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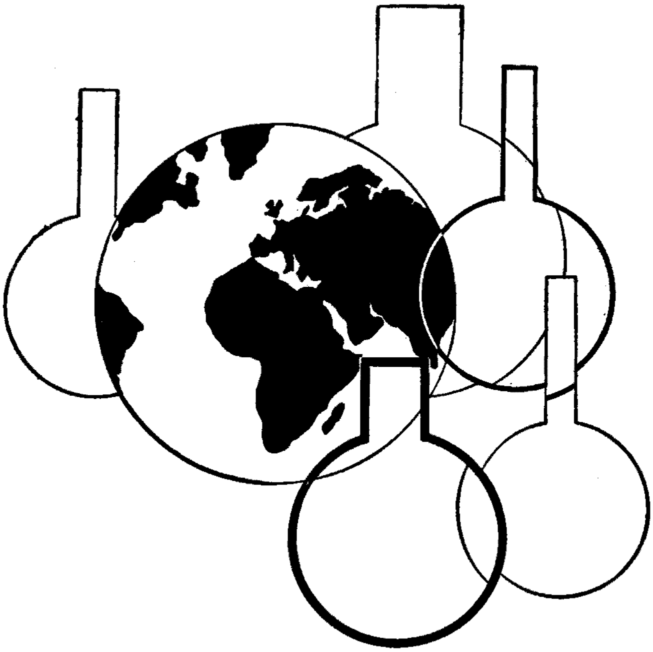

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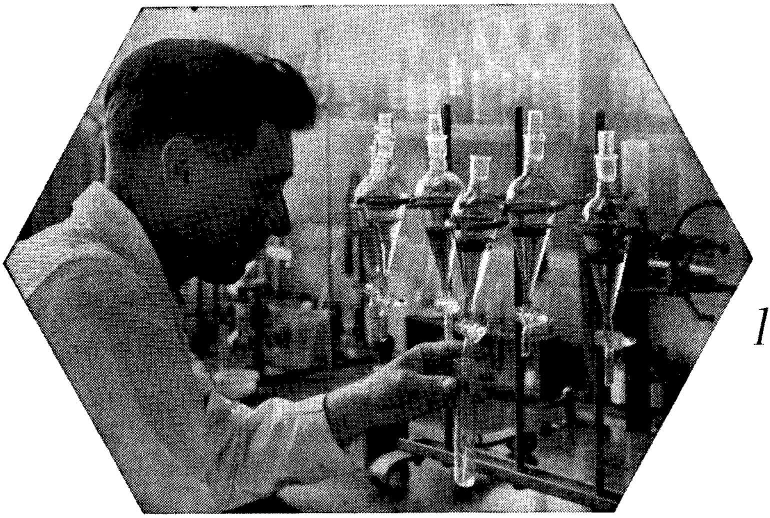

Incidental information

No.13

Items of interest from our laboratory notebooks

▶ Most analysts know about 1,10-phenanthroline and many use it for iron determinations. Not so many people seem to know that **4,7-diphenyl-1,10-phenanthroline** is twice as sensitive as 1,10-phenanthroline in the colorimetric determination of iron. There are several papers on the subject but the latest is *Analyst*, 83 (1958) 80. The reagent is also called **Bathophenanthroline,** and we make it.

▶ Then, again the substitution of methyl groups in the 2,9 position has the interesting effect of making the reagent insensitive to iron and we then have a selective and sensitive reagent for copper (see *Anal. Chem.*, 28 (1956) 1158). Hopkin & Williams make **2,9-dimethyl-1,10-phenanthroline** (sometimes called **Neocuproin**).

▶ One does not think of sulphate as a radical one can determine absorptiometrically, but this is now possible for low concentrations. **Barium chloranilate** is the reagent and there are two papers on the subject—*Anal. Chem.*, 29 (1957) 281 and *Anal. Chem.*, 30 (1958) 202. Hopkin & Williams make it.

▶ Hopkin & Williams Ltd. were also early off the mark with supplies of the remarkable new colour-producing reagent for fluoride ions, **3-aminomethylalizarin-N,N-diacetic acid,** described by Belcher, Leonard and West (*Talanta*, 2 (1959) 92). This important reagent is already available from stock.

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THE DETERMINATION OF ^{235}U BY THE ISOTOPE DILUTION METHOD

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(Received January 2nd, 1960)

INTRODUCTION

One of the problems associated with the use of enriched uranium fuelled reactors is that of costing for the quantity of ^{235}U consumed, both by fission and by neutron capture, in the reactor. For some transactions a value may be calculated from reactor power levels, irradiation times etc., but where these factors are uncertain it is highly desirable that there should be available a method of assessing ^{235}U usage which is quite independent of the irradiation history of the fuel elements.

Methods involving the determination of the radioactivity of fission products are, to a greater or lesser extent, dependent upon a knowledge of irradiation conditions and "cooling" time, although in principle a method might be based on the determination of a stable fission product. Other methods could be envisaged for application to intact fuel elements but these would seem to offer formidable practical problems. However, as the quantity of ^{235}U originally present in a charge of fuel elements is clearly defined, and as the average usage may be of the order of 20%[1], one attractive approach would consist of a determination of the ^{235}U content of the irradiated fuel elements, thus giving the quantity consumed by difference. This would require a representative sample of the fuel elements and to obtain this by any method other than one involving their total dissolution would seem extremely difficult if not impossible. However this dissolution usually represents the first stage in a chemical processing plant, so an aliquot of plant feed solution could conveniently provide a sample suitable for a ^{235}U determination. This estimate could be based on a determination of total uranium combined either with an isotopic analysis or with corrections for production of ^{236}U and loss of ^{238}U, but the most fundamental approach would be a direct determination of the ^{235}U content and for this the isotope dilution method would seem the most suitable technique. This method involves the addition of a known quantity of tracer (in this case ^{233}U or natural uranium) to the sample, followed by chemical separation of the uranium and a mass spectrometric determination of the ^{235}U/^{233}U or ^{235}U/^{238}U isotope ratio. The quantity of ^{235}U may then be calculated from the quantity of tracer added and the appropriate isotope ratio, so the method does not require a quantitative recovery of the uranium.

Thus the purpose of the work described in this paper has been an attempt to find the precision of the isotope dilution method for the determination of ^{235}U in solutions which simulate diluted samples of the feed solution in a chemical plant designed to process enriched uranium–aluminium alloy reactor fuel. The published data for the Dounreay Chemical Plant have been used to define typical solution conditions[1].

The technique has already been applied to the determination of uranium in fuel element dissolver solutions at the Idaho chemical processing plant using a ^{233}U tracer[2,3]. In one paper the coefficient of variation for "cold" samples was reported as 0.22% for solutions of uranium concentration 5–20 g/l, and 1.1% for solutions in the range 0.5–3.2 g/l; for process samples the overall coefficient of variation was 2.7%[2]. In a later paper a series of standard deviations was quoted for a range of sample-spike ratios, and a minimum value of 0.56% obtained for a ratio of unity; in this case the overall value quoted for plant solutions was 1.85%[3]. Uranium was separated from the plant solutions by remote liquid–liquid extraction using 3% T.B.P./*n*-hexane, followed by a hydrogen peroxide precipitation[4]. Normally an aliquot of plant solution containing 1–2 mg uranium was taken, but occasionally the method was used for as little as 50–100 μg. A total of 50 μg of uranium (sample and tracer) was used for the mass spectrometric analysis.

The method has also been successfully used for the determination of natural uranium in sea-water using ^{235}U (93%) as the tracer[5]. In this case a total quantity of 0.6 μg of uranium was separated chemically and used for the mass spectrometric analysis, and the average coefficient of variation was approximately 0.5%.

Either natural uranium or ^{233}U could be used as the tracer for the required determination of ^{235}U. The former is readily available and has practically no associated health hazard, but its use involves additional mass spectrometry for it is necessary to determine the ^{238}U/^{235}U ratio for the plant solutions alone, as well as after the addition of the natural uranium tracer. The use of ^{233}U permits a direct determination of ^{235}U (for solutions which may be assumed to contain no ^{233}U) and so might be expected to yield slightly more precise results. In the interests of making a complete investigation both tracers were used in this work.

In any attempt to achieve high accuracy by the isotope dilution method it is necessary to ensure that no systematic errors are introduced by mass discrimination in the ion source or detector of the mass spectrometer. This may be achieved either by calibrating the mass spectrometer with mixtures of known quantities of ^{233}U and ^{235}U or of natural uranium and ^{235}U, or more simply by calibrating the tracer against a ^{235}U standard under the same conditions as those subsequently used for samples, and then using the tracer concentration determined in this way for the calculation of the ^{235}U content of the solutions under test. In either case any random error in the measurement must be included in the final assessment of the precision of the method. The second method was used in this work for it avoided the need for a gravimetrically standardised solution of ^{233}U.

It was considered that the final accuracy of the method should be at least better than 1%. Previous work has shown that 0.5% could be achieved fairly readily for the average standard deviation of a single value[5]. Thus for a calibration based on ten replicate analyses, and a determination of ^{235}U in a given solution based on six replicate analyses, the equivalent value of three times the overall standard error for the final mean value would be 0.8%. This should apply to a determination made using ^{233}U tracer. For one using natural uranium it was proposed to take two further aliquots from each solution to permit a determination of the ^{238}U/^{235}U ratio of the fuel element uranium, and this measurement would introduce an additional small uncertainty.

It is clearly desirable that if such a method is to be used on a routine basis for plant solutions the activity levels should be small enough to permit the addition of tracer to aliquots, and the separation of uranium for mass spectrometry to be made in a fume hood with little or no shielding. A typical feed solution in a chemical processing plant might be as follows: Al 2.5 *M*; Hg 0.02 *M*; ^{235}U 3.2 g/l; fission product activity 570 curies/l[1]. This corresponds to an activity level of ~ 180 μC/μg ^{235}U, so a portion of diluted feed solution sufficient for 6–8 determinations, each made with 2 μg ^{235}U, will contain only 2–3 mC of fission product activity. Also a set of six aliquots each containing 2 μg of ^{233}U represents a relatively safe quantity of α-activity to handle in a dry state in a well ventilated fume hood.

Thus a procedure may be envisaged in which an aliquot of feed solution (or a series of aliquots combined to be representative of a number of batches of fuel elements) is taken from a chemical separation plant, diluted in a cave, and a portion containing a few millicuries of β-γ activity removed for analysis. The following account describes an investigation of the precision which should be feasible for the determination of ^{235}U in such a solution. Four test solutions have been prepared, each containing uranium, aluminium and mercury in the appropriate proportions, and aliquots containing ~ 2 μg ^{235}U taken for replicate analyses. The investigation has been made on an essentially inactive basis, but the presence of fission products would be unlikely to have any significant effect for the concentration of any one of these is low with respect to uranium, and the chemical separation used is one which is known to remove the majority of fission products. It is worth stressing that the precision of the results reported later refers only to the analytical method. It includes no allowance for errors associated with taking a sample from a plant or with its dilution, or for errors which might arise from continuous operation of a plant as opposed to batch operation.

PREPARATION OF SOLUTIONS

a. ^{235}U standard

About 0.6 g of enriched ^{235}U oxide (93%) was weighed as U_3O_8 after being heated to a constant weight at 850° and 950°. An impurity analysis for the sample amounted to only ~ 0.02% of the uranium. The oxide was dissolved in nitric acid and diluted to a concentration of ~ 35 μg ^{235}U/g.

An aliquot of this solution was diluted to a concentration of ~ 2 μg/g, and this dilute solution used to calibrate the tracers; four more aliquots were used to prepare the solutions under investigation.

b. Solutions under investigation

In addition to the chemical composition of a plant feed solution it is necessary to consider the range of uranium isotopic compositions which might be encountered. The uranium supplied to a reactor of the Dounreay type contains, in the first instance, 93% ^{235}U[1]; it will be assumed that the rest is ^{238}U, although in fact there will probably be a small quantity of ^{234}U. In the reactor some 20% of the ^{235}U is consumed by fission, or by conversion to ^{236}U, and the resultant deficiency of ^{235}U may be made good in the chemical processing plant by the addition of more 93% ^{235}U. Thus as the fuel is cycled between the reactor and the chemical plant there will be a build up of the isotopes ^{234}U, ^{236}U, ^{237}U and ^{238}U[1]. However only changes in the ^{238}U/^{235}U ratio need be considered, for only these will affect determinations made using a natural uranium tracer. If losses of ^{238}U in the reactor are ignored, then in the course of seven cycles the ^{238}U/^{235}U ratio of the material returned to the plant will increase from $\sim$ 0.09 to $\sim$ 0.2.

Four solutions were prepared by mixing solutions containing ^{235}U (93%), natural uranium, aluminium nitrate, mercuric nitrate, and hydrochloric acid. Their approximate compositions were as follows:

Solution 1: ^{235}U (93%) 2 μg/g, natural uranium —, Al 40 μg/g, Hg 1 μg/g, HCl 5 *N*, ^{238}U/^{235}U ratio 0.06.

Solution 2: ^{235}U (93%) 2 μg/g, natural uranium 0.2 μg/g, Al 40 μg/g, Hg 1 μg/g, HCl 5 *N*, ^{238}U/^{235}U ratio 0.15.

Solution 3: ^{235}U (93%) 2 μg/g, natural uranium 0.5 μg/g, Al 40 μg/g, Hg 1 μg/g, HCl 5 *N*, ^{238}U/^{235}U ratio 0.3.

Solution 4: ^{235}U (93%) 2 μg/g, natural uranium 1.8 μg/g, Al 40 μg/g, Hg 1 μg/g, HCl 5 *N*, ^{238}U/^{235}U ratio 1.

Solutions 1, 2 and 3 were prepared to simulate the range of ^{238}U/^{235}U ratios which might arise during the recycling of fuel between the reactor and the chemical plant. Solution 4 was chosen in view of the possible extension of the method to less enriched material.

c. Tracers

^{233}U tracer. A solution of ^{233}U was prepared with a concentration of $\sim$ 3 μg/g in 5 *N* hydrochloric acid. The sample had the following isotopic composition: ^{233}U 99.68%, ^{234}U 0.24%, ^{235}U 0.02%, ^{238}U 0.06%.

Natural uranium tracer. About 0.9 g of "Specpure" U_3O_8 was heated to constant weight at 850° and 950°, dissolved in nitric acid and diluted to a concentration of 120 μg/g. One aliquot was diluted to a concentration of $\sim$ 4 μg/g; this dilute solution was calibrated against the ^{235}U standard, and used to determine the ^{235}U content of solutions 1, 2 and 3. A more concentrated solution ($\sim$ 20 μg/g) was used to determine the ^{235}U content of solution 4. These solutions were also made 5 *N* in hydrochloric acid. An impurity analysis for the same batch of "Specpure" U_3O_8 amounted to 0.04%.

ADDITION OF TRACERS

For each determination an aliquot of the tracer and of the sample was weighed into a polythene bottle.

a. Choice of mixing ratio

For a determination using ^{233}U as the tracer the most suitable ^{235}U/^{233}U ratio is unity, and in this series of determinations the values were included by the range 0.8–1.2.

For a determination made using natural uranium it is also necessary to measure the ^{238}U/^{235}U ratio for the sample before the addition of the tracer. If the ^{238}U/^{235}U ratio of the sample is R_S, and that of the mixture after the addition of tracer R_M, then errors in R_S will be effective in the difference $R_M - R_S$. To minimise uncertainties caused by any errors in the measurement of R_S, R_M was usually chosen to be approximately $10 \times R_S$; thus an error of 1% in R_S would cause one of only $\sim 0.1\%$ in $R_M - R_S$. Values of R_S and R_M are shown in Table I.

TABLE I

VALUES OF R_S AND R_M FOR ^{235}U STANDARD AND SOLUTIONS UNDER INVESTIGATION

Solution	R_S	R_M
^{235}U standard	0.06	1 – 1.5
solution 1	0.06	1.2 – 1.3
solution 2	0.15	1.7 – 1.8
solution 3	0.30	2.8 – 3.5
solution 4	0.97	6.4 – 10.2

b. Calibration of tracers

^{233}U tracer: 10 aliquots were mixed with aliquots of the ^{235}U standard.

^{238}U tracer: 10 aliquots were mixed with aliquots of the ^{235}U standard.
3 aliquots of the ^{235}U standard only were taken to permit a determination of its ^{238}U/^{235}U ratio.

The mixtures were evaporated to dryness in small beakers and transferred to mass spectrometer filaments as described below.

c. Determination of ^{235}U in solutions under investigation

From each of the four solutions the following aliquots were taken: 6 aliquots for the determination of ^{235}U with ^{233}U tracer, 6 aliquots for the determination of ^{235}U with natural uranium tracer, and 2 aliquots for the determination of the ^{238}U/^{235}U ratio for the sample.

CHEMICAL SEPARATION OF URANIUM

All solutions had been conditioned to be 5 *N* in hydrochloric acid, so a solvent extraction procedure using tri(iso-octyl)amine[6] could be applied directly to the mixtures of samples and tracers. Bromine water was added to the solutions to promote oxidation of uranium to the six valence state; this was not necessary for the present series of determinations, but it was done in order to ensure that this addition could cause no interference with the separation. However if the method were to be applied to solutions in which the uranium was not necessarily in the six valence state, it would be advisible to check the efficiency of this oxidation under the appropriate experimental conditions. The uranium was extracted with a 5% solution of tri(iso-octyl)amine in xylene and back-washed into water. The final solution was washed with xylene to minimise organic contaminants. The two phases were mixed by flushing them rapidly into and out of a blunt-ended spitzer for 30–50 seconds; the mixture was then separated in a centrifuge, and the required phase removed with a pointed spitzer.

The following procedure was used:

1. To the solution (1–3 ml) add 2 drops of bromine water and 1 ml of 5% (v/v) tri(iso-octyl)amine/xylene: mix, centrifuge, separate; 2. Repeat step 1; 3. Add 0.5 ml xylene: mix, centrifuge, separate; 4. To combined xylene fractions add 1 ml of water:

mix, centrifuge, separate; 5. Repeat step 4; 6. To combined water fractions add 1 ml of xylene: mix, centrifuge, separate; 7. Repeat step 6.

The procedure was checked using ^{233}U and ^{237}U as radioactive tracers, and also with a mixture of fission products obtained from an irradiated uranium-graphite pellet after ~ 150 days "cooling". The γ-spectrum showed the main components of this mixture to be zirconium, niobium, cerium and ruthenium. The separation of uranium was usually 90% or better, and the final solution contained 1–2% only of the fission product β,γ-activity.

The distribution of the γ-activity after the separation was determined in one experiment and found to be as follows:

original aqueous phase	96%;
washed tri(iso-octyl)amine-xylene extract	3%;
final aqueous solution	1%.

Usually two samples were treated together and the separation then required 20–30 minutes. Any one aliquot usually contained about 2 μg of ^{235}U, which in practice, for a solution from the Dounreay plant, would be associated with ~ 360 μC of fission product activity[1]. With the above procedure this should be reduced to ~ 15 μC in 10 min, and the final product should contain only ~ 5 μC of fission product activity.

PREPARATION OF SAMPLES FOR MASS SPECTROMETRY

The solutions of purified uranium were evaporated to dryness in small platinum dishes (fluorimeter trays) and organic matter destroyed by oxidation with nitric and perchloric acids. A little nitric acid was then added to the platinum dish, evaporated to small volume, transferred to a glass plate, and there evaporated to dryness; this process was repeated 2 or 3 times, and produced a deposit on the glass plate which was clearly visible, and which could easily be dissolved in a drop of water and transferred to a mass spectrometer filament. Subsequent experience with plutonium analyses has shown that a more concentrated deposit may be produced by using an indented microscope slide treated with "repelcote".

CONTAMINATION

Polythene and glassware were normally used once only; they were washed with nitric acid and rinsed thoroughly with water. The platinum dishes were fused first with sodium bisulphate and then with fusion mixture, and finally were immersed in boiling nitric acid. After the second fusion the dishes were checked in a fluorimeter and any indicating more than 0.002–0.004 μg uranium were recleaned. Gram quantities of uranium were not treated in the laboratory during the period in which this work was carried out, but otherwise no special precautions were taken to avoid atmospheric contamination.

A check on contamination by natural uranium was provided by measurements of the ^{238}U/^{235}U ratios for the aliquots to which ^{233}U tracer had been added. When the determination of the ^{235}U/^{233}U ratio had been completed a few measurements were made of the ^{238}U/^{235}U ratio. Atmospheric contamination would be indicated by variation of the ^{238}U/^{235}U ratio between aliquots from any one solution. The variation observed was not significant and would correspond to only 0.1–0.2% of the natural uranium added as tracer in the parallel series of determinations.

Contamination from reagents would show as a difference between the average ^{238}U/^{235}U ratio found for solution 1, and the value found directly by measurements with larger quantities ($\sim$ 25 μg) of the ^{235}U standard. Again the differences were barely significant and were equivalent to a contamination level of only 0.001–0.002 μg natural uranium.

MASS SPECTROMETRY

Isotopic analyses were made by the multi-filament technique using two Metropolitan-Vickers M.S.5 type mass spectrometers:

Determinations involving ^{233}U tracer were made with the prototype M.S.5.

Determinations with natural uranium tracer were made using a production instrument.

Neither could be said to be operating ideally so the results reported later represent values obtained under average working conditions.

a. Prototype instrument (^{233}U determinations)

Considerable difficulty was experienced with H.T. breakdown in the ion source. This was never explained satisfactorily and its main effect was to reduce the rate of analysis from a possible 3 samples per day to an average 2 samples per day. Little trouble was caused by background. The side filament carrying the sample was heated by a stabilised current.

b. Production instrument (natural uranium determinations)

No difficulty was caused by H.T. breakdown in the ion source, but for some samples the hydrocarbon background was troublesome. The current supply for the sample filament was not stabilised; also the Sorenson regulator was not working, but in our opinion this made little difference to the stability of ion beams, provided the mains voltage to the electronic units was maintained between certain fixed limits by means of a "Variac". The provision for scanning a spectrum was superior to the arrangement on the prototype instrument for it permitted a comparison of two isotopes to be made over shorter intervals of time.

c. General comments

Before they were used for the analysis of samples all filament units were cleaned in the mass spectrometer for 10–15 minutes, and then checked for contamination under normal operating conditions. Sources carrying samples were placed in the instrument and the filaments run at temperatures a little below the normal operating ones until the hydrocarbon background had fallen to an acceptable level. The samples were then analysed under such conditions that the contribution of ^{238}U from impurity in the filament material should be less than 2 mV. The most abundant isotope in the sample was usually recorded on the 5-V or 10-V ranges; occasionally for the ^{233}U determinations the 1-V or 2-V ranges were used. About 40 measurements of the isotope ratio were made for each sample.

EVALUATION OF RESULTS

Results were calculated using the following equations:

a. *^{233}U determinations*

$$y = z(R'_M - R'_T) \times \frac{235}{233} \qquad (1)$$

where z = mass of ^{233}U added, y = mass of ^{235}U in the sample, R'_T = ^{235}U/^{233}U ratio for the ^{233}U tracer, R'_M = ^{235}U/^{233}U ratio for the mixture of sample and tracer.

b. Natural uranium determinations

$$y = w\,\frac{R_T - R_M}{R_M - R_S} \times \frac{1}{R_T} \times \frac{235}{238} \qquad (2)$$

where w = mass of ^{238}U added, y = mass of ^{235}U in the sample, R_T = ^{238}U/^{235}U ratio of natural uranium, R_S = ^{238}U/^{235}U ratio for the sample, R_M = ^{238}U/^{235}U ratio for the mixture of sample and tracer.

CALCULATION OF RANDOM ERRORS

For a set of measurements the standard deviation of a single value may be calculated as:

$$\sigma = \sqrt{\frac{\Sigma\,(\bar{x} - x)^2}{(n-1)}}$$

The standard deviation of the mean value may be taken as the standard error:

$$\sigma_m = \frac{\sigma}{\sqrt{n}}$$

When 6 or 10 measurements have been made, the standard error has been taken to represent the uncertainty in the mean value; when only 2 or 3 measurements have been made the standard deviation has been used. The appropriate uncertainty (expressed as a percentage and denoted by *s.e.*) has been calculated for each function used in the calculation and an overall value found:

$$s.e._{\text{total}} = \sqrt{\Sigma\,(s.e.)^2}$$

The uncertainty finally quoted with each result is 3 × $s.e._{\text{total}}$.

a. *^{233}U determinations*

The precision of the final result for a given solution involves two sources of error: the random error in the determination and that in the calibration of the tracer.

b. Natural uranium determinations

For a determination made using natural uranium as a tracer there are several more sources of random error, but most of these are small. The various sources of error are:

(1) Random error in the calibration of the natural uranium tracer. (2) Random error in the determination. (3) When the ^{238}U/^{235}U ratio used for a determination is somewhat different from unity (solutions 3 and 4), a range factor has to be used in the calculation of the isotope ratio R_M. If the percentage error introduced into the isotope ratio by the uncertainty in the range factor is [$s.e.(RF/R_M)$], then the error in the final result is:

$$[s.e.(RF/R_M)] \times \frac{R_M}{R_M - R_S} \times \frac{R_T - R_S}{R_T - R_M}$$

(4) Errors also arise from the measurement of R_S, the ^{238}U/^{235}U ratio of the sample before addition of tracer. If the random error in the ratio is [$s.e.(R_S)$] the uncertainty introduced into a determination is:

$$[s.e.(R_S)] \times \frac{R_S}{R_M - R_S}$$

(5) Similarly there is the effect of the error in the range factor (if required):

$$[s.e.(RF/R_S)] \times \frac{R_S}{R_M - R_S}$$

The errors described under (4) and (5) occur both in a determination and in the calibration of the tracer, but as the function $R_S/(R_M - R_S)$ usually has a value in the range 0.05–0.1, their effect is relatively small.

RESULTS

a. Calibration of tracers

The values in Tables II and III were calculated using equations (1) and (2), the measured isotope ratios, and the gravimetric value for the concentration of the ^{235}U standard. These measured tracer concentrations were then used with equations (1) and

TABLE II

^{233}U TRACER

Sample number	*$^{235}U/^{233}U$ ratio*	*Concentration of ^{233}U µg/g*	*Mean value*
29	1.131	3.195	
30	1.120	3.197	
31	1.013	3.197	
32	0.915	3.202	
33	0.965	3.192	3.200 µg/g
34	1.019	3.201	
35	1.131	3.201	Standard deviation of a single value ≡ 0.16%
36	0.951	3.208	
37	0.980	3.202	Standard error of mean value ≡ 0.05%
38	0.937	3.209	

TABLE III

NATURAL URANIUM TRACER

Sample number	*$^{238}U/^{235}U$ ratio*	*Concentration of ^{238}U µg/g*	*Mean value*
39	1.274	3.785	
40	1.274	3.785	
41	1.205	3.796	
42	1.319	3.799	
43	1.264	3.776	3.788 µg/g
44	1.265	3.791	
45	1.037	3.788	Standard deviation of a single value ≡ 0.20%
46	1.465	3.794	
47	1.502	3.777	Standard error of mean value ≡ 0.06%
48	1.259	3.789	
49	0.0639		
50	0.0636		
51	0.0636		

(2) to determine the ^{235}U content of solutions 1–4. (The above values are based on directly measured isotope ratios. If the conventional discrimination correction of $\sqrt{238/235}$ is applied to the results in Table III, the value found for the concentration of *total* natural uranium is 3.839 µg/g. This may be compared with the value 3.832 µg/g based on the mass of natural uranium oxide used to prepare the tracer solution).

b. Results for solutions under investigation (Tables IV, V and VI)

TABLE IV

RESULTS OBTAINED USING ^{233}U TRACER

Solution	*Sample number*	*$^{235}U/^{233}U$ ratio*	*Concentration of ^{235}U µg/g*	*Mean value*
Solution 1	1	0.936	1.925	
	2	0.961	1.940	
	3	0.931	1.924	1.935 µg/g
	4	0.946	1.931	
	5	0.978	1.935	Standard deviation of a single value ≡ 0.57%
	6	1.031	1.954	
				Standard error of mean value ≡ 0.23%
Solution 2	15	0.978	1.955	
	16	0.981	1.960	
	17	0.937	1.955	1.957 µg/g
	18	0.928	1.958	
	19	0.972	1.958	Standard deviation of a single value ≡ 0.10%
	20	0.926	1.958	
				Standard error of mean value ≡ 0.04%
Solution 3	52	0.980	1.947	
	53	1.053	1.947	
	54	0.969	1.953	1.951 µg/g
	55	0.900	1.959	
	56	0.982	1.948	Standard deviation of a single value ≡ 0.24%
	57	1.020	1.949	
				Standard error of mean value ≡ 0.10%
Solution 4	66	0.926	1.915	
	67	0.875	1.909	
	68	0.956	1.917	1.913 µg/g
	69	0.992	1.913	
	70	0.820	1.914	Standard deviation of a single value ≡ 0.16%
	71	0.983	1.910	
				Standard error of mean value ≡ 0.07%

TABLE V

RESULTS OBTAINED USING NATURAL URANIUM TRACER

Solution	*Sample number*	*$^{238}U/^{235}U$ ratio*	*Concentration of ^{235}U µg/g*	*Mean value*
Solution 1	7	1.233	1.945	
	8	1.301	1.939	
	9	1.160	1.939	1.939 µg/g
	10	1.241	1.945	
	11	1.195	1.932	Standard deviation of a single value ≡ 0.31%
	12	1.197	1.931	
	13	0.0638		Standard error of mean value ≡ 0.13%
	14	0.0653		

TABLE V (continued)

Solution	*Sample number*	*$^{238}U/^{235}U$ ratio*	*Concentration of ^{235}U µg/g*	*Mean value*
Solution 2	21	1.762	1.962	
	22	1.823	1.950	
	23	1.825	1.960	1.957 µg/g
	24	1.817	1.956	
	25	1.743	1.957	Standard deviation of a single value ≡ 0.21%
	26	1.822	1.957	
	27	0.1536		Standard error of mean value ≡ 0.08%
	28	0.1554		
Solution 3	58	3.405	1.946	
	59	3.210	1.984	
	60	3.491	1.955	1.961 µg/g
	61	3.103	1.966	
	62	3.364	1.962	Standard deviation of a single value ≡ 0.67%
	63	2.809	1.956	
	64	0.2976		Standard error of mean value ≡ 0.27%
	65	0.2972		
Solution 4	72	8.72	1.922	
	73	6.64	1.917	
	74	10.25	1.932	1.922 µg/g
	75	7.78	1.917	
	76	6.45	1.918	Standard deviation of a single value ≡ 0.29%
	77	8.67	1.923	
	78	0.9682		Standard error of mean value ≡ 0.12%
	79	0.9681		

TABLE VI

SUMMARY OF RESULTS FOR SOLUTIONS UNDER INVESTIGATION

	Concentration expected µg/g	*Concentration determined using ^{233}U tracer µg/g*	*Concentration determined using natural uranium tracer µg/g*
Solution 1			
value	1.932	1.935 ± 0.014	1.939 ± 0.010
3 × s.e.$_{\text{Total}}$		± 0.72%	± 0.51%
discrepancy		+ 0.16%	+ 0.35%
Solution 2			
value	1.957	1.957 ± 0.004	1.957 ± 0.008
3 × s.e.$_{\text{Total}}$		± 0.20%	± 0.39%
discrepancy		+ 0.03%	+ 0.01%
Solution 3			
value	1.948	1.951 ± 0.006	1.961 ± 0.017
3 × s.e.$_{\text{Total}}$		± 0.33%	± 0.85%
discrepancy		+ 0.12%	+ 0.68%
Solution 4			
value	1.913	1.913 ± 0.005	1.922 ± 0.008
3 × s.e.$_{\text{Total}}$		± 0.25%	± 0.42%
discrepancy		+ 0.03%	+ 0.47%

* The uncertainty quoted with each result is 3 × total standard error. The discrepancies are based on the differences between values expressed to a further place of decimals.

The mean values of the errors and discrepancies recorded in Table VI are as follows:

(*a*) for determinations made using ^{233}U tracer the mean value of 3× total standard error is 0.37%, and the mean value of the discrepancy is +0.09%;

(*b*) for determinations made using natural uranium tracer the mean value of 3× total standard error is 0.55%, and the mean discrepancy +0.38%.

DISCUSSION

a. ^{233}*U determinations*

For the determinations made using the ^{233}U tracer, the discrepancies between the values found and those expected are less than 0.2% and are not significant. The mean value of 3 × (total standard error) is equivalent to 0.37%, so if a value of 0.1% is assumed for errors in the preparation of the ^{235}U standard the overall accuracy of a determination based on six replicate analyses should be of the order of 0.5%.

The values found for the standard deviation of a single value are, for the four solutions, 0.57%, 0.10%, 0.24% and 0.16% respectively, giving a mean value of 0.27%. The standard error for the calibration of the tracer is equivalent to 0.05%, and making allowance for this the average standard deviation becomes 0.275%. If this value is used to assign limits to the "concentrations expected" listed in Table VI then of the twenty-four individual determinations made for the four solutions, twenty lie within the range $\pm 1\ \sigma$, three within the range $\pm 1\ \sigma$ to $\pm 2\ \sigma$, and for one determination (number 6) the random error is considerably greater than $2\ \sigma$. The distribution which might be expected theoretically is 16 : 7 : 1. Thus the mean overall value of 3 × standard deviation is 0.83%. If a value of 0.1% is again assumed for errors in the preparation of the ^{235}U standard, the overall accuracy ($3\ \sigma$) for a measurement based on a single determination should be of the order of 1%.

b. Natural uranium determinations

The determinations made using natural uranium as the tracer show some evidence of a small positive bias. The discrepancy may be attributed to random error for solution 1 (2 standard errors) but it is becoming significant for solution 3 (2.4 standard errors) and is quite significant for solution 4 (3.3 standard errors). It is possible that for solutions 3 and 4 systematic errors of the order of a few tenths of a per cent could have been caused by contributions from hydrocarbon background. This has not been established but much of the data is consistent with the suggestion.

The relative abundances of the various peaks of the background observed in a mass spectrometer may well vary from sample to sample, and also over the course of an isotopic analysis; in the absence of an exact relation all that can be stated is that the background peaks at mass numbers 233, 235 and 238 can be of comparable size (*e.g.* in one case 0.5 : 0.7 : 1), although this may not necessarily be true for every analysis. The effects of such a background should be negligible in the determination of a ^{238}U/^{235}U ratio of nearly unity; however as the ratio to be determined becomes increasingly different from one, it also becomes increasingly sensitive to background errors for the less abundant isotope is recorded using a more sensitive range of the amplifier. For the conditions under which the various ratios were measured the average errors introduced by a background of 1 mV at each of mass numbers 235 and 238 would be as follows: solution 1, solution 2, and calibration, ~0.02%

(^{238}U/^{235}U ratio 1.2–1.8; ^{235}U peak usually recorded on 5-V range); solution 3, ~0.07% (^{238}U/^{235}U ratio 3.0–3.5; ^{235}U peak usually recorded on 2-V range); solution 4, 0.1–0.2% (^{238}U/^{235}U ratio 6–10; ^{235}U peak recorded on 1-V or 2-V range). Thus only solutions 3 and 4 need be considered.

