ANALYTICA CHIMICA ACTA

International monthly devoted to all branches of analytical chemistry
Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 34, No. 1, 1–124, January 1966

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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 34, No. 1, January 1966

THE POSSIBILITY OF A TRULY ABSOLUTE METHOD OF SPECTROGRAPHIC ANALYSIS

A quantitative expression is given for the relation between the concentration of an element in a sample and the line intensity when a low current d.c. carbon arc with anode excitation is employed. With this equation, the concentration of an element can be determined without previous establishment of a working curve.

L. DE GALAN,
Anal. Chim. Acta, 34 (1966) 2–8

ELEMENTAL SURVEY ANALYSIS BY NEUTRON ACTIVATION: SIMPLIFIED ESTIMATION OF UPPER LIMITS

A procedure is described for the rapid estimation of concentration upper limits of elements not observed in a sample by routine instrumental reactor neutron activation analysis. Experimental and theoretical justifications of time-saving steps are given, and necessary precautions in the use of the procedure are discussed. Tables for use with the procedure are included.

H. R. LUKENS, JR.,
Anal. Chim. Acta, 34 (1966) 9–16

DETERMINATION OF MAGNESIUM AND ZINC IN HUMAN BRAIN TISSUE BY ATOMIC ABSORPTION SPECTROSCOPY

A rapid, interference-free method is presented for the determination of magnesium and zinc in human brain tissue by atomic absorption spectroscopy. Several experimental parameters were investigated, and interference studies were run on each of the analysis elements. A wet oxidation method of lipoid rich brain tissue is described which is rapid and effective. The analyses of many different brain samples, including various sections of individual brain samples, are indicated showing both dry and wet weights. The elemental sensitivity is 0.04 p.p.m. for zinc and 0.01 p.p.m. for magnesium.

T. L. CHANG, T. A. GOVER AND W. W. HARRISON,
Anal. Chim. Acta, 34 (1966) 17–23

THE AMPEROMETRIC TITRATION OF HEXAORGANODITIN COMPOUNDS WITH ELECTROLYTICALLY GENERATED IODINE, BROMINE OR SILVER ION

Coulometric titrations with amperometric end-points, utilizing iodine, bromine or silver ion, were applied to the analyses of several organo-ditin compounds. The various experimental conditions are discussed. It is shown that trimethyltriphenylditin can be determined in mixtures containing hexaphenylditin.

G. TAGLIAVINI,
Anal. Chim. Acta, 34 (1966) 24–31

A RAPID IODINE RADIOCHEMICAL PROCEDURE

A radiochemical procedure was developed to determine fission yields and radiation characteristics of short-lived iodine fission products. Iodine was separated from other fission products of uranium in less than 10 sec after completion of irradiation. High decontamination factors of iodine from Sn, Sb, Te, Xe, Cs and Ba, and high chemical yields were obtained. The sample was prepared by dissolving uranium peroxide in molten periodic acid; the melt was cooled, ground and mixed with activated carbon. After irradiation, the periodic acid was decomposed by heat and the gaseous iodine formed was collected in carbon tetrachloride or in a cooled counting chamber. Higher temperatures could be used than in conventional aqueous systems, thus enhancing the exchange of carrier and fission product iodine.

A. E. Greendale, D. L. Love and A. A. Delucchi,
Anal. Chim. Acta, 34 (1966) 32–40

AN AUTOMATIC ABSORPTIOMETRIC METHOD FOR THE DETERMINATION OF NITRATE

A method has been developed for the determination of nitrate with the Technicon Autoanalyser in the range 2–10 p.p.m. The method depends on the reduction of nitrate to nitrite by hydrazine in alkaline solution, with copper as a catalyst. The nitrite produced diazotises sulphanilamide and the product is coupled with N-(1-naphthyl)ethylenediamine, to give a red dye, the absorbance of which is measured at 550 mμ. A relative standard deviation of 3–4% is obtained.

D. R. Terrey,
Anal. Chim. Acta, 34 (1966) 41–45

FRACTIONAL SUBLIMATION OF VARIOUS METAL β-DIKETONE CHELATES

The vacuum fractional sublimation of various metal β-diketone chelates was compared with the fractional sublimation of the metal acetylacetonates reported earlier. Characteristic recrystallization temperature zones are reported for a number of metal acetylacetonates, acetyltrifluoroacetonates, hexafluoroacetylacetonates, benzoylacetonates, and benzoyltrifluoroacetonates. The substitution of a trifluoromethyl for a methyl group in the ligand molecule increased the volatility of the corresponding metal chelates, but this increased volatility did not lead to improved separations by fractional sublimation. In particular, the hexafluoroacetylacetonates tended to recrystallize as microcrystals in diffuse zones which extended over much of the sublimation tube and the benzoyltrifluoroacetonates tended to distill rather than sublime, with the liquids flowing down the wall of the tube. The best separations were achieved among the metal acetylacetonates. The chelates studied are generally stable and can be recovered from the sublimation apparatus in near quantitative yields. Separations of mixtures of Be, Mg and Cr; Fe, Mg and Al; and Fe and Al were studied critically. Although the separations were not complete, they compared favorably with some reported gas chromatographic separations.

E. W. Berg and F. R. Hartlage, Jr.,
Anal. Chim. Acta, 34 (1966) 46–52

A NEW REACTION FOR THE IDENTIFICATION AND DETERMINATION OF PERCHLORATE

PART I. DETECTION OF PERCHLORATE

Perchlorate is extracted into methyl isobutyl ketone from aqueous solutions of copper(II) ions containing azide ions and an excess of 2,2′-dipyridyl. The yellow color of the organic phase can be used for the detection of perchlorate. A procedure is given which allows the identification of 3 μg of perchlorate. Considerably larger amounts of nitrate, chlorate, chloride and several other anions can be tolerated. By performing the test with the help of the Weisz ring oven technique, a limit of identification of 0.15 μg of perchlorate can be attained.

P. Senise,
Anal. Chim. Acta, 34 (1966) 53–58

SEPARATION AND MEASUREMENT OF CESIUM-137 IN PRECIPITATION

In rainwater samples containing fallout debris of recent origin, the ^{137}Cs absorption peak in a γ-ray scintillation spectrum contained, and was often completely obscured by, contributions from other γ-ray emitting radionuclides, so that the ^{137}Cs activity could not be determined directly. Precipitation samples were collected with rain funnels and passed through Dowex 50W-X12 cation-exchange columns. The ^{137}Cs was selectively eluted with 0.5 M ammonium nitrate. The absolute recovery of ^{137}Cs was complicated by the presence of airborne sediments that were invariably collected with the sample and could irreversibly fix ^{137}Cs from the rainwater.

J. E. Johnson, D. W. Wilson, G. M. Ward and R. D. Thompson,
Anal. Chim. Acta, 34 (1966) 59–63

THE DETERMINATION OF TRACES OF CADMIUM BY ANODIC STRIPPING POLAROGRAPHY

(in French)

A systematic study of the factors influencing the determination of traces of cadmium by anodic stripping at a hanging mercury drop electrode has been made. The limits of application of the method have been widened and the studies have allowed the method to be made as sensitive and accurate as possible.

E. Martin, D. Monnier and W. Haerdi,
Anal. Chim. Acta, 34 (1966) 64–70

SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF CALCIUM AFTER SEPARATION FROM CONCENTRATED LITHIUM CHLORIDE SOLUTION BY ION EXCHANGE

(in German)

Calcium was separated from 1–2 M solutions of lithium chloride by means of Wofatit CP cation exchanger. Calcium was quantitatively separated from lithium by elution with 1 M ammonium chloride. Calcium was eluted with hydrochloric acid and, eventually, measured spectrophotometrically at 567 mμ after addition of buffer and cresolphthalexone. The sensitivity was found to be 0.002 μg Ca/cm^2 and Beer's law was obeyed up to 15 μg Ca. With 1 g of lithium, the limit of determination was 10^{-4}% Ca.

J. Bosholm,
Anal. Chim. Acta, 34 (1966) 71–77

GRAVIMETRIC DETERMINATION OF ZIRCONIUM WITH A NEW AZOPYRAZOLONE DERIVATIVE

3-Methyl-5-oxo-1-phenyl-2-pyrazolin-4-ylazo-2′-(6′,8′-naphthalenedisulfonic acid) (disodium salt) is proposed as a new reagent for the gravimetric determination of zirconium. The precipitate formed at pH 1–1.5 can be weighed directly and there are few interferences.

G. Popa, G. Baiulescu, C. Greff and S. Moldoveanu,
Anal. Chim. Acta, 34 (1966) 78–82

GAS CHROMATOGRAPHIC FRACTIONATION AS A SUPPLEMENT AND REPLACEMENT FOR LABORATORY DISTILLATION

A preparative gas chromatograph which accommodates sample injection volumes of <1 ml–$>$ 200 ml is described. Traps adequate for the quantitative recovery of a similar range of component volumes are also described. Materials, costs and details of operation are discussed. A diverse set of case histories is presented to show that such an instrument is entirely capable of supplementing and replacing normal distillations.

A. B. Carel and G. Perkins, Jr.,
Anal. Chim. Acta, 34 (1966) 83–100

GAS-VOLUMETRIC DETERMINATIONS BY MEANS OF HYPODERMIC SYRINGES: THE DETERMINATION OF HYPOPHOSPHITE

(Short Communication)

T. N. Tischer, A. D. Baitsholts and E. P. Przybylowicz,
Anal. Chim. Acta, 34 (1966) 101–104

DETECTION OF VOLATILE CARBON-14 LABELED COMPOUNDS BY A MODIFIED GAS CHROMATOGRAPHY–IONIZATION CHAMBER TECHNIQUE

(Short Communication)

E. R. White and H. G. Davis,
Anal. Chim. Acta, 34 (1966) 105–107

AN ION-EXCHANGE METHOD FOR THE DETECTION OF ESTERS

(Short Communication)

M. Qureshi and S. Z. Qureshi,
Anal. Chim. Acta, 34 (1966) 108–111

INVESTIGATIONS ON TESTS FOR PHOSPHATE AND SILICATE BY THE RING-OVEN METHOD

(Short Communication)

Y. A. Gawargious, L. J. Ottendorfer and S. W. Bishara,
Anal. Chim. Acta, 34 (1966) 111–114

ULTRAMICROCOULOMETRIC TITRATION OF CHROMIUM(VI)

(Short Communication)

G. D. Christian and F. J. Feldman,
Anal. Chim. Acta, 34 (1966) 115–119

RAPID ISOLATION OF RADIO-SILVER AND CERTAIN OTHER RADIO-ELEMENTS FROM SOLUTION: APPLICATION TO A SEARCH FOR ^{121}Ag IN ^{235}U FISSION

(Short Communication)

H. V. Weiss and W. L. Reichert,
Anal. Chim. Acta, 34 (1966) 119–122

ANALYTICA CHIMICA ACTA

Vol. 34 (1966)

ANALYTICA CHIMICA ACTA

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ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Anal. Chim. Acta, Vol. 34 (1966)

PRINTED IN THE NETHERLANDS

EDITORIAL

This issue of Analytica Chimica Acta heralds the expansion of the journal to three volumes a year. Shortly after its inception in 1948, the Journal had to be expanded to two volumes a year to accommodate the increasing amount of material submitted for publication. The number of papers considered worthy of publication has continued to increase, with the result that the time between acceptance of a paper and its final publication has become a source of dismay to the Editors, Publishers and Authors.

In the belief that the scientific community should be served as expeditiously as possible, we consider expansion to three volumes a year to be the best course of action. It is felt that a significant increase in the already high percentage of papers rejected would result in the loss of a substantial amount of worthwhile information. Likewise, shortening papers to the essential core would not only create hardship for authors who would have to expend time and effort in revisions, but would also result in losses of freedom. We firmly believe in the virtues of personal opinion and individual expression, and in the value of the cross-fertilization of ideas which results when scientists are given freedom to discuss their work fully.

We accept the responsibility of publishing worthwhile contributions as quickly as possible and in this regard we draw attention to the revised information for authors which appears inside the cover of this issue. Correctly prepared manuscripts can be handled more rapidly at all stages from submission to final publication.

Our general editorial policy is to provide a reputable means of publication for significant contributions to analytical chemistry, whether theoretical or applied. We hope that our efforts in this direction will receive as much encouragement in the future as they have in the past.

P.W.W.
A.M.G.M.

THE POSSIBILITY OF A TRULY ABSOLUTE METHOD OF SPECTROGRAPHIC ANALYSIS

L. DE GALAN
Laboratory of Analytical Chemistry, University of Amsterdam, Amsterdam (The Netherlands)

(Received May 18th, 1965)

Like any other analysis, emission spectrochemical analysis is based on a relation between a measured signal, in this case *the intensity* E of a spectral line, and the concentration c_{an} of the element in a sample.

$$E = f\ (c_{an}) \qquad (1)$$

Although a linear relationship between E and c_{an} favours the precision of the analysis, this is not essential, since in general the function $f(c)$ is established by means of standard mixtures containing known amounts of the element to be analysed.

For such a procedure to be applicable, it is necessary that the function $f(c)$ is reproducible from one analysis to another. When the analysis conditions are subject to irregular variations, it is often possible to use a second element as a reference and to establish a relation

$$E = g\ (c_{an}, c_{ref}) \qquad (2)$$

which meets the demands of constancy required in analysis. At the same time the reference element may be chosen in such a way as to make the function g linear with respect to the concentration of the analysis element, but again this is not a prerequisite.

For arc and spark techniques utilized in spectrographic analysis, the second method of analysis is the one commonly employed. The reference element, which is called the internal standard here, allows for fluctuations in external conditions, and especially for variations in excitation conditions in the light source.

However, care is required in selecting a suitable internal standard and in general this choice is directed by the nature of the element to be determined[1]. Also, the internal standard procedure implies extra work in preparing samples and carrying out the analysis. Therefore, methods avoiding this complication and based upon eqn. (1) have received attention; at first for semi-quantitative analyses only, but in recent years for precise analysis too[2].

In the spectrochemical literature such analyses are referred to as being *absolute*[2], although they differ in no way from the procedures commonly employed in spectrophotometry, polarography etc., where this description has not found acceptance. In our opinion it is more appropriate to speak of absolute methods of analysis, when no calibration curve is constructed at all, and the concentration c_{an} is derived directly from the measured signal E. Thus, classical gravimetric and volumetric analysis represent absolute methods of analysis. Obviously, such a procedure requires establishment of a sufficiently accurate theoretical or empirical expression for the function f(c), knowledge of certain characteristic constants and measurement of the signal E in absolute units.

In emission spectroscopy such a procedure has not so far been attempted. Lack of a reliable expression for the function f(c) and insufficient knowledge of characteristic constants are the main problems. However, in the past decade increasing attention has been paid to the accurate determination of transition probabilities. Moreover, a complete expression for the function f(c) can be given for at least one source of excitation: the low current d.c. carbon arc with anode excitation. Therefore, it is worthwhile to reconsider the possibility of truly absolute spectrographic analysis based on eqn. (1), especially since more stable sources of excitation are being developed[3,4].

AN EXPRESSION FOR THE FUNCTION f(c)

To derive an expression for the observed line intensity in dependence of the element concentration in the sample, we start with the relation between emitted radiation J and vapour concentration n:

$$J_q = A_q g_q h\nu_q \frac{(1-\alpha)}{Z} n \, e^{-V_q/kT} \qquad (3)$$

where J_q is the radiation energy emitted per unit volume, in unit time within a particular atomic transition q; J will be called emittance,
A_q is the transition probability,
g_q is the statistical weight of the upper level,
$h\nu_q$ is the energy difference between the levels,
V_q is the excitation energy,
T is the temperature,
k is Boltzmann's constant,
Z is the partition function of the atom,
n is the total concentration of the element under consideration in the discharge zone; it includes atoms and ions,
α is the degree of ionization of the element, which can be calculated from temperature and electron concentration by means of SAHA's equation.

The constants ν and A appearing in this equation are the characteristic constants of the analytical method. Whereas the frequency ν is very accurately known, the transition probabilities A are accurately known for a small number of transitions only. This restricts the possibility of absolute analysis to some twenty elements.

Equation (3) can be transformed to yield an expression of the form of eqn. (1) with the following considerations.

(*a*) The photographically measured line intensity E is the integral of the emittance J over the diameter of the source and the exposure time. With a special optical arrangement and an ABEL transformation it is possible to derive J from measured intensities E[5]; we shall denote this by $J = \mathrm{Tr}(E)$.

(*b*) To measure E in absolute units (erg/cm^2) the optical arrangement must be calibrated with a standard light source of known radiance, such as a tungsten ribbon lamp.

(*c*) At any point in the discharge zone the vapour concentration n of the element is proportional to the rate of entry Q, denoting the number of atoms of the element evaporating from the sample electrode in unit time. The proportionality factor Ψ is a measure of the velocity, with which the particles of the element are transported through the discharge volume[6]. Integrating eqn. (3) over the exposure time t_e we obtain

$$\mathrm{Tr}(E) = \int_0^{t_e} \mathrm{const} \cdot Aghv \frac{(1-\alpha)}{Z} \frac{Q}{\Psi} \mathrm{e}^{-V/kT} \mathrm{d}t \tag{4}$$

where the constant is determined by calibration with the standard light source. When the excitation conditions in the source are constant during the exposure, the degree of ionization α, the temperature T, the partition function Z, and the transport factor are independent of time and we obtain after rearranging

$$\int_0^{t_e} Q\,\mathrm{d}t = K \frac{Z\Psi}{(1-\alpha)A} \mathrm{e}^{V/kT} \mathrm{Tr}(E) \tag{5}$$

where all accurately known constants have been taken together (K).

The integral on the left hand side of this equation denotes the amount of element entering the discharge zone within the exposure time t_e. In general this quantity is unknown. However, by extending the exposure over the total time t_b, required to volatilize the sample in the supporting electrode completely, we make sure that all the element present enters the discharge zone. In that case the integral is equal to $M \cdot c_{an}$, where M is the weight of the sample charged into the electrode, and c_{an} is the weight percentage of the required element. Practice shows that it is possible to obtain reasonably constant excitation conditions over the entire burning period of the sample[5].

A more fundamental problem is the evaluation of the transport factor Ψ. Apart from the fact that for most light sources the absolute magnitude of this factor is not known, it is definitely not permissible to take it as equal for all elements. Indeed, the transport velocity of an element depends on the characteristics of the light source and element[7]. Recently, the author has described a study of the d.c. carbon arc with anode excitation. For this type of light source a very simple expression was obtained for the transport factor in the middle of the arc[5]:

$$\Psi = \frac{Q}{n} = 300 \cdot 10^{\alpha} \ (\mathrm{cm^3/sec}) \tag{6}$$

where α is degree of ionization. When this is substituted into eqn. (5), we obtain finally

$$\int_0^{t_b} Q\,\mathrm{d}t = M \cdot c_{an} = 300 \cdot k \frac{Z}{(1-\alpha)A} 10^{\alpha} \mathrm{e}^{V/kT} \mathrm{Tr}(E) \tag{7}$$

This expression is of the form of eqn. (1) and it can be utilized for truly absolute analysis. Indeed, the constant K is found from simple calibration with a standard light source, and temperature and electron concentration can be measured, where-after partition function Z, degree of ionization α, and the exponent V/kT can be calculated; finally, the intensity E can be measured and the ABEL transform can be evaluated[5].

The accuracy of the analysis is determined by the accuracy of the value substituted for A. In favourable cases absolute transition probabilities are known to within 10%. The appearance of the temperature in eqn.(7) makes high demands on the undisturbed measurement of this parameter. Systematic errors may result from a systematic deviation of the measured temperature. Again, this is not a principal objection to the method, because this difficulty is removed, when accurate methods for measuring arc temperatures have been developed. In the present investigation the same temperature scale was used as that applied in establishing eqn.(6). As has been discussed elsewhere, the factor 300 in this equation is determined by the scale of reference for the temperature[5]. Consequently, systematic errors of this kind need not be feared.

EXPERIMENTAL

Details of optical arrangement, calibration with standard light source and measurement of temperature and electron concentration have been described previously[5]; the exposure conditions are stated in Table I.

TABLE I

SPECTROGRAPHIC OPERATING CONDITIONS

Spectrograph	Zeiss Qu-24 medium quartz prism
Slit width	10 μ
Current	10 A, direct current
Open circuit voltage	250 V
Electrodes	Ultra Carbon Co., Bay City, Michigan, U.S.A.; supporting anode (4 mm internal diameter × 12 mm deep, graphite), carbon cathode
Arc gap	10 mm
Exposure	to completion
Emulsion	Ilford N-40 Process Plate
Photographic processing	4 min at 20° in I.D.-2
Sample	50-mg test substance; 20-mg top layer consisting of graphite powder, spectroscopic buffer and matrix compound only

To test the method of analysis outlined above, test mixtures of the elements aluminium, tin, gallium, gold, silver, zinc and magnesium in excess silicon dioxide were prepared. The last two elements were necessary to measure temperature and electron concentration; they were also made the object of analysis.

One part of the mixture was diluted with graphite powder, yielding a test substance of overall composition $SiO_2:C=1:2$; to another part of the mixture were added equal amounts of lithium fluoride and graphite powder, so that the overall composition of this second test substance was $SiO_2:LiF:C=1:1:1$. All compounds were of "Specpure" quality; the absence of self-absorption was checked.

Smoothness of evaporation and constancy of excitation were checked with moving plate exposures and found to be satisfactory for both substances. The silicon/carbon mixture yielded an arc temperature of 6300°K; the addition of the spectroscopic buffer lithium fluoride reduced the arc temperature to about 5600°K. The electron pressure was 10^{-3} atm in both cases.

The analysis lines used in the investigation and the relevant absolute transition probabilities are summarized in Table II. Obviously, the systematic error of the analysis is restricted to some 10%; of course, the direction of this error may vary from one element to another. The random error in determining the concentration c_{an} is at least of the same magnitude, because the random error in measuring line intensities exerts an influence through the spectroscopically measured temperature and degree of ionization; also, the ABEL transformation produces an increase of random error[5]. On the other hand, the random error is reduced by repeating the observations. In general the accuracy of an experimental result is expected to be about 25%.

TABLE II

ANALYSIS LINES AND TRANSITION PROBABILITIES

Element and line	*Trans. prob. $gA(10^8/sec)$*	*Estimated error (%)*	*Reference*
Ag I 3280	6.95	5	8
Al I 3082	2.56	10	9,10
Au I 2675	3.54	10	8
Ga I 2874	6.98	10	9,10
Mg I 2852	9.10	10	9
Sn I 2863	1.95	25	11
Zn I 3076	0.00105	10	12

DISCUSSION

The results of the analysis are presented in Table III. The accuracy can be read from the last column, where the logarithmic differences are stated between the experimental value and the true value of the weight percentage of an element in the

TABLE III

ACCURACY OF ABSOLUTE ANALYSIS

Matrix	*Element*	*Weight percentage c_{an}*		*Logarithmic difference*
		True value	*Exp. value*	
	Ag	0.002	0.002	0
	Al	0.15	0.25	+0.2
	Au	0.10	0.06	−0.2
$SiO_2 : C = 1 : 2$	Ga	0.20	0.16	−0.1
	Mg	0.0015	0.0008	−0.2
	Sn	0.10	0.1	0
	Zn	2.0	2.5	+0.1
	Ag	0.0010	0.001	0
	Al	0.015	0.025	+0.2
	Au	0.10	0.08	−0.1
$SiO_2 : C : LiF = 1 : 1 : 1$	Ga	0.030	0.015	−0.3
	Mg	0.002	0.004	+0.3
	Sn	0.040	0.04	0
	Zn	6.0	7.5	+0.1

Mean arithmetic deviation 10^{-3}.

sample. Both the magnitude and the sign of the deviations are seen to vary among the elements. The maximum inaccuracy in estimating the concentration is a factor two; the general error is about 35%, which agrees with expectation.

Obviously, this marks the method as a semi-quantitative one. Considered from a practical standpoint, it compares unfavourably with other semi-quantitative methods of analysis. Although the present method does not require preparation of standard samples or construction of working curves, this advantage is outweighed by the fact that measurement of temperature and electron concentration in the arc and the reduction of measured line intensity to concentration with eqn.(7) are tedious and time-consuming procedures.

It must be borne in mind, however, that such objections as limited accuracy and complicated calculation may be overcome in future. The availability of more accurate transition probabilities and development of more stable light sources will lead to a decrease of systematic and random error. At the same time it can be expected that the awkward ABEL transformation may be avoided by using effective values for temperature and electron concentration (*i.e.* averaged over the diameter of the source) and by substituting intensity E instead of $\mathrm{Tr}(E)$ into eqn.(7). When the excitation conditions in the source are well defined and reproducible, one single measurement of temperature and electron concentration will suffice and a nomogram of eqn.(7) is then easily constructed.

At present the theoretical implications of the results are more important than the question of immediate practical applicability. The agreement between the expected level of accuracy and the experimentally observed deviations shows the principal possibility of truly absolute analysis. It also proves that eqn.(7) is a correct expression for the relation between observed spectral line intensity E and sample concentration c_{an}.

Of course, the validity and applicability of eqn.(7) are restricted to the excitation source for which eqn.(6) was established: the low current d.c. carbon arc with the lower supporting electrode made the anode. In other sources the transport velocity of elements can be quite different[7] and accordingly, the transport factor Ψ will be different. The fact that the present results were obtained with the same equipment as employed in constructing eqn.(6) does not reduce their importance, but confirms the validity of this expression. Since the elements gold and silver were not used in the previous investigation, these elements represent new and independent examples. Also, the matrix compounds in the test substances differ from those employed previously (aluminium oxide, lithium fluoride, potassium fluoride).

Although eqn.(6) is an empirical relation, derived from experimental observations, an approximate theoretical explanation has been given[5]. The results of a more extensive theoretical study of transport phenomena in the d.c. arc will be published shortly.

Finally, we mention an application of eqn.(7), which may be of more immediate use. When the sample concentration of an element is known, eqn.(7) can be utilized to calculate the absolute value of the transition probability of a spectral line. This procedure should be useful to obtain transition probabilities of very weak spectral lines, which cannot be compared directly with strong lines of the spectrum on account of interfering self-absorption.

As an example, we determined the transition probability of the line Al I 3057

Å, which can be observed in the arc spectrum when the sample concentration of aluminium exceeds 10%. For this high aluminium concentration the reference lines of the simple aluminium spectrum are subject to very serious self-absorption. For example, the theoretical value for the intensity ratio of the doublet lines Al I 3091 and Al I 3082 Å is 2; this value is measured, if the aluminium concentration in the sample is 0.01%. If the aluminium concentration is 10%, however, the experimental value for this ratio is as low as 1.1.

If the transition probability of the line Al I 3057 Å is determined by direct comparison with the line at 3082 Å, we measure a value of $gA(3057)/gA(3082) = 7.5$, or $gA(3057) = 2 \cdot 10^9$/sec. On the other hand, if the transition probability of the line is derived from eqn.(7), we measure $gA(3057) = 6 \cdot 10^7$/sec, which value is much more plausible. Because the procedure for measuring transition probabilities is completely similar to the absolute analysis, the accuracy of the resulting estimate is restricted to about a factor 1.5; we consider this rather promising for such difficult transitions.

SUMMARY

A quantitative expression is given for the relation between the concentration of an element in a sample and the line intensity when a low current d.c. carbon arc with anode excitation is employed. With this equation, the concentration of an element can be determined without previous establishment of a working curve.

RÉSUMÉ

Une expression quantitative est donnée pour la relation entre la concentration d'un élément dans un échantillon et l'intensité de la raie émise, dans le cas d'un spectre d'arc, avec excitation anodique. Grâce à cette équation, la concentration d'un élément peut être déterminée sans établissement préalable d'une courbe.

ZUSAMMENFASSUNG

Es wird ein quantitativer Ausdruck angegeben für die Beziehung zwischen der Linienintensität und der Konzentration eines Elements in der Probe bei Anwendung eines Gleichstromkohlebogens mit anodischer Anregung. Dieser Ausdruck ermöglicht eich- und leitprobenfreie quantitative Analysen.

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ELEMENTAL SURVEY ANALYSIS BY NEUTRON ACTIVATION: SIMPLIFIED ESTIMATION OF UPPER LIMITS

H. R. LUKENS, JR.
General Atomic Division, General Dynamics Corporation, San Diego, Calif. 92112 (U.S.A.)
(Received April 7th, 1965)

With suitably high neutron fluxes, neutron activation analysis has been shown to have very good analytical sensitivity for most elements[1]. The fact that it can be employed in a non-destructive manner with the aid of γ-ray spectrometry[2] makes it especially suitable for elemental survey analyses of unknown samples. In practice, a relatively small number of elements often dominate the γ-ray spectrum of an irradiated sample by virtue of their relative concentrations and analytical sensitivities. Naturally, only upper limits of concentration can be obtained for the majority of elements not evidenced in the γ-ray spectrum. Measures that can be taken to simplify the usually arduous task of computing upper limits in this type of work are described herein.

The dominant γ-rays evidenced in a complex γ-ray spectrum in effect represent "noise", or "background", with respect to one another and particularly with respect to the measurement of the less prominent elements. If upper limits for the many elements not discernible in the spectrum are computed with reference to the "noise" in the regions in which their individual γ-ray peaks would appear, the computations are quite tedious. This is especially true if random irradiation and measurement times are employed. However, if calculations are made for a restricted analytical regimen, the weight of each element required to obtain a given peak intensity can be defined in advance and used in all subsequent analyses. Furthermore, if limit calculations are made with respect to approximate rather than exact peak regions, the number of such regions needed to account for all limits can be greatly reduced.

While upper limits may sometimes be the best information obtainable, they may often be economically desirable. Also, in many analytical situations the exact determination of the amounts (or concentrations) of one or more specified elements present in a sample is not really necessary, or does not warrant the expenditure of the additional effort needed to ascertain them — a reasonably firm upper limit may be quite adequate. For example, if specifications or requirements merely stipulate that the manganese content of a sample should not exceed 10 p.p.m., and it can rapidly be shown that the sample contains < 2 p.p.m. Mn, it would be pointless to carry out a more detailed analysis which ascertained that the actual value was, say, 0.15 ± 0.01 p.p.m. Mn. The rapid method of estimating upper limits for many elements, from neutron activation analysis γ-ray spectrum data, developed in this paper enables one to set upper limits for many elements with only two irradiations of the sample (non-destructive). If the upper limit thus established for a particular element is higher than the specification value, more detailed analysis, possibly including post-irradiation radiochemical separations, may be warranted.

EXPERIMENTAL

A fairly simple procedure is recommended for general neutron activation survey analysis. A weighed sample is irradiated for 1 min, allowed to decay for 1 min,

TABLE I

72-ELEMENT SURVEY

(1-Min irradiation at a thermal-neutron flux of $4.3 \cdot 10^{12}$ n/cm^2/sec ($3.5 \cdot 10^{12}$ F.S. Flux) and 1-min decay)

E_γ(MeV)	*Element*	*μg^a*	*Indicator*	*E_γ(MeV)*	*Element*	*μg^a*	*Indicator*
0.042	Nb	1	6.6m Nb-94m	0.46	I	0.26	25m Tc-131
0.051	Rh	0.07	4.4m Rh-104m	0.51	Cu	6	12.8h Cu-64
0.058	Ir	0.15	1.4m Ir-192m	0.51	Os	2	9.5m Os-190m
0.059	Co	0.5	10m Co-60m	0.53	Xe	2	15.6m Xe-135m
0.064	Re	0.08	18.7m Re-188m	0.56	Rb	0.5	1.0m Rb-86m
0.08	Ho	4	27h Ho-166	0.56	As	10	26.5h As-76
0.084	Tm	2000	127d Tm-170	0.566	Sb	1.2	2.8d Sb-122
0.089	Lu	1	3.7h Lu-176m	0.62	Br	4	17.6m Br-80m
0.108	Dy	0.0008	1.3m Dy-165m	0.66	Ag	0.07	24s Ag-110
0.11	Nd	0.5	12m Nd-151	0.72	Ru	60	4.5h Ru-105
0.127	Cs	3	2.9h Cs-134m	0.74	Ce	300	60s Ce-139m
0.13	W	0.3	1.6m W-185m	0.75	Zr	5000	17h Zr-97
0.14	Sc	0.025	19.6s Sc-46m	0.84	Mg	20	9.5m Mg-27
0.14	Ge	0.6	49s Ge-75m	0.84	Ga	7	14h Ga-72
0.147	Yb	25	1.9h Yb-177	0.85	Mn	0.2	2.58h Mn-56
0.15	Te	5	25m Te-131	0.85	Fe	4000	2.58h Mn-56
0.162	Se	0.6	17.5s Se-77m	0.90	Pb	200,000	66.9m Pb-204m
0.163	Ba	14	84m Ba-139	0.92	Y	8.6	17s Y-89m
0.18	Ta	11	16.5m Ta-182m	0.96	Eu	0.2	9.3h Eu-152m
0.19	Kr	1	13s Kr-86m	0.97	Tb	2500	73d Tb-160
0.19	Mo	20	15m Mo-101	1.27	In	0.008	54m In-116
0.19	Pd	1	4.8m Pd-109m	1.29	A	35	1.8h A-41
0.20	O	30,000	29s O-19	1.37	Na	9	15h Na-24
0.20	Hg	10	5.5m Hg-205	1.44	V	0.04	3.76m V-52
0.25	Sm	0.18	24m Sm-155	1.44	Cr	300	3.76m V-52
0.308	Er	6	7.5h Er-171	1.49	Ni	800	2.56h Ni-65
0.32	Ti	4	5.8m Ti-51	1.53	K	500	12.5h K-42
0.33	Sn	13	9.5m Sn-125	1.57	Pr	135	19.1h Pr-142
0.337	Pt	5	1.3m Pt-197m	1.6	F	30	11s F-20
0.36	Gd	6	3.7m Gd-161	1.6	La	20	40.2h La-140
0.39	Sr	5	2.8h Sr-87m	1.64	Cl	12	37m Cl-38
0.412	Au	0.43	2.7d Au-198	1.78	Al	0.2	2.3m Al-28
0.43	Cd	40	50m Cd-111m	1.78	Si	20	2.3m Al-28
0.44	Ne	13	38s Ne-23	1.78	P	60	2.3m Al-28
0.44	Zn	200	13.9h Zn-69m	3.1	S	5000	5m S-37
0 443	Hf	0.9	5.5h Hf-180m	3.1	Ca	150	8.8m Ca-49

[a] Micrograms per 1000 counts/min in the photopeak. Short-lived species corrected for decay during 1-min count.

then measured for 1 min by multichannel γ-ray spectrometry. The sample is then irradiated for 30 min and measured with the spectrometer for a known period of time at one hour, one day, and 8 days after termination of the irradiation. Each γ-ray peak is identified, and appropriate concentrations of the contributing elements calculated. Upper limits are estimated for the remaining elements from the gross spectrum.

In the author's laboratory, the short irradiation is performed in a pneumatic transfer system which terminates in a vacant fuel-element position in the core of a TRIGA Mark I nuclear reactor, operating at 250 kW. At this power level the sample is exposed to a thermal-neutron flux of $4.3 \cdot 10^{12}$ n/cm^2/sec and a fission-spectrum

TABLE II

68-ELEMENT SURVEY

(30-Min irradiation at a thermal-neutron flux of $1.8 \cdot 10^{12}$ n/cm^2/sec ($1.5 \cdot 10^{12}$ F.S. Flux) and 60-min decay)

E_γ(MeV)	*Element*	μg[a]	*Indicator*	*E_γ(MeV)*	*Element*	μg[a]	*Indicator*
0.033	Kr	0.06	114m Kr-83m	0.443	Hf	0.2	5.5h Hf-180m
0.051	Rh	3200	4.4m Rh-104m	0.46	I	0.08	25m I-131
0.059	Co	4	10m Co-60m	0.48	Y	100	3.2h Y-90m
0.074	Pt	1.2	31m Pt-199	0.51	F	1000	1.9h F-18
0.08	Ho	0.26	27h Ho-166	0.51	Cu	0.4	12.8h Cu-64
0.084	Tm	120	127d Tm-170	0.55	Br	2	36h Br-82
0.088	Pd	7.6	13.6h Pd-109	0.56	As	1.4	26h As-76
0.102	Sm	0.12	47h Sm-153	0.566	Sb	0.8	2.8d Sb-122
0.104	Se	16	57m Se-81m	0.66	Ag	200	253d Ag-110m
0.127	Cs	0.24	2.9h Cs-134m	0.686	W	0.04	24h W-187
0.133	Hg	3.4	24h Hg-197m	0.72	Ru	4.4	4.5h Ru-105
0.14	Mo	20	67h Mo-99	0.75	Zr	340	17h Zr-97
0.15	Sn	6	41m Sn-123	0.84	Mg	2600	9.5m Mg-27
0.15	Te	2	25m Te-131	0.84	Al	8000	9.5m Mg-27
0.155	Re	0.24	17h Re-188	0.84	Ga	4.4	14h Ga-72
0.163	Ba	1.6	84m Ba-139	0.85	Mn	0.012	2.58h Mn-56
0.2	Nd	2.8	1.8h Nd-149	0.85	Fe	700	2.58h Mn-56
0.208	Lu	0.12	6.8d Lu-177	0.89	Sc	4.4	83d Sc-46
0.21	Ge	16	11h Ge-77	0.90	Pb	3000	67m Pb-204m
0.233	Xe	40	2.3d Xe-133m	0.96	Eu	0.012	9.3h Eu-152m
0.281	Os	2	30h Os-193	1.12	Ta	20	115d Ta-182
0.294	Ce	40	33.4h Ce-143	1.27	In	0.002	54m In-116
0.30	Tb	11	73d Tb-160	1.28	Si	30,000	6.6m Al-29
0.308	Er	0.3	7.5h Er-171	1.29	A	5	1.8h A-41
0.32	Ti	1040	5.8m Ti-51	1.37	Na	1.2	15h Na-24
0.32	Cr	180	27d Cr-51	1.44	V	400	3.8m V-52
0.325	Ir	0.1	19h Ir-194	1.49	Ni	60	2.6h Ni-65
0.35	Dy	0.01	2.3h Dy-165	1.53	K	40	12h K-42
0.36	Gd	2.4	18h Gd-159	1.57	Pr	8	19.1h Pr-142
0.39	Sr	0.6	2.8h Sr-87m	1.60	La	1.4	40h La-140
0.396	Yb	4	4.2d Yb-175	1.64	Cl	2.8	37m Cl-38
0.412	Au	0.03	2.7d Au-198	1.85	Rb	80	17m Rb-88
0.43	Cd	10	50m Cd-111	2.35	Nb	1600	13h Nb-92m
0.44	Zn	34	14h Zn-69m	3.1	Ca	4000	8.8m Ca-49

[a] Micrograms per 1000 counts/min in the photopeak.

neutron flux of $3.5 \cdot 10^{12}$ n/cm²/sec. The longer irradiation is carried out with the sample placed in a specimen rack that rotates around the core. The thermal-neutron and fission-spectrum neutron fluxes in this position are $1.8 \cdot 10^{12}$ n/cm²/sec and $1.5 \cdot 10^{12}$ n/cm²/sec, respectively, during 250-kW operation. Spectra are obtained in 200 channels of a γ-ray spectrometer.

The following Tables are based on the foregoing specifications and the use of a solid 3-in. diameter by 3-in. high NaI(Tl) scintillation detector, shielded by 4 in. of lead with a cadmium–copper lining. A sample size of 1 ml is assumed, and the counting arrangement includes placement of a 0.5-in. plastic β-particle absorber between the detector and the sample. Otherwise, closest geometry is employed. Each Table indicates the number of micrograms of element required for the measurement of 1000-photopeak counts in 1 min. Table I is given for the 1-min irradiation and Tables II, III, and IV are given for decays of one hour, one day, and 8 days, respectively, following the 30-min irradiation. The listing in each Table is in the order of increasing γ-ray energy. The values embodied in the Tables represent a composite of data accumulated at General Atomic and includes previous work by YULE[3], in connexion with the examination of very pure materials.

TABLE III

54-ELEMENT SURVEY

(30-Min irradiation at a thermal-neutron flux of $1.8 \cdot 10^{12}$ n/cm²/sec ($1.5 \cdot 10^{12}$ F.S. Flux) and 24-h decay)

E_γ(MeV)	Element	μg[a]	Indicator	E_γ(MeV)	Element	μg[a]	Indicator
0.074	Os	1.5	14h Os-191m	0.44	Zn	110	14h Zn-69m
0.08	Ho	0.5	27h Ho-166	0.482	Hf	21	44.6d Hf-181
0.084	Tm	120	172d Tm-170	0.482	W	1.2	24h W-187
0.088	Pd	30	13.6h Pd-109	0.494	Ba	760	11.5d Ba-131
0.094	Dy	10	2.3h Dy-165	0.50	Ru	180	40d Ru-103
0.102	Sm	0.16	47h Sm-153	0.51	Cu	1.6	12.8h Cu-64
0.133	Hg	6.8	24h Hg-197m	0.52	Cd	38	53h Cd-115
0.136	Pt	40	4.3d Pt-193m	0.532	Nd	250	11.1d Nd-147
0.14	Mo	26	67h Mo-99	0.55	Br	3.2	36h Br-82
0.15	Kr	90	4.4h Kr-85m	0.56	As	2.8	26h As-76
0.155	Re	0.33	17h Re-188	0.566	Sb	1.0	2.8d Sb-122
0.161	Sn	10,000	14d Sn-117m	0.605	Cs	36	2.1y Cs-134
0.191	In	30	50d In-114m	0.66	Ag	200	253d Ag-110m
0.208	Lu	0.14	6.8d Lu-177	0.75	Zr	900	17h Zr-97
0.21	Ge	70	11h Ge-77	0.84	Ga	15	14h Ga-72
0.233	Xe	55	2.3d Xe-133m	0.85	Mn	7.6	2.58h Mn-56
0.27	Se	170	120d Se-75	0.89	Sc	4.4	83d Sc-46
0.283	Ce	70	33.4d Ce-143	0.96	Eu	0.072	9.3h Eu-152m
0.30	Tb	11	73d Tb-160	1.08	Rb	800	19.5d Rb-86
0.308	Er	1.4	7.5h Er-171	1.09	Fe	40,000	45d Fe-59
0.317	Ir	0.4	74.4d Ir-192	1.12	Ta	20	115d Ta-182
0.32	Cr	180	27d Cr-51	1.17	Co	44	5.3y Co-60
0.36	Te	110	8d I-131	1.37	Na	3.6	15h Na-24
0.36	Gd	6	18h Gd-159	1.53	K	160	12h K-42
0.39	Sr	240	2.8h Sr-87m	1.57	Pr	11	19.1h Pr-142
0.396	Yb	5	4.2d Yb-175	1.60	La	1.6	40h La-140
0.412	Au	0.038	2.7d Au-198	2.35	Nb	5800	13h Nb-92m

[a] Micrograms per 1000 counts/min in the photopeak.

TABLE IV

40-ELEMENT SURVEY

(30-Min irradiation at a thermal-neutron flux of $1.8 \cdot 10^{12}$ n/cm^2/sec ($1.5 \cdot 10^{12}$ F.S. Flux) and 192-h decay)

E_γ(MeV)	*Element*	*μg*[a]	*Indicator*	*E_γ(MeV)*	*Element*	*μg*[a]	*Indicator*
0.08	Ho	30	27h Ho-166	0.482	Hf	23	44.6d Hf-181
0.084	Tm	125	127d Tm-170	0.482	W	160	24h W-187
0.102	Sm	1.9	47h Sm-153	0.494	Ba	1160	11.5d Ba-131
0.133	Hg	850	24h Hg-197m	0.50	Ru	200	40d Ru-103
0.136	Pt	130	4.3d Pt-193m	0.510	Sr	8700	64d Sr-85
0.14	Mo	90	67h Mo-99	0.532	Nd	390	11.1d Nd-147
0.155	Re	330	17h Re-188	0.55	Br	80	36h Br-82
0.161	Sn	15,000	14d Sn-117m	0.56	As	250	26h As-76
0.191	In	33	50d In-114m	0.566	Sb	5.5	2.8d Sb-122
0.208	Lu	0.28	6.8d Lu-177	0.605	Cs	36	2.1y Cs-134
0.233	Xe	400	2.3d Xe-133m	0.66	Ag	250	253d Ag-110m
0.27	Se	180	120d Se-75	0.89	Sc	4.6	83d Sc-46
0.283	Ce	80	33.4d Ce-143	1.08	Rb	1000	19.5d Rb-86
0.30	Tb	12	73d Tb-160	1.09	Fe	45,000	45d Fe-59
0.317	Ir	0.43	74.4d Ir-192	1.12	Ta	21	115d Ta-182
0.32	Cr	220	27d Cr-51	1.17	Co	44	5.3y Co-60
0.36	Te	200	8d I-131	1.28	Eu	240	16y Eu-154
0.36	Gd	4000	18h Gd-159	1.37	Na	9000	15h Na-24
0.396	Yb	16	4.2d Yb-175	1.52	Pr	4500	19.1h Pr-142
0.412	Au	0.23	2.7d Au-198	1.60	La	29	40h La-140

[a] Micrograms per 1000 counts/min in the photopeak.

A composite Table (Table V) is given to indicate the preferred Table for computing the upper limit of each element considered. The fact that continued decay of a complex sample enhances the opportunity of observing a long-lived isotope is taken into account by indicating the longest reasonable decay period, provided that a shorter period does not offer much greater sensitivity. Also, since short-lived interferences are frequently intense, reasonable alternatives to the use of Table I are indicated in parentheses wherever possible. In practice, the lowest upper limit computed for an element from several sets of data is, of course, the one that should be reported.

DISCUSSION

The foregoing procedure and associated Tables can be quite helpful in the survey of samples by means of neutron activation analysis. However, they do not abridge the necessity for arbitrary decisions with respect to data interpretation. The analyst will wish to choose amongst a variety of possible procedures, depending on the degree of precision required in any particular case.

A comprehensive treatment of data interpretation is not intended here. However, a rapid method of manually obtaining approximate upper-limit values is suggested for use where order-of-magnitude precision will suffice. This approach consists of integrating the counts collected during 1 min in each 0.1-MeV energy

TABLE V

OPTIMUM SPECTRA FOR LIMIT CALCULATIONS

Element	*Table*[a]				*Element*	*Table*				*Element*	*Table*			
	I	*II*	*III*	*IV*		*I*	*II*	*III*	*IV*		*I*	*II*	*III*	*IV*
O	x				Ge	x		(x)		La			x	
F	x				As			x		Ce				x
Ne	x				Se	x			(x)	Pr			x	
Na			x		Br			x		Nd	x			
Mg	x				Kr		x			Eu			x	
Al	x				Rb	x				Gd			x	
Si	x				Sr		x			Tb				x
P	x				Y		x			Dy	x			
S	x				Zr			x		Ho			x	
Cl		x			Nb	x				Er		x		
A		x			Mo				x	Tm				x
K			x		Ru		x			Yb				x
Ca	x				Rh	x				Lu				x
Sc	x			(x)	Pd	x			(x)	Hf		x		
Ti	x				Ag	x				Ta				x
V	x				Cd			x		W		x		
Cr				x	In		x			Re	x		(x)	
Mn		x			Sn		x			Os			x	
Fe		x			Sb			x		Ir				x
Co	x			(x)	Te		x			Pt		x		
Ni		x			I		x			Au			x	
Cu			x		Xe	x		(x)		Hg			x	
Zn			x		Cs		x			Pb		x		
Ga			x		Ba		x							

[a] Table I contains sensitivities relevant to a 1-min irradiation and 1-min decay. Tables II, III and IV contain sensitivities relevant to decays of 1 h, 1 day, and 8 days, respectively, following a 30-min irradiation.

interval and arbitrarily taking 10% of each total as representative of upper limits for appropriate elements.

For example, if 10,000 counts/min were collected in the 0.4–0.5 MeV region (with no photopeak evident in this region) at 1 h after a 30-min irradiation by the described procedure, one could say, approximately, that there were less than 1000 counts/min in the region due to Au, Cd, Zn, Hf, I, or Y. In this case the limits for these elements could be read directly from Table II. If a photopeak was evidenced in the region, its assignment would be determined and the quantitative value of the particular element computed; however, the other elements would be treated in the fashion described. Of course, where a definite assignment cannot be given to a photopeak, its net counting rate is used as the basis of computing upper limits for the several possible radioisotopes it may represent in accordance with standard practice.

The foregoing approach has been found to be reasonable in practice and usually compares quite favorably with more detailed upper-limit calculations. For example, where the "noise" in the 0.3–0.4 MeV region (the photopeak region of ^{159}Gd) was 5659 counts/min (due to ^{56}Mn), the limit was taken to be < 1.4 μg of Gd (Table II conditions). The standard deviation of the noise level in this region was, by itself, of little use, since the average activity at the ends of the region exceeded that of the region itself (*i.e.*, a straight baseline did not apply). A detailed analysis, which utilized the shape of the ^{56}Mn spectrum in the region in question and the standard deviation of the noise, gave an upper limit value of < 0.6 μg of Gd. Essentially the same degree of limit comparison was found in the estimation of ^{110}Ag activity limits where ^{56}Mn was present. In each case, decay of ^{56}Mn permitted verification that the less-than values were not exceeded by the element in question.

The upper limits obtained in the above procedure can be obtained very rapidly, and they seldom differ by a factor of more than 5 from those obtained by detailed analysis. This is fairly obvious, for the standard deviation of any number of gross counts between 4 and 2500, which is simply the square root of the number, does not differ by more than a factor of five from 10% of the number. Furthermore, in a detailed limit estimate the error of the gross sample measurement must be combined with the errors associated with other measurements: *i.e.*, the determination of the exact contribution of each interference to the energy interval in question will have an error probability that must be considered. The effect of the combined errors and confidence-level considerations is to extend considerably the upper end of the range scale over which the factor of 5 holds true. Thus, the 3 standard-deviation confidence level of a 40,000 count measurement with a single shape correction is within a factor of 5 of the 10% criterion.

Refinement of the described data interpretation procedure may sometimes be required. The 0.1-MeV energy interval is fairly compatible with the resolution of the detector over much of the energy scale; but an increasing range of intervals, of from about 0.03 to 0.15 MeV, over the full energy scale would provide a somewhat better match in this respect. However, this point is minor compared to the fact that no gross energy interval can truly represent all of the γ-rays that fall therein. Thus, the 0.3–0.4-MeV region of Table II includes both the 0.30-MeV γ-ray of ^{160}Tb and the 0.396-MeV γ-ray of ^{174}Yb. The former would be better placed in a 0.25–0.35-MeV interval and the latter in a 0.35–0.45-MeV interval. It is recommended, however, that adjustments of intervals to accommodate this sort of "end effect" be reserved for cases where use of the original arbitrary interval will result in a significant error.

The chief criterion with respect to possible "end effect" error in a given interval is concerned with the adjacent intervals. If, for example, the 0.2–0.3-MeV interval has nearly the same level of activity at 1 h after a 30-min irradiation as does the 0.3–0.4-MeV interval, the estimation of Os, Ce, Tb, Er, Ti, Cr, and Ir limits from the counts in the 0.3–0.4-MeV interval will be reasonable. However, if the activities in the two regions are widely different, a special energy interval of the spectrum will be required for estimation of limits for these elements (*cf.* Table II).

As in other applications of neutron activation analysis, the analyst must be prepared to recognize and take into account certain facets of sample behavior that may be present. The presence of lithium, boron, or several other particular elements can cause less exposure of the sample to neutrons than would be the case if these elements were absent. Fast-neutron reactions must be recognized: for example, the ^{56}Fe(n, p)^{56}Mn reaction in a core irradiation will give an apparent 50 p.p.m. of Mn in a sample of iron, and the ^{27}Al(n, α)^{24}Na reaction gives the same amount of ^{24}Na as 1000 p.p.m. of sodium in a sample of aluminum.

The given experimental and data interpretation procedure permits very rapid elemental surveys for many types of samples. Where the major sample constituents are insensitive to neutron activation or give rise primarily to very short-lived isotopes (*e.g.* H, Li, Be, C, O, etc.) a γ-ray spectrum relevant to any of the Tables I through IV can be reduced in 30 min or less. Where the matrix gives rise to substantial amounts of radioactivity, the time for interpretation of a spectrum may be increased. The intensity and half-lives of major-constituent radioactivity influence data interpretation. Thus, a major amount of chlorine may render Tables I and II relatively useless, but Tables III and IV could be used for rapid interpretation of data taken at one and 8 days after irradiation. Despite such occasional limitations, the procedure has proven to be very useful in these laboratories, since it frequently permits a rapid and economical elemental survey.

SUMMARY

A procedure is described for the rapid estimation of concentration upper limits of elements not observed in a sample by routine instrumental reactor neutron activation analysis. Experimental and theoretical justifications of time-saving steps are given, and necessary precautions in the use of the procedure are discussed. Tables for use with the procedure are included.

RÉSUMÉ

On décrit un procédé d'estimation rapide pour des concentrations dépassant les limites de l'analyse habituelle par activation au moyen de neutrons. Le mode opératoire est donné, de même que des tables et les précautions nécessaires à prendre.

ZUSAMMENFASSUNG

Es wird ein Verfahren beschrieben, das eine schnelle Bestimmung von Elementkonzentrationen gestattet, die kleiner sind als diejenigen, die mit der routinemässigen Neutronenaktivierungsanalyse bestimmt werden können. Experimentelle und theoretische Begründungen von zeitsparenden Schritten werden angegeben und notwendige Vorsichtsmassnahmen bei Anwendung des Verfahrens diskutiert.

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DETERMINATION OF MAGNESIUM AND ZINC IN HUMAN BRAIN TISSUE BY ATOMIC ABSORPTION SPECTROSCOPY

T. L. CHANG, T. A. GOVER AND W. W. HARRISON
Department of Chemistry, University of Virginia, Charlottesville, Va. (U.S.A.)
(Received April 15th, 1965)

Atomic absorption spectroscopy is rapidly becoming a very important method for trace metal determinations in biological materials. This mainly arises from the accuracy, sensitivity, and freedom from interference shown by the absorption technique. PARKER[1] has determined magnesium, calcium, and zinc in animal tissue in his studies of mineral inter-relationships in animal nutrition. WILLIS has determined zinc and cadmium directly in urine samples without sample pretreatment[2] and has provided a detailed description of the analysis of blood serum for magnesium[3] and potassium and sodium[4]. Other reports have shown the applicability of atomic absorption to the determination of magnesium in such biological samples as bone[5] and feces[6]. FUWA *et al.*[7] recently described the determination of zinc in biological fluids.

This study describes a rapid and relatively interference-free method for the determination of magnesium and zinc in human brain tissue. A convenient and reliable wet digestion method is described for the treatment of brain tissue with its high lipoid content.

EXPERIMENTAL

Reagents

A standard zinc stock solution (1000 p.p.m.) was prepared by dissolving 1.245 g of Specpure-grade zinc oxide (Johnson, Matthey & Co.) in a minimum of dilute hydrochloric acid and diluting to 1000 ml with distilled water. A standard magnesium stock solution (1000 p.p.m.) was prepared by dissolving 1.658 g of Specpure-grade magnesium oxide (Johnson, Matthey & Co.) in a minimum of dilute hydrochloric acid and diluting to 1000 ml with distilled water. Working standards of lower concentration were prepared by appropriate dilution. All other reagents were of analytical grade.

Apparatus

The single beam, DC atomic absorption unit consisted of a Hitachi-Perkin Elmer Model 139 spectrophotometer in conjunction with a Perkin Elmer slot atomizer-burner, a Westinghouse hollow-cathode lamp, and assorted optical equipment mounted on a Cenco 66 cm optical bench. A quartz lens system collimated the slit restricted resonance beam through the air–acetylene flame and then focused the beam on the entrance slit of the monochromater. The Westinghouse WL-22607 zinc tube and the WL-22604 calcium–magnesium–aluminum tube were powered by a Kepco Model ABC 425M 0.05% regulated DC power supply (Kepco, Inc., Flushing, N.Y.), operated in the constant current configuration. The 12-cm atomizer-burner was operated under the following conditions: 2.2 l/min acetylene, 7.1 l/min atomizer air, and 10.9 l/min auxiliary air. The sample uptake rate was 7.0 ml/min. The atomizer-burner introduced 8% of the aspirated sample into the flame. Optimum sensitivity was obtained when the collimated analyzing beam was directed through the flame 5.0 mm above the burner surface. A DC solenoid shutter system mounted on an adjustable slit in front of the tube allowed the hollow cathode radiation to be cut off. An HTV R106 photomultiplier was used as a detector in the Model 139 photomultiplier attachment.

Procedure

Brain tissue contains a considerable amount of lipoid which is difficult to digest by conventional wet procedures. Nitric acid alone, a mixture of nitric acid and hydrochloric acid, or a mixture of nitric acid and hydrogen peroxide will dissolve the tissue, but the lipoid remains undigested. Addition of sulfuric acid to any of the above solutions produces char, indicating the necessity of further oxidation with a stronger oxidant. ALLAN[8] used a mixed acid of 85% nitric acid and 15% perchloric acid to digest fertilizer and plants. However, it was found that direct addition of this mixed acid to brain tissue samples sometimes caused spontaneous ignition of tissue fragments as the oxidation proceeded. Therefore, a two-step digestion is used, as suggested by SMITH[9].

Digest the sample in 100% nitric acid on a hotplate until the bulk of the sample has dissolved. Then add about one-fifth by volume of 70% perchloric acid (*vs.* nitric acid). Continue heating the digestion solution to the dense white fumes of perchloric acid, at which point the lipoid portion becomes completely digested. One gram of wet tissue consumes about 4–5 ml of mixed acid. After cooling, the concentrate is transferred to a suitable volumetric flask and diluted to volume with distilled water to give a final concentration of appropriate absorbance.

Samples were cut into slices of 2–3 mm thickness and dried at 150° overnight. For zinc determination, a sample with a wet weight of about 5 g was digested and diluted to 50 ml in a volumetric flask to give an absorbance between 0.15–0.25. Magnesium was best determined by measuring the absorbance of 5 ml of the above solution diluted to 100 ml. If a separate tissue sample was used, a sample with a wet weight of about 1 g was digested and diluted to 250 ml. This solution gave an absorbance between 0.2 and 0.4 corresponding to a solution containing 0.5 to 1 p.p.m. magnesium.

RESULTS AND DISCUSSION

Zinc

Between 2000 Å and 6000 Å, zinc(I) has two resonance lines, 2138.6 Å and 3075.9 Å[10]. The 2138.6 Å line shows intense absorption, while the 3075.9 Å line exhibits no measurable absorption at the concentrations employed in this study. There are no other significant lines emitted from the zinc hollow-cathode tube in the region of 2138.6 Å, allowing the use of wide slits.

The current applied to the hollow-cathode tube sharply affects the sensitivity of zinc determination. As indicated in Fig. 1, the absorbance drops sharply and linearly with increase of current. The 6 mA current, however, requires a photomultiplier dynode voltage which introduces considerable noise. Therefore, a 10 mA current was selected due to its better signal-to-noise ratio.

Working curves were established (Fig. 2) with solutions containing 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0 and 5.0 p.p.m. of zinc analyzed at 2138.6 Å, 0.5 mm slit width, and 10 mA applied current. Beer's law was followed up to 2.5 p.p.m. for all tube currents.

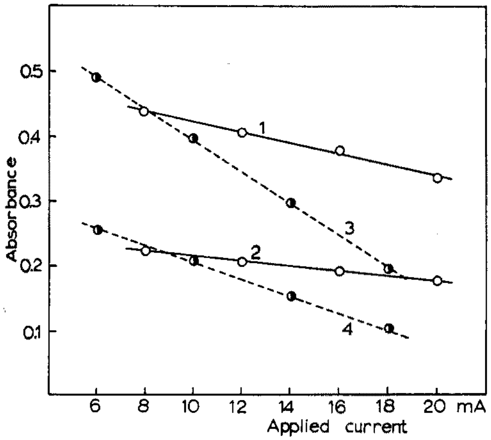

Fig. 1. Effect of hollow-cathode tube current on zinc and magnesium absorption. (1) 1.0 p.p.m. Mg; (2) 0.5 p.p.m. Mg; (3) 3.0 p.p.m. Zn; (4) 1.5 p.p.m. Zn.

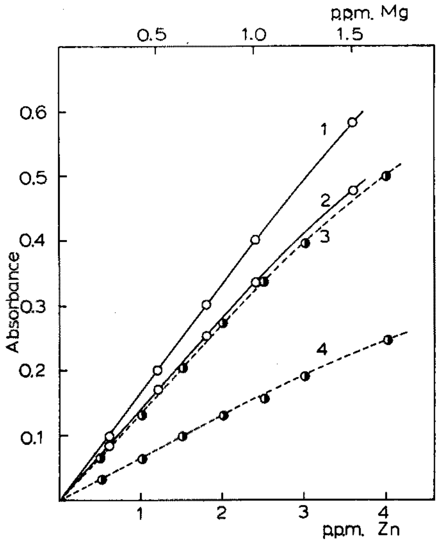

Fig. 2. Working curves for magnesium and zinc at different hollow cathode tube current. (1) Mg, 10 mA; (2) Mg, 18 mA; (3) Zn, 10 mA; (4) Zn, 18 mA.

The sensitivity under these optimum conditions was 0.04 p.p.m. for a reproducible absorbance reading of 0.005 unit. Because of the stability of the system, a smaller absorbance reading could actually be determined.

As indicated by ALLAN[11], no interference of foreign ions was found. To a solution containing 2 p.p.m. of zinc, the following common ions in 1000 p.p.m. concentration were added: K^+, Na^+, Mg^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Sr^{2+}, Mn^{2+}, Fe^{3+}, Cr^{3+}, Al^{3+}, Au^{4+}, Mo^{6+}, Cl^-, NO_3^-, ClO_4^-, SO_4^{2-} and PO_4^{3-}. No change in zinc absorption was noted. This study as well as that by PARKER[1] showed that the presence of hydrochloric acid, nitric acid, perchloric acid or sulfuric acid influences the zinc absorption only slightly.

As a further check on possible interference, the standard addition method was employed to determine the recovery of added zinc in brain tissue samples. The results (Table I) indicate that the contents of brain tissue do not interfere with the determination of zinc by atomic absorption.

Magnesium

Between 2000 Å and 6000 Å, only 3 magnesium emission lines, 2852.1 Å, 2802.7 Å and 2795.5 Å, are significantly absorbed by magnesium in the flame. The 2852.1 Å line is a resonance absorption line for magnesium(I), while the other two represent transitions terminating in the ground state of magnesium(II). A 1 p.p.m. magnesium solution absorbs 56% of the incident 2852.1 Å resonance radiation. A 100 p.p.m. magnesium solution absorbs 22% at the 2802.7 Å line and 41% at the 2795.5 Å line. These measurements were taken at an applied current of 18 mA and 0.1 mm slit width. The 2852.1 Å line was chosen for this work.

TABLE I

RECOVERY OF ADDED Zn FROM BRAIN TISSUE DIGESTIONS

Sample no.	*Zn contained (p.p.m.)*	*Zn added (p.p.m.)*	*Total Zn (p.p.m.)*	*Recovered (p.p.m.)*	*% Recovered*
1	0.82	0	0.82	0.82	100
2	0.82	0.50	1.32	1.34	101
3	0.82	1.00	1.82	1.80	99
4	0.65	0	0.65	0.65	100
5	0.65	0.50	1.15	1.13	98
6	0.65	1.00	1.65	1.62	98
7	0.56	0	0.56	0.56	100
8	0.56	0.50	1.06	1.06	100
9	0.56	1.00	1.56	1.55	99

TABLE II

RECOVERY OF ADDED Mg FROM BRAIN TISSUE DIGESTIONS

Sample no.	*Mg contained (p.p.m.)*	*Mg added (p.p.m.)*	*Total Mg (p.p.m.)*	*Recovered (p.p.m.)*	*% Recovered*
1	0.35	0	0.35	0.35	100
2	0.35	0.20	0.55	0.55	100
3	0.35	0.40	0.75	0.74	99
4	0.35	0.60	0.95	0.93	98
5	0.29	0	0.29	0.29	100
6	0.29	0.20	0.49	0.50	102
7	0.29	0.40	0.69	0.69	100
8	0.29	0.60	0.89	0.88	99

Since the 2852.1 Å line has no closely adjacent lines, a wider slit may be used with no loss in absorption sensitivity. A constant absorption reading for a given magnesium concentration was found up to a slit of 1.0 mm.

The effect of the hollow cathode tube current on magnesium absorption was studied with a series of standard magnesium solutions (Fig. 1). As with zinc, the sensitivity decreased with an increase of applied current, although the slope of this plot was less than for zinc. For a current change from 8 mA to 18 mA, the decrease was 19% for magnesium compared with 56% for zinc. Since at lower currents the analysis sensitivity, as well as the lifetime of the hollow cathode lamp, is increased significantly, a 10 mA current was selected for the analytical determinations.

Under optimum conditions, *i.e.*, 2852.1 Å, 0.2 mm slit width and 10 mA applied current, a working curve was obtained (Fig. 2) with a series of solutions containing 0.25 p.p.m. to 1.5 p.p.m. magnesium. A linear relationship was obtained up to 1.0 p.p.m. for all lamp current studied. The sensitivity, based on a reproducible absorption reading of 0.005 unit, was 0.01 p.p.m.

Interference studies were conducted with the ions previously mentioned. Of these, only aluminum showed any significant effect, as has been reported[12]. Although measures have been described[13,14] to overcome such interference, the aluminum content of brain tissue is so low that it does not affect the magnesium absorption reading.

The presence of perchloric acid, sulfuric acid, nitric acid or hydrochloric acid was found to influence the magnesium absorbance only slightly. The standard addition method was also employed to check recovery rates of magnesium added to brain samples. The results, tabulated in Table II, indicated that interferences from the biological matrix were absent.

Samples from 21 different brains were analyzed. The white matter and grey matter of brain tissue were analyzed separately.

The results are shown in Table III. Reproducibility for duplicate samples taken from the same brain was within $\pm 2\%$. Dry weight comparisons indicated a considerably higher zinc content and a slightly higher magnesium content in the white matter section of the brain. However, the data are too limited to permit generalization. TIPTON[15] found by spectrographic analysis an average brain zinc content of 16.8 μg/g in wet tissue.

The atomic absorption method is quite rapid, simple, and easily adaptable to routine analyses. The suggested procedure should also be suitable for the determination of other trace elements in tissue.

The authors express their appreciation to Dr. M. G. NETSKY, University of Virginia Medical School, who supplied the tissue samples.

SUMMARY

A rapid, interference-free method is presented for the determination of magnesium and zinc in human brain tissue by atomic absorption spectroscopy. Several experimental parameters were investigated, and interference studies were run on each of the analysis elements. A wet oxidation method of lipoid rich brain tissue is described which is rapid and effective. The analyses of many different brain samples, including various sections of individual brain samples, are indicated showing both dry and wet weights. The elemental sensitivity is 0.04 p.p.m. for zinc and 0.01 p.p.m. for magnesium.

RÉSUMÉ

Les auteurs décrivent une méthode rapide et sélective pour le dosage du magnésium et du zinc dans les tissus de cerveau humain, par spectroscopie par absorption atomique. On a examiné plusieurs paramètres expérimentaux et on décrit une méthode d'oxydation par voie humide. Sensibilité: 0.04 p.p.m. pour le zinc et 0.01 p.p.m. pour le magnésium.

TABLE III

MAGNESIUM AND ZINC CONTENT OF HUMAN BRAIN TISSUE AS DETERMINED BY ATOMIC ABSORPTION

Sample no.	*Volatile content* (%)	*Grey matter*				*Volatile content* (%)	*White matter*			
		Magnesium		*Zinc*			*Magnesium*		*Zinc*	
		μg/g wet	*μg/g dry*	*μg/g wet*	*μg/g dry*		*μg/g wet*	*μg/g dry*	*μg/g wet*	*μg/g dry*
10	80.5	120	615	11.8	60.8	72.0	152	524	14.0	48.3
11	80.7	127	660	15.4	80.0	70.8	160	552	10.5	36.2
12	81.8	128	706	14.2	78.2	72.4	161	585	12.8	46.3
13	81.4	126	680	14.0	75.6	75.4	152	622	10.1	41.3
18	83.3	103	620	13.1	78.5	74.0	151	586	10.2	39.5
23	82.8	112	650	13.1	76.5	69.8	178	592	11.2	37.5
24	84.1	113	714	13.2	83.2	73.9	163	625	10.5	40.4
35	83.4	108	658	14.3	86.4	73.8	159	612	9.2	34.7
39	83.7	126	774	12.5	74.7	74.2	168	651	8.5	32.0
40	83.5	105	613	13.3	81.0	68.2	150	480	10.4	33.0
58	85.6	114	788	12.1	83.8	73.4	154	579	10.6	39.8
59	79.2	107	514	12.5	60.0	68.9	159	508	10.7	34.2
61	84.5	108	701	13.7	88.4	75.2	138	559	10.3	41.7
63	82.6	135	777	12.8	73.6	72.5	156	582	9.9	36.1
64	82.8	112	650	12.5	71.5	72.8	140	518	10.4	38.2
66	80.0	108	720	11.5	76.6	68.9	148	462	9.3	28.7
67	84.7	109	710	12.2	79.5	72.9	144	530	10.1	37.2
70	78.3	118	723	12.0	74.2	72.0	145	518	9.3	33.1
72	85.0	109	720	12.5	83.4	72.9	140	518	11.2	41.4
94	84.9	103	685	12.9	90.0	71.5	151	530	10.6	37.0
95	84.6	110	713	12.6	83.6	71.0	148	510	10.7	36.8
Average	82.7 ±1.7	114 ±8	685 ±49	12.9 ±0.7	78.0 ±6.1	72.2 ±1.6	153 ±8	554 ±43	10.5 ±0.7	37.7 ±3.6

ZUSAMMENFASSUNG

Es wird eine schnelle, störungsfreie Methode angegeben zur Bestimmung von Magnesium und Zink in menschlichen Gehirngeweben mittels der atomaren Absorptionsspektroskopie. Es wurden verschiedene experimentelle Parameter undersucht und eine schnelle, wirksame, nasse Oxydationsmethode für die lipoidreichen Gewebe beschrieben. Die Empfindlichkeit beträgt 0.04 p.p.m. für Zink und 0.01 p.p.m. für Magnesium.

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THE AMPEROMETRIC TITRATION OF HEXAORGANO-DITIN COMPOUNDS WITH ELECTROLYTICALLY GENERATED IODINE, BROMINE OR SILVER ION

GIUSEPPE TAGLIAVINI
Institute of Analytical Chemistry, University of Padua, Padua (Italy)

(Received April 14th, 1965)

Methods for the coulometric determination of hexaethyldilead and hexamethylditin with iodine and bromine, respectively, were previously described[1,2]. A compound of the type R_6M_2 (where R is ethyl or methyl, and M is Pb or Sn) in an alcoholic solution containing halide ions, X^-, was placed in the anodic compartment of an electrolysis cell, where it underwent the following reaction:

$$R_3M{-}MR_3 + X_2 \rightarrow 2\ R_3MX$$

due to the X_2 electrolytically produced under constant current at the platinum anode. The end-point was observed by a rise in the indicator current, caused by excess of halogen, between a second pair of platinum electrodes sensitive to the X_3^-/X^- redox system[3]. An amperometric plot of indicator current *vs.* generation time was obtained photographically in order to ensure an accurate determination.

In this earlier work, iodine was employed for the coulometric–amperometric titration of hexaethyldilead, because its rate of reaction was always greater than the rate of electrolytic generation of the halogen. This was not verified for hexamethylditin, for which bromine had to be used.

It was therefore clear that for a definite rate of generation of halogen, the titration depended upon an appropriate reaction rate. The reaction rate can be modified not only by changing the temperature, but obviously also by choosing a proper value of X^- according to the equilibrium:

$$X_2 + X^- \rightleftharpoons X_3^-$$

The present study was designed to verify which of the following compounds could be titrated with bromine and which could be iodinated: hexaethyl-, hexapropyl-, hexabutyl-, hexaphenyl-, and trimethyltriphenylditin.

In addition, since the quantitative reaction

$$Et_6Pb_2 + 2\ Ag^+ \rightarrow 2\ Et_3Pb^+ + 2\ Ag$$

had previously been verified for hexaethyldilead[4], the possibility of titrating each of the above-mentioned compounds by means of electrolytically generated silver ion to an amperometric end-point[3], was examined. Conditions were also studied whereby a selective titration of one species in the presence of another could be carried out by the utilization of a complexing agent (quinoline) for silver.

EXPERIMENTAL

Chemicals and reagents

Hexamethylditin. Trimethyltin bromide was reduced by sodium in liquid ammonia by KRAUS AND SESSIONS' method[5]; the hexamethylditin was recrystallized from light petroleum (b.p. 60–80°) at −78°; m.p. 23°.

Hexaethylditin and hexapropylditin. These compounds were prepared by the above method[6]. Et_6Sn_2: b.p. 161–162° at 23 mm; Pr_6Sn_2: b.p. 144° at 15.5 mm Hg.

Hexabutylditin. This compound is commercially available from Fluka. It was distilled under vacuum before use.

Trimethyltriphenylditin. This compound was prepared by KRAUS AND BULLARD's method[7] in liquid ammonia from trimethyltin chloride with sodium triphenyltin. When the solid product of this reaction was dissolved in ether and a series of extractions with water was made, a residue was obtained from the organic layer consisting of a mixture of trimethyltriphenyl- and hexaphenylditin. By a series of recrystallizations from chloroform and methanol, a compound melting at 104° was obtained.

Hexaphenylditin. This compound was prepared in liquid ammonia from triphenyltin chloride and sodium[6]. The solid residue was recrystallized from benzene, yielding a product melting at 229°.

Methanol, ethanol and benzene were purified from C. Erba reagents (Milano, Italy). Alcoholic sodium iodide, bromide and lithium nitrate solutions were prepared from RP C. Erba reagents. No reducing substances were found.

Apparatus

The indicator and the anode generator electrodes, as well as a variable speed stirrer, were placed in the titration cell. In order to stabilize the sensitivity of the indicator system, the stirrer speed was adjusted by means of a stroboscopic disc. A stirrer speed of 1,000 rev./min. was used. The indicator system employed in the halogenations consisted of two platinum wire electrodes, 20 mm long and 0.9 mm in diameter. For silver ion titrations, metallic silver electrodes of the same size were employed. The applied potential difference across the two electrodes was usually 100 mV.

The recording of the plot, indicator current *vs.* generation time, was carried out by means of a galvanometer (sensitivity, $1.42 \cdot 10^{-9}$ A/mm min) and a photographic drum system.

The generator electrodes consisted of 1 × 1 cm platinum foil squares or silver foil squares of the same dimensions. The cathode was always separated from the anodic compartment. The generator current, produced by an amperostatic power supply, was read potentiometrically by means of a standard resistor. The employed generator currents were from approximately 1 to 5 mA.

Procedure

The solid substances, trimethyltriphenyl- and hexaphenylditin, were stable enough to be weighed before being dissolved in a known volume of ethanol, previously degassed with dry nitrogen. The pure fractions of the other compounds were transferred by vacuum distillation into thin-walled glass ampoules cooled by liquid air and then sealed by flame. The ampoules were weighed before and after distillation. They were broken open in a known volume of alcohol in order to obtain *ca.* 10^{-3} *M* solutions. The bottles containing the solutions were kept under nitrogen and fitted with an automatic microburet. The latter was inserted directly into the cell for the coulometric–amperometric determination. In this way known volumes of solution were added to 60 ml of anode solution, also degassed with nitrogen and containing known amounts of NaI, NH_4Br or $LiNO_3$, depending on whether iodination, bromination or silver ion titration was to be carried out.

As shown in Figs. 1–3, the end-points were readily observed and were obtained by extrapolating the linear part of the indicator current caused by excess reagent, to the zero current line. After the end-point the slope of the rising curve of the reagents considered and that of the blank must be the same.

RESULTS

Iodination

Even when the iodide concentration was greatly reduced, analytically correct results were obtained only for hexaethylditin. In Table I the results obtained for various quantities of hexaethylditin are reported. Figure 1 illustrates the influence of varying iodide concentrations on the amperometric plot.

TABLE I

IODINATION OF HEXAETHYLDITIN IN METHANOL
(0.01 *M* NaI, 0.09 *M* $LiNO_3$ at 25°)

Run no.	*Coulombs calculated*	*Generator current ($A \cdot 10^3$)*	*Generation time (sec)*	*Coulombs found*	*% Error*
1	0.250	1.8	140	0.252	+0.8
2	0.500	2.0	252	0.504	+0.8
3	1.250	4.0	311	1.244	−0.5

Bromination

All the ditin compounds could be determined with bromine except for hexaphenylditin. Even at elevated temperatures and with a bromide concentration of 0.01*M*, the hexaphenyl compound gave unsatisfactory results. Table II reports the data obtained. The amperometric plots were of the same type as previously reported for hexamethylditin[6].

Silver ion titration

The silver ion titrations were based on the following equation:

$$R_3Sn\text{–}SnR_3 + 2\,Ag^+ \rightarrow 2\,R_3Sn^+ + 2\,Ag$$

This reaction was verified for three of the compounds: hexaphenyl-, hexamethyl- and trimethyltriphenylditin. Known amounts of the substances dissolved in ethanol or alcohol–benzene mixture were added to alcoholic silver nitrate. Metallic silver was thus precipitated and then separated and titrated by VOLHARD's method. Sodium

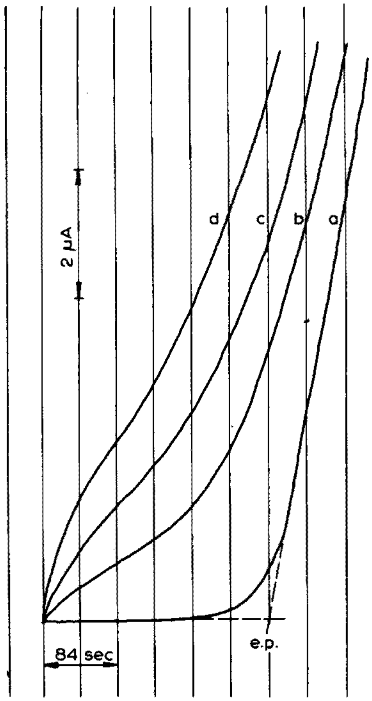


Fig. 1. Effect of varying iodide concentration on iodination of hexaethylditin (Run 2, Table I). (a) 0.01 *M*; (b) 0.05 *M*; (c) 0.075 *M*; (d) 0.1 *M* NaI.

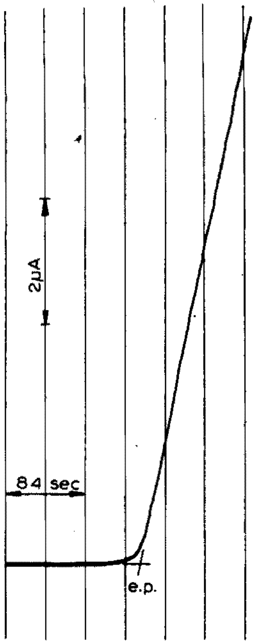


Fig. 2. Silver ion titration of hexamethylditin (Run 17, Table IV).

TABLE II

BROMINATION OF R_6Sn_2 COMPOUNDS IN METHANOL
(0.1 *M* NH_4Br at 20°)

Run no.	*Compound*	*Coulombs calculated*	*Generator current (A · 10³)*	*Generation time (sec)*	*Coulombs found*	*% Error*
4	$(C_2H_5)_6Sn_2$	0.205	1.5	138	0.207	+1.0
5	$(C_2H_5)_6Sn_2$	0.410	3.1	131	0.406	−1.0
6	$(C_2H_5)_6Sn_2$	1.025	4.8	214	1.027	+0.2
7	$(C_3H_7)_6Sn_2$	0.200	1.5	134	0.201	+0.5
8	$(C_3H_7)_6Sn_2$	0.400	3.2	124	0.397	−0.8
9	$(C_3H_7)_6Sn_2$	1.000	4.5	223	1.004	+0.4
10	$(C_4H_9)_6Sn_2$	0.210	1.4	151	0.212	+0.9
11	$(C_4H_9)_6Sn_2$	0.420	3.2	131	0.419	−0.2
12	$(C_4H_9)_6Sn_2$	1.050	4.7	222	1.043	−0.7
13	$(CH_3)_3Sn{-}Sn(C_6H_5)_3$	0.215	1.6	136	0.218	+1.4
14	$(CH_3)_3Sn{-}Sn(C_6H_5)_3$	0.430	3.3	130	0.429	−0.2
15	$(CH_3)_3Sn{-}Sn(C_6H_5)_3$	1.075	4.9	220	1.078	+0.3

fluoride or sodium tetraphenylborate was added to the filtrate to precipitate the triphenyl and trimethyl ions, respectively. The results obtained are reported in Table III.

TABLE III

REACTION OF R_6Sn_2 COMPOUNDS WITH $AgNO_3$ AT ROOM TEMPERATURE

Compound	*R_6Sn_2 g-mole · 10^3*	*$AgNO_3$ g-mole · 10^3*	*Me_3Sn^+ found g-ion · 10^3*	*Ph_3Sn^+ found g-ion · 10^3*	*Ag found g-at · 10^3*
$(C_6H_5)_6Sn_2$	0.5	1	—	1.05	0.98
$(CH_3)_6Sn_2$	0.255	0.5	0.47	—	0.505
$(CH_3)_3Sn–Sn(C_6H_5)_3$	0.3	0.6	0.59	—	0.58

TABLE IV

SILVER ION TITRATION OF R_6Sn_2 COMPOUNDS IN ETHANOL

(0.1 *M* $LiNO_3$ at 20°)

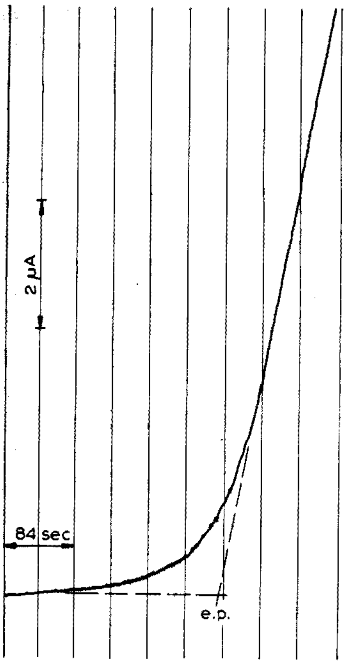
Run no.	*Compound*	*Coulombs calculated*	*Generator current ($A \cdot 10^3$)*	*Generation time (sec)*	*Coulombs found*	*% Error*
16	$(CH_3)_6Sn_2$	0.210	1.5	140	0.210	0.0
17	$(CH_3)_6Sn_2$	0.420	3.0	141	0.423	+0.7
18	$(CH_3)_6Sn_2$	1.050	4.6	227	1.044	−0.6
19	$(C_2H_5)_6Sn_2$	0.205	1.5	137	0.205	0.0
20	$(C_2H_5)_6Sn_2$	0.410	3.0	136	0.408	−0.5
21	$(C_2H_5)_6Sn_2$	1.025	4.3	238	1.023	−0.2
22	$(C_3H_7)_6Sn_2$	0.200	1.5	133	0.199	−0.5
23	$(C_3H_7)_6Sn_2$	0.400	3.1	130	0.403	+0.8
24	$(C_3H_7)_6Sn_2$	1.000	4.4	227	0.998	−0.2
25	$(C_4H_9)_6Sn_2$	0.210	1.5	140	0.210	0.0
26	$(C_4H_9)_6Sn_2$	0.420	3.3	127	0.419	−0.2
27	$(C_4H_9)_6Sn_2$	1.050	4.5	233	1.048	−0.2
28	$(CH_3)_3Sn–Sn(C_6H_5)_3$	0.215	1.7	127	0.216	+0.5
29	$(CH_3)_3Sn–Sn(C_6H_5)_3$	0.430	3.5	123	0.430	0.0
30	$(CH_3)_3Sn–Sn(C_6H_5)_3$	1.075	4.5	239	1.075	0.0
31	$(C_6H_5)_6Sn_2$	0.372	1.5	248	0.372	0.0
32	$(C_6H_5)_6Sn_2$	0.744	3.0	247	0.741	−0.4
33	$(C_6H_5)_6Sn_2$	1.488	3.0	497	1.491	+0.2

TABLE V

SILVER ION TITRATION OF $Me_3SnSnPh_3–Ph_6Sn_2$ MIXTURES IN ETHANOL : BENZENE (80 : 20)

($LiNO_3$ 0.1 *M* at 20°)

Run no.	*$(CH_3)_3Sn–Sn(C_6H_5)_3$ Coulombs calc.*	*$(C_6H_5)_3Sn–Sn(C_6H_5)_3$ Coulombs calc.*	*[Quinoline] (M)*	*Generat rent (A*
34	0.718	—	—	1.95
35	0.718	0.025	0.03	1.85
36	0.359	0.276	0.03	1.86
37	0.150	1.69	0.03	0.9
38	0.150	6.76	0.03	0.9
39	0.150	6.76	0.03	0.9



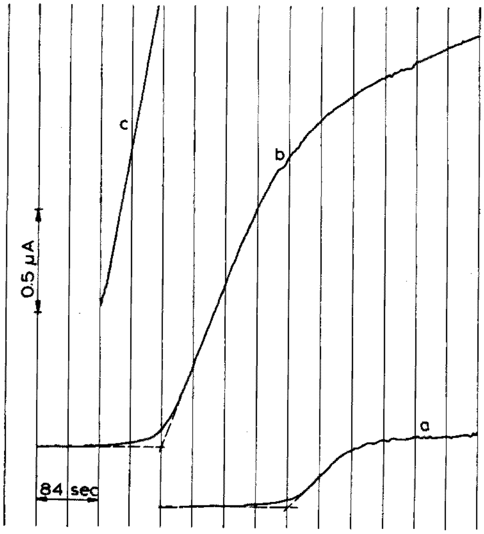


Fig. 3. Silver ion titration of hexaphenylditin (Run 32, Table IV).

Fig. 4. Silver ion titration of a hexaphenyl-, trimethyltriphenylditin mixture. (a) Run 39, Table V; (b) Run 37, Table V; (c) blank.

Coulometric–amperometric titrations were possible for all the compounds under consideration (Table IV). Figure 2 shows an amperometric plot obtained for hexamethylditin. Similar diagrams for all the compounds except hexaphenylditin, were obtained. A typical diagram of the hexaphenyl compound obtained under identical experimental conditions is shown in Fig. 3. A comparison of Figs. 2 and 3 leads one to conclude that the reaction rate with silver ion for all compounds other than hexaphenylditin is quite fast. Since the reaction rate can be influenced by the presence of a complexing agent for silver ion:

$$Ag^+ + 2\,L \rightleftharpoons AgL_2^+ \quad (L = \text{quinoline})$$

Time (sec)	*$(CH_3)_3Sn\text{–}Sn(C_6H_5)_3$ Coulombs found*	*% Error*	*% Weight $(C_6H_5)_3Sn\text{–}Sn(C_6H_5)_3$*
367	0.716	−0.3	0
387	0.716	−0.3	4.5
193	0.359	0.0	51.1
168	0.151	+0.6	94.0
168	0.151	+0.6	98.5
164	0.148	−1.3	98.5

quinoline was added to the anodic solution, further reducing the reaction rate of hexaphenylditin, so that titration of even small amounts of trimethyltriphenylditin could be carried out in mixtures with hexaphenylditin. This is quite interesting, in view of the fact that KRAUS AND BULLARD's method[7] for the preparation of the trimethyltriphenyl compound gives a mixture of the two.

After a systematic study, it was concluded that a very accurate titration could be made even for small amounts of the mixed ditin compound in a large excess of hexaphenylditin. Because of the extreme accuracy in reaching the end-point, satisfactory results could also be obtained for small quantities of hexaphenylditin in an excess of trimethyltriphenylditin. Results are reported in Table V; amperometric plots referring to runs 37 and 38 are given in Fig. 4.

From these plots one compound could be determined in the presence of another. The slopes of the titration curves *a* and *b* varied from the blank *c*, obviously because of the subsequent reaction of hexaphenylditin. The indicator current reached a constant value, indicating that the reaction rate of hexaphenylditin was equal to the generation rate of the silver ion. Nevertheless, the extrapolated equivalence points were in good agreement with the calculated values.

Such analyses can be carried out under conditions where the specific velocity constants relative to the individual species are known. Studies on the kinetics of the iodination and silver ion reactions with the organometallics discussed in this paper are in progress.

The author expresses his thanks to Prof. L. RICCOBONI for helpful discussion. The financial support of the Consiglio Nazionale delle Ricerche, Roma (Italy) is gratefully acknowledged.

SUMMARY

Coulometric titrations with amperometric end-points, utilizing iodine, bromine or silver ion, were applied to the analyses of several organo-ditin compounds. The various experimental conditions are discussed. It is shown that trimethyltriphenylditin can be determined in mixtures containing hexaphenylditin.

RÉSUMÉ

L'auteur propose une méthode coulométrique avec indication ampérométrique du point équivalent, utilisant iode, brome ou ion argent. Ce procédé a été appliqué au dosage de nombreux composés organiques de l'étain (R_6Sn_2). Les différentes conditions d'expérience sont discutées. Cette méthode permet le dosage de Me_3Sn–$SnPh_3$ dans des mélanges Ph_6Sn_2–Me_3Sn–$SnPh_3$.

ZUSAMMENFASSUNG

Die Analyse mehrerer organischer Dizinnverbindungen wurden mittels coulometrischer Titration und unter Anwendung amperometrischer Endpunktsanzeige und Jod, Brom oder Silberionen durchgeführt. Verschiedene experimentelle Bedingungen werden diskutiert. Es wird gezeigt, dass Trimethyltriphenyldizinn in Mischungen die Hexaphenyldizinn enthalten bestimmt werden kann.

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A RAPID IODINE RADIOCHEMICAL PROCEDURE*

A. E. GREENDALE, D. L. LOVE AND A. A. DELUCCHI
U. S. Naval Radiological Defense Laboratory, San Francisco, Calif. 94135 (U.S.A.)

(Received May 21st, 1965)

A rapid (< 10 sec) radiochemical procedure was needed for the determination of fission yields and radiation characteristics of short-lived iodine isotopes. A fast procedure was needed also for the determination of the independent fission yields of those iodine isotopes which are not themselves short-lived but which have short-lived precursors. Requirements for such an iodine procedure are: accurate measurement of the elapsed time between fission and iodine separation; fast collection of iodine after separation, in order that gaseous iodine decay products may be assayed; good decontamination from the precursors Sn, Sb and Te and descendants Xe, Cs and Ba for fission yield studies; good decontamination from gross fission products for radiation measurements; and finally radiochemical exchange of the fission-product iodine with carrier iodine before iodine separation.

GLENDENIN AND METCALF[1] have pointed out that the interchange between freshly formed radio-iodine and carrier iodine is often slow and incomplete in aqueous solutions. Because of this difficulty in attaining radiochemical exchange with added iodine carrier, present radiochemical procedures are quite time-consuming. A radiochemical iodine procedure[1,2] widely employed at present uses sodium hypochlorite and hydroxyammonium chloride in successive steps to insure radiochemical exchange with the iodine carrier, followed by carbon tetrachloride–aqueous extractions with nitrite and hydrogen sulfite for separation of the iodine. Such a separation typically takes 20 min to perform.

In the present procedure a non-aqueous system at an elevated temperature (about 130°) is used to obtain a rapid exchange of fission product iodine with carrier iodine. In one rapid step, the carrier iodine and fission product iodine are converted to gaseous iodine, which is easily removed from the other elements, collected, and assayed.

EXPERIMENTAL

Reagents and sample preparation

Periodic acid (Matheson, Coleman and Bell 99.5% H_5IO_6) was stored in a vacuum desiccator before use.

Uranium-235 (93.2%) was converted to the peroxide[3] ($UO_4 \cdot 2H_2O$) by precipitation from a uranyl nitrate solution with hydrogen peroxide, washed, dried below 100°, and ground to a powder. After one week or more, uranium-235 as the peroxide could be satisfactorily assayed by comparing the gross γ-activity with that of a known mass of ^{235}U. The uranium peroxide was dissolved in molten periodic acid

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* This work was supported in part by the U.S. Atomic Energy Commission.

in a weight ratio of 1:14 and heated in an oil bath to 135°. The clear melt was cooled and ground to a powder in a dry box. This powder (600 mg) was intimately mixed with 90 mg of activated carbon (Atlas Powder Co., Grade S-51) and transferred to a tared graphite capsule of 7 mm O.D., 6 mm I.D., and 21 mm long. The exact amount added was determined by difference. A graphite plug cemented in place with "Duco Cement" prevented loss of contents. The capsule was γ-counted as a further check on the mass of ^{235}U. Since periodic acid is hygroscopic, the capsule was kept in a small screw-top vial until it was to be irradiated. The capsules must be made up within a few days of the time of irradiation, since the periodic acid slowly decomposes at room temperature in the presence of activated carbon.

Apparatus

The same pneumatic system[4] that was used in the rapid separation of antimony[5] and tin[6] transported the uranium-filled graphite capsule to and from the reactor. Detail 1-A of Fig. 1 shows the rabbit containing the graphite capsule. The external dimensions were the same as those of the rabbit previously used to transport aqueous solutions of fissionable uranium[4]. After irradiation, the 0.002-in. thick Teflon diaphragm in the base of the rabbit was cut by the stainless steel cutter shown in Detail 1-B of Fig. 1, allowing the graphite capsule to pass into the reaction vessel (B) of the iodine apparatus. This cutter replaced the hypodermic needles originally used[4].

The apparatus for the separation of iodine is shown in Fig. 1. A transfer tube (A) connected a reaction vessel (B) to the cutter and the pneumatic system. A resistance heater (D), in series with a variable transformer, maintained the reaction vessel temperature above 125°, and a 1000-W projector bulb (C) provided heat to initiate the decomposition of the periodic acid contained in the graphite capsule. A medium sintered-glass filter (E) trapped the particulate matter from the reaction vessel but allowed the gaseous iodine to pass through. A stopcock (F) permitted the easy removal of the iodine with CCl_4 at the end of the experiment. A column (H) was filled with 4-mm glass beads to give a large surface area for the collection of iodine. A container (I) held CCl_4 for wetting the glass beads and for flushing the iodine from the beads, and an overflow chamber (J) prevented the CCl_4 in the column from being lost when the vacuum was applied during the collection of iodine. A heat gun (K; Master Appliance Mfg., Co., Racine, Wisconsin) heated the glass parts A, E and G above 125° to prevent condensation of iodine, with a shroud (L) directing the hot air stream to the desired locations.

In order to obtain γ-ray spectra of the short-lived fission product iodine at the earliest possible time, another apparatus was designed so that the released iodine gas could be rapidly transferred to and collected near a γ-ray detector. To accomplish this, the sintered-glass funnel and CCl_4 trap previously described (parts E, I, J, H, G and F in Fig. 1) were replaced by the apparatus shown in Fig. 2. This apparatus consisted basically of a heated teflon tube which was used to transport the iodine gas to a point near the γ-ray detector and a cooled chamber which was used to trap the iodine on its arrival. Other auxiliary equipment is also shown in Fig. 2. A 1-l vessel (A) contained: Dow Corning Silicone fluid, an immersion heater, a stirrer, an inlet and outlet thermometer to measure the temperature of the oil flowing through the system (140° at outlet and 125° at inlet of oil bath), and a thermocouple connected to a regulator (B) which supplied power to the immersion heater. A small centrifugal

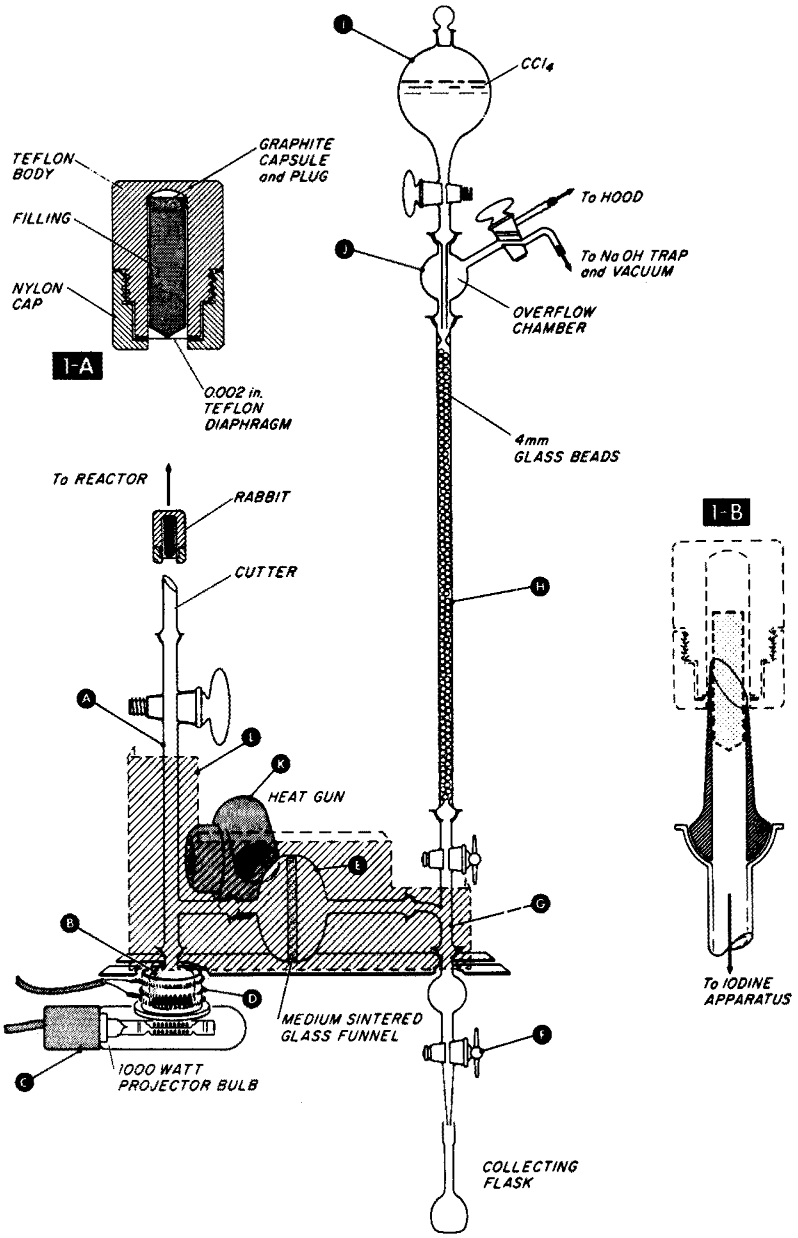

Fig. 1. Iodine separation apparatus.

pump (C) circulated the heated oil through neoprene tubing, which surrounded the semi-transparent Teflon spaghetti tubing. A coil of nickel tubing (D), heated by a Meker-type burner, supplied heated air for flushing the iodine out of the sintered-glass funnel (E). Details of the oil jacket around the Teflon tubing are shown in the inset at (F) along with an exploded view of the iodine collection chamber at (G).

Iodine was transferred from the separation apparatus to the chamber, 15 feet away, within 3 sec. A vacuum flask (H) contained dilute sodium hydroxide to trap any iodine which might get past the counting chamber. While the iodine transfer was being made, a negative pressure of 10 in. of mercury was maintained in the flask. The tubes going into the counting chamber could be easily removed and the holes in the chamber stoppered. The iodine within the chamber could be dissolved in CCl_4 and quantitatively removed for a chemical yield determination.

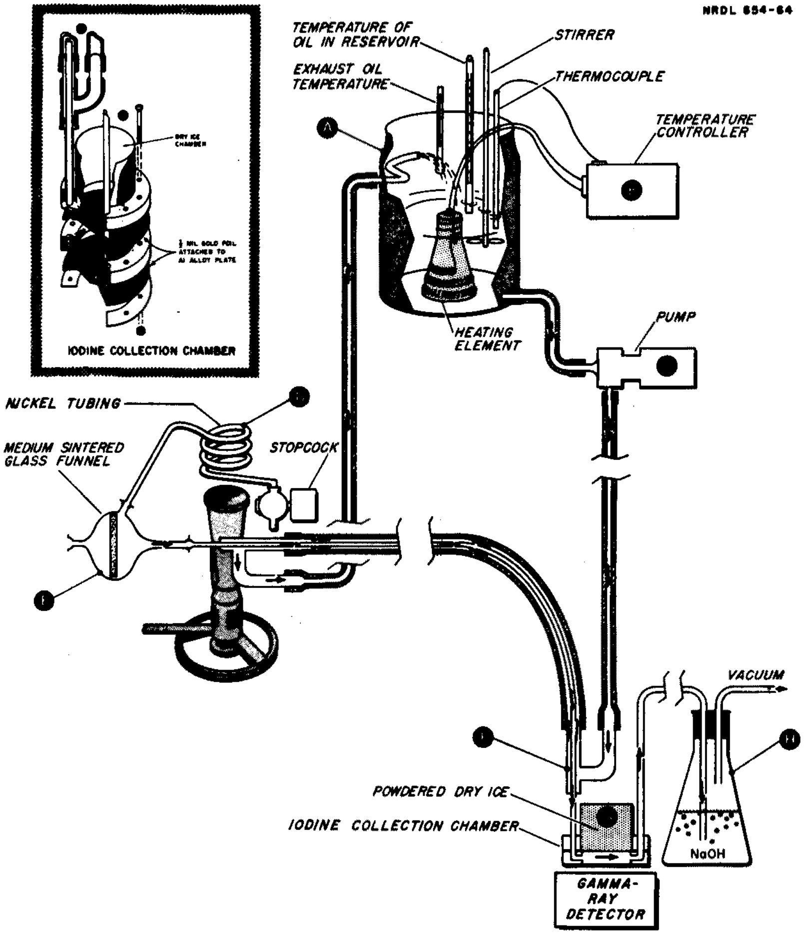

Fig. 2. Apparatus for obtaining early-time spectra.

Procedure

The apparatus is assembled as shown in Fig. 1 and connected to the rabbit transfer system. The glass parts A, B, E and G are then heated to about 125° by the resistance heater and heat gun. The glass beads are wetted by passing CCl_4 through the column. The excess CCl_4 is discarded and valve (F) is closed. The rabbit containing the graphite capsule, which had been filled with uranium peroxide, periodic acid, and activated carbon, is sent into the reactor. The vacuum (valve near J) and the projector bulb are turned on before the rabbit returns from a predetermined time in the reactor. Within 2 sec after the arrival of the graphite capsule in vessel (B), the reaction starts. The graphite capsule breaks open and the gaseous iodine moves rapidly through the glass frit at (E) and deposits on the glass beads wet with CCl_4. The reaction is completed within 4 sec after the end of the irradiation The resistance heater and projector bulb are turned off. The vacuum (valve near J) is turned off to bring the system to atmospheric pressure. With the valve near G closed, about 6 ml of CCl_4 (previously marked on the column) is added. After standing for a few seconds, the iodine–CCl_4 solution is run into a volumetric flask or other suitable container and made up to volume with CCl_4 rinses. The chemical yield is 70–80%. The chemical yield is readily obtained by a spectrophotometric measurement of iodine in an aliquot of the CCl_4 solution.

DISCUSSION

Choice of reagents

In earlier work on the rapid separations of Sb[5], As[5] and Sn[6], it was found that a gaseous separation of the desired element offers significant advantages in speed of separation, transfer to the collection point, and ease of decontamination from mixed fission products. Elemental iodine is easily handled as a gas if the apparatus is heated slightly to prevent condensation. The violet iodine gas can be followed visually during the reaction, thus simplifying the timing of the start and the duration of the reaction. A column of glass beads wet with CCl_4 readily absorbs the gaseous iodine, and the iodine is easily leached off with fresh CCl_4 into a flask for counting and assay. Aliquots of the solution of iodine in CCl_4 can be measured photometrically to give the chemical yield. Since this is a nondestructive measurement, the aliquot can be combined with the original sample, if desired.

Periodic acid has a number of properties which make it a good iodine carrier. Molten periodic acid is a good solvent for the oxides of uranium. With heat, the periodic acid breaks down readily to give gaseous iodine, the only other products being oxygen and water. By using a relatively large mass (561 mg) