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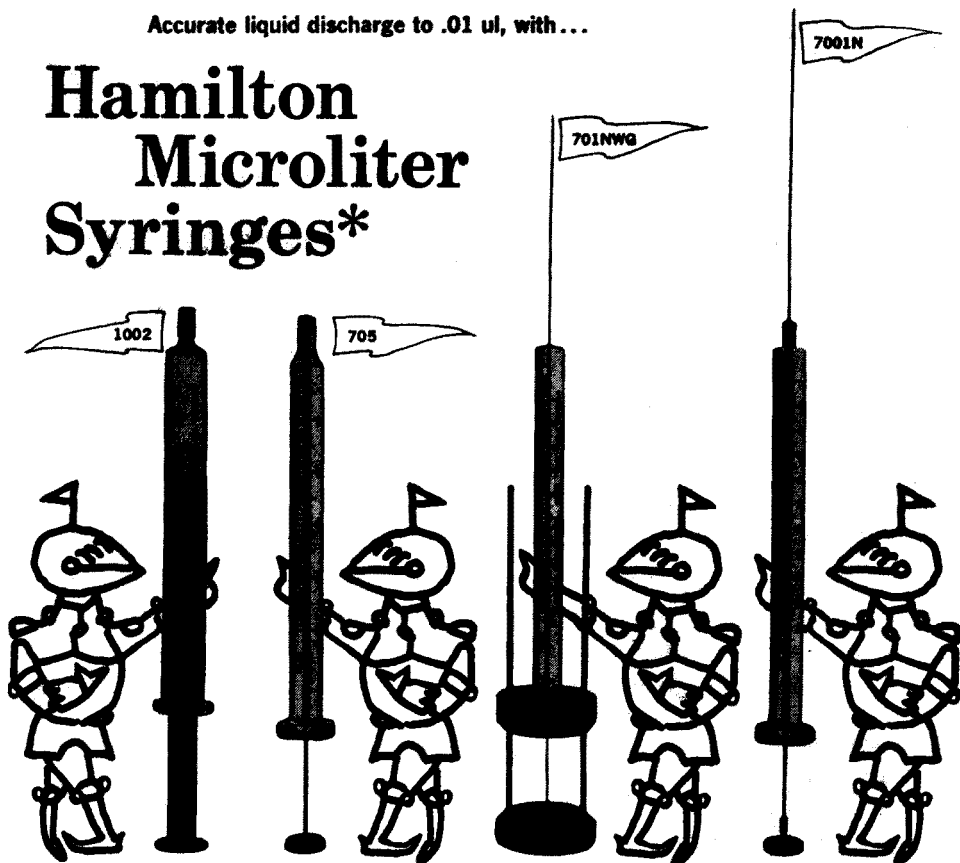
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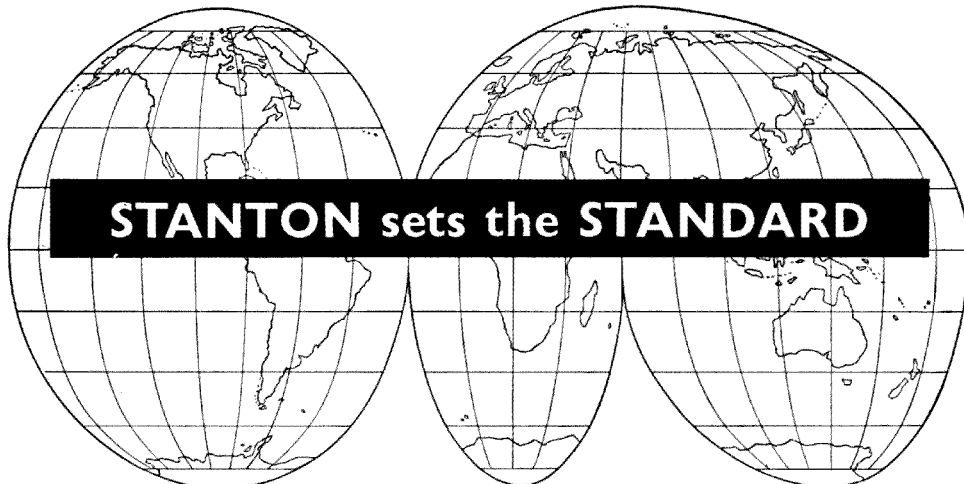
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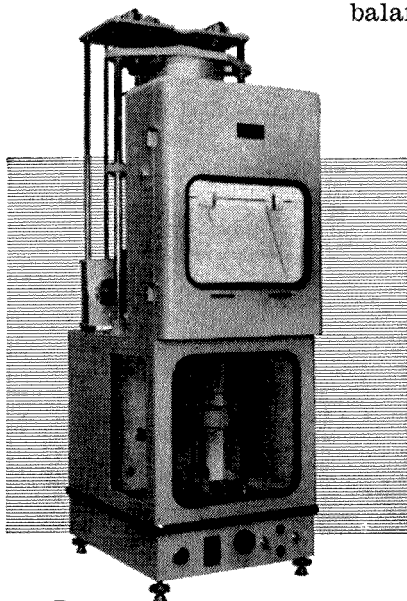
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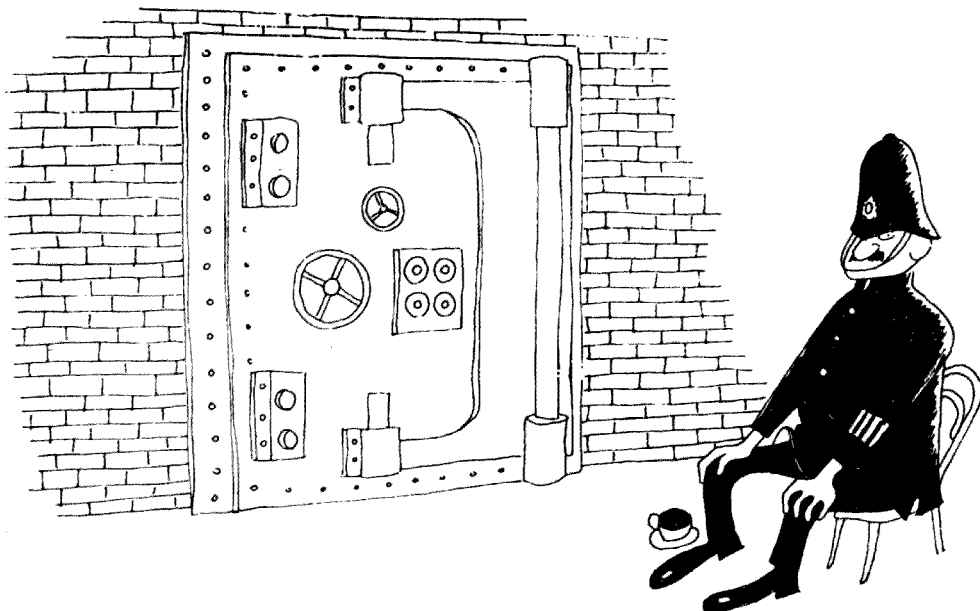


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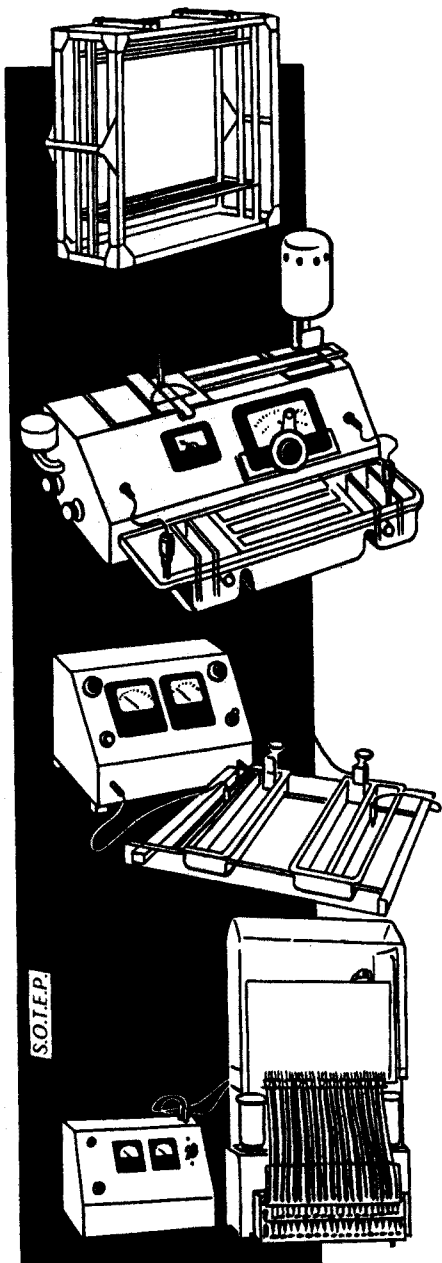
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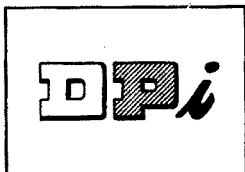
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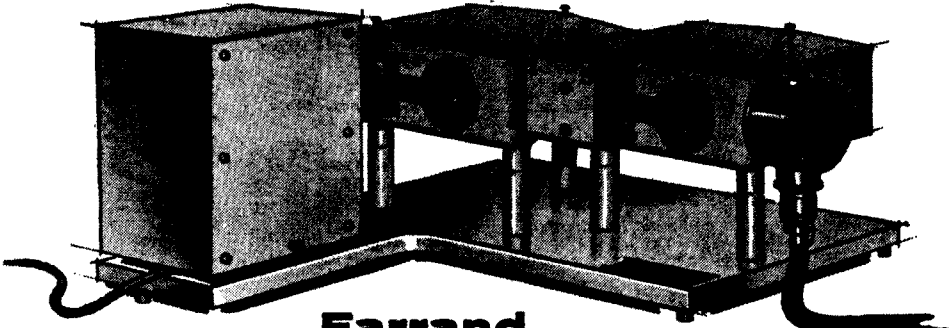
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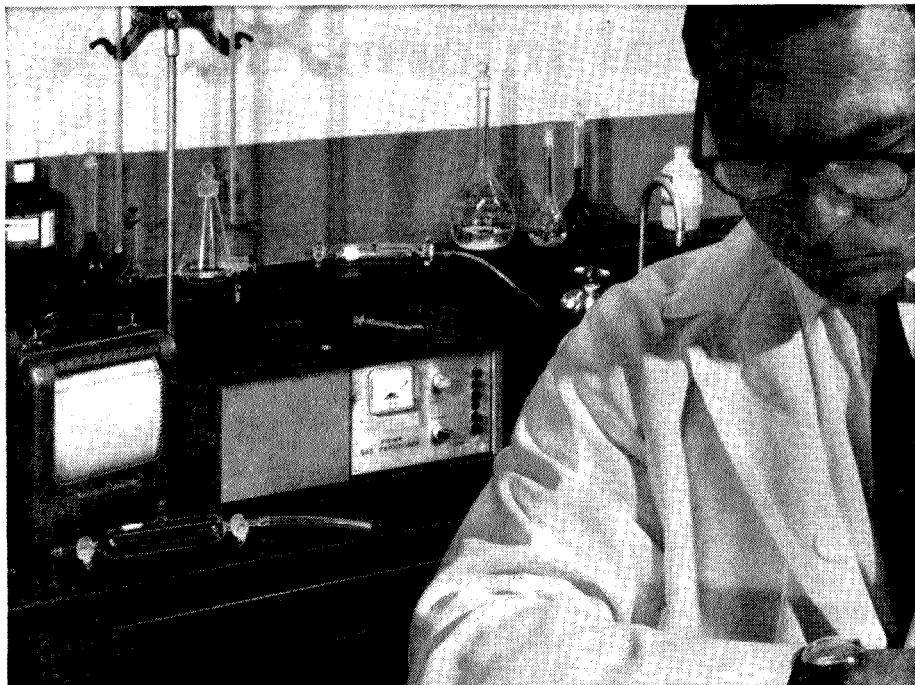
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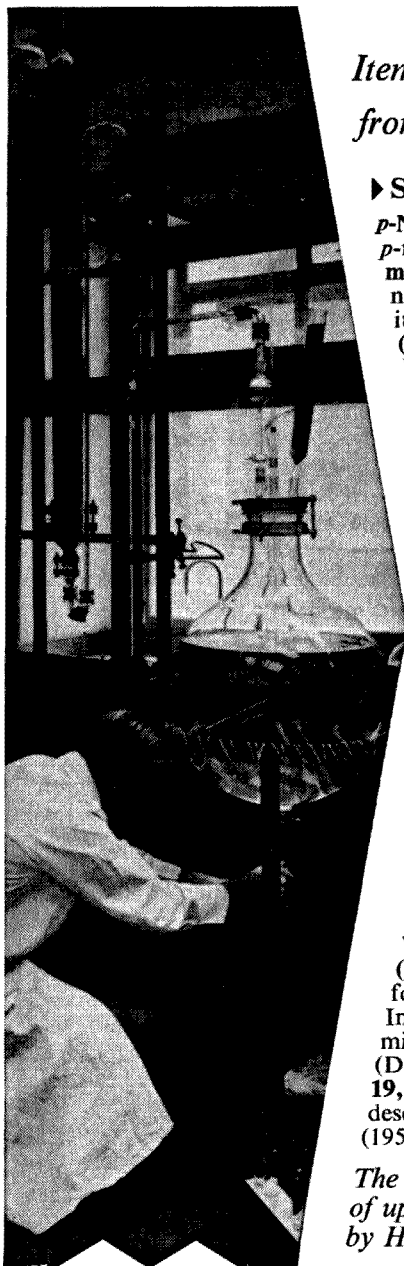


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## A COMPARISON OF THREE METHODS OF DETERMINING THE CONCENTRATION OF URANIUM IN SEA WATER

J. D. WILSON, R. K. WEBSTER, G. W. C. MILNER,  
G. A. BARNETT AND A. A. SMALES

*Chemistry Division, U.K.A.E.A. Research Group, Atomic Energy Research Establishment, Harwell  
(Great Britain)*

(Received July 15th, 1960)

### INTRODUCTION

Earlier measurements of the concentration of uranium in sea water have been reviewed by KOCZY<sup>1</sup>, and a number of results have also been tabulated by RONA, GILPATRICK AND JEFFREY<sup>2</sup>. It is clear from the results quoted in these papers that there are considerable variations in the uranium concentrations quoted by different observers, and that there is little agreement as to whether the uranium concentration varied with the locality and the depth at which the sample is taken. HERNEGGER AND KARLIK<sup>3</sup> for example, found a uranium concentration of 1.3  $\mu\text{g/l}$  which was fairly independent of the depth at which the samples were taken, whilst both KOCZY<sup>1</sup> and NAKANISHI<sup>4</sup> found that the concentration increased up to a depth of 500 to 1,000 m after which it remained fairly constant. NAKANISHI's average value of 2.8  $\mu\text{g/l}$  for depths below 500 m is, however, twice that obtained by KOCZY.

Large variations in the results of analyses of samples taken from different locations is understandable in the case of coastal waters, but is less so in the case of deep sea samples, and the table given by RONA, GILPATRICK AND JEFFREY shows that different observers have obtained results ranging from 0.7 to 3.5  $\mu\text{g/l}$  for samples taken from near the surface in the same areas of the North Atlantic and North Pacific Oceans.

In view of the wide range of results which have been reported it would clearly be unsatisfactory to rely solely on any one analytical method in a new determination of uranium in sea water, and whilst a new polarographic method<sup>5</sup> for uranium in sea water was being developed in this laboratory the opportunity was taken to analyse a number of the sea water samples by the isotopic dilution (involving mass spectrometry) and the fluorimetric methods as well.

A second reason for doing this was to demonstrate that the differences in the results obtained by earlier workers were not primarily due to the different analytical techniques employed, *viz.*, D.C. polarography<sup>6</sup>, fluorimetry<sup>4</sup>, fission counting<sup>7</sup>, and the isotopic dilution method<sup>8</sup>.

An alternative explanation of some of the variations in the values which have been reported previously might be found in the fact that often no checks were made on the chemical yields in the extraction and concentration steps *in the actual analyses*. It was usually assumed that these recoveries were the same as those found in trial experiments with known amounts of uranium (although these recoveries were not

always 100%). The experiments with radioactive tracers which are quoted in a previous paper<sup>5</sup> from this laboratory show, however, that it is extremely difficult to obtain recoveries of uranium from sea water reproducible to within 10% by the usual extraction procedures, so that the effect of variable chemical losses must be considered.

Some form of uranium tracer was used in all the methods described in this paper; <sup>237</sup>U for the methods using pulse polarography<sup>5</sup> and fluorimetry, and <sup>235</sup>U in the isotopic dilution method. In this way the effects of the variable chemical yields in the extraction steps were always known or eliminated. It may be observed that the mean value of  $3.33 \pm 0.08 \mu\text{g/l}$  for English Channel and Bay of Biscay waters obtained by the three methods is quite close to the value of  $3.33 \mu\text{g/l}$  found for water from the North Atlantic and the Gulf of Mexico by RONA, GILPATRICK AND JEFFREY<sup>2</sup>, who also used an isotopic dilution method.

In addition to giving a *consistent* value for the uranium content of sea water, the results permitted a comparison of the precision of the three methods to be carried out and indicated some possible sources of error in this determination. Details of the polarographic method<sup>5</sup> have already been given, and enough details of the isotopic dilution and fluorimetric methods are given in this paper to enable a proper comparison to be made.

#### THE ISOTOPIC DILUTION METHOD

The isotopic dilution method which was used involved the measurement of the <sup>238</sup>U/<sup>235</sup>U ratio in sea water extracts after the <sup>235</sup>U tracer had been added to the original sea water. The tracer had the isotopic composition <sup>234</sup>U — 1.03%, <sup>235</sup>U — 93.41%, <sup>236</sup>U — 0.125%, <sup>238</sup>U — 5.44%, whereas natural uranium consists mainly of <sup>238</sup>U (99.3%). The concentration of the solution of this tracer was determined by calibration against a standard solution of natural uranium, so that in effect the natural uranium in sea water is compared against a standard solution of natural uranium and systematic errors which might be introduced by mass discrimination are eliminated.

In principle the measurement of the <sup>238</sup>U/<sup>235</sup>U ratio makes the results obtained by the isotopic dilution procedure independent of the chemical yield; in practice if the contamination level from reagents, etc. is significant, small errors may be introduced if the chemical yield differs between a uranium determination and a blank determination. The uranium blanks in the method which is described were small, however, so this error was very small.

The determinations fell into two groups. Some preliminary measurements were made using a 6" radius of curvature 60° sector mass spectrometer fitted with a simple D.C. amplifier detector. 1.5-l samples of sea water were used, the uranium being coprecipitated with aluminium phosphate and then purified by solvent extraction as the nitrate into ethyl acetate. In addition to being time consuming, this method gave rather high uranium blanks and its use was discontinued. The later determinations were made with a Metropolitan-Vickers M.S.5 mass spectrometer. This is a 12" radius of curvature 90° sector instrument incorporating an electron multiplier detector, and its high sensitivity enabled much smaller samples of sea water to be analysed. The method which is described below involves the extraction of the uranium 8-hydroxyquinoline (oxine) complex into chloroform from 100-ml aliquots of sea water, and it is much shorter than the first method investigated.



*Experimental method*

Acidify the sea water immediately it is collected, with 2 ml of conc. nitric acid per l. Weigh about 2 g of  $^{235}\text{U}$  tracer solution and 100 g of sea water into a polythene bottle, mix thoroughly, and allow to stand for 1 or more days to reach equilibrium. Then transfer the solution to a 250-ml separating funnel and add 1 ml of 20% w/v ammonium acetate and 1 ml of 0.1 M ethylenediaminetetraacetic acid disodium salt (EDTA). Adjust to between pH 6.5 and 7 by the addition of ammonium hydroxide using B.D.H. universal indicator, and then add 1 ml of a 6% w/v solution of oxine in alcohol. Extract the uranium complex with 3 ml of chloroform, add a further 1 ml of the oxine solution and make two more extractions with 3 ml and 2 ml of chloroform respectively. Evaporate the combined extracts to dryness in a platinum tray and ignite to remove any organic residue. Wash the tray with a small quantity of hot nitric acid and evaporate the washings to dryness on a circular glass plate or microscope slide. Dissolve the visible deposit in a small drop of water, and transfer to the sample filament of a mass spectrometer surface ionisation source. Then carry out an isotopic analysis.

*Results for uranium in sea water*

Table I shows the values obtained for the uranium content of coastal sea water using the co-precipitation of the uranium with aluminium phosphate from 1.5-l samples of sea water. Samples 'A' and 'B' were both taken at the same time and at the same place, but sample 'A' was stored in a 35-l polythene bottle, whilst sample 'B' was stored in a 5-l glass bottle.

The results in Table II were obtained using the recommended extraction procedure

TABLE I  
THE CONCENTRATION OF URANIUM IN SEA WATER  
BY ISOTOPIC DILUTION- $\text{AlPO}_4$  CO-PRECIPITATION METHOD

Sample	Uranium concentration (corrected for blank)				Mean value	Coefficient of variation
'A'	3.33	3.33	3.34	3.34	3.3 <sub>4</sub> $\mu\text{g/l}$	0.17%
'B'	3.62	3.65			3.6 <sub>3</sub> $\mu\text{g/l}$	0.5%
Blank	0.07	0.09			0.08 $\mu\text{g}$	—
Calibration of tracer	2.87	2.87	2.87	2.89	2.87 <sub>4</sub> $\mu\text{g/ml}$	0.4%

TABLE II  
THE CONCENTRATION OF URANIUM IN SEA WATER  
BY ISOTOPIC DILUTION-8-HYDROXYQUINOLINE EXTRACTION METHOD

Sample	Blank	Uranium concentration (corrected for blank)			Mean value	Coefficient of variation
1. Weymouth Bay	0.0008 $\mu\text{g}$	3.30	3.32		3.3 <sub>1</sub> $\mu\text{g/l}$	0.28%
2. Bay of Biscay (4,210 m)	0.0025 $\mu\text{g}$	3.29	3.30	3.34	3.3 <sub>1</sub> $\mu\text{g/l}$	0.76%
3. Sample 16 (25°S., 145°W., 3,500 m)	0.0023 $\mu\text{g}$	2.99	2.99	3.01	3.0 <sub>0</sub> $\mu\text{g/l}$	0.47%
4. Sample 21 (43°50'S., 105°30'W.)	0.0019 $\mu\text{g}$	3.24	3.25	3.26	3.2 <sub>5</sub> $\mu\text{g/l}$	0.34%
5. Calibration of tracer	—	0.166	0.165	0.166	0.165 <sub>7</sub> $\mu\text{g/g}$	0.38%

and an M.S.5 mass spectrometer. The Weymouth Bay coastal water quoted in Table II was a sample taken a year later than samples 'A' and 'B' in Table I, and was stored in a 45-l glass carboy. In view of the close agreement between the results for this sample and for sample A, even though quite different chemical separations were used, it seems probable that the small bottle containing sample B was contaminated. Samples 16 and 21 were kindly supplied by Dr. E. RONA, Oak Ridge Institute of Nuclear Studies. These results are given only as an illustration of the precision of the method, and are not included in the average value which is quoted later, for this refers only to English Channel and Bay of Biscay sea waters.

#### *A discussion of the errors*

The results are calculated from the equation

$$x = y \cdot \frac{R_{238} - T_{238}}{N_{238} - R_{238}} \cdot \frac{234 N_{234} + 235 + 238 N_{238}}{234 T_{234} + 235 + 236 T_{236} + 238 T_{238}}$$

where  $x$  is the mass of natural uranium to be measured,  $y$  is the mass of tracer added, and  $N$ ,  $T$  and  $R$  refer to the isotope ratios (all with reference to the 235 isotope) for the normal, tracer and mixed element respectively. The same equation is used for the calibration of the tracer against the standard uranium solution, though  $x$  is then the known and  $y$  the unknown quantity. If it is assumed that the uranium in the standard solution and in the sea water has the same isotopic composition, the last factor in equation (1) is common to both the calibration and the determination and so cancels.

There are then three sources of error to be considered, (a) the determination of  $y$  the quantity of tracer, (b) contamination, and (c) random errors involved in the determination for sea water.

#### *The error in the calibration of the tracer*

This is made up as follows:

(1) Random error in the mass spectrometric calibration, standard error for the mean of 4 determinations equivalent to 0.19%. (2) Dilution errors, 2 standard flasks grade A limits -0.02% and 1 pipette, coefficient of variation -0.11%. (3) Mass of  $U_3O_8$  in standard solution, coefficient of variation -0.07%. (4) Stoichiometry of  $U_3O_8$ .

The error in (4) is not easy to assess, but if it is assumed to be small<sup>8</sup>, the overall coefficient of variation for the calibration is 0.24%.

#### *Contamination from the reagents*

A number of blank determinations using the oxine extraction were made in order to investigate the contamination. By changing the proportions of the reagents it was possible to show that most of the uranium blank came from the oxine itself, thus the blank correction for sample 1 in Table II refers to a smaller quantity of oxine than that used for samples 2, 3 and 4. Since the quantity of oxine which was used was kept constant in each series of measurements, there should be little variation in the blank correction, which was  $0.0023 \pm 0.0003 \mu\text{g}$  (mean of six measurements). The quantity of uranium which was measured in a determination was about  $0.3 \mu\text{g}$  so that the blank correction represents about 0.8% of the amount measured, and the uncertainty in a single blank correction represents only 0.1%.

*Random errors in a determination*

Examination of equation (1) shows that any error in the measurement of the  $^{238}\text{U}/^{235}\text{U}$  ratio for the mixture of sample and tracer will be magnified in the calculation of  $x$ , and that the magnification is a minimum for a value of  $R_{238} \approx \sqrt{N_{238}T_{238}}$ . In this case, the optimum value for  $R$  is 2.8, whereas a ratio of about 1 was used in this work. The magnification factors for the ratios 2.8 and 1.0 are only 1.04 and 1.07 respectively, so that little precision is lost by using ratios of about unity, and the uncertainty in an amplifier range factor is then avoided.

The  $^{238}\text{U}/^{235}\text{U}$  ratio for uranium in sea water was not determined, and the accepted value of 137.8 for natural uranium was assumed instead. It can be shown that an error of 1% in this assumed ratio will introduce one of only 0.015% into the measurement.

The coefficients of variation of the four results in Table II have a mean value of 0.46% and the mean coefficient of variation for a single determination, combined with a single blank measurement and including calibration errors is 0.52%. This value may be compared with a mean figure of 2.2% for the results reported by RONA, GILPATRICK AND JEFFREY<sup>2</sup>.

## THE FLUORIMETRIC METHOD

The very sensitive fluorimetric method for uranium has been used previously for the direct measurement of uranium in river waters<sup>9</sup>. However, this procedure could not be used for sea water without some modification for it involves the direct evaporation of the sample in a fluorimeter tray and the large residue from sea water (mainly sodium chloride) cannot be dissolved in the usual quantities of flux. A preliminary solvent extraction of the uranium into chloroform as its oxine complex was again used and  $^{237}\text{U}$  tracer was employed to measure the chemical yield.

*Experimental method*

The solvent extraction of the uranium was carried out in a similar way as in the isotopic dilution method. The following differences should be noted, however. 100 ml of the sample was taken and mixed with about 0.1 ml of a  $^{237}\text{U}$  tracer solution (containing  $\sim 0.1 \mu\text{C}$ ). The preparation of  $^{237}\text{U}$  has already been described<sup>5</sup>. The solution was *boiled* and then left overnight to allow the  $^{237}\text{U}$  to exchange with the natural uranium. The chloroform extracts were collected together and made up to 10 ml in a standard flask. 2 ml of this solution was transferred to a cylindrical polythene container ('Polytainer') placed in a well type crystal in a  $\gamma$ -counter, and at least 10,000 counts were recorded for this and for a standard solution. The chemical yield was measured in this way. The fluorimetric estimation was carried out as follows:

Place three clean fluorimeter dishes in position on a hot peripheral heating block<sup>9</sup> and add a total of 2 ml of the chloroform extract to each, adding 0.5 ml at a time, and allowing the chloroform to evaporate completely between the additions. Add 0.25 ml of a solution of magnesium carbonate in glacial acetic acid (1 mg/ml magnesium) adding the liquid slowly to prevent the dissolving 8-hydroxyquinoline from creeping up the sides of the platinum dish. Then add 0.5 ml of a solution of uranium containing 0.1  $\mu\text{g}/\text{ml}$ , as an internal standard, to one dish only. Continue heating, and when all the dishes are dry, gently flame off the organic matter and bring each dish momentarily to a red heat. Add 0.5 g of a mixed sodium carbonate-fluoride flux to each

dish and place in position on a platinum gauze over a gas burner. Fuse at the lowest possible temperature, and keep molten for about five minutes, swirling the melt occasionally. Allow the dishes to cool slowly, and when they are quite cold, measure the fluorescence in a fluorimeter. Re-fuse briefly, allow to cool, and check that the maximum degree of fluorescence has been reached. Calculate the uranium content of the sample by the standard method<sup>9</sup>.

### Results

Six sea water samples, collected from various depths in the Bay of Biscay, were analysed by the fluorimetric method, and the results are given in Table III.

Earlier experience with the fluorimetric method showed that it was desirable to measure the chemical yield with a radioactive tracer, for the results which were obtained without the addition of tracer were significantly lower than those values obtained by other methods. When the chemical yields were measured with the <sup>237</sup>Cf tracer it became clear that it was essential to use such a tracer, for chemical yields as low as 74% were recorded. Unless a tracer is used it must be assumed that the results may be systematically too low.

#### A DISCUSSION OF THE RESULTS OBTAINED BY THE DIFFERENT METHODS

The results of the analyses of a number of sea waters by the isotopic dilution (I.D.), pulse polarographic (P.P.) and fluorimetric methods (F) are summarised in Table III. It can be seen that there is no difference within the limits of experimental error between the results obtained for English Channel (coastal) and Bay of Biscay (deep sea) samples. Similarly, if there is any variation of the uranium concentration with depth, it is so small as to be less than the experimental errors in both the polarographic and fluorimetric methods, and only accurate analyses made by the isotopic dilution

TABLE III  
A COMPARISON OF THE RESULTS OF ANALYSES OF SEA WATER BY THREE METHODS

Origin of sample	Method of analysis		
	Isotopic dilution, µg/l uranium	Pulse polarography, µg/l uranium	Fluorimetry with tracer, µg/l uranium
1. Bay of Biscay, stored in polythene			
1. 7 metre depth	—	3.5 ± 0.2	3.5 ± 0.3
2. 570 metre depth	—	3.5 ± 0.2	3.0 ± 0.8
3. 975 metre depth	—	3.6 ± 0.2	3.2 ± 0.3
4. 1990 metre depth	—	3.2 ± 0.2	3.1 ± 0.3
5. 2815 metre depth	—	3.3 ± 0.2	3.4 ± 0.2
6. 4210 metre depth	3.31 ± 0.06	3.4 ± 0.2	3.3 ± 0.4
		Mean = 3.41 ± 0.17 <sup>a</sup>	Mean = 3.25 ± 0.23 <sup>a</sup>
2. Weymouth Bay			
1. Stored in polythene	3.34 ± 0.04	—	—
2. Stored in glass	3.63 ± 0.06 <sup>b</sup>	—	—
3. Stored in glass	3.31 ± 0.04	—	—
4. Stored in glass	—	3.37 ± 0.08	—

<sup>a</sup> Estimated from the actual spread of the results.

<sup>b</sup> Assumed to be a contaminated sample.

method are likely to detect any variation. The errors which are quoted are 3 times the estimated standard error of the mean value.

The results for Bay of Biscay waters by the three different methods are  $3.31 \pm 0.06$  (I.D. — 3 analyses),  $3.41 \pm 0.17$  (P.P. — 9 analyses, see Ref.<sup>5</sup>) and  $3.25 \pm 0.23$  (F — 6 analyses). Assigning equal weight to each of these values gives a mean value of  $3.32 \mu\text{g}$  of uranium per l. In a similar way an average value of  $3.34 \mu\text{g/l}$  is obtained for the Weymouth Bay water, and on assuming no significant difference between the waters from the two sampling points, an overall average of  $3.33 \pm 0.08 \mu\text{g/l}$  is found. This value is in good agreement with that of  $3.39 \mu\text{g/l}$  ( $3.31 \mu\text{g/kg}$ ) found by RONA, GILPATRICK AND JEFFREY<sup>2</sup> for waters from the North Atlantic and the Gulf of Mexico.

#### A COMPARISON OF THE METHODS OF ANALYSIS

The three methods may be compared on the basis of the precision and accuracy of each, the man hours and the time taken to achieve such accuracy and the cost of the equipment. It is first necessary to distinguish between the *time* taken for an analysis and the man hours (or effort) involved. The time for an analysis may be taken as the time interval between the receipt of a sample and the reporting of the result. The effort, however, is not proportional to the time because in all three methods it is necessary to allow the same time (1 day) for isotopic equilibrium to be established. Because of this, the disparity in the time taken by the various analytical methods is much less than the disparity in the man hours involved.

The three methods, as they have been described in this and in an earlier paper<sup>5</sup>, have been taken as the basis for the comparisons and the results are given in Tables IV and V. Table IV shows an analysis of the way in which the time and effort is distributed amongst the various operations, whilst Table V gives a comparison of the methods. No attempt has been made to take account of the numerous variations which

TABLE IV  
THE TIME AND EFFORT REQUIRED FOR VARIOUS OPERATIONS

Operation	Pulse polarographic method	Isotopic dilution method	Fluorimetric method
1. Addition of tracer and isotopic exchange			
<i>Time</i>	1 day	1 day	1 day
2. Extraction of Uranium	2 extractions, 1 back extraction, and 2 evaporations (usually 6 samples simultaneously)	1 extraction and 2 evaporations (5 samples simultaneously)	1 extraction and 1 evaporation (1 sample at a time)
<i>Effort</i>	8 man hours per sample	$2\frac{1}{2}$ man hours per sample	2 man hours per sample
3. Measurement of radiochemical yield	100,000 counts on standard and unknown at 2000 c.p.m.	—	10,000 counts on standard and unknown at 200 c.p.m.
<i>Effort</i>	2 man hours per sample	nil	2 man hours per sample
4. Measurement of total uranium			
<i>Effort</i>	5 man hours per sample	$1\frac{1}{2}$ to 2 man hours per sample	$1\frac{1}{2}$ man hours per sample

Note: blank determinations count as one actual analysis.

are possible — for example, variations in the number of samples extracted simultaneously, or in the division of time between extraction and measuring processes.

In interpreting the data given in Tables IV and V, the following points should be borne in mind:

1. In all the methods the measurements were repeated as often as possible in order to obtain a high precision. With the mass spectrometer, for example, about 15 complete scans were recorded for any one sample to give about 30 estimates of the  $^{238}\text{U}/^{235}\text{U}$  ratio. Clearly the precision could be improved by recording more ratios, but to achieve a significant improvement would require a substantial increase in the

TABLE V  
A COMPARISON OF THE THREE METHODS OF ANALYSIS

	<i>Pulse polarographic method</i>	<i>Isotopic dilution method</i>	<i>Fluorimetric method</i>
1. Precision of method:			
For radiochemical yield	1.1%	—	1.3%
For uranium estimation	0.7%	0.52%	3%
<i>Overall Coefficient of Variation</i>	1.4% (estimated)	0.52% (measured)	5% (measured)
2. Minimum time for analysis	3 days	2 days	1.5 days
3. Effort per sample	15 man hours	~ 5 man hours	~ 6 man hours
4. Size of sample required	4 l	100 ml	100 ml

time needed both for recording and for measuring ratios. The precision of the fluorimetric method is not improved by making more measurements on each tray, but only by making measurements on a greater number of melts since the irreproducibility of the fusion is the limiting factor. The number of melts which can be made is limited by the amount of uranium extracted. In the polarographic method the number of measurements on each sample is limited by deterioration of the final solution when left in the cell overnight.

2. No account has been taken of the time needed for the calibration of the  $^{235}\text{U}$  tracer in the isotopic dilution method, or of the time required to prepare  $^{237}\text{U}$  for the other methods. The calibration need be done only infrequently, and the preparation of enough  $^{237}\text{U}$  for 2 weeks work takes about 1 day, once the ion-exchange column containing  $^{241}\text{Pu}$  has been set up. Whilst both the tracer calibration and  $^{237}\text{U}$  separations would add considerably to the time taken for a single analysis, they form only an insignificant part of the time involved in a large number of analyses.

3. The time taken in measuring the background count rate has not been included in the time spent in counting the  $^{237}\text{U}$ , since it is usual to record the background count rate over a long period of time whilst other work is being done.

These tables show that the isotopic dilution method is to be preferred, but this involves expensive equipment. The cost of equipment for this method may be reduced by using a smaller and less sensitive mass spectrometer (not available commercially), but this would involve using larger sea water samples (1–2 l) and consequently a relatively cumbersome and time-consuming chemical procedure.

Although the costs for equipment in the other two methods are lower, these methods could only be considered as replacements for the isotopic dilution method if the precision of the results could be improved. The higher overall coefficient of variation for the results by polarography arises mainly from errors in counting the  $^{237}\text{U}$ . The observed coefficient of variation for a single count is 0.8%. As the coefficient of variation calculated for 100,000 counts is only 0.3%, the greater part of the counting error must arise from errors in transferring the sample solution to a polythene container and from irreproducibility in positioning the container in the well of the NaI crystal of the  $\gamma$ -counter. By exercising greater precautions it may be possible to improve the precision in this part of the determination. The coefficient of variation of 0.7% for recording and measuring the polarographic peaks is based on a measured coefficient of variation of 1% for a single measurement of peak height. It might be possible to improve on this by paying more attention to the reproducibility of the conditions within the polarographic cell, since the instrument is more reproducible than this.

In the fluorimetric method, the value of the coefficient of variation of the counting operation could be reduced to about 0.8% by taking greater precautions, but the precision of the fluorimetric measurement could only be improved by analysing each sample many times. It would be necessary to make at least 100 determinations to approach the precision of the isotopic dilution method.

#### CONCLUSIONS

It has been shown that there are at least three methods which can be used to obtain accurate values for the uranium content of sea water samples. If the cost is of no consequence, the isotopic dilution method is the best of the methods examined in this work.

The analyses which have been made for sea water samples from Weymouth Bay and from the Bay of Biscay show little difference in the uranium concentration and give a mean value of  $3.33 \pm 0.08 \mu\text{g per l}$ .

#### ACKNOWLEDGEMENTS

The assistance of Dr. B. A. LOVERIDGE in preliminary chemical work on the isotopic dilution method employing aluminium phosphate and of Mr. J. W. MORGAN for measurements in the isotopic dilution-8-hydroxyquinoline method is gratefully acknowledged.

#### SUMMARY

A stable isotopic dilution method and a fluorimetric method for the measurement of the concentration of uranium in sea water are described. In both methods the uranium is extracted from the sea water into chloroform using 8-hydroxyquinoline.  $^{237}\text{U}$  is used as a tracer in the fluorimetric method. The results obtained by these two methods and by a pulse polarographic method are compared, and give a mean value of  $3.33 \pm 0.08 \mu\text{g per l}$  for the uranium content of samples of English Channel and Bay of Biscay water. The precision of the methods improves in the order fluorimetry, pulse polarography, isotopic dilution.

#### RÉSUMÉ

Les auteurs ont effectué une étude de comparaison entre la méthode par dilution isotopique et la méthode fluorimétrique pour le dosage de l'uranium dans l'eau de mer. Dans les deux cas, on procède à l'extraction du complexe uranium-hydroxy-8-quinoléine dans le chloroforme. Les résultats ont été comparés avec ceux obtenus par une méthode polarographique.

## ZUSAMMENFASSUNG

Beschreibung einer Isotopen-Verdünnungsmethode und einer fluorimetrischen Methode zur Bestimmung von Uran in Meerwasser. Die Abtrennung aus dem Meerwasser erfolgt durch Extraktion des Uran-8-Oxychinolin Komplexes mit Chloroform. Die erhaltenen Werte werden mit den Ergebnissen einer polarographischen Methode verglichen.

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*Anal. Chim. Acta*, 23 (1960) 505-514

## DECOMPOSITION OF FERROCYANIDE IN ANALYSIS

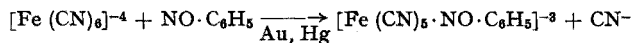
## IV. NEW SPOT TEST FOR GOLD\*

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Under ultraviolet light<sup>1</sup> and in the presence of certain cations (Hg<sup>2-5</sup>, Au<sup>6,7</sup>, Pt<sup>6</sup>, Ag<sup>4,5</sup>, Pd<sup>8</sup>) ferrocyanide(II) and nitrosobenzene react to yield the violet pentacyanide complex<sup>3,9</sup>:



Since this complex is intensely coloured, methods based on this reaction are very sensitive. For example, the method for spectrophotometric determination of mercury<sup>3</sup> can be applied to concentrations as small as 10<sup>-7</sup> moles of mercury/l, while methods for the photometric determination of gold<sup>7</sup> (0.2-13 p.p.m.) and palladium<sup>8</sup> (5 · 10<sup>-6</sup>-8 · 10<sup>-4</sup> moles/l) are only slightly less sensitive.

Spot tests based on the same principle have the following sensitivities:

Hg<sup>5</sup>: 0.002 µg/drop; Ag<sup>10</sup>: 0.004 µg/drop;

Pd<sup>8</sup>: 0.02 µg/drop; some aromatic nitrosocompounds<sup>11</sup>: 0.02-1 µg/drop.

The spot test described in the present paper has the sensitivity of 0.05 µg/drop and it is suitable for the detection of gold in solutions containing foreign cations.

\* Part III in *Mikrochim. Acta*, (1960) 586.



## EXPERIMENTAL

*Reagents*

$\text{HAuCl}_4$ : A 0.005-*M* solution was used as stock solution. Diluted solutions were prepared fresh every day by dilution with distilled or redistilled water in Pyrex or Jena glassware.

$\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ : A 0.5% solution was used. For the detection of gold at concentrations near the limit of sensitivity, the solution must be prepared fresh daily and kept away from direct sunlight.

$\text{C}_6\text{H}_5 \cdot \text{NO}$ : A saturated aqueous solution was obtained by dissolving an excess of the substance in distilled water at 70° (on a water bath). The solution must be prepared fresh every 8 to 10 days. The nitrosobenzene was prepared by oxidation of aniline with Caro's acid<sup>12</sup>.

Acetate buffer: 1-*M* solution, pH 5.0.

Solution "A": A 4 to 1 mixture of nitrosobenzene and acetate buffer solutions.

TABLE I  
INTERFERENCE OF CATIONS  
Concentration of Au: 0.5  $\mu\text{g}/\text{drop}$  ( $5 \cdot 10^{-5}$  moles/l)

Cation	Conc. of cation in moles/l or Au : Me (by weight)	Effect on sensitivity
K	0.10	None
Na	0.10	None
Mg	0.03	None
Ca	0.10	None
Sr	0.10	None
Ba	0.10	None
Zn	1 : 80	Strong decrease <sup>a</sup>
Mn	1 : 80	Strong decrease <sup>a</sup>
Co	1 : 20	Considerable decrease <sup>a</sup>
Ni	1 : 20	Considerable decrease <sup>b</sup>
Cr <sup>+3</sup>	1 : 20	Considerable decrease
Al	1 : 80	Strong decrease
	1 : 20	Considerable decrease
Fe <sup>+3</sup>	1 : 20	Strong decrease <sup>a</sup>
	1 : 10	Considerable decrease <sup>a</sup>
As(AsO <sub>2</sub> <sup>-</sup> )	1 : 20	Considerable decrease
Cd	1 : 80	Slight <sup>a</sup>
Cu <sup>+2</sup>	1 : 20	Slight. After warming it is necessary to add NaOH.
Bi	1 : 20	Strong decrease
	1 : 10	Considerable decrease
Pb	1 : 80	Considerable decrease
U(UO <sub>2</sub> <sup>+2</sup> )	1 : 40	Considerable decrease
	1 : 20	Slight
Pt(PtCl <sub>6</sub> <sup>-2</sup> )	$5 \cdot 10^{-3}$	Slight. No effect on decomposition!
Hg	0.01	Hg gives the same effect but can be masked by KI. KI must be added.
	$4 \cdot 10^{-5}$	
Ag	0.01	The effect is almost completely prevented. Slight influence if KI added.
	$1 \cdot 10^{-4}$	No effect in presence of KI.

<sup>a</sup> 3 drops of  $\text{K}_4[\text{Fe}(\text{CN})_6]$ .

<sup>b</sup> 2 drops of  $\text{K}_4[\text{Fe}(\text{CN})_6]$ .

## PROCEDURE

A drop of  $K_4[Fe(CN)_6]$  solution was placed in the depression of a porcelain spot plate followed by a drop of solution "A", and then a drop of the test solution. A parallel blank test was run with a drop of distilled water. After a short period, or on heating to about 30 to 40°, a pink or violet colour appeared, while the blank remained colourless or faintly yellow. The colour appeared very quickly on heating, but its intensity was not increased by further heating. Sunlight has an effect similar to that of the gold ion, hence the experiments must be conducted in the shade or in the light of an incandescent lamp.

*Sensitivity*

The action of gold on ferrocyanide is strongly affected by the acidity of the solution; for optimum sensitivity the pH must be correct. An acetate buffer maintaining a pH of 5.0 has proved best, pH 4.1 and 6.2 giving significantly lower sensitivities. It has been also ascertained that optimum sensitivity is obtained with a 0.5% solution of potassium ferrocyanide and a saturated solution of nitrosobenzene.

The sensitivity of this spot test for the pure system was investigated with the following results:

Limit of identification 0.05  $\mu$ g/drop (0.05 ml) and

Concentration limit 1 : 1,000,000.

*Interference of cations*

Of the cations investigated (Table I) only mercury and silver react analogously; mercury in low concentrations does not react immediately at room temperature, and silver does not react even after protracted waiting, hence gold can be detected in the presence of those cations. On heating, both metals give stronger colorations, which make the detection of gold unreliable. Previous investigations<sup>5,10</sup> have shown that iodides in high concentrations completely inhibit the reactions of mercury and silver; further tests showed the mercury and silver interferences with the reaction for gold can be eliminated by the addition of iodides. Moreover, this addition accelerates the reaction with gold, so that no heating is necessary.

Heavy metals that yield coloured precipitates with ferrocyanide ( $Fe^{+3}$ ,  $Cu^{+2}$ ,  $UO_2^{+2}$ ) also interfere with the detection of gold, but this interference can be readily eliminated by warming during the test, and then destroying the precipitate by making the solution alkaline (see Table I). Unfortunately, this expedient breaks down when the concentration of the interfering ion is too high.

Large amounts of certain cations, although they do not give intensely coloured precipitates, considerably lower the sensitivity of the test; others have no effect even at very high concentrations (see Table I).

*Interference of anions*

The effect of some anions on the activity of gold has also been studied. Most anions do not interfere even at high concentrations. Thiosulphate, sulphite and cyanide at high concentrations considerably lower the sensitivity, and may even inhibit the action of the gold ion. Iodides accelerate the reaction significantly, presumably by reducing  $Au^{+3}$  to  $Au^+$ . The results of these experiments are summarized in Table II.

TABLE II  
INTERFERENCE OF ANIONS  
Concentration of Au: 0.5  $\mu\text{g}/\text{drop}$  ( $5 \cdot 10^{-5}$  moles/l)

Anion	Conc. of anion in moles/l	Effect on sensitivity
$\text{NO}_3^-$	0.10	None
$\text{SO}_4^{2-}$	0.01	None
$\text{CH}_3\text{COO}^-$	0.10	None
$\text{Cl}^-$	0.10	Slight
	0.01	None
$\text{Br}^-$	0.10	Slight
	0.01	None
$\text{I}^-$	0.10	The reaction is faster and more sensitive
$\text{CNS}^-$	0.10	Slight
$\text{CN}^-$	0.01	Strong decrease
$\text{B}_4\text{O}_7^{2-}$	0.01	None
$\text{C}_2\text{O}_4^{2-}$	0.10	Slight
$\text{SO}_3^{2-}$	0.10	The reaction is completely inhibited
	$2 \cdot 10^{-4}$	Considerable decrease
$\text{HPO}_4^{2-}$	0.10	Slight
$\text{S}_2\text{O}_8^{2-}$	0.01	The reaction is completely inhibited
	$1 \cdot 10^{-3}$	The reaction is completely inhibited
	$1 \cdot 10^{-4}$	Strong decrease

## SUMMARY

A very selective spot test for gold has been developed based on the effect of gold(III) on the decomposition of ferrocyanide in the presence of nitrosobenzene. The sensitivity is 0.05  $\mu\text{g}/\text{drop}$  and the concentration limit 1 : 1,000,000. Mercury and silver react analogously, but can be masked with iodide, which also improves the sensitivity. Interferences of iron(III), copper(II) and uranyl ion can be avoided.

## RÉSUMÉ

Les auteurs ont mis au point une nouvelle réaction à la touche, sensible et sélective, pour l'identification de l'or. Elle est basée sur l'influence de  $\text{Au}^{+3}$  sur la décomposition des ferrocyanures, en présence de nitrosobenzène.

## ZUSAMMENFASSUNG

Es wird eine neue Tüpfelprobe für Gold beschrieben. Die empfindliche und selektive Reaktion beruht auf dem Einfluss von  $\text{Au}^{+3}$  auf die Zersetzung von Ferrocyanid in Gegenwart von Nitrosobenzol.

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THE INFLUENCE OF ACIDS AND SALTS ON THE USE OF  
CHROMOUS CHLORIDE AS A REDUCING TITRANT

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The importance of chromous chloride as a reducing titrant for the determination of metal ions is well known. The early work of ZINTL *et al.*<sup>1</sup> consisted mainly of determining the optimum conditions whereby chromous solutions could be successfully used for the determination of mercury(II), iron(III), silver(I) and gold(III). In recent years, MURAKI<sup>2</sup> and LINGANE AND NIEDRACH<sup>3</sup> have carried out studies on similar lines. LINGANE AND NIEDRACH used a platinum indicator electrode to study the reduction of quadri- and hexavalent selenium and tellurium with chromous ions, and attempted to find conditions of acidity under which accurate results could be obtained.

Although many workers have employed the chromous–chromic system in potentiometric work, very little has been done to investigate systematically the factors influencing such titrations. This communication deals with our investigations on potentiometric titration of copper sulphate with chromous chloride solution in presence of various acids and their salts. The probable role of hydrogen and chloride ions is also discussed.

## EXPERIMENTAL

*Chromous chloride solution*

The behaviour and stability of chromous solutions are likely to vary from sample to sample depending on the mode of preparation, the presence of foreign ions and the method of storage; a special method was therefore used for the preparation of the solution free from foreign ions, and for its storage. The method recommended by BALTHIS AND BAILAR<sup>4</sup> with a slight modification was followed. Chromic chloride was reduced with zinc and hydrochloric acid and the chromous chloride thus obtained was converted to chromous acetate by adding sodium acetate, an inert atmosphere being maintained. The acetate was then washed free of zinc salt (by suction device under CO<sub>2</sub> atmosphere) and dissolved in air-free, ice-cold 1.0 *N* hydrochloric acid. The solution so obtained contained an equivalent amount of acetic acid as a product of the reaction. To obtain a completely 'neutral' solution twice the volume of freshly distilled ice-cold alcohol was added when a copious precipitate of chromous chloride separated. It was filtered by suction and repeatedly washed with ice-cold 90% alcohol. The precipitate was then dissolved in the required amount of ice-cold water to give the deep blue chromous chloride solution free from any foreign ion. This method gave the purest aqueous solution, which was stored in a STONE<sup>5</sup> type bottle and remained stable for months.

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*Strength of chromous chloride solution*

The chromous chloride solution must be standardized regularly; a quick and accurate method was evolved. 5.0 ml of 0.1 *N* potassium permanganate acidified with 15.0 ml of 2 *N* sulphuric acid was transferred to a 100-ml beaker and covered with a layer (about 0.5 cm thick) of kerosene. 2.0 ml of chromous chloride solution was then transferred to the permanganate keeping the tip of the burette under the layer of kerosene. The mixture was stirred and set aside for 5 min to ensure complete oxidation of chromium(II), and the excess of permanganate was titrated potentiometrically with 0.05 *N* ferrous sulphate (Fig. 1). For estimating total chromium the method adopted by FORBES AND RICHTER<sup>6</sup> was employed.

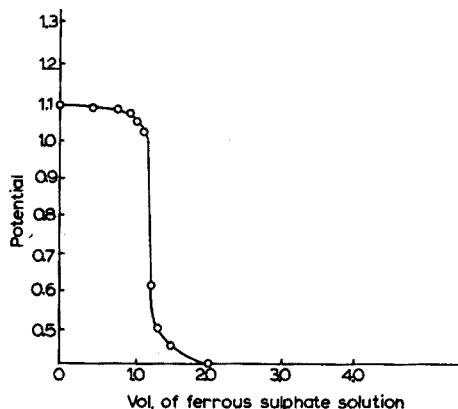


Fig. 1. Standardisation of chromous chloride solution.

## PROCEDURE

A Tinsley Potentiometer type 3387B with lamp-scale, galvanometer arrangement was used for potential measurements. The electrodes used were a smooth platinum wire and Beckman Fibre type calomel electrode. 5.0 ml of 0.1 *N* copper sulphate solution was placed in an air-tight cell. Varying amounts of the reagents were added and the total volume was made up to 30.0 ml with the requisite amount of air-free water. The air in the cell was then completely displaced by passing a rapid current of nitrogen for about 15 min. The contents in the cell were then titrated with chromous chloride using the micro-burette attachment. Some typical titration curves are given in Fig. 2 and the observations are summarised in Table I.

## DISCUSSION

The second break of the titration curves was usually pronounced, but sharp breaks in the first stage were only obtained in presence of hydrochloric acid and potassium chloride separately or together. At high concentrations of this acid and salt the white precipitate of cuprous chloride did not appear and sharp breaks were obtained in the first stage of reduction. With sulphuric acid, the second break was fairly sharp, but with the sodium salt or a mixture of the acid and the salt, typical titration curves were not obtained. In a large number of experiments it was found that although the chloride ions (also from potassium or ammonium chloride) gave typical titration

TABLE I

Strength of  $\text{CrCl}_2$  solution = 0.2739 *M* (permanganate method);  $\text{Cr}^{+3}/\text{Cr}^{+2} = 0.1508$ ; temp. =  $25 \pm 0.1^\circ$

Reagent	Conc. of the reagent	Strength of $\text{CrCl}_2$ from		Nature of curve	
		1st break	2nd break	1st break	2nd break
<i>temp. = 25 ± 0.1°</i>					
1. ('Neutral' solution)		0.2858	0.2739	F.S.	S.
2. HCl	0.1 <i>N</i>	0.2809	0.2739	S.F.	S.
HCl	0.2 <i>N</i>	0.2777	0.2688	F.S.	S.
HCl	0.5 <i>N</i>	0.2739	0.2667	S.	S.
HCl	1.0 <i>N</i>	0.2739	0.2667	S.	S.
HCl	2.0 <i>N</i>	0.2748	0.2631	S.	S.F.
3. KCl	0.1 <i>N</i>	0.2809	0.2777	F.	S.
KCl	0.2 <i>N</i>	0.2809	0.2739	F.S.	S.
KCl	0.5 <i>N</i>	0.2777	0.2681	S.	S.
KCl	1.0 <i>N</i>	0.2777	0.2667	S.	S.
KCl	1.5 <i>N</i>	0.2732	0.2631	S.	S.
KCl	2.0 <i>N</i>	0.2777	0.2613	S.	S.
4. $\text{H}_2\text{SO}_4$	0.1 <i>N</i>	0.2703	0.2739	Q.F.	F.S.
$\text{H}_2\text{SO}_4$	0.2 <i>N</i>	0.2732	0.2739	Q.F.	S.
$\text{H}_2\text{SO}_4$	0.5 <i>N</i>	(0.2703)	0.2703	Q.F.	S.
$\text{H}_2\text{SO}_4$	1.0 <i>N</i>	(0.2631)	0.2683	Q.F.	S.
$\text{H}_2\text{SO}_4$	2.0 <i>N</i>	(0.2631)	0.2681	Q.F.	S.
5. $\text{Na}_2\text{SO}_4$	0.1 <i>N</i>	(0.2631)	0.2717	F.	S.
$\text{Na}_2\text{SO}_4$	0.5 <i>N</i>	—	0.2703	Q.F.	S.
$\text{Na}_2\text{SO}_4$	1.0 <i>N</i>	—	0.2717	Q.F.	S.
$\text{Na}_2\text{SO}_4$	1.5 <i>N</i>	—	0.2703	Q.F.	S.
6. HAc	0.1 <i>N</i>	(0.2631)	0.2703	F.S.	S.
HAc	0.5 <i>N</i>	(0.2564)	0.2717	F.	S.
HAc	1.0 <i>N</i>	—	0.2703	Q.F.	S.
HAc	2.0 <i>N</i>	—	0.2718	Q.F.	F.S.
7. NaAc	0.1 <i>N</i>	—	(0.2597)	Q.F.	F.
NaAc	0.2 <i>N</i>	—	—	Q.F.	Q.F.
8. KCl + HCl	0.1 <i>N</i> , 0.1 <i>N</i>	0.2758	0.2739	F.S.	S.
KCl + HCl	1.0 <i>N</i> , 0.1 <i>N</i>	0.2748	0.2667	S.	S.
KCl + HCl	0.1 <i>N</i> , 1.0 <i>N</i>	0.2732	0.2667	Q.F.	S.
KCl + HCl	1.0 <i>N</i> , 1.0 <i>N</i>	0.2748	0.2631	Q.S.	S.
9. $\text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$	0.1 <i>N</i> , 0.1 <i>N</i>	0.2631	0.2703	F.	S.
$\text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$	0.1 <i>N</i> , 1.0 <i>N</i>	0.2564	0.2739	Q.F.	S.
$\text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$	1.0 <i>N</i> , 0.1 <i>N</i>	(0.2564)	0.2739	Q.F.	S.
$\text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$	1.0 <i>N</i> , 0.7 <i>N</i>	—	—	Q.F.	S.
10. HAc + NaAc	0.1 <i>N</i> , 0.1 <i>N</i>	0.2564	0.2703	Q.F.	S.
HAc + NaAc	1.0 <i>N</i> , 0.1 <i>N</i>	—	(0.2607)	Q.F.	F.
11. KCl + HAc	0.1 <i>N</i> , 0.1 <i>N</i>	0.2631	0.2703	S.	S.
KCl + HAc	1.5 <i>N</i> , 0.5 <i>N</i>	0.2739	0.2631	S.	S.
KCl + HAc	0.5 <i>N</i> , 1.5 <i>N</i>	0.2703	0.2667	S.	S.
KCl + HAc	1.0 <i>N</i> , 1.0 <i>N</i>	0.2703	0.2564	S.	S.

TABLE I (continued)

Reagent	Conc. of the reagent	Strength of CrCl <sub>2</sub> from		Nature of curve <sup>a</sup>	
		1st break	2nd break	1st break	2nd break
<i>temp. = 55 ± 0.1°</i>					
1. ('Neutral' solution)		0.2703	0.2703	F.	S.
2. HCl	0.5 N	0.2703	0.2667	S.	S.
	1.0 N	0.2703	0.2667	S.	S.
	2.0 N	0.2667	0.2603	S.	S.
3. KCl	0.5 N	0.2777	0.2703	F.	S.
	1.0 N	0.2703	0.2703	F.S.	S.
	2.0 N	0.2703	0.2597	F.S.	F.S.
4. KCl + HCl	1.0 N, 1.0 N	0.2703	0.2564	Q.S.	F.S.
5. H <sub>2</sub> SO <sub>4</sub>	0.5 N	(0.2564)	0.2631	Q.F.	S.
	1.5 N	—	0.2667	Q.F.	S.
6. HAc	1.5 N	(0.2703)	0.2667	F.	F.
7. H <sub>2</sub> SO <sub>4</sub> + Na <sub>2</sub> SO <sub>4</sub>	1.0 N, 1.0 N	(0.2500)	0.2703	F.	F.
8. KCl + HAc	0.5 N, 1.0 N	0.2732	0.2703	S.	S.
	1.0 N, 1.0 N	0.2732	0.2739	Q.S.	S.
9. NH <sub>4</sub> Cl	0.5 N	0.2703	0.2667	S.	S.
	1.5 N	0.2732	0.2631	S.	F.
10. NH <sub>4</sub> Cl + HAc	0.5 N, 1.0 N	0.2703	0.2667	F.	S.
	1.0 N, 1.0 N	0.2732	0.2631	F.	S.

<sup>a</sup> F = flat; S = sharp; Q.F. = quite flat; Q.S. = quite sharp; S.F. = slightly flat; F.S. = fairly sharp.

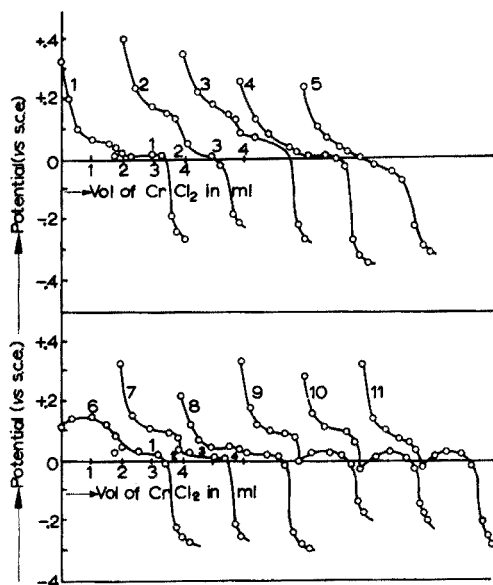
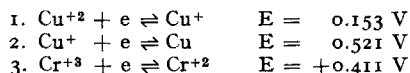


Fig. 2. Titration curves of CuSO<sub>4</sub> against CrCl<sub>2</sub> in presence of: at 25°, (1) neutral medium; (2) 1 N HCl; (3) 1 N KCl; (4) 1 N H<sub>2</sub>SO<sub>4</sub>; (5) 1 N Na<sub>2</sub>SO<sub>4</sub>; (6) 1 N HAc; (7) 1 N KCl + 1 N HCl; (8) 1 N H<sub>2</sub>SO<sub>4</sub> + 1 N K<sub>2</sub>SO<sub>4</sub>, at 55°, (9) 1 N HCl; (10) 1 N HCl + 1 N KCl; (11) 1 N NH<sub>4</sub>Cl.

curves with two breaks, the presence of acids was highly desirable since this helped in the rapid attainment of a steady electrode potential.

The potentials of the various systems involved are:



The equivalence potential for system (a), first break =  $(-0.153 + 0.140)/2 = 0.1285 \text{ V}$  and for system (b), second break =  $(-0.521 + 0.410)/2 = -0.055 \text{ V}$ .

Although the theoretical values of the equivalence potentials at the two stages of the reaction were not strictly realised, the deviations did not affect the determination of the strength of the solution. Results coinciding with the actual value (0.2739 *M* as determined by the permanganate method) were achieved by considering the second stage for lower concentrations of HCl or KCl or both, while higher concentrations of these electrolytes gave concordant values even at the first stage of reduction. With the other electrolytes, only in a few scattered cases (low concentrations of  $\text{H}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  and KCl at the first stage, KCl and at  $58^\circ$ , and  $\text{NH}_4\text{Cl}$  and HAc) were the values obtained approximately the same as the actual concentration of chromous chloride solution. Titrations at high temperatures (as recommended by other workers) did not appear to be preferable; at high temperatures the values obtained were lower than the actual values even though the high temperature helped in the rapid attainment of equilibrium.

Since the reaction  $\text{Cr}^{+2} + \text{Cu}^{+2} \rightleftharpoons \text{Cu}^+ + \text{Cr}^{+3}$  involves two unstable ions, the necessary condition for carrying out the titration appears to be to stabilise both of them. This is possible with complexing agents<sup>6,7</sup> such as KCl, HCl,  $\text{NH}_4\text{Cl}$  etc.; better results can, however, be achieved when sufficient hydrogen ions are also added to prevent hydrolysis.

In determining conditions for the use of chromous chloride in oxidation-reduction titrations, it is necessary to consider not only factors influencing the stability of chromous ions but also the nature of the metal ion undergoing reduction. Addition of HCl or KCl would not only influence the stability of the chromous ions but would also form complexes<sup>8</sup> such as  $\text{K}_2\text{CuCl}_3$ ,  $\text{K}_3\text{CuCl}_4$ ,  $\text{H}_2\text{CuCl}_3$ , etc. with copper(I). It is highly probable that favourable conditions for the appearance of the first break are achieved by the formation of these complexes. An interesting and new aspect in these titrations is the role of ammonium chloride, which was found to be quite useful in the titrations. Results on the behaviour of chromium(II) and (III) at the dropping mercury electrode confirm this<sup>9</sup>; the anodic half wave potential for chromium(II) in ammonium chloride was higher than that in hydrochloric acid so that ammonium ions exerted a greater influence than hydrogen ions in determining the nature of the reaction.

#### ACKNOWLEDGEMENT

Thanks are due to Prof. M. O. FAROOQ, lately Head of the Chemistry Department, for providing facilities.

#### SUMMARY

The potentiometric titration of copper sulphate with chromous chloride solution is studied in presence of varying concentrations of acids and salts. Chloride ions are essential and hydrogen ions desirable. High temperatures are unsuitable.



## RÉSUMÉ

Les auteurs ont effectué une étude sur l'influence d'acides et de divers sels sur le comportement du sulfate de cuivre, lors de titrages potentiométriques au moyen de chlorure de chrome(II).

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über den Einfluss von Säuren und verschiedener Salze bei der potentiometrischen Titration von Kupfersulfat mit Chrom-(II)-chlorid.

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*Anal. Chim. Acta*, 23 (1960) 518-523

## DOSAGE DIRECT DE CALCIUM ET DE MAGNÉSIUM EN PRÉSENCE DE FER, ALUMINIUM ET TITANE PAR LE SEL DISODIQUÉ DE L'ACIDE ÉTHYLÈNEDIAMINÉTÉTRACÉTIQUE (EDTA)

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(Reçu le 13 mai 1960)

## INTRODUCTION

Les dosages du calcium et du magnésium à l'aide de réactifs modernes, en passe de devenir „classiques”, tels que le complexon III ont fait l'objet de très nombreuses publications examinées notamment dans les ouvrages de base de PRIBIL, SCHWARZENBACH ET FLASCHKA<sup>1-3</sup>.

Parmi les avantages de cette méthode il faut citer: une certaine spécificité, une grande rapidité, une bonne sensibilité et précision.

Toutefois, dans le cadre des analyses de ces deux éléments, dans les produits tels que les silicates naturels (argiles, kaolins, feldspath, etc. . .) ou complexes (émaux, frites, etc. . .), ce dosage devient nettement plus long car il nécessite: d'une part la séparation préalable de l'aluminium, du fer, du titane et éventuellement du manganèse et du chrome, qui, comme on le sait, gênent ce dosage et, d'autre part, l'élimination des sels ammoniacaux formés au cours de cette opération. La précipitation des hydroxydes des éléments cités par les méthodes classiques à l'ammoniaque<sup>4,5</sup>, peut en-

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traîner une certaine absorption du calcium sur le précipité formé et apporter dans le cas de l'analyse de faibles teneurs de calcium, un élément d'erreur. La séparation plus sélective des hydroxydes par l'ammoniaque -urée, préconisée par le C.O.B.E.A.<sup>6</sup>, n'entraîne pratiquement pas le calcium comme nous avons pu le constater sur des solutions synthétiques<sup>7</sup>. Cependant, même dans ce cas, les fortes quantités d'urée et d'ammoniaque introduites dans le milieu, obligent l'analyste à procéder à leur élimination toujours longue et fastidieuse.

Cet état de choses nous a incités à rechercher un moyen, permettant les dosages de calcium et magnésium en présence d'aluminium, fer et titane aux teneurs moyennes de ces éléments généralement présentes dans les silicates. Des techniques existent pour le masquage de l'aluminium et du fer par la triéthanolamine<sup>1,2,8,9</sup> et des métaux lourds par le cyanure de potassium<sup>10</sup>.

L'action de la triéthanolamine est efficace en milieu fortement alcalin ( $\text{pH} \geq 12$ ) et convient bien pour le dosage du calcium; en présence de fer la coloration brune formée disparaît lors de l'addition de la solution potassique. Dans le cas du dosage du magnésium la nécessité de travailler à  $\text{pH} 10$ , pour éviter la précipitation de la magnésie en milieu alcalin plus élevé, diminue considérablement l'effet protecteur de ce réactif. En outre, le fer présent dans le milieu analysé perturbe par son effet oxydant le virage du noir ériochrome T, employé comme indicateur<sup>8</sup>.

Le cyanure de potassium forme avec certains cations des groupes analytiques I et II des complexes très stables, mais, pour obtenir le masquage de ces cations, il est nécessaire d'utiliser un excès de réactif, ce qui rend cette technique difficilement utilisable. En effet, d'une part le cyanure en forte concentration influe sur le  $\text{pH}$  (effet d'hydrolyse) et d'autre part, les complexes cyanurés, étant colorés, peuvent gêner la perception du virage des indicateurs. Enfin, l'inconvénient des manipulations systématiques d'importantes quantités de cyanure de potassium se passe de commentaires.

Pour ces multiples raisons, nous avons été amenés à approfondir ce problème, car les moyens cités ne présentaient qu'une solution partielle dans notre cas.

#### PARTIE EXPÉRIMENTALE

Nous envisagerons deux cas: celui du calcium en présence de l'aluminium, du fer et du titane et celui de la somme de calcium + magnésium en présence de ces trois éléments.

##### *Dosage direct de calcium*

Nous avons, d'abord, vérifié l'action masquante de la triéthanolamine sur des solutions à différentes concentrations d'aluminium, fer et titane, à côté du calcium et déterminé les teneurs limites tolérables de ces trois éléments, soit, respectivement, 50 mg, 50 mg et 5 mg (exprimés en oxydes:  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  et  $\text{TiO}_2$ ). Nous avons pu ainsi doser sur des silicates cet alcalino-terreux par le complexon III en présence de murexide (indicateur) et de triéthanolamine (agent masquant). Les résultats de certains de ces essais sont consignés dans le Tableau I.

Toutefois, le virage de la murexide déjà délicat à saisir dans le cas d'un dosage de calcium après séparation préalable de l'aluminium, du fer et du titane, devient encore moins perceptible lorsque la titration est effectuée d'une façon directe. Le mélange d'indicateur composé de murexide et de vert-naphtol B<sup>11</sup> n'est pas plus avantageux.

TABLEAU I

DOSAGES DE CALCIUM ET MAGNÉSIUM PAR COMPLEXOMÉTRIE SUR DES PRODUITS NATURELS

	<i>Après élimination de Fe, Ti, Al</i>		<i>En présence de Fe, Ti, Al</i>	
	CaO %	MgO %	CaO %	MgO %
Schiste	2.24	1.52	2.32	1.60
Granit	2.40	0.61	2.52	0.60
Granit	1.04	0.04	1.12	traces
Granit	0.22	1.76	0.20	1.85
Grès	2.35	1.18	2.34	1.20
Argile	0.53	0.42	0.53	0.40
Ciment	63.7		64.00	
Dolomie	35.70	16.17	36.00	16.07
Calcaire	56.00		56.02	traces
Feldspath	0.35	0.08	0.30	traces
Argile marneuse	20.07	1.12	19.85	1.19
Feldspath	2.00	1.34	1.90	1.33
Feldspath	2.24	traces	2.10	traces
Argile marneuse	23.87	1.51	23.21	1.35

Un nouvel indicateur, la calcéine permet d'effectuer de très bons dosages du calcium par le complexon III à pH 12, le virage de la teinte vert-jaune à la teinte rose est beaucoup plus net que celui de la murexide. Toutefois, nous avons constaté, ainsi que l'a fait THOMPSON<sup>12</sup>, que la calcéine en présence de triéthanolamine ne vire pas au moment de la fixation des ions Ca<sup>+2</sup> par l'EDTA. Ce fait a conduit cet auteur à abandonner l'emploi de la calcéine. Nous avons trouvé qu'une addition d'acide tartrique au milieu analytique permettait de percevoir très nettement le virage de cet indicateur. Dans ce cas la teneur limite d'aluminium que l'on peut tolérer dans la solution à analyser se trouve portée à 150 mg, exprimés en oxyde, celles de titane et fer étant respectivement 5 mg et 10 mg (en oxyde de l'élément).

L'acide tartrique donne avec l'aluminium, le fer et le titane des complexes qui sont caractérisés par leur insensibilité vis-à-vis des alcalins. Les solutions potassique ou sodique loin de précipiter les hydroxydes stabilisent les complexes formés dans ce cas.

A titre d'exemple, nous donnons dans les Tableaux II et III des valeurs pour Ca trouvées sur des solutions synthétiques et sur des ciments, suivant le mode opératoire qui sera décrit en annexe.

#### *Dosage du magnésium en présence de Al, Fe et Ti*

Nous avons signalé dans l'introduction les difficultés qui se présentent dans le cas du dosage du magnésium, effectué dans un milieu contenant Al, Fe et Ti. Bien entendu, lorsque le calcium accompagne le magnésium, c'est la somme Ca + Mg qui est dosée suivant les conditions opératoires définies pour le magnésium seul. Différentes techniques ont été essayées parmi lesquelles nous citons: la réduction du fer par l'acide ascorbique, le masquage par le cyanure de potassium<sup>1,2,8,10,11</sup>, la formation de complexe par l'EDTA à pH 4-4.5 et l'emploi de différents indicateurs<sup>13,14</sup>. Dans tous les cas les résultats trouvés ont été assez décevants.

La seule méthode qui nous a donné des résultats satisfaisants, dans le cas des silicates, a été le dosage du magnésium en présence de triéthanolamine, d'acide tartrique et de noir ériochrome T (indicateur). La présence d'acide tartrique permet d'effectuer

le dosage dans une zone de pH élevé. La magnésie ne précipite pas, le fer se trouve complexé, reste en solution et n'entre pas en réaction avec l'EDTA. L'influence de la triéthanolamine en est d'autant plus efficace, l'aluminium, le fer et le titane ne sont plus gênants jusqu'à respectivement 50 mg, 10 mg et 10 mg exprimés en oxydes.

Le mode opératoire de ce dosage se trouve décrit en annexe et quelques résultats sont donnés dans les Tableaux I et IV.

#### DISCUSSIONS DES RÉSULTATS

Des essais effectués sur des solutions synthétiques et sur des silicates très différents par leur structure minéralogique et leurs compositions tels que schistes, marnes, argiles, feldspaths, kaolins, granits, etc. . . montrent la possibilité d'un dosage direct de calcium en présence d'aluminium, fer et titane. Les résultats trouvés dans ce cas sont très voisins de ceux obtenus par dosage complexométrique après séparation des hydroxydes.

En déterminant directement le calcium sur une partie aliquote de la solution provenant de l'attaque sulfo-fluorhydrique de la matière silico-alumineuse, on supprime très certainement l'erreur possible, due à la perte d'une certaine quantité de cet élément adsorbé sur le précipité colloïdal des hydroxydes d'aluminium, de fer et de titane, obtenu par le procédé classique à l'ammoniaque. D'autre part, on diminue dans le cas d'un dosage direct la quantité d'impuretés introduites par les réactifs employés au cours d'une telle précipitation. Certains dosages à blanc donnent jusqu'à 0.5% de CaO, apportés de la sorte.

Ces quelques considérations formulées pour le calcium sont également valables pour le magnésium, réserve faite toutefois pour le taux de contamination généralement

TABLEAU II

DOSAGE DIRECT DU CALCIUM SUR SOLUTION SYNTHÉTIQUE EN MILIEU TARTRIQUE  
AVEC LA CALCÉINE (INDICATEUR) EN PRÉSENCE DE Al, Fe ET Ti

Complexon 0.05 M				CaO mg trouvé		Moyenne
CaO mg	Al <sub>2</sub> O <sub>3</sub> mg	Fe <sub>2</sub> O <sub>3</sub> mg	TiO <sub>2</sub> mg			
5.32	150			5.32	5.32	5.32
2.66	70	10	5	2.66	2.66	2.66
1.33	70	10	5	1.40	1.40	1.40
0.532	70	10	5	0.56	0.56	0.56
0.266	70	10	5	non dosable avec complexon 0.05 M		
Complexon 0.01 M				CaO mg trouvé		Moyenne
CaO mg	Al <sub>2</sub> O <sub>3</sub> mg	Fe <sub>2</sub> O <sub>3</sub> mg	TiO <sub>2</sub> mg			
2.66	70	10	5	2.404	2.52	2.52
1.33	70	10	5	1.26	1.26	1.26
0.532	70	10	5	0.61	0.61	0.61
0.266	70	10	5	0.28	0.28	0.28
2.66	70	5	2	2.57	2.57	2.57
1.33	70	5	2	1.28	1.31	1.31
0.532	70	5	2	0.67	0.61	0.61
0.266	70	5	2	0.28	0.28	0.28
2.66	70	2	1	2.604	2.604	2.604
1.33	70	2	1	1.316	1.316	1.28
0.532	70	2	1	0.56	0.56	0.56
0.266	70	2	1	0.28	0.25	0.28

TABLEAU III  
DOSAGE DIRECT DU CALCIUM EN MILIEU TARTRIQUE DANS LES CIMENTS

Echantillons analysés	CaO %				
	Gravimétrie	Complexon III			
Ciment type A (en présence de SiO <sub>2</sub> )		65.90	65.57	65.57	65.90
Ciment type A (après séparation de SiO <sub>2</sub> )	65.00	66.10	66.02	66.10	66.10
Ciment type B (en présence de SiO <sub>2</sub> )		63.84	63.84	63.84	63.84
Ciment type B (après séparation de SiO <sub>2</sub> )	64.00	64.40	64.40	64.40	
Ciment type L (après séparation de SiO <sub>2</sub> )	45.30	45.80	45.80	45.80	

bien plus faible apportée par les réactifs pour ce dernier élément. Il est superflu de mettre en évidence les avantages de la rapidité de la méthode. Le gain de temps obtenu par le dosage direct est considérable; il se chiffre par de nombreuses heures de travail. La sensibilité, les limites de détection et l'ordre de grandeur de la précision, restent les mêmes que ceux des analyses complexométriques en général. Les essais comparatifs effectués sur le calcium avec la murexide et la calcéine sont nettement plus favorables pour ce dernier réactif. La netteté du virage obtenu est assez remarquable, aussi bien en absence qu'en présence des éléments „gênants”: Al, Fe, Ti.

Pour le magnésium, signalons que le virage déjà quelque peu délicat à percevoir en absence des hydroxydes le devient encore plus lors du dosage direct effectué selon la méthode décrite dans ce travail.

TABLEAU IV  
DOSAGE DIRECT DE MgO EN MILIEU TARTRIQUE EN PRÉSENCE DE Al, Fe ET Ti  
(sur solutions synthétiques)  
Complexon 0.05 M

MgO mg	Al <sub>2</sub> O <sub>3</sub> mg	Fe <sub>2</sub> O <sub>3</sub> mg	TiO <sub>2</sub> mg	MgO mg trouvé			
8.8	50	10	5	8.8	8.6	8.8	8.8
4.4	50	10	5	4.4	4.4	4.4	4.4
2.2	50	10	5	2.2	2.2	2	2.2
1.1	50	10	5	1	1	1.1	1
0.44	50	10	5	0.43	0.43	0.43	0.43
0.22	50	10	5	0.21	0.21	0.21	0.21

Nous attirons l'attention du lecteur sur cet inconvénient, tout en lui signalant que des études sont en cours pour trouver une amélioration à ce manque de sensibilité. A cet égard, l'*o*-cresolphtaléine complexone semble donner un virage plus net (violet → incolore) que celui observé avec le noir ériochrome T et peut être utilisé à sa place.

#### CONCLUSION

L'analyse du calcium et du magnésium dans des produits complexes, tels que les silicates, effectuée sur une attaque sulfo-fluorhydrique de la matière au cours de laquelle la silice est éliminée par volatilisation, nécessite la séparation préalable de

l'aluminium, du fer, du titane et, éventuellement du manganèse et du chrome, puis, des sels ammoniacaux formés au cours de cette opération.

Différentes techniques examinées en vue de doser le calcium et le magnésium en présence d'aluminium, fer et titane, nous ont donné des résultats partiellement satisfaisants. La méthode trouvée apporte des avantages certains dans le cas du dosage direct du calcium et malgré certains inconvénients constatés pour le dosage du magnésium, réunit de nouvelles conditions d'analyse.

Cette technique est basée sur l'utilisation de l'acide tartrique et de la triéthanolamine (binôme complexifiant), de la calcéine et du noir ériochrome T (indicateurs), et du complexon III (réactif titrant).

#### ANNEXE

##### *Mode opératoire*

##### *Principe*

Les sels de Al, Fe et Ti sont masqués par l'acide tartrique et la triéthanolamine et de ce fait, Ca et Mg forment seuls des complexes avec l'EDTA. La fin de ces réactions est décelée par des indicateurs appropriés qui changent de coloration dès la disparition des ions  $\text{Ca}^{+2}$  et  $\text{Mg}^{+2}$  de la solution analysée.

##### *Réactifs utilisés*

Acide sulfurique,  $d = 1.83$ ; Acide fluorhydrique à 40%; Acide chlorhydrique,  $d = 1.19$ ; Acide tartrique à 2%; Solution d'hydroxyde de potassium environ 4 N: Dissoudre 228 g d'hydroxyde de potassium dans 1000 ml d'eau distillée; Indicateur à base de calcéine: broyer 0.100 g de calcéine dans 100 g de chlorure de sodium; Solution de complexon III (dihydrate du sel disodique de l'acide éthylène diamine tétraacétique) exactement 0.01 M: Peser 3.721 g de complexon III, les dissoudre dans de l'eau distillée, ajuster à 1000 ml; Solution de complexon III, 0.05 M: Peser 18.605 g de complexon III, les dissoudre dans de l'eau distillée ajuster à 1000 ml; Solution exacte à 1 g/l CaO: Peser 1.7846 g de carbonate de calcium, le dissoudre dans de l'eau distillée additionnée de 3 à 5 ml de HCl,  $d = 1.19$ . Compléter à 1000 ml; Solution à 1 g/l MgO: Peser 6.1160 g de sulfate de magnésium  $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$ , le dissoudre avec de l'eau distillée, ajuster à 1000 ml. Note: On peut utiliser également le nitrate ou le chlorure de magnésium); Triéthanolamine; Ammoniaque,  $d = 0.92$ ; Noir ériochrome T; Chlorure d'ammonium; Indicateur à base de noir ériochrome T: broyer 0.300 g de noir ériochrome avec 100 g de  $\text{NH}_4\text{Cl}$ .

##### *Dosage du calcium*

##### *Pratique du dosage*

A la solution chlorhydrique à doser qui doit être amenée à un volume d'environ 50 ml et contenir plus de 0.30 mg de CaO, ajouter: 10 ml de solution d'acide tartrique à 2%; 10 ml d'hydroxyde de potassium et environ 100 mg d'indicateur calcéine. La solution prend une coloration jaune-vert.

Titrer avec une solution étalon de complexon III, 0.01 M ou 0.05 M suivant les quantités de calcium à doser, jusqu'à virage de la coloration au *rose stable*.

*Remarques*

Dans le cas d'une faible teneur en Ca (moins de 0,30 mg dans la solution à doser), il est nécessaire d'ajouter un certain volume de solution à 1 g/l CaO qui sera déduit du résultat obtenu.

Moins il y a de Ti et Fe dans la solution plus le virage est net; il est bon par conséquent de faire en sorte que les quantités présentes de ces deux éléments soient inférieures respectivement à 5 mg (Ti) et 10 mg (Fe) dans la solution à doser.

*Calcul*

1 ml de solution de complexon 0,05 M correspond à 2,804 mg de CaO. 1 ml de solution de complexon 0,01 M correspond à 0,561 mg de CaO.

*Dosage de l'ensemble calcium et magnésium**Pratique du dosage*

A la solution chlorhydrique à doser qui doit occuper un volume d'environ 50 ml et contenir plus de 1 mg de MgO, ajouter: 10 ml de solution d'acide tartrique à 2%; 10 à 15 ml de triéthanolamine; mélanger avec soin et ajouter encore, 10 ml d'ammoniaque et environ 1 g d'indicateur noir ériochrome T. La solution prend une coloration rouge violet. Titrer avec le complexon 0,05 M jusqu'à virage au bleu violet. Les gouttes de complexon tombant dans la solution y forment des filets bleus au début du dosage, puis deviennent blanches lorsque le magnésium est complexé.

*Remarques*

Il est conseillé de réaliser le dosage rapidement à l'aide d'une burette au 1/20 de ml, car on utilise afin de bien percevoir le virage le complexon 0,05 M dont chaque goutte correspond à une quantité importante de MgO. Dans le cas de faibles quantités de MgO (< 5 mg), il est nécessaire d'ajouter 5 ml de solution à 1 g/l de MgO, et d'en tenir compte dans le calcul.

*Calcul de la teneur en magnésium*

1 ml de complexon 0,05 M correspond à 2,016 mg de MgO.

*Application à l'analyse des silicates**Attaque du produit*

On opère sur le produit broyé, passé au tamis 21 AFNOR (mailles de 0,1 mm) et séché à 110°, jusqu'à poids constant. 1 g environ est pesé sur une balance de précision au 1/10 de mg, dans une capsule de platine et soumis à l'attaque acide HF/H<sub>2</sub>SO<sub>4</sub> à la température du bain de sable: 240° environ. On répète 3 fois l'addition de HF puis on reprend le résidu sec par de l'eau distillée et 10 ml de HCl dans un bécher. On porte à l'ébullition jusqu'à dissolution complète, puis après refroidissement, on introduit en fiole jaugée de 250 ml et on ajuste au volume avec de l'eau distillée. Les dosages décrits sont effectués sur des prises aliquotes de 25 ml, soit sur 1/10 de la prise d'essai.

*Pratique du dosage*

Mode opératoire décrit pages 524 et 525.

*Remarques*

Il est possible d'opérer ces dosages sur les solutions issues d'attaques au carbonate de l'échantillon, après l'insolubilisation de la silice par HCl ou HCl-gélatine.

## RÉSUMÉ

Les dosages de calcium et de magnésium à l'aide du sel disodique de l'acide éthylène-diamine tétraacétique dans des produits tels que les silicates naturels (argiles, kaolins, feldspaths, marnes, etc. . .) ou complexes (émaux, frites) comme ils étaient pratiqués avant cette étude, étaient relativement longs car ils nécessitaient d'une part la séparation préalable de l'aluminium, fer, titane et autres métaux lourds, d'autre part, l'élimination des sels ammoniacaux formés au cours de cette opération. Dans ce travail plusieurs méthodes ont été examinées en vue de doser le calcium et le magnésium en présence de fer, titane et aluminium. Elles diffèrent, entre elles, surtout par le choix des réactifs destinés à complexifier les ions gênants. La méthode trouvée donne des résultats tout à fait comparables à ceux obtenus après séparation des éléments Al, Fe et Ti. Elle est basée sur l'utilisation de l'acide tartrique et de la triéthanolamine (binome complexifiant), de la calcéine et du noir ériochrome T (indicateur) et du complexon III (réactif titrant). Le mode opératoire détaillé de cette technique est donné en annexe.

## SUMMARY

Description of a volumetric method for the determination of Ca and Mg in the presence of Al, Fe and Ti by titration with Complexon III; tartaric acid and triethanolamine are present. Calcein and eriochrome black are used as indicators.

## ZUSAMMENFASSUNG

Beschreibung einer volumetrischen Methode zur Bestimmung von Ca und Mg neben Al, Fe und Ti durch Titration mit Komplexon III in Gegenwart von Weinsäure und Triäthanolamin und mit Calcein und Eriochromschwarz als Indikatoren.

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DIALLYLDITHIOCARBAMIDOHYDRAZINE (DALZIN) AS  
AN ANALYTICAL REAGENT  
DETERMINATION OF PALLADIUM AND ITS SEPARATION FROM  
NICKEL, ZINC AND COPPER

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Dalzin has been used for the determination and separation of a number of metals<sup>1</sup>. Further investigation has shown that palladium can be quantitatively precipitated from hot solutions by Dalzin at pH 3.1-4.5, while most of the common ions and other platinum metals remain in solution. Copper, mercury and silver interfere, but the interference of copper can be eliminated by complexing with EDTA and precipitating palladium at a pH below 4.5. Nickel and zinc can be determined in the filtrate after raising the pH as usual.

EXPERIMENTAL

Chemicals used were all of A.R. quality. A palladium solution was prepared from palladium chloride (Johnson and Matthey) and standardized gravimetrically as palladium dimethylglyoxime. pH measurements were made with Philips pH meter.

*Composition of palladium complex*

Palladium was precipitated at pH *ca.* 4 by the method given below and the precipitate was dried at 105° to constant weight. A weighed quantity was decomposed with aqua regia and evaporated several times with concentrated hydrochloric acid and the residue was taken up with this acid and diluted to 100 ml. Palladium in the solution was determined by the dimethylglyoxime method. The complex was found to have the composition Pd(C<sub>8</sub>H<sub>12</sub>N<sub>4</sub>S<sub>2</sub>) H<sub>2</sub>O (Pd. calc. 30.22%, found 29.93%).

*Determination of palladium*

The palladium chloride solution (30-60 mg Pd) was neutralised with ammonia and diluted to about 100 ml and the pH was adjusted with a freshly prepared solution of citric acid. The solution was heated on a water-bath and 25 ml of a hot alcoholic 1.0% solution of the reagent was added with constant stirring. The brick-red precipitate was allowed to settle and was filtered through a weighed sintered glass crucible. Filtrates were kept for pH determinations. The precipitate was washed with hot water and acetone, dried at 105° and weighed (Pd factor = 0.3022). The results are shown in Table I.

TABLE I

Weight of Pd compound g	Pd found g	Pd taken g	pH
0.0983	0.02971	0.03024	2.2
0.1177	0.03557	0.03629	2.7
0.1198	0.03620	0.03629	3.1
0.1998	0.06040	0.06049	3.5
0.1594	0.04818	0.04839	4.0
0.1795	0.05425	0.05444	4.5
0.1180	0.03567	0.03629	4.8
0.1775	0.05364	0.05444	5.1

*Separation of Pd-Ni and Pd-Zn*

A solution of palladium containing nickel or zinc was treated as in the above procedure. Nickel or zinc was estimated in the filtrate with the same reagent as previously described<sup>1</sup>. The results are shown in Table II.

TABLE II

Pd compound g	Pd found g	Pd taken g	Ni found g	Ni taken g	Zn found g	Zn taken
0.0998	0.03006	0.03024	0.07791	0.07801		
0.1201	0.03629	0.03629	0.02922	0.02925		
0.1396	0.04219	0.04234	0.05832	0.05850		
0.1596	0.04825	0.04839	0.04335	0.04388		
0.1795	0.05425	0.05444			0.04158	0.04175
0.1797	0.05431	0.05444			0.02487	0.02505
0.1001	0.03026	0.03024			0.04168	0.04175
0.1003	0.03032	0.03024			0.06231	0.06212

TABLE III

	Wt. of foreign ion mg	Wt. of Pd compound g	Pd found g	Pd taken g
Cu	50	0.1179	0.03562	0.03629
	100	0.1200	0.03626	0.03629
Be	50	0.1595	0.04828	0.04839
	100	0.1806	0.05458	0.05444
Mg	50	0.1398	0.04225	0.04234
	50	0.1596	0.04828	0.04839
Ca	100	0.1795	0.05425	0.05444
	200	0.1003	0.03032	0.03024
Ba	100	0.1003	0.03032	0.03024
	200	0.1003	0.03032	0.03024
Sr	100	0.1004	0.03034	0.03035
	200	0.1005	0.03037	0.03038
Th	25	0.1795	0.05425	0.05444
	50	0.1795	0.05425	0.05444
Ce	25	0.1794	0.05423	0.05444
	50	0.1803	0.05446	0.05446
Mn	25	0.1808	0.05462	0.05444
	50	0.1792	0.05416	0.05444

*Determination in presence of various ions*

Solutions of palladium containing other ions were treated as above. Copper was kept in solution with the aid of EDTA. The ions studied are given in Table III.

## SUMMARY

Palladium is precipitated quantitatively by Dalzin at pH *ca.* 4, and can be determined. It is separated from nickel and zinc which can be determined in the filtrate with the same reagent.

## RÉSUMÉ

Les auteurs ont mis au point une méthode de dosage gravimétrique du palladium au moyen de diallyldithiocarbamido-hydrazine ("Dalzine"); il est possible d'effectuer une séparation d'avec Ni, Zn et Cu.

## ZUSAMMENFASSUNG

Beschreibung einer gravimetrischen Bestimmung von Palladium mit Hilfe von Diallyldithiocarbamido-hydrazin mit Angaben über Trennungen von anderen Metallen.

## REFERENCE

<sup>1</sup> N. K. DUTT AND K. P. SEN SARMA, *Anal. Chim. Acta*, 15 (1956) 21, 102.

*Anal. Chim. Acta*, 23 (1960) 531-533

## THE GRAVIMETRIC DETERMINATION OF CADMIUM WITH THE SODIUM SALT OF 1-PHENYL-TETRAZOLINE-5-THIONE

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The acid, 1-phenyl-tetrazoline-5-thione, has the structure indicated in Fig. 1. Structure II has been proposed as the enolized form of structure I<sup>1,2</sup>. Infrared absorption data, however, have shown that I is the preferred structure of the compound and that the thiol form is not present<sup>3</sup>. Investigations by Lieber\* and his associates have shown

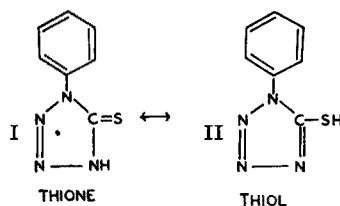


Fig. 1. 1-Phenyl-tetrazoline-5-thione.

that the 1-tetrazoline thionyl group is electron withdrawing and that the hydrogen residing on the nitrogen atom at position four of the heterocyclic ring is acidic. The

\* Our attention was called to this compound by Professor Eugene Lieber of Roosevelt University.

$pK_a$  of this hydrogen is 3.65 at 25°. It is completely dissociated in 0.1 *N* sodium hydroxide and even in a buffered solution of pH 7.5, the dissociation is nearly complete<sup>4</sup>. Thus the compound readily forms salts. The sodium salt has been used as the reagent in our studies.

#### *Reagent preparation*

The 1-phenyl-tetrazoline-5-thione is easily prepared by refluxing a mixture of phenyl isothiocyanate and sodium azide, at a mole ratio of 1 : 1.5, in water (100 ml of water per 0.1 mole isothiocyanate) for four hours. The resulting mixture is extracted with ether to remove the unreacted phenyl isothiocyanate and is then acidified with hydrochloric acid, precipitating the tetrazoline compound from solution. The product is collected on filter paper, washed with cold water and recrystallized from hot water, giving white needles melting at 149°–150°<sup>5</sup>.

The sodium salt of the tetrazoline compound is prepared by dissolving the acid form in 20% sodium hydroxide solution. The resulting solution is evaporated to dryness, and the sodium salt is extracted with absolute ethanol which will not dissolve the sodium carbonate formed from the excess sodium hydroxide. The alcoholic solution of the sodium salt is then carefully evaporated to dryness and the solid material is extracted with water. The final form of the sodium salt is obtained from this solution by evaporating until the needles of the sodium salt form when the solution is chilled. The second extraction is used to separate any organic impurities which may be present after the ethanol extraction. The sodium salt obtained above is very soluble in water. Solutions have been made which contain approximately 64 g solute per 100 ml solution.

#### *Study of the reagent*

In using the reagent in the precipitation of metal ions, the control of the pH of the solution is important. Below pH 5, the water insoluble acid form of the reagent is regenerated. When the precipitation is attempted in very basic solutions, there occurs some decomposition of the reagent which yields sulfide-like materials.

Qualitative studies employing the sodium salt of the reagent gave precipitates with cobalt, nickel, zinc, silver, cadmium, mercury and lead. All of these precipitates are white in color with the exception of cobalt which, at first, yields a bluish-white precipitate which turns intensely blue upon standing. The rate of this color change is analogous to a clock reaction and is temperature and concentration dependent. No precipitation was observed with the alkali or alkaline earth metals. Precipitates were obtained with chromium, copper, tin, antimony and bismuth. It was determined, however, that these latter precipitates were actually regenerated reagent in various stages of decomposition.

Sensitivity determinations were performed on cobalt, zinc, nickel, cadmium and lead. Cadmium, lead and zinc gave precipitates at concentrations of 1, 2, and 6 p.p.m. respectively.

Since there are few good weighing forms for cadmium, the high sensitivity of the cadmium precipitation gave promise for a new weighing form for the gravimetric determination of cadmium. The cadmium precipitate which is a white crystalline material, has been found by analysis to contain a 2 : 1 mole ratio of the tetrazole to cadmium.

The molecular weight of the compound, which contains 24.08% cadmium, is 466.85. The compound has a molar solubility of  $2.0 \cdot 10^{-5}$  moles per liter at 25° and a solubility product of  $3.03 \cdot 10^{-14}$  at this temperature. The cadmium precipitate may be readily dried at 110°.

The gravimetric determination of cadmium was carried out using aqueous 5% and saturated solutions of the reagent. The amount of cadmium determined varied from 1–40 mg. A standard cadmium solution was prepared from reagent grade  $\text{Cd}(\text{NO}_3)_2$  and standardization by electrodeposition indicated a concentration of 2.039 mg cadmium per ml. This solution was used for the larger cadmium samples and was diluted for the smaller samples. The volume of the sample solution prior to precipitation was adjusted to approximately 50 ml.

The reagent was added dropwise to the cadmium solutions which were heated to just below their boiling point. After the addition of a few drops of the reagent, the solutions were stirred briefly and then allowed to stand until the precipitate, which started to form immediately, was noticed to form aggregates. The remaining portion of the reagent solution was then added with stirring. The samples were filtered using medium porosity porcelain filtering crucibles. Approximately 125 ml distilled water was used to wash and transfer the precipitates, which were dried at 110° until constant weight was attained. The results of these determinations are summarized in Tables I

TABLE I  
CADMIUM PRECIPITATION WITH SATURATED REAGENT SOLUTION

<i>mg Cd taken</i>	<i>mg Cd recovered</i>	<i>Average recovery</i>	<i>Average deviation</i>
40.8	40.5	40.6	0.6/1000
40.8	40.6		
40.8	40.6		
40.8	40.6		
20.4	20.1	20.3	6/1000
20.4	20.2		
20.4	20.2		
20.4	20.4		
20.4	20.4		
5.1	4.8	4.9	24/1000
5.1	4.8		
5.1	5.0		
5.1	5.0		
5.1	5.1		
1.0	0.8	0.9	92/1000
1.0	0.8		
1.0	0.8		
1.0	0.9		
1.0	0.9		
1.0	1.0		
1.0	1.0		
1.0	1.0		
1.0	1.0		
1.0	1.0		
1.0	1.0		
1.0	1.0		
1.0	1.1		

and II. A series of experiments were carried out using 10% ethanol to reduce the solubility of the precipitate. These results are summarized in Table II. Coprecipitation studies were made with manganese and magnesium since these elements are often found in cadmium alloys. The results in Table II<sup>f</sup> indicate negligible coprecipitation.

## DISCUSSION

In the comparison of Tables I and II, it is seen that the quantitative recovery of cadmium is very similar with both the saturated and 5% solutions of the reagent. The results obtained when using the saturated solution generally show a higher degree of accuracy and better precision, especially with the larger cadmium samples. Also in Table II, there are results of the precipitation of cadmium employing ethanol to depress the solubility of the precipitate. The improvement of the accuracy is such that the added effort is not warranted. The presence of ethanol tends to make the transfer of the precipitate more difficult and time-consuming.

Preliminary investigations have indicated that this reagent may also be useful for the determination of lead and zinc.

TABLE II  
CADMIUM PRECIPITATION WITH 5% REAGENT SOLUTION

<i>mg Cd taken</i>	<i>mg Cd recovered</i>	<i>Average recovery</i>	<i>Average deviation</i>
40.8	40.1	40.4	4/1000
40.8	40.3		
40.8	40.4		
40.8	40.6		
20.4	19.8	20.3	14/1000
20.4	20.5		
20.4	20.5		
20.4	20.5		
5.1	4.5	4.8	21/1000
5.1	4.8		
5.1	4.8		
5.1	4.9		
1.0	0.7	0.9	100/1000
1.0	0.8		
1.0	0.8		
1.0	0.8		
1.0	0.9		
1.0	1.0		
1.0	1.0		
1.0 <sup>a</sup>	0.7	1.0	150/1000
1.0 <sup>a</sup>	0.9		
1.0 <sup>a</sup>	1.1		
1.0 <sup>a</sup>	1.1		
1.0 <sup>b</sup>	0.8	0.9	50/1000
1.0 <sup>b</sup>	0.9		
1.0 <sup>b</sup>	0.9		
1.0 <sup>b</sup>	1.0		

<sup>a</sup> Precipitate washed with 10% EtOH solution.

<sup>b</sup> Cadmium precipitated in and washed with 10% EtOH solution.

TABLE III  
 CADMIUM PRECIPITATION IN PRESENCE OF MANGANESE AND  
 MAGNESIUM WITH SATURATED REAGENT SOLUTION

<i>mg Cd taken</i>	<i>mg Mn taken</i>	<i>mg Mg taken</i>	<i>mg Cd recovered</i>	<i>Average mg Cd recovered</i>
20.4	5.0	none	20.3	20.4
20.4	5.0	none	20.4	
20.4	10.0	none	20.4	20.4
20.4	10.0	none	20.4	
20.4	none	5.0	20.3	20.4
20.4	none	5.0	20.4	
20.4	none	10.0	20.3	20.4
20.4	none	10.0	20.4	
20.4	5.0	5.0	20.3	20.4
20.4	5.0	5.0	20.5	
20.4	none	none	20.3	20.4
20.4	none	none	20.3	
20.4	none	none	20.4	
20.4	none	none	20.5	

## SUMMARY

The use of the sodium salt of 1-phenyl-tetrazoline-5-thione provides a good method for the quantitative determination of cadmium, yielding a crystalline precipitate which is easily filtered and brought to constant weight. The precision of the determination is fair and the accuracy is generally within 0.2 mg. The main limitation of the reagent is that it is not specific in its action and it might be necessary to effect a prior separation since cadmium is often found to be alloyed with lead and zinc.

## RÉSUMÉ

Le sel de sodium de la phényl-1-tétrazoline-thione-5 peut être utilisé comme réactif pour le dosage gravimétrique du cadmium. Cependant cette méthode est peu spécifique et une séparation préalable est souvent nécessaire.

## ZUSAMMENFASSUNG

Das Natriumsalz des 1-Phenyl-tetrazolin-5-thions kann zur gravimetrischen Bestimmung von Cadmium verwendet werden. Da das Reagenz wenig spezifisch ist, müssen störende Elemente, vor allem Blei und Zink, vorher entfernt werden.

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## AN IMPROVED TITRIMETRIC METHOD FOR DETERMINING SULPHUR TRIOXIDE IN FLUE GAS

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### INTRODUCTION

The presence of a few parts per million of sulphur trioxide in flue gas has caused serious problems due to the deposition of sulphuric acid on the low temperature parts of oil-fired boilers. The concentration of sulphur trioxide is a measure of the corrosive nature of the flue gas and its determination is therefore important.

The measurement of sulphur trioxide concentrations in the range 0–50 p.p.m. v/v in the presence of a large excess (2,000–3,000 p.p.m. v/v) of sulphur dioxide<sup>1–3</sup> is usually carried out in two stages:

(1) Quantitative absorption of the sulphur trioxide from a sample of flue gas in an aqueous solution of isopropanol, which inhibits oxidation of sulphur dioxide.

(2) Determination of microgram quantities of sulphur trioxide in the aqueous isopropanol.

In most techniques described in the literature<sup>1,3–5</sup> sulphate in the aqueous isopropanol has been determined turbidimetrically; this technique possesses limited sensitivity and precision, and is rather time-consuming.

A titrimetric method for determining sulphate<sup>6</sup> was applied by SEIDMAN<sup>7</sup> to the measurement of sulphur trioxide in flue gas: the lower limit for the determination was 10 p.p.m. v/v of sulphur trioxide in the flue gas. For application in modern power stations, it is desirable that the lower limit should be not more than 0.5 p.p.m. SO<sub>3</sub> v/v, corresponding to about 0.25 p.p.m. SO<sub>3</sub> v/v in the isopropanol solution\*.

This paper presents the results of work on a titrimetric determination for flue gas analysis and compares the results with others obtained using an established turbidimetric technique<sup>3</sup>.

### EXPERIMENTAL

In alcoholic solution, barium ions form a complex with Thoron (the sodium salt of 1-(*o*-arseno-phenyl-azo)-2-naphthol-3 : 6 disulphonic acid). Thoron in aqueous alcoholic solution is yellow; the barium complex has a peak of optical absorption at 550 m $\mu$ , and appears pink. In this method of analysis, Thoron is added to the solution of sulphate which is then titrated with barium perchlorate in 4 : 1 isopropanol : water to a change of colour from yellow to pink.

It was found by visual observation that the most dilute titrant which gave a rea-

\* Using the C.E.R.L. absorption apparatus<sup>3</sup>, flue gas is sampled at 1.0 l/min for about 15 min. The sulphur trioxide is absorbed in a total of 100 ml of aqueous isopropanol.



sonably sharp end-point was 0.0025 *M*. At this concentration the end-point could always be determined to within 1 drop (0.02 ml) of titrant (equivalent to 4 μg of SO<sub>3</sub>) when the titration was carried out in diffused sunlight. There was no gain in precision on further dilution, as the end-point became less distinct. When an "EEL" photoelectric indicator was used to observe the end-point the concentration of the titrant could be reduced to 0.0005 *M*, and the precision of the method was increased at the lower limit of its range. It was possible by this means to decrease the limit of detection to 2 μg SO<sub>3</sub>. This is equivalent to about 0.1 p.p.m. v/v of SO<sub>3</sub> in the sampled gas if a 50-ml aliquot of the sample solution is titrated.

The interference of sulphur dioxide reported by FRITZ AND YANNAMURA<sup>6</sup> was investigated. Different quantities of sulphate, as sulphuric acid, in 4 : 1 isopropanol : water containing 60 μg/ml of SO<sub>2</sub> were titrated with 0.0025 *M* barium perchlorate\*. A graph relating the volume of titrant and the quantity of sulphate added gave a straight line with a small positive intercept on the titrant axis. This "blank" was shown by means of turbidimetric determinations to be equivalent to the small amount of sulphate in the sulphur dioxide solution; there was no interference by sulphur dioxide at the concentration investigated.

The apparent pH of the synthetic solutions and of samples obtained from flue gas was between 3.5 and 4.0 (indicated by a glass electrode). This is within the range of apparent pH (2.5–4.0) stated by FRITZ AND YANNAMURA<sup>6</sup> to be necessary for the end-point to be visible, therefore no adjustment was necessary.

The precision of the method was determined at three levels of sulphate concentration in the presence of 60 μg/ml of dissolved sulphur dioxide, using the technique described in the Appendix.

The results are compared in Table I with those obtained by the turbidimetric method<sup>3</sup>. The lowest concentration quoted was determined using 0.0005 *M* titrant and a photometric end-point indicator.

TABLE I  
PRECISION OF TITRIMETRIC AND TURBIDIMETRIC METHODS

Quantity of sulphate taken, μg SO <sub>3</sub>	Concentration in solution, μg SO <sub>3</sub> /ml	Equivalent concentration in flue gas, p.p.m. SO <sub>3</sub> v/v	Titrimetric method (see Appendix)		Turbidimetric method <sup>a</sup>	
			Number of determinations	Standard deviation, μg SO <sub>3</sub> *	Number of determinations	Standard deviation, μg SO <sub>3</sub>
500	25.0	46.7	12	2.0	9	9.0
250	12.5	23.4	—	—	10	5.0
200	10.0	18.7	12	2.0	—	—
50.0	2.5	4.7	12	2.0	10	2.0
8.00	0.16	0.3	10	0.6	—	—

\* Standard deviation of the results of single determinations about the mean value.

#### CONCLUSION

The titrimetric method is quicker, more precise, and more sensitive than the turbidimetric method, which it would replace with advantage; it requires less manipulation and the reagents used are stable over long periods. The titrimetric procedure could be used to complete the flue gas analysis at the sampling site and is suitable for routine application to industrial plant.

\* Sample solutions from the absorption apparatus usually contain about 30 μg/ml of SO<sub>3</sub>.

## APPENDIX

*Titrimetric method for determining sulphur trioxide in flue gas**Reagents*

*Barium perchlorate, 0.0025 M*: Dissolve about 0.84 g of anhydrous barium perchlorate in 1000 ml of 4 : 1 isopropanol : water. Adjust the apparent pH of the solution to between 2.5 and 4.0 by adding perchloric acid. Standardise the solution by titrating with standard sulphuric acid using the procedure described below.

*Thoron indicator, 0.04%*: Dissolve 0.04 g Thoron in 100 ml of distilled water.

*Sulphuric acid, 0.00125 N*: Prepare from a gravimetrically standardised solution of sulphuric acid in water, so that the resulting solution is 4 : 1 isopropanol : water. 1 ml of this solution is equivalent to 50.0  $\mu\text{g}$  of sulphur trioxide.

*Procedure*

These instructions are for the analysis of the 4 : 1 isopropanol : water solution from the absorption apparatus<sup>3</sup>. Transfer to a conical flask a convenient aliquot (10–50 ml) of the solution containing preferably between 50  $\mu\text{g}$  and 500  $\mu\text{g}$  of  $\text{SO}_3$ . Add 5 drops of the indicator solution for each 20 ml of the test solution. Titrate with the barium perchlorate solution to the appearance of a pink colour. The end-point is most easily seen in diffused sunlight.

## ACKNOWLEDGEMENTS

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## SUMMARY

The titration of sulphate in 4 : 1 isopropanol : water by barium perchlorate to the colour change of Thoron has been applied to the determination of low concentrations of sulphur trioxide (0–50 p.p.m.) in flue gas containing a large excess of sulphur dioxide (2,000–3,000 p.p.m.). The lower visual limit of the end-point was attained using 0.0025 *M* titrant: in determinations of between 50  $\mu\text{g}$  and 500  $\mu\text{g}$   $\text{SO}_3$  the standard deviation of the results was 2  $\mu\text{g}$   $\text{SO}_3$ . The range of application of the method was further extended by observing the end-point photometrically; 0.0005 *M* titrant gave a standard deviation of 0.6  $\mu\text{g}$  in determinations of 8  $\mu\text{g}$   $\text{SO}_3$ . No interference was given by dissolved sulphur dioxide at concentrations up to 60  $\mu\text{g}/\text{ml}$ , that is, twice the usual maximum. The improved titrimetric procedure is more precise and more sensitive than the turbidimetric methods previously used.

## RÉSUMÉ

Le titrage des sulfates, en milieu isopropanol-eau (4 : 1) par le perchlorate de baryum, en présence de thoron comme indicateur, a été appliqué au dosage de l'anhydride sulfurique en faibles teneurs (0–50 p.p.m.  $\text{SO}_3$ ) dans des gaz de cheminées, renfermant un gros excès d'anhydride sulfureux (2000 à 3000 p.p.m.). Cette méthode titrimétrique est plus précise et plus sensible que les méthodes turbidimétriques utilisées jusqu'à présent.

## ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung kleiner Mengen Schwefeltrioxyd neben grossen Mengen Schwefeldioxyd in Abgasen. Die in wasserhaltigem Isopropanol gebildete Schwefelsäure wird mit Bariumperchloratlösung in Gegenwart von Thoron als Indikator titriert. Die Endpunktsbestimmung kann visuell oder photometrisch erfolgen. Die beschriebene Methode ist genauer als das nephelometrische Verfahren.

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## SUR LA STABILITÉ THERMIQUE DES ÉTALONS ANALYTIQUES. IX\*

CLÉMENT DUVAL

avec la collaboration technique de

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(Reçu le 5 juillet 1960)

Poursuivant l'étude des substances utilisables comme étalons, nous présentons les 12 corps suivants: bromure de potassium, carbonate de guanidine, acétate de cadmium, anhydride phtalique, acide *o*-phtalique, sulfate de lanthane, citrate de lithium, sulfate de cobalt, sulfate de magnésium, acide malonique, acide succinique et sulfate de potassium.

Toutes ces substances ont été chauffées sur une thermobalance à enregistrement photographique, avec échauffement linéaire de 300° par heure et avec des poids de substance de l'ordre de 200 mg. Les spectres infrarouges ont été réalisés sur poudre, entre 6 et 15  $\mu$ , sur le spectromètre Perkin-Elmer 21, avec optique de chlorure de sodium.

### *Bromure de potassium*

Ce sel est toujours sec et anhydre. Son poids ne change pas jusqu'à 800°; la droite de thermolyse n'est pas reproduite.

Il ne donne évidemment pas de spectre infrarouge dans la région étudiée.

### *Carbonate de guanidinium*

Le carbonate de guanidinium est anhydre et stable au moins jusqu'à 150°; après quoi, la décomposition se fait en trois temps avec libération complète du creuset (Fig. 1).

Le spectre infrarouge a fourni trois bandes fortes pour 1662, 1545 et 1392  $\text{cm}^{-1}$ , relatives au groupement C=NH et au groupement NH<sub>2</sub>, ainsi que la bande forte caractéristique du groupement CO<sub>3</sub> à 880  $\text{cm}^{-1}$ .

### *Acétate de cadmium*

Le produit qui nous a servi contenait deux molécules d'eau qu'il a perdues entre 63 et 190° (Fig. 2). Un palier relatif à l'acétate anhydre s'étend alors jusqu'à 286°; la décomposition se produit brusquement et le palier de l'oxyde CdO commence dès 344°.

\* Pour le huitième mémoire de cette série, voir *Anal. Chim. Acta*, 23 (1960) 257.

\*\* Adresse: 11, rue Pierre Curie, Paris, 5.

Le spectre infrarouge présente les bandes suivantes, communes à la plupart des acétates: 1640 (f), 1554 (TF), 1418 (TF), 1345 (aF), 1046 (aF), 1020 (aF), 945 (aF)  $\text{cm}^{-1}$ .

#### *Anhydride phtalique*

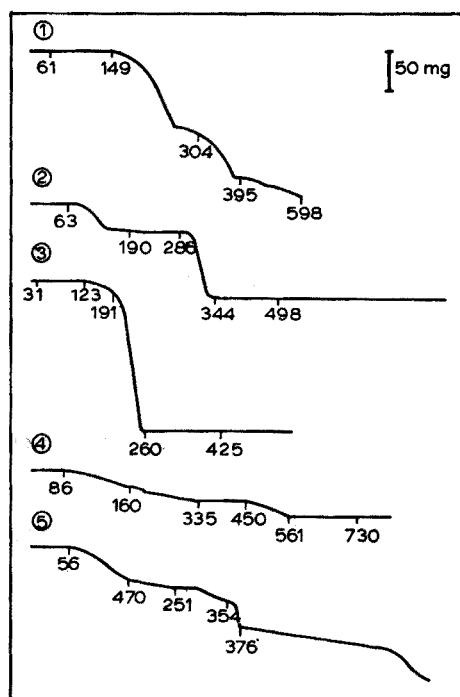
Ce corps se montre bien sec et anhydre et reste stable jusque vers  $123^\circ$ . Il se sublime alors rapidement et le creuset est vide à  $260^\circ$  (Fig. 3).

Le spectre infrarouge présente les bandes suivantes: 1900 (aF), 1843 (F), 1784 (aF), 1731 (F), 1598 (aF), 1471 (F), 1388 (aF), 1363 (F), 1335 (aF), 1283 (aF), 1254 (F), 1243 (f), 1211 (f), 1174 (aF), 1105 (F), 1067 (aF), 1006 (F), 902 (TF), 886 (f), 837 (F), 798 (F), 731 (f), 710 (TF), 676 (F)  $\text{cm}^{-1}$ .

#### *Acide o-phtalique*

La courbe représentative de thermolyse est identique quant à la forme à celle de l'anhydride. Cet acide est sec et stable jusqu'à  $187^\circ$ ; après quoi il se déshydrate et se sublime et le creuset est complètement vide à  $279^\circ$ .

Nous avons enregistré le spectre infrarouge qui présente les maxima d'absorption suivants: 1685 (TF), 1587 (aF), 1493 (aF), 1403 (F), 1304 (f), 1281 (F), 1270 (f), 1070 (aF), 1003 (f), 923 (f), 903 (aF), 828 (f), 797 (aF), 737 (aF), 690 (f), 672 (aF)  $\text{cm}^{-1}$ .



Figs. 1-5.

#### *Sulfate de lanthane*

Le sulfate à 8 molécules d'eau que nous avons utilisé est stable jusque à  $86^\circ$ . Il donne naissance de  $338$  à  $450^\circ$  à un palier horizontal correspondant sans doute à un mélange.

Le produit anhydre  $\text{La}_2(\text{SO}_4)_3$  apparaît à  $560^\circ$ ; il est préférable de le peser plutôt que le corps de départ (Fig. 4).

Le spectre infrarouge permet de mesurer les bandes de fréquences: 1621 (F), 1420 (F), 1140 (F), 1098 (aF), 1080 (aF), 984 (aF), 657 (aF)  $\text{cm}^{-1}$ .

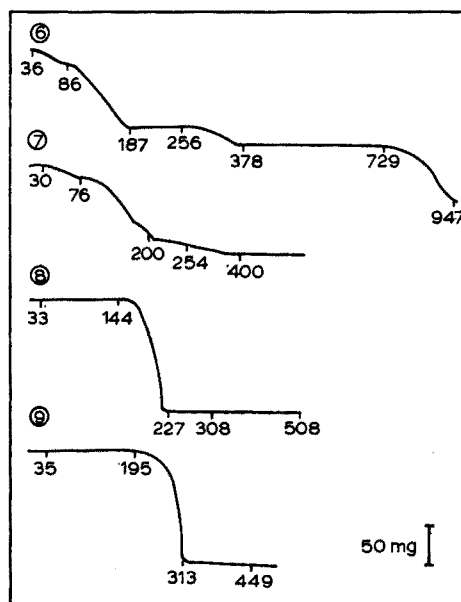
#### *Citrate de lithium*

Le produit de départ contient 4 molécules d'eau et il conserve son état d'hydratation jusqu'à  $56^\circ$ ; il devient anhydre vers  $251^\circ$  puis se décompose progressivement en abandonnant, au-dessus de  $930^\circ$ , de l'oxyde de lithium plus ou moins carbonaté (Fig. 5).

Nous observons sur le spectre infrarouge les bandes de fréquences suivantes: 1689 (aF), 1595 (TF), 1423 (aF), 1402 (aF), 1388 (aF), 1282 (aF), 1253 (aF), 1110 (aF), 1087 (aF), 1035 (aF), 947 (f), 903 (F), 834 (F)  $\text{cm}^{-1}$ .

#### *Sulfate de cobalt*

Le sulfate de cobalt commercial a été recristallisé une fois dans l'eau; le calcul en donne 7 molécules d'eau. Cet heptahydrate n'est pas stable; déjà, il perd du poids dès  $36^\circ$ ; le palier de l'hexahydrate n'est pas nettement marqué et entre  $187^\circ$  et  $256^\circ$  s'étend un autre palier légèrement oblique correspondant assurément à un mélange.



Figs. 6-9.

La déshydratation est achevée à  $378^\circ$  et le palier du sulfate anhydre s'étend jusqu'à  $730^\circ$ . C'est évidemment sous cette forme que l'on obtient les résultats les plus sûrs en vue d'une pesée de précision. Au-dessus de cette température l'anhydride sulfurique se dégage en se dissociant et, vers  $950^\circ$ , on aboutit à l'oxyde  $\text{Co}_3\text{O}_4$  (Fig. 6).

Le spectre d'absorption infrarouge présente trois bandes fortes pour 1087 et 983  $\text{cm}^{-1}$  correspondant au groupement  $\text{SO}_4$  et 1634  $\text{cm}^{-1}$  relative aux bandes habituelles de l'eau.

*Sulfate de magnésium*

Ce sel, sorti du flacon, présente 7 molécules d'eau qu'il ne conserve que jusque vers 36°. Il n'y a pas, au cours de la dissociation, de palier très net pour les différents hydrates, avec notre vitesse de chauffe (Fig. 7), c'est pourquoi nous recommandons de porter le corps au-dessus de 400° pour obtenir le sulfate anhydre.

Le spectre d'absorption infrarouge est tout à fait identique à celui du sulfate de cobalt, avec les bandes fortes de 1643, 1084 et 983  $\text{cm}^{-1}$ .

*Acide malonique*

Ce corps est stable et anhydre jusqu'à 144°. Il se décompose alors rapidement jusqu'à 227° et le creuset est débarrassé des dernières traces de carbone vers 420° (Fig. 8).

Le spectre enregistré présente les bandes caractéristiques suivantes: 1735 (f), 1703 (aF), 1437 (f), 1416 (F), 1397 (aF), 1387 (f), 1312 (F), 1257 (aF), 1217 (TF), 1172 (TF), 960 (f), 932 (f), 917 (F), 897 (tf), 769 (TF), 654 (TF)  $\text{cm}^{-1}$ .

*Acide succinique*

L'acide succinique se présente également anhydre et est stable jusqu'à 195°. Il se produit alors une brusque décomposition jusque vers 313° et à partir de 449° le creuset est complètement vide (Fig. 9).

Dans le spectre infrarouge, on relève les bandes suivantes: 1689 (TF), 1416 (TF), 1323 (f), 1306 (F), 1200 (TF), 1175 (aF), 918 (aF), 890 (f), 802 (F)  $\text{cm}^{-1}$ .

*Sulfate de potassium*

Nous avons chauffé du sulfate de potassium provenant de différents flacons; tous ont perdu au maximum, 1/200 de leur poids en les chauffant jusque vers 800°. On peut, sans doute, attribuer cette perte à une petite trace d'acide sulfurique occlus.

Le spectre d'absorption infrarouge présente bien les deux bandes fortes correspondant au groupement  $\text{SO}_4$  pour 1115 et 981  $\text{cm}^{-1}$ .

## RÉSUMÉ

Cette neuvième étude a porté sur la stabilité thermique et l'enregistrement du spectre d'absorption infrarouge, entre 6 et 15  $\mu$  pour douze substances proposées comme étalons en chimie analytique.

## SUMMARY

A report is given of the infra-red spectra and the thermal stability of twelve substances that are used as standards in chemical analysis.

## ZUSAMMENFASSUNG

Es werden die UR-Spektren sowie das thermische Verhalten von zwölf Substanzen, die in der analytischen Chemie als Standardsubstanzen verwendet werden, beschrieben.

# IMPURITY DETERMINATION BY THERMAL ANALYSIS

## I. THE MELTING CURVE OF A GRADUALLY FROZEN SAMPLE

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### INTRODUCTION

The interpretation of melting curves is based on the assumption that thermodynamic equilibrium prevails throughout the solid and the liquid phase during the determination of the curve. A number of experimental circumstances resulting in insufficient thermodynamic equilibrium have been discussed in a previous paper<sup>1</sup>. Attention has been paid to the limited mass transfer in the liquid and it has been shown that its influence may be neglected under suitable experimental conditions<sup>2</sup>.

Thus far, no attention has been paid to the influence of the rate of mass transfer *in the solid*. As is obvious a limited rate of mass transfer in the solid has no effect on the attainment of thermodynamic equilibrium, when *no solid solutions* occur in the solid-liquid system. However, when the system contains mixed crystals the approach of thermodynamic equilibrium between the entire solid and the liquid is seriously affected when the rate of mass transfer in the solid is limited.

Since mass transfer in the solid can hardly be promoted by external means and the diffusion constants in solids lie in the range of  $10^{-10}$  to  $10^{-12}$   $\text{cm}^{-1} \text{sec}^{-1}$  (those of liquids are  $10^{-4}$  to  $10^{-5}$   $\text{cm}^{-1} \text{sec}^{-1}$ ), it even must be concluded that mass transfer within the solid is negligible under the experimental conditions usually applied in the determination of heating curves. Consequently only the surface layer of the solid participates in the thermodynamic equilibrium and the bulk of the solid is not in thermodynamic equilibrium during the determination of the melting curve.

These conclusions are used as the starting point for the interpretation of heating curves which is developed in this paper. On the basis of the new interpretation some discrepancies mentioned in the literature can be solved.

A further consequence of the lack of mass transfer in the solid is that the pretreatment of the sample influences the shape of the melting curve. This influence is absent when cooling curves are determined which start with the liquid sample.

However, since rates of crystallisation may be slow compared to rates of melting, serious deviations from the equilibrium temperatures may occur on cooling<sup>1</sup>. Therefore a heating curve obtained by starting with a solid sample is preferable.

Two cases of pretreatment of the sample may be distinguished:

1. The solid sample has been obtained by *slow freezing* of the liquid.
2. The solid sample has been obtained by *sudden freezing* of the liquid.

The present paper deals with gradually frozen samples. The heating curves of samples obtained by quick freezing will be discussed in another paper.

*Relation between temperature and fraction liquid of a binary solid-liquid system which is slowly frozen*

Since only the surface layer of the solid participates in the thermodynamic equilibrium, the amount of solid involved is negligible compared to the bulk of the solid. Since diffusion in the liquid is sufficiently large, the total amount of liquid present at a certain moment participates in the thermodynamic equilibrium.

Suppose that the total amount of liquid equals a fraction  $y$  of the total sample and let the concentration of the liquid be  $X_L$  (mol-fraction). The fraction of the sample which is solid is  $(1 - y)$ . Now suppose that the amount of solid increases with  $d(1 - y)$ . The concentration of this tiny deposit of solid is  $X_s$  which is coexistent with the liquid concentration  $X_L$ . Owing to the law of conservation of matter:

$$X_s \cdot d(1 - y) = -d(X_L y) \quad (1)$$

is valid, hence:

$$-\frac{dy}{y} = \frac{dX_L}{X_L - X_s} \quad (2)$$

According to thermodynamics (provided  $X_L$  and  $X_s$  are small)

$$(X_L - X_s) = \frac{Q}{RT^2} \Delta T \quad (3)$$

where

$$\begin{aligned} Q &= \text{heat of fusion in cal/mol.} \\ R &= \text{gas constant in cal/degree mol.} \\ T &= \text{temperature in } ^\circ\text{K} \\ \Delta T &= \text{depression of melting point in } ^\circ\text{C.} \end{aligned}$$

Further, if  $X_L$  is small, the following equation may be considered as a fair approximation:

$$X_L = K_L \Delta T \quad (4)$$

where  $K_L$  is a constant. Substitution of eqns. (3) and (4) in eqn. (2) yields:

$$-\frac{dy}{y} = \frac{K_L R T^2 d(\Delta T)}{Q \cdot \Delta T}$$

Integration of the above equation results in:

$$-\ln y = \frac{RT^2}{Q} K_L \ln \Delta T + C \quad (5)$$

The concentration in the liquid  $X_L$  will be equal to  $X$  (the concentration in the total sample) when  $y = 1$ . Since, according to eqn. (4),  $(\Delta T)_{y=1} = K_L/X$ , the integration constant  $C$  will be equal to:

$$C = -\frac{RT^2}{Q} K_L \ln \frac{K_L}{X} \quad (6)$$

Combination of eqns. (5) and (6) results in:

$$\ln y = \frac{RT^2}{Q} K_L \ln \frac{X}{K_L \Delta T} \quad (7)$$



When no solid solutions are formed the constant  $K_L$  equals  $Q/RT^2$  and eqn. (7) reduces to the simple and well-known equation of White obtaining to systems which show no miscibility in the solid phase:

$$y = \frac{RT^2}{Q} \frac{X}{AT} \quad (8)$$

It may be useful to note that eqn. (7) is not restricted to solid-liquid systems. It is valid for any binary system showing a phase transition under the condition that the bulk of one of the phases is excluded from further exchange with the other phase. Since on heating of a slowly frozen sample the reverse process occurs, eqn. (7) is valid for the heating (melting) curve of a gradually frozen sample.

As was mentioned in the introduction, heating curves are preferred to cooling curves, because of the lack of *thermal* equilibrium on cooling. It is stressed that a limited lack of thermal equilibrium does not necessary imply perceptible deviations in the concentration of the coexisting phases. This view is fully confirmed by the experimental results mentioned below.

#### EXPERIMENTAL CHECK ON EQUATION (7)

An experimental check on eqn. (7) was carried out with two systems showing solid solutions, *viz.*: diphenyl (main component)–phenanthrene and tin (main component)–bismuth. Each component was carefully purified beforehand. Then the constant  $K_L$  of each system was determined independently of the heating curve:

Several mixtures of each system were prepared by weighing, followed by thorough mixing in the liquid phase. The mixtures were frozen and then their *final* melting point was determined as follows. The (macro) samples were slowly heated and a thermometer was inserted; heating was continued until a minute fraction of solid was present and then the sample was kept under adiabatic conditions and the temperature was read. At this moment the concentration of the liquid does not perceptibly differ from the total concentration of the sample. This method yields results which are more reliable and reproducible than temperature readings taken at the moment the "last" crystal disappears (at that moment the contacting surface of solid and liquid is too small).

The final melting points thus found were plotted as a function of the concentration. The constant  $K_L$  of each system may then be read from the graph according to eqn. (4).

The heats of fusion ( $Q$ ) of the main components were derived from the literature<sup>4</sup>.

Subsequently, melting curves were determined on samples of known composition by means of the thin-film apparatus<sup>5</sup> operating according to the so-called dynamic method. The pretreatment of the sample consisted of melting the sample followed by gradual solidification within 30–60 min. The results obtained are presented in the first two columns of the Tables I, II and III. The third columns of these tables mention the depressions calculated with the aid of eqn. (7). Agreement between the temperatures observed and those calculated is striking. (The accuracy of the temperature readings is not better than 0.01°). For comparison, the depressions calculated on the basis of the equation which is valid in case of equilibrium between the liquid and the *total* mass of solid are listed in the fourth column of each table. This equation reads:

$$y = \frac{RT^2}{Q} \frac{X}{\Delta T} + \frac{K_s RT^2}{Q} \quad (9)$$

where  $K_s$  is the depression constant of the *initial* melting point. This constant was calculated from eqn. (3) and the already known value of  $K_L$ .

Clearly the difference between the depressions found and those calculated from eqn. (9) must increase when the fraction liquid ( $y$ ) decreases. This is confirmed by the results.

TABLE I  
DEPRESSIONS FOUND AND CALCULATED OF A SAMPLE OF DIPHENYL CONTAINING  
0.181 mol% OF PHENANTHRENE

Fraction liquid $y$	Depression $\Delta T$ in °C		
	Found	Calculated on the basis of local equilibrium. (eqn. 7)	Calculated on the basis of total equilibrium. (eqn. 9)
0.1	0.41	0.40	0.22
0.2	0.22	0.24	0.18
0.3	0.17	0.17	0.14
0.4	0.14	0.14	0.12
0.5	0.13	0.12	0.10
0.6	0.10	0.10	0.09
0.7	0.08	0.08	0.08

TABLE II  
DEPRESSIONS FOUND AND CALCULATED OF A SAMPLE OF DIPHENYL CONTAINING  
0.762 mol% OF PHENANTHRENE

Fraction liquid $y$	Depression $\Delta T$ in °C		
	Found	Calculated on the basis of local equilibrium (eqn. 7)	Calculated on the basis of total equilibrium (eqn. 9)
0.1	1.85	1.86	0.95
0.2	1.03	1.02	0.77
0.3	0.77	0.77	0.64
0.4	0.62	0.61	0.55
0.5	0.54	0.53	0.49
0.6	0.47	0.48	0.43
0.7	0.42	0.43	0.39

TABLE III  
DEPRESSIONS FOUND AND CALCULATED OF A SAMPLE OF TIN CONTAINING 0.300 mol% OF BISMUTH

Fraction liquid $y$	Depression $\Delta T$ in °C		
	Found	Calculated on the basis of local equilibrium (eqn. 7)	Calculated on the basis of total equilibrium (eqn. 9)
0.1	2.82	2.90	1.84
0.2	1.82	1.83	1.40
0.3	1.42	1.41	1.22
0.4	1.18	1.15	1.08
0.5	1.02	1.00	0.98
0.6	0.92	0.92	0.90

## DISCUSSION

The above results show that a formula derived on the assumption of local equilibrium (eqn. 7) fits the experimental melting curves more closely than a formula derived on the assumption of total equilibrium (eqn. 9). It may now be worthwhile to discuss the method by which the content of impurity in an unknown sample may be derived from the heating curve on the basis of the local equilibrium equation. Two methods of impurity determination are normally available, *viz.*: the so-called absolute and comparative methods. The absolute method demands only one heating curve. The data derived from the heating curve when combined with thermodynamic data (the depression constant and the distribution coefficient which are usually determined separately) may yield the amount of impurity. The comparative method demands two melting curves, one of the sample as such and one of the same sample after addition of a known amount of impurity.

*Impurity determination by the absolute method*

According to eqn. (7) a plot of  $\ln y$  versus  $\ln \Delta T$  gives a straight line. The slope of this line gives the value of

$$-\frac{RT^2}{Q} K_L$$

and the line intersects the  $\ln y$ -axis at

$$\ln y = \frac{RT^2}{Q} K_L \ln X/K_L$$

These data combined with the value of  $RT^2/Q$  (derived from the curve or from elsewhere) enable the value of  $K_L$  and  $X$  to be calculated by simple algebra. This procedure is possible provided that the melting point  $T_s$  of the pure main component is exactly known. When  $T_s$  is unknown, its value may be derived from the curve in the following way. Three values of  $y$  *viz.*  $y_1$ ,  $y_2$  and  $y_3$  are chosen and the corresponding temperatures  $T_1$ ,  $T_2$  and  $T_3$  are read from the curve. The pertaining values of  $\Delta T$  are  $T_s - T_1$ ,  $T_s - T_2$  and  $T_s - T_3$ . From eqn. (7) it may be derived that:

$$\frac{\ln y_1/y_2}{\ln y_2/y_3} = \frac{\ln (T_s - T_2)/(T_s - T_1)}{\ln (T_s - T_3)/(T_s - T_2)} \quad (10)$$

The lefthand term of this equation is known; if its value is  $a$  then:

$$\left(\frac{T_s - T_3}{T_s - T_2}\right)^a = \frac{T_s - T_2}{T_s - T_1}, \quad \text{or}$$

$$(T_s - T_2)^{a+1} = (T_s - T_3)^a (T_s - T_1) \quad (11)$$

Now a series of plausible values of  $T_s$  is chosen and the values of the left and right terms of equation (11) are plotted as a function of  $T_s$ . The point of intersection of the two plots yields the desired value of  $T_s$ . This method of calculation, the determination of  $T_s$  included, has been applied to the data represented in the Tables I, II and III. The results are listed in Table IV. The results show that this method, although somewhat laborious, can give satisfactory results.

TABLE IV

COMPARISON OF THE AMOUNTS OF IMPURITY ADDED AND FOUND BY CALCULATION ACCORDING TO AN ABSOLUTE METHOD BASED ON EQUATION (7)

Substance	Impurity added	Found
Diphenyl	0.181 mol %	0.18 mol %
Diphenyl	0.762 mol %	0.74 mol %
Tin	0.300 mol %	0.28 mol %

*Impurity determination by the comparative method*

Eqn. (7), rewritten in its exponential form, reads:

$$y = \left( \frac{X}{K_L \Delta T} \right)^{\frac{RT^2}{Q} K_L}, \text{ or}$$

$$(y)^{-\frac{Q}{RT^2 K_L}} = \frac{K_L}{X} (T_s - T)$$

In the following the temperatures obtaining to the heating curve of the sample are denoted by  $T_y$ , whereas those obtaining to the sample to which a known extra mol-fraction  $p$  of the impurity has been added, are denoted as  $T_{y'}$ . The difference of two temperatures obtaining to the first curve is:

$$T_{y_1} - T_{y_2} = \frac{X}{K_L} \left\{ (y_1)^{\frac{-Q}{RT^2 K_L}} - (y_2)^{\frac{-Q}{RT^2 K_L}} \right\}$$

The difference of the corresponding temperatures of the second curve (read at the same values of  $y_1$  and  $y_2$ ) is:

$$T'_{y_2} - T'_{y_1} = \frac{X + p}{K_L} \left\{ (y_1)^{\frac{-Q}{RT^2 K_L}} - (y_2)^{\frac{-Q}{RT^2 K_L}} \right\}$$

Thus:

$$\frac{T_{y_2} - T_{y_1}}{T'_{y_2} - T'_{y_1}} = \frac{X}{X + p} \quad (12)$$

from which  $x$  may be solved. The above equation is identical with the equation previously derived by one of us<sup>5</sup> on the basis of the assumption of total equilibrium.

#### CONCLUSIONS

The equation obtaining to the comparative method of impurity determination, *viz.* eqn. (12), is applicable to a gradually frozen sample showing local equilibrium as well as to a sample showing total equilibrium. However, when the absolute method is applied, the equation valid for total equilibrium (eqn. 9) differs from eqn. (7) which is valid for total equilibrium of gradually frozen samples. These conclusions suggest a possible explanation of the discrepancy between authors who obtained satisfactory results on the impurity determination of solid solutions<sup>5</sup> and those who did not<sup>6,7</sup>.

## SUMMARY

A temperature-heat content relation is presented for binary systems which show solid solutions. Contrary to previous equations, the present equation accounts for the very restricted rate of diffusion in the solid. The equation is based on local equilibrium during freezing and melting. The equation obtaining to the comparative method of impurity determination and applicable to a gradually frozen sample is identical to the equation previously derived on the basis of total equilibrium. The corresponding equations of the absolute method differ considerably. Experiments confirm the local equilibrium theory and show the inadequacy of the total equilibrium theory.

## RÉSUMÉ

Les auteurs ont effectué une étude sur la détermination des impuretés par analyse thermique, à l'aide de la courbe de fusion d'un échantillon refroidi lentement.

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Bestimmung des Reinheitsgrades durch thermische Analyse der Substanzproben, die einer langsamen Abkühlung unterworfen waren.

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DETECTION AND COLORIMETRIC DETERMINATION  
OF POLYNITRO AROMATIC COMPOUNDS

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## INTRODUCTION

Some new tests for polynitro compounds are investigated in this paper. As the literature on the utilization of polynitro organic compounds in organic analysis is so extremely extensive, any new analytical methods for these compounds should be capable of extensive modification and application.

Benzene, which interferes with hematopoiesis, has been determined in the air by nitration to *m*-dinitrobenzene followed by reaction with alkaline butanone or acetone and measurement of the resultant violet color<sup>1-3</sup>.

In a similar fashion, toluene, xylene, and chlorobenzene have also been determined by nitration to a *m*-dinitrobenzene derivative<sup>4,5</sup>. Recently a nitration test for polynuclear hydrocarbons was described in which pyrene, benzo[a]pyrene, chrysene,

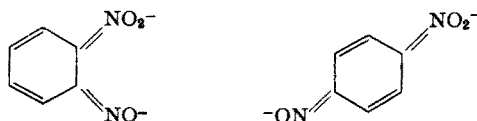
*Anal. Chim. Acta*, 23 (1960) 551-556

etc., could be detected in mixtures<sup>6</sup>. This test has been modified into a specific method for pyrene and its derivatives<sup>7</sup>. The latter procedure consisted of the preparation of polynitro pyrene derivatives which gave a blue color in alkaline solution. The method has been applied to the detection of pyrene in polluted air, auto exhaust fumes, and incinerator effluent.

Polynitro compounds have also been used as reagents in the analysis for creatinine<sup>8</sup> and 17-oxo steroids<sup>9</sup> in body fluids.

All these analytical procedures are examples of the general reaction of an aromatic compound containing two or three electron-attracting groups in meta positions with a suitably activated anion in alkaline solution to give a violet to purple quinonoidal anion<sup>10</sup>. Compounds such as *o*- and *p*-dinitrobenzene are reported to give colorless and yellow colors, respectively, in such a reaction<sup>11,12</sup>.

However, *o*- and *p*-dinitrobenzenes are said to react with organic compounds which serve as hydrogen donors in an alkaline medium to give blue-violet and red quinonjic dyes, respectively<sup>13</sup>, *e.g.*



A third group of analytical methods is much more difficult to define as to mechanism. These methods include (a) the reaction of 1,2- and 1,4-dinitrobenzenes in alkaline solution with compounds containing the cyclopentadiene CH<sub>2</sub> group to give blue to green dyes<sup>14</sup> and (b) the reaction of 2,2'-dinitrobiphenyl and other polynitro compounds with dialkyl and aralkyl ketones to give violet and blue dyes<sup>15</sup>. The former reaction has been used to detect fluorene and the benzofluorenes in the air; the latter reaction has been used for the detection of dialkyl and aralkyl ketones.

In this paper these latter two reactions are applied to the detection or determination of polynitro aromatic compounds.

## EXPERIMENTAL

### Reagents

All compounds were obtained from the Fisher Chemical Co., Aldrich Chemical Co., and the K and K Laboratories or were prepared by standard literature procedures in the laboratory. Where necessary, chemicals were purified to a constant melting point.

### Equipment

A Cary Model 11 Recording Spectrophotometer was used for wave length measurements. For time studies and preliminary investigations, an American Optical Company Rapid Scan Spectrophotometer was used.

### Spot test procedure

To one drop (0.02 ml) of 25% aqueous tetraethylammonium hydroxide in a spot plate was added one drop of 5% fluorene (or 50% butanone) in dimethylformamide. Then one drop of the dimethylformamide test solution was added. The colors and identification limits are given in Tables I and II. For detection on paper the procedure was the same except that 1  $\mu$ l of dimethylformamide test solution was added in the last step. In Table I the substitution of butanone for fluorene as a reagent gives almost identical results, except where noted in the table.

### Colorimetric procedure

To 5 ml of the dimethylformamide test solution was added 5 ml of 0.1% fluorene in dimethylformamide, followed by 1 ml of 10% aqueous tetraethylammonium hydroxide and dilution to

TABLE I  
COLORS AND IDENTIFICATION LIMITS FOR POLYINITRO COMPOUNDS DETECTED  
WITH THE FLUORENE TEST

Compound	Color <sup>a</sup>	Ident. limit, $\mu\text{g}$	
		Paper <sup>b</sup>	Spot plate
1,2-Dinitrobenzene	B	0.1	0.4
1,3-Dinitrobenzene	B <sup>c</sup>	0.1	0.2
1,4-Dinitrobenzene	G	0.1	0.2
1,2-Dinitro-4,5-dichlorobenzene	G <sup>e</sup>	0.1	0.5
2,3-Dinitro-N,N-dimethylaniline	G	0.5	2.5
2,4-Dinitrochlorobenzene	V <sup>d</sup>	0.05	0.2
2,4-Dinitrotoluene	B <sup>d</sup>	0.02	0.1
2,4-Dinitrophenylacetic acid	B <sup>d</sup>	0.01	0.2
2,4-Dinitroaniline	R <sup>d</sup>	0.01	0.2
3,5-Dinitrobenzoic acid	V <sup>e,d</sup>	0.1	0.2
3,5-Dinitrobenzoyl chloride	R <sup>e,d</sup>	0.05	0.1
Dinitromesitylene	G	2	2
Picryl chloride	R <sup>d</sup>	0.05	0.1
Picric acid	R <sup>d</sup>	0.05	0.1
2,4,6-Trinitrofluorene	R <sup>d,f</sup>	0.01	0.2
2,4'-Dinitrobiphenyl	B	0.5	1.
4,4'-Dinitrobiphenyl	YG	5.	10.
2,2'-Dinitrobiphenyl	B	0.5	1.
1,4-Dinitronaphthalene	G	0.05	0.5
1,6-Dinitropyrene	B	0.05	0.1
6,12-Dinitrochrysenes	R	60.	0.5
1,3,6-Trinitropyrene	B <sup>d</sup>	0.05	0.2
1,3,6,8-Tetranitropyrene	B <sup>d</sup>	0.01	0.05

<sup>a</sup>B = blue; G = green; V = violet; R = red; Y = yellow.

<sup>b</sup>Colors not as stable on paper as on the spot plate.

<sup>c</sup>Purple in butanone procedure.

<sup>d</sup>Fluorene or butanone not necessary in the test.

<sup>e</sup>Blue in butanone procedure.

<sup>f</sup>Blue in fluorene test on paper.

TABLE II  
COLORS AND IDENTIFICATION LIMITS FOR MISCELLANEOUS COMPOUNDS  
DETECTED WITH THE BUTANONE OR FLUORENE TESTS

Compound	Butanone test		Fluorene test	
	Color	I.L., $\mu\text{g}$	Color	I.L., $\mu\text{g}$
3-Nitroazobenzene	V	0.1	B	0.2
<i>m</i> -Bisphenylazobenzene	B	0.5	G <sup>a</sup>	0.1
3-Acetylazobenzene	R <sup>b</sup>	1	R <sup>b</sup>	2
$\beta$ ,3-Dinitrostyrene	R <sup>a</sup>	1	R <sup>a</sup>	2
4-Nitrobenzal-3-nitroaniline	R <sup>c</sup>	1	B <sup>c</sup>	0.5

<sup>a</sup>Blue in paper test.

<sup>b</sup>Yellow in paper test.

<sup>c</sup>Yellow-green in paper test.

50 ml with dimethylformamide. The absorption spectrum was then determined within 3 min. The wave length maxima and molar absorbances obtained with some polynitro compounds are shown in Table III. The results obtained in substituting other reagents for fluorene in the colorimetric determination of *o*-dinitrobenzene are presented in Table IV. In all cases the wave length maxima and the molar absorbance values were read directly after diluting the solution to the mark.

TABLE III  
 COLORIMETRIC DETERMINATION OF AROMATIC POLYNITRO  
 COMPOUNDS WITH THE FLUORENE REAGENT

Compound	Color <sup>a</sup>	$\lambda_{max}$ , $m\mu$	$\epsilon \cdot 10^{-3}$
<i>o</i> -Dinitrobenzene	B	695	20.
<i>p</i> -Dinitrobenzene	G	705	16.
1,4-Dinitronaphthalene	G	738	13.
1,6-Dinitropyrene	G	655	13.
6,12-Dinitrochrysene	R	560	25.

<sup>a</sup>B = blue; G = green; R = red.

TABLE IV  
 EFFECT OF CHANGE OF REAGENT ON COLORIMETRIC DETERMINATION  
 OF *o*-DINITROBENZENE

Reagent, 0.1% in DMF	Color <sup>a</sup>	$\lambda_{max}$ , $m\mu$	Molar absorbance $\epsilon \cdot 10^{-3}$
Fluorene	B	695	20
2-Ethylfluorene	B	698	19
2-Bromofluorene	B	705	20
2-Fluorofluorene	B	700	18
2-Acetylfluorene	G	715	18
2-Benzoylamino fluorene	V	595	6.0
		660	6.0
Indene	B	660 <sup>b</sup>	16
4H-Cyclopenta[d, e, f]phenanthrene	G	655	19
		700	20
11H-Benzo[b]fluorene	G	717	12

<sup>a</sup>B = blue; G = green; V = violet.

<sup>b</sup>Also shoulders at 600 and 700  $m\mu$ .

#### DISCUSSION OF SPOT TESTS

Unlike previously described color tests for polynitro compounds, *o*-, *m*-, and *p*-dinitrobenzene derivatives gave positive results, at least in the qualitative procedures. In other tests *m*-dinitro derivatives will usually give a color reaction while the *o*- and *p*-isomers will not, or vice versa, but the present test is considered a general test for most polynitro aromatic compounds. Not only that, but in the present method a brilliant, easily visible blue to green color was obtained for most tested dinitro aromatic compounds (Table I). Fluorene is used in this test, although butanone can be substituted with almost identical results. The few tested trinitro and tetranitro compounds gave the same color in alkaline dimethylformamide alone as was obtained with fluorene or butanone. With most of the other polynitro compounds, the presence of fluorene or butanone was necessary in the test procedure for the development of the color.

A few miscellaneous compounds were also tested and were found to give positive results even though in some cases a nitro group was not present. However, fairly strong electronegative groups were present (Table II). The positive results for these compounds can be explained, to some extent, as due to the general reaction of an aromatic compound containing two or three electron-attracting groups in the *meta* position with a suitably activated anion in alkaline solution to form a highly colored



anion<sup>10</sup>. Consequently, compounds, such as 3-nitroazobenzene, 3-acetylazobenzene, 2-nitrofluorenone, etc., would be expected to give positive results.

The following compounds gave negative results in the spot test procedures: nitrobenzene, *p*-nitrophenol, *p*-nitroanisole, 4-nitro-1,2-xylene, 5-nitroacenaphthene, 1-nitropyrene 8-nitroquinoline, *p*-nitrocinnamic acid, 4,4'-dinitrobiphenyl, 1,5-dinitronaphthalene, and tetranitromethane.

#### DISCUSSION OF COLORIMETRIC PROCEDURE

Attempts to obtain quantitative results for *m*-dinitrobenzene by the colorimetric procedure were unsuccessful due to the rapid decolorization of the solution. The color obtained in the fluorene colorimetric procedure for *o*-dinitrobenzene gradually fades. A fresh solution has a molar absorbance of about 20,500. In 15 min the molar absorbance was 19,800; in 60 min the value had dropped to 19,300. For *p*-dinitrobenzene the color faded more rapidly (Fig. 1).

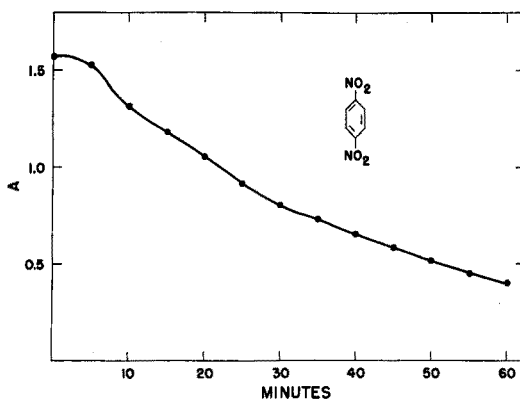


Fig. 1. Effect of time on the colorimetric determination of *p*-dinitrobenzene ( $10^{-4} M$ ) with fluorene at  $\lambda_{\max} 705 m\mu$  by the standard procedure.

In the colorimetric determination of *o*-dinitrobenzene the use of higher or lower concentrations of the fluorene reagent decreased the color intensity. With the higher concentrations of fluorene ( $\sim 10\%$ ), bands were also formed at 455, 485 and 520  $m\mu$  at the expense of the 695- $m\mu$  band.

Compounds containing strong electronegative groups other than the nitro groups could be expected to give the color reaction. For example, in the fluorene test, 3-nitroazobenzene gave a prominent band at 590  $m\mu$ ,  $\epsilon$  20,000, with a shoulder at 700  $m\mu$ . Similarly, 1,3-bis-phenylazobenzene gave a dye with  $\lambda_{\max}$  665  $m\mu$ ,  $\epsilon$  29,000. This latter value was obtained after 15–20 min standing as the color intensity takes that long to develop.

Other polynuclear hydrocarbons containing the cyclopentadiene moiety can be substituted for fluorene in the colorimetric procedure (Table IV). With 4H-cyclopenta[d, e, f]phenanthrene as reagent, a doublet was obtained in the absorption spectrum of the dye derived from reaction of the reagent with *o*-dinitrobenzene. With *m*-dinitro-

benzene an unstable series of colors was observed, while with *p*-dinitrobenzene a prominent band was produced at 670 m $\mu$  with a shoulder at 700 m $\mu$  (Fig. 2).

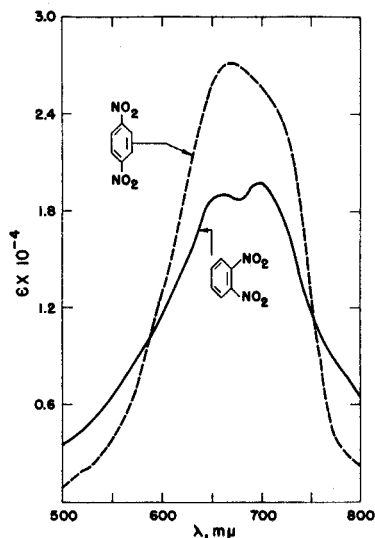


Fig. 2. Visible absorption spectra of the 4H-cyclopenta[d, e, f]phenanthrene procedure for the determination of *o*-dinitrobenzene (—) and *p*-dinitrobenzene (---). Both  $10^{-4}$  M.

#### SUMMARY

A sensitive new spot test for polynitro aromatic compounds is introduced. In most cases a blue to green color is obtained using fluorene (or some other polynuclear cyclopentadiene derivative) as the reagent. A colorimetric procedure for the analysis of *o*- and *p*-dinitro compounds is also presented.

#### RÉSUMÉ

Une nouvelle réaction sensible est proposée pour l'identification des composés aromatiques polynitrés. On obtient avec le fluorène comme réactif une coloration bleue à verte. Une méthode de dosage colorimétrique est décrite.

#### ZUSAMMENFASSUNG

Aromatische Polynitroverbindungen geben mit Fluoren blaue bis grüne Färbungen. Diese Reaktion kann zum Nachweis wie auch zur colorimetrischen Bestimmung der aromatischen Polynitroverbindungen verwendet werden.

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SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM(III)  
WITH EDTA

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## INTRODUCTION

Spectrophotometric determinations of chromium are generally based on the oxidizing action of chromium(VI) and require stringent conditions for accurate results. Very few methods are based on the complex-formation of chromium(III) in aqueous solution. This is probably due to the slow reactions of the strongly hydrated chromium(III) ions.

UBERBACHER AND DROSCHER<sup>1</sup> used the violet coloured chromium(III)-oxalate complex for the spectrophotometric determination of chromium.

An extremely stable complex of chromium(III) is formed with EDTA<sup>2</sup> but its formation is very slow at room temperature although it proceeds rapidly on heating. Several investigators have drawn attention to the possibility of a spectrophotometric determination of chromium by means of this complex<sup>3-6</sup>. In general their results are contradictory with respect to the dependence of the colour on pH, interferences by other ions, the excess of EDTA, etc. We therefore made a critical investigation of the conditions for the spectrophotometric determination of chromium(III) with EDTA.

As our results agree in many respects with those obtained by PŘIBIL AND KLUBALOVA<sup>3</sup>, the publication of these authors can be taken as a starting point. PŘIBIL AND KLUBALOVA<sup>3</sup> found that the complex is readily formed in neutral or weakly acidic solutions simply by heating the solution containing chromium(III) and EDTA for 15 min. The purple coloured solution formed on heating turns blue on addition of alkali. When the pH rises above 11, complete decomposition of the complex takes place and Cr(OH)<sub>3</sub> precipitates.

## EXPERIMENTAL PART

All chemicals used were of analytical grade. The content of the chromium(III) stock solutions was determined by the classical gravimetric procedure. A Unicam SP 500 spectrophotometer was used for all extinction measurements.

## RESULTS

*The chromium(III)-EDTA complex**Influence of the pH*

We carried out a systematic investigation of the influence of the pH on the colour of the complex (ammonia-ammonium chloride and acetic acid-sodium acetate buf-

fers were used). In acid solution two maxima occur, one at 395  $m\mu$  and another of larger intensity at 545  $m\mu$ . In alkaline medium the first maximum occurs at the same wavelength, but the extinction is considerably lower. The second maximum shifts to a higher wavelength, 590  $m\mu$ , and here the extinction is also lower. Table I gives the wavelength at which the second maximum occurs and the corresponding values of the molecular extinction coefficient.

TABLE I  
DEPENDENCE OF THE SECOND MAXIMUM ON pH

pH	Wavelength at which second maximum occurs	Corresponding molar extinction coefficient
0.85	545	147
1.50	545	157
2.00	545	171
3.03	545	198
3.60	545	203
4.00	545	201
5.37	545	201
6.19	545	197
7.13	550	172
8.60	583	129
9.00	590	123
10.20	590	122
10.60	590	122
10.90	590	122

The second maximum proved to be most suitable for analytical purposes and accurate measurements showed that in two pH ranges the extinction is independent of the pH, *viz.*, at pH 3–6 and at pH 9–11.

#### Validity of Beer's law

We observed no deviation from Beer's law in either pH range. The molecular extinction coefficients of both maxima were calculated from 10 extinction measurements, being 201.2 (standard deviation 0.6) in acid medium (pH 3–6) at 545  $m\mu$ , and 122.1 (standard deviation 0.3) in alkaline medium (pH 9–11).

#### Interferences

In agreement with PŘIBIL AND KLUBALOVA<sup>3</sup> we found that:

- (a) The extinction is independent of the excess of EDTA and of the time of heating. The colour is perfectly stable on standing.
- (b) The following elements do not affect the formation of the complex and the resulting extinction: alkali metals; alkaline earth metals; elements of the H<sub>2</sub>S group with the exception of copper; aluminium, manganese and zinc. Of the more common anions, chloride, nitrate, acetate and sulphate do not interfere (PŘIBIL *et al.*<sup>3</sup> mention an interference of sulphate ions, but we did not observe any interference even when the amount of sulphate was one hundred times that of chromium).
- (c) Of the more common metals, only copper, iron, cobalt and nickel, which give coloured complexes with EDTA, interfere with the determination of chromium.

*Determination of chromium as chromium(III)-EDTA complex  
in presence of other metals*

Unfortunately, iron and nickel often occur in samples containing chromium. PŘIBIL *et al.*<sup>3</sup> therefore tried to develop a procedure for the separation of chromium(III) from these elements; potassium hydroxide and hydrogen peroxide were added to precipitate the interfering elements as their hydroxides and convert chromium to chromate. After filtration the chromate must be reduced to chromium(III) before the determination with EDTA. PŘIBIL stated that this reduction is incomplete with most common reducing agents. He used EDTA itself for the reduction of chromate to chromium(III). When potassium dichromate was used initially, the results of the determination as the EDTA complex were lower than expected from the results given directly by chromium(III), but they were reproducible and correct when used with an auxiliary calibration curve. However, when interfering elements were present and hydrogen peroxide had to be used for the separation, PŘIBIL found that it was impossible to remove the last traces of peroxide. According to PŘIBIL, the peroxide interferes with the chromium(III)-EDTA determination because it increases the extinction. This increase has an upper limit and he therefore added an excess of hydrogen peroxide to each determination. This resulted in a third calibration curve.

We reinvestigated these statements and at room temperature we could find no effect of hydrogen peroxide on the extinction at  $545\text{ m}\mu$  of an acid chromium(III)-EDTA solution, even when 100 ml of the solution of the complex contained 8 ml of 30% hydrogen peroxide. The extinction at  $395\text{ m}\mu$  increased but this was due to absorbance by hydrogen peroxide and was directly proportional to its amount. In alkaline medium and at higher temperatures the chromium(III)-EDTA complex was completely destroyed by hydrogen peroxide and chromium was converted to the hexavalent state.

We also proved spectrophotometrically that the reduction of dichromate by EDTA, as carried out by PŘIBIL, is not complete. In some, but not all, cases the spectrum of the reduced solution contained the characteristics of the spectrum of the dichromate ion. This fact could also be explained: as PŘIBIL mentions, not all the peroxide is decomposed by boiling; the residual amount could oxidize the residual dichromate in acid medium, to form blue chromium peroxide,  $\text{CrO}_5$ , or red perchromates. These colours were found in solutions that were oxidized with hydrogen peroxide to chromate and subsequently reduced to chromium(III) by means of EDTA.

Because of all these complications from oxidation to chromate and subsequent reduction, we concluded that a method which did not involve an oxidation, should be preferred. We succeeded in developing a few suitable procedures in which oxidation could be avoided before the determination as chromium(III)-EDTA. The three procedures given below cover practically all the cases likely to be met in practice.

*Procedures A and B*

The first two procedures (A and B) utilize the separation of chromium(III) by means of TAA (thioacetamide) and EDTA. (In previous papers<sup>7-9</sup> we have described the determinations of zinc, copper and iron by means of EDTA and TAA.)

We have shown<sup>7</sup>, that addition of calcium chloride and TAA to an ammoniacal solution containing EDTA precipitates all the common group III elements, with the excep-

tion of chromium(III), provided that the solution is heated in a water bath before the addition of calcium chloride, because of the slow formation of the chromium(III)-EDTA complex at room temperature. It should therefore be possible to make use of this separation for the determination of chromium in presence of other group II and group III elements.

*Procedure A* can be used when cobalt and nickel are absent. The group II elements are precipitated if necessary (only when copper is present), in acid medium with TAA and the other interfering element (iron) as hydroxide, without the use of TAA, in ammoniacal medium. For the simple case when only group III elements are present, with the exception of cobalt and nickel, procedure A is as follows:

Place 2.5 ml of a solution, containing 0.15-4 mg of chromium(III) in a 15-ml centrifuge tube. If necessary, oxidize iron(II) to iron(III) with bromine water and heat to remove the excess of bromine. Add 1 ml of 0.2 M EDTA solution and heat for 30 min in a water bath at 90°. Cool and add ammonia until the colour of the solution changes from purple to blue. Add 1 ml of buffer pH 10, and 1 ml of 0.6 M calcium chloride solution and heat for another 30 min in a water bath at 95°. Cool, centrifuge and pour the supernatant liquid into a 25-, 50- or 100-ml volumetric flask, containing buffer solution of pH 10 or 4. Wash twice with 1 ml of a slightly ammoniacal 2% ammonium chloride solution into the flask, make up to the mark and measure the extinction at 590 or 545 m $\mu$ , depending on the buffer used.

The results of some of the determinations of small amounts of chromium in presence of 4 mg of iron are shown in Table II.

TABLE II  
DETERMINATION OF DIFFERENT AMOUNTS OF CHROMIUM IN PRESENCE OF 4 mg OF IRON(III)

Wavelength of extinction measurement in m $\mu$	Cr(III)		Error in %
	present	found	
590	3.83 mg	3.84 mg	+0.25
545	0.765	0.776	+1.5
545	0.383	0.389	+1.5
545	0.383	0.387	+1.0
545	0.153	0.153	0
545	0.153	0.151	-1.3
545	0.153	0.152	-0.7

Very similar results were obtained when Al, Mn, and Zn were also added in the same amounts as iron. It may therefore be concluded that small amounts of chromium can be determined in this way in presence of relatively large amounts of Fe, Al, Mn and Zn.

#### Note

The same procedure can be used when group II elements are present, with the exception of copper. When copper is present it can be precipitated in acid solution with TAA before the precipitation of group III elements, or procedure B can be used.

*Procedure B* is used when cobalt or nickel is present; TAA is used to precipitate the interfering elements, Co, Ni and Cu. Of course procedure B could be followed in

all cases, but procedure A is generally preferred, because the spectrophotometric determination can be carried out in acid solution (at  $545\text{ m}\mu$ ). When the group III elements have been precipitated as sulfides with TAA, acidification of the filtrate results in turbidity which interferes with the extinction measurement, hence the extinction of the alkaline solution must be measured (at  $590\text{ m}\mu$ ) when procedure B is applied. We have already shown<sup>7</sup>, that group II and III elements, which interfere with this determination of chromium, can be precipitated by the addition of TAA and calcium chloride to the ammoniacal solution containing EDTA.

Procedure B is as follows. Place 2.5 ml of a solution, containing 0.7–4 mg of chromium(III) in a 15-ml centrifuge tube. Neutralize the solution with dilute ammonia (if a permanent precipitate appears, dissolve in a drop of hydrochloric acid). Add 3 ml of 0.2 M EDTA, heat for 30 min in a water bath at  $90\text{--}95^\circ$ , cool to  $70^\circ$ , add a few drops of ammonia (colour changes from purple to blue), 1 ml of buffer solution pH 10, 1.5 ml of an 8% solution of TAA and 200 mg of calcium chloride ( $\text{CaCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ ). Heat for 30 min in a water bath at  $80\text{--}85^\circ$ . Centrifuge, remove the supernatant liquid by suction through a G4 glass filter stick. Wash twice with 2–3 ml water and combine the three filtrates in a 100-ml volumetric flask containing 20 ml of buffer solution pH 10. Make up to the mark and measure the extinction at  $590\text{ m}\mu$ .

Typical results obtained by this procedure, in presence of various elements, are given in Table III. It can be seen that only nickel interferes.

TABLE III  
DETERMINATION OF CHROMIUM IN PRESENCE OF GROUP II AND GROUP III ELEMENTS

Other elements present, mg							Cr(III), mg		Error in %
Fe	Al	Zn	Mn	Co	Cu	Ni	present	found	
6	6	6	6	—	—	—	3.83	3.87	+ 1.0
3	3	3	3	3	3	—	3.83	3.88	+ 1.3
3	3	3	3	3	3	—	3.06	3.06	0
3	3	3	3	3	3	—	2.30	2.32	+ 0.9
3	3	3	3	3	3	—	1.54	1.57	+ 1.9
3	3	3	3	3	3	—	0.765	0.780	+ 1.9
—	—	—	—	—	—	3	3.83	4.42	+ 15

#### Notes

I. In the volumetric flask, the excess of TAA decomposes slowly, forming small amounts of hydrogen sulfide. It is therefore necessary to use absolutely cation-free distilled water, in order to avoid interference of traces of heavy metal sulfides.

II. The presence of nickel generally causes complications:

(a) Part of the nickel remains colloidal. This can be partly prevented by the addition of cobalt(II); nickel sulfide then coprecipitates with cobalt sulfide. Even then, however, the precipitation of nickel sulfide is usually only complete after several days.

(b) When precipitates of nickel sulfide come into contact with atmospheric oxygen, they can be oxidized so that some nickel dissolves<sup>10</sup> and causes in positive errors in the determination of chromium.

In spite of many efforts we were unsuccessful in developing a satisfactory quantitative separation of chromium(III) from nickel(II) which does not require a long time.

*General remark with respect to procedures A and B*

Larger amounts of the interfering elements than those mentioned in Tables II and III should be avoided, because decantations from centrifuge tubes with very large amounts of precipitate cannot be carried out satisfactorily.

Chromium(III) determinations in presence of larger amounts of these elements can be carried out by taking smaller amounts of the sample containing 0.2–1 mg of chromium.

*Procedure C*

Although procedures A and B gave correct results except in the presence of nickel, we tried to develop a procedure for the determination of chromium(III) in presence of nickel and perhaps other elements, which did not require a separation. We tried to utilize the following qualitatively observed facts.

(a) The chromium(III)–EDTA complex is formed very slowly at room temperature, whereas the complexes of the interfering elements are formed practically instantaneously.

(b) The complexes of the interfering elements absorb at 545 and 590  $m\mu$ , but to a much smaller extent than the chromium(III)–EDTA complex.

It should therefore be possible to determine chromium(III) in acid solution in presence of interfering metal ions by means of two extinction measurements at 545  $m\mu$ , one mixture with EDTA being heated and the other unheated. The difference of the two extinction measurements  $\Delta E$  should then be equal to  $\Delta \epsilon cd$  in which  $\Delta \epsilon$  is the difference of the molecular extinction coefficients of the chromium(III)–EDTA complex and of chromium(III) itself.

The following results show that the requirements for this simple determination of chromium are fulfilled.

(a) *The velocity of the formation of the chromium(III)–EDTA complex.* We studied the increase in the extinction at 545  $m\mu$  with time in a 4-cm cell at room temperature of two 100-ml solutions containing about 10 mg of chromium, 5 ml of 0.2 M EDTA and buffered at pH 3.5 or 4 with acetic acid–acetate buffers. The increase of the extinction was linear with time during the first two hours. The extinction of the pure chromium(III) solution was 0.088 and that of the corresponding chromium(III)–EDTA solution after complex formation of the complex 1.52. The increase in the extinction at the beginning was 0.0005 per minute at pH 3.5 and 0.001 per minute at pH 4. These values prove that when a pH value of 3.5 is chosen and the extinction of the unheated solution is measured within 6 min the error in the determination caused by the formation of the EDTA complex is less than 0.2%.

(b) *Rate of formation of the interfering complexes, their molar extinction values and their behaviour on heating.* We found that the EDTA complexes of iron(III), nickel and copper were formed immediately after addition of EDTA to the metal ion solutions at pH 3.5 and 4. The extinction values were not affected by heating the solutions. The molar extinction values at the wavelength under consideration (545  $m\mu$ ) were 4 for the iron(III)-complex, 5 for the nickel-complex and 3.5 for the copper-complex. Therefore no interference of iron(III), nickel and copper is to be expected in procedure C.

Although the cobalt(II)–EDTA complex is formed immediately at room temperature and the molar extinction coefficient is small, cobalt interferes because the extinction increases when the cobalt(II)–EDTA solution is heated, owing to the



oxidation of the complex to Co(III)-EDTA, which is favoured by the decrease of the Co(III)/Co(II) oxidation potential in the presence of EDTA. Because the increase in the extinction of the cobalt(II)-EDTA solution on heating is small, interference with the determination of chromium(III) only occurs when cobalt is present in larger amounts than chromium.

Procedure C is as follows. It is applicable for chromium(III) solutions containing 0.1-1.5 mg of chromium per ml (about  $10^{-2}$ - $10^{-3}$  M Cr(III)) and various amounts of other metals.

Treat 5 ml of the solution in a test-tube with such an amount of 5% ammonia that the next drop of ammonia would cause precipitation of a metal hydroxide. Add 3 ml of 0.2 M EDTA (more when very large amounts of other metals are present). Heat the tube for 30 min in a water bath at 90-95°. Cool and transfer the liquid quantitatively to a 100-ml volumetric flask containing 10 ml of buffer pH 3.5 (prepared by diluting a mixture of 48 ml of acetic acid and 4.6 g of sodium acetate to 100 ml with water). Make up to the mark and measure the extinction in a 4-cm cell at 545 m $\mu$ . (For very small chromium concentrations, use a 50-ml flask, containing 5 ml of buffer solution.) Transfer another 5-ml aliquot of the original chromium(III) solution directly to another 100-ml volumetric flask containing 10 ml of buffer pH 3.5. Add water to a volume of 90-95 ml and then add 3 ml (more if necessary) of 0.2 M EDTA. Make up to the mark and measure the extinction immediately at 545 m $\mu$  in a 4-cm cell. The difference of the two extinction values  $\Delta E = \Delta \epsilon \cdot c \cdot d$ , where  $\Delta \epsilon$  (the difference between the molar extinction coefficients of chromium(III)-EDTA and chromium(III)) is 189.6 and  $d = 4$ . The calculated  $c$  is simply related to the concentration of the original unknown solution.

Some of the results of determinations of chromium according to procedure C in presence of other elements are given in Table IV.

TABLE IV  
DETERMINATIONS OF CHROMIUM IN PRESENCE OF OTHER METALS

Concentrations of other metal ions present (mmol)							Concentration of chromium (mmol)		Error %
Al	Fe(III)	Zn	Mn	Co	Ni	Cu	present	found	
—	20	—	—	—	20	20	8.86	8.92	+ 0.7
20	10	10	10	—	10	10	2.21	2.21	0
20	10	10	10	—	10	10	2.21	2.21	0
40	20	20	20	—	20	20	2.21	2.23	+ 0.9
40	20	20	20	—	20	20	2.21	2.24	+ 1.4
—	80	—	—	—	40	40	3.55	3.56	+ 0.3
—	80	—	—	—	40	40	3.55	3.59	+ 1.1
—	—	—	—	60	—	—	8.86	9.84	+ 11
—	—	—	—	20	—	—	8.86	9.22	+ 4
—	—	—	—	6	—	—	8.86	8.95	+ 1

The same procedure was applied to the determination of chromium in a N.B.S. chromium-nickel-steel (101  $d$ ), after dissolution of the alloy in concentrated hydrochloric acid. The alloy contained more than 70% Fe, about 0.2% Cu, 9% Ni, many traces of other elements and 18.67% Cr. We found with procedure C 18.70% and 18.73% Cr.

## Notes

1. Any iron(II) must be oxidized to iron(III) with bromine water; the excess bromine is removed by boiling.

2. Contrary to procedures A and B, procedure C requires two aliquots of the same solution for the determination of chromium. 25 ml of the unknown solution, however, are sufficient (corresponding to at least 2.5 mg chromium).

3. As can be seen from Table IV accurate results for the determination of chromium can be obtained in presence of large amounts of the other elements under consideration, with the exception of cobalt. When the amount of cobalt present is smaller than the amount of chromium the error is negligible.

4. A great advantage of procedure C over A and B is that no separations are used. The time required for the determination of the chromium(III) content of a solution is less than an hour irrespective of the amounts and nature of the other elements under consideration (with the exception of cobalt).

## SUMMARY

The spectrophotometric determination of chromium(III) as the chromium(III)-EDTA complex<sup>3</sup> has been critically investigated. The separation of chromium(III) from interfering elements by oxidation to chromate and subsequent reduction is unsatisfactory. Separation by means of TAA and EDTA is suggested; good results were obtained except in presence of nickel. A rapid method is also described for the determination of chromium(III); no separation is needed and results are accurate, except when more cobalt than chromium is present.

## RÉSUMÉ

Le dosage spectrophotométrique du chrome(III), sous forme du complexe Cr(III)-EDTA, proposé par PŘIBIL n'étant pas entièrement satisfaisant, deux autres procédés sont décrits, l'un avec séparation, sans oxydation du chrome(III); l'autre sans aucune séparation.

## ZUSAMMENFASSUNG

Beschreibung von zwei spektrophotometrischen Methoden zur Bestimmung von Cr(III) als Cr(III)-EDTA Komplex. Bei der einen Methode werden die störenden Elemente als Hydroxyde und Sulfide gefällt, bei der anderen Methode ist keine Trennung notwendig.

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SPECTROPHOTOMETRIC DETERMINATION OF SELENIUM(IV) WITH  
1,1'-DIANTHRIMIDE

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## INTRODUCTION

The organic reagent 1,1'-dianthrimide is normally used for spectrophotometric determination of small amounts of boron, the colour of the boron 1,1'-dianthrimide complex being developed in concentrated sulfuric acid by heating. During an investigation of the elements interfering in this determination it was found that germanium<sup>1</sup> and tellurium<sup>2</sup> also formed complexes with 1,1'-dianthrimide. Further investigations have shown that selenium reacts similarly, and in the present paper the use of 1,1'-dianthrimide for spectrophotometric determination of selenium is described.

No reference is made in the literature to the use of 1,1'-dianthrimide for the detection or determination of selenium.

## INSTRUMENTS AND REAGENTS

*Instruments*

Extinction measurements were made with a Zeiss spectrophotometer PMQ II, a matched set of 0.500-cm glass cells being used.

*Reagents*

The sublimed selenium dioxide was of purum quality. 1,1'-Dianthrimide, concentrated sulfuric acid (95–97%), fuming sulfuric acid (about 20% SO<sub>3</sub>) and other chemicals were of reagent grade quality. A series of sulfuric acids of varying strength was prepared by adding fuming acid or distilled water to concentrated sulfuric acid, the exact concentration being finally determined by titration. Ordinary distilled water from an all-metal still was used.

*Glassware*

All solutions were prepared and heated in 50-ml bottles (Jena Geräteglas) with ground-in glass stoppers.

*Heat treatment*

The solutions were heated in a thermostatically controlled drying oven of standard construction.

## EXPERIMENTAL DATA

*Standard solutions*

Selenium dioxide (70.3 mg) was dissolved in about 25 ml of 1% sodium hydroxide

solution. After dilution in a volumetric flask to 50 ml with 1% sodium hydroxide solution, the standard solution (containing 1 mg of selenium per ml) was stored in a plastic bottle. Another standard solution of selenium (containing 0.2 mg of selenium per ml) was prepared by diluting 10 ml to 50 ml with 1% sodium hydroxide solution. The 1% sodium hydroxide solution served as a blank.

1,1'-Dianthrimide (1.250 g) was dissolved in 96.12% sulfuric acid. The solution was diluted to 250 ml with the same acid and contained 5 mg of reagent per ml.

#### *Absorption curves*

In Fig. 1, curve 1, an absorption curve of the selenium 1,1'-dianthrimide complex is plotted. Curve 2 (Fig. 1) shows the absorption curve of a solution of 1,1'-dianthrimide.

The solutions measured photometrically were prepared in the following way. For curve 1, 0.6 ml of the selenium standard solution containing 0.2 mg of selenium per ml, 5 ml of the 1,1'-dianthrimide standard solution and 20 ml of 97.85% sulfuric acid were pipetted into a 50-ml bottle. The bottle was stoppered and the solution was mixed and then kept in the oven for 16 h at 70°. After cooling to room temperature the extinction at different wavelengths was measured against a blank consisting of 0.6 ml of 1% sodium hydroxide solution, 5 ml of 1,1'-dianthrimide standard solution and 20 ml of 97.85% sulfuric acid. The blank was also heated for 16 h at 70°. Curve 2 is the absorption curve of the blank solution measured against 96.12% sulfuric acid.

In this investigation the excess of 1,1'-dianthrimide was about 40 times the amount of selenium present. The high extinction values of the blank (as seen in Fig. 1, curve 2) can therefore be reduced considerably.

From Fig. 1 it is seen that the selenium 1,1'-dianthrimide complex has two absorption maxima at 480 and 585 m $\mu$ .

#### *Effect of concentration of sulfuric acid*

Before plotting calibration curves the effect of the concentration of sulfuric acid

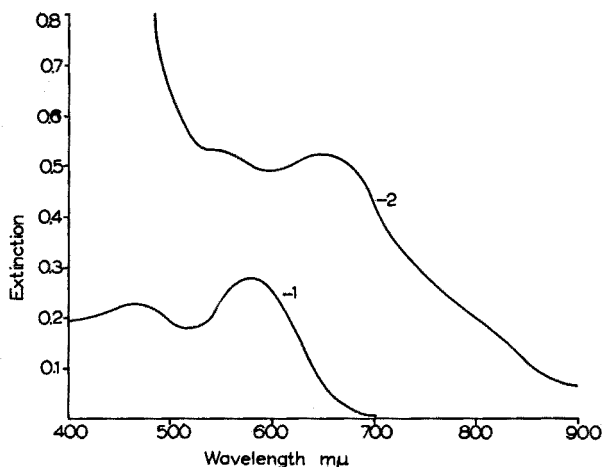


Fig. 1. Curve 1: Absorption curve of the selenium 1,1'-dianthrimide complex. Curve 2: Absorption curve of 1,1'-dianthrimide.

on the development of the colour of the complex was investigated for solutions heated for 16 h at 70°. A series of solutions was prepared in which the concentrations of selenium and 1,1'-dianthrimide were kept constant, while the concentration of sulfuric acid was varied.

0.1 ml of the selenium standard solution containing 1 mg of selenium per ml, 5 ml of 1,1'-dianthrimide standard solution and 20 ml of sulfuric acid of varying strength were pipetted into 50-ml bottles. The solutions were heated for 16 h at 70°, and the extinctions were measured at the wavelengths of the two absorption maxima against a series of blanks containing 0.1 ml of 1% sodium hydroxide solution, 5 ml of 1,1'-dianthrimide standard solution and 20 ml of the different acids. The extinction data obtained are given in Table I.

TABLE I  
EFFECT OF CONCENTRATION OF SULFURIC ACID ON THE DEVELOPMENT OF THE COLOUR OF  
THE SELENIUM 1,1'-DIANTHRIMIDE COMPLEX

Concentration (%) of the 20 ml of sulfuric acid added:	82.67	86.38	92.78	94.56	96.12	97.85	99.45
Extinction at 480 m $\mu$	0.285	0.362	0.386	0.338	0.324	0.364	0.578
Extinction at 585 m $\mu$	0.445	0.501	0.525	0.469	0.418	0.432	0.610

It can be seen that the concentration of sulfuric acid is critical. In the present investigation 96.12% acid was employed for preparing the calibration curve.

#### Calibration curves

Calibration curves were plotted by measuring the extinctions of a series of solutions containing varying known amounts of selenium. Into a series of 50-ml bottles were pipetted known volumes up to 1 ml from the standard solutions of selenium. Volumes of less than 1 ml were diluted to that volume with the blank solution. Then 5 ml of 1,1'-dianthrimide standard solution and 20 ml of 96.12% sulfuric acid were added, and the solutions were heated for 16 h at 70°. The extinctions were finally measured at the wavelengths of the two absorption maxima against a blank prepared and heated in the same way. The calibration data are given in Table II; it can be seen that a positive deviation from the Beer-Lambert law was obtained within the concentration range examined.

TABLE II  
EXTINCTION DATA FOR THE DETERMINATION OF SELENIUM WITH 1,1'-DIANTHRIMIDE

Se(mg) taken (C):	0.02	0.06	0.10	0.14	0.18	0.20	0.25
Extinction at 480 m $\mu$ (E <sub>1</sub> )	0.026	0.123	0.308	0.500	0.710	0.850	1.222
Extinction index at 480 m $\mu$ (E <sub>1</sub> /C)	1.30	2.05	3.08	3.57	3.99	4.25	4.89
Extinction at 585 m $\mu$ (E <sub>2</sub> )	0.025	0.167	0.408	0.645	0.880	1.033	1.456
Extinction index at 585 m $\mu$ (E <sub>2</sub> /C)	1.25	2.78	4.08	4.61	4.89	5.17	5.82

*Effect of temperature and heating time*

In concentrated sulphuric acid selenium and 1,1'-dianthrimide react very slowly. The rate of reaction increases with the temperature, but even at 70° the colour development is relatively slow. At temperatures above 70° a red colour appeared in addition to the colour of the complex; this colour probably originated from a decomposition product of 1,1'-dianthrimide. Consequently, a heating temperature above 70° cannot be recommended. A prolonged heating period also resulted in the appearance of the red decomposition product. A heating time of 16 h was used in this investigation.

*Influence of foreign ions*

On the basis of unpublished work on ions interfering in the determination of boron with 1,1'-dianthrimide, it can be deduced that the following ions interfere in the determination of selenium: B<sup>3+</sup>, Ge<sup>4+</sup>, Te<sup>4+</sup>, Br<sup>-</sup> (oxidized in concentrated sulfuric acid) and F<sup>-</sup>. The interference from fluoride ions is probably due to attack on glass and release of boron.

The following ions were found not to interfere in amounts given in brackets in mg per 25 ml: Ag<sup>+</sup>(2); Al<sup>3+</sup>(5); Ba<sup>2+</sup>(50); Bi<sup>3+</sup>(1); Ca<sup>2+</sup>(100); Cd<sup>2+</sup>(50); Co<sup>2+</sup>(20); Cr<sup>3+</sup>(10); Cu<sup>2+</sup>(20); Fe<sup>2+</sup>(20); Li<sup>+</sup>(10); Mg<sup>2+</sup>(20); Mn<sup>2+</sup>(10); Na<sup>+</sup>(130); Ni<sup>2+</sup>(20); Pb<sup>2+</sup>(1); Si<sup>4+</sup>(1); Sn<sup>2+</sup>(20); Ti<sup>4+</sup>(1); Tl<sup>+</sup>(10); Zn<sup>2+</sup>(50); Cl<sup>-</sup>(200); Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>(0.01); PO<sub>4</sub><sup>3-</sup>(100) and SO<sub>4</sub><sup>2-</sup>(138).

*Composition and stability constants of the 1,1'-dianthrimide complexes*

The composition and the stability constant of the boron 1,1'-dianthrimide complex have been determined previously<sup>3,4</sup>. The complex was found to have the mole ratio 1 : 1, and the stability constant (in 93.8% sulfuric acid and at 70°) was found to be 1.4 · 10<sup>5</sup>.

Investigations of the complexes of 1,1'-dianthrimide with germanium, tellurium and selenium showed that these complexes also have 1 : 1 mole ratios. Work on the stability constants, rates of formation etc. of these complexes is in progress and will be published later.

## SUMMARY

In concentrated sulfuric acid selenium and 1,1'-dianthrimide form a complex with mole ratio 1 : 1 and with absorption maxima at 480 and 585 mμ. The complex formation can be utilized for spectrophotometric determination of up to about 0.2 mg of Se per 25 ml. Interfering ions are boron, germanium, tellurium, bromide and fluoride.

## RÉSUMÉ

Une méthode spectrophotométrique est proposée pour le dosage du sélénium. On utilise comme réactif la dianthrimide-1,1'.

## ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Selen mit Hilfe von 1,1'-Dianthrimid.

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## ÉTUDE POLAROGRAPHIQUE DU GERMANIUM BIVALENT

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## INTRODUCTION

Il existe relativement peu d'études polarographiques sur le germanium. La réduction du germanium(IV) a été signalée par plusieurs auteurs<sup>1-4</sup>; en milieu alcalin, la réduction se fait en un stade à l'état métallique et le courant limite de diffusion diminue progressivement au-dessus du  $\text{pH} = 8,5^4$ .

Réduit par l'acide hypophosphoreux, Ge(II) donne, en milieu acide, une vague anodique d'oxydation  $\text{Ge(II)} \rightarrow \text{Ge(IV)}$ , puis, à un potentiel plus négatif, une vague de réduction  $\text{Ge(II)} \rightarrow \text{Ge}^{5-7}$ .

Il nous a paru intéressant de soumettre ce dernier système à une étude détaillée en vue d'obtenir des renseignements à la fois sur la chimie des solutions de germanium, encore très mal connues, et sur les phénomènes électrochimiques de cet élément. Cette publication comporte un certain nombre de résultats se rapportant à l'influence sur les deux vagues de germanium(II), de la concentration en acide hypophosphoreux et du pH.

## DÉTAILS EXPÉRIMENTAUX

Tous les polarogrammes ont été obtenus, soit au moyen d'un appareil manuel, soit au moyen d'un appareil enregistreur Sargent dont l'échelle des potentiels est spécialement étalonnée. La transformation des courbes en  $\log(i_a - i)/i$  par exemple, en fonction du potentiel, a été effectuée en corrigeant les courants mesurés de la chute ohmique.

La réduction du germanium à la valence 2 est faite par l'acide hypophosphoreux  $\text{H}_3\text{PO}_2$  ( $\text{p}K = 1,0$ ); toutefois, comme Ge(II) s'oxyde instantanément à l'air, nous avons été obligés de réaliser un appareil permettant d'effectuer toutes les manipulations à l'abri de l'air: la réduction de la solution de Ge(IV) se fait à la température du bain-marie, sous atmosphère d'azote, la solution est amenée à un titre donné au moyen d'eau désoxygénée et enfin introduite dans une burette graduée. Les introductions dans la cellule polarographique se font également entièrement à l'abri de l'oxygène. Les précautions à prendre pour obtenir des résultats quantitatifs sont très sévères étant donné que les solutions sont toujours diluées en germanium et que, en plus, on a observé que l'introduction de traces d'oxygène provoque une oxydation *immédiate* de Ge(II) en Ge(IV).

La réduction totale d'une solution de germanium  $5 \cdot 10^{-3} M$  par  $\text{H}_3\text{PO}_2 \sim 1,7 N$  à la température du bain-marie est obtenue après 2 h 30 de chauffage.

\* Cette étude fait partie de la thèse de doctorat: „*Contribution au dosage et à l'étude polarographique du germanium*” (1958).

## RÉSULTATS ET DISCUSSION

Comme nous l'avons déjà signalé, Ge(II), en milieu  $H_3PO_2$ , donne deux vagues de même hauteur: la vague anodique correspondant à l'oxydation  $Ge(II) \rightarrow Ge(IV)$  est caractérisée par un potentiel  $E^{1/2}$  égal à  $-0.149 \pm 0.003$  V/S.C.E., tandis que la vague cathodique — réduction  $Ge(II) \rightarrow Ge$  — est située à  $-0.515 \pm 0.002$  V/S.C.E.; les constantes du courant de diffusion (DDC), pour une concentration en  $[H_3PO_2] = 1.09$  N valant:

$$(DDC)_o = 3.36 \mu A \text{ mg}^{-2/3} \text{ sec}^{1/2}$$

$$(DDC)_a = 3.40 \mu A \text{ mg}^{-2/3} \text{ sec}^{1/2}$$

ces valeurs — potentiels  $E^{1/2}$  et DDC — sont constantes pour des concentrations en germanium variant entre  $5 \cdot 10^{-3}$  et  $1.5 \cdot 10^{-4}$  ion g/l.

Nous allons examiner maintenant l'influence de la concentration en acide hypophosphoreux et du pH sur les vagues polarographiques ( $E^{1/2}$ ,  $i_a$ , morphologie de la vague) en vue d'approfondir nos connaissances sur la chimie et l'électrochimie des solutions de germanium bivalent.

TABLEAU I

1ère série d'essais:  $2.5 \cdot 10^{-3}$  M Ge + 0.008% gélatine  
 $(m^{\frac{2}{3}} \cdot \theta^{\frac{1}{2}})$  à  $-0.7$  V/S.C.E. = 1.83;  $(m^{\frac{2}{3}} \cdot \theta^{\frac{1}{2}})$  à  $-0.002$  V/S.C.E. = 1.82  $\text{mg}^{\frac{2}{3}} \cdot \text{sec}^{-\frac{1}{2}}$

$[H_3PO_2]N$ de la solution à polarographier	$(i_a)_o$ $\mu A$	$(D.D.C.)_o$ $\mu A \text{ mg}^{-\frac{2}{3}} \text{ sec}^{\frac{1}{2}} (mM)^{-1} \times \text{lit.}$	$(i_a)_a$ $\mu A$	$(D.D.C.)_a$ $\mu A \text{ mg}^{-\frac{2}{3}} \text{ sec}^{\frac{1}{2}} (mM)^{-1} \times \text{lit.}$
4.50	13.2	2.88	13.0	2.86
3.82	13.6	2.97	13.4	2.95
3.45	13.8	3.02	13.6	2.99
2.90	14.2	3.10	14.2	3.12
2.43	14.5	3.17	14.5	3.19
1.91	14.8	3.24	14.8	3.25
1.09	15.6	3.41	15.6	3.43
0.82	15.6	3.41	15.6	3.44

2ème série d'essais:  $5 \cdot 10^{-4}$  M Ge + 0.008% gélatine  
 $(m^{\frac{2}{3}} \cdot \theta^{\frac{1}{2}})$  à  $-0.7$  V/S.C.E. = 1.81;  $(m^{\frac{2}{3}} \cdot \theta^{\frac{1}{2}})$  à  $-0.002$  V/S.C.E. = 1.805  $\text{mg}^{\frac{2}{3}} \cdot \text{sec}^{-\frac{1}{2}}$

$[H_3PO_2]N$ de la solution à polarographier	$(i_a)_o$ $\mu A$	$(D.D.C.)_o$ $\mu A \text{ mg}^{-\frac{2}{3}} \text{ sec}^{\frac{1}{2}} (mM)^{-1} \times \text{lit.}$	$(i_a)_a$ $\mu A$	$(D.D.C.)_a$ $\mu A \text{ mg}^{-\frac{2}{3}} \text{ sec}^{\frac{1}{2}} (mM)^{-1} \times \text{lit.}$
4.72	2.60	2.87	2.56	2.84
3.21	2.80	3.09	2.80	3.10
1.71	2.96	3.27	2.92	3.24
1.06	3.08	3.40	3.04	3.37
1.05	3.08	3.40	3.08	3.41
0.52	3.12	3.45	3.08	3.41
0.36	3.08	3.40	3.06	3.39
0.29	3.12	3.45	3.12	3.46
0.25	3.08	3.40	3.04	3.37

(a) Influence de la concentration en  $H_3PO_2$ 

Pour une concentration constante en Ge(II), on observe une diminution progressive des hauteurs des deux vagues lorsque la concentration en  $H_3PO_2$  augmente (voir Tableau I).



Cette diminution de  $(i_d)_a$  et  $(i_d)_c$  peut être due soit à l'augmentation de la viscosité du milieu, soit à une modification de la dimension de la particule diffusante. D'après la relation de Stokes-Einstein, on sait que le coefficient de diffusion  $D$  doit être inversement proportionnel à la viscosité  $\eta$  du milieu et, comme le courant limite  $i_d$  est proportionnel à  $D^{1/2}$  (équation d'Ilkovic), on peut s'attendre à ce que  $i_d \eta^{1/2}$  soit une constante s'il s'agit d'un effet de viscosité. Les mesures ont été faites au viscomètre d'Oswald à  $25^\circ \pm 0.5$  par rapport à l'eau distillée ( $\rho_0 = 0.9919$  g/cm<sup>3</sup>,  $t_0 = 209$  sec):

$$\frac{\eta_s}{\eta_0} = \frac{\rho_s}{\rho_0} \cdot \frac{t_s}{t_0}$$

Le Tableau II montre que le produit de  $i_d$  par  $\eta^{1/2}$  est bien constant à moins de 1% près, ce qui constitue la précision de la mesure des courants en polarographie ordinaire.

TABLEAU II

Série de mesures no. 1:  $\circ$  (rapporté à une concentration  $5 \cdot 10^{-4}$  M en Ge)  
Série de mesures no. 2:  $\triangle$  ( $5 \cdot 10^{-4}$  M en Ge)

Série	[H <sub>3</sub> PO <sub>2</sub> ] en N	(i <sub>d</sub> ) <sub>c</sub> en $\mu$ A	t <sub>s</sub> min	$\rho_s$ g/cm <sup>3</sup>	$\eta_s/\eta_0$	$i_d[\eta_s/\eta_0]^{1/2}$
$\triangle$	4.72	2.60	5'15''	1.109	1.685	3.38
$\circ$	4.50	2.64	5'12''	1.106	1.660	3.39
$\circ$	3.82	2.72	4'53''	1.089	1.540	3.37
$\triangle$	3.21	2.80	4'40'' <sup>6</sup> / <sub>10</sub>	1.076	1.456	3.38
$\triangle$	1.71	2.96	4'12''	1.039	1.255	3.32
$\triangle$	1.06	3.08	3'54'' <sup>6</sup> / <sub>10</sub>	1.024	1.160	3.32
$\circ$	1.06	3.10	3'55''	1.024	1.162	3.35
						moyenne = 3.36 $\pm$ 0.02

L'influence de la concentration en H<sub>3</sub>PO<sub>2</sub> sur les potentiels de demi-vague et sur la forme de la courbe est de nature à nous fournir des indications précieuses. Les résultats expérimentaux sont groupés dans le Tableau III.

Tableau III contient non seulement les potentiels de demi-vague des vagues anodiques et cathodiques mais également les pentes des droites  $\theta_a$  et  $\theta_c$  obtenues en représentant les vagues en fonction de

$$\log \frac{(i_d)_c - i}{i} \text{ et } \log \frac{-i}{i - (i_d)_a};$$

les pentes permettent alors de calculer  $(n\alpha)_c$  et  $(n\beta)_a$ ,  $\alpha$  et  $\beta$  étant les coefficients d'activation et  $n$  le nombre d'électrons intervenant dans la réaction lente, ainsi qu'il résulte de l'équation théorique d'une vague irréversible.

De l'ensemble de ces résultats, il résulte que:

(1) la vague cathodique correspond à la réduction du germanium(II) à l'état métallique, en formant vraisemblablement un amalgame: elle est du type réversible ( $\alpha = 1$ ) et donne un nombre d'électrons  $n = 2$ .

(2) le déplacement du potentiel  $(E^{1/2})_c$  avec l'augmentation de la concentration en acide hypophosphoreux vers des potentiels plus négatifs semble indiquer l'existence d'un complexe hypophosphoreux de Ge(II).

(3) la vague anodique possédant un D.D.C. sensiblement égal à celui de la vague

TABLEAU III

Sol:  $5 \cdot 10^{-4}$  M Ge + 0.008% gélatine  
 Série  $\odot$  : essais - mai 1957  
 Série  $\square$  : essais - janvier 1957  
 Séries  $\triangle$  et  $\times$  : essais - mai - juin 1956.

Série	$[H_3PO_2]_N$	$\log[H_3PO_2]$	$\frac{E^{\ddagger}}{V/S.C.E.}$	$\frac{E^{\ddagger}}{V/S.C.E.}$	$R$ Ohms	$\theta_c$ mV	$\theta_a$ mV	$(n\alpha)_c$	$(n\alpha)_a$
$\odot$	4.72	+0.674	-0.539	-0.142	600	31.2	58.7	1.90	1.00
$\odot$	3.21	+0.506	-0.531	-0.143	550	31.7	60.0	1.86	0.99
$\odot$	1.71	+0.232	-0.524	-0.146	850	30.5	61.2	1.94	0.97
$\odot$	1.06	+0.027	-0.512	-0.152	900	30.0	61.5	1.97	0.96
$\odot$	1.05	+0.024	-0.513	-0.150	950	30.0	63.2	1.97	0.93
$\times$	0.94	-0.028	-0.512	-0.176	900	30.0	56.2	1.97	1.05
$\square$	0.76	-0.117	-0.509	-0.158	—	—	—	—	—
$\times$	0.75	-0.125	-0.505	-0.157	950	30.0	58.7	1.97	1.00
$\square$	0.72	-0.143	-0.505	—	—	—	—	—	—
$\triangle$	0.64	-0.194	-0.501	—	—	—	—	—	—
$\square$	0.58	-0.233	-0.503	-0.157	—	—	—	—	—
$\times$	0.54	-0.269	-0.498	-0.176	1650	30.0	61.5	1.97	0.98
$\odot$	0.52	-0.286	-0.500	-0.156	1250	32.4	63.7	1.83	0.93
$\triangle$	0.50	-0.298	-0.497	—	—	—	—	—	—
$\square$	0.49	-0.308	-0.498	-0.157	—	—	—	—	—
$\triangle$	0.42	-0.377	-0.494	—	—	—	—	—	—
$\odot$	0.37	-0.437	-0.492	-0.160	1450	30.0	62.5	1.97	0.95
$\odot$	0.29	-0.542	-0.485	-0.169	1900	30.0	60.0	1.97	0.90
$\odot$	0.25	-0.605	-0.482	-0.171	1400	—	—	—	—
$\times$	0.21	-0.684	-0.480	—	1650	30	58.7	1.97	1.00

Les indications  $c$  et  $a$  se rapportent respectivement à la vague cathodique et anodique.

cathodique, correspond par conséquent à l'oxydation Ge(II) — Ge(IV). La valeur de  $n\beta$  indique indubitablement le caractère irréversible de cette réaction d'électrode et le léger déplacement de  $(E^{1/2})_a$  en fonction de la concentration en acide hypophosphoreux semble confirmer le fait que Ge(II) est complexé par l'acide en question.

Si l'on examine maintenant les déplacements de  $E^{1/2}$  en fonction de la concentration en acide hypophosphoreux, on trouve, pour la vague cathodique, une variation linéaire aussi bien en portant  $(E^{1/2})_c$  en fonction de  $\log [H_3PO_2]$  que en fonction de  $\log [H_2PO_2]^-$ ; les pentes de ces droites permettent de déterminer la valeur du nombre de particules dans le complexe (puisque  $n = 2$ ) et l'on trouve, dans le premier cas,  $n = 1.83$  et dans le second 3.3.

Il est impossible, sur la base de ces données, de trancher entre les complexes  $Ge(H_3PO_2)_2^{+2}$  ou  $Ge(H_2PO_2)_3^-$ .

Les cas de la vague anodique est trop complexe et la discussion des résultats ne mène à aucune hypothèse ayant quelque valeur.

#### (b) Influence du pH

L'influence du pH est représentée dans la Fig. 1. Il n'est pas possible de faire une

discussion détaillée de ces résultats dans le cadre de cet article. Nous voudrions simplement indiquer les conclusions essentielles qui en résultent:

Notons d'abord que la diminution de  $i_d$  observée à  $\text{pH} > 1.0$  représente un état d'équilibre réversible et qu'il ne s'agit pas du résultat d'une précipitation d'hydroxyde; on observe d'ailleurs simultanément un déplacement de  $E^{1/2}$  dans le sens des poten-

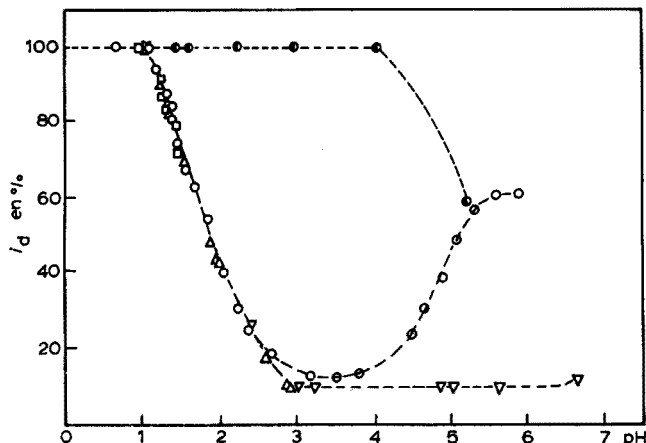


Fig. 1. Variation de  $i_d$  en % en fonction du pH, (sol.  $5 \cdot 10^{-4}$  M Ge(II) + 0.25 M  $\text{H}_3\text{PO}_2$  + 0.008% gélatine).  $\circ$  : avec NaAc seul (mesures 1957);  $\square$  : avec NaAc seul (mesures 1956);  $\triangle$  : avec NaOH seul;  $\nabla$  : avec biphthalate de K + NaOH;  $\bullet$  : avec  $\text{K}_2\text{C}_2\text{O}_4$  0.05 M + KOH.

tiels négatifs pour les deux vagues; des mesures turbidimétriques n'ont laissé apparaître aucune indication de formation de solution colloïdale. Il semble plutôt s'agir d'une transformation progressive du complexe par exemple  $\text{Ge}(\text{H}_3\text{PO}_2)_2^{+2} \rightarrow \text{Ge}(\text{H}_2\text{PO}_2)_2$ , au fur et à mesure de l'augmentation du pH, nouvelle forme irréductible ou en tous cas avec une vitesse très faible.

L'augmentation de la vague, en milieu acétique à  $\text{pH} > 4$ , semble indiquer la transformation du complexe hypophosphoreux en complexe acétique.

Enfin, l'étude en milieu hypophosphoreux et oxalique à différentes concentrations et différents pH — étude portant sur le courant limite et sur la forme de la vague — tend à montrer que l'on assiste progressivement, avec l'accroissement du pH au delà de 1, à la formation de complexe oxalique,  $\text{Ge}(\text{C}_2\text{O}_4)$  s'oxydant en  $\text{Ge}(\text{C}_2\text{O}_4)_3^{-2}$  vers  $\text{pH} = 3$ . La diminution ultérieure à  $\text{pH} > 4$  doit être attribuée à la formation d'un sel basique insoluble.

#### RÉSUMÉ

Les auteurs ont fait une étude polarographique des vagues de réduction et d'oxydation de Ge(II) dans différents milieux — notamment acide hypophosphoreux et acide oxalique — en fonction du pH et de la concentration. La vague de réduction de Ge(II) dans  $\text{H}_3\text{PO}_2$  1.09 N est caractérisée par  $E^{1/2} = -0.515 \pm 0.002$  V/S.C.E. et une constante du courant de diffusion de  $3.36 \mu\text{A mg}^{-2/3} \text{sec}^{1/2}$  tandis que pour la vague d'oxydation, on trouve  $E^{1/2} = -0.149 \pm 0.03$  V/S.C.E. et D.D.C. =  $3.40 \mu\text{A mg}^{-2/3} \text{sec}^{1/2}$ . Cette étude fournit des indications sur les complexes formés.

#### SUMMARY

The authors made a polarographic study of the oxidation and reduction waves of Ge(II) in different media — hypophosphorous acid and oxalic acid in particular — in relation to pH and

concentration. In 1.09  $N$   $H_3PO_2$  the reduction wave of Ge(II) is characterized by  $E^{1/2} = -0.515 \pm 0.002$  V/S.C.E. and a diffusion current constant of  $3.36 \mu A \text{ mg}^{-2/3} \text{ sec}^{1/2}$ , whereas for the oxidation wave these values are  $E^{1/2} = -0.149 \pm 0.003$  V/S.C.E. and D.D.C. =  $3.40 \mu A \text{ mg}^{-2/3} \text{ sec}^{1/2}$ . This study gives some information about the complexes that are formed.

#### ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über den Einfluss von pH und Konzentration auf den Verlauf der Oxydations- und Reduktionskurven bei der polarographischen Bestimmung von Ge(II) in verschiedenen Medien.

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## THE POLAROGRAPHIC DETERMINATION OF THIOETHANOLAMINE AND ITS DISULFIDE IN THE PRESENCE OF ONE ANOTHER

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Thioethanolamine and its disulfide have been found to afford protection against ionizing radiation for a number of biological systems<sup>1-4</sup>. In order to elucidate the mechanism of protection of these compounds, it is necessary to determine thioethanolamine in the presence of its disulfide at the physiological pH value of 7.4.

Most methods for the determination of the disulfide group involve prior reduction with subsequent determination of the mercaptan formed. IJIMA AND EGUCHI<sup>5</sup> have reported a method for disulfide based on the color produced after reaction of the disulfide group with copper sulfate and sodium thiosulfate. BENESCH AND BENESCH<sup>6</sup> proposed an indirect titration procedure involving back titration of the excess of added iodoacetamide. The anodic polarography of sulfur compounds in petroleum and its fractions has been reported by DRUSHEL AND MILLER<sup>7</sup>.

The procedure described in the present paper is a direct polarographic method involving the mercury dissolution wave.

#### REAGENTS AND APPARATUS

Thioethanolamine as the hydrochloride was obtained from Evans Chemetics, Inc., New York City. The disulfide of thioethanolamine ( $\beta$ ,  $\beta'$ -diaminoethyl disulfide dihydrochloride) was obtained from K & K Laboratories, Inc., Jamaica, New York.

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All other reagents were of "analytical grade". Polarograms were run in a CLARK and LUBS buffer of pH 7.4, ionic strength 0.2 M.

A Leeds and Northrup Electro-Chemograph, Type E, was used throughout. The dropping mercury electrode had a capillary constant ( $m^{2/3}t^{1/6}$ ) of  $2.211 \text{ mg}^{2/3} \text{ sec}^{-1/2}$ . A Lingane H-cell fitted with a potassium chloride-agar plug and a saturated calomel electrode was used as the polarographic cell. This cell was placed in a water bath thermostated at  $25 \pm 0.2^\circ$ . Nitrogen gas was bubbled through the test solutions for fifteen minutes prior to each run and a nitrogen atmosphere was maintained above the solution during the course of the run. Commercial tank nitrogen (Southern Oxygen Co.) was purified by passing the gas through two solutions of chromous sulfate and one of buffer before entering the H-cell.

#### DISCUSSION OF RESULTS

In Fig. 1 are shown the polarograms of thioethanolamine and its disulfide in a buffer medium of pH 7.4. Thioethanolamine has a half-wave potential of  $-0.420 \text{ V vs. SCE}$  and its disulfide has a half-wave potential 200 mV more negative. The wave of the disulfide exhibits a maximum which can be suppressed by the addition of two drops of a 0.2% solution of gelatin. Thioethanolamine was found to give a linear current-concentration relationship over the concentration range of  $2 \cdot 10^{-5}$  to  $10^{-2}$  molar and the disulfide over the range of  $7.5 \cdot 10^{-6}$  to  $7.5 \cdot 10^{-3}$  molar. These substances could be

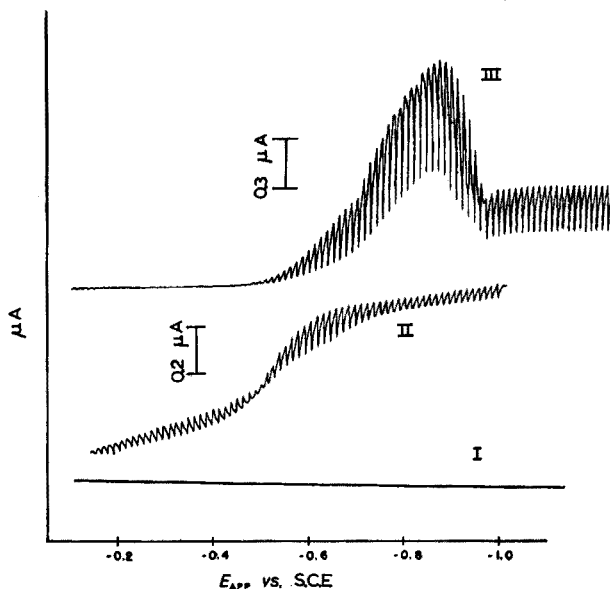


Fig. 1. Polarograms of thioethanolamine and its disulfide in a buffer solution of pH 7.4. Curve I. Supporting electrolyte alone. Curve II.  $10^{-4} \text{ M}$  thioethanolamine. Curve III.  $7.5 (10^{-4}) \text{ M}$  disulfide of thioethanolamine.

determined singly with an average error of less than 2%. In admixture, the disulfide could be determined in the presence of a 100-fold excess of thioethanolamine and the

mercaptan in the presence of a 10-fold excess of the disulfide with an average error of less than 5%.

#### *Effect of air*

In the buffer medium in which this determination is performed, thioethanolamine is rapidly air oxidized to the disulfide. A polarogram run on thioethanolamine showed no disulfide to be present. After exposure of the test solution to the air for 30 min, the wave for the mercaptan had completely disappeared and was replaced by the wave for the disulfide.

This sensitivity to air oxidation makes it necessary to deaerate both the thioethanolamine and the buffer solution prior to mixing and to add the test solution to the buffer in a manner which excludes all but traces of air. This can be accomplished by placing the buffer solution in the polarographic cell, flushing with nitrogen gas, and adding the thioethanolamine solution from a pipette, the tip of which is below the surface of the buffer solution.

#### ACKNOWLEDGEMENT

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#### SUMMARY

A direct polarographic method has been developed for the determination of thioethanolamine and its disulfide in the presence of one another. Thioethanolamine may be determined over the concentration range of  $2 \cdot 10^{-5}$  to  $10^{-2}$  molar and its disulfide over the range of  $7.5 \cdot 10^{-6}$  to  $7.5 \cdot 10^{-3}$  molar with an average error of 2%. Thioethanolamine may be determined in the presence of a 10-fold excess of the disulfide and the disulfide in the presence of a 100-fold excess of the mercaptan. Precautions must be taken to exclude air from the system due to the rapid oxidation of the thioethanolamine to its disulfide.

#### RÉSUMÉ

Une méthode polarographique est proposée pour le dosage de la thioéthanolamine et de son disulfure, en présence l'un de l'autre. En raison de la rapidité d'oxydation de la thioéthanolamine, il est nécessaire d'éliminer complètement l'air.

#### ZUSAMMENFASSUNG

Beschreibung einer polarographischen Methode zur Bestimmung von  $\beta$ -Mercaptoäthylamin neben der entsprechenden Disulfidverbindung. Wegen der leichten Oxydierbarkeit der Mercaptoverbindung muss unter Luftausschluss gearbeitet werden.

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MACRO- ET MICRODOSAGE DE TRACES DE COBALT  
DOSAGES SPECTROPHOTOMÉTRIQUE ET POLAROGRAPHIQUE DU  
COBALT DANS LES ACIERS MA 2 B, EDELWEISS

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DOSAGE SPECTROPHOTOMÉTRIQUE

Il est nécessaire de connaître la teneur en cobalt des matériaux utilisés dans la construction des réacteurs atomiques et susceptibles de recevoir un flux intense et prolongé de neutrons. En effet, il faut éviter, dans la mesure du possible, la formation de trop grandes quantités de cobalt 60, isotope de longue période, émetteur de rayons  $\gamma$  pénétrants.

Parmi les divers procédés de séparations proposés pour le dosage du cobalt dans les aciers, citons celui de SMOCZKIEWICZOWA ET MIZGALSKI<sup>1</sup> qui utilisent la chromatographie sur papier et de SAYLER ET AWEET<sup>2</sup> qui effectuent une séparation électrolytique sur anode. Dans ce dernier cas, les quantités d'échantillons nécessaires sont relativement très grandes puisque la solution doit renfermer 10 mg environ de cobalt; il ne semble donc pas qu'elle puisse s'appliquer au dosage d'aciers très pauvres en cobalt. D'autres auteurs déposent le cobalt sur une cathode de mercure, puis dissolvent celle-ci dans une atmosphère d'azote. Il est aussi proposé une extraction à l' $\alpha$ -nitroso- $\beta$ -naphthol<sup>3,4</sup>. PEPKOWITZ ET MARLEY<sup>5</sup> ont mis au point une méthode rapide et précise de dosage du cobalt par le tétraphénylarsonium mais elle n'est pas suffisamment sensible, semble-t-il, pour le dosage de faibles traces de cobalt dans les alliages. Citons encore GRAUE *et al.*<sup>6</sup> dont la méthode a été spécialement établie pour les alliages destinés à la construction des réacteurs. Ils partent de 1 g d'échantillon; le fer est éliminé par extraction à l'éther chlorhydrique ou par entraînement à l'oxyde de zinc.

Pour le dosage, la plupart des auteurs utilisent la méthode spectrophotométrique et comme réactif le nitroso-sel R, particulièrement sensible. Nous proposons une détermination du cobalt dans l'acier 18/8 par ce même réactif, le mode opératoire est basé sur l'étude systématique que nous avons faite sur cet élément tant en ce qui concerne les séparations que la détermination spectrophotométrique. La précision et la sensibilité de la méthode ont été déterminées, les pertes et contaminations ont été évaluées<sup>7-9</sup>.

Cette méthode est plus sensible que celles proposées dans la littérature, grâce à un mode opératoire différent, à l'emploi de microcuvettes et d'un photomultiplicateur. On peut doser des traces de cobalt comprises entre 0.01  $\mu\text{g}$  et 50  $\mu\text{g}$  dans les milieux les plus complexes, tant chimiques que biologiques, avec précision et sans difficultés spéciales.

Bien que la plupart du temps, une telle sensibilité ne présente pas une absolue

nécessité, même pour des matériaux destinés à l'énergie atomique, elle a néanmoins le très grand avantage de permettre d'opérer sur de très faibles quantités d'échantillon. On diminue le temps nécessaire aux diverses opérations, certaines d'entre elles peuvent même être supprimées et on évite du même coup la présence de trop grandes quantités d'ions étrangers, le fer dans le cas particulier. On peut objecter qu'en diminuant la prise dans de telles proportions, la moindre perte ou la plus faible contamination sont susceptibles de provoquer de grandes erreurs. Cet argument est sans valeur car les réactifs utilisés sont purifiés de telle sorte que le blanc est très souvent négligeable et de toute façon, il peut être déterminé très exactement. De plus, en réduisant la quantité d'échantillon, on réduit du même coup la quantité des réactifs nécessaires et par conséquent les contaminations. Quant aux pertes, nous verrons qu'elles diminuent avec la prise et qu'elles ne sont pas plus fortes, proportionnellement sur 100 mg que sur 1 mg d'échantillon (v. Tableaux I et II). Il est du reste possible de les évaluer avec précision par addition, à la solution initiale, d'un indicateur radiochimique, en l'occurrence le cobalt 60, dont l'activité  $\gamma$  est mesurée, au compteur à scintillation, au début puis à la fin des opérations analytiques. La perte d'activité correspond de façon très exacte aux pertes de cobalt au cours de l'analyse.

Cet indicateur radiochimique permet aussi de contrôler l'efficacité des séparations et de suivre pas à pas la marche de l'analyse. Cette manière de faire a considérablement facilité la mise au point de la méthode. Evidemment, nous sommes placés dans des conditions particulièrement avantageuses car notre indicateur a une longue période et les rayons  $\gamma$  qu'il émet, très pénétrants, sont particulièrement faciles à compter avec précision. De plus, le processus présente une grande sensibilité.

Les densités optiques ont été mesurées au spectrophotomètre "Beckman DU avec ou sans photomultiplicateur et les mesures d'activité  $\gamma$  au moyen d'un scintillateur P 20 B équipé d'un cristal creux et relié à un compteur "Tracerlab 1000 scaler". Pour le marquage des solutions, nous avons utilisé le cobalt 60 (solution ayant une activité de 1  $\mu\text{C}/\text{ml}$  et renfermant 0.18  $\mu\text{g}/\text{ml}$  de cobalt total).

#### *Pureté des réactifs*

Nous avons utilisé des acides "Merck pro anal."; le cobalt s'y trouve en quantité négligeable. Quant au citrate de sodium, régulateur de pH et agent complexant, il contient au maximum 0.5  $\mu\text{g}$  de cobalt par 100 g. Toutes les solutions ont été préparées avec de l'eau bidistillée préalablement traitée aux échangeurs de cations. Un blanc permet de faire les corrections des erreurs provenant des contaminations.

#### MACRODOSAGE

##### *Mode opératoire*

On dissout 100 à 500 mg d'acier dans 15 ml d'eau régale (l'analyse sur 1 g, proposé par certains auteurs n'est pas à recommander ici). On porte à ébullition pour éliminer le chlore et on ajoute de temps en temps un peu d'eau distillée afin d'éviter une évaporation à sec qui provoquerait la formation d'oxydes de fer hydratés difficiles à mettre en solution. On contrôle le départ du chlore au moyen de papier iodo-ami-donné. Lorsque l'opération est terminée, on reprend par l'acide chlorhydrique concentré de telle sorte qu'on obtienne un volume de 10 à 15 ml.

Pour marquer cette solution, on introduit 2 ml de l'étalon cobalt 60 renfermé dans une éprouvette, dans le cristal creux et on en mesure l'activité totale. Ces deux ml



sont ensuite introduits dans la solution chlorhydrique renfermant l'échantillon, puis on compte de nouveau l'activité de l'éprouvette vide pour en déterminer l'activité résiduelle. La différence de ces deux comptages donne l'activité de notre solution. Au début des opérations analytiques, on obtient avec l'étalon dont la composition est donnée ci-dessus, 10,000 à 12,000 c.p.m. Le cobalt 60 va jouer le rôle d'indicateur radioactif de pertes. Si on fait parallèlement une analyse avec étalon interne, on procédera de façon identique pour le marquage.

#### *Extraction du fer*

La quantité de fer est telle que celui-ci saturerait la résine dont la masse a été réduite autant que possible et le cobalt ne serait plus alors retenu quantitativement. Il faut donc éliminer la plus grande partie du fer par extraction. On transvase la solution dans une ampoule à décanter de 250 ml, on y ajoute 50 ml d'acide chlorhydrique 9 N et 40 ml d'éther saturé d'acide chlorhydrique concentré. Après agitation énergique pendant quelques minutes (l'équilibre entre les phases s'établit très rapidement lorsqu'on prend l'éther comme solvant organique), on laisse reposer 15 min, puis on sépare les phases. L'opération d'extraction est répétée trois fois; on élimine ainsi la plus grande partie du fer de la solution aqueuse. Si les opérations sont bien conduites la phase éther-HCl ne présente aucune activité; il n'y a donc pas de perte de cobalt au cours de ces opérations.

#### *Séparation sur résine*

La solution aqueuse verte qui résulte de l'extraction précédente et qui renferme le cobalt est chauffée à 60° au bain-marie pour éliminer l'éther qui y est dissous. Son volume est de 60 ml environ et la teneur en acide, qui convient bien à la séparation sur résine, n'a pas été modifiée par les opérations précédentes. Il faut en effet éviter toute variation de concentration en acide chlorhydrique, qui pourrait provoquer une rétention du nickel et du chrome sur la résine, le cobalt ne serait plus alors retenu quantitativement.

On fait donc passer la solution ci-dessus sur une colonne de 120 mm de hauteur et 8 mm de diamètre, ce qui correspond à un volume apparent de la résine Dowex I-X 8 (100/200 mesh) de 6 ml environ (celle-ci a été préalablement lavée avec 30 ml HCl 0.01 N, puis imprégnée de 10 ml HCl 9 N). La solution récupérée au bas de la colonne ainsi que les solutions acides de lavage ne doivent pas présenter d'activité notable. On perçoit, dans la partie supérieure de la résine, un anneau brun dû aux traces de fer, le cobalt se fixe immédiatement au-dessous. Quant au nickel et au chrome, ils traversent quantitativement la colonne. Le cobalt est élué par 30 ml d'une solution d'acide chlorhydrique 4 N. On reçoit, au bas de la colonne un liquide légèrement coloré en jaune vert qui renferme le cobalt et de petites quantités de résine, gênantes pour la détermination spectrophotométrique.

#### *Élimination de la résine*

On ajoute du citrate de sodium cristallisé à la solution, de telle sorte que la concentration soit de 10%. On porte au pH 8.2, tout d'abord par addition d'une solution concentrée d'hydroxyde de sodium en refroidissant, puis avec une solution normale d'hydroxyde de sodium. On transvase dans une ampoule à décanter de 200 ml et on extrait avec 5 ml d'une solution de 0.05% de dithizone dans l'éther. L'opération est

répétée jusqu'à ce que la couleur de la solution étherée ne change plus. On élimine ainsi les traces de résine. On termine par un lavage de cette dernière avec 5 ml d'éther pur et on mesure alors l'activité de la phase aqueuse, elle doit être négligeable.

#### *Destruction de la dithizone*

Les diverses solutions de dithizonate de cobalt dans l'éther ainsi que l'éther de lavage sont réunis dans une ampoule à décanter de 100 ml. On lave deux fois avec 2 ml d'acide chlorhydrique 0.1 *N* puis on transvase dans une capsule de pyrex et on ajoute 5 ml d'acide perchlorique. La capsule est recouverte d'un verre de montre creux renfermant un peu d'eau qui joue le rôle condensateur et on place le tout sur une plaque chauffante à 200°. Après deux heures environ, la dithizone est détruite quantitativement, la solution devient incolore. 5 ml d'une solution molaire de chlorure de potassium sont ajoutés, puis on évapore à sec et reprend par 1 ml d'acide chlorhydrique concentré, puis nouvelle évaporation à sec, nouvelle addition de 1 ml d'eau distillée, pour éliminer cette fois toute trace d'acide chlorhydrique. Le résidu de la capsule est repris par de l'eau distillée, ajoutée par petites fractions qu'on introduit dans un ballon de 5 ml jusqu'au trait de jauge.

#### *Détermination spectrophotométrique*

La solution est diluée, si nécessaire, de telle sorte qu'elle ne renferme pas plus de 2 à 3  $\mu\text{g/ml}$  et pas moins de 0.01  $\mu\text{g/ml}$  de cobalt. (Lorsque la teneur de cobalt dans l'acier est très faible, on ajoute après la destruction de la dithizone, 1 ml de la solution de chlorure de potassium au lieu de 5 ml. Le résidu, après élimination de l'acide chlorhydrique sera repris par 1 ml d'eau distillée).

Dans un tube à centrifuger de 5 ml, on introduit 1 ml de la solution précédente, 2 ml de tampon acétique de pH 6 (acétate de sodium à 10% additionné d'acide acétique glacial) et 0.5 ml d'une solution de nitroso-sel R à 0.05%. Le tube est placé une minute dans un bain-marie bouillant pour développer la coloration; puis on ajoute 0.5 ml d'acide nitrique concentré et on maintient au bain-marie 30 sec.

TABLEAU I  
ANALYSE DU COBALT DANS L'ACIER PHOENIX MA 2 B

Analyse	Prise (g)	Etalon interne ( $\mu\text{g}$ )	Activité		Pertes (%)	Co trouvé ( $\mu\text{g}$ )	Co dans prise (%)
			avant (c.p.m.)	après (c.p.m.)			
1	0.5	—	11884	9734	18	225	0.045
2	0.5	—	12094	9561	21	210	0.042
3	0.1	—	11914	10126	15	44	0.044
4	0.1	—	11937	10407	16	42	0.042
5	0.1	—	11902	9758	18	41	0.041
6	0.1	—	12124	7271	40*	44	0.044
7	0.1	49.6	12014	9488	21	92	0.042
8	0.1	69.4	11987	8882	26	114	0.045
9	0.1	—	12342	10512	15	46	0.046
10	0.1	—	12385	10779	13	42	0.042
11	0.1	49.6	12332	9863	20	95	0.045
12	0.1	69.4	12455	10091	19	112	0.043
Valeur moyenne . . . . .							0.0434

\* Cet écart n'est pas imputable aux séparations elles-mêmes, mais à une perte accidentelle.

Après refroidissement dans un courant d'eau, on complète au trait de jauge avec de l'eau bidistillée puis on centrifuge pendant 20 min pour rendre la solution optiquement vide. Cette dernière est introduite dans une cuve de 1 cm d'épaisseur et on mesure au spectrophotomètre Beckman la densité optique, à  $\lambda = 520 \text{ m}\mu$ , par rapport à un blanc, qu'on obtient en procédant exactement comme il a été fait pour l'échantillon.

Nous avons effectué une série de 12 dosages sur le même acier en partant de prises de 0.5 g et 0.1 g; les résultats sont donnés dans le Tableau I.

Les pertes ont été déterminées par la mesure des activités au début et à la fin de l'analyse.

Pour les analyses 7, 8, 11 et 12, une quantité connue de cobalt a été ajoutée au moment de la mise en solution de la prise (étalon interne), la marche du dosage étant par ailleurs identique.

En prenant les précautions nécessaires, il est possible de maintenir les pertes entre 15 et 20% et de les évaluer à, au moins, 5% près. Nous ne l'avons pas fait, car l'indicateur radioactif permet de les déterminer très exactement.

#### *Étude statistique de la précision de la méthode*

Elle a été faite sur les résultats des analyses 3 à 12, pour des prises de 0.1 g. L'écart type sur cette série de déterminations est de 0.485. Pour une probabilité de 95%, on aura un écart de  $\pm 1.1 \mu\text{g}$ ; le résultat est donc compris entre 41.9 et 44.1  $\mu\text{g}$ , c'est-à-dire entre 0.0419 et 0.0441%.

#### MICRODOSAGE

La sensibilité de la méthode que nous avons mise au point permet d'effectuer les dosages du cobalt dans les aciers sur des prises beaucoup plus faibles que celles nécessaires au macrodosage. L'expérience nous a montré que les pertes ne sont proportionnellement pas plus grandes, par contre les opérations sont plus rapides. Pour des quantités d'échantillons comprises entre 1 mg et 10 mg, il n'est pas nécessaire d'effectuer une préextraction du fer à l'éther chlorhydrique, car il n'y a pas suffisamment de cet ion pour saturer la résine. En partant de 10 mg d'échantillon par exemple, le fer est fixé dans la moitié supérieure de la résine et le cobalt est retenu quantitativement sur celle-ci. Enfin, il suffit d'une seule extraction à la dithizone pour récupérer la totalité du cobalt.

Dans toutes les analyses que nous avons faites, il n'a pas été pris de précautions spéciales pour éviter les pertes au cours des diverses opérations analytiques, car celles-ci ont été déterminées par indicateur radiochimique. Des pertes allant jusqu'à 34% n'entachent pas la précision du dosage, comme on peut s'en rendre compte en examinant les résultats donnés dans le Tableau II.

#### *Mode opératoire*

Lorsqu'on effectue la détermination du cobalt par microdosage, certaines modifications et simplifications peuvent être apportées au mode opératoire donné précédemment.

En premier lieu, la mise en solution est beaucoup plus rapide; 5 ml d'eau régale sont suffisants pour l'effectuer. Pour les prises de 10 mg, le marquage se fait au moyen de 1 ml de la solution de cobalt actif dilué 10 fois; pour les prises de 1 mg, au moyen

de 1 ml de la même solution diluée 100 fois. Après avoir chassé le chlore, on reprend par l'acide chlorhydrique 9 N de manière à obtenir un volume final d'environ 10 ml. Comme nous l'avons signalé plus haut, il est inutile de procéder à l'extraction du fer.

L'extraction par la dithizone en solution étherée ne nécessite que 5 ml de réactif; elle est suivie de deux lavages à l'éther (5 ml).

La destruction du dithizonate au moyen d'acide perchlorique est plus rapide du fait de la faible quantité de réactif présent; une heure suffit en général pour obtenir une décoloration complète.

La reprise du résidu final, après minéralisation de la dithizone est faite au moyen de 2 ml d'eau bidistillée.

Les résultats obtenus sont donnés dans le Tableau II.

TABLEAU II  
RÉSULTATS DE L'ANALYSE DE L'ACIER EDELWEISS "PHOENIX MA 2 B" SUR PRISES MICRO

Prises acier (mg)	Co récupéré (%)	Densité optique	Co trouvée (µg)	Co dans la prise (%)
10	78.8	0.088	4.53	0.0453
10	89	0.0995	4.54	0.0454
10	75.3	0.085	4.58	0.0458
10	77.9	0.086	4.49	0.0449
			Valeur moyenne	0.0453
1	66	0.015	0.461	0.0461
1	90.5	0.020	0.449	0.0449
1	88.2	0.020	0.460	0.0460
			Valeur moyenne	0.0457

\* Déduction faite du cobalt introduit comme traceur, soit 0.02 µg pour les prises de 10 mg et 0.002 µg pour les prises de 1 mg et corrections faites pour les pertes.

La quantité de cobalt introduite par le citrate (3 g) est de 0.015 µg. Il n'y a donc pratiquement pas de correction à apporter au résultat si l'on effectue des prises de 100 mg ou davantage.

Les résultats donnés sur les prises de 10 mg et de 1 mg doivent par contre tenir compte de ce facteur et l'on obtient finalement les valeurs suivantes:

Prises de 10 mg:  $4.53 - 0.015 = 4.515 \mu\text{g}$ , ce qui donne une teneur de 0.0452% Co.

Prises de 1 mg — moyenne:  $0.457 - 0.015 \mu\text{g}$ , teneur de 0.0442% Co.

#### DOSAGE POLAROGRAPHIQUE

(polarographe à rayons cathodiques)

Comme nous l'avons signalé par ailleurs, le dosage polarographique du cobalt est gêné par la présence de zinc même si celui-ci est en petites quantités. Il est introduit dans nos dosages par les acides nitrique et perchlorique nécessaires à la minéralisation du dithizonate. Les essais de purification de ces acides n'ont pas permis d'éliminer cet élément. Après distillation ils renferment autant de zinc sinon plus qu'avant et pourtant nous avons montré, au moyen de zinc 65, que l'ion initialement présent dans l'acide n'est pas entraîné lors de cette opération, le distillat ne présentant aucune radioactivité. Nous n'avons pas encore recherché les causes de cette contamination. Le mode opératoire a dû être quelque peu modifié pour éviter l'extraction à la dithizone. Lors de l'élution du cobalt fixé sur la résine Dowex, on prélève des fractions successives de 2 ml. Comme la solution initiale a été marquée au cobalt 60, l'activité

de chacune de ces fractions est mesurée et l'on conserve pour le dosage celle qui est la plus riche en cobalt. Les ions de cet élément fixés sur la colonne restent groupés lors de l'éluat de sorte qu'il est possible d'obtenir, dans une seule fraction de 2 ml, le 90% du cobalt total. La faible quantité de résine contenue dans un si petit volume ne gêne pas le dosage polarographique. Il est évident que seul le marquage au moyen d'un traceur radioactif permet de travailler de la manière décrite. Pour donner à la méthode toute la sûreté désirable, il est nécessaire de procéder à un étalonnage interne plutôt que de se référer à une courbe d'étalonnage. Pour cela, on conserve l'une des fractions d'éluat qui suit celle renfermant la quasi totalité de cobalt et qui ne présente plus d'activité. On y ajoute une quantité connue de cobalt (égale approximativement à celle renfermée dans l'échantillon). On effectue sur les deux fractions les mêmes opérations, ce qui permet de réduire les erreurs au minimum.

### Marche de l'analyse

Les essais préliminaires nous ont montré que l'on n'obtient de résultats valables que si la quantité de cobalt est égale ou supérieure à 1  $\mu\text{g}$ . Dans ces conditions, l'erreur est inférieure à 10%. Nous avons effectué les analyses sur des prises de 10 mg, les différents stades en sont : la mise en solution selon le processus décrit à la page 578, un marquage au cobalt 60, le passage sur colonne de résine Dowex dont les conditions sont données à la page 579. L'éluat se fait au moyen d'acide chlorhydrique 4 N et l'éluat recueilli en fractions de 2 ml. Celle d'entre elles présentant l'activité maximum est retenue pour le dosage, une des suivantes, d'activité nulle servira d'étalon externe ; elle sera additionnée d'une quantité connue de cobalt. Ces deux fractions sont évaporées à sec, on y ajoute 1 ml d'une solution de chlorure de potassium 0.1 N ; on évapore à sec, reprend par de l'eau distillée, évapore à sec une nouvelle fois pour chasser toute trace d'acide et reprend par deux à trois ml d'eau distillée. Après passage d'azote purifié pour chasser l'oxygène, on polarographie.

Les nombreux essais à blanc que nous avons faits ne donnent pas de saut au polarographe. Il n'y a donc pas de contamination au cours des opérations et les réactifs n'en renferment pas suffisamment pour gêner le dosage. Le Tableau III donne les principales valeurs obtenues.

C'est la valeur moyenne qui a permis de calculer les résultats donnés dans la sixième colonne.

Le dosage polarographique est moins sensible que le dosage spectrophotométrique, mais il donne de bons résultats lorsque la quantité de cobalt présente est suffisante. Il a l'avantage d'être plus simple et plus rapide.

TABLEAU III

Prise actier (mg)	Activité ajoutée (c.p.m.)	Activité recueillie		Saut ( $\mu\text{A}$ )	Co trouvé $\mu\text{g}^a$	Co dans la prise %
		(c.p.m.)	%			
9.60	28,650	25,284	88.3	1.007	4.41	0.0459
9.60	28,650	25,240	88.1	1.027	4.51	0.0469
9.60	28,650	27,210	94.9	1.034	4.21	0.0438
9.60	28,650	24,928	87.0	0.980	4.34	0.0452

\* Nous avons utilisé deux étalons ; l'un donne un saut de 0.827  $\mu\text{A}$  pour 3.20  $\mu\text{g}$  de cobalt et l'autre 1.670  $\mu\text{A}$  pour 6.40  $\mu\text{g}$ .

TABLEAU IV  
 CARACTÉRISTIQUES DE NOS DIFFÉRENTES MÉTHODES  
 APPLIQUÉES AU DOSAGE DU COBALT DANS UN ACIER 18/8

	Méthode spectrophotométrique		Polarographie	Activation avec étalon interne
	macro	micro		
Poids des échantillons	100 mg	1 mg	10 mg	1 à 5 mg
Effets — des pertes	nul	nul	nul	nul
— des contaminations	corrigé par un blanc		corrigé par un blanc nul	
Principales causes d'erreurs	coloration du réactif, mesure de D		mesure de la vague en présence d'im- puretés	mesure du pic du cobalt 58
Ordre de grandeur des erreurs	4%	8%	6%	5%
Indicateur radioactif	nécessaire		nécessaire	
Dosage: limite absolue	0.02 $\mu\text{g}$	0.005 $\mu\text{g}$	0.1 $\mu\text{g}$	0.2 $\mu\text{g}$
Dosage: limite relative	0.01 $\mu\text{g/ml}$	0.01 $\mu\text{g/ml}$	0.5 $\mu\text{g/ml}$	—
Résultats	0.043%	0.045%	0.045%	0.049%

## REMERCIEMENTS

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## RÉSUMÉ

Il est proposé une méthode de dosage spectrophotométrique permettant de déterminer la concentration de cobalt dans un acier 18/8, sur 0.1 à 0.5 g pour le macrodosage et sur 1 mg pour le microdosage; les erreurs sont comprises entre 4 et 6%. La méthode consiste à extraire le fer, à séparer le cobalt sur résine Dowex I-X 8 et à déterminer la densité optique du complexe cobalt-nitroso-sel R. La limite de sensibilité du dosage est de 0.01  $\mu\text{g/ml}$ . Le microdosage se fait en micro-cuve avec un photomultiplicateur; il permet de doser encore 0.005  $\mu\text{g}$  de cobalt. Il est aussi proposé une méthode polarographique moins sensible (0.5  $\mu\text{g/ml}$ ) mais plus rapide. Les erreurs sont du même ordre de grandeur.

## SUMMARY

A spectrophotometric method for the determination of cobalt in 18/8 steel is described. Iron is removed by solvent extraction, cobalt is separated by means of an ion-exchange resin and converted to the nitroso-R-salt complex, the optical density of which is then measured. The method can be applied on the macro- and on the micro-scale. The limit of error lies between 4 and 6%; the limit of identification is 0.005  $\mu\text{g}$  cobalt. A less sensitive (0.5  $\mu\text{g/ml}$ ) but more rapid polarographic method is also described.

## ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Kobalt in 18/8 Stahl. Eisen wird durch Lösungsmittel-Extraktion entfernt, das Kobalt mit einem Austauschharz abgetrennt und in den Nitroso-R-Salz Komplex übergeführt, dessen optische Dichte dann gemessen wird. Das Verfahren kann als Makro- und Mikromethode angewandt werden. Die Fehlergrenze liegt zwischen 4 und 6%. Erfassungsgrenze: 0.005  $\mu\text{g}$  Kobalt. Ferner wird eine weniger empfindliche (0.5  $\mu\text{g/ml}$ ), aber raschere polarographische Methode beschrieben.

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## CURRENT-TIME CHARACTERISTICS OF THE RAPIDLY DROPPING MERCURY ELECTRODE

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Dropping mercury electrodes (DME) with short drop times have been considered unsuitable as indicator electrode in polarography because of the presence of the maximum of the second kind owing to the "Spüleeffekt"<sup>1</sup>; only a few papers on such an electrode have been published<sup>2</sup>. KOONS studied the properties of the DME with a normal rate of mercury flow but a very short drop time under the high pressure applied to the electrode<sup>3</sup>. Recently, KARCHMER carried out a systematic investigation on DMEs with a short drop time and used the electrode for the polarographic determination of dissolved oxygen in natural and effluent waters<sup>4</sup>. In previous papers<sup>5,6</sup>, the present authors have pointed out that the rapidly dropping mercury electrode (RADME), whose drop time is less than 1 sec, seems to be one of the most suitable indicator electrodes in alternating current (a.c.) polarography. It was also shown in direct current (d.c.) polarography that, in the presence of a sufficient amount of surface-active substances (SAS), the maximum of the second kind seems to be completely suppressed and current-voltage curves similar to those at the conventional DME are observed at the RADME<sup>6</sup>. In this paper, the characteristics of the RADME in stationary and flowing media are investigated by measurements of the current-time curves during the life of a mercury drop.

## REAGENTS AND APPARATUS

The standard solution of mercury(II) was prepared by dissolving a known amount of purified mercury metal in concentrated nitric acid. The standard solutions of lead nitrate and cadmium nitrate were prepared from guaranteed grade reagents and standardized amperometrically against standard ethylenediaminetetraacetate solution<sup>7</sup>. Polyoxyethylene lauryl ether (LEO) was obtained from Nikko Co., Tokyo ("Nikkol BL-10"). All other chemicals used were of analytical reagent grade. Redistilled water was used for the preparation of the solutions.

Current-voltage curves were recorded with a Yanagimoto Y-GR Model 2 Galva-recorder (pen-recording polarograph) or measured with a manual apparatus similar to that of KOLTHOFF AND LINGANE<sup>8</sup>. In the measurement of current-time curves, the ohmic potential drop (less than 2 mV) across the standard variable resistance  $R$  (Fig. 1) was amplified by the d.c. amplifier (Fig. 2) and recorded with the mechanical oscillograph (N-6 type of Yokogawa Electric Works Co.). The characteristics of the

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conventional DME and the RADME used in the present study are shown in Table I. A saturated calomel electrode of large surface area was used as the anode, and was connected to the electrolytic solution by a Hume and Harris-type agar bridge<sup>9</sup>. All measurements in stationary media were made in a thermostat at  $25.0 \pm 0.1^\circ$ . The dissolved oxygen in the solution was expelled by passing pure nitrogen gas. The current-voltage and current-time curves presented in this paper are corrected for residual currents.

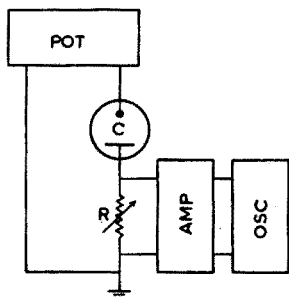


Fig. 1. Circuit for the measurement of current-time curves: POT, applying potentiometer; C, electrolysis cell; R, standard variable resistance; AMP, d.c. amplifier; OSC, mechanical oscillograph.

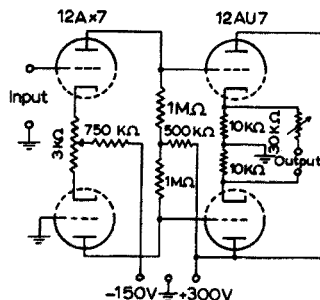


Fig. 2. Circuit of the d.c. amplifier.

TABLE I  
CHARACTERISTICS OF THE CONVENTIONAL DME AND THE RADME

Electrode	Rate of flow of mercury <i>m</i> , mg/sec	Drop time $\tau$ , sec
DME <sup>a</sup>	2.43 <sub>8</sub>	3.68 <sub>9</sub>
RADME <sup>b</sup>	20.4 <sub>3</sub>	0.67 <sub>0</sub>

<sup>a</sup> Measured in an air-free 0.1 *M* KCl-0.005% gelatin solution; open circuit; height of the mercury column, 45 cm

<sup>b</sup> Measured in an air-free 0.1 *M* HNO<sub>3</sub> solution; open circuit; height of the mercury column, 50 cm

All experiments in the flowing media were carried out in a thermostat of  $25 \pm 1^\circ$  with the electrolysis cell as shown in Fig. 3. The flow rate of the solution was varied by changing the speed of rotation of stirrer S which was rotated by a synchronous motor. Preliminary experiments showed that the current-voltage curves in flowing media were not affected appreciably by a slight change in the position of the tip of the RADME.

#### RESULTS

One of the examples which show the effect of polyoxyethylene lauryl ether (LEO) on the current-voltage curves observed at the RADME in stationary media is shown in Fig. 4. Fig. 5 presents the current-time curves of cadmium(II) which were obtained with the RADME in stationary 0.1 *M* potassium nitrate solutions in the presence and the absence of LEO. The plots of  $\log i$  vs.  $\log t$  of those current-time curves are



given in Fig. 6. Similar results were also obtained with lead(II) in 0.1 *M* potassium nitrate solutions and with mercury(II) in 0.1 *M* nitric acid solutions.

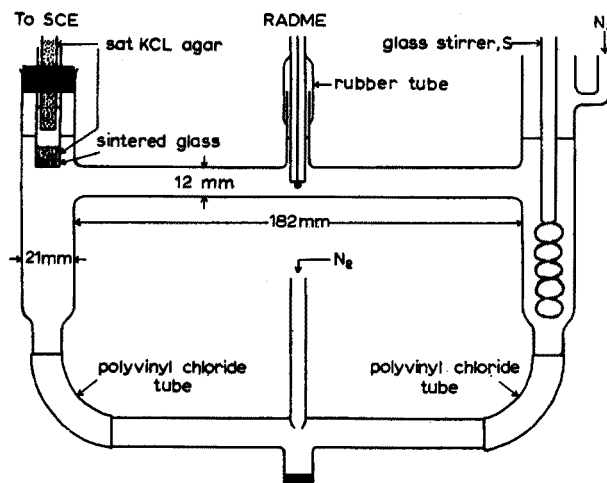


Fig. 3. Electrolysis cell for flowing media.

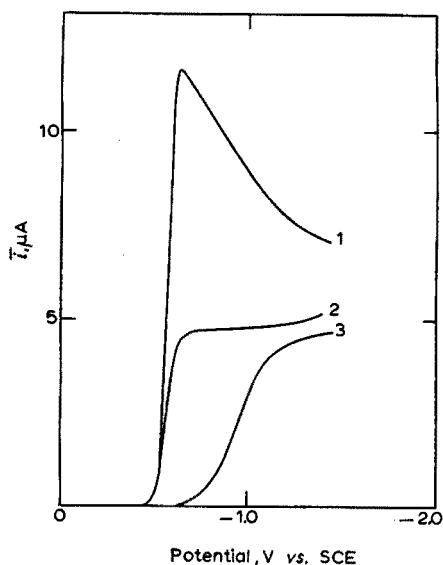


Fig. 4. Current-voltage curves of  $2.00 \cdot 10^{-4} M$   $Cd(NO_3)_2$  in 0.1 *M*  $KNO_3$  in the absence and in the presence of LEO. Concentration of LEO: (1) 0; (2)  $5 \cdot 10^{-5} M$ ; (3)  $5 \cdot 10^{-4} M$ .

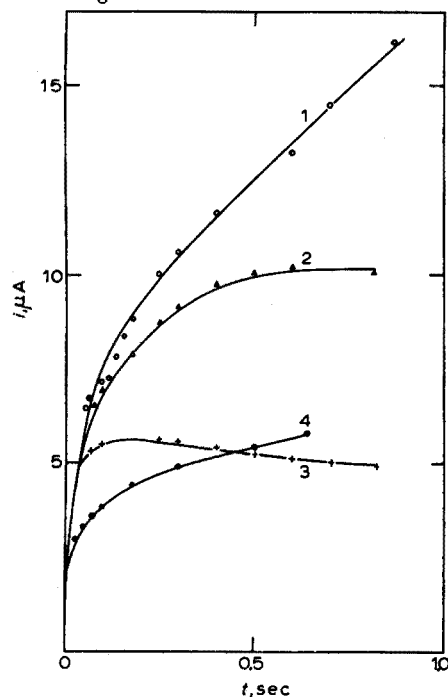


Fig. 5. Current-time curves of  $2.00 \cdot 10^{-4} M$   $Cd(NO_3)_2$  in 0.1 *M*  $KNO_3$  in the absence and in the presence of LEO. Concentration of LEO: (1) 0 ( $-0.65$ ); (2) 0 ( $-1.00$ ); (3)  $5 \cdot 10^{-5} M$  ( $-1.00$ ); (4)  $5 \cdot 10^{-4} M$  ( $-1.4$ ). The values in parentheses are the electrode potentials in V vs. SCE where the current-time curves are measured.

The effect of the flow of the solution on the current-voltage and current-time curves was investigated in 0.1 M potassium nitrate solutions of lead(II). In general, the current-voltage curves were not disturbed appreciably by the flow of the solution. It was also found that, in the presence of  $5 \cdot 10^{-4}$  M LEO, the limiting current at the RADME was kept constant within the experimental error unless the flow rate of the

TABLE II  
EFFECT OF THE FLOW RATE OF THE SOLUTION ON THE LIMITING CURRENT OF  $2.14 \cdot 10^{-4}$  M  $\text{Pb}(\text{NO}_3)_2$  IN 0.1 M  $\text{KNO}_3$  SOLUTION CONTAINING  $5 \cdot 10^{-4}$  M LEO

Flow rate, cm/sec	Limiting current		
	at $-0.80$ V	at $-1.00$ V	at $-1.40$ V
0	4.80	4.80	4.65
0.57	4.77	4.80	4.62
1.79	4.78	4.76	4.54
3.26	4.78	4.74	4.60
8.94	6.39	6.44	6.27

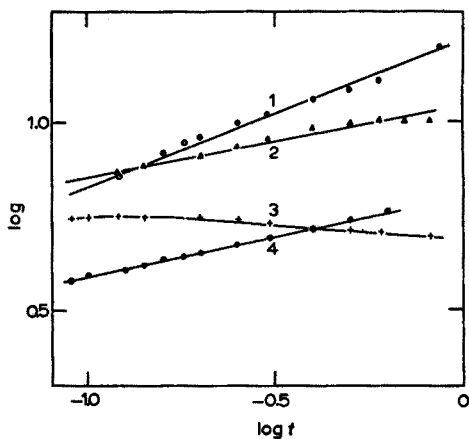


Fig. 6. Relations between  $\log i$  and  $\log t$  of the corresponding current-time curves in Fig. 5.

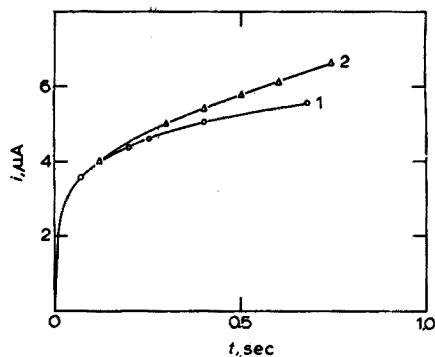


Fig. 7. Effect of the flow rate of the solution on the current-time curves of  $2.14 \cdot 10^{-4}$  M  $\text{Pb}(\text{NO}_3)_2$  in 0.1 M  $\text{KNO}_3$  containing  $5 \cdot 10^{-4}$  M LEO at the potential of  $-0.80$  V vs. SCE. Flow rate: (1) 0; (2) 1.8 cm/sec.

solution exceeded about 3 cm/sec (Table II). Fig. 7 shows the current-time curves which were obtained with lead(II) in stationary and flowing media at the potential where lead(II) gives the limiting current.

#### DISCUSSION

The relation between the instantaneous current  $i$  and the time  $t$  during the life of a drop of the DME is generally considered to be represented by the equation:

$$i = kt^x \quad (1)$$

where  $k$  and  $x$  are the constants determined by the nature of the mass-transfer process.

From eqn. (1) the average current  $\bar{i}$  during the life of a drop is expressed by the relation,

$$\bar{i} = \frac{I}{\tau} \int_0^{\tau} i dt = \frac{I}{1+x} i_{\tau} \quad (2)$$

where  $\tau$  is the drop time and  $i_{\tau}$  the instantaneous current at  $t = \tau$ . If the current is controlled by the diffusion, the value of  $x$  should be equal to 0.167 according to the Ilkovic equation. This prediction has been examined by many investigators<sup>10</sup>, and the value of  $x$  of the diffusion-controlled limiting current observed at the conventional DME has been found experimentally to be nearly equal to 0.2 except for the initial part of the current-time curve. On the other hand, if the current is controlled by the convection, the value of  $x$  is expected to be 0.5 from theoretical considerations<sup>11</sup>. This has been experimentally verified in the case of the limiting current obtained with the rotated dropping mercury electrode<sup>11,12</sup>. Therefore, if the current is controlled by both diffusion and convection, the value of  $x$  must be between 0.167 and 0.5.

TABLE III  
CHARACTERISTICS OF THE LIMITING CURRENTS WITH THE RADME IN THE ABSENCE OF SAS

Ionic species:	Hg(II) <sup>a</sup>			Pb(II) <sup>b</sup>		Cd(II) <sup>c</sup>	
	Electrode potential, V vs. SCE:	0	-0.50	-0.80	-0.45	-1.00	-0.65
$x$	0.215	0.317	0.286	d	0.160	0.358	0.237
$I/(1+x)$	0.828	0.760	0.778	d	0.862	0.730	0.808
$\bar{i}/i_{\tau}$	0.824	0.748	0.788	d	0.888	0.707	0.891

<sup>a</sup>  $2.10 \cdot 10^{-4} M$  Hg(NO<sub>3</sub>)<sub>2</sub> - 0.1 M HNO<sub>3</sub>.

<sup>b</sup>  $2.00 \cdot 10^{-4} M$  Pb(NO<sub>3</sub>)<sub>2</sub> - 0.1 M KNO<sub>3</sub>.

<sup>c</sup>  $2.00 \cdot 10^{-4} M$  Cd(NO<sub>3</sub>)<sub>2</sub> - 0.1 M KNO<sub>3</sub>.

<sup>d</sup> Cannot be determined because of the anomalies of the current-time curves.

TABLE IV  
CHARACTERISTICS OF THE LIMITING CURRENTS OBTAINED WITH THE RADME IN THE PRESENCE OF  $5 \cdot 10^{-4} M$  LEO

Ionic species:	Hg(II) <sup>a</sup>			Pb(II) <sup>b</sup>		Cd(II) <sup>c</sup>
	Electrode potential, V vs. SCE:	0	-0.50	-0.80	-0.80	-1.00
$x$	0.241	0.207	0.217	0.197 (0.230)	0.194	0.211
$I/(1+x)$	0.806	0.829	0.822	0.837 (0.809)	0.838	0.828
$\bar{i}/i_{\tau}$	0.796	0.819	0.781	0.826 (0.775)	0.820	0.829

<sup>a</sup>  $2.10 \cdot 10^{-4} M$  Hg(NO<sub>3</sub>)<sub>2</sub> - 0.1 M HNO<sub>3</sub> -  $5 \cdot 10^{-4} M$  LEO.

<sup>b</sup>  $2.00 \cdot 10^{-4} M$  Pb(NO<sub>3</sub>)<sub>2</sub> - 0.1 M KNO<sub>3</sub> -  $5 \cdot 10^{-4} M$  LEO.

<sup>c</sup>  $2.00 \cdot 10^{-4} M$  Cd(NO<sub>3</sub>)<sub>2</sub> - 0.1 M KNO<sub>3</sub> -  $5 \cdot 10^{-4} M$  LEO.

Values in parentheses are those obtained in flowing media (flow rate, 1.8 cm/sec).

The results of the analysis of the current–time curves which were obtained with the RADME under various conditions are summarized in Tables III and IV. The average current was determined by the graphical integration of the current–time curve. In the absence of LEO, the value of  $\alpha$  at potentials near the electrocapillary maximum, where the maximum of the second kind is the most pronounced, is usually larger than 0.3, as shown in Table III. This means that the current under these conditions is controlled by diffusion as well as by convection due to the "Spüleffekt". On the other hand, Table IV shows that the values of  $\alpha$  of the limiting current obtained with the RADME in the solutions containing  $5 \cdot 10^{-4} M$  LEO are between 0.19 and 0.25 in all cases. This indicates that, in the presence of a sufficient amount of SAS, the "Spüleffekt" is completely eliminated and the limiting current at the RADME is mainly controlled by the diffusion. It must be mentioned here that, in the presence of  $5 \cdot 10^{-5} M$  LEO, no maximum of the second kind appears on the current–voltage curve (Fig. 4), while the current–time curve (Fig. 5(3)) clearly shows the effect of convection on the limiting current.

It is very interesting that the limiting current at the RADME is independent of the flow rate of the solution within a certain range (Table II). The results of the current–time curves (Fig. 7 and Table IV) also indicate that the limiting current observed at the RADME in the presence of a sufficient amount of SAS is not affected appreciably by the flow of the solution. Similar results have been reported by KARCHMER with the limiting current of oxygen in the potassium chloride solutions<sup>4</sup>. These facts may be explained in the following way. The thickness of the diffusion layer at the surface of the DME is proportional to the square-root of time<sup>13</sup>. Therefore, the thickness of the diffusion layer established during the life of a mercury drop is thinner at the RADME than at the conventional DME, and the current at the RADME is less sensitive to the movement of the bulk solution.

From the experimental results mentioned above, it is concluded that the characteristics of the limiting current at the RADME in the presence of a sufficient amount of SAS, e.g.  $5 \cdot 10^{-4} M$  LEO, are similar to those at the conventional DME. The fact that the limiting current obtained with the RADME is not affected appreciably by the flow of the solution unless the flow velocity exceeds a certain critical value suggests that the RADME is a suitable indicator electrode in d.c. polarography in flowing media.

#### ACKNOWLEDGEMENT

The authors thank Dr. M. MATSUO, Tohoku University, for his kind advice in constructing the direct current amplifier. They also thank the Ministry of Education for the financial support granted for this research.

#### SUMMARY

The properties of the rapidly dropping mercury electrode (RADME) in stationary and flowing media were studied by measurement of the current–time curve during a drop-life. In the absence of surface-active substance (SAS), the limiting current observed at the RADME in the potential region where the maximum of the second kind appears, was shown to be controlled by both diffusion and convection. However, in the presence of a sufficient amount of SAS, the maximum of the second kind was completely suppressed and the characteristics of the limiting current at the RADME were similar to those at the conventional DME. It was also shown that the limiting current of lead(II) obtained with the RADME in 0.1 *M* potassium nitrate solutions containing  $5 \cdot 10^{-4} M$  polyoxyethylene lauryl ether was almost independent of changes in flow rate of the solution up to about 3 cm/sec. These results suggest that the RADME is a suitable indicator electrode in d.c. polarography in flowing media.

## RÉSUMÉ

Une étude a été effectuée sur les caractéristiques de l'électrode à gouttes de mercure rapide, dans divers milieux. Les résultats obtenus montrent qu'une telle électrode peut être utilisée comme électrode indicatrice en polarographie à courant continu ("flowing media").

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Eigenschaften der schnell-tropfenden Quecksilber-elektrode in stationärem und fließendem Medium. Die Ergebnisse zeigen, dass diese Elektrode als Indikatorelektrode bei der Gleichstrom-polarographie mit fließendem Medium verwendet werden kann.

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## BOOK REVIEWS

*Modern methods of analysis of copper and its alloys*, by CHARLES M. DOZINEL, translated by GEORGE R. ANDRASO, Georges Thone, Liège, 1960, 239 pp., price \$ 32.00.

The important position occupied by the copper industry has made it necessary to analyse a great number of copper-containing materials. Consequently there has been a great increase in the scientific literature on this subject during the last ten years. When performing such analyses it is in many cases necessary to make a prolonged and laborious study of the original papers in order to obtain the necessary information concerning the most reliable method.

This book is designed to overcome this difficulty to a certain extent by providing a compact source for the widely spread information. Unpublished laboratory reports as well as scientific journals have been consulted in compiling this summary. Some procedures that seemed doubtful have been tested to ensure reliability. For more than twenty elements that can be present in copper alloys, the existing modern analytical methods in the field of gravimetry, titrimetry, electrolysis, polarography, and colorimetry, as well as combined procedures are reviewed. Some reliable procedures are treated more extensively so that in these cases the original papers need not be consulted. At the beginning, two separate chapters are devoted to a survey of the spectrographic methods—emission, X-ray and mass spectrography—and to practical data on qualitative and quantitative chemical wet methods. Finally some general considerations are devoted to important problems in connection with industrial analysis, mainly concerning rationalization.

The bibliography contains 767 references. Some more or less important procedures and books concerning the five chemical methods discussed have, however, been overlooked, and the references

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are not always given in the same way. Also new methods such as radiochemistry, which is already being used to determine traces of metals in copper alloys, are not discussed.

The price of the book is rather high when compared with that of other similar publications, but as far as research and consulting the literature are concerned, industrial laboratories will be able to save much time by using this work.

VERBEEK (Ghent)

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*X-Ray Absorption and Emission in Analytical Chemistry, Spectro-chemical Analysis with X-Rays*, H. A. LIEBHAFSKY, H. G. PFEIFFER, E. H. WINSLOW and J. DE ZAMANY, John Wiley, New York, 1960, 357 pages, Prix \$ 13.50.

Les méthodes d'analyses physico-chimiques se multiplient. La plupart d'entre elles sont remarquables, tant par la sensibilité que par la rapidité des dosages. Elles font appel aux chapitres les plus divers de la physique moderne, aussi le chimiste est-il souvent fort embarrassé lorsqu'il doit faire un choix. Il n'est pas facile de se familiariser avec des méthodes si spéciales et de se rendre compte des possibilités qu'elles offrent tant en ce qui concerne les substances qu'il est possible de doser que les conditions dans lesquelles s'effectuent les analyses et la précision des résultats.

Heureusement que certains spécialistes de ces questions ont écrit cet ouvrage, effectuent le travail de synthèse, d'épuration grâce auquel d'autres auteurs que ceux de l'utilisation des rayons X pour l'identification et le dosage de l'analyste, lui permettant de se faire rapidement une idée du problème.

L'ouvrage de LIEBHAFSKY *et coll.* répond très exactement à ce que l'analyste lui-même lui demande; il donne une vue d'ensemble du problème, sans vains bavardages, sans détails inutiles. Au lecteur de faire son choix, d'étudier le chapitre qui le concerne. Le style est simple, posé clair et bien ordonné. Peut-être les auteurs auraient-ils pu dresser une liste des termes et des symboles utilisés avec leurs définitions exactes.

Dans un premier chapitre intitulé origine et propriétés des rayons X, l'auteur s'initie sans grandes difficultés aux principes de bases sur lesquels reposent les méthodes suivantes traitent des mesures de l'intensité des rayons X, de l'absorption des rayons X, des rayons X poly- et monochromatiques, de la détermination des épaisseurs, de la spectrométrie des rayons X, de l'équipement et de la reproductibilité. Tout le problème a été traité avec des exemples sont donnés, tels que le dosage des métaux dans les minerais, les métaux dans les essences, du chlore dans les plastiques. Un chapitre est consacré au dosage des métaux. Il est encore possible de doser, par cette méthode, des quantités de l'ordre de quelques microgrammes terminent l'ouvrage, qui donnent les valeurs de l'absorption critique, des rayons X, de leurs longueurs d'onde caractéristiques, etc.

Présentation parfaite, dessins, figures et photographies très soignées.

D. MONNIER (Genève)

*Anal. Chim. Acta*, 23 (1960) 592

*Analytical Chemistry of Titanium Metals and Compounds* by MAURICE CODELL, Interscience, New York, 1959, 378 + xiii pp., price \$ 12.00.

Although analytical procedures for the examination of titanium-bearing minerals and titanium-based pigments have been available for more than twenty years, it is only comparatively recently that the metal titanium has become commercially important and analytical methods for its examination have become available. With rapid advances in metallurgical methods of extraction, melting and fabrication of the metal, production of titanium has increased considerably and this has added to the importance of this relatively new analytical field.

There is little doubt that by bringing together, into a single volume, published information on this subject, DR. CODELL has made a useful contribution to analytical chemistry and enhanced the value of his book by drawing widely on information afforded by unpublished American reports.

The technical standard of this publication is generally high, but a major criticism is that almost

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without exception the recommended methods are of American origin and a more cosmopolitan approach to the subject is justified, particularly when so much information on the subject has been published elsewhere.

Part I contains chapters on the general chemistry of the subject; sampling, dissolution, general methods of separation, emission spectrographic procedures, vacuum line methods and methods for determining titanium. The section on vacuum methods is particularly informative and the relatively complicated apparatus well illustrated.

In Part II methods are detailed for determining more than twenty metals in titanium and its alloys, and for most of these, several procedures are given, thus providing for the determination of trace and alloying amounts of elements in question. At the beginning of each procedure the chemical principles involved are briefly discussed, and elements which interfere in specified determinations are enumerated. The work is, therefore, by no means merely a manual of laboratory methods. The uses and limitations of each procedure are also indicated, thus affording a useful guide to the analyst in his choice of method. The procedures described are generally based on well established principles, and it is noteworthy that use has been made of analytical methods involving polarographic and ion-exchange principles. There is little in this particular section to arouse adverse comment, but it is surprising to find that no reference is made to volumetric methods for determining aluminium. For instance, following precipitation of aluminium oxinate (p. 110), it is more expedient, and just as reliable, to complete this determination by titration using a standard solution of potassium permanganate/tromide than by the recommended gravimetric method. In some instances a complexometric titration might be used to advantage, e.g. in the determination of aluminium with nickel (p. 198).

Part III of the book deals with the determination of non-metallics in titanium and its alloys and includes methods for the determination of hydrogen, carbon, silicon, nitrogen, phosphorus, boron, oxygen, and chlorine. In the introduction to this section of the book, each procedure is prefaced by an informative discussion of the high standard of the methods described. In the hydrogen determination, however, difficulties are not emphasised. The range of this determination is stated on page 200, but the method described, would generally be considered suitable for percentages greater than about 0.005%.

In Part IV, the analysis of titanium-base materials, including titanium tetrahydride, is very well covered and presumably these procedures are the property of the department of E.I. DuPont de Nemours. The methods are based on the high technical standard and clarity of presentation are such that the book is remarkably free from obvious typographical errors, although on page 308 (pp. 308 and 310) lithopone is spelled incorrectly, and in the same section lithopone is twice referred to as  $ZnS-PbSO_4$ .

There is no doubt that this book will be useful to all concerned with the analysis of titanium-bearing materials and should be regarded as a worthy contribution in the field of analytical chemistry.

D. F. Wood (Birmingham)

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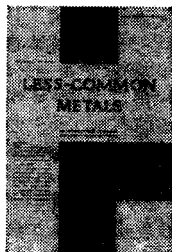
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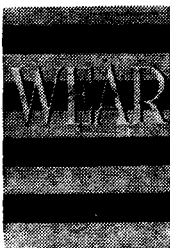
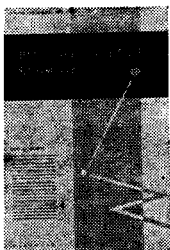
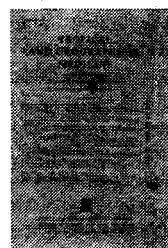
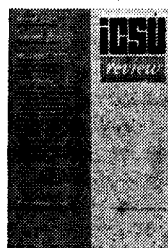
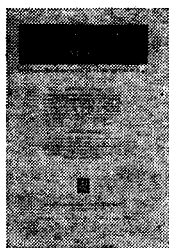
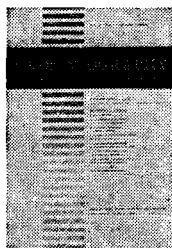
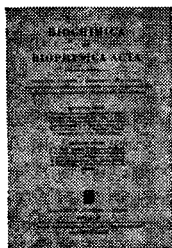
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