Before each isotopic analysis was made the sample was heated to a temperature just below the normal operating value and left until the background (monitored at mass numbers 230, 231, and 233) had fallen to an acceptable level. Ideally the background at mass number 233 should be at least less than 1 mV; however it was sometimes difficult to distinguish a background of 1 mV from the noise level of the amplifier, and it was also considered that if the investigation were to be of any real value it should proceed at an average rate of two mass spectrometric analyses per day. For solution 3 an examination of the mass spectrometer records shows that for five of the six determinations the peak at mass number 233 had fallen to 1–5 mV by the beginning of the isotopic analysis; similar sized peaks at mass numbers 235 and 238 would introduce an error of 0.1–0.3%. For sample 59 the peak at mass number 233 was much larger, falling from a value of ~ 40 mV at the beginning of the isotopic analysis to ~ 3 mV by the end of the analysis. For solution 4 special care was taken to minimise the effects of background and in this case, as the samples were so large (2 μg ^{235}U; 10–20 μg ^{238}U), it was possible to reduce the relative size of background peaks by decreasing the gain of the electron multiplier. An examination of the mass spectrometer charts shows that for analysis 75 the abundance of the peak at mass number 233 was less than 0.1 mV. For the remaining samples however the peak at mass number 233 may well have been 0.5–1 mV, but usually it could not be distinguished adequately from the noise level to permit identification or precise measurement.

While the data and the mass spectrometric records may be consistent with the introduction of small errors by hydrocarbon background, in the absence of a precise relation between the abundances of the various background peaks it would be difficult to prove that a bias had arisen in this way. However further support is given by the mass spectrometric analyses 64, 65, 78 and 79. These were the isotopic analyses

TABLE VII

RESULTS CALCULATED FROM ISOTOPIC ANALYSES 64, 65, 78 AND 79

Sample number	*$^{238}U/^{235}U$ ratio*	*Concentration of ^{235}U μg/g*
Solution 3		
64	0.2976	1.938
65	0.2972	1.941
mean value		1.940 ± 0.012 μg/g
cf. concentration expected		1.948 μg/g
3 × *s.e.*$_{\text{Total}}$		± 0.63%
discrepancy		— 0.43%
Solution 4		
78	0.9682	1.912
79	0.9681	1.912
mean value		1.912 ± 0.004 μg/g
cf. concentration expected		1.913 μg/g
3 × *s.e.*$_{\text{Total}}$		± 0.20%
discrepancy		— 0.04%

for the uranium present in solutions 3 and 4, but as the preparation of these solutions involved the addition of known quantities of natural uranium the isotopic analyses may also be used to calculate the ^{235}U contents. These results are recorded in Table VII. If the background suggestion is accepted then for solution 3 if a positive bias is introduced into results based on the measurement of $^{238}U/^{235}U$ ratios of ~ 3, a negative bias might be expected for these ratios of ~ 0.3; for solution 4 the $^{238}U/^{235}U$ ratio is now ~ 1 instead of 6–10 so no bias would be expected.

The results obtained for the four solutions yield the following estimates of precision. The mean value of 3 × (total standard error) for a determination based on six replicate analyses and two isotopic analyses is 0.55%, and for a determination based on a single isotopic dilution determination combined with a single isotopic analysis the mean value of 3 × standard deviation is 1.2%. Thus the precision achieved by the method using natural uranium tracer is somewhat worse than that found using ^{233}U tracer, and in addition, for the analyses described in this paper, there is a mean bias of 0.4%.

CONCLUSIONS

The results obtained using ^{233}U as a tracer show an average precision ($3\,\sigma$) of 0.37% for a value based on six replicate analyses and 0.83% for one based on a single determination. No significant bias was observed. For the determinations made using a natural uranium tracer the corresponding mean values of the precision ($3\,\sigma$) are 0.55% and 1.2% respectively, and there is a mean bias of +0.4%. The inferior results obtained using the natural uranium tracer appear to be due to the following reasons:

(a) Additional measurements are involved, namely the determination of R_S, the $^{238}U/^{235}U$ ratio of the samples. In fact the uncertainty introduced by these measurements was relatively small. In the worst case (solution 2) its effect was to increase the overall standard error by a quarter, and for the four solutions the average value of 3 × (total standard error) was increased from 0.50% to 0.55%.

(b) Uncertainties are introduced when the ratio R_M is somewhat different from unity. The two ion beams are then measured on different sensitivity ranges so the uncertainty in a range factor calibration is introduced, and errors in the location of the base line become more important. It also seems probable that small errors may have been introduced by hydrocarbon background. If this contribution should vary from sample to sample then in addition to causing a small bias it would form a further source of random error.

(c) The current supply for the sample filament in the ion source was not stabilised.

A method based on the use of ^{233}U as a tracer would seem to be very suitable for the required determination of ^{235}U. The average measures of precision are given above, but an allowance must also be made for errors associated with the preparation of a ^{235}U standard (*e.g.* stoichiometry of the oxide, etc.) so a precision and accuracy of about 1% should be feasible for a single determination, and about 0.5% for a measurement based on six replicate analyses. In addition to this specific problem it is possible that the method could be used for other routine determinations of ^{235}U. Methods based on a determination of total uranium will also usually require an isotopic analysis of the uranium, and in view of the high isotopic purity of the ^{233}U tracer it is likely that this analysis could often be made satisfactorily in the presence of the tracer. Thus, where the precision of a single determination is adequate, the isotope dilution method could form an alternative or at least a supplementary method of analysis for relatively little further effort than that already required for the isotopic analysis.

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SUMMARY

This paper describes an examination of the precision which might be achieved by using an isotopic dilution method for the determination of ^{235}U in the feed solution of an enriched uranium fuel chemical processing plant such as the Dounreay M.T.R. chemical plant. Four solutions were prepared to simulate diluted samples of feed solution; they contained uranium with an isotopic content ranging from 93% ^{235}U to 50% ^{235}U. Separation of uranium was made by solvent extraction with tri(iso-octyl)amine, and isotopic analyses were then made using two Metropolitan-Vickers M.S.5 mass spectrometers. Both ^{233}U and natural uranium were examined as possible tracers. Using ^{233}U as the tracer the results for the four solutions yield a mean precision ($3\ \sigma$) of 0.37% for a result based on six replicate analyses, and 0.83% for one based on a single analysis. These values include the random errors involved in the mass spectrometric calibration of the tracer, but not errors associated with the gravimetric preparation of a ^{235}U standard, or those which would be concerned with taking a sample from a plant.

The results obtained using a natural uranium tracer are less satisfactory, and possible explanations are suggested.

RÉSUMÉ

Les auteurs ont effectué l'étude d'un dosage de l'uranium-235, par dilution isotopique. La séparation de l'uranium se fait par extraction dans un solvant. Les analyses isotopiques ont été faites au moyen de deux spectromètres de masse. En utilisant l'uranium-233 comme traceur, on arrive à une précision moyenne de 0.37%. Les résultats obtenus avec l'uranium naturel comme traceur sont moins satisfaisants.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von Uran-235 nach dem Isotopenverdünnungsverfahren. Die Abtrennung des Urans erfolgt durch Extraktion mit einem organischen Lösungsmittel. Zur Isotopenanalyse werden zwei Massenspektrometer verwendet. Mit Uran-233 als Tracer erreicht man eine mittlere Genauigkeit von 0.37%. Natürliches Uran als Tracer ist weniger geeignet.

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STUDIES ON COORDINATION COMPOUNDS

XVIII. FORMATION CONSTANTS OF SOME METAL SALTS OF HYDROXYQUINONES

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INTRODUCTION

Several of the hydroxyquinones have important analytical applications. Most of these involve interactions with metal ions. Yet there have been almost no quantitative studies on the equilibria involved in these interactions. Hence, the present investigation was undertaken using the technique which was found to be useful in the case of the nitrosonaphthols[1]. Kojic acid, chlorokojic acid, and 3-hydroxyflavone were included for comparison.

EXPERIMENTAL*

Materials

5-Hydroxy-1,4-naphthoquinone (juglone) (Aldrich Chemical Co. Inc.) was recrystallized from ethyl alcohol: m.p. 152°; reported 153°[2]. 2-Hydroxy-1,4-naphthoquinone (lawsone) (Aldrich Chemical Co., Inc.) was recrystallized from ethyl alcohol: m.p. 189°(d); literature 190°[3]. 2-Hydroxy-3-methyl-1,4-naphthoquinone (phthiocol) was prepared from 2-methylnaphthoquinone by the method of FIESER[4]: m.p. 172°; reported 173°. 2-Hydroxy-3-(3′-methylcrotyl)-1,4-naphthoquinone (Aldrich Chemical Co., Inc.) was recrystallized from ethyl alcohol: m.p. 136°. 1-Hydroxy anthraquinone (Bios Laboratories, Inc.) was recrystallized from purified dioxane and dried at 110°: m.p. 190°; reported 192°[5]. 1,2-Dihydroxyanthraquinone (alizarin) (National Aniline Division) was recrystallized from absolute ethanol and dried at 115°: m.p. 289°; reported 290°[6]. 1,2-Dihydroxy-3-nitroanthraquinone (3-nitroalizarin) (Eastman Organic Chemicals) was recrystallized from purified dioxane and dried at 115°: m.p. 242°; reported 244°[7]. Sodium 3-alizarin sulfonate (Eastman Organic Chemicals) was a certified product and used as supplied. 1,3-Dihydroxyanthraquinone was prepared by Dr. H. D. KIVLIGHN: m.p. 264–265°; reported 262–263°[8]. 1,2,7-Trihydroxyanthraquinone (K & K Laboratories, Inc.) was recrystallized three times from dioxane. 1,8-Dihydroxyanthraquinone (chrysazin) (Eastman Organic Chemicals) was recrystallized from ethyl alcohol: m.p. 190°; reported 191°[9]. Kojic acid (Corn Products Refining Co.) was purified by sublimation: m.p. 154–156°; reported 154°[10]. Chlorokojic acid (Aldrich Chemical Co., Inc.) was recrystallized from water: m.p. 165°; reported 166°[11]. 3-Hydroxyflavone (Eastman Organic Chemicals) was recrystallized from ethanol: m.p. 171°; reported 170°[12].

1,8-Dihydroxyanthrone. Five grams of purified 1,8-dihydroxyanthraquinone in a 200-ml round bottom flask with a reflux condenser was mixed with 5 g of tin powder and 40 ml glacial acetic acid. The mixture was heated to boiling and, over a period of 8 h, 5 g conc. hydrochloric acid was added dropwise. The yellow precipitate was filtered, dried and recrystallized from ethanol: m.p. 178°; reported 178°[13].

1,8,10-Trihydroxyanthrone. Ten grams of 1,8-dihydroxyanthraquinone was dissolved in 250 ml warm chlorobenzene. To this was added the Raney nickel prepared by washing 20 g of the commercial catalyst with acetone followed by chlorobenzene. Hydrogen was started at 50 lb/in.² and 27° and was complete in 3 h. The solution was warmed and filtered and the catalyst warmed with

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* All melting points are uncorrected.

200 ml ethanol. The yellow crystals (2.6 g) which resulted upon combining and chilling the filtrates were recrystallized twice from Skellysolve C: m.p. 160–61°*.

Equilibrium measurements

All measurements were made in 75 vol % dioxane–water solutions at a constant temperature of 30.0° ± 0.1°. The apparatus, techniques and methods of calculation were those previously described[1] except for two differences. The solution of tetramethylammonium hydroxide used in titrations was made up in 75 vol % dioxane-water solution exactly like the solution being titrated. The calculations were extended to include the reliability in the average values on the basis of the 95% confidence interval[14,15]. The values of the dissociation constants are assembled in Table I and those for the formation constants in Table II. Both the low solubility and the weak acidity of several of the compounds under study caused difficulties.

TABLE I

VALUES FOR pK IN 75 VOL % DIOXANE–WATER SOLUTION AT 30°

	pK_1	pK_2
2-Hydroxy-1,4-naphthoquinone	8.05±0.03	
2-Hydroxy-3-methyl-1,4-naphthoquinone	9.56±0.03	
2-Hydroxy-3-(3′-methylcrotyl)-1,4-naphthoquinone	10.32±0.05	
5-Hydroxy-1,4-naphthoquinone	13.29±0.03	
1-Hydroxyanthraquinone	14.29±0.02	
1,2-Dihydroxyanthraquinone	10.73±0.03	
1,8-Dihydroxyanthraquinone	13.06±0.02	
1,2-Dihydroxy-3-nitroanthraquinone	6.28±0.05	14.08±0.2
1,2,7-Trihydroxyanthraquinone	10.48±0.04	
Kojic acid	12.29±0.03	
Chlorokojic acid	12.02±0.02	
3-Hydroxyflavone	13.98±0.03	
Sodium 3-alizarin sulfonate (in water solution)	6.12	10.80

1,2,3-Trihydroxyanthraquinone was too insoluble in 75% dioxane for any measurements. On treating sodium 3-alizarin sulfonate with tetramethylammonium hydroxide a copious precipitate formed. Because of the dark red color which developed early in the titrations of the hydroxyquinones, the solutions which contained metal ions were filtered to make certain that the final system was homogeneous. No calculations were made for those systems which had even a small amount of precipitate. These included all of the metal ions in the cases of 1,2-dihydroxyanthraquinone and 1,2,7-trihydroxyanthraquinone. The anthrones were too weakly acid to permit measuring the pK's.

Infrared absorption spectra

All spectra were obtained with a Perkin-Elmer, model 21 recording infrared spectrophotometer, using sodium chloride optics. The spectra in the solid phase were made by incorporating the materials in potassium bromide pellets[16,17]. The frequencies of selected absorptions are given in Table III.

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* These directions were supplied by Dr. W. B. Wheatley of Bristol Laboratories Inc. who adapted them from K. ZAHN AND H. KOCH, *Ber.*, 71 (1938) 172.

TABLE II

VALUES FOR FORMATION CONSTANTS OF THE COMPLEXES OF HYDROXYQUINONES AND HYDROXY-γ-PYRONES WITH SEVERAL BIVALENT METAL IONS AT 30° IN 75 VOL% DIOXANE

	UO_2^{+2}	Cu^{+2}	Be^{+2}	Ni^{+2}	Co^{+2}	Zn^{+2}	Cd^{+2}	Mn^{+2}	UO_2^{+2}	Cu^{+2}	Be^{+2}	Ni^{+2}	Co^{+2}	Zn^{+2}	Cd^{+2}	Mn^{+2}
2-Hydroxy-1,4-naphthoquinone	7.27 ±0.02	6.77 ±0.05	5.62 ±0.13	5.59 ±0.03	5.71 ±0.03	6.14 ±0.02	5.35 ±0.04		6.07 ±0.02	5.68 ±0.02	4.62 ±0.02	5.29 ±0.06	5.07 ±0.06	5.41 ±0.02	4.88 ±0.02	
2-Hydroxy-3-methyl-1,4-naphthoquinone	8.39 ±0.03	7.73 ±0.07	ppt.	6.46 ±0.02		6.80 ±0.03			7.20 ±0.05	6.44 ±0.03	ppt.	5.61 ±0.02		6.00 ±0.03		
2-Hydroxy-3-(3′-methylcrotyl)-1,4-naphthoquinone	8.73 ±0.05	8.18 ±0.04	ppt.	6.61 ±0.07	6.57 ±0.05	7.08 ±0.05			7.30 ±0.06	7.36 ±0.03	ppt.	5.86 ±0.04	5.54 ±0.05	6.08 ±0.07		
5-Hydroxy-1,4-naphthoquinone	11.84 ±0.05	11.24 ±0.05	ppt.	8.96 ±0.03	8.66 ±0.03	ppt.	ppt.	ppt.	10.53 ±0.08	9.67 ±0.04	ppt.	7.66 ±0.07	7.55 ±0.09	ppt.	ppt.	ppt.
1-Hydroxyanthraquinone	ppt.	12.04 ±0.04	12.01	9.47 ±0.03	ppt.	ppt.	ppt.	9.03 ±0.06	ppt.	10.83 ±0.04	11.44	8.74 ±0.06	ppt.	ppt.	ppt.	8.80 ±0.05
1,8-Dihydroxyanthraquinone	12.13 ±0.06	ppt.	ppt.	8.64 ±0.03	8.52 ±0.04	ppt.	ppt.	ppt.	11.03 ±0.04	ppt.	ppt.	7.92 ±0.07	7.86 ±0.07	ppt.	ppt.	ppt.
Kojic acid	—	—	10.07 ±0.06	9.72 ±0.03	9.46 ±0.03	10.38 ±0.03	9.81 ±0.03	9.81 ±0.03	10.23 ±0.02	10.13 ±0.02	7.81 ±0.05	7.57 ±0.04	7.49 ±0.02	8.58 ±0.03	7.43 ±0.06	7.47 ±0.06
Chlorokojic acid	—	ppt.	9.57 ±0.07	9.22 ±0.03	8.87 ±0.03	9.74 ±0.03	8.72 ±0.02	ppt.	9.93 ±0.03		8.63 ±0.05	7.42 ±0.06	7.14 ±0.07	8.01 ±0.05	7.32 ±0.03	ppt.
3-Hydroxyflavone	—	13.20 ±0.05		ppt.	9.91 ±0.04	11.03 ±0.06	9.70 ±0.02	ppt.		11.13 ±0.05		ppt.	ppt.	9.79 ±0.04	8.41 ±0.03	ppt.

TABLE III

SIGNIFICANT PEAKS IN THE INFRARED SPECTRA OF HYDROXYQUINONES AND HYDROXY-γ-PYRONES

	Solvent	*Hydroxyl*	*Carbonyl*		*C = C*
2-Hydroxy-1,4-naphthoquinone	KBr	3175br	1681s	1693s	1596s
2-Hydroxy-3-methyl-1,4-naphthoquinone	KBr	3340br	1662sh	1652s	1595s
	$CHBr_3$	3140br	1670s	1652s	1600s
2-Hydroxy-3-(3′-methylcrotyl)-1,4-naphthoquinone	KBr	3333s	1662s,sh	1643s	1595s
5-Hydroxy-1,4-naphthoquinone	KBr	3070br	1670s	1647s	1603s
1-Hydroxyanthraquinone	KBr	3077br	1672s	1639s	1593s
	$CHBr_3$	3020s			
1,2-Dihydroxyanthraquinone	KBr	3340br	1662s	1634s	1587s
1,3-Dihydroxyanthraquinone	KBr	3378br	1671sh	1638s	1595s
	CCl_4	2907			
3-Nitro-1,2-dihydroxyanthraquinone	KBr	3175br	1681s	1642s	1590s
	CCl_4	2951 2840	1681	1629	
1,8-Dihydroxyanthraquinone	KBr	3077br	1678s	1628	1603sh
1,2,7-Trihydroxyanthraquinone	KBr	3300br	1670s	1640sh	1595s
1,8-Dihydroxyanthrone	KBr	3000br 3330sh		1613s	1600s
1,8,10-Trihydroxyanthrone	KBr	2970br 3440sh		1634sh	1608s
Kojic acid	KBr	3175br		1664	1622s
Chlorokojic acid	KBr	3175br		1656	1632
3-Hydroxyflavone	KBr	3180		1630sh	1609s
	CCl_4	3320		1628	1550v.br

br = broad; s = sharp; sh = shoulder.

DISCUSSION

Dissociation constants

The values of the dissociation constants show a number of interesting points. Perhaps the most startling of these is the large difference ($\sim 10^5$) in the dissociation constants of juglone and lawsone. The difference probably is to be attributed largely to the difference in the strength of hydrogen bonding in a six-*vs.* a five-membered ring[18]. However, the fact that the carbonyl group is adjacent to the hydroxy group in lawsone and not in juglone also may be important. Substitution of alkyl groups in the lawsone molecule has the usual inductive effect of markedly reducing the acidity, apparently the more so, the larger the group. Further, the difference ($\sim 10^4$) in the dissociation constants of kojic acid and lawsone shows that a marked effect on the stability of the ring formed by hydrogen bonding may be produced by a change in the adjacent ring.

The acidity of 1-hydroxyanthraquinone ($pK = 14.29$) differs by only a factor of 10 from that of the corresponding naphthoquinone, lawsone. The effect of a fused benzo ring is much the same when values for kojic acid and 3-hydroxyflavone are compared. The nitro group in 3-nitroalizarin greatly increases the acidity of the proton of the adjacent OH group but has much less effect on the proton of the OH group adjacent to the carbonyl group (see below). The effect of the sulfonate group is similar since the pK's for alizarin in water at 18° are 8.18 and 11.94[19].

The substitution of $ClCH_2^-$ for $HOCH_2^-$ in kojic acid increases the acidity as would be expected but not by any great amount.

The pK's of such weak acids are best determined by some means other than simple titration. By measurements of the EMF of cells, KIVLIGHN[20] found the following values for 70% dioxane solution at 25°:

	pK_1	pK_2
1-Hydroxyanthraquinone	13.15	
2-Hydroxyanthraquinone	10.86	
1,2-Dihydroxyanthraquinone	9.93	16.37
1,4-Dihydroxyanthraquinone	12.23	13.92
1,5-Dihydroxyanthraquinone	12.66	15.23
1,8-Dihydroxyanthraquinone	11.89	15.15
2,6-Dihydroxyanthraquinone	10.32	12.75

While these values are different from those found in this investigation, the agreement is as good as might be expected considering the different conditions of the two sets of measurements. Some studies on the variation of pK with mole fraction of dioxane were made. In 70 volume % dioxane-water at 30° the following values were obtained: 1,2-dihydroxyanthraquinone, 9.91 and 1,8-dihydroxyanthraquinone, 11.97. KIVLIGHN's values show the difference in acidity of a hydrogen-bonded and a non-hydrogen-bonded OH group and indicate that both OH groups in 1,8-dihydroxyanthraquinone are hydrogen-bonded to the same carbonyl group. They also make evident why only pK_1 for these compounds can be determined titrametrically and why no pK at all for the reduction products of 1,8-dihydroxyanthraquinone can be obtained titrametrically.

Formation constants

For the compounds comprising the present study two customary generalizations hold: (1) for a related group of compounds and a common metal ion, the weaker the acid, the more stable the complex and (2) for a given chelating group, the order of stability of metal ion associations is $UO_2 > Cu > Zn > Be > Ni > Co > Mn, Cd$.

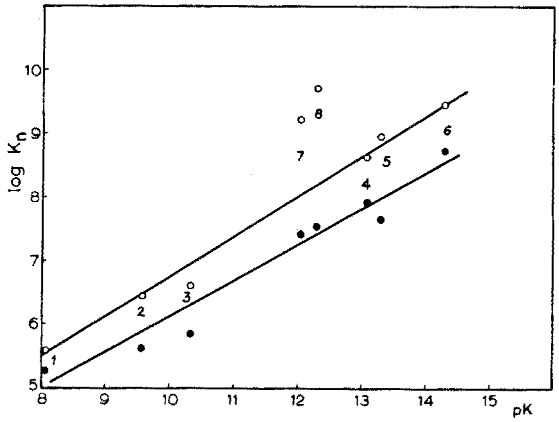

Fig. 1. Plot of log K_n for the nickel salts *vs.* pK of the ligand: o = log K_1; ● = log K_2; 1 = 2-hydroxy-1,4-naphthoquinone; 2 = 2-hydroxy-3-methyl-1,4-napthoquinone; 3 = 2-hydroxy-3(3'-methylcrotyl)-1,4-naphthoquinone; 4 = 1,8-dihydroxyanthraquinone; 5 = 5-hydroxy-1,4-naphthoquinone; 6 = 1-hydroxyanthraquinone; 7 = chlorokojic acid; 8 = kojic acid.

The beryllium compounds are thus relatively less stable than usual[21–23]. Insolubility of complexes prevented the determination of formation constants in several cases. The metal derivatives of lawsone are significantly more stable than those of juglone. It is not safe to conclude that, contrary to findings with other types of compounds [diamines and triamines[24,25] α- and β-(S-ethylmercapto)alkanoic acids[26], α- and β-aminopolyalkanoic acids[27,28]], six-membered chelate rings are here more stable than five-membered rings, because lawsone is a much weaker acid than juglone. The plot of pK *vs.* log K (Fig. 1) for the nickel derivatives indicates that the latter is the more likely explanation. Kojic acid differs too much in type from the hydroxyqui-

TABLE IV

SIGNIFICANT PEAKS IN THE INFRARED SPECTRA OF VARIOUS ANTHRAQUINONES

Compound	*Medium*	*Hydroxyl frequencies*		*Carbonyl frequencies*		*Ref.*
Anthraquinone	Mull			1676		30
	Mull			1675s		29,32
2-Methyl	Mull			1675		29
1-Hydroxy	Mull			1673	1636	30
	Mull			1667	1631s	29
	Mull		3058	1672	1635	32
2-Hydroxy	Mull	3509		1673		30
	Mull	3344s		1667s		29
1-Hydroxy-2-methyl	Mull			1696s	1634s	29
1-Hydroxy-2,4-dichloro	C_6Cl_6		2857			33
2-Hydroxy-3-methyl	Mull	3311s		1658s		29
2-Hydroxy-1-nitro	C_6Cl_6	3497sh				31
2-Hydroxy-3-nitro	C_6Cl_6		3185br			31
1,2-Dihydroxy	Mull	3380		1660	1636	30
	Mull	3367m		1658s	1634s	29
	C_6Cl_6	3320s	2967br			31
1,2-Dihydroxy-3-nitro	C_6Cl_6			1680	1640	31
1,3-Dihydroxy	Mull	3380		1675	1635	30
	Mull	3413s		1675m	1637s	29
	C_6Cl_6	3571s	3077br			31
1,4-Dihydroxy	Mull			1627		30
	Mull			1626		29
	Mull		2924	1626		32
1,5-Dihydroxy	Mull			1639		30
	Mull			1634		29
	Mull		2967	1636		32
1,8-Dihydroxy	Mull			1675	1622	30
	Mull			1678s	1621s	29
	C_6Cl_6		3101br			31
1,8-Dihydroxy-3-methyl	Mull			1675s	1621s	29
2,3-Dihydroxy	Mull	3472s	3268s	1675s		29
2,6-Dihydroxy	Mull	3300s		1656s		29
2,7-Dihydroxy	Mull		3195m	1653s		29
1,2,3-Trihydroxy	Mull	3378m		1650s	1626s	29
1,2,4-Trihydroxy	Mull	3226m			1621s	29
1,2,5-Trihydroxy	Mull	3333m			1626s	29
1,2,6-Trihydroxy	Mull	3356s	3279w	1650s		29
1,2,7-Trihydroxy	Mull	3390w	3310s	1647s		29
1,2,8-Trihydroxy	Mull	3378m		1661m	1621s	29
1,3,4-Trihydroxy	Mull	3330			1632	30
1,4,8-Trihydroxy	Mull				1605s	29
1,4,5,8-Tetrahydroxy	Mull				*ca.* 1595	30
		3333			1590	32

nones for any rigorous comparison. However, the noticably greater value of log K_1 for the kojic and chlorokojic acid derivatives is interesting.

Infrared spectra

It was hoped that the infrared spectra as well as the dissociation constants of the hydroxyquinones would furnish information about the relative stability of hydrogen bonds in the compounds under study. This difference was expected to be manifest in the magnitude of the shifts of the hydroxyl and carbonyl absorptions from their normal positions. This expectation was not fully realized. Although the shifts seem to be of the relative magnitudes expected, other structural factors appear to have a much greater effect. The spectra of the anthraquinones have been rather thoroughly studied and data on pertinent compounds are assembled in Table IV. Certain generalizations have been drawn from these and other data[29].

1. Those compounds containing α, β-hydroxyl give a sharp band 3600–3150 cm^{-1}. 2. Those compounds containing an α-hydroxyl show a broad band at lower frequencies. Oftentimes this is completely obscured. 3. Those compounds having one α-hydroxyl show two carbonyl bands: one at 1675–1647 cm^{-1} and a stronger one between 1637 and 1621 cm^{-1}. 4. Those compounds having an α-hydroxyl at each carbonyl show one carbonyl band at 1645–1608 cm^{-1}. 5. Those compounds with two α-hydroxyls in the 1 and 8 positions show two carbonyl bands: one at 1678–1661 cm^{-1} and a stronger one at 1626–1616 cm^{-1}. 6. The average $C = C$ stretching frequency is greater than 1757 cm^{-1} in the 1,4- or 1,5-dihydroxy compounds and less than 1575 cm^{-1} in 1,4,5-trihydroxy. For the 1,4,5,8-tetrahydroxy compound, the $C = O$ and $C = C$ stretching frequencies are indistinguishable.

These observations on anthraquinone derivatives show clearly the effect of hydrogen chelation (hydrogen-bonding) in shifting the positions of the hydroxyl and carbonyl frequencies and in broadening the absorption bands, especially that for hydroxyl. The anthrones show the frequencies characteristic of a doubly hydrogen-bonded carbonyl and the hydrogen-bonded hydroxyl with the addition of the non-hydrogen-bonded hydroxyl in the case of 1,8,10-trihydroxyanthrone.

The absorption of the free carbonyl in juglone, which corresponds structurally to the anthraquinones, is in the same region as that of the anthraquinones (1672 cm^{-1}) although the hydrogen-bonded carbonyl is not shifted to as great an extent (1647 cm^{-1}) as in the anthraquinones. The absorption of the hydroxyl resembles that of the α-hydroxyanthraquinones. However, lawsone differs from juglone in that absorption due to the free carbonyl and the hydrogen bonded hydroxyl appear at higher frequencies (1681 cm^{-1} and 3175 cm^{-1}, respectively) whereas the absorption due to the hydrogen-bonded carbonyl in lawsone is at a lower frequency than in juglone. The expected difference due to the different strengths of the hydrogen bond in the two instances is not found. The marked influence of substitution in the 3-position of lawsone on the position of the free carbonyl absorption is surprising. The hydroxyl absorption of kojic and chlorokojic acids and 3-hydroxyflavone resembles that of lawsone whereas the carbonyl absorption resembles that of the 3-substituted lawsones. Also the absorption due to $C = C$ in these compounds is very close to that due to $C = O$.

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SUMMARY

Formation constants of various metal derivatives of four hydroxynaphthoquinones, two hydroxyanthraquinones, and three hydroxy-γ-pyrones have been measured in 75 vol% dioxane. The acidity of those of the above compounds which form 5-membered hydrogen chelate rings is greater than that of those which form similar 6-membered rings. The shifts of the hydroxy and carbonyl frequencies in the infrared spectra of these compounds are influenced by too many factors to be useful in distinguishing between the 5- and 6-membered rings.

RÉSUMÉ

Lors d'une étude sur les composés de coordination, les auteurs ont déterminé les constantes de formation de quelques dérivés métalliques d'hydroxyquinones (4 hydroxynaphthoquinones, 2 hydroxyanthraquinones et 3 hydroxy-γ-pyrones).

ZUSAMMENFASSUNG

Es werden die Bildungskonstanten verschiedener Metallderivate von vier Hydroxynaphtochinonen, zwei Hydroxyanthrachinonen und drei Hydroxy-γ-pyronen angegeben.

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PYROMELLITEIN INDICATORS

III. LAKE FORMATION

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The author has previously[1] discussed the pyromellitein indicators, prepared by condensing pyromellitic acid dianhydride (PMDA) with phenols by methods used for the preparation of phenolphthalein. Some of these indicators have been found to form colored lakes with metallic hydroxides.

Laboratory procedure

All of the experiments were run in semi-micro test tubes, by taking 1 drop samples of the ions, as made up for qualitative analysis, diluting to 1 ml, adding 1 drop of indicator, and observing any reaction which took place (Table II). If no precipitate formed, the solution was made basic with either 3 *N* NH_4OH (Table III) or 3 *N* NaOH (Table IV).

TABLE I

Indicator designation	*Phenol condensed*	*No. of phenols condensed per mole of PMDA*
A	Phenol	2
B	Phenol	4
C	Oxine	2
D	Oxine	4
E	Resorcinol	2
F	Resorcinol	4
G	Phenol Resorcinol	2 2
H	Brominated product of F	

TABLE II

COLORS OF PRECIPITATES FORMED IN WEAKLY ACID SOLUTION

Indicator	*Hg_2^{+2}*	*Pb^{+2}*	*Sb^{+3}*	*Sn^{+4}*	*Fe^{+3}*	*Fe^{+2}*	*Cr^{+3}*
D	—	—	—	—	—	Green	—
E	Yel.	Yel.	—	—	—	—	—
F	—	—	Yel.	—	(Red Br.)	—	—
G	Brn.	—	—	—	—	—	—
H	Red	—	Red	Orange	Red	—	Red

Note : Precipitates with Sb^{+3} and Sn^{+4} form on dilution. White precipitates formed by dilution are not listed. Pb^{+2} precipitates *very* small (haze).

TABLE III

COLORS OF LAKES FORMED IN SOLUTION BASIC WITH NH_3

Indicator	Hg^{+2}	Bi^{+3}	Sb^{+2}	Sn^{+2}	Fe^{+3}	Al^{+3}	Cr^{+3}
D	—	—	—	—	$Fe(OH)_3$	Grn.	$Cr(OH)_3$
E	Pink	Yel.	—	—	,,	—	,,
F	(Red Br.)	(Red Br.)	Yel.	Orange	,,	(Red Br.)	,,
G	Pink	Pink	—	—	,,	—	,,
H	Red	Bright Red	Red	Pink	,,	Red	Red

TABLE III (continued)

Indicator	Co^{+2}	Ni^{+2}	Mn^{+2}	Fe^{+2}	Mg^{+2}	Be^{+2}	Ce^{+3}
D	Grn.	—	Brn.[a]	(Gray Grn.)	—	—	Grn.
E	Gray	—	(Dk. Brn.)[b]	Grn.	Pink	—	Lt. Brn.
F	Orange	—	(Red Brn.)[b]	Brn.	Orange	Orange	Red Brn.
G	Gray	—	(Dk. Brn)[b]	Grn.	Pink		Lt. Brn.
H	Red	Red	Red[b]	Dk. Red	Bright Red	—	Deep Red

[a] Possibly $MnO(OH)_2$.
[b] Indicator removed from solution; fluorescence destroyed.

TABLE IV

COLORS OF LAKES FORMED IN THE PRESENCE OF NaOH[a]

Indicator	Hg^{+2}	Bi^{+3}	Cu^{+2}	Mg^{+2}
E	Pink	Yel.	Grn.[b]	Pink
F	(Red Brn.)	(Red Brn.)	Yel. Grn.[b]	Orange
G	Pink	Pink	Grn.[b]	Pink
H	Red	Red	Purple	Bright Red

[a] Slight excesses of NaOH removed indicator from colored lakes in most cases. Those listed in Table III are those which seemed to be most stable.
[b] Colors of the copper lakes may be due to a suspension of colloidal $Cu(OH)_2$ suspended in the indicators.

The ions tested were grouped according to the classical scheme of analysis, as follows:

Ag^+, Hg_2^{+2}, Pb^{+2}, Hg^{+2}, Bi^{+3}, Cu^{+2}, Cd^{+2}, As^{+3}, Sb^{+3}, Sn^{+4}, Sn^{+2}, Fe^{+3}, Al^{+3}, Cr^{+3}, Ce^{+3}, Fe^{+2}, Ni^{+2}, Co^{+2}, Mn^{+2}, Zn^{+2}, Be^{+2}, Ba^{+2}, Sr^{+2}, Ca^{+2}, Mg^{+2}

Of these ions some gave colors of such intensity that more experiments were run to determine the lower limits at which lakes were detected. These experiments were carried out by preparing solutions which were 200 p.p.m. with regard to the ion being used and dilution of this solution. Results are shown in Table V. If the lower limit is greater than 200 p.p.m., a line is shown in this table.

All indicators were prepared in concentrations of 0.100 g per 100 ml of solution, a drop of 0.1 *N* NaOH being added to aid solution. For purposes of tabulation, these

TABLE V

LOWEST ION CONCENTRATIONS (p.p.m.) GIVING DETECTABLE LAKES[a]

Indicator	*Mg^{+2}*	*Ni^{+2}*	*Bi^{+3}*	*Sb^{+3}*	*Ce^{+3}*	*Cr^{+3}*
E	50	50	—	—	100	—
F	12.5	25	—	—	100	200
G	12.5	50	—	—	100	—
H	1.5	25	100	100	50	100

[a] Lakes formed by making 1 ml of solution and 1 drop of indicator just basic with 1 *N* NH_3.

indicators will be designated by letters (Table I), according to the type of phenol and the number of phenolic groups condensed.

DISCUSSION

Indicators A, B, and C gave white precipitates or very weakly colored precipitates which have therefore been omitted in the tabulations. The very low indicator concentrations (amounting to the neighborhood of 0.1 millimole per l in the final mixture) producing intense colors seem to show the possibility of use of some of these in micro analysis. This is particularly true of the one designated as H, the brominated tetraresorcinol pyromellitein. The mercurous mercury compounds are destroyed by basic solutions, but might be used to determine mercurous mercury in the presence of silver and lead in solutions weakly acidified with dilute HNO_3. For qualitative testing, the use of indicator H for bismuth and for magnesium seems to have the greatest potential, since the indicator will show up the "water white" $Bi(OH)_3$, and since it gives an excellent stable color with magnesium but not with the other group IV metals.

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SUMMARY

The pyromellitein indicators previously described have been used to form lakes with a large number of ions. The brominated tetraresorcinol pyromellitein in particular forms brightly colored lakes with magnesium hydroxide which should be of interest in detecting this ion in very low concentrations.

RÉSUMÉ

Les indicateurs de la classe des pyromellitéines, décrits dans un article précédent, peuvent réagir avec un certain nombre de cations, en formant des laques. Un nouveau réactif très sensible est proposé pour l'identification du magnésium.

ZUSAMMENFASSUNG

Die in einer früheren Arbeit beschriebenen Pyromellitein Indikatoren bilden Farblacke mit einer grossen Anzahl von Jonen. Das bromierte Tetraresorcin-pyromellitein bildet mit Magnesiumhydroxyd einen stark gefärbten Lack, der als Nachweis für Magnesium dienen kann.

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HEMATOXYLIN AS INDICATOR IN THE CHELATOMETRIC TITRATION OF METALS

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Hematoxylin is obtained from Campeche wood and has been used as an indicator in the titration of aluminum with EDTA[1] and as a colorimetric reagent for aluminum[2] and other elements[3,4]. Hematoxylin itself does not give color reactions with metals; these are due to hematein, its oxidation product. In the present work the possibilities of using hematoxylin as an indicator in the titration of metals other than aluminum with EDTA are studied.

Reagents and apparatus

EDTA. A 0.025 *M* solution was prepared from 9.3 g of disodium ethylenediaminetetraacetate dihydrate diluted to one liter with water. It was standardized against zinc metal dissolved in dilute nitric acid, with Eriochrome Black T as indicator[5].

Standard bismuth solution. A 0.025 *M* solution was prepared from metallic bismuth (A.R.) by dissolution in nitric acid and dilution to one liter with 1 + 99 nitric acid. It was standardized with EDTA using Pyrocatechol Violet as indicator[6].

Standard zirconium solution. A 0.025 *M* solution was prepared from zirconyl chloride (A.R.) dissolved in hydrochloric acid (1 + 9). It was standardized with EDTA using Eriochrome Cyanine R as indicator[7].

Indicator. 0.2 g of hematoxylin (Merck, Germany) ($C_{16}H_{14}O_6 \cdot H_2O$) was dissolved in 1 ml of ammonia and 20 ml of distilled water; after 10 minutes it was acidified with 5 ml of acetic acid. This solution was stable for at least 3 months.

All the other reagents used were of A.R. quality.

The titrations were made with a Metrohm Piston Burette, Model E 274, 20-ml capacity.

The pH was measured with a Beckman Potentiometer, model Zeromatic, with glass and calomel electrodes.

Experimental procedure

A known volume of the standard metallic solution was transferred to a 250-ml beaker and diluted to about 150 ml with distilled water; the pH was adjusted with one or more of the following solutions: 1 + 99 nitric acid, 1 + 9 hydrochloric acid or 25% ammonium acetate. Ten drops of the indicator were added and the solution was titrated with EDTA, the burette tip being immersed and with the aid of magnetic stirring.

When necessary, the final pH was measured with the potentiometer.

Titration of bismuth

Excellent results were obtained for the determination of bismuth. The titration was successful at pH 1 to 2. If the pH was greater than 2, precipitation occurred and there was no color change on addition of EDTA. If the pH was less than 1 an orange-red color appeared, which made the end-point color change poor.

The color change of the indicator was from red to yellow and was very sharp and clear. Some typical results are given in Table I.

TABLE I

Bismuth present (mg)	*Bismuth found (mg)*	*Difference (mg)*
5.04	5.09	+0.05
10.08	10.14	+0.06
35.29	35.29	0.00
60.49	60.60	+0.11
100.82	100.83	+0.01

The titration was selective: lead, cadmium, zinc, aluminum, nickel, cobalt, calcium, barium, magnesium, silver and the alkali metals did not interfere. Small quantities of copper (about 30 mg) could be tolerated. Anions that precipitate bismuth, *e.g.* chloride, fluoride and phosphate, or that complex bismuth, *e.g.* tartrate and citrate, interfered. Reducing agents such as sulphite, bleached the indicator.

Iron(III) interfered, but its interference could be eliminated by the procedure described below.

Titration of bismuth in the presence of iron(III)

A few drops of 5% potassium thiocyanate were added to the acidic solution (pH 1–2) followed by a freshly prepared solution of 10% ascorbic acid, until discoloration was complete and 3 or 4 drops were present in excess. Then the indicator was added and the solution titrated immediately with EDTA.

TABLE II

TITRATION OF BISMUTH IN THE PRESENCE OF OTHER SUBSTANCES

(bismuth present: 50.41 mg)

Substance	*Amount*	*ml of EDTA required*	*Difference (ml)*
Na_2SO_4	1.0 g	9.42	+0.02
KNO_3	1.0 g	9.43	+0.03
NH_4NO_3	1.0 g	9.42	+0.02
$MgSO_4 \cdot 7\ H_2O$	0.2 g	9.40	0.00
$Ba(NO_3)_2$	0.2 g	9.40	0.00
$AgNO_3$	0.2 g	9.44	+0.04
$Co(NO_3)_2$	44.1 mg Co	9.44	+0.04
$NiSO_4$	44.1 mg Ni	9.46	+0.06
$Cu(NO_3)_2$	6.4 mg Cu	9.46	+0.06
$Cu(NO_3)_2$	31.8 mg Cu	9.45	+0.05
$Al(NO_3)_3$	27.0 mg Al	9.44	+0.04
$Al(NO_3)_3$	54.0 mg Al	9.40	0.00
$Ca(NO_3)_2$	0.10 g Ca	9.38	—0.02
$Zn(NO_3)_2$	0.10 g Zn	9.40	0.00
$Cd(NO_3)_2$	0.10 g Cd	9.40	0.00
$Pb(NO_3)_2$	0.10 g Pb	9.44	+0.04
$Fe(NO_3)_3$	30 mg Fe	9.44[a]	+0.04
$Fe(NO_3)_3$	50 mg Fe	9.43[a]	+0.03
$Fe(NO_3)_3$	100 mg Fe	9.36[a]	—0.04
$Fe(NO_3)_3$	100 mg Fe	9.45[a]	+0.05

[a] Fe(III) previously reduced with ascorbic acid.

The reverse titration of the EDTA with a solution of bismuth was possible. In this case the pH could be greater. This offers various possibilities for the determination of other metals by adding an excess of EDTA and back-titrating with a standard solution of bismuth.

TABLE III

TITRATION OF EDTA WITH A STANDARD SOLUTION OF BISMUTH

ml of 0.025 M Bi^{+3} solution		*Difference*	*pH at the end-point*
Calculated	*Found*		
10.64	10.70	+0.06	1.5
10.64	10.69	+0.05	2.3
10.64	10.71	+0.07	4.8

Titration of zirconium

In this case the color changed from red to pinkish-yellow but this was not very sharp; a very sharp color change was obtained by screening with 2 or 3 drops of 1% methylene blue. The color change was then from purple to greyish-green. The optimum pH was between 1.0 and 1.5.

TABLE IV

Zirconium present (mg)	*Zirconium found (mg)*	*Difference (mg)*
19.64	19.66	+0.02
19.64	19.68	+0.04
22.80	22.78	—0.02
22.80	22.82	+0.02
22.98	22.96	—0.02
22.98	22.92	—0.06
27.36	27.33	—0.03
34.20	34.15	—0.05
47.88	47.73	—0.15

TABLE V

TITRATION OF ZIRCONIUM IN THE PRESENCE OF OTHER SUBSTANCES
(zirconium present: 19.64 mg)

Substance	*Amount*	*ml of EDTA*	*Difference (ml)*
NaCl	1.0 g	8.81	—0.05
KBr	1.0 g	8.85	—0.01
KNO_3	1.0 g	8.83	—0.03
$MgCl_2 \cdot 6\ H_2O$	0.2 g	8.83	—0.03
$Al(NO_3)_3$	27 mg Al	8.89	+0.03
$Al(NO_3)_3$	54 mg Al	8.90	+0.04
$Ca(NO_3)_2$	100 mg Ca	8.79	—0.07
$Cd(NO_3)_2$	100 mg Cd	8.84	—0.02
$Co(NO_3)_2$	100 mg Co	8.83	—0.03
$Pb(NO_3)_2$	100 mg Pb	8.84	—0.02
$Zn(NO_3)_2$	100 mg Zn	8.86	0.00

The titration was less selective than that of bismuth. Copper was partially titrated even in small quantities. Iron, even in the presence of ascorbic acid, caused a poor color change. Anions that precipitate or complex zirconium, *e.g.* phosphates, fluoride or tartrate, interfered.

The reverse titration was not satisfactory because the color change was not sharp and it was easy to overshoot the equivalence point.

Titration of other metals

Lead reacted with hematoxylin at about pH 6 producing a blue color which changed to pink on addition of EDTA, but the results obtained were not satisfactory.

Copper reacted with hematoxylin to give a purple color; the color change on addition of EDTA depended on the pH and there was always a series of transition colors up to yellow (or green, for higher concentrations of copper). The results obtained were bad.

Several other metals, *e.g.* cadmium, cobalt, nickel, gave a violet or purple color with hematoxylin in alkaline media. With excess of EDTA this color changed to red but the contrast between the two colors was very poor.

SUMMARY

Hematoxylin is suggested as an indicator in the titration of several metals with EDTA. Bismuth and zirconium were readily determined in acidic medium. Several other metals also gave color reactions, but the color changes on addition of EDTA were not sharp.

RÉSUMÉ

L'auteur a étudié le comportement de l'hématoxiline, comme indicateur, lors du dosage de divers métaux, au moyen de l'EDTA. Les résultats obtenus lors du titrage du bismuth et du zirconium sont satisfaisants.

ZUSAMMENFASSUNG

Es wurde Hämatoxylin auf seine Eignung als Indikator bei der Titration von Metallen mit EDTA untersucht. Gute Werte werden bei der Titration von Bismut und Zirkonium erhalten.

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CHELATING AGENTS CONTAINING TWO 8-QUINOLINOL FUNCTIONS

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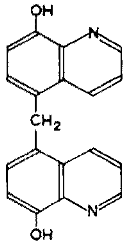
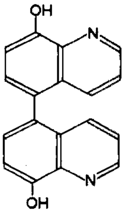
It has been stated that 8,8'-dihydroxy-5,5'-biquinolylmethane (I) and several closely related compounds are similar to 8-quinolinol in reactions with metals but are more sensitive[1]. Except for these observations there appears to be no other published information on the effects of more than one 8-quinolinol function per molecule on chelating properties.



I



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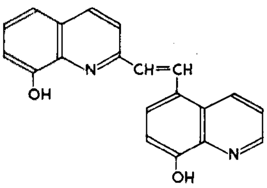

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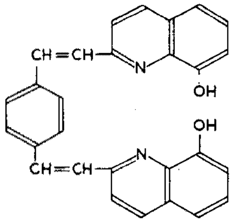

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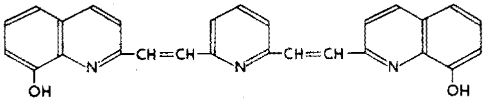

V

Five such reagents, three of them new compounds, were prepared for this study. Reaction of 8-quinolinol with formaldehyde in cold concentrated sulfuric acid[2] readily yielded I. Oxidation of 8-quinolinol with ferric sulfate[3] gave 8,8'-dihydroxy-5,5'-biquinolyl (II) but in very poor yields. Three new compounds were prepared by condensing 8-hydroxyquinaldine with 5-formyl-8-quinolinol[4], terephthaldialdehyde, and pyridine-2,6-dialdehyde respectively to give III, IV, and V. Of these III is the only one subjected to any investigation beyond the preparation at the present time. Both IV and V are extraordinarily insoluble in most solvents.

An attempt was made to evaluate the relative acid–base properties of I, II, and III by a spectrophotometric measurement of absorbancy as a function of pH (Fig. 1). The poor solubility of these reagents in water forced the comparison to be performed in 20% EtOH and even in this solvent at a concentration of only 4 mg per liter III precipitated at neutral pH values and thus was not investigated in the neutral to basic range.

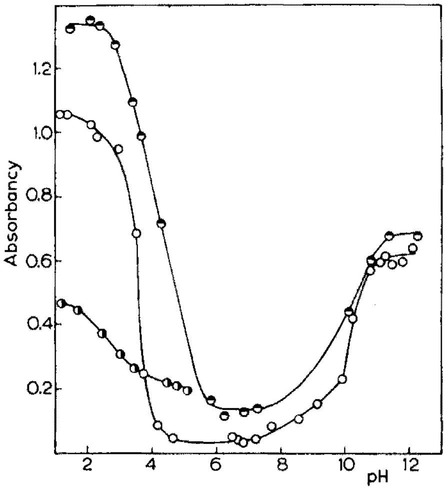

Fig. 1. Absorbancy *versus* pH curves: ◓ I at 258 mμ; ○ II at 258 mμ; ◑ III at 263 mμ.

Four possible ionization stages may be formulated for the dihydrochlorides of these compounds, and it was therefore rather surprising that only three spectrophotometrically distinct forms, representing only two ionization stages, were experimentally detected. In view of the nearly identical acid properties of the two N^+—H functions and their wide separation in the molecule it seems plausible to assume that pK_1 and pK_2 overlap to such an extent that they are not individually detectible. Thus the mid-point of the nearly vertical portions of the curves near pH 3–4 may be regarded as the average of pK_1 and pK_2. A similar argument may be applied to pK_3 and pK_4 which represent the ionizations of the two phenolic hydrogens. It is obvious that the $pK_{1av.}$ for the N^+—H groups is subject to much greater variation than the $pK_{2av.}$ for the phenolic groups (Table I); since the N^+—H dissociations are so much stronger, it is reasonable that they should exhibit greater vulnerability to structural factors. In any case, the presence of two 8-quinolinol functions per molecule gives a noticeable weakening of the base strength of the nitrogens but little change in the acidity of the phenolic groups.

TABLE I

APPARENT IONIZATION CONSTANTS OF 8-QUINOLINOLS IN 20% ALCOHOL

Compound	*Apparent $pK_{1(av.)}$*	*Apparent $pK_{2(av.)}$*
I	4.2	10.0
II	3.6	10.1
III	*ca.* 3.0[a]	—[a]
8-Quinolinol	4.9	10.3

[a] Accurate results for the first ionization of III were not obtainable because of precipitation, and for the same reason no effort was made to estimate the phenolic ionization.

Available comparative data for the ionization constants of other dihydroxy aromatic compounds are limited in number, but appear to give ratios of K_1 to K_2 generally much less than 100[5-7], except for hydroxyls ortho to each other or otherwise affected by specific steric interactions. Indeed for special cases, the ratio of K_1 to K_2 has been found to be less than the well-known statistical value of 4, and most remarkably, even less than unity[8].

TABLE II

ABSORPTION MAXIMA OF BIS-8-QUINOLINOLS IN 0.1 *N* ALCOHOLIC HYDROCHLORIC ACID

Compound			
I	257 (4.86)	311 (3.34)	380 (3.64)
II	257 (4.17)	311 (3.42), 320^{s}(3.39)	380 (3.64)
III	264 (4.65)	320 (4.23)	400–15 (4.45)
IV	264 (4.32)	325 (4.27)	420 (4.77)
V	300 (4.65)	360 (4.50)	386 (4.55)

Absorption maxima of all compounds in approximately 0.1 *N* alcoholic hydrochloric acid (Table II) were similar to the spectrum of 8-quinolinol in this solvent except for the shifts to longer wavelengths and higher absorbancies that might be expected from the extension of the conjugated system or the approximate doubling of the molecular weight.

A few chelates of compounds I, II and III were prepared and analyzed to establish whether both functions in these molecules can participate in chelation at once. Compound I formed chelates with both ferric and aluminum ions containing a 3:1 mole ratio of reagent to metal; thus, only one chelating function per molecule is used. Free hydroxyl groups could be demonstrated both by acetylation with acetic anhydride and pyridine and by infrared spectra. Similarly copper and zinc formed 2:1 compounds. Although II gave a 3:1 ratio of reagent to metal with aluminum, a 1:1 composition was noted with copper, nickel and zinc, indicating that both chelating functions in the molecule are used. A possible explanation for this effect might be formation of an oligomer with the metal acting as the connecting link between units, another possibility is simply incomplete chelation, the remaining valence bonds of the metal being used in reaction with hydroxyl or other ions that tend to produce an insoluble product. III forms a red-brown 2:1 chelate with cupric ion, and apparently only one chelating function per molecule is utilized.

In qualitative tests both I and II formed chelate compounds quite similar to those of 8-quinolinol in color and general pH response, and III resembled 8-hydroxyquinaldine in these respects.

EXPERIMENTAL

Preparation of compounds

The oxidation of 8-quinolinol with ferric sulfate to yield 8,8′-dihydroxy-5,5′-biquinolyl[3] was modified to give a yield of about 25%. Ferric sulfate (40 g) was added to 10 g 8-quinolinol in 2700 ml water with stirring, and the mixture heated 15–30 min. Then a solution of 15 g NaOH in 300 ml water was added at a rate to maintain the pH between 5 and 7 for 8–9 h at the boiling point. After standing over night the mixture was filtered and the black precipitate was warmed with a little concentrated hydrochloric acid until it became orange. After filtration the orange solid was dissolved in the minimum amount of water and concentrated hydrochloric acid added to precipitate the bright yellow dihydrochloride dihydrate. This could be washed with acetone, dissolved in water, and the solution neutralized to precipitate the white free base, decomposing above 310°. Bromination of the compound with standard bromate–bromide in an acid solution consumed four equivalents of bromine, indicating dibromination, probably in the 7,7′ positions. This bromination was quantitative and could be used to analyze the chelate compounds. Infrared spectra of the hydrochloride in KBr pellet form showed principal maxima at 3.03, 3.48, 6.14, 6.27, 6.43, 6.81, 7.21, 7.68, 8.35, 8.64, 9.28, 11.01, 11.75, 12.35 and 12.92 μ; the free base had principal bands at 2.99, 6.14, 6.30, 6.63, 6.80, 7.05, 7.15, 7.29, 7.82, 8.03, 8.31, 8.42, 8.67, 8.98, 9.64, 11.03, 11.86, 12.08, 12.28, 12.63 and 14.00 μ.

The preparation of I was readily accomplished by the method of SCHÜLLER[2]. The free base showed infrared maxima at 3.0, 6.15, 6.30, 6.64, 6.76, 7.03, 7.29, 7.83, 8.13, 8.36, 8.66, 9.30, 9.42, 10.04, 10.58, 11.01, 11.96, 12.10, 12.80 and 14.31 μ.

Compound III was obtained by heating 0.02 mole (3.2 g) 8-hydroxyquinaldine with 0.02 mole 5-formyl-8-quinolinol[4] in 10 ml acetic anhydride for 6 h. The resulting solution was poured into water, filtered and the precipitate saponified by heating for an hour with 20% sodium hydroxide solution. After neutralization of the solution with hydrochloric acid the precipitated product was filtered and recrystallized from alcohol containing 10% hydrochloric acid, yielding the dihydrochloride as orange crystals, melting at 233°. Principal infrared absorption bands for the dihydrochloride were observed at 3.6 (broad), 6.25, 6.43, 7.35, 7.60, 8.09, 8.62, 9.20, 11.45, 11.80, 12.19, 12.87 and 13.12 μ. Calcd. for $C_{20}H_{14}N_2O_2 \cdot 2HCl$: N, 7.20; found: N, 7.13.

A similar condensation of 8-hydroxyquinaldine with terephthaldialdehyde gave IV, as the dihydrochloride. Neutralization gave the free base m.p. 215°. Principal infrared bands were observed at 3.7 (broad), 6.24, 6.51, 6.62, 6.80, 7.00, 7.04, 7.20, 7.55, 7.70, 8.00, 8.27, 8.63, 9.19, 10.38, 11.52, 12.00, 13.40, and 14.72 μ. Calcd. for $C_{28}H_{20}N_2O_2 \cdot 2HCl$: N, 5.74; found: N, 5.63.

A similar reaction of two moles of 8-hydroxyquinaldine with 2,6-pyridine dialdehyde gave V as the trihydrochloride, m.p. 232°. Calcd. for $C_{27}H_{19}N_3O_2 \cdot 3HCl$: N, 8.00; found: N, 8.24.

Ionization constants and spectra

Stock solutions of I, II, and III containing 7.56, 4.90 and 4.30 mg per liter respectively in dilute hydrochloric acid were prepared. Portions (5.00 ml) of each were pipetted into 25-ml flasks, 5 ml ethanol added, and the solutions diluted with hydrochloric acid or dilute sodium hydroxide to 25.00 ml. An ionic strength of approximately 0.1 was provided by the addition of the necessary amount of potassium chloride to each before dilution. The apparent pH of the solutions was measured with a Beckman Model G pH meter calibrated against aqueous buffers. The spectra were recorded from 356–220 mμ with a Beckman DK-2 Spectrophotometer; a few of the solutions were also measured throughout the visible spectrum as well.

Separate alcoholic acid solutions were employed to obtain the spectra of Table II.

Infrared spectra were determined in KBr pellets on a Baird AB-2 Spectrophotometer with NaCl prism from 2–16 μ.

Chelate compounds

Since the formulas of the metal chelates were the principal point of interest, some preparations were conducted with both 2:1 and 1:1 ratios of reagent to metal ion when the ion was divalent, and with both 3:1 and 3:2 ratios for the trivalent ions. With I and ferric ion only a black 3:1 product was isolated and the same ratio was found for the yellow aluminum chelate; the presence of free hydroxyl groups in the latter was shown both by acetylation with acetic anhydride in pyridine and by absorption in the 3.0-μ region of the infrared spectrum. With the divalent ions copper and zinc, I formed only the 2:1 chelates. Reaction of III with copper also gave a red-brown 2:1 product. Reaction of II with aluminum gave the 3:1 product expected, but with copper, nickel and zinc this reagent yielded chelates analyzing for the 1:1 mole ratio.

All products were precipitated under the conditions normally employed for the preparation of the corresponding chelates of 8-quinolinol[9], and the dried samples were analyzed by ignition of weighed portions to the metal oxides. With II some analyses were also performed by bromination.

ACKNOWLEDGEMENT

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SUMMARY

Ionization constants, spectra and some metal chelate formulas of several chelating agents containing two 8-quinolinol functions per molecule have been investigated. In general, only one of the chelating functions appears to be used in the formation of insoluble metal chelates. However, 8,8′-dihydroxy-5,5′-biquinolyl may show exceptions to this rule with some divalent ions.

RÉSUMÉ

Les auteurs ont effectué une étude sur plusieurs agents de chélation, renfermant deux radicaux d'hydroxy-8-quinoléine par molécule. Ils ont examiné les constantes d'ionisation, les spectres et les formules de quelques chélates métalliques.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über chelatbildende Verbindungen, die zwei 8-Oxychinolingruppen pro Molekül enthalten. Ionisationskonstanten, Spektren und Strukturen einiger Metallchelate wurden bestimmt.

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DETERMINATION OF SMALL AMOUNTS OF CHLORIDE BY VOLHARD TITRATION*

EVALUATION OF OPERATOR DETERMINATE END-POINT ERROR

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The applicability of the Volhard titration to the determination of small amounts of chloride[1] in solid-rocket oxidants (ammonium nitrate, ammonium perchlorate, and potassium perchlorate) has not been ascertained prior to this time. In the course of determining the optimum experimental parameters of the Volhard titration, the recognition and empirical evaluation of the operator determinate end-point error was required. The determination and use of this value, or use of a procedure which eliminates the need of its evaluation, is required when one titrates in solutions of high ionic strength, and is applicable to all analyses involving back-titrations and visual end-point detection.

The original Volhard[2] titration of silver has been utilized for the determination of chloride in acid solution. An excess of silver ion is added (1), and the excess is titrated with thiocyanate ion (2), in the presence of ferric ions, which serve as an internal

$$Ag^+ + Cl^- \rightarrow AgCl_{(s)} \tag{1}$$

$$Ag^+ + CNS^- \rightarrow AgCNS_{(s)} \tag{2}$$

indicator through formation of the familiar dark red coloration of the iron(III) monothiocyanate ion. In order to prevent metathesis of the silver chloride to silver thiocyanate (3) which occurs in the vicinity of the end-point[3,4], nitrobenzene is added

$$AgCl + CNS^- \rightarrow AgCNS + Cl^- \tag{3}$$

as coagulating agent[5]. After the equivalence point has been reached, a slight excess of thiocyanate ion is required to develop sufficient ferric thiocyanate ion to permit visual perception (4):

$$Fe^{+3} + CNS^- \rightarrow Fe\,CNS^{+2} \tag{4}$$

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* This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NASw-6, sponsored by the National Aeronautics and Space Administration.

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The absolute magnitude of the concentration of $FeCNS^{+2}$ at the end-point will depend upon the sensitivity of the operator's eye and the ionic equilibria established by the conditions of the titration. The error introduced because of these parameters is determinate and varies between operators, henceforth this error shall be called the operator determinate end-point error. Because thermodynamic equilibria data is available, or can be estimated, for all the ionic species involved in the titration, it is possible to calculate the total determinate error incurred at the end-point of the Volhard titration. However, in the estimation of small quantities of chloride with the aid of the Volhard titration, the operator determinate end-point error is large with respect to theoretical errors resulting from over titration at the end-point. Consequently, an expedient to alleviate the calculation of the thermodynamic concentration of species in the solution is to empirically evaluate the operator determinate end-point error and appraise the merits of the titration after suitable correction for this error. The empirical evaluation is a superior approach because of limitations of adequate mathematical expressions for the diverse ion effects at the high ionic strengths encountered. A rigorous discussion of the operator determinate end-point error, $F[(FeCNS^{+2})_t, \mu]$, the free chloride in solution, Cl^-, and their dependence upon the visual perception of the operator, $(FeCNS^{+2})_t$, and the ionic strength, μ, is given below.

Significance of the operator determinate end-point error

Equations 1, 2, and 4 may be written in terms of the thermodynamic relationships (5), (6) and (7).

$$(Ag^+)\,(Cl^-) = \frac{K_{AgCl}}{\gamma_{Ag^+}\,\gamma_{Cl^-}} \tag{5}$$

$$(Ag^+)\,(CNS^-) = \frac{K_{AgCNS}}{\gamma_{Ag^+}\,\gamma_{CNS^-}} \tag{6}$$

$$\frac{(FeCNS^{+2})}{(Fe^{+3})\,(CNS^-)} = K_f\,\frac{\gamma_{Fe^{+3}}\,\gamma_{CNS^-}}{\gamma_{FeCNS^{+2}}} \tag{7}$$

where K and γ are activity products and activity coefficients of the product or species denoted by the subscript; K_f is the activity formation constant of the ferric monothiocyanate ion.

The excess of ferric ion is sufficient that the analytical concentration and equilibrium concentration are approximately equal; *i.e.*,

$$(Fe^{+3})_0 = Fe^{+3} + FeCNS^{+2} \simeq Fe^{+3} \tag{8}$$

when this condition is satisfied, eqn. (7) is equivalent to

$$\frac{(FeCNS^{+2})_t}{(Fe^{+3})_0\,(CNS^-)} = K_f\,\frac{\gamma_{Fe^{+3}}\,\gamma_{CNS^-}}{\gamma_{FeCNS^{+2}}} \tag{9}$$

where $(FeCNS^{+2})_t$ is the concentration of ferric monothiocyanate ion required to be visually perceptible by the operator, and the ions with subscript o represent the analytical concentration of such ions. At the end-point of the titration, the total number of millimoles of chloride, silver, and thiocyanate present in the mixture are given by eqns. (10), (11) and (12):

$$(\mathrm{Cl^-})_0 = (\mathrm{Cl^-}) + \mathrm{AgCl}_{(s)} \tag{10}$$

$$(\mathrm{Ag^+})_0 = (\mathrm{Ag^+}) + \mathrm{AgCl}_{(s)} + \mathrm{AgCNS}_{(s)} \tag{11}$$

$$(\mathrm{CNS^-})_0 = (\mathrm{CNS^-}) + \mathrm{AgCNS}_{(s)} + (\mathrm{FeCNS^{+2}})_t \tag{12}$$

combining eqns. (10), (11) and (12).

$$(\mathrm{Cl^-})_0 = (\mathrm{Ag^+})_0 - (\mathrm{CNS^-})_0 + (\mathrm{FeCNS^{+2}})_t + (\mathrm{CNS^-}) - (\mathrm{Ag^+}) + (\mathrm{Cl^-}) \tag{13}$$

By incorporation of eqns. (5), (6) and (9), eqn. (13) becomes

$$\begin{aligned}(\mathrm{Cl^-})_0 = {} & (\mathrm{Ag^+})_0 - (\mathrm{CNS^-})_0 + (\mathrm{FeCNS^{+3}})_t + \frac{(\mathrm{FeCNS^{+2}})_t\, \gamma_{\mathrm{FeCNS}^{+2}}}{(\mathrm{Fe^{+3}})_0 K_f\, \gamma_{\mathrm{Fe}^{+3}}\, \gamma_{\mathrm{CNS}^-}} \\ & - \frac{(\mathrm{Fe^{+3}})_0\; K_{\mathrm{AgCNS}}\, K_f\, \gamma_{\mathrm{Fe}^{+3}}}{(\mathrm{FeCNS^{+2}})_t\, \mathrm{Ag^+}\, \gamma_{\mathrm{FeCNS}^{+2}}} + \frac{(\mathrm{FeCNS^{+2}})\; K_{\mathrm{AgCl}}\, \gamma_{\mathrm{FeCNS}^{+2}}}{(\mathrm{Fe^{+3}})_0\, K_{\mathrm{AgCNS}}\, K_f\, \gamma_{\mathrm{Fe}^{+3}}\, \gamma_{\mathrm{Cl}^-}}\end{aligned} \tag{14}$$

or, the number of millimoles of chloride present in the sample is

$$(\mathrm{Cl^-})_0 = (N_{\mathrm{AgNO_3}})\,(V_{\mathrm{AgNO_3}}) - (N_{\mathrm{KCNS}})\,(V_{\mathrm{KCNS}}) + F[(\mathrm{FeCNS^{+2}})_t,\, \mu] + (\mathrm{Cl^-})\,[(\mathrm{FeCNS^{+2}})_t,\, \mu] \tag{15}$$

where N is the normality and V is the volume in milliliters of the solution noted by the subscript, $(\mathrm{Cl^-})[\mathrm{FeCNS^{+2}})_t,\, \mu]$ indicates that the free chloride concentration is a function of $(\mathrm{FeCNS^{+2}})_t$ and the activity coefficients, hence the ionic strength, μ, and

$$F[(\mathrm{FeCNS^{+2}})_t,\, \mu] = (\mathrm{FeCNS^{+2}})_t + (\mathrm{CNS^-}) - (\mathrm{Ag^+}) \tag{16}$$

The term $F[(\mathrm{FeCNS^{+2}})_t,\, \mu]$ is defined as the operator determinate end-point error.

Evaluation of the operator determinate end-point error

In a manner analogous to the preceeding discussion, for the standardization or titration of a blank, eqn. 15 may be reduced to

$$N_{\mathrm{KCNS}} = \frac{(N_{\mathrm{AgNO_3}})\,(V_{\mathrm{AgNO_3}}) + F[(\mathrm{FeCNS^{+2}})_t,\, \mu]}{V_{\mathrm{KCNS}}} \tag{17}$$

Hence, if $F[(\mathrm{FeCNS^{+2}})_t,\, \mu]$ is significant with respect to $(N_{\mathrm{AgNO_3}})\,(V_{\mathrm{AgNO_3}})$, the normality calculated for potassium thiocyanate is not independent of the ratio $V_{\mathrm{AgNO_3}}/V_{\mathrm{KCNS}}$. However, if the ratio is (1) determined at the same ionic strength (constant activity-coefficient ratios), (2) by the same operator [constant $(\mathrm{FeCNS^{+2}})_t$], and (3) exactly the same volume of potassium thiocyanate used in the standardization (17) is required for the back titration of the excess of silver nitrate in the chloride determination (15), then

$$(\mathrm{Cl^-})_0 = N_{\mathrm{AgNO_3}}\,[V_{\mathrm{AgNO_3}\,(s)} - V_{\mathrm{AgNO_3}\,(b)}] + (\mathrm{Cl^-})\,[(\mathrm{FeCNS^{+2}})_t,\, \mu] \tag{18}$$

where the subscripts s and b represent titrations of the sample and a blank of the same excess of thiocyanate, respectively. In other words, a titration in conformance with the three conditions given above would yield results which are low by only the free chloride-ion concentration, which for most cases is negligible.

The absolute magnitude of the operator determinate end-point error, $F[(FeCNS^{+2})_t, \mu]$, was evaluated in the following manner: rewriting (17), the following expression was obtained

$$V_{KCNS} = \frac{N_{AgNO_3}}{N_{KCNS}} V_{AgNO_3} + \frac{F[(FeCNS^{+2})_t, \mu]}{N_{KCNS}} \qquad (19)$$

By plotting volume of KCNS *vs.* volume of $AgNO_3$, a straight line, the slope of which is N_{AgNO_3}/N_{KCNS} and intercept is $F[FeCNS^{+2})_t, \mu]$, is obtained.

TABLE I

EVALUATION OF THE OPERATOR DETERMINATE END-POINT ERROR

0.05101 N $AgNO_3$		*0.05646 N $AgNO_3$*	
V_{KCNS} *ml*	V_{AgNO_3} *ml*	V_{KCNS} *ml*	V_{AgNO_3} *ml*
1.77	1.99		
1.77	2.02	4.61	5.00
2.50	2.94	4.61	5.00
2.65	3.14	4.63	5.00
4.81	5.77	4.65	5.00
5.07	6.10	9.16	10.00
7.82	9.48	9.17	10.00
7.90	9.60	9.17	10.00
9.86	12.00	9.18	10.00
9.91	12.10	22.61	25.00
12.32	15.04	22.62	25.00
12.39	15.11		
14.65	17.96		
14.79	18.04		
17.12	20.98		
17.19	21.04		

With 0.05101 *N* $AgNO_3$, $V_{KCNS} = 0.81130$, $V_{AgNO_3} = + 0.116$
With 0.05646 *N* $AgNO_3$, $V_{KCNS} = 0.89935$, $V_{AgNO_3} = + 0.127$

Table I lists the results obtained from titrations of varying amounts of $AgNO_3$ with KCNS, as well as the results obtained from least-squares analysis of the straight line produced from plotting V_{KCNS} *vs.* V_{AgNO_3}. Two different silver nitrate solutions, of strengths 0.05101 *N* and 0.05646 *N*, were used. 0 122 ml is the average value of $F[(FeCNS^{+2})_t, \mu]/N_{KCNS}$. The pooled standard deviation of this result is 0.0126 ml. This is the amount of the thiocyanate solution required to obtain an end-point. The operator determinate end-point error is calculated to be $7.66 \cdot 10^{-6}$ moles.

From the slopes of the two curves, the normality of KCNS may be evaluated as follows:

when $$N_{AgNO_3} = 0.05101, \quad \frac{N_{AgNO_3}}{N_{KCNS}} = 0.81130$$

then

$$N_{KCNS} = 0.06287$$

and when

$$N_{AgNO_3} = 0.05646, \frac{N_{AgNO_3}}{N_{KCNS}} = 0.89935$$

then

$$N_{KCNS} = 0.06278$$

and it is found the normalities are in agreement by 1.4 parts per thousand.

It is interesting to compare the value of the operator determinate end-point error and the "end-point error" reported by other investigators. Several investigators[3,6,7] find that an analytical concentration of 10^{-5} M of thiocyanate ion is sufficient to produce a perceptible color in a solution containing approximately 0.015 M ferric ion and 0.6 M nitric acid. Using a concentration formation constant (at an ionic strength of 0.6 M) of 139 for the formation of ferric monothiocyanate ion[8,9], the theoretical amount of $FeCNS^{+2}$ necessary to be perceptible is about $6.7 \cdot 10^{-6}$ M. In the work presented in this paper the volume of solution was about 160 ml, hence the analytical concentration of thiocyanate that is necessary for an end-point is $4.8 \cdot 10^{-5}$ M, which leads to a calculated amount of $FeCNS^{+2}$ of about $2.3 \cdot 10^{-5}$ M, when the ferric concentration is 0.0067 M.

The fact that 3.4 times the amount of $FeCNS^{+2}$ is required in this work than others, may lie partly in the fact that the "end-point blank" is usually determined in solutions which do not contain nitrobenzene and silver chloride and silver thiocyanate precipitates. In the carefully executed work of SWIFT *et al.*[7], it was noted that the concentration of $FeCNS^{+2}$ required for end-point detection increased when a silver chloride precipitate was present, in fact at the optimum ferric concentration, a 1.95-fold increase is calculated. The work presented here is the only one in which the actual conditions of the end-point are entirely simulated.

A larger contribution to the increased amount of $FeCNS^{+2}$ required to reach end-point is probably due to lack of sensitivity of the eye of the operator. This is a factor which must be appraised for each operator as an individual.

It should be reported here that KEYS[10], by means of novel micromanipulations, was able to achieve a sensitivity of 0.001 mg of chloride in a 10-ml solution, which is equivalent to $3 \cdot 10^{-6}$ M, however, this only represents the reproducibility of his method; no attempts to evaluate the accuracy of the method were made.

EXPERIMENTAL PROCEDURE

This procedure takes advantage of the possibility of eliminating the operator determinate end-point error by specifying that the ratio of silver nitrate solution to potassium thiocyanate solution be determined with the same volume of potassium thiocyanate solution as will be employed in the subsequent analysis. The theory underlying this expedient has been discussed and summarized above (18).

Reagents

1. *Silver nitrate solution, 0.05 N.* Weigh approximately 8 to 9 g of dry, reagent-grade $AgNO_3$ to the nearest milligram and dissolve in distilled water; dilute to exactly one liter.

Calculate the normality as follows:

$$N = \frac{W_{AgNO_3}}{169.89}$$

where W_{AgNO_3} is the weight of silver nitrate. Freshly prepared solutions of silver nitrate in distilled water need not be standardized.

2. *Ferric alum indicator.* Dissolve 200 g of ferric ammonium sulfate in 300 ml of distilled water. Heat to the boiling-point and add 25 ml of reagent-grade nitric acid. Filter, cool, and store in a Pyrex bottle.

3. *Potassium thiocyanate solution, 0.05 N.* Dissolve 4.8 to 5.0 g of reagent-grade potassium thiocyanate in distilled water and dilute to one liter. Standardize this solution against standard silver nitrate as follows: Transfer 5.00 ml of 0.05 N $AgNO_3$ to a 500-ml Erlenmeyer flask, and add 150 ml of distilled water and 8 ml of 1 : 1 nitric acid. Add 1 ml of nitrobenzene, 1 to 2 ml of ferric alum indicator, and titrate with potassium thiocyanate solution to a permanent red-brown color. Calculate the normality of the potassium thiocyanate solution as follows:

$$N = \frac{V_{AgNO_3}}{V_{KCNS}} \times N_{AgNO_3}$$

Procedure

Transfer a weighed portion of the sample which contains 2 to 20 mg of chloride salt to a 500-ml Erlenmeyer flask and dissolve in 150 ml of distilled water; it is permissible to assist solution by heat. Add 8 ml of 1:1 nitric acid to the cold solution and mix well. From a 10-ml buret, add a measured excess of 5 ml of standardized 0.05 N silver nitrate solution and mix well; then add 1 ml of nitrobenzene, and vigorously swirl the flask in order to coagulate the precipitate. Allow the precipitate to settle and carefully add a little more 0.05 N silver nitrate solution to the supernatant liquid; if an excess has been added, no turbidity will appear. Again swirl the flask in order to coagulate the precipitate; the supernatant liquid must not be milky. The 5-ml excess of silver nitrate can not readily be estimated initially; however, with use of results of the initial titration, one can easily calculate the total amount of silver nitrate to give a 5-ml excess in succeeding titrations of the same sample.

Add 1 to 2 ml of ferric alum indicator and titrate with 0.05 N potassium thiocyanate solution to a permanent red-brown color.

Calculate the per cent chloride salt content as follows:

$$\% \text{ chloride salt} = \frac{M\,(aA - bB)}{10W}$$

where, M = molecular weight of the chloride salt being titrated, 53.50 for ammonium chloride, or 74.56 for potassium chloride. a = normality of silver nitrate solution. b = normality of potassium thiocyanate solution. A = volume of silver nitrate solution, (ml). B = volume of potassium thiocyanate solution, (ml). W = weight of sample, (g).

RESULTS

A summary of results of chloride determinations of synthetic chloride-in-ammonium nitrate and ammonium perchlorate mixtures is shown in Table II. The method recommended above for the calculation of the chloride content was not used, but rather the introduction of the calculated operator determinate end-point error (calculated above) as well as the calculated potassium thiocyanate normality into eqn. 15 to arrive at an equivalent "net" volume of silver nitrate consumed was used.

TABLE II

VOLHARD DETERMINATION OF SMALL CHLORIDE CONTENTS IN AMMONIUM NITRATE AND AMMONIUM PERCHLORATE

Salt	*NH_4Cl taken mg*	*$AgNO_3$ ml*	*KCNS ml*	*Net $AgNO_3$ ml*	*NH_4Cl found mg*	*Error mg*
None	0.00	5.01	4.62	0.01	0.03	+0.03
None	3.89	5.09	3.55	1.28	3.87	—0.02
None	9.73	8.77	5.12	3.21	9.70	—0.03
None	12.16	10.00	5.48	4.04	12.20	+0.04
None	19.08	9.91	3.34	6.33	19.12	+0.04
None	38.92	19.31	5.90	12.85	38.82	—0.10
30.0 g NH_4NO_3	0.00	5.04	4.60	0.06	0.18	+0.18
30.0 g NH_4NO_3	3.89	5.12	3.53	1.33	4.02	+0.13
30.0 g NH_4NO_3	3.82	4.19	2.72	1.30	3.93	+0.11
30.0 g NH_4NO_3	4.85	5.43	3.55	1.62	4.89	+0.04
30.0 g NH_4NO_3	7.27	6.54	3.79	2.46	7.43	+0.16
30.0 g NH_4NO_3	9.70	9.08	5.37	3.24	9.79	+0.09
30.0 g NH_4NO_3	11.46	7.27	3.20	3.85	11.63	+0.17
30.0 g NH_4NO_3	19.10	9.34	2.80	6.36	19.21	+0.11
24.4 g NH_4ClO_4	0.00	5.00	4.58	0.04	0.12	+0.12
22.1 g NH_4ClO_4	4.86	10.00	7.62	1.66	5.01	+0.15
23.8 g NH_4ClO_4	6.08	5.00	2.87	1.94	5.86	—0.20
26.9 g NH_4ClO_4	7.30	7.00	4.30	2.35	7.10	—0.20
23.8 g NH_4ClO_4	12.16	10.00	5.53	3.98	12.02	—0.08
26.0 g NH_4ClO_4	12.16	10.00	5.43	4.10	12.39	+0.23

$N_{AgNO_3} = 0.05646$; Net $V_{AgNO_3} = V_{AgNO_3} - 1.112\ (V_{KCNS} - 0.12)$

As mentioned previously, this result should be low by the amount of free chloride in the solution at the end-point. For most cases of the normal Volhard titration (ionic strength about 0.6 M), $(Cl^-)F(FeCNS^{+2})$ is negligible, however, this has not been ascertained at high ionic strengths. In particular, when small amounts of chloride (50–500 p.p.m.) are to be determined with reasonable accuracy, the required sample size becomes very large and the ionic strength will be greater than 4 M. Strictly speaking, it is necessary to standardize the potassium thiocyanate solution at this high ionic strength. However, by recognizing the fact that although the activity coefficients evaluated at 0.6 M and 4.3 M are considerably different, the ratios of activity coefficients at these two ionic strengths are not too different. The studies presented here were facilitated by making an approximation that the activity coefficient ratios are identical. The value of the operator determinate end-point error was evaluated at the usual ionic strength (about 0.6 M), and this value was utilized in the calculation of chloride contents titrated in media of high ionic strengths (up to 4.3 *M*). The results of these studies show that the amount of free chloride ion in solution at the end-point is negligible with respect to the concentration level of chloride present in the sample, or small enough to be masked with the indeterminate error of the measurement. Consequently, the approximation of constant activity coefficient ratios at ionic strengths of 0.6 *M* and 4.3 *M* proves to be valid, or if there is any discrepancy it is small enough to be hidden in the indeterminate error of the measurements.

Slightly high results of titrations of chloride in ammonium nitrate media were obtained; hence a small "salt effect" is indicated. However, the accuracy at this concentration level of chloride ion is adequate for most purposes. Because a 0.1-ml change in the net volume of silver nitrate leads to a change of 0.30 mg of ammonium chloride, the apparent "salt effect" discerned could easily be attributed to reproducibility variations; however, the constancy of direction of this variation affirms the belief of a small "salt effect". When expressed in absolute percent, chloride contents of 0.000 to 0.064% were determined with an average error of 0.0004%.

The randomness of direction of the apparent error of the titration of chloride in ammonium perchlorate infers that there is no "salt effect." The apparent error of this titration is greater than that obtained when titrating in ammonium nitrate media, but considering the low chloride ion level, the accuracy is quite satisfactory. When expressed as absolute per cent ammonium chloride, contents of 0.000 to 0.051% were determined with an average error of 0.0007%.

TABLE III

VOLHARD DETERMINATION OF SMALL CHLORIDE CONTENTS IN POTASSIUM PERCHLORATE

Salt	*KCl taken mg*	*$AgNO_3$ ml*	*KCNS ml*	*Net $AgNO_3$ ml*	*KCl found mg*	*Result*		
						Avg mg	*s^a mg*	*Error mg*
None	2.89	6.54	4.79	0.78	2.97			
		7.51	5.61	0.74	2.81			
		4.08	2.81	0.77	2.93	2.90	0.08	+0.01
None	7.23	6.36	3.76	1.87	7.11			
		6.73	4.05	1.89	7.19			
		5.05	2.72	1.85	7.04	7.11	0.08	−0.12
8.0 g $KClO_4$	0.00	4.80	4.05	−0.04	−0.15			
		5.06	4.27	−0.08	−0.30			
		5.45	4.56	−0.02	−0.08	−0.18	0.11	−0.18
8.0 g $KClO_4$	2.89	4.05	2.85	0.69	2.62			
		4.10	2.88	0.70	2.66			
		6.14	4.50	0.74	2.81	2.70	0.10	−0.19
8.0 g $KClO_4$	7.23	5.07	2.75	1.83	6.96			
		6.45	3.92	1.77	6.73			
		5.77	3.31	1.84	7.00	6.90	0.15	−0.33

$N_{AgNO_3} = 0.05101$; Net $V_{AgNO_3} = V_{AgNO_3} - 1.233\ (V_{KCNS} - 0.12)$

[a] Standard deviation

The results of titrations of chloride determinations of synthetic chloride-in-potassium perchlorate mixtures is shown in Table III. Because of the sparing solubility of potassium perchlorate, the sample was dissolved in 200 ml of water at 50°, then the solution was allowed to cool to room temperature; potassium perchlorate crystals separate. The chloride content of this mixture was then determined by the procedure above. As would be expected from coprecipitation of chloride within the crystals of potassium perchlorate, the results of this determination are all low. The achieved accuracy is not as great as anticipated, but the results are acceptable. When expressed as absolute per cent potassium chloride, contents of 0.000 to 0.090 were determined with an average error of 0.0030% and reproducibility of 0.0015%. Another adaptation of the Volhard procedure was examined and abandoned; namely, addition of excess silver nitrate to the hot solution of potassium chloride and perchlorate. Coprecipitation of the excess silver nitrate occurred to such a degree that results comparable to those obtained when handling cool solutions (as above) were observed.

In conclusion, this study has shown that good results for the Volhard determination of small amounts of chloride ion in oxidizers can be achieved if the ratio of strengths of the potassium thiocyanate and silver nitrate solutions and the determination of the chloride are 1) carried out by the same operator and 2) exactly the same number of milliliters of potassium thiocyanate are used in each instance.

SUMMARY

The applicability of the Volhard titration to the determination of small amounts of chloride in solutions of high ionic strength has been examined. A rigorous derivation of the operator determinate end-point error, which is applicable to all analyses involving back-titrations and visual end-point detection, is presented together with a method for its empirical evaluation. Employ of the operator determinate end-point error has enabled determination of small amounts of chloride (0.00 to 0.090%) in ammonium nitrate, ammonium perchlorate, and potassium perchlorate with an average absolute error of 0.0004%, 0.0007%, and 0.0015%, respectively.

RÉSUMÉ

Les auteurs ont appliqué la méthode de VOLHARD au dosage de faibles teneurs en chlorure dans des solutions de force ionique élevée. On a pu doser des teneurs en chlorure de 0.000 à 0.09% dans le nitrate d'ammonium, le perchlorate d'ammonium et le perchlorate de potassium, avec un erreur de 0.0004%, 0.0007% et 0.0015%, respectivement.

ZUSAMMENFASSUNG

Es wird die Anwendung der Titrationsmethode nach VOLHARD zur Bestimmung kleiner Mengen von Chlorid in Gegenwart hoher Jonenkonzentrationen beschrieben und auf die einzuhaltenden Bedingungen hingewiesen.

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ANALYTICAL CHEMISTRY OF ZIRCONIUM

I. *o*-CRESOTIC ACID AND 4-AMINOSALICYLIC ACID IN THE DETERMINATION OF ZIRCONIUM

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Among the more important methods for the determination of zirconium are the gravimetric procedures involving precipitation of zirconium with cupferron[1], phosphate[2], mandelic acid[3], *m*-dinitrobenzoic acid[4], some phenolic acids[5] and *m*-cresoxy acetic acid[6]. To these may be added *o*-cresotic acid and 4-aminosalicylic acid. The precipitate is voluminous and settles quickly.

EXPERIMENTAL

Reagents

o-Cresotic acid (sodium salt) recrystallised; 4-amino salicylic acid (sodium salt) B.D.H.; zirconyl chloride, E. Merck, G.R.

Determination of zirconium

To the hot (80°) solution is added a 1% solution of the precipitant until precipitation is complete. The precipitate is digested for 10 min, filtered through Whatman paper No. 42, washed with hot water, dried and finally ignited to oxide before weighing. A few representative results are shown in Table I.

TABLE I

o-Cresotic acid		*4-Aminosalicylic acid*	
ZrO_2 taken (mg)	*ZrO_2 found (mg)*	*ZrO_2 taken (mg)*	*ZrO_2 found (mg)*
2.464	2.440	2.464	2.400
12.320	12.280	12.320	12.180
24.640	24.580	30.800	30.800
123.220	123.180	123.220	123.080
246.440	246.380	246.440	246.300

Both *o*-cresotic acid and 4-aminosalicylic acid proved to be efficient precipitants but *o*-cresotic acid was the more sensitive. The precipitate with *o*-cresotic acid was much more granular and easily filterable than that with 4-aminosalicylic acid.

Effect of hydrogen ion concentration on precipitation

In order to compare the efficiency of these acids at different hydrogen ion concentrations zirconium was determined at different pH values which were obtained by the addition of sodium acetate buffers. The results are shown in Table II.

TABLE II

pH	*ZrO_2 taken (mg)*	*ZrO_2 found (mg)*	
		o-Cresotic acid	*4-Aminosalicylic acid*
1.4	24.64	24.58	24.68
3.3	31.40	31.38	31.38
4.6	31.40	31.28	31.28
5.0	31.40	31.38	31.08
5.4	31.40	31.38	31.18

It can be seen that the recoveries of zirconium with 4-aminosalicylic acid decreased as the pH of the solution increased; the optimum pH range was 1.4–3.3. In the case of *o*-cresotic acid precipitation was quantitative at all pH values studied.

Determination of zirconium in presence of other ions

Ions such as bismuth(III), chromium(III), cerium(IV), manganese(II), molybdenum(VI) and vanadium(IV) did not interfere in these determinations of zirconium. But it is not possible to separate zirconium from thorium, the latter being quantitatively precipitated at all pH values. Double precipitation is needed if iron(III), copper(II) or uranyl ions are present as these form coloured complexes in solution.

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SUMMARY

o-Cresotic acid and 4-aminosalicylic acid are suitable for quantitative precipitation of zirconium; the precipitate is ignited and weighed. The optimum pH ranges are 1.4–5.4 and 1.4–3.3, respectively.

RÉSUMÉ

L'acide *o*-crésotique et l'acide amino-4-salicylique ont été utilisés avec succès pour le dosage gravimétrique du zirconium.

ZUSAMMENFASSUNG

o-Kresotinsäure und Amino-4-salicylsäure eignen sich zur gravimetrischen Bestimmung von Zirkonium.

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ANION EXCHANGE STUDIES OF URANIUM(VI) IN SULPHATE AND CARBONATE SOLUTIONS

SEPARATION FROM MIXTURES

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Uranium(VI) forms strong anionic complexes of the type $[UO_2(SO_4)_2]^{-2}$ and $[UO_2(SO_4)_3]^{-4}$ in sulphuric acid solutions; the formation constants for these complexes are 350 and 2500 respectively[1]. The anionic carbonate complex $[UO_2(CO_3)_3]^{-4}$ is much stronger, hence many ion exchange separations of uranium from commonly associated cations are possible. PREUSS AND KUNIN[1], and GRINSTEAD *et al.*[2] recovered uranium from carbonate and sulphate leach systems. BANERJEE AND HEYN[3] separated uranium from bismuth by anion exchange in sulphuric acid solution, at pH 1.0 – 1.5. Using essentially the same principle, SUSIC[4] worked out separation methods of uranium from cerium, alkali metals, and a few divalent metals. MURTHY[5] employed a carbonate medium for the anion-exchange separation of uranium from vanadium; vanadate was adsorbed along with the uranium complex, but was removed by elution with sodium carbonate solution and finally uranium was eluted with sodium chloride solution. Uranium(VI) also forms anionic chloro- and nitrato-complexes[6,7], which permits anion exchange separations of uranium from vanadium, iron etc.

However, systematic anion-exchange studies of uranium are lacking. The present paper describes the anion exchange behaviour of uranium(VI) in sulphate and carbonate systems, which are the two principal leach liquors of uranium. The strongly basic, quaternary ammonium type anion exchanger, Dowex 21K, was employed. Hydrochloric, nitric, sulphuric and perchloric acids and sodium chloride, ammonium chloride, sodium nitrate and sodium sulphate were studied as eluting agents. Uranium was separated from the important fission product elements *e.g.*, cerium, zirconium, caesium, silver and cadmium, from vanadium and also from phosphate and molybdate.

APPARATUS AND REAGENTS

Apparatus

Ion-exchange column and Cambridge pH meter.

The ion-exchange column was similar to that previously described[8]; a resin bed, 1.4 × 14.5 cm, was used.

Reagents

The chemicals used were of reagent grade, unless otherwise specified.

A uranium solution was prepared from uranyl nitrate hexahydrate (Mallinckrodt A.R.) and standardized by the usual oxine method. For ion-exchange runs, *ca.* 25 mg of uranium was taken.

Dowex 21K (Dow Chemical Cy., Midland, Mich., U.S.A.), 50–100 mesh, chloride-form anion exchange resin was pre-treated by alternate washing with 1 *N* hydrochloric acid, water and 0.5 *N* sodium hydroxide followed by water. After being slurried into the column, it was washed at a flow-rate of 2 ml/min with 1 *N* hydrochloric acid and then with water till the resin bed was free from chloride. For ion-exchange runs in sulphate or carbonate medium, the resin was converted to the appropriate form by washing with 10% sulphuric acid or 10% sodium carbonate solution and washed with distilled water till free from sulphate or carbonate.

EXPERIMENTAL, RESULTS AND DISCUSSION

Ion-exchange behaviour studies

A. Sulphate system. An aliquot of the uranyl nitrate solution was evaporated to fumes with sulphuric acid in a 50-ml beaker so that uranyl sulphate was formed. This was dissolved in a little water and the pH adjusted to 1.0–1.5 with 0.01 *N* sulphuric acid and 0.01 *N* sodium hydroxide by means of a pH meter. This solution, containing an anionic sulphate complex of uranium, was passed through the resin bed at a rate of 1 ml per minute. The resin was washed with 50 ml of water and then with 200 ml of the different eluants at the same flow rate. The eluants were hydrochloric acid (0.25, 0.50, 1.0 and 2.0 *M*), nitric acid (0.25, 0.50, 1.0 and 2.0 *M*), perchloric acid (0.25, 0.50, 1.0 and 1.5 *M*), sulphuric acid (1, 2 and 3 *M*), ammonium chloride (1, 3, 5 and 10%), citric acid (pH 5.0 – 5%) and sodium hydroxide (1%). The effluent batch (200 ml) was evaporated nearly to dryness with 5 ml of sulphuric acid and 2 ml of perchloric acid (70%) to destroy any organic matter from the resin, and uranium was determined gravimetrically by the oxine method.

TABLE I

BEHAVIOUR OF THE ANIONIC SULPHATE COMPLEX OF URANIUM(VI) TOWARDS VARIOUS ELUTING AGENTS

Uranium = 24.76 mg. Wt. of resin = 9.5420 g (oven-dried)

No.	*Eluting agents*	*Eluant concentration, M*	*Total uranium recovery, %*
1	$HClO_4$	0.25	106.2
	$HClO_4$	0.5	97.6
	$HClO_4$	1.0	97.0
	$HClO_4$	1.5	96.8
2	HNO_3	0.25	96.8
	HNO_3	0.5	100.3
	HNO_3	1.0	103.9
	HNO_3	2.0	93.5
3	H_2SO_4	0.25	95.0
	H_2SO_4	1.0	98.5
	H_2SO_4	2.0	103.8
	H_2SO_4	3.0	100.9
4	HCl	0.25	96.0
	HCl	0.5	95.8
	HCl	1.0	104.4
	HCl	2.0	80.0
5	NH_4Cl	1%	79.9
	NH_4Cl	3%	83.6
	NH_4Cl	5%	105
	NH_4Cl	10%	100.5
6	NaOH	1%	2.2

The results (Table I) show that essentially quantitative elution was possible with 200 ml of perchloric acid (0.25 – 1.5 *M*), nitric acid (0.25 – 2.0 *M*), sulphuric acid

(0.25 – 3 *M*) and hydrochloric acid (0.25 – 1.0 *M*). The elution was incomplete with higher concentrations of hydrochloric acid presumably owing to the formation of the $[UO_2Cl_4]^{-2}$ complex[9]. Citric acid at pH 5.0 (5%), tartaric acid (5%) and sodium hydroxide (0.5%) failed to elute uranium; with 1% sodium hydroxide only about 2% uranium was recovered. Ammonium chloride (5–10%) gave quantitative recovery of uranium. For routine work perchloric acid (0.5 – 1.0 *M*) is preferred because it is easily volatilized in the assaying step and does not form anionic chloro-complexes. The eluting agents may be arranged in order of decreasing efficiency: $ClO_4^- > NO_3^{-2} > SO_4^{-2} > Cl^- > OH^-$. This falls in line with the qualitative series[10] expressing the decreasing selectivity of Dowex 21K for various anions: $CNS^- > I^- > NO_3^- > Br^- > CN^- > HSO_4^- \simeq HSO_3^- > NO_2^- > Cl^- > HCO_3^- > CH_3COO^- > OH^- > F^-$.

B. Carbonate system. The anionic carbonate complex, $[UO_2(CO_3)_3]^{-4}$ was prepared as follows. A known aliquot of uranyl nitrate solution was converted to sulphate as before and dissolved in water and the solution was carefully neutralised with solid sodium carbonate. Then 5 g of sodium carbonate was added, and the solution was diluted to 50 ml, boiled if necessary, and cooled to room temperature. The uranium solution was run through the resin column at a rate of 1 ml per minute. The resin was washed with 50 ml of water and 200 ml of the eluant was passed at a rate of 2 ml per minute. The eluants were sodium chloride (2, 4, 5, 10%), ammonium chloride (5, 10%), sodium nitrate (5, 10%) and sodium sulphate (10%). The effluent batch was boiled with 10 ml of 8 *N* nitric acid to expel carbon dioxide, cooled and neutralised with ammonia and finally uranium was analysed as the oxinate.

Sodium chloride (5–10%), ammonium chloride (10%) and sodium nitrate (5–10%) permitted quantitative elution. Lower concentrations of these eluants and also sodium sulphate — even 10% — gave incomplete elution (Table II).

TABLE II

BEHAVIOUR OF ANIONIC CARBONATE COMPLEX OF URANIUM TOWARDS VARIOUS ELUTING AGENTS

Resin = 9.5420 g (oven dried)

No. agents	*Eluting agents*	*Eluant concentration, %*	*Total uranium recovery, %*
1	NaCl	2[a]	35.2
	NaCl	4	58.7
	NaCl	5	96.8
	NaCl	10	102.5
2	NH_4Cl	5	51.8
	NH_4Cl	10	98.5
3	$NaNO_3$	5	105.5
	$NaNO_3$	10	95.8
4	$Na_2SO_4 \cdot 10\,H_2O$	10	10.8

[a] Elution with 300 ml

Ion-exchange separations

A. Sulphate system. The separations of uranium from zirconium, cerium, caesium, silver, cadmium and vanadium are based on the fact that the anionic sulphate complex of uranium(VI) is quantitatively retained by the anion exchanger, whereas the cations which do not form anionic complexes pass through the column.

In each case the mixture was processed as in the above preparation of the anionic uranium sulphate complex. After the adsorption, the column was washed with 50 ml of 0.05 *M* sulphuric acid and 50 ml of water; finally uranium was eluted from the resin with 200 ml of 0.5 *M* perchloric acid and determined as described above.

The results (Table III) show that, except in mixtures containing thorium, essentially quantitative separations were obtained. Thorium was adsorbed under the same conditions as uranium[11]. High results were obtained with U : Th ratios greater than 10 : 1 owing to coelution of thorium with uranium. The separation of these metals in any ratio seems to be possible by selective elution; uranium is first eluted with *ca.* 0.25 *M* sulphuric acid and thorium is then eluted with 1 *M* or stronger acid. However this was not further examined, since cation-exchange separation[8] is much simpler. Those cations which give precipitates in sulphate medium interfere, *e.g.* barium, strontium, calcium and lead. Anions are adsorbed with uranium. However, the method may be extended to cover a large number of cations, and may be used for the purification of uranium from commonly associated cations.

TABLE III

ION-EXCHANGE SEPARATION IN SULPHATE SYSTEM

U = 23.77 mg

No.	*Foreign ion added, mg*		*Uranium recovery* %
1	Zr	24.10	95.9
2	Zr	2.4	103.4
3	Zr	95.0	106.8
4	Ce(IV)	22.32	106.3
5	Ce(IV)	2.8	96.7
6	Ce(IV)	44.6	100.4
7	Cs	24.0	105.3
8	Cs	100.0	102.9
9	V(V)	24.5	96.5
10	V(V)	2.5	100.6
11	Ag	2.5	101.0
12	Ag	25	103.4
13	Cd	2.5	101.4
14	Cd	25.5	99.9
15	Th	2.3	109.0
16	Th	22.5	160.4

B. Carbonate system. Many metal ions, particularly those of the heavy metals, precipitate in carbonate medium, and their separation from uranium is not possible. However, uranium can be separated from commonly associated anions, *e.g.* phosphates and other anions, *e.g.* molybdate, by selective elution. The method is virtually an extension of that proposed by MURTHY[5]. Phosphate or molybdate was adsorbed along with uranium and was removed with 10% sodium carbonate; finally uranium was eluted with 5% sodium chloride.

The free acid in the uranium solution (sulphate) was neutralized with sodium carbonate, the desired anion was added and the mixture was made 10% with respect to sodium carbonate as described before. The solution was run through the column at a flow rate of 1 ml per minute. The bed was washed with 30 ml of 10% sodium carbonate at 2 ml per minute. The phosphate or molybdate was eluted with 200 ml of 10% sodium carbonate and uranium was then eluted with 200 ml of 5% sodium chloride at 2 ml per minute. The last traces of phosphate or molybdate were removed before elution of uranium began. The separations obtained are shown in Table IV. Large scale separations could be effected with larger ion-exchange columns.

TABLE IV

ION-EXCHANGE SEPARATIONS IN CARBONATE SYSTEM

U = 23.77 mg

No.	*Foreign ion added, mg*		*Uranium found mg*	*Uranium recovery %*
1	PO_4^{-3}	25	22.98	96.7
2	PO_4^{-3}	250	22.70	95.4
3	PO_4^{-3}	100	24.50	102.9
4	$Mo_7O_{24}^{-6}$	24	23.90	100.4
5	$Mo_7O_{24}^{-6}$	240	23.52	98.9

The results in Tables I–IV are reproducible to within ± 5%

ACKNOWLEDGEMENT

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SUMMARY

The anion-exchange behaviour of uranium(VI) in two important leach systems, sulphate and carbonate, is described. Hydrochloric, nitric, sulphuric and perchloric acids and sodium chloride, ammonium chloride, sodium nitrate and sodium sulphate were tested as eluants on a Dowex 21K column. In the sulphate system uranium is separated from fission product elements, *e.g.* cerium, zirconium, caesium, silver, cadmium, and from vanadium; in the carbonate system, it is separated from phosphate and molybdate.

RÉSUMÉ

Une étude a été effectuée sur le comportement chromatographique de l'uranium(VI). On a pu, en solution sulfatée, le séparer sur colonne de Dowex 21K (échangeur d'anions) d'avec les éléments de produit de fission importants, Ce, Zr, Cs, Ag, Cd et V et, en solution carbonatée, d'avec phosphate et molybdate.

ZUSAMMENFASSUNG

Eine Untersuchung über das chromatographische Verhalten von Uran(VI) hat gezeigt, dass es sich von den wichtigsten Spaltprodukten (Ce, Zr, Cs, Ag, Cd und V) über einer Dowex 21K Kolonne mit Sulfatlösung trennen lässt. Mit Karbonatlösung kann eine Trennung von Phosphat und Molybdat erzielt werden.

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CHROMATOGRAPHIC SEPARATION OF INORGANIC ANIONS ON SPECIALLY PREPARED CALCIUM SULPHATE STICKS

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Inorganic ions can be separated by a simplified chromatographic technique with various adsorbents[1]; of these, calcium sulphate in the form of specially prepared sticks is most effective for obtaining rapid separations, the identification being complete in less than 10 min. The method has already been used for the qualitative separation of about a dozen cations[2,3].

This paper records the extension of the method to the rapid qualitative separation of inorganic anions.

EXPERIMENTAL

The sticks were prepared as previously described[3], except that the proportion of calcium sulphate ($CaSO_4 \cdot 2H_2O$) to plaster of Paris was 45 : 55 instead of 55 : 45. The technique was similar to that described previously[3].

RESULTS

Separation of phosphate from phosphite

Neutral solutions (pH 6.5–7) were used. After being washed with water, the stick was made just dry and sprayed with silver nitrate reagent. A distinct yellow band appeared a little above the point of application of the test solution. After 2 minutes, a broad black band appeared at quite a large distance above the yellow band. The first patch of white silver phosphite at this position could scarcely be seen until it became reduced to black metallic silver.

Separation of arsenate from arsenite

This was done in the same way as the phosphate–phosphite separation. Two distinct bands appeared. The chocolate arsenate band appeared just above the application point while the yellow arsenite band appeared farther up the stick.

Separation of arsenate from phosphite

In this case, after spraying with silver nitrate, the chocolate arsenate band appeared just above the application point while the broader black phosphite band was the same as mentioned above.

Separation of arsenite from phosphite

Again, the same procedure was used. A quite broad yellow band of arsenite appeared a little above the application point and after about two minutes a distinct broader black band of phosphite appeared considerably above it.

Separation of thiosulphate from thiocyanate

The stick was washed with water containing 10% acetone; water alone caused imperfect separation. A mixture (1 : 1) of 0.2 N ferric nitrate and 0.2 N silver nitrate was used as the spray. The bands were broad and clearly separated. The red ferric ferri-thiocyanate band lay above the black silver sulphide band, the sulphide being formed by the rapid decomposition of silver thiosulphate. The latter band appeared just above the application point.

Separation of ferricyanide from thiocyanate

The stick was washed with water, allowed almost to dry, and sprayed with ferric chloride reagent. Two equally broad bands were obtained, one red and one brown. The stick was then sprayed with a dilute solution of ferrous ammonium sulphate. The brown band nearest the application point turned deep blue. The red ferric ferri-thiocyanate band remained unaltered and could be confirmed by bleaching with mercuric chloride solution.

Separation of ferrocyanide from thiocyanate

Water alone was used for washing. Distinct blue and red bands were formed with ferric chloride reagent. The blue band appeared a little above the application point with the red band a little above it. The latter could be bleached with mercuric chloride solution.

Separation of ferrocyanide from ferricyanide

The wash water contained 15% *n*-propyl alcohol; water alone gave imperfect separation. The stick was sprayed with copper sulphate reagent. Two bands appeared, upper chocolate and lower green, separated by a considerable distance. The green band appeared just above the application point and the chocolate band considerably farther up. Ferric chloride was also used to identify the separated ions as blue and brown bands. When the moist stick was treated with sulphur dioxide the brown band turned blue.

SUMMARY

Specially prepared calcium sulphate sticks are suitable adsorbents in the chromatographic separation of inorganic anions. Separations of various binary mixtures of phosphate, phosphite, arsenate, arsenite, thiosulphate, thiocyanate, ferricyanide and ferrocyanide are possible.

RÉSUMÉ

Une méthode chromatographique est proposée pour la séparation d'anions, utilisant des baguettes de sulfate de calcium, spécialement préparées.

ZUSAMMENFASSUNG

Beschreibung einer chromatischen Methode zur Trennung der Anionen mit Hilfe von Calciumsulfat in Form von Stäbchen.

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THE DETERMINATION OF STRONTIUM IN ROCKS AND BIOLOGICAL MATERIALS

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INTRODUCTION

Owing to the biological importance of strontium-90, it is desirable that the path of natural strontium from the soil through vegetable matter and animals should be understood. The administration of radioactive tracers to living subjects can give only relative information on retention, distribution, and excretion and can seldom give the absolute concentration of the natural element. Therefore there is a need for accurate strontium analyses at trace levels in a wide range of botanical and biological specimens, as well as in soils and rocks. Emission spectrography is a suitably rapid technique, but there is always the possibility of unsuspected suppression or enhancement of emitted lines by other constituents in the sample. It is therefore desirable that the reference standards for spectrographic analysis shall be as nearly as possible identical to the sample, both in chemical composition and physical form. Both neutron activation and stable dilution analyses offer ways of determining the strontium content of materials with sufficient accuracy and precision so that these may be used later as reference standards for spectrographic work.

A number of authors have established methods for determining strontium by neutron activation. BROOKSBANK, LEDDICOTE AND MAHLMANN[1] have studied strontium in animal tissues, while SOWDEN AND STITCH[2] have published a series of neutron activation analyses carried out on samples of human bone. BOWEN[3] and BOWEN AND DYMOND[4] have used neutron activation for determining strontium in sea water, marine organisms, plants and soils. HUMMEL AND SMALES[5] obtained a slightly lower figure than that reported by BOWEN AND DYMOND for strontium in sea water and confirmed it by stable isotope dilution analysis. HARRISON AND RAYMOND[6] developed an analytical scheme for the rapid determination of strontium in excreta using the induced strontium-87m isotope.

Because most of these methods have been restricted in their application, we have sought to establish a radiochemical procedure which is adequate for the assay of natural strontium in a wide variety of matrices and to compare these results with an independent series of figures obtained by stable isotope dilution analysis.

Hitherto, the stable isotope dilution technique has been concerned mainly with geological age work, but its use for the determination of strontium in standard rock samples has been reported[7,8]. The method is based upon the addition of a known quantity of enriched strontium-84 tracer to the sample, followed by the estimation of the quantity of normal strontium (mainly ^{88}Sr) from the change in the $^{84}Sr/^{88}Sr$ isotope ratio. Interference can be caused only by elements with isobars. In this case the isobaric elements are krypton and rubidium. Krypton does not produce ions with the thermal emission source used for strontium; rubidium has isotopes of mass 85 and 87 only, and so does not interfere with the determination of the $^{84}Sr/^{88}Sr$ isotope ratio unless it is present in very large quantities. Thus the only likely source of systematic error is contamination, but with fairly simple precautions this may be restricted to 0.3 μg, and the appropriate blank correction applied.

NEUTRON ACTIVATION ANALYSIS

Outline of the methods

The strontium-89 isotope

This procedure is applicable to the determination of strontium in rocks and minerals where an exceptional degree of radiochemical decontamination is required and where there may be some doubt whether the shortened scheme, using the strontium-87m isotope, will be adequate. The nuclear reaction is:

$^{88}Sr(n,\gamma)^{89}Sr$; $^{89}Sr \rightarrow {}^{89}Y$ (stable); activation cross-section, 0.005 barns.

Samples and strontium standards are sealed into silica phials and irradiated in the highest available neutron flux. The activated material is dissolved in the presence of carrier strontium. Successive treatments with fuming nitric acid precipitate the strontium and eliminate the bulk of the calcium and other interfering induced activities. Three pairs of scavenges follow: acid sulphide (antimony carrier), alkaline sulphide (cobalt carrier), and hydroxide scavenge (ferric iron carrier). The strontium is precipitated as the carbonate, converted to the nitrate, dissolved in water and fed to an ion-exchange column. Strontium, essentially free of calcium, is eluted chromatographically from the column and recovered from the appropriate fraction of the eluate by oxalate precipitation. After being washed, the strontium oxalate is dissolved, reprecipitated, washed, slurried on to an aluminium counting tray, dried under an infra-red lamp, weighed and beta-counted. The observed activity is corrected for chemical yield and compared with the activity of the strontium reference standards which have undergone the same irradiation and chemical treatment.

The radiochemical technique requires a period of about nine hours which is too long to permit the same separations to be used with adequate sensitivity for the shorter-lived (2.7 h) isotope, strontium-87m.

The strontium-87m isotope

The abbreviated procedure, using the strontium-87m isotope, is appropriate for botanical or biological specimens where the calcium/strontium ratio is not much greater than 1600:1. Other cations capable of high induced specific activities during a three hour irradiation may be present in amounts not greater than trace level. The nuclear reaction is:

$^{86}Sr(n,\gamma)^{87m}Sr$; ^{87m}Sr (isomeric transition) $\rightarrow {}^{87}Sr$(stable); activation cross-section 1.5 barns.

After irradiation for two and a half to three hours, the phials are opened and the contents dissolved in the presence of strontium carrier. Calcium is eliminated by a succession of four fuming nitric acid precipitations of strontium nitrate. Two scavenges with ferric hydroxide remove extraneous activity. The ion-exchange step is omitted and therefore radio-barium must be removed by duplicate precipitations with barium carrier. Strontium is recovered as the oxalate and prepared for beta-counting as in the ^{89}Sr method.

Experimental discussion

Samples need not be ashed before irradiation. Silica phials are most suitable for irradiations lasting more than a few hours, but shorter irradiations can be carried out successfully with the samples sealed in short lengths of polythene tubing. The low melting point of polythene is an advantage with biological samples, such as milk powder, which are likely to char at the higher temperatures needed to seal off a silica phial.

Each standard contains 100 μg of strontium (natural isotopic abundance) in the form of a 0.1-g aliquot of a solution of 1 mg strontium per ml. The standard solution is transferred into the weighed phials by a dropping pipette and rubber bulb. The pipettes are made with a slender tip lightly treated upon the outside with "Repelcote" (Hopkins and Williams Ltd.), or a similar solution of water-repellent silanes in carbon tetrachloride, to prevent the standard solution being drawn up between the walls of the phial and the pipette tip.

Decontamination from interfering radioactivity offers no problem with the exception of radio-calcium. The calcium/strontium ratio in bone ash is about 1600 and the ratio of the induced radioactivities will be approximately 4 at the time of beta-counting if the strontium-87m method is used. A decontamination factor of 10^3 for calcium-45 is therefore adequate. In the case of rocks analysed by the strontium-89 method, the calcium/strontium ratio may be in the vicinity of 2000 and the ratio of induced activities at the time of counting will then be about 5400. A decontamination factor of 10^7 for calcium-45 is the minimum acceptable for the strontium-89 method.

Three fuming nitric acid precipitations[9,10] of strontium nitrate (8 ml of fuming nitric acid to 5 ml of solution) give a separation from calcium with a decontamination factor of better than 1000 which is sufficient for the strontium-87m scheme; but nitric acid separations alone would be a tedious means of obtaining the decontamination factor of 10^7 which is necessary in the strontium-89 procedure. A chromatographic ion-exchange step is therefore added to purify the strontium from the last traces of calcium and obtain an overall decontamination factor of at least 10^7 from calcium-45.

LERNER AND RIEMAN[11] described the separation of calcium, strontium, and barium on a column of "colloidal Dowex-50" (less than 120 mesh) and their method has been modified to obtain a clear separation of small quantities on a very much smaller column. Addition of 0.05 M citric acid to 1 M lactic acid (pH adjusted to 7 with concentrated ammonium hydroxide) improves the behaviour of strontium on a 4 gram column of Zeo-Karb 225 (7 mm × 155 mm, 50 μ resin particles).

Four grams of air dried resin are weighed out and wetted with the eluent. When the resin has ceased to swell, it is slurried into the glass tube. The column is washed for an hour with the lactate–citrate eluent at 20 ml/h and for another hour with demineralised water. If the column is not prepared in this manner, the separation of calcium and strontium becomes unpredictable. The active solution is fed on to the column as a neutral solution of nitrates and the column washed with two ml of water before beginning the elution. The exact positions of calcium and strontium were checked by using radio-tracers in preliminary experiments and a typical elution curve is shown in Fig. 1.

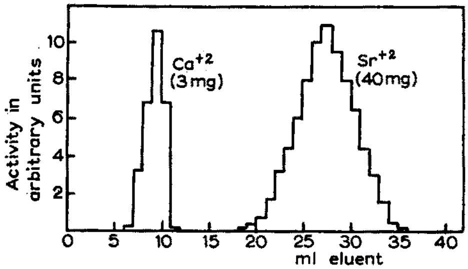

Fig. 1. The elution of calcium and strontium from a 7 mm × 155 mm columm of Zeo-Karb 225 (4 grams of dried resin) with 1 *M* ammonium lactate, 0.05 *M* ammonium citrate at pH 7.

The radiochemical purity of the separated strontium-87m sources can be demonstrated by following the decay of the isotope over at least ten half-lives. Irradiation induces a small proportion of strontium-89 and the activity due to this nuclide appears as a constant (54 day half-life) tail to the decay of the shorter-lived isotope. If the decay curves of the sample and standards plotted upon the same time base can be superimposed, they are of equal radiochemical purity. Subtraction of the "tail" from the decay curve should yield a linear decay curve on semi-logarithmic paper with a half-life very close to 162 min if no other impurities are present.

It is not practicable to prove the radiochemical purity of separated strontium-89 by recording the decay because the half-life is too long to give a decisive answer in a reasonable length of time. Instead, the beta-energies of the sample sources may be compared with the energy of the standards by measuring the source activity through a series of aluminium absorbers and plotting an "absorber curve", *i.e.* the logarithm of activity against absorber thickness. All the experimental curves were coincident with the curves obtained from pure strontium standards.

A few percent of radio-calcium shows up very clearly on an absorber curve by a well-defined increase in the negative slope in the region of 0.50 mg Al/cm^2. Emitters with beta-energies close to that of strontium-89 (1.46 MeV) will not be revealed.

Interfering nuclear reactions

There are several possible nuclear reactions (other than the n,γ-reaction on stron-

TABLE I

SIGNIFICANT STRONTIUM ISOTOPES ARISING FROM THE FISSION OF URANIUM-235 BY THERMAL NEUTRONS

Nuclide	*Half-life*	*Fission yield*	*Beta-energy MeV*	*Proportion*	*Gamma-energy MeV*	*Proportion*
Sr-89	54 day	4.8%	1.46	100%	—	—
Sr-90	28 y	5.9%	0.54	100%	—	—
Sr-91	9.7 h	5.9%	0.62	7%	1.413	7%
			1.09	33%	1.025	33%
			1.36	29%	0.747	7%
			2.03	4%	0.66	22%
			2.66	27%	0.64	33%
Sr-92	2.7 h	6.1%	?	100%	—	—

tium) which may produce radio-strontium: 1. Fission of uranium; 2. Fission of plutonium; 3. Fission of thorium; 4. *n,α* on zirconium; 5. *n,p* on yttrium.

The fission of uranium and plutonium is initiated by thermal neutrons, but the latter may be disregarded as it is an artificial element which is not likely to be met in natural samples. The fission of thorium[12] and the reported *n,α*-reactions on zirconium[13,14] require fast neutrons. The important strontium isotopes arising from fission of uranium-235 are shown in Table I together with related nuclear data[15].

The relative activities of the strontium isotopes which may be expected from the irradiation of a microgram of natural uranium in a thermal flux of 10^{12} neutrons/cm^2-sec can be calculated by the following equation:

$$\text{d.p.m.}/\mu\text{g uranium} = 6.06 \times 10^5\, \varnothing \left(1 - e^{-\frac{0.693t}{t_{\frac{1}{2}}}}\right)$$

where $\varnothing$ is the fission yield of the nuclide sought, $t_{\frac{1}{2}}$ its half-life, and t the time of irradiation.

Calculated activities for strontium under two conditions of irradiation are given in Table II. Table III shows the strontium activity found experimentally and the ratio of the activities of irradiated strontium and fission product strontium. Interference by uranium is proportionately less by the strontium-89 method.

TABLE II

RELATIVE ACTIVITY OF STRONTIUM ISOTOPES ARISING FROM THE THERMAL NEUTRON FISSION OF URANIUM

Nuclide	*3-h irradiation and 10-h cooling period*	*14-day irradiation and 1-week cooling period*
^{89}Sr	44 d.p.m./μg U	3640 d.p.m./μg U
^{90}Sr	0.3 d.p.m./μg U	36 d.p.m./μg U
^{91}Sr	3380 d.p.m./μg U	(decayed)
^{92}Sr	1475 d.p.m./μg U	(decayed)
Totals	4899 d.p.m./μg U	3676 d.p.m./μg U

TABLE III

OBSERVED INDUCED ACTIVITY IN STRONTIUM AND THE ACTIVITY OF STRONTIUM ARISING FROM THE FISSION OF URANIUM

Irradiation and the analytical procedure	*Irradiated natural strontium*	*Fission product strontium*	*Activity ratio*
3-h irradiation ^{87m}Sr method of analysis with added sulphide scavenges	40 c.p.m./μg Sr	720 c.p.m. Sr/μg U	18.0
	62 c.p.m./μg Sr	1200 c.p.m. Sr/μg U	19.4
	30 c.p.m./μg Sr	580 c.p.m. Sr/μg U	19.3
14-day irradiation ^{89}Sr method of analysis	71 c.p.m./μg Sr	825 c.p.m. Sr/μg U	11.6
	65 c.p.m./μg Sr	714 c.p.m. Sr/μg U	11.0
	57 c.p.m./μg Sr	588 c.p.m. Sr/μg U	10.3
	20 c.p.m./μg Sr	220 c.p.m. Sr/μg U	11.0

The international standard granite, G-1 (see Table VII), contains 3.6 p.p.m. of uranium[16] and the same investigators report 0.5 p.p.m. of uranium in the diabase, W-1. The strontium content of these rocks is about 250 p.p.m. and 170 p.p.m. so the fission strontium correction is approximately 14% and 2.5% of the observed activity in the final sources respectively.

Similar comparisons were carried out with thorium, zirconium, and yttrium to determine the levels at which they interfere significantly with a strontium determination. If the acceptable interference level is taken to be 1% of the induced strontium activity, then the relative quantities of each element which can be tolerated without requiring a correction are shown in Table IV.

TABLE IV

THE RELATIVE QUANTITIES OF URANIUM, THORIUM, ZIRCONIUM AND YTTRIUM WHICH WILL CAUSE AN ERROR OF 1% IN THE DETERMINATION OF STRONTIUM BY NEUTRON ACTIVATION

14-day irradiation and 7-days cooling	Uranium	0.0009	times the weight of strontium
	Zirconium	180	times the weight of strontium
	Yttrium	3.3	times the weight of strontium
3-h irradiation and 10-h cooling	Uranium	0.00055	times the weight of strontium
	Thorium	0.4	times the weight of strontium
	Zirconium	750	times the weight of strontium
	Yttrium	250	times the weight of strontium

ANALYTICAL PROCEDURE

The strontium-89 activation procedure

Prepare irradiation phials and weigh 0.1–0.4 g of sample into each phial and seal it. Also prepare two or more standards each containing 100 μg of strontium (standard solution containing 1 mg Specpure strontium per ml). If uranium is present in the samples, prepare several uranium standards (5 μg uranium in solution). Clean the phials externally and pack into an irradiation can. Irradiate for 1–3 weeks at the highest available neutron flux and allow the induced activity to decay for several days before commencing the radiochemistry.

Open the phials and dissolve water or acid-soluble inorganic materials in 5 ml of strontium carrier solution (12 mg Sr/ml) and 1 ml of dilute nitric acid. Add 18 ml of fuming nitric acid. Chill the solution in an ice bath for five minutes before centrifuging. Discard the supernatant acid and dissolve the precipitate in 5 ml of water. Add 8 ml of fuming nitric acid, chill and centrifuge. Repeat the nitrate precipitation twice. If large quantities of sulphate are present in the sample, a carbonate metathesis step precedes the first nitrate precipitation to ensure exchange between radiostrontium and the carrier.

Wet-oxidise organic material by the procedure of G.F. SMITH[17]. First clean the irradiated silica phials externally by heating at 60–70° in a few hundred ml of water containing 20–30 g of strontium nitrate. Remove, rinse, and dry the phials. Relieve internal pressure by breaking the tip off the phial with forceps and then break open at the neck. Place the body of the phial and its contents in a 50-ml beaker containing 4 ml of 72% perchloric acid, 2 ml of concentrated nitric acid, 5 ml of strontium carrier solution, and two drops of 2 *M* sodium chromate solution as a catalyst. Heat cautiously on a hotplate to keep the reaction going steadily without loss by spraying or boiling. When all visible organic matter has been destroyed, remove the broken phial with a pair of glass forceps bent from 2 mm glass rod. Rinse the phial with a few drops of water on removal. Continue the oxidation until the solution changes colour from green to orange. Remove the beaker from the hotplate and cool before pouring the acid into a 50-ml centrifuge tube. Rinse the beaker once with 2 ml of water and add the water to the centrifuge tube. Rinse the beaker with 9 ml of fuming nitric acid, in small portions, and pour the rinsings into the tube, thus precipitating strontium nitrate. Chill the tube and its contents for five minutes in an ice bath. Centrifuge, and discard the acid. Dissolve the strontium nitrate in 5 ml of water. Add 8 ml of fuming nitric acid, chill, centrifuge, and repeat the nitrate precipitation twice to separate the strontium from radio-calcium.

Rock samples are attacked by a sodium peroxide frit.[18] Weigh 3 g of dry granular sodium peroxide into a 25-ml nickel crucible. Break open the irradiation phial and tap the contents into the crucible (Caution: radioactive dust). Mix well using a glass stirring rod 2 mm in diameter. Level the peroxide by tapping the side of the crucible then dust 1 g of sodium peroxide evenly over the surface which must be well covered if the frit is to be successful. Place the crucible in a muffle furnace at 480 ± 20° for twenty to thirty minutes. Remove the crucible from the furnace and plunge the lower half into a beaker of ice-cold water for a minute—a surface colour change indicates when the centre of the mass is cool. Turn the crucible upside down over the mouth of a 400-ml conical beaker containing the dissolving solution and tap the bottom sharply to release the cake. Prepare the dissolving solution as follows:
100 ml water (demineralised); 30 ml industrial methylated spirits; 10 ml concentrated hydrochloric acid; 5 ml strontium carrier solution (12 mg Sr/ml).

The peroxide frit dissolves without violence in the presence of the alcohol. If the reaction is too slow, reduce the quantity of alcohol. Gentle warming aids the final stage of dissolution, but the quantity of acid is sufficient for complete solution. Addition of excess acid will lead to the precipitation of silicic acid.

To remove silica, add 10–20 mg of iron to the warm solution and then add concentrated ammonium hydroxide slowly with stirring until slightly ammoniacal. Filter the precipitate immediately and rinse the beaker several times with water, pouring the rinsings through the filter paper. To the filtrate add 50 ml of 4 *N* sodium carbonate solution. Digest the precipitate on a warm hotplate until the bulk of it begins to settle. Centrifuge. Discard the supernatant solution and add 3 ml of water to the precipitate followed by 9 ml of fuming nitric acid. Chill, centrifuge, and discard the acid. Complete the preliminary separation of the bulk of the calcium by repeating the nitrate precipitation three times, using 5 ml of water and 8 ml of fuming nitric acid for each precipitation.

Strontium and uranium standards are unloaded into 5 ml of strontium carrier solution and the first nitrate precipitation carried out adding 8 ml of fuming nitric acid. The precipitate is dissolved in 5 ml of water and 8 ml of fuming nitric acid added. Repeat the precipitation twice.

After the last fuming nitric acid precipitation, wash the centrifuged strontium nitrate with 5–10 ml of anhydrous industrial methylated spirits. Make the addition quickly with rapid swirling, centrifuge, and discard the alcohol wash. Dissolve the strontium nitrate in 20 ml of water and add 2 ml of 5 *N* hydrochloric acid to make the solution 0.5 *N* in acid. Add 10 mg of antimony carrier and three or four drops of 5 *N* ammonium sulphide reagent. Digest the precipitate in a water bath near the boiling point until it coagulates. Filter, and repeat the scavenge on the filtrate. Test for complete precipitation by adding a drop of sulphide reagent. Discard the precipitates. Add two or three drops of bromothymol blue indicator to the filtrate and then add concentrated ammonia to the neutral point (colour change: yellow to green) followed by six drops in excess. Add 10 mg of cobalt carrier and complete the scavenge as for antimony. Test for complete precipitation of the final cobalt scavenge. Avoid a large excess of ammonium sulphide reagent because it must be destroyed later before attempting the iron hydroxide scavenges.

To the filtrate from the final sulphide scavenge add 0.5 ml of hydrogen peroxide (20 vol) and 5 mg of ferric iron carrier. Insufficient peroxide is indicated by the dark colour of a ferrous sulphide precipitate. If too great an excess of sulphide has been added, a cloud of free sulphur is seen on adding the peroxide. Completion of the oxidation is indicated by the presence of light brown ferric hydroxide. Digest the ferric hydroxide briefly in the water bath. Filter, and repeat the precipitation on the filtrate. Filter while hot and discard the precipitates.

Recover the strontium by heating the solution to 80–90° and adding 10–15 ml of 4 *N* sodium carbonate solution. Digest, centrifuge, and discard the supernatant solution. Wash the precipitate once with water, centrifuge, and discard the washing solution. Add 3 ml of water to the strontium carbonate in the centrifuge tube and run in 9 ml of fuming nitric acid. Chill in an ice bath, centrifuge, and discard the acid. Wash the strontium nitrate with 10–15 ml of anhydrous industrial methylated spirits. Centrifuge and discard the alcohol. Dissolve the nitrate in 2 ml of water and feed to the prepared ion-exchange column (see Experimental Discussion). Rinse the centrifuge tube with 2 ml of water and add to the column as soon as the level of the first 2 ml of solution has dropped to the resin surface. Commence elution with 1 *M* ammonium lactate and 0.05 *M* ammonium citrate as soon as the level of the small volume of wash water falls to the surface of the resin. Collect the eluent in a graduated cylinder. Discard the first nineteen millilitres to pass through the column (calcium is found in the 7–13 ml fraction) and collect the 19–37 ml fraction containing the strontium in another receiver.

Precipitate the strontium with an equal volume (18–20 ml) of saturated ammonium oxalate solution. Permit the slow-forming precipitate to settle before centrifuging. Discard the supernate. Wash the precipitate twice with water, centrifuge, and discard the washings. Dissolve the strontium oxalate in 20 ml of water and a minimum volume (about 1 ml) of 5 *N* hydrochloric acid. Heat to 80–90° in the water bath and very slowly add concentrated ammonium hydroxide dropwise with constant swirling until a permanent precipitate begins to form. Set aside in the water bath to digest for a few minutes and then make ammoniacal. Too rapid addition of ammonia in the second precipitation results in an amorphous precipitate which creeps and is difficult to wash and to slurry evenly on to the counting tray. Cool, centrifuge, and discard the solution. Wash the strontium oxalate twice with 10–15 ml portions of water and twice with similar volumes of anhydrous industrial methylated spirits. Centrifuge each time and discard the washings. Slurry the precipitate with anhydrous alcohol and use a dropping pipette and rubber bulb to transfer the slurry from the centrifuge tube to a weighed beta-counting tray. Tap the tray lightly to settle the precipitate compactly on the bottom of the tray, then dry under an infra-red lamp. Weigh the sources and beta-count.

Correct the observed beta-activity for the background of the counter and, if the range of counts between standards and samples is unduly high, make the appropriate corrections for counter dead-time. Calculate the chemical yield of the source on the basis of the initial quantity of carrier used (60 mg Sr carrier = 132.6 mg of $SrC_2O_4 \cdot H_2O$) and correct the observed activity accordingly. Apply the appropriate factor to correct the beta-count for the self-absorption of the source. Calculate the factor '*f*' for the standards:

$$'f' = \frac{\mu\text{g strontium irradiated}}{\text{corrected activity (c.p.m.)}} = \mu\text{g Sr/c.p.m.}$$

Multiply the corrected activity of the samples by '*f*' to find the weight of strontium originally present in the sample. From this figure and the weight of sample taken, calculate the strontium content.

The strontium-87m activation procedure

Irradiate the samples in either silica phials or polythene ampoules for 2½–3 hours together with strontium standards. Allow the very short-lived activities to decay for two hours before unloading the samples. Dissolve the materials as described in the method for strontium-89 using only 36 mg of strontium carrier, and precipitate the strontium as nitrate. Centrifuge and discard the acid. Dissolve the strontium nitrate in 5 ml of water and add 8 ml of fuming nitric acid. Repeat this precipitation with nitric acid twice (repeat three times for samples like bone ash with a high calcium/strontium ratio). Wash the final precipitate with anhydrous alcohol as already described and dissolve it in 20 ml of water.

Sulphide scavenges are omitted and the two ferric hydroxide scavenges follow immediately upon the last strontium nitrate precipitation. Make the solution slightly ammoniacal and add 5 mg of ferric iron carrier. Digest briefly near the boiling point to aid filtration. Filter, and repeat the hydroxide precipitation with additional iron carrier.

Carefully neutralise the filtrate from the hydroxide scavenges with nitric acid (bromothymol blue indicator). Add to the neutral solution 1 ml of 6 *N* acetic acid, 2 ml of 6 *M* ammonium acetate, and 10 mg of barium carrier. Put the centrifuge tube in the water bath and heat almost to boiling. Precipitate barium by the slow addition of 1 ml of 1.5 *M* sodium chromate reagent. Swirl the contents of the tube constantly as the reagent is added. Digest for a few minutes in the water bath, centrifuge and filter. (The precipitate is finely divided, but does not pass through the filter paper if it is centrifuged before filtration). Repeat the scavenge on the filtrate, adding 10 mg of barium slowly to the hot solution.

Add 2 ml of concentrated ammonium hydroxide to the filtrate from the second barium scavenge. Heat to 80–90° and add 5–10 ml of saturated ammonium oxalate solution. Allow the solution to cool. Centrifuge, and discard the supernate. Wash the precipitated strontium oxalate twice with water, centrifuging each time, and discard the washings. Dissolve the precipitate and reprecipitate it as in the strontium-89 method. Wash twice with water, twice with anhydrous alcohol, and slurry on to a weighed beta-counting tray. Dry under an infra-red lamp, weigh, and beta-count the source. Correct the observed activity for chemical yield (36 mg Sr carrier = 79.6 mg $SrC_2O_4 \cdot H_2O$), self-absorption in the source, and for decay during the counting interval. Compare the corrected activity with that of the standards which have been treated similarly.

Correction factors for absorption and backscatter of radiation from strontium-89 and strontium-87m sources

For the long-lived isotope, irradiate 5–10 mg of strontium (as strontium carbonate, "Specpure") for two weeks in a flux of 10^{12} neutrons/cm^2-sec and allow a cooling period of one week. Dissolve the irradiated strontium in the presence of 60 mg of carrier strontium and pass the strontium through the complex analytical method to ensure radiochemical purity. Before the final oxalate precipitation, add a further 300 mg of strontium carrier and dilute the solution five-fold. Heat the solution to 80–90° and complete the precipitation with 5–10 ml of saturated ammonium oxalate solution and ammonium hydroxide. Centrifuge, wash the oxalate precipitate thoroughly with water and then with anhydrous methylated spirits. Slurry the strontium oxalate on to weighed counting trays endeavouring to produce a series of twelve sources between 30 and 85 mg at intervals of 5 mg. In practice it is simpler to obtain a random distribution of weights. Dry the sources under an infrared lamp, weigh and count. The precipitate can be washed off the trays with alcohol and the sources re-made for a second series of observations.

Correct the observed activity for the background of the beta-counter, and if necessary for the dead-time of the counter. Plot the specific activity (c.p.m./weight in mg) against the source weights as shown in Fig. 2. Draw a smooth curve through the experimental points. In the range between 30 and 50 mg the curve is fairly flat and this value of the specific activity is conveniently taken as the reference value and all others referred to it. Correction factors for selected weights are calculated from the smoothed curve of Fig. 2 and plotted as in Fig. 3. Corrections are almost negligible and need be applied only when particular care is being taken to eliminate all possible sources of error.

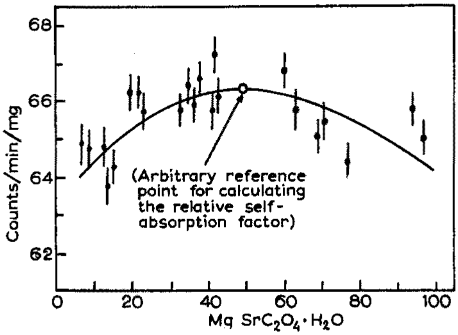

Fig. 2. Variation of specific activity of strontium-89 with source weight.

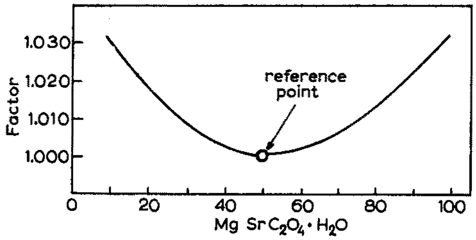

Fig. 3. The relative correction factor for the self-absorption of strontium-89 sources.

For the strontium-87m isotope, no more than 5 mg of strontium need be irradiated for 2½–3 h in order to have ample activity after radiochemical purification (abbreviated method). Add about 200 mg of additional strontium carrier before the final oxalate precipitation, dilute the solution as before and complete the precipitation. After the sources are dried, weigh and count them. Correct the observed activity for decay over the period of counting. Plot the results (see Fig. 4) in the same manner as for strontium-89.

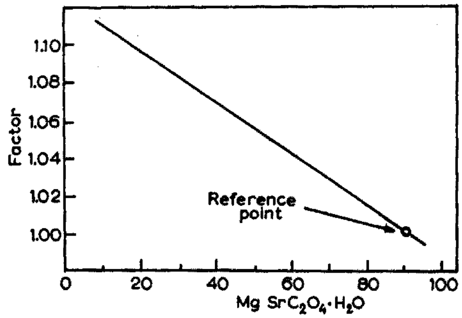

Fig. 4. The relative correction factor for the self-absorption of strontium-87m sources.

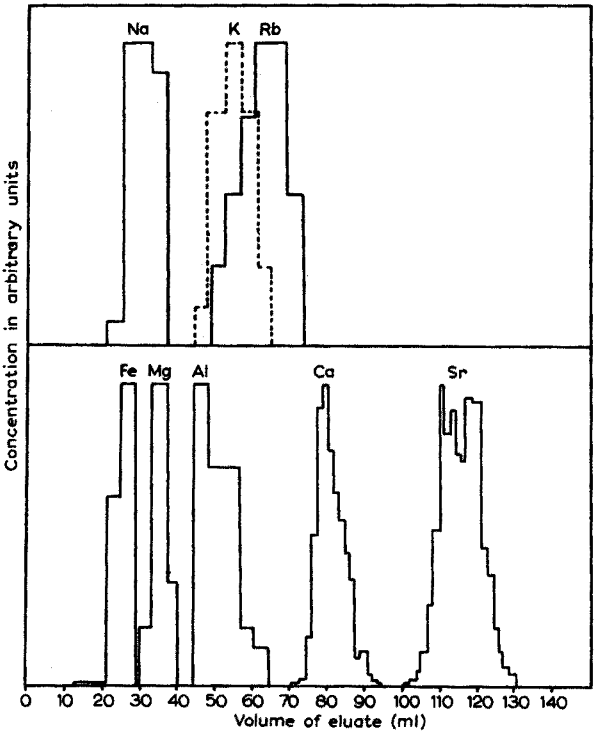

Fig. 5. The elution of Fe, Na, Mg, Al, K, Rb, Ca and Sr from a 12 mm × 210 mm column of Zeo-Karb 225 (15 grams of dry resin) with 2.5 *N* hydrochloric acid. (For clarity the alkali metals are plotted separately from the other elements.)

STABLE ISOTOPE DILUTION ANALYSIS

Experimental discussion

This method requires the addition of a known quantity of enriched strontium-84 tracer to the sample, followed by separation of strontium in a state of purity suitable for a mass spectrometric analysis. Normal strontium (82.5% ^{88}Sr) may then be determined from the difference between the ^{84}Sr/^{88}Sr isotopic ratios of the tracer and of the mixture.

After the addition of tracer the samples were dissolved either in a mixture of hydrofluoric and perchloric acids, or in one of nitric and perchloric acids. Samples of bone ash and soil leachings were first treated with very dilute hydrochloric acid over a period of 1–2 h to avoid losses by spraying. Strontium was then separated by cation-exchange chromatography, the method being very similar to one described by ALDRICH[19]. The sample was placed on a column of Zeo-Karb 225 and eluted with 2.5 N hydrochloric acid. The strontium fraction was evaporated to dryness, again after the addition of nitric acid, and then used in the mass spectrometer. Fig. 5 shows the relative elution positions found for Fe, Na, Mg, Al, K, Rb, Ca and Sr. A mixture of suitable salts of these elements was dissolved in 2.5 N hydrochloric acid, placed on the column, eluted, and 36 fractions of 3–4 ml collected. The first six of these elements were located by emission spectroscopy; these analyses were kindly made by Mr. F. T. BIRKS, Analytical Chemistry Branch, Harwell. Calcium and strontium were located with radioactive tracers.

ALDRICH[20] stated that some of the aluminium was often present in the strontium fraction, so the elution position of this element was checked under a variety of conditions. In each case about 100 mg of aluminium was placed on the column, eluted, and located in the fractions by precipitation with ammonia. Provided an aluminium salt was merely dissolved in hydrochloric acid and then eluted from the column the elution position found was similar to that shown in Fig. 5. If the aluminium salt was first treated with a mixture of hydrofluoric and perchloric acids, either alone or mixed with granite (G–1), it was eluted from the column by a smaller volume, usually appearing in the fraction 15–25 ml, presumably because of the formation of a fluoride complex. The elution position of strontium was also determined under various conditions, but no significant variation was found.

It must be emphasized that the elution curve shown in Fig. 5 shows only the *relative* elution positions of the various elements. The absolute positions may vary between apparently similar batches of resin and it is essential to make an investigation with radioactive strontium tracer for each batch. For example in one case, after the columns had been refilled with fresh resin, strontium required a smaller volume of acid for complete elution, and if the fraction collected had been based on the initial calibration it could have contained as little as 0.1 – 1% of the strontium. Under these conditions any contamination acquired after the ion-exchange stage would have a disproportionately large effect and could cause extremely large errors.

For samples containing high strontium concentrations it was possible to make a determination without an ion-exchange separation. The sample and tracer were merely dissolved in nitric acid and a portion used directly for a mass spectrometric analysis. Large rubidium beams were produced in the mass spectrometer, but by heating the sample on the filament overnight, rubidium could be evaporated from the sample and the rubidium ion beam intensity reduced to a negligible level; an analysis could then be made for strontium. Results obtained in this way were of poor precision but agreed well with later determinations made with a separation. Table V records these analyses and also the mean values and standard deviations of later determinations made with a separation. In the case of sample 7 this direct analysis for strontium was made in the presence of a 400-fold excess of calcium.

TABLE V

DETERMINATIONS OF STRONTIUM IN SOIL LEACHINGS MADE BOTH DIRECTLY AND AFTER AN ION-EXCHANGE SEPARATION

Sample	*Direct determinations p.p.m.*		*Comparison determinations p.p.m.*
Soil leachings (West Virginia) (Sample No. 7)	610 620 660	630	616.5 ± 1.2
Soil leachings (Mississippi) (Sample No. 8)	2890 2940 3150	2990	2973 ± 38

Isotopic analyses were made with a 6″ radius of curvature 60° sector mass spectrometer containing a surface ionisation source and the conventional detector system of a Type 954 electrometer valve and a dc-amplifier. The measured $^{84}Sr/^{88}Sr$ isotopic ratios were used to calculate the quantity of strontium in a sample with the following equation:

$$x = y \cdot \frac{R_T - R_M}{R_M - R_N} \cdot \frac{84R_{N_4} + 86R_{N_6} + 87R_{N_7} + 88}{84R_{T_4} + 86R_{T_6} + 87R_{T_7} + 88}$$

where: x = the mass of strontium present in the sample; y = the mass of strontium tracer added; R_M = the $^{84}Sr/^{88}Sr$ isotope ratio for the mixture; R_N = $^{84}Sr/^{88}Sr$ isotope ratio of normal strontium; R_T = the $^{84}Sr/^{88}Sr$ isotope ratio of tracer strontium; R_{N_4} = the $^{84}Sr/^{88}Sr$ isotope ratio of normal strontium; R_{N_6} = the $^{86}Sr/^{88}Sr$ isotope ratio of normal strontium, etc.

The strontium-84 tracer had the following measured isotopic composition: ^{84}Sr 50.5%, ^{86}Sr 12.0%, ^{87}Sr 3.6%, ^{88}Sr 33.9%. The concentration of a solution of this tracer was determined by isotope dilution with a standard prepared from Johnson Matthey's "Specpure" strontium carbonate. About 1 g of strontium carbonate was dried at 180° for 24 h and used to prepare a solution of accurately known concentration of about 10 μg/ml. Aliquots of this dilute standard were added to aliquots of the tracer and the $^{84}Sr/^{88}Sr$ ratios of the mixtures determined. The coefficient of variation for five determinations of the concentration was 1.5%.

Blank corrections were determined by processing a portion of the tracer under the same conditions as those used for the samples. A blank correction was not usually greater than 0.3 μg. It never represented more than 4% of the quantity of strontium determined, and the average blank correction was about 1%. Hydrochloric acid was purified by distillation in quartz apparatus, and water by mixed bed ion exchange. Otherwise AnalaR grade reagents were used. All evaporations were made under glass or silica covers. Solutions came into contact only with platinum, silica or polythene.

The cation-exchange columns were washed with 300 ml of 2.5 *N* hydrochloric acid before each series of determinations.

ANALYTICAL METHOD

Preparation of cation-exchange columns

The resin used is Zeo-Karb 225, particle size 50 μ diameter, supplied by "The Permutit Company Ltd". Place 2 lb of resin in a suitable tube and wash with ~20 l of 2.5 *N* hydrochloric acid. Wash the resin thoroughly with water, and then spread out on filter paper to dry for several days. When dry, store in a polythene bottle and mix thoroughly. This provides sufficient dry resin for about thirty columns.

Weigh out 15 g of resin and transfer as a slurry into a column. A piece of ½″ polythene tube 10–12″ long fitted with a silica tip forms a suitable container. The resin is retained with a plug of cotton wool at each end. Wash the column with 300 ml of 2.5 *N* hydrochloric acid before each determination.

Determine the elution position for strontium with one column. Place an aliquot of strontium-89 tracer on the column and elute with 2.5 *N* hydrochloric acid. Discard the first 60 ml of eluate and then collect 3–5 ml fractions. To each fraction add 10 mg of strontium carrier, neutralise with ammonia and add excess sodium carbonate reagent. Wash the precipitate first with water and then with industrial methylated spirits, and transfer as a slurry in industrial methylated spirits on to an aluminium tray for beta-counting.

TABLE VI

THE STRONTIUM CONTENT IN p.p.m. OF EIGHT INTERNATIONAL SAMPLES OF BIOCHEMICAL INTEREST DETERMINED BY NEUTRON ACTIVATION AND STABLE ISOTOPE DILUTION, TOGETHER WITH COMPARATIVE SPECTROGRAPHIC RESULTS

Sample No.	*Material*	*Neutron activation results*		*Isotope dilution results*	*Spectrographic results*
		strontium-89 method	*strontium-87m method*		
1	Alfalfa	124	128	118 120 126 121.5 ± 5	120, 100, 100
2	Clover and rye grass	64	68	64 67 65 ± 2	55
3	Milk powder (Utah)	8 ± 1	7 ± 1	7.3 7.3 7.8 7.5 ± 0.3	7 ± 1
4	Milk powder (Italy)	8 ± 1	6 ± 1	5.8 6.2 6.4 6.2 ± 0.4	7 ± 1
5	Bone ash (Baltimore, N.J.)	310	306	293 314 325 311 ± 17	240
6	Bone ash (Camden, N.J.)	445	431	427 428 440 432 ± 10	300
7	Soil leachings (West Virginia)	658	656	615.5 616.5 618 617 ± 9	880, 710, 890
8	Soil leachings (Mississippi)	3000	2980	2930 2980 3010 2975 ± 60	3500

Treatment of samples

Weigh out a suitable aliquot of strontium-84 tracer in a platinum dish and evaporate to dryness. Weigh out the sample and decompose with hydrofluoric and perchloric acids, or with nitric and perchloric acids. Dissolve the residue in 3 ml of 2.5 *N* hydrochloric acid and place on a column. Wash with 1–2 ml of water and then elute with 2.5 *N* hydrochloric acid. Collect the strontium fraction in a polythene bottle and evaporate to dryness in the original platinum dish. Heat to redness to decompose organic material. Add a few ml of nitric acid and evaporate to dryness. Dissolve the residue in one drop of demineralised water and transfer to the filament of a mass spectrometer source unit.

RESULTS AND DISCUSSION

The results of strontium analyses by neutron activation and isotope dilution on

TABLE VII

THE STRONTIUM CONTENT IN p.p.m. OF TWO STANDARD ROCK SAMPLES, TWO MISCELLANEOUS SAMPLES OF BONE ASH AND FOUR OF SODIUM SULPHATE

(The precision of the neutron activation figures is estimated to be about ±3%)

Material		*Neutron activation strontium-89 method*	*Stable isotope dilution*		*Comparative analyses*[a]
Granite, G-1		252[b]	224 238 240 241	236 ± 9	233 I.D., Herzog[7] 262 I.D., Turekian[8] 287 E.S., Turekian[8] 120 E.S., Murata[8] 220 E.S., Harvey[8] 250 E.S., Ahrens[8] 280 E.S., Nockolds[8] 900 E.S., Mitchell[8]
Diabase, W-1		172[b]	177 177 181 184	180 ± 4	177 I.D., Herzog[7] 178 I.D., Turekian[8] 172 E.S., Turekian[8] 120 E.S., Murata[8] 180 E.S., Harvey[8] 180 E.S., Nockolds[8] 250 E.S., Ahrens[8] 420 E.S., Mitchell[8]
Bone ash No. 37 (from Dr. S. R. Stitch)		143	—		144 N.A., Sowden and Stitch[2]
Bone ash No. 38 (from Dr. S. R. Stitch)		136	—		146 N.A., Sowden and Stitch[2]
Sodium sulphate	I	12	—		
	II	41	41.6 42.3	42 ± 2	
	III	13	—		Sample supplied as a test. Believed to be 2 p.p.m. in Sr, spiked with a further 10 p.p.m.
	IV	58	51		

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[a] I.D. = Isotope dilution. E.S. = Emission spectroscopy. N.A. = Neutron activation.

[b] Corrected for presence of uranium.

TABLE VIII

THE STRONTIUM CONTENTS OF SAMPLES FROM THE SKAERGAARD INTRUSION, EAST GREENLAND

Sample	*Uranium content p.p.m. and method of determination*	*Strontium content p.p.m. calculated from total Sr radioactivity*	*Correction for uranium (p.p.m. Sr)*	*Strontium content corrected mean value p.p.m.*
E.G. 1851 Perpendicular Feldspar Rock	0.3 Estimated	244 246 250 249	—2	245
E.G. 4328 Upper Ferrogabbro	0.4–0.5 Fluorimetry	188 187 196 193	—4	187
E.G. 4329 Upper Ferrogabbro	0.4 Estimated	221 217 224 221	—4	217
E.G. 4330 Fayalite Ferrogabbro	2 Estimated	457 453 464 464	—18	442
E.G. 4332 Hedenbergite Granophyre	1.1 Radioactivation	255 256 248 252	—7	246
E.G. 4427 Middle Gabbro	0.27 Fluorimetry	177 175 171 169	—2	171
E.G. 4489 Transgressive Granophyre Sill	3.5 Radioactivation	336 326 319 332 333	—23	306
E.G. 4507 Chilled Marginal Gabbro	0.2 Radioactivation	268 268 269	—1	267
E.G. 4526 Gabbro Picrite	0.07 Radioactivation	112 116 114 115	—	114
E.G. 5181 Lower Ferrogabbro	0.1 Fluorimetry	309 317 298 313	—1	308

eight international samples of biochemical interest are given in Table VI. Almost a year elapsed between the series of analyses employing the strontium-89 isotope and those using the strontium-87m method. Replicate neutron activation analyses lead to an estimated precision of 3% with the exception of the results on milk powders where the uncertainty is higher because the quantity of strontium is close to the lower limit of the procedure. The uncertainty quoted for each result obtained by stable isotope dilution analysis represents the overall standard deviation for the set of determinations and for the calibration of the strontium-84 tracer. The last column of Table VI shows the independent spectrographic analyses submitted by Mr. F. W. J. GARTON (U.K.A.E.A., Woolwich Outstation).

Omitting the results on milk powders, the average agreement between the two neutron activation methods is ±2% of the mean. Bearing in mind the estimated precision of 3%, neither method appears to suffer from an inherent bias. The figures obtained by stable isotope dilution and neutron activation are in satisfactory agreement, with the possible exception of the sample of West Virginia Soil Leachings. The spectrographic figures also agree within the estimated accuracy of the data (±20%) with the results obtained by the other methods on the first four samples in Table VI. The spectrographic results are notably lower for the bone ash and higher for the soil leachings than the figures obtained by neutron activation and isotope dilution.

Table VII sets out comparative analytical results for two samples of bone ash (supplied by Dr. S. R. STITCH, Radiobiological Unit, Medical Research Council, A.E.R.E.), four samples of sodium sulphate, and samples of standard granite, G-1, and standard diabase, W-1.

Table VIII reports a series of neutron activation analyses for the strontium content of certain rocks from the East Greenland Skaergaard intrusion. These samples were kindly supplied by Prof. L. R. WAGER and Dr. E. A. VINCENT of the Department of Geology and Mineralogy, University of Oxford. A uranium standard was irradiated with each of these samples and a correction for fission product strontium applied to the sample analyses in proportion to their uranium content. The figures for the uranium content were obtained from either fluorimetric or neutron activation analyses or, where no analyses were available, from estimates based upon analyses of other comparable rocks. The average correction was 3%.

SUMMARY

Methods are described for the determination of strontium in a variety of materials by neutron activation and by stable isotope dilution. The samples for neutron activation analysis, together with strontium standards, are irradiated in a high neutron flux for a few hours (strontium-87m, 2.7 hour half-life) or for a week or more (strontium-89, 54 day half-life). After dissolving in the presence of strontium carrier, samples and standards are subjected to radiochemical purification. The beta activity induced in the samples and standards is compared and the quantity of strontium in the sample calculated by proportion. Somewhat less than one microgram of strontium can be determined. For stable isotope dilution analysis, the sample is mixed with a known quantity of strontium-84 tracer and dissolved in a mixture of hydrofluoric and perchloric, or nitric and perchloric acids. Strontium is then usually separated by cation-exchange chromatography it is possible to obtain spectrometric analysis, but for samples with large strontium concentrations before making the mass results without a separation. The main source of systematic error is strontium contamination, but with simple precautions this may be restricted to 1–4% of the quantity of strontium determined and a correction applied.

RÉSUMÉ

Des méthodes radiochemiques sont décrites pour le dosage du strontium, soit par activation au moyen de neutrons, soit par dilution isotopique. Pour l'analyse par activation, on irradie dans un flux de neutrons simultanément l'échantillon à analyser et un strontium étalon; on compare les activités bêta et on peut alors calculer la teneur en strontium de l'échantillon. Pour l'analyse par dilution isotopique, l'échantillon est mélangé avec un traceur (strontium-84) et dissous dans un mélange d'acides. Le strontium peut être ensuite séparé par chromatographie avant de procéder à l'analyse spectrométrique de masse.

ZUSAMMENFASSUNG

Beschreibung radiochemischer Methoden zur Bestimmung von Strontium durch Aktivierung mit Neutronen oder nach der Isotopen-Verdünnungsmethode. Bei dem Aktivierungsverfahren wird eine Strontiumprobe als Vergleichssubstanz mit-bestrahlt. Durch Vergleich der Aktivitäten lässt sich der Strontiumgehalt berechnen. Bei der Isotopen-Verdünnungsmethode wird die Substanz mit Strontium-84 als Tracer gemischt, das Strontium über einen Jonenaustauscher abgetrennt und anschliessend massenspektrometrisch bestimmt.

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EFFECT OF ABSORBANCY UPON RAMAN INTENSITIES IN LIQUIDS

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In recent studies carried out by the author on the Raman effect in liquid an extremely noticeable effect upon Raman intensities was observed which was directly correlated to the absorbancy of the materials being studied. Placzek[1] and several recent authors[2,3] have considered the alteration in Raman intensity as the exciting line enters an absorption band. It is stated that the intensity rises due to a resonance phenomenon which results in an increase in the transition probability. In addition to the resonance phenomenon encountered it is also felt in the light of recent studies[4] that the absorbancy of the material in question quite frequently plays a deciding factor in the resultant Raman intensity. Consequently it was felt desirable to apply absorbancy laws to the Raman process. In particular the physical circumstance of peripheral illumination by means of a helical lamp upon a Wood's model Raman tube was considered[5].

Raman excitation of a liquid can be visualized as occurring in three steps: light traverses the solution, interacts with the solution producing Raman radiation, and then traverses the solution until it is collected at the monochromator slit. For the particular case of illumination of a Wood's tube we may consider that illumination by a helical lamp can be pictured as illumination by a cylinder of light. The light from a given cross section of the Raman tube then passes the length of the tube and is gathered by a suitable lens. For a given cross section of the tube light must travel a path r, see Fig. 1, to the point of excitation O. The excitation intensity at O is given by the Lambert-Beer law:

$$I_1/I_0 = e^{-a_1 c r(\theta)}$$

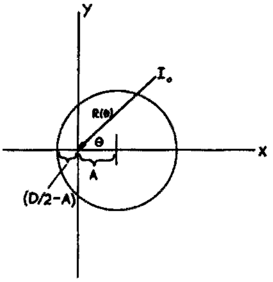

Fig. 1. Cross section of the Raman tube.

where I_1 and I_0 are respectively the final and initial intensity; a, the absorbancy coefficient for the Raman excitation line; c, the concentration of solute; and $r(\theta)$, the distance r as a function of radial angle of illumination. If now we consider the full range of r and integrate the intensity over the whole cross section of the tube we find the illumination intensity at a given cross section is:

$$I_1/I_0 = \frac{4\pi}{a_1^2 c_1^2} (1 + e^{-a_1 c_1 D} - 2\, e^{-a_1 c_1 D/2})$$

where D is the diameter of the tube. The contribution of axial illumination is not considered in this expression as its contribution is small relative to radial illumination. The material at a given point of illumination may scatter by either a Raman or Rayleigh process. The former process may be represented as:

$$I_2/I_1 = K_1 c_1$$

where K_1 is the transition probability of the Raman process, and c_1 is the concentration of specie undergoing excitation. The Rayleigh scattering process may originate from either the solvent or solute; thus for the Rayleigh process we have:

$$I_2/I_1 = K_{\text{solvent}}\, c_{\text{solvent}} + K_{\text{solute}}\, c_{\text{solute}}$$

The light reaching the condensing lens must travel a path along the length of the tube from the point of excitation. In most liquids the case of back scattering is negligible and will not be considered. The total intensity at the face of the Wood's tube is given by the integration of light intensity over the length of the tube L:

$$I_f/I_2 = 1/a_2 c_1 (1 - e^{-a_2 L c_1})$$

where a_2 is the absorbancy coefficient for the Raman line. The complete process for

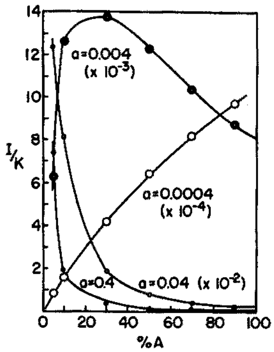

Fig. 2. Calculated intensity for variation in a ($a_{11} = a_{12}$), $D = 5.1$ cm, $L = 20.3$ cm.

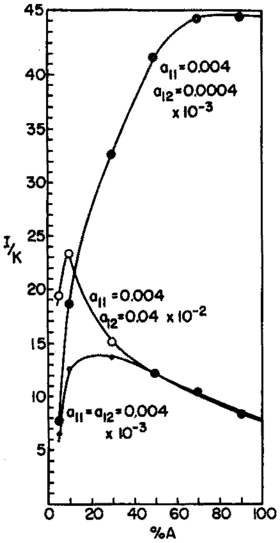

Fig. 3. Calculated intensity for variation in a_{11}, a_{12}, $D = 5.1$ cm, $L = 20.3$ cm.

Raman scattering is thus given by:

$$I_1/I_0 \cdot I_2/I_1 \cdot I_1/I_2 = I_f/I_0$$

or:

$$I_f/I_0 = \frac{4\pi}{a_1^{\,2} c_1^{\,2}} \left[e^{-a_1 c_1 D} + 1 - 2\, e^{-a_1 c_1 D/2}\right] \left[K_1 c_2\right] \left[1/a_2 c_1 \left(1 - e^{-a_1 L c_1}\right)\right]$$

For the Rayleigh scattering process the K_1c_1 term is substituted by:

$$\Sigma\, K_1' c_1'$$

i.e. the summation of scattering from all components present. The variation in intensity with concentration as effected by the parameters is shown in Figs. 2 through

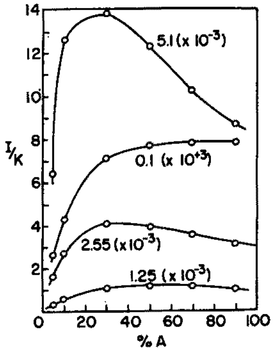

Fig. 4. Calculated intensity for variation in D, $a = 0.004$, $L = 20.0$ cm.

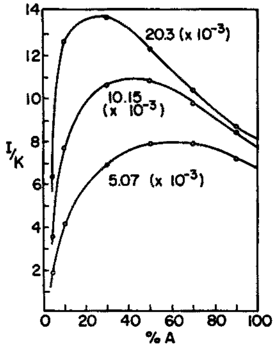

Fig. 5. Calculated intensity for variation in L, $a = 0.004$, $D = 5.1$ cm.

5. In Fig. 2 it is to be noted that there is a general trend of increasing intensity for decreasing absorbancy coefficient also we see that for high absorbancy coefficient the intensity rises to a maximum, the more abruptly the larger the absorbancy coefficient, and then drops, again the more abruptly the larger the coefficient. As the absorbancy coefficient diminishes the trend is reversed until at low absorbancy coefficient, the trend is completely increasing with concentration. Fig. 3 shows the effect of independently altering a_1 and a_2. Fig. 4 shows the effect produced on the intensity by alteration of the diameter of the Wood's tube. For large diameter the intensity goes through a maximum and then declines. This maximum becomes less prominent the smaller the diameter of the tube. It is to be noted that the total intensity falls in general with decreasing diameter. Finally in Fig. 5 the variation in length of Wood's tube is considered. For greatest length of Wood's tube the intensity again proceeds through a maximum and then declines. With decreasing tube length the overall intensity fall and the maximum becomes less pronounced. Thus the absorbancy coefficient of a given material may be seen to indicate desirable physical sizes of equipment as well as preferable concentration ranges for study.

ACKNOWLEDGEMENT

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SUMMARY

An equation is proposed relating Raman intensity of liquids to the absorbancy of the liquid and geometric factors in the design of the Raman tube. Calculations are carried out which show the effect of concentration on intensity for variation in absorbancy, length and diameter of Raman tube.

RÉSUMÉ

Une équation est proposée, montrant la relation entre l'intensité Raman dans les liquides et leur absorption, ainsi que les dimensions du tube Raman (longueur, diamètre).

ZUSAMMENFASSUNG

Die Beziehungen zwischen Raman Intensität, und Absorptionsfähigkeit von Flüssigkeiten sowie der Einfluss der geometrischen Faktoren der Raman Röhren werden durch eine Gleichung ausgedrückt.

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

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INTRODUCTION

The organic reagent 1,1'-dianthrimide is normally applied for spectrophotometric determination of small amounts of boron. In an earlier publication[1] the photometric determination of germanium with 1,1'-dianthrimide was described; in the present paper the determination of tellurium with 1,1'-dianthrimide is proposed. The reactions of boron, germanium and tellurium with 1,1'-dianthrimide take place in concentrated sulphuric acid, the colours of the complexes being developed by heating.

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

INSTRUMENTS AND REAGENTS

Instruments

Extinction measurements were made with a Zeiss spectrophotometer PMQ II, 0.5-cm glass cells being used.

Reagents

The spectrographically standardized tellurium dioxide (Johnson, Matthey & Co.) contained the following amounts of impurities: 2 p.p.m. tin; 1 p.p.m. copper, iron, lead, magnesium, silicon and sodium; and less than 1 p.p.m. calcium, manganese and silver. Concentrated sulphuric acid (95–97%) and other chemicals (including 1,1'-dianthrimide) were of reagent grade quality. The strength of the stock solution of sulphuric acid was determined volumetrically and found to be 96.12%. Ordinary distilled water from an all-metal still was used. The solutions were prepared and heated in 50-ml bottles (Jena Geräteglass) with ground glass stoppers. The solutions were heated in a thermostatically controlled drying oven of standard construction.

Standard solutions

Tellurium dioxide (62.5 mg) was dissolved in some ml of 1% sodium hydroxide solution. After dilution to 50 ml with 1% sodium hydroxide solution, the standard solution was stored in a plastic bottle. This solution contained 1 mg of tellurium per ml. A 1% solution of sodium hydroxide served as blank. 1,1'-Dianthrimide (1.250 g) was dissolved in 96.12% sulphuric acid, and the solution was diluted to 250 ml with the same acid. The solution contained 5 mg of 1,1'-dianthrimide per ml.

EXPERIMENTAL

Absorption curves

The absorption curve of a 10^{-4} *M* solution of 1,1'-dianthrimide in concentrated sulphuric acid gave (when measured against concentrated sulphuric acid) small and nearly constant extinction values in the range 500 to 700 mμ. At lower wavelengths the extinction increased rapidly, and at higher wavelengths the extinction decreased.

In more concentrated solutions (about 10^{-3} *M*) of 1,1′-dianthrimide a broad absorption band appeared at about 650 mμ; in more dilute solutions (about 10^{-5} *M*) a maximum was observed at about 350 mμ.

The complex between tellurium and 1,1′-dianthrimide showed two absorption maxima at 550 and 600 mμ. (The absorption maxima of the boron 1,1′-dianthrimide and the germanium 1,1′-dianthrimide complexes are found at about 630 and 660 mμ, respectively).

Effect of concentration of sulphuric acid

Before testing the validity of the Lambert-Beer law, the effect of concentration of sulphuric acid on the development of the colour was investigated for solutions heated for 16 h at 70°.

A series of solutions was prepared in which the concentrations of tellurium and 1,1′-dianthrimide were kept constant, while the concentration of sulphuric acid was varied. 0.2 ml of the tellurium standard solution, 20 ml of the different sulphuric acids and 5 ml of the 1,1′-dianthrimide solution were pipetted into 50-ml bottles. The series of blank solutions prepared contained 0.2 ml of 1% sodium hydroxide solution, 20 ml of sulphuric acid and 5 ml of 1,1′-dianthrimide standard solution. After heating, the extinctions of the sample solutions were measured against the corresponding blanks at the wavelength of the absorption maximum 600 mμ. The data obtained are given in Table I.

TABLE I

EFFECT OF CONCENTRATION OF SULPHURIC ACID ON THE DEVELOPMENT OF THE COLOUR OF THE TELLURIUM 1,1′-DIANTHRIMIDE COMPLEX

Concn. (in per cent) of the sulphuric acid added	82.67	86.38	92.78	96.12	97.85	98.75	99.45
Extinctions at 600 mμ	0.066	0.126	0.230	0.310	0.336	0.334	0.212

It is seen from Table I that the strength of sulphuric acid was not critical when the concentration of the 20 ml of acid added was within the range 96.12 to 98.75%. Above and below this range lower extinction data were obtained.

Calibration curve

On the basis of the above results a calibration curve was plotted for a series of solutions containing 20 ml of 97.85% sulphuric acid. Into 50-ml bottles were pipetted 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 ml of tellurium standard solution. Volumes of less than 0.6 ml were diluted to that volume with 1% sodium hydroxide solution. Then 20 ml of 97.85% sulphuric acid and 5 ml of 1,1′-dianthrimide standard solution were added. The blank solution consisted of 0.6 ml of 1% sodium hydroxide solution, 20 ml of 97.85% sulphuric acid and 5 ml of 1,1′-dianthrimide standard solution. After 16 h of heating at 70° the extinctions of the sample solutions were measured against the blank at 600 mμ. The data obtained are given in Table II.

It is seen from Table II that a negative deviation from the Lambert-Beer law was obtained within the concentration range examined.

TABLE II

CALIBRATION CURVE FOR THE DETERMINATION OF TELLURIUM WITH 1,1'-DIANTHRIMIDE

Mg tellurium taken (A)	*Extinction (E)*	*Extinction index (E/A)*
0.1	0.168	1.68
0.2	0.332	1.66
0.3	0.470	1.57
0.4	0.588	1.47
0.5	0.700	1.40
0.6	0.840	1.40

Effect of temperature

In concentrated sulphuric acid tellurium and 1,1'-dianthrimide react very slowly. The rate of reaction increases with temperature, but even at 70° the colour development was quite slow.

On the basis of unpublished results from an investigation of the boron 1,1'-dianthrimide complex, it is possible to indicate the effect of higher heating temperatures. When solutions of boron and the reagent were heated at 80° or higher, the extinctions decreased compared with solutions heated at 70°. At higher temperatures a red colour appeared in addition to the colour of the complex, the red colour probably originating from a decomposition product of 1,1'-dianthrimide. Consequently, a heating temperature above 70° cannot be recommended for the formation of the tellurium 1,1'-dianthrimide complex.

Effect of heating time

A relatively long heating time was necessary to obtain equilibrium conditions. The solutions were heated for 16 h at 70°; a longer time caused a decreased extinction, probably again owing to decomposition of the complex.

Influence of foreign ions

On the basis of an investigation of the ions interfering in the determination of boron with 1,1'-dianthrimide, it is possible to obtain information about the ions interfering in the determination of tellurium. The following ions interfere: boron, germanium(IV), bromide (oxidized in concentrated sulphuric acid) and fluoride. The interference of fluoride is probably due to attack on glass and release of boron.

SUMMARY

Tellurium and 1,1'-dianthrimide form a coloured complex with absorption maxima at 550 and 600 mμ, which can be used spectrophotometrically. Boron and germanium are known to react similarly; bromide and fluoride interfere.

RÉSUMÉ

Une méthode spectrophotométrique est proposée pour le dosage du tellure au moyen de dianthrimide-1,1'. Ce réactif réagit également avec le bore et le germanium. La réaction est perturbée par les anions Br^- et F^-.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Bestimmung von Tellur mit Dianthrimid-1,1' beschrieben. Bor, Germanium, Brom und Fluor stören.

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SIMULTANEOUS DETERMINATION OF SILICON AND PHOSPHORUS IN THE PRESENCE OF EACH OTHER

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The most widely used method for the determination of silicon and phosphorus is the spectrophotometric method. This involves the formation of the yellow silicomolybdate and phosphomolybdate, followed by reduction of these complexes to molybdenum blue.

During the investigation leading to the colorimetric determination of silicon in the presence of phosphorus, PAUL AND POVER[1] reported the separation of silicomolybdate from phosphomolybdate by selective extraction of the latter with ethyl acetate. Reduction of the silicomolybdate in the aqueous phase provided an accurate and reliable method for determination of silicon in the presence of phosphorus.

The possibility of simultaneously determining phosphorus in the solvent phase was considered. De SESA AND ROGERS[2] have reported the simultaneous determination of silicon and phosphorus by measurement of the total absorbance of the yellow molybdate at 332 mμ, extraction of the phosphomolybdate with isoamyl acetate and measuring the absorbance of the organic phase at 330 mμ. Correction of the total absorbance in the aqueous phase for phosphorus, using the previously determined absorbance index of phosphomolybdate, gave the silicon content.

This technique though feasible was time-consuming. However, while investigating the solvent extraction technique, a spectrophotometric method was developed for the simultaneous determination of silicon and phosphorus as molybdenum blue.

This paper reports the investigations leading to this method and the tests conducted on the procedure.

EXPERIMENTAL

Reagents

All reagents were of AnalaR grade. Distilled water was used throughout.

Silicate solutions: Solutions of soluble silica were prepared by fusing 10.0 mg of finely divided quartz with 0.5 g of powdered sucrose and 1.5 g of sodium peroxide in a Parr-bomb, and dissolving the melt in 100 ml water in a polythene beaker. Further solutions of silicate were prepared by dilution.

Phosphate solutions: A stock solution of phosphorus was prepared by dissolving 0.50 g of sodium dihydrogen phosphate (dihydrate) and diluting to 100 ml. Further solutions of phosphate were prepared from it by dilution.

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Amino-naphthol-sulphonic acid reagent: 0.20 g of 1-amino-2-naphthol-4-sulphonic acid, 2.4 g sodium sulphite ($7H_2O$) and 12.0 g sodium metabisulphite dissolved in water and made up to 100 ml. The reagent was kept in a dark bottle and freshly prepared weekly.

Silicon and phosphorus determination

Silicon and phosphorus were determined by the same colorimetric method. This involved the formation of yellow molybdates of silicon and phosphorus, and their reduction to the corresponding heteropoly blue with 1-amino-2-naphthol-4-sulphonic acid reagent. The silico-heteropoly blue was measured at 690 mμ and the phospho-heteropoly blue at 660 mμ. The reagents which were found to give accurate and reproducible results for both silicon and phosphorus determination are given in the order in which they were added:

2.0 ml silicate (60 to 10 μg) or phosphate (50 to 400 μg), 2.0 ml hydrochloric acid (*N*), 1.0 ml perchloric acid (72%), 4.0 ml ammonium molybdate solution (5%), 0.5 ml 1-amino-2-naphthol-4-sulphonic acid reagent.

Blanks made with 2 ml distilled water and the standard reagents, were used to set the colorimeter to read 100% transmission before the optical density of the test material was measured.

PROCEDURE FOR SIMULTANEOUS DETERMINATION OF SILICON AND PHOSPHORUS

2.0 ml of the test solution were pipetted into a 50-ml separating funnel, followed by 2.0 ml hydrochloric acid. 1.0 ml perchloric acid was then added and the solution shaken for about 1 min. 4.0 ml ammonium molybdate solution were added and the solution mixed by shaking for about 3 min, after which 0.5 ml of 1-amino-2-naphthol-4-sulphonic acid reagent was added with continuous shaking. The resulting solution was allowed to stand for 10 min for maximum colour to develop. The contents of the separating funnel were then extracted with 20.0 ml of diethyl ether for 30 sec. The aqueous phase was separated and its optical density measured immediately at 690 mμ against a similarly treated blank. The colour of the organic phase was measured at 660 mμ against a solvent blank.

RESULTS

In Table I is recorded the extraction of phospho- and silico-heteropoly blue by various solvents. 98.3% of the phospho-heteropoly blue was extracted by *n*-propyl acetate,

TABLE I

SOLVENT EXTRACTION OF HETEROPOLY BLUE OF PHOSPHORUS AND SILICON

Solvent	*Phosphate found in solvent phase after extraction of phosphate blue*[a] *μg*	*Silica found in aqueous phase after extraction of silicate blue*[b] *μg*
ethyl acetate	300	50
n-propyl acetate	295	52
isopropyl acetate	295	52
n-butyl acetate	—	53
isobutyl acetate	294	56
isoamyl acetate	235	60
diethyl ether	295	59
chloroform	<5	60
tetrachloroethane	<5	60
carbon tetrachloride	<5	60
benzene	<5	60
petroleum ether (b.p. 40–60°)	<5	60

[a] Initial phosphate concentration 300 μg/2 ml.
[b] Initial silicate concentration 60 μg/2 ml.

isopropyl acetate, isobutyl acetate and diethyl ether. Isoamyl acetate extracted the phospho-heteropoly blue to the extent of 79.3% while ethyl acetate was 100% efficient. *n*-Amyl acetate and dibutyl ether were found to bleach the molybdenum blue to a yellowish – green colour. The phospho-heteropoly blue was not extracted by any of the hydrocarbon (or chlorinated hydrocarbon) solvents tested.

The important criterion for the selection of a suitable solvent for studies of this kind, is that the solvent must possess selective extraction properties for phospho-heteropoly blue and silico-heteropoly blue *i.e.* the solvent must be capable of quantitatively extracting one without extracting the other. Of the solvents that were found to extract the phospho-heteropoly blue efficiently diethyl ether alone did not extract silico-heteropoly blue to any great extent, 1.7% of the silicate being extracted at the concentration tested. Ethyl acetate, although 100% efficient for the extraction of the phospho-heteropoly blue, was found to extract the silico-heteropoly blue to the extent of 16.7%. Silico-heteropoly blue, like phospho-heteropoly blue was not extracted by any of the hydrocarbons (or chlorinated hydrocarbons) tested.

TABLE II

EXTRACTION OF PHOSPHO- AND SILICO-HETEROPOLY BLUE BY DIETHYL ETHER

Phosphate present in aqueous phase before extraction μg	*Phosphate found in aqueous phase after extraction* μg	*Silicate present before extraction* μg	*Silicate found in solvent phase after extraction* μg
50	<5	20	<1
100	<5	30	<1
200	5	40	<1
300	7	50	<1
400	12	60	1

These preliminary studies indicated that among the solvents tested for selective solvent extraction of the heteropoly blue of phosphorus and silicon, diethyl ether was the most suitable. A detail study of the selective solvent extraction of phospho- and silico-heteropoly blue by this solvent was, therefore, made. The results of these studies (Table II) demonstrated that over a range of phosphate concentration (25 μg to 200 μg/ml), the phospho-heteropoly blue was efficiently extracted by diethyl ether. At the same time, the silico-heteropoly blue was not extracted to any significant extent between silicate concentrations of 10 μg to 25 μg/ml. The phosphate and silicate concentrations used in these studies included both the upper and lower limits of concentrations that the methods of estimation are capable of accurately determining.

TABLE III

ACCURACY OF CALIBRATION CURVES FOR PHOSPHORUS AND SILICON DETERMINATION

Phosphate content present μg	*Phosphate content found* μg	*Silicon content present* μg	*Silicon content found* μg
280	292	64	63
200	200	52	50
150	150	40	38
75	75	36	35
40	42	29	28

Fig. 1 shows the standard graph for the phospho-heteropoly blue in the solvent phase, while that for the silico-heteropoly blue after diethyl ether extraction, is given in Fig. 2. These graphs being linear, demonstrate that under the standard conditions adopted the blue colour in both the solvent phase and the aqueous phase was proportional to concentration. These calibration curves were tested at various concentrations of phosphate and silicate and were found to give accurate results (Table III).

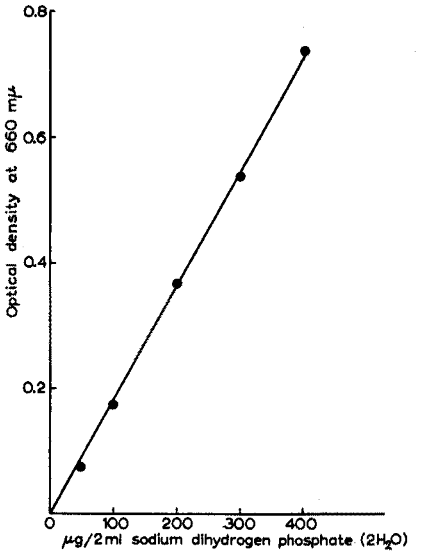

Fig. 1. Calibration graph for phosphorus determination after diethyl ether extraction of phospho-heteropoly blue.

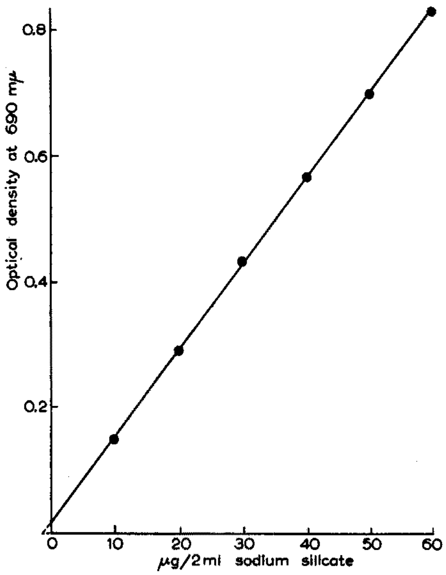

Fig. 2. Calibration graph for silicon determination after diethyl ether extraction of silico-heteropoly blue.

To conclude these studies, the recoveries of phosphate and silicate in mixtures of each other were determined by this method of determination utilizing the solvent extraction technique with diethyl ether. The results of these experiments, recorded in Table IV, demonstrate that this method of simultaneous determination of phosphorus and silicon is accurate and reproducible.

TABLE IV

SIMULTANEOUS DETERMINATION OF PHOSPHATE AND SILICATE IN MIXTURES OF EACH OTHER BY SOLVENT EXTRACTION OF PHOSPHO- AND SILICO-HETEROPOLY BLUE

Mixtures	*Phosphate present in mixture μg*	*Phosphate found after extraction μg*	*Silica present in mixture μg*	*Silica found after extraction μg*
A	400	390	55	56
B	300	315	37	38
C	200	196	27	25
D	100	97	40	39
E	50	51	10	10
F	25	26	13	13

DISCUSSION

The method described in this paper permits the simultaneous determination of phosphorus and silicon in the presence of each other. The major weakness of the method is that due to the relatively large volume of solvent that is employed in the extraction of the phospho-heteropoly blue, the method is not as sensitive in the determination of phosphorus as it is in the determination of silicon. Nevertheless, the method is capable of detecting accurately 12 μg/ml of phosphate. The method has the advantages of being simple, rapid and accurate.

When 1.0 ml of 1-amino-2-naphthol-4-sulphonic acid reagent was used to reduce phosphomolybdate to the phospho-heteropoly blue, it was found that although diethyl ether extracted the phospho-heteropoly blue completely, nevertheless as a "residual" blue colour was always present in the aqueous phase. This will affect the silicon determinations when both silicate and phosphate are present. Addition of 0.5 ml of the aminonaphthol sulphonic acid reagent however, gave excellent results for both silicon and phosphorus determinations.

The explanation of this finding is that under normal conditions, molybdic acid will react with 1-amino-2-naphthol-4-sulphonic acid reagent to produce a blue colour when excess of these reagents are present in the reaction mixture. Perchloric acid, when added in suitable amounts, prevents the development of this blue colour. In the present investigation, 2.0 ml perchloric acid (72%) when employed with 0.5 ml of 1-amino-2-naphthol-4-sulphonic acid reagent (0.2%) gave good results. However, if higher concentrations of reducing agent is used, proportionately larger amounts of perchloric acid should also be used.

It was found that when sodium sulphite solution (30%) was used as the reducing agent to effect the production of phospho- and silico-heteropoly blue instead of 1-amino-2-naphthol-4-sulphonic acid reagent, neither the phospho-heteropoly blue nor the silico-heteropoly blue could be extracted by ethyl acetate, *n*-propyl acetate, isopropyl acetate, *n*-butyl acetate, isobutyl acetate, isoamyl acetate, diethyl ether, petroleum ether (b.p. 40–60°), benzene, chloroform, carbon tetrachloride or tetrachloroethane.

ACKNOWLEDGEMENTS

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SUMMARY

An accurate and reproducible colorimetric method for the simultaneous determination of phosphorus and silicon in the presence of each other is reported. The method involves the selective extraction of phospho-heteropoly blue by diethyl ether.

RÉSUMÉ

Une méthode est décrite pour le dosage colorimétrique du phosphore et du silicium, en présence l'un de l'autre.

ZUSAMMENFASSUNG

Beschreibung einer colorimetrischen Methode zur Bestimmung von Phosphor und Silizium nebeneinander.

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THE SUPPRESSION OF CALCIUM INTERFERENCE IN THE FLAME PHOTOMETRIC DETERMINATION OF EXCHANGEABLE SODIUM IN SOILS

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INTRODUCTION

In the analysis of sodium using a flame photometer of the filter type, calcium usually interferes because of failure of the radiation filter used to isolate the sodium doublet at 589.0–589.6 mμ to completely exclude radiation from calcium. While this interference can be considerably reduced by the careful choice of filters[1], it cannot be completely eliminated. Steps must be taken to offset or prevent this interference either by applying a correction for the amount of calcium present, by removal of the calcium, or by chemical suppression of its radiation. This is particularly important for samples low in sodium and high in calcium, as is often the case in ammonium chloride leachates of soils. If a correction is made for calcium it is essential to ensure that no interference occurs with the calcium emission.

A method in which calcium interference is completely suppressed would have obvious advantages over one in which a correction is applied, particularly for samples where analysis for calcium is not required.

WILLIAMS[2] has shown that aluminium and phosphate both markedly depress calcium emission in ammonium chloride solution and WILLIAMS AND TWINE[3] have shown that these ions can suppress calcium interference with sodium in the analysis of plant material. The present investigation was made to examine the possibility of using aluminium or phosphate to suppress calcium interference in the flame photometric determination of sodium in ammonium chloride leachates of soils.

EXPERIMENTAL

The results were obtained using an E.E.L. flame photometer with a gelatine filter to isolate the sodium radiation at 589.0–589.6 mμ. The gases used were air and a proprietary bottled gas similar to "calor" gas.

Stock solutions were prepared as follows:

Calcium : Calcium carbonate was dissolved in a slight excess of hydrochloric acid. The solution was boiled to expel carbon dioxide and, after cooling, made to volume.

Aluminium chloride : Aluminium metal was dissolved in a slight excess of hydrochloric acid and the solution adjusted to volume.

Other stock solutions were prepared from ammonium chloride, sodium chloride, ammonium dihydrogen phosphate and aluminium ammonium sulphate.

Soils were leached with normal ammonium chloride and sodium and calcium determined as described by WILLIAMS[2] except that to allow comparisons to be made, lanthanum chloride was not added before adjusting to volume, but was added in 1 ml of solution to a 20-ml aliquot.

RESULTS AND DISCUSSION

Suppression of calcium interference

Results of the examination of solutions to test the effect of aluminium and phosphate on the suppression of calcium interference with sodium in normal ammonium chloride solution are given in Table I.

TABLE I

THE EFFECT OF ALUMINIUM AND PHOSPHATE ON THE INTERFERENCE OF CALCIUM WITH 2.5 p.p.m. OF SODIUM IN NORMAL AMMONIUM CHLORIDE SOLUTION

Addition p.p.m.	*Galvanometer reading*			
	Calcium added p.p.m.			
	0	*50*	*100*	*200*
Nil	29	35	41	53
250 Al	29	31	32	45
400 Al	30	30	30	34
400 Al + 400 P	31	31	31	32
500 Al[a]	31	32	32	33
800 Al + 800 P[b]	38	38	38	38

[a] Added as aluminium ammonium sulphate.
[b] Added as aluminium ammonium sulphate and phosphoric acid.

These results show that aluminium alone and aluminium together with phosphate were effective in suppressing interference from calcium, but for complete suppression of interference in solutions containing up to 200 p.p.m. of calcium, aluminium and phosphorus in excess of 400 p.p.m. of each were necessary. Complete suppression at this level of calcium was obtained with approximately 800 p.p.m. of both aluminium and phosphorus added as a solution of ammonium alum and phosphoric acid. Further tests showed that these concentrations gave complete suppression of interference from 250 p.p.m. of calcium while with 500 p.p.m. of calcium the galvanometer reading was increased only from 38 to 40.

These results suggest that satisfactory suppression of calcium interference in ammonium chloride leachates of soils should be achieved by the addition of similar amounts of aluminium and phosphate. This can be done by the addition of 2 ml of a solution containing 15 g of aluminium ammonium sulphate (ammonium alum) and 2 ml of phosphoric acid ($d = 1.70$) per 100 ml to 20 ml of ammonium chloride leachate. The sodium concentration can then be determined by reference to a calibration curve prepared from normal ammonium chloride standards to which corresponding amounts of the aluminium-phosphoric acid solution have been added.

Examination of soils

As a check on the proposed method a group of soils was leached with normal ammonium chloride, and sodium was determined with the flame photometer both by suppression of calcium interference as proposed, and by applying a correction for calcium interference after reading both sodium and calcium following addition of 2000 p.p.m. of lanthanum as suggested by WILLIAMS[2]. The results are given in Table II.

TABLE II

A COMPARISON BETWEEN EXCHANGEABLE SODIUM IN SOILS DETERMINED BY SUPPRESSION OF CALCIUM INTERFERENCE AND BY CORRECTION FOR CALCIUM INTERFERENCE

Sample No.	*Exchangeable calcium m.e. per 100 g*	*Exchangeable sodium m.e. per 100 g*	
		Ca correction	*Ca suppression*
1	56.6	0.521	0.551
2	40.8	5.65	5.76
3	36.8	0.311	0.316
4	35.2	0.109	0.125
5	31.9	2.97	3.01
6	24.0	0.085	0.087
7	21.4	0.371	0.380
8	16.1	0.330	0.381
9	13.5	0.082	0.078
10	11.5	2.14	2.11
11	10.2	0.127	0.122
12	10.0	0.513	0.522
13	9.4	0.267	0.249
14	7.8	0.197	0.207
15	6.6	0.133	0.139
16	4.0	0.172	0.178
17	3.3	0.118	0.122
18	0.5	0.061	0.061

These results show that satisfactory agreement was obtained between the two methods. In general the values obtained when calcium interference was suppressed tended to be slightly higher than when a correction was made. However, the difference was small and the results indicate that the aluminium–phosphoric acid solution had given satisfactory suppression of calcium interference over the whole range of soils which included some with high calcium: sodium ratios.

SUMMARY

An examination of the effects of aluminium and phosphate on the interference of calcium with sodium analysis using a flame photometer of the filter type showed that these ions could be used to suppress this interference.

A method is proposed for the satisfactory suppression of calcium interference in the determination of exchangeable sodium in ammonium chloride leachates of soils.

RÉSUMÉ

L'emploi de l'aluminium et du phosphate permet de supprimer l'interférence du calcium lors du dosage du sodium par photométrie de flamme. Une méthode est proposée pour le dosage du sodium dans des terres.

ZUSAMMENFASSUNG

Die durch Calcium verursachte Störung der flammenphotometrischen Bestimmung von Natrium kann durch Zusatz von Aluminium und Phosphat ausgeschaltet werden. Es wird eine Methode beschrieben zur Bestimmung von Natrium in Erdproben.

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DETERMINATION OF METAL IONS BY MEANS OF TAA AND EDTA

II. DETERMINATION OF COPPER

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INTRODUCTION

In a previous paper[1] attention was drawn to new possibilities for rapid metal determinations by means of the combined use of thioacetamide (TAA) and ethylenediaminetetraacetic acid (EDTA). For the determination of copper in the TAA–EDTA system, the use of EDTA and calcium chloride is not necessary, because copper, being a group II element, precipitates with TAA in acid medium.

The spectrophotometric method with aminoacetic acid, described by ZIEGLER[2] is preferred for the determination of copper. According to ZIEGLER, only a few elements of the third group interfere in this method. The molar extinction coefficient (34.3 for the flat-maximum at 735 mμ, as measured with a Unicam SP 500 spectrophotometer) is somewhat low, but a more sensitive method which is not subject to interferences is not available. The method, however, is entirely acceptable for the present purpose where intermediate amounts of copper rather than traces were involved. ZIEGLER's statement that the colour is very stable and that small amounts of nitric acid do not interfere was confirmed. This is very important because the metal sulfides have to be dissolved by means of nitric acid.

The observations of ZIEGLER permitted the assumption that addition of TAA to an acid solution containing a mixture of metal ions, would separate copper from all the elements that interfere with its determination by means of aminoacetic acid. Dissolution of the precipitate in nitric acid and treatment according to the method of ZIEGLER would then give the correct copper content of the mixture.

EXPERIMENTAL

Reagents

Aminoacetic acid, AnalaR, a 10% solution in water containing 4% sodium citrate.

Procedure

The determinations are carried out in 15-ml centrifuge tubes. To 4–8 ml of a neutral (or slightly acid) solution, containing not less than 2.5 mg copper, add 1–2 ml of 4 *N* hydrochloric acid and 1 ml of aqueous 6% TAA solution. Heat for 20 min in a water bath at 90°. Centrifuge and remove the supernatant liquid by suction through a G4 glass filter stick as shown in Fig. 1 of the previous paper[1]. Remove as little as possible of the precipitate from the centrifuge tube into the glass filter. Wash the precipitate after filtration three times with 1–2 ml of water and remove the washing water in the same way. Dissolve the precipitate in the centrifuge tube and on the filter in a few drops of 60% nitric acid. Place the combined solutions in a 50-ml volumetric flask. Add 25 ml of the colour reagent and dilute to the mark. The sodium citrate in the reagent solution adjusts the pH of the final solution to between 2.9 and 4.1. Measure the extinction in a 4-cm cell in a Unicam SP 500 spectrophotometer at 735 mμ. In some cases (especially when lead was present), it was necessary to centrifuge the coloured solution before measuring the extinction.

Remarks

I. The decanted liquids always contain small (not always visible) amounts of copper sulphide. Therefore filtration is essential. When polypropylene centrifuge tubes were used, it seemed possible in some cases to discard the decanted liquid directly without using glass filters. II. It is advisable to use a good electric centrifuge (*e.g.* 3000 r.p.m.).

RESULTS

I. *Determination in presence of group II elements*

The results of the determinations of copper in presence of other group II elements are shown in Table I.

TABLE I

DETERMINATION OF COPPER IN PRESENCE OF OTHER GROUP II ELEMENTS

Amounts of other elements in mg							*mg Cu present*	*mg Cu found*	*error in %*
Hg	*Pb*	*Cd*	*As*	*Sb*	*Sn*	*Bi*			
			4	4	4		4.00	4.00	0.0
			4	4	4		4.00	4.02	+0.5
			4	4	4		4.00	3.98	−0.5
4	4	4					4.00	3.98	−0.5
4	4	6					4.00	3.98	−0.5
16	16	16					2.50	2.52	+0.8
16	16	16					2.50	2.52	+0.8
4	4	4	4	4	4		2.50[a]	2.45	−2.0
4	4	4	4	4	4		2.50[a]	2.45	−2.0
			16	16	16		2.50[a]	2.45	−2.0
			16	16	16		2.50[a]	2.50	0.0
4	4	4	4	4	4		2.50	2.52	+0.8
4	4	4	4	4	4		2.50	2.50	0.0
			16	16	16		2.50	2.52	+0.8
						16	5.00	5.16	+3.2
						16	5.00	5.02	+0.4
						16	5.00	5.26	+5.2

[a] Experiments carried out in polypropylene centrifuge tubes (the decant liquid was discarded without filtration).

Table I shows that copper can be determined with fair accuracy in presence of twenty-fold amounts of other group II elements other than bismuth, which interferes causing positive errors.

The lowest amount of copper that can be determined accurately by this method is 2.5 mg, because of the low sensitivity of the spectrophotometric method. Smaller copper concentrations can be determined similarly by taking larger volumes. In Table II the results of the determinations of 2.5 mg copper are shown; 100-ml centrifuge tubes were used and 10–20 ml of hydrochloric acid was added but the method was otherwise the same as described above. In this way copper concentrations as small as $4 \cdot 10^{-4}$ *M* were determined with fair accuracy.

TABLE II

DETERMINATIONS OF SMALLER COPPER CONCENTRATIONS

Amounts of other elements in mg						*mg Cu present*	*mg Cu found*	*error in %*
Hg	*Pb*	*Cd*	*As*	*Sb*	*Sn*			
2	2	2				2.50	2.49	—0.4
			2	2	2	2.50	2.50	0.0
			2	2	2	2.50	2.49	—0.4

II. *Determination of copper in presence of group III elements*

KRIJN[3] has already described the macro determination of copper by precipitation with TAA in the presence of group III elements and subsequent iodometric determination. Group II elements generally interfere with this iodometric determination. As was expected, determinations of copper by the method proposed in the present paper showed that group III elements do not interfere.

SUMMARY

Copper can be determined in presence of the common group II and group III elements by precipitation with TAA in acid solution and subsequent spectrophotometric determination as the copper(II)-aminoacetic acid complex. Only bismuth interferes. Copper was determined in concentrations as small as $4 \cdot 10^{-4}$ *M* and in presence of As, Sb, Sn, Pb, Cd, Hg and all group III elements.

RÉSUMÉ

Le cuivre peut être dosé en présence des éléments les plus communs des groupes II et III, par précipitation avec TAA, en solution acide, suivie d'une détermination spectrophotométrique du complexe cuivre(II)-acide aminoacétique. Seul le bismuth gêne.

ZUSAMMENFASSUNG

Kupfer kann in Gegenwart der häufig vorkommenden Elemente der zweiten und dritten Gruppe quantitativ bestimmt werden durch Fällung mit TAA in säurer Lösung und folgende spektrophotometrische Bestimmung als Kupfer(II)-aminoessigsäures Komplex. Nur Wismut stört die spektrophotometrische Bestimmung. Dieses Metall darf also nicht anwesend sein. Kupfer wurde nach dieser Methode in Konzentrationen bis $4 \cdot 10^{-4}$ *M* bestimmt, in Anwesenheit von As, Sb, Sn, Pb, Cd, Hg und die Metalle der dritten Gruppe.

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THE RELATION OF CATALYST ACIDITY TO THE ELECTRODE POTENTIAL RECORDED IN AN AUTOMATIC TITRATION*

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The strength and amount of surface acidity on catalysts has been a subject of considerable interest to the petroleum processing industry[1-9]. It has been proposed[2] that the acid sites are effective in the formation of carbonium ions from hydrocarbons, and relations have been found[3,5,9] between surface acidity and cracking or polymerization activity. Of the various methods reported for the determination of catalyst acidity and strength, the titration of a non-aqueous suspension with *n*-butylamine, with the use of indicators of various pK_a values for the end-point determination, has received considerable attention in this laboratory. The original method described by BENESI[1] involved the batchwise titration of a suspension, followed by the addition of indicators to portions of the suspension. However, two disadvantages of the use of indicators in the determination were apparent. These were (a) the limitation of the method to materials with sufficient lack of color to enable indicator color changes to be seen, and (b) the tediousness of the technique, which involves careful manipulations and observations by trained personnel. The first of these objections can be mitigated by mixing light colored standards with the samples. This modification of the technique, however, intensifies the second factor. These limitations suggested an investigation of a potentiometric titration technique which would be equally applicable to dark and light colored catalysts, involve essentially no manual manipulations, and give a permanent record of the test on a recorder chart strip.

Titration of an aqueous suspension of silica has been described by BOLT[10], in which a glass electrode was immersed in the suspension and a calomel electrode was connected by a bridge of 3% agar in the silica dialyzate. Potentiometric titrations in aqueous media have also been described with regard to the total exchange capacity of soils[11] and ion-exchange resins[12]. Batchwise titration of clay, alumina, and quartz in ethanol have been described by GOATES, ANDERSON AND WILLIS[13,14]. The potentiometric titration of clay and resin suspensions in alcohol–water–aniline mixtures was described by GANGULY, MUKHERJEE AND GHOSH[15]. The direct application of these methods offered little or no improvement in either speed or automatic operation over the procedure of batchwise butylamine equilibration and indicator tests. Since catalyst samples characterized in this laboratory by the indicator technique were available (data in Figs. 5 and 6), it was decided to approach the problem by a continuous and recorded titration. After experimentation with various solvents, electrodes, and

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methods of instrumentation, a technique was found for titrating ground catalyst suspensions with a dilute solution of butylamine in acetonitrile, in such a manner as to yield curves characteristic of the catalysts. The titration can be performed, and the data recorded, with an automatic titrator, so that operator time is involved only in the preparation of samples, the setting up of the instrument, and the interpretation of the recorded potential curve.

EXPERIMENTAL

In order to find the best conditions for a completely automatic method of measurement, various conditions were investigated regarding the feed rate of the reagent solution to the catalyst, the preparation of a homogeneous catalyst slurry, the rate of stirring, and the optimum normality of the titrating base. Within limits, any of the experimental conditions may be varied, and still yield titration curves clearly differentiating catalysts of various acidity characteristics. In the course of the work described here changes were made to the equilibration period at the start of the experiment, and these affected the initial potential readings shown in various figures. The following procedure is suggested as a most suitable way of handling this test on a routine basis.

One gram of sample, ground to pass a 200-mesh sieve, is pretreated by calcination in a 25-ml Erlenmeyer flask for three hours at 500°. The flask, while still in the furnace, is stoppered with a standard taper stopper, then immediately placed in a desiccator to cool. It is transferred quantitatively with reagent grade acetonitrile into a 250-ml beaker and diluted to a total volume of 150 ml. Standard glass and calomel electrodes are immersed in the slurry and a glass stirrer set to a speed just below that creating turbulence. After a 5-min equilibration period, the titration is started, with 0.008 molar butylamine in acetonitrile introduced to the slurry at a constant rate of 0.4 ml per minute. A Precision-Dow Dual Recordomatic Titrometer provides the mechanism for the constant rate of flow of titrant and the recording of the potential curve. The catalyst samples used in these experiments are listed in Table I.

TABLE I

CATALYST SAMPLES

Name	*Source*	*Principal components*	*Area*
S-46	Houdry Co., Philadelphia	87–13% Silica–alumina	315 m²/g
AAA	American Cyanamid Co., New York	75–25% Silica–alumina	452 m²/g
DA-5 Silica–magnesia	Davison Chemical Co., Baltimore	70–30% Silica–magnesia	500 m²/g
F-10	Aluminum Co. of America, Pittsburgh	Alumina	125 m²/g
Cabosil M-5	Godfrey L. Cabot, Inc., Boston	Silica	175–200 m²/g

RESULTS

Comparative data for typical catalyst substrates

The recorded data for four catalyst samples, including three different types, are shown in Fig. 1. The four samples were all titrated under the same experimental conditions. Both Houdry S-46 and Aerocat Triple A silica–alumina show similar but distinguishable curves. It was known from results using a butylamine batchwise titration and indicators on a spot plate that the S-46 contained about 0.19 mequivs. of acid sites strong enough to turn an indicator of pK_a —8.2, and a distribution of sites to a total of 0.33 mequivs./g. The Triple A contained about 0.30 mequivs. of the very strong sites, and a total of about 0.35 mequivs./g. The titration curves qualitatively and semi-quantitatively agreed with these results.

The silica–magnesia sample had a surface with only weakly acidic sites, as determined with Hammett indicators. This was again found to be the case when it was titrated electrometrically, as the initial electrode potential was approximately half that found for a system containing strong surface acidity. The silica–magnesia electrometric titration curve decreased in slope very slowly, indicating a large amount of weak acid sites. This corresponded to the titration with indicators in which 1.2 mequivs./g of weakly acidic sites were noted.

The F-10 alumina sample had about 0.04 mequivs./g of weak acid sites. The titration curve, which is easily distinguished from the silica–magnesia, indicated a total acidity somewhat in excess of this value.

When replicate samples were titrated under the same conditions, the reproducibility of the electrode potential curve was ±5 mV.

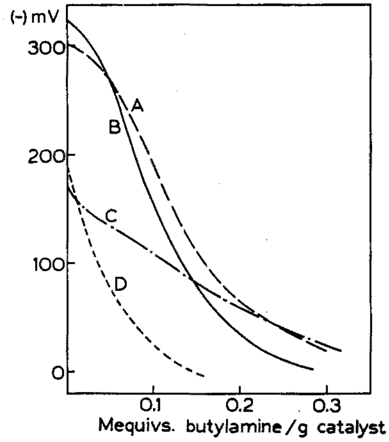

Fig. 1. Titration of typical catalyst bases. A. Triple A silica–alumina; B. S-46 silica–alumina; C. silica–magnesia; D. F-10 alumina.

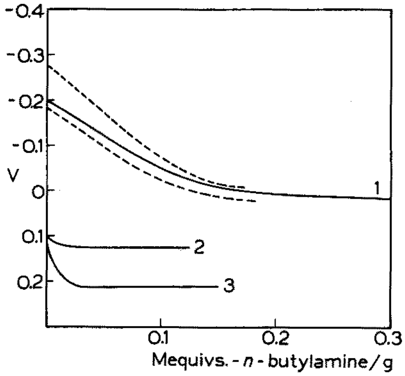

Fig. 2. The application of the titration to dark colored, metal promoted, catalyst samples.

Pre-equilibrated samples

As the titrations were done with a slow but constant feed of *n*-butylamine titrant, the relation of these results to batch titration results depended on the effective equilibration of the slurry with the added titrant. Samples of Houdry S-46 silica–alumina catalyst were contacted with various amounts of butylamine by shaking for three hours at room temperature, before the titration. The results in Table II compare the influence of pre-equilibrated and titrated base on the electrode potential. The first incremental addition, 0.025 mequivs./g appeared to need a slower feed rate for equilibration. However, the equilibration was satisfactory for greater amounts of amine.

TABLE II

A COMPARISON OF THE EFFECTS OF PRE-EQUILIBRATION, AND TITRATION WITH BASE, ON THE ELECTRODE POTENTIAL OF A HOUDRY S-46 SILICA–ALUMINA CATALYST SLURRY

	Change in electrode potential	
Amounts of added butylamine	*Pre-equilibration*	*Continuous automatic titration*
0.025 mequivs./g	90 mV	50 mV
0.050 mequivs./g	130 mV	130 mV
0.100 mequivs./g	230 mV	250 mV
0.150 mequivs./g	290 mV	320 mV

Applications to metal promoted samples

Since the major types of acid surface catalysts can readily be differentiated by the automatic titration technique, an unknown sample can be characterized by the similarity of its titration curve to that of other materials of known acidity. In Fig. 2, the experimental titration curves are shown for three dark colored, metal promoted, catalyst samples whose acidity could not be directly determined with indicators. As these catalysts are presently part of an experimental program of commercial interest they cannot be more explicitly defined here. The illustration merely shows the application of the technique to this type of sample. Sample 1 falls between the curves of the unpromoted catalyst pre-equilibrated with 0.075 and 0.100 mequivs. of butylamine per gram. Therefore, 0.075 to 0.100 mequivs./g of strong acid sites have been covered or deactivated by the promotion treatment, leaving approximately 0.20 mequivs./g of strong and medium strength acid sites. In contrast, the sample 2 curve of a different substrate shows no appreciable acidity, and sample 3 appears slightly basic.

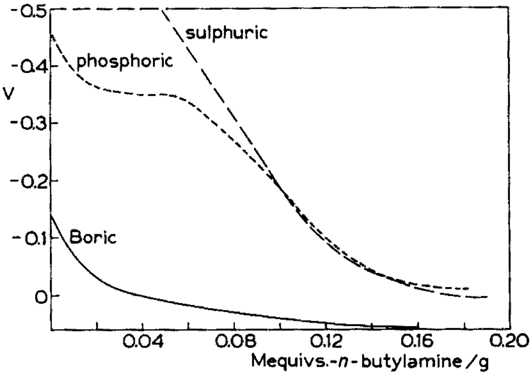

Fig. 3. The titration of mounted mineral acids on silica.

Titration of mounted acid samples

In Fig. 3, the curves depict the titration of three mineral acids mounted on Cabosil M-5, a non-porous silica. The technique described by BENESI[16] was used to contact the silica with 0.1 millimoles of phosphoric, and 0.2 millimoles of boric acid per gram of catalyst. The curves indicate the strength of the acids in the correct order, the initial voltage of the mounted sulfuric being off-scale of the instrument. If the available mounted acid was the same as the amount impregnated, the first ionizable hydrogen of the sulfuric and phosphoric acids was titrated in the range shown, but only a portion of one hydrogen of the boric acid was titrated. A similar observation was made by BENESI[1] for the amine titration with Hammett indicators.

THEORY AND TREATMENT OF DATA

The physical system in this measurement consists of a dispersed solid in a non-aqueous solvent. The measured electrode potential may arise from several sources including;

(a) The standard electrode potential of the calomel electrode, (*i.e.* the $Hg-HgCl_2$ interface).

(b) The liquid junction potential between the aqueous potassium chloride solution inside the sleeve of the calomel electrode and the dispersion in acetonitrile outside the electrode.

(c) The difference in potential across the glass membrane separating the dispersion in acetonitrile and the aqueous buffer solution inside the electrode, and

(d) The potential of the sensing electrode within the glass electrode (*i.e.* the Ag-AgCl interface).

Since (a) remains unchanged during an experiment, and (d) responds directly to (c) the effects (b) and (c) may account for the potentiometric curve. The effect (b), if present, does not appear to change appreciably during a titration. Thus the addition of butylamine solution to a non-acidic solid dispersion, or to the solvent alone, did not change the electrode potential to any extent.

Therefore, it appears that the electrode potential is determined primarily by the acid environment given to the outside of the glass electrode membrane by immersion in the finely divided acid-surfaced particles. The measured electrode potential may reflect the properties of the solid dispersion with regard to its weight concentration, particle size, strength and number of surface acid sites, and other surface effects.

TABLE III

EFFECT OF PARTICLE SIZE ON THE ELECTRODE POTENTIAL

Particle diameters-microns	*Measured initial potential V*	*Mequivs. of n-butylamine per gram of solid required to produce zero potential*
590–840	—0.08	0.01
297–420	—0.15	0.015
149–297	—0.18	0.06
105–149	—0.25	0.07
74–105	—0.31	0.14
44–74	—0.37	0.25
Smaller than 44	—0.37	0.25

In practice, the effect of certain of these factors may be determined, and thereafter held constant. For example, tests were made (Table III) of the effect of changing particle size on the electrode potential of a Houdry S-46 sample and it was found that a minimum particle size must be used before the maximum effect of the slurry on the electrode potential appears. Of the other factors, the strength of the surface acid is the variable with the greatest effect on the electrode potential.

In the interpretation of these data it was desired to plot the curves in a manner more directly showing the distribution of acid strength on the catalyst surface than the recorded potential curve. The topographical similarity of these recorded curves to the differential heats of adsorption of butylamine on attapulgite obtained by CHESSICK AND ZETTLEMOYER[17] was noted. Following a procedure used by DRAIN AND MORRISON[18] for heats of adsorption of argon on rutile, CHESSICK AND ZETTLEMOYER calculated a site energy distribution function $g(E)$ from the slope of the plot of the differential heat of adsorption (ΔH_d) against the moles of adsorbed butylamine, as

$$\frac{dN}{d(\Delta H_d)} = g(\Delta H_d)$$

Without implying an identity of thermodynamic quantities, the potentiometric titration curves may be treated in an analogous fashion by a plot of dN/dE *vs.* dE, where N is the moles of added butylamine, and E is the electrode potential. Differential plots of this type are compared in the Figs. 4 and 5 with histograms of the acidity distribution of the same materials as obtained by a modification of the Benesi technique, in which the indicator is added to a dried portion of the catalyst on a spot plate. The differential representation seems to yield in these cases a satisfactory picture of the acid strength distribution on the catalyst surface. From the theoretical point of view, a more complex treatment of the data is necessary, but in this simple

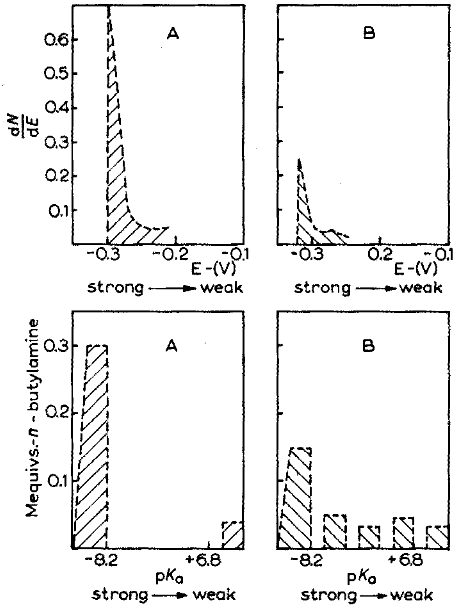

Fig. 4. A comparison of the differential plots of the titrations with the acidity distribution found with Hammett indicators. A. Triple A silica-alumina; B. S-46 silica-alumina.

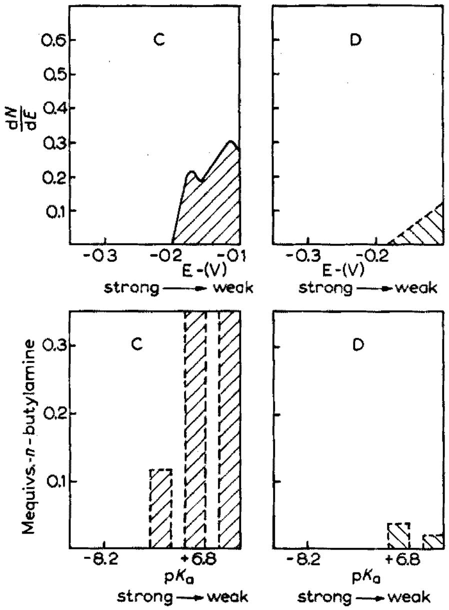

Fig. 5. A comparison of the differential plots of the titrations with the distribution found with Hammett indicators. C. silica-magnesia; D. F-10 alumina.

treatment advantage is taken of the primary sensitivity of the electrode potential to the strength of the surface acid sites in the catalyst slurry.

CONCLUSIONS

The continuous and recorded electrometric titration of slurries described here provides a convenient and reproducible method of screening prepared and treated solid catalyst for surface acid strength and concentration. The measurement is most readily used in the comparative testing of unknown samples against standards whose acidity has been characterized by an alternate method. It is particularly valuable to laboratory operations in which surface acidity data are of continuous interest for a flow of samples, as the technique is largely automated.

ACKNOWLEDGEMENT

The authors wish to thank Dr. N. D. Coggeshall, Gulf Research and Development Company, for his guidance and suggestions.

SUMMARY

The potentiometric titration of catalyst slurries in acetonitrile has been used for the determination of the surface acidity of catalysts. The technique is equally applicable to dark and light colored catalysts, involves essentially no manual manipulations, and gives a permanent record of the test on a recorder chart strip. The potentiometric titration curves of various types of catalysts and catalyst substrates with butylamine are shown. The titration curves are consistent with knowledge of catalyst acidity from batchwise titration with indicators; and are sensitive to previous equilibration with the basic titrant and to the covering of surface acid by metallic promoters. The automatic titration is a useful screening tool for characterization of samples in catalyst development programs.

RÉSUMÉ

La détermination de l'acidité de la surface des catalyseurs peut être effectuée par titrage potentiométrique au moyen de la butylamine. Une méthode automatique est décrite.

ZUSAMMENFASSUNG

Die Bestimmung des Säuregrades der Oberfläche von Katalysatoren kann durch potentiometrische Titration mit Butylamin erfolgen. Es wird eine automatische Methode beschrieben.

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STUDIES IN POLAROGRAPHIC ANALYSIS

II. AMPEROMETRIC TITRATION OF TELLURITE WITH POTASSIUM PERMANGANATE

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The potentiometric titration of tellurite with potassium permanganate has been studied under a variety of conditions[1,2]. Good results can be obtained when the titrations are performed in 0.1 N sodium hydroxide, and when the titrated solutions are 0.1 to 10^{-4} N. These concentrations lie within the range of polarographic analysis, hence we have examined the amperometric titration of tellurite with permanganate in alkaline solutions. The titration is possible because the diffusion currents of permanganate[3] and tellurite[4] vary with the concentration of the reducible materials. Amperometric titrations are of practical importance because of their simplicity and rapidity; the equivalence point can be determined from a few readings on each side of the end-point. Moreover, it is not necessary to titrate slowly near the end-point, whereas in potentiometric titrations the equilibrium becomes sluggish as the concentrations of the reactants decrease.

EXPERIMENTAL

Solutions

Potassium permanganate solutions 0.1396 and 0.090 N were prepared by the method of STAMM[5] and standardised with sodium oxalate; 0.0108 and 0.005 N solutions were prepared by appropriate dilution.

Sodium tellurite solutions 0.0605 and 0.0518 N were prepared by dissolving the solid in twice-distilled water and standardising against potassium permanganate[2]; $6.05 \cdot 10^{-4}$ up to $2.07 \cdot 10^{-3}$ N solutions were prepared by dilution with twice-distilled water.

Apparatus and technique

The diffusion current was measured by a Radiometer Polarograph. The capillary characteristics measured in open circuit at a mercury height of 40 cm were $m = 1.992$ mg/sec and $t = 3.33$ sec. For a titration, 5 ml of the *ca.* 10^{-3} M tellurite solution was made 0.05 or 0.1 N to sodium hydroxide and placed in the polarographic cell and purified nitrogen was bubbled through it for about 20 min. The nitrogen stream was then placed over the solution. The applied potential was adjusted to −0.8 V, −1 V, −1.4 V or −1.7 V *vs.* S.C.E. After the diffusion current of the tellurite solution alone had been measured, the permanganate solution was added from a burette. Nitrogen gas was then bubbled for two min in order to mix the reactants and to remove any dissolved oxygen. After each addition of the permanganate, the diffusion current was recorded. The diffusion current corrected for dilution was calculated and plotted against the volume of permanganate added. The end-point corresponding to the intersection of the two branches of the titration curve was obtained by interpolation.

RESULTS AND DISCUSSION

The amperometric titration curves of tellurite in alkaline solutions by potassium permanganate are shown in Figs. 1 and 2. The curves in Fig. 1 show the titration of tellurite solutions with 0.00216 M potassium permanganate solution in presence of 0.05 N - 0.1 N NaOH at —0.8 and —1.0 V; the curve is approximately reversed L-shaped. At these potentials neither tellurite nor tellurate (obtained by the oxidation or initially added to combine with the manganese(IV) formed) are reduced at the dropping mercury electrode. The initial current (—0.5 to 0.7 μA) represents the residual current. The current then increases slowly along branch A of the curves as the permanganate solution is added because manganese(IV) produced from the reaction,

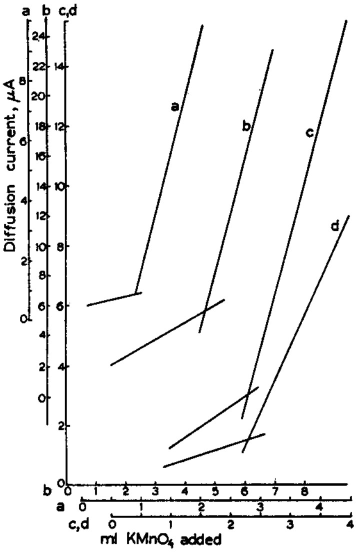

Fig. 1. a. 10 ml 6.05 · 10^{-4} N Te^{+4} titrated with 0.00648 N $KMnO_4$ in 0.1 N NaOH, in absence of telluric acid at —0.8 V. b. 5 ml 6.05 · 10^{-3} N Te^{+4} titrated similarly in presence of telluric acid at —1 V. c. 10 ml 1.513 · 10^{-3} N Te^{+4} titrated similarly in presence of telluric acid at —0.8 V. d. As in c in absence of telluric acid.

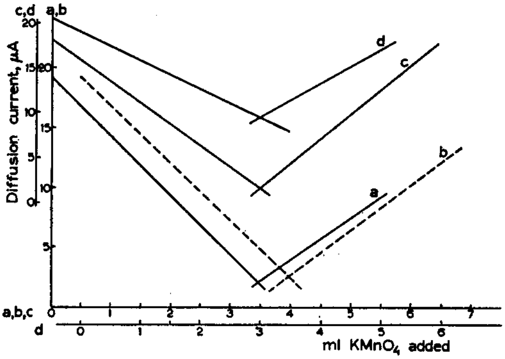

Fig. 2. 5 ml 2.07 · 10^{-3} N Te^{+4} titrated with 3 · 10^{-3} N $KMnO_4$ in 0.05 N NaOH at a, —1.7 V; b, c, d, —1.4 V.

$$3\ Te^{+4} + 2\ Mn^{+7} \rightarrow 3\ Te^{+6} + 2\ Mn^{+4}$$

is reduced at the dropping mercury electrode (D.M.E.) to manganese(II) when telluric acid is present.

When all the tellurite has been oxidised, the current increases rapidly, owing to the reduction of the permanganate added, along branch B of the titration curve. The intersect of the two branches gives the end-point.

The curves obtained at —1.4 V are V-shaped (*cf.* Fig. 2); at this potential tellurite is reduced at the D.M.E. and the initial current corresponds to the tellurium(IV) concentration. As permanganate is added tellurite is oxidised but tellurate is not reduced at —1.4 V at the D.M.E., and the current decreases continuously as the tellurium(IV) concentration decreases. When the end-point has been passed, the current increases again owing to the reduction of the excess permanganate. As in the

TABLE I

Vol. and normality of tellurite	*Alkalinity N*	*Normality*[a] *of $KMnO_4$ (N)*	*Vol. of $KMnO_4$ to tellurite*		*Error %*	*Remarks*
			Potentiometric	*Amperometric*		
10 ml $1.513 \cdot 10^{-3}$ *N*	0.1	0.00648 *N*	2.335	2.325	—0.43	—0.80 V telluric acid
10 ml $6.05 \cdot 10^{-4}$ *N*	0.1	0.00648 *N*	0.934	0.938	+0.43	—0.8 V no telluric acid
10 ml $1.513 \cdot 10^{-3}$ *N*	0.1	0.00648 *N*	2.335	2.325	—0.43	—0.8 V no telluric acid
5 ml $6.05 \cdot 10^{-3}$ *N*	0.1	0.00648 *N*	4.669	4.70	+0.66	—1 V telluric acid
5 ml $2.07 \cdot 10^{-3}$ *N*	0.05	$3 \cdot 10^{-3}$ *N*	3.45	3.470	+0.58	—1.7 V
5 ml $2.07 \cdot 10^{-3}$ *N*	0.05	$3 \cdot 10^{-3}$ *N*	3.45	3.475	+0.72	—1.4 V
5 ml $2.07 \cdot 10^{-3}$ *N*	0.05	$3 \cdot 10^{-3}$ *N*	3.45	3.44	—0.29	—1.4 V
5 ml $2.07 \cdot 10^{-3}$ *N*	0.05	$3 \cdot 10^{-3}$ *N*	3.45	3.437	—0.38	—1.4 V

[a] Normality is based on a valency change = 3 *i.e.* from 7 to 4. The values were obtained by multiplying the normalities determined by the oxalate method (*i.e.* 0.0108 and 0.005) by 0.6.

case of Fig. 1 the end-point is obtained by extrapolating the linear portions of the V-shaped curve.

In these titrations the normality of NaOH was kept at 0.05 – 0.1 *N*; at this alkalinity dilute tellurite solutions reduce permanganate to manganese dioxide. At higher alkalinities, manganate is also formed as a reduction product and erroneous results are obtained.

The end-points obtained from the titration curves are shown in the third column of Table I. The amperometric method gives results which are in reasonable agreement with those of the potentiometric method. The amperometric method has the advantage of speed; a titration requires only 15 min after deaerating the solution whereas the potentiometric titration needs 30–40 min.

SUMMARY

Tellurite was titrated amperometrically with permanganate in presence of 0.05 – 0.1 *N* NaOH and in presence or absence of telluric acid. At —0.8 and —1 V reversed L-shaped curves were obtained; at —1.4 V, the curves were V-shaped. The results agreed with those of potentiometric titrations.

RÉSUMÉ

Le titrage de tellurite a été effectué par ampérométrie, au moyen de permanganate, en milieu alcalin. Les résultats trouvés sont satisfaisants et concordent avec ceux obtenus par potentiométrie.

ZUSAMMENFASSUNG

Beschreibung eines amperometrischen Titrationsverfahrens zur Bestimmung von Tellurit mit Permanganat in alkalischer Lösung. Es werden die gleichen Resultate erhalten wie mit der potentiometrischen Methode.

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Short Communications

The recovery of chloroform from dithizone residues

The use of large quantities of chloroform solutions of dithizone for determining lead and zinc in agricultural and geochemical materials necessitated some means for the recovery of chloroform.

Extraction with concentrated sulphuric acid, followed by distillation from lime has been employed by BIDDLE[1] and HUBBARD[2] for the recovery of chloroform from dithizone residues. MULLIN AND RILEY[3] found that prolonged contact of chloroform with either sulphuric acid or lime rendered it unfit for the preparation of dithizone solutions. Chloroform that was badly contaminated with photochemical oxidation products when purified by the above procedure caused immediate oxidation of dithizone. MULLIN AND RILEY[3] obtained pure, stable chloroform by distilling the dithizone residues through a layer of 10% sodium sulphite solution; shaking the distillate with 3% hydroxylamine hydrochloride solution or 10% sodium sulphite solution and distilling the product from lime or active charcoal into 1% of its volume of ethyl alcohol.

The recovery method proposed here involves breaking down the lead and zinc dithizonates with alkaline EDTA solution. The lead and zinc EDTA complexes and the dithizone go into the aqueous phase leaving oxidised dithizone (diphenylthiocarbodiazone) in the chloroform. Phosgene is hydrolysed by the alkaline solution to ammonium chloride and ammonium carbonate and the diphenylthiocarbodiazone is removed by treatment with active charcoal. The recovered chloroform is finally distilled into 1% of its volume of ethyl alcohol.

Procedure

250 ml 0.1 *M* EDTA (disodium salt) solution, 250 ml distilled water and 50 ml NH_4OH ($d = 0.88$) were added to 1-l dithizone residues in a 2-l separating funnel. The contents of the funnel were shaken vigorously for 2 min, during which time the chloroform layer usually changed from reddish-blue to green. If the chloroform layer was still coloured reddish-blue, the alkaline EDTA solution was discarded and the above treatment was repeated. The green chloroform layer was transferred to another 2-l separating funnel and shaken for 2 min with 500 ml distilled water containing 25 ml ammonium hydroxide ($d = 0.88$). The layers were allowed to separate and the orange-yellow chloroform phase was run into a 2-l separating funnel and shaken well for 2 min with 30–40 g active charcoal. After filtration, the clear chloroform solution was distilled, the first 50–60 ml of distillate being discarded. Brown glass bottles containing 1% of their volume of ethyl alcohol (96%) were used as receivers. These were swirled several times during the distillation.

In order to test the suitability of the product, 1.0 ml of a 0.0015% dithizone solution in pure chloroform was diluted to 20 ml with the recovered chloroform. The optical density of the solution was measured at 620 mμ in a 1-cm cell. After storage in dark at ~5° for 5 days the optical density was again measured.

DISCUSSION

Chloroform recovered by the proposed method was suitable for analytical purposes; there was no change in the optical densities of dithizone solutions prepared from it after 5 days storage in the dark at ~5°. A batch of dithizone residues contaminated with phosgene gave a satisfactory product when purified by the proposed method. The time taken for the proposed method was approximately 2 hours as against 5 hours for that of MULLIN AND RILEY. Although the proposed method has only been applied to residues containing lead and zinc dithizonates, it should be applicable to other dithizonates provided they are easily dissociated and contain metals which react with EDTA.

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Thorium-EDTA complexes — A conductometric study

The disodium salt of ethylenediaminetetraacetic acid (EDTA) complexes thorium[1]. CABELL[2] studied this system potentiometrically; he indicated that in addition to the 1 : 1 complex, a 2 : 1 complex was formed and that the complex ThY_2 was less stable than ThY. This note reports a conductometric study of thorium–EDTA complexes.

Standard solutions of thorium nitrate and EDTA were prepared from AnalaR reagents. All conductivity measurements were made on a conductivity bridge (Industrial Instruments Inc., U.S.A. Model Re 216-B). An aliquot of standard thorium nitrate was placed in the conductivity cell, diluted to 15.2 ml and titrated with EDTA. A typical curve is given in Fig. 1(a). Two inflections were obtained corresponding to 1 : 1 and 1 : 2 complexes between thorium and EDTA.

The presence of two complexes was also observed when EDTA was placed in the cell and titrated with thorium nitrate. A typical curve is given in Fig. 1(b). The stoichiometric relationship between thorium and EDTA was checked by titrating different concentrations of thorium nitrate with EDTA. Table I gives the results obtained which indicate the formation of two complexes. From the shape of the curve — inflection 2 of Fig. 1(a) and inflection 1 of Fig. 1(b) — it can be seen that the higher complex was more dissociated[3]; this confirms CABELL's results.

When a mixture of thorium nitrate and EDTA in the molar ratio of 1 : 1 was titrated conductometrically with sodium hydroxide, the acid liberated corresponded to 2 equivs. of thorium. When the ratio of thorium nitrate to EDTA was 1 : 2, no acid was liberated, which indicates that the reactions are:

$$Na_2H_2Y + Th(NO_3)_4 \rightarrow ThY + 2\,HNO_3 + 2\,NaNO_3$$

$$ThY + 2\,HNO_3 + 2\,NaNO_3 + Na_2H_2Y \rightarrow H_4ThY_2 + 4\,NaNO_3.$$

This conductometric study thus confirms that 1 : 1 and 1 : 2 complexes are formed between thorium and EDTA.

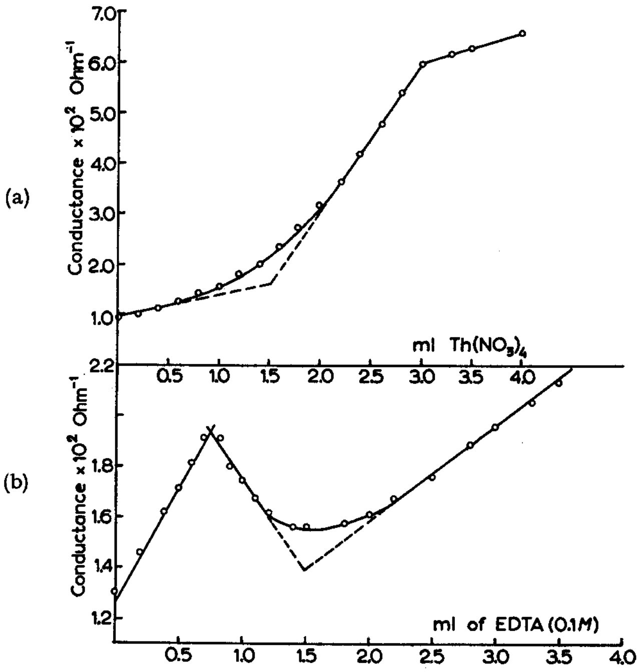

Fig. 1(a). Titration of EDTA (15.2 ml of 0.0148 *M*) with thorium nitrate (0.07511 *M* of thorium); (b) Titration of thorium nitrate (15.2 ml of 0.00494 *M* thorium) with EDTA.

TABLE I

TITRATION OF Th WITH EDTA

Th taken for titration mg	*Concentration at 1st inflection in 10^3 M*		*Concentration at 2nd inflection in 10^3 M*	
	Th	*EDTA*	*Th*	*EDTA*
4.36	1.22	1.20	1.21	2.44
8.71	2.41	2.40	2.35	4.90
17.43	4.71	4.70	4.50	8.90
26.40	6.90	6.92	6.48	12.74

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[1] F. J. WELCHER, *The analytical uses of ethylenediaminetetraacetic acid*, Van Nostrand, New York, 1958.
[2] M. J. CABELL, *Analyst*, 77 (1952) 859.
[3] G. SCHWARZENBACH, *Complexometric titrations*, Interscience, New York, 1957, p. 9.

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REVUES DE LIVRE

Handbuch der mikrochemischen Methoden, Band 1/Teil 2, *Waagen und Wägung*, von A. A. BENEDETTI-PICHLER. *Geräte für die anorganische Mikrogravimetrie*, von FRIEDRICH HECHT, Springer Verlag, Vienne, 191 Abb. IV + 307 Seiten. 1959. Ganzleinen $ 19,05, bei Verpflichtung zur Abnahme des gesamten Handbuches, Ganzleinen $ 15,25.

Il y a quelque temps, nous avions le plaisir de présenter aux lecteurs des *Analytica Chimica Acta* le volume I,1 de cette série. Peu après, parut le volume II,1 et aujourd'hui nous avons entre les mains le volume I,2. Ainsi que son titre l'indique, l'ouvrage est composé de deux parties, la première concernant les balances et la pesée, la seconde, l'appareillage utilisé en microgravimétrie minérale. Il est tout à fait superflu de présenter les auteurs, tous deux étant des autorités dans le domaine de l'analyse microchimique.

La première partie, concernant les balances, comprend les chapitres suivants: *Allgemeiner Teil.* Präzision und Genauigkeit. Die Präzision der Wägungen. Die Genauigkeit der Wägung. *Präzisionshebelwaagen.* Allgemeine Beschreibung der Waage. Allgemeine Beschreibung von bei Waagen benutzten Zusatz- oder Hilfsgeräten. Theorie der gleicharmigen Hebelwaage. Beschreibung der Leistungsfähigkeit einer Präzisionshebelwaage. Aufstellen und Reinigen von Präzisionshebelwaagen. Allgemeine Ratschläge zur Behandlung von Präzisionswaagen. Wägung durch Massenvergleich. Austarieren. Neigungswägung und Eichung der Waage. Ausführung von Proportionalwägungen. Ausführung der Gauss'schen Doppelwägung. Ausführung von Substitutionswägungen. Neuerungen an mikrochemischen Waagen. *Mikrowaagen.* Das Bauen von Mikrowaagen. Die Teile der Balkenwaagen. Wägungsprinzipien und ihre Anwendung; Mikrowaagen. Literatur am Ende jedes Kapitels. Namen- und Sachverzeichnis.

Ne pouvant pas entrer davantage dans les détails, nous nous contenterons de signaler ici que tous les problèmes ayant trait à la pesée et aux microbalances sont analysés par l'auteur avec beaucoup de clarté et sur une base scientifique. Pour une fois encore, Monsieur BENEDETTI-PICHLER a su allier la théorie à la pratique d'une manière très heureuse. Le chapitre II traite plus spécialement des balances à fléau; on y trouvera toutes les indications nécessaires pour leur installation et entretien. Quant au IIIme et dernier chapitre, il est consacré à la construction et installation des balances à fil de quartz, de même qu'à l'installation et la manipulation des autres balances microchimiques de haute sensibilité.

La seconde partie du livre, consacrée aux ustensiles servant à l'analyse microgravimétrique, est composée des chapitres suivants: *Eigenschaften der für die Mikroanalyse geeigneten Wägungsformen. Vorbereitungen zur Analyse.* Probenahme. Einwaage. Lösen und Aufschliessen. *Reagensbehälter. Rückstandbestimmungen.* Organische und anorganische Substanzen. *Fällen und Fällungsgeräte.* Fällungsgefässe. Fällen. Rühren. Mikrorückflusskühler. Einleiten, bzw. Überleiten von Gasen. Mikropipetten. Pinzetten. Tiegelzangen. *Filtration, Filtergeräte, Auswaschen.* Verfahren nach F. EMICH und seiner Schule. Verfahren nach F. PREGL und seiner Schule. Filtration mittels der Zentrifuge. *Lösen und Umfällen von Niederschlägen. Trocknen der Niederschläge. Glühen der Niederschläge. Abdampfen.* Geräte. Methodisches. *Abrauchen. Methodik nach* J. DONAU. *Dichtebestimmung von Flüssigkeiten.* Literatur am Ende jedes Kapitels. Namen- und Sachverzeichnis.

Monsieur HECHT avait déjà traité ce sujet dans la partie générale de son traité classique de microanalyse. Néanmoins, il ne s'agit pas ici d'une simple reprise du sujet, mais plutôt d'un travail de compilation où l'on trouvera toutes les données concernant l'emploi des différents vases, ustensiles et autres appareils microchimiques préconisés depuis la naissance de la microchimie jusqu'à nos jours. La microélectrolyse sera traitée dans un autre volume de la série, aussi ne fait-elle pas partie du livre présent.

Nous sommes heureux d'avoir entre les mains un recueil aussi complet des techniques microchimiques minérales, recueil qui épargnera à bien de chimistes des recherches fastidieuses dans le très vaste champ de la bibliographie chimique.

En concluant, nous tenons à recommander vivement cet excellent livre, persuadés qu'il rendra bien des services aux microanalystes.

I. KAPÉTANIDIS (Genève)

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Treatise on Analytical Chemistry, (en trois parties) par I. M. KOLTHOFF ET P. J. ELVING, assistés de E. B. SANDELL, 1ère partie, Vol. 1, *Théorie et pratique*, The Interscience Encyclopedia, Inc., New York, 1959, 809 pages, Prix: $ 17.50.

Ces auteurs ont entrepris une oeuvre d'envergure, celle de faire un ouvrage comprenant tous les chapitres de la chimie analytique, tant classique que moderne, tant pratique que théorique, une sorte de vaste encyclopédie. Elle comprendra trois parties ayant pour titre: théorie et pratique, la chimie analytique des éléments, analyse des produits industriels et elle sera constituée d'un nombre important de volumes, encore non défini, semble-t-il. Le sujet est si vaste que les auteurs ont dû s'adjoindre de nombreux collaborateurs, pour le premier volume, le seul sorti de presse à ce jour, il y en a 15. C'est dire que chaque partie est traitée par un spécialiste particulièrement averti tant au point de vue théorique que pratique.

Le volume 1 comprend deux sections. La section A a pour titre général: La chimie analytique, ses objectifs, son rôle et ses limites. Les principaux chapitres sont: les méthodes de l'analyse chimique, les erreurs en analyse chimique, précision et exactitude, échantillonnage. La section B, intitulée: application des principes chimiques à l'analyse, traite des éléments et composés, du poids atomique, de l'équilibre chimique, de la représentation graphique, des potentiels d'électrodes, de la nature et de la détermination du pH, de la notion acide–base, de la force des acides et des bases et des courbes de neutralisation qui en découlent, de l'équilibre acide–base en milieu non-aqueux, de la complexométrie, du mécanisme des réactions d'oxydo–réduction, des équilibres d'oxydo–réduction et des courbes de titration, de la solubilité des précipités (formation, propriétés, pureté), des équilibres et des réactions de précipitation. Cette section n'est pas terminée, on en trouvera la suite dans le prochain volume.

Il est difficile de se faire une opinion d'un ouvrage d'une telle ampleur sur un premier volume. On peut néanmoins en tirer quelques remarques. Ce traité ne s'adresse qu'aux lecteurs ayant déjà de solides bases de chimie analytique, aux étudiants avancés, comme aux chimistes qui se destinent à l'industrie ou à la recherche pure. Ce livre va loin et profond et donne une foule de renseignements qu'on ne trouve pas dans d'autres ouvrages. C'est un vrai traité de chimie générale. Quelques chapitres sont entièrement consacrés à la physico–chimie et donnent de tels détails qu'on peut se demander s'ils ne seraient pas plus à leur place dans un livre spécialisé. Les auteurs peuvent répondre à cette objection en montrant que les phénomènes physico–chimiques sont présentés de telle sorte que les applications analytiques en découlent tout naturellement, avec une logique rigoureuse et c'est vrai pour la plus grande partie des chapitres écrits par des physico–chimistes qui ont pensé analytique.

Ce livre renferme des parties très remarquables, susceptibles d'ouvrir de nouveaux horizons; telles sont, par exemple, celles qui traitent des représentations graphiques, des équilibres acide–base où les auteurs, après CHARLOT, adoptent la théorie de BRÖNSTED, qui est certainement la mieux adaptée à la chimie analytique. Citons encore le chapitre sur la conception du pH et celui des réactions entre complexes.

Ce premier volume fait bien augurer de la suite de cet ouvrage qui deviendra, nous en sommes certains, un des outils indispensables tant au chercheur qu'au chimiste de l'industrie, de même qu'à celui qui est chargé d'enseigner les principes et les applications de la chimie analytique. Inutile de louer la présentation, le soin avec lequel les graphiques, les figures, les tableaux sont présentés. C'est la coutume des éditions américaines.

D. MONNIER (Genève)

Anal. Chim. Acta, 23 (1960) 202–203

Gas Chromatography Abstracts 1958, par C. E. H. KNAPMAN ET C. G. SCOTT, Butterworths, London, 1960, 262 p. Prix: 42 s.

Les auteurs présentent une bibliographie très complète des travaux effectués en chromatographie gazeuse jusqu'à fin 1958. Il y a 1468 références, chacune d'elles comprend le titre de l'article, le nom des auteurs et de l'ouvrage et un court résumé de 2 à 6 lignes. En outre ce livre renferme un index des auteurs et une table des matières fort bien comprise grâce à laquelle il est possible de trouver rapidement les articles parus dans un domaine particulier tel que par exemple considération théorique, appareillage, détecteur, colonnes, gaz entraineur, etc.

À l'intérieur de chacune de ces rubriques, les sujets sont classés par ordre alphabétique. Compilation intelligente et qui rendra les plus grands services à tous ceux qui ont recours à cette remarquable méthode de séparation et de dosage.

D. MONNIER (Genève)

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Gmelins Handbuch der anorganischen Chemie, 8. Auflage, Verlag Chemie, G.m.b.H., Weinheim/Bergstrasse. *Alphabetische Folge zur Systematik der Sachverhalte* (Sonderband), in deutscher und englischer Sprache, 1959, IV, 109 Seiten, Kartoniert DM 30.—, Ganzleinen DM 35.—.

Zu dem 1957 erschienenen Sonderband *Systematik der Sachverhalte* ist jetzt als Ergänzung der Sonderband *Alphabetische Folge zur Systematik der Sachverhalte* erschienen. Durch die Mitaufnahme einer grossen Anzahl von Begriffen und Synonyma, die im systematischen Teil nicht berücksichtigt waren, hat sich die Zahl der Stichworte auf etwa 5.000 erhöht. Jedes Stichwort ist mit einer Schlüsselzahl versehen, die dem seit Jahren beim Gmelin Institut bewährten System der Klassifizierung der Begriffe entspricht. Diese Schlüsselzahlen eignen sich gleichzeitig als Grundlage für automatische Dokumentationsverfahren. Der Band enthält neben dem deutschen Verzeichnis auch einen englischen Index mit den entsprechenden Schlüsselzahlen. Dieser Index dürfte besonders den auf dem Literaturgebiet tätigen Chemiker interessieren.

K. EDER (Genf)

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ANNOUNCEMENT

The twelfth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy will be held at the Penn-Sheraton Hotel in Pittsburgh, Pennsylvania, U.S.A., from February 27 through March 3, 1961. About 150 papers will be presented on all phases of analytical chemistry and spectroscopy. A symposium entitled *New Frontiers in Optics and Spectroscopy* will be sponsored jointly by the Pittsburgh Conference and the Optical Society of America.

Original papers are invited on all phases of analytical chemistry, spectroscopy, and nucleonics applied to analysis. The final date for receipt of abstracts is October 15, 1960. Two abstracts should be submitted in triplicate. The first abstract should be limited to 150 words to be printed in the program. The second abstract should be of approximately 500 words to help the Program Committee evaluate and classify the paper. A letter sent with the abstracts should list the names of authors, laboratory in which the work was done, and the current addresses of the authors. All correspondence should be addressed to:

> Dr. WILLIAM F. HARRIS, Program Chairman of the Twelfth Annual Pittsburgh Conference,
> Research Laboratories, Westinghouse Electric Corporation, Pittsburgh 35, Pennsylvania,
> U.S.A.

In addition to the program of technical papers, there will be an exhibition of the newest instrumentation for analysis. More than seventy-five companies will display instruments, chemicals, and equipment.

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Short communications:

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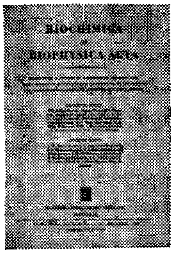
LESS-COMMON METALS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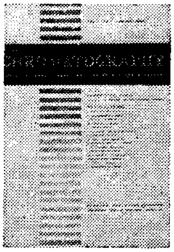

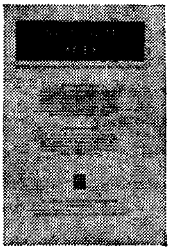

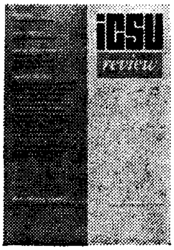
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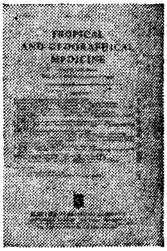

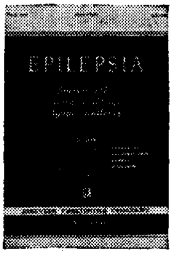
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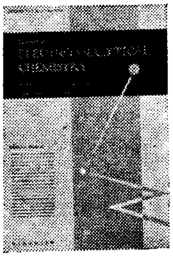

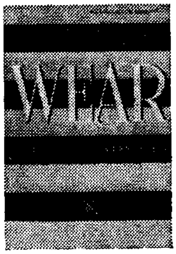
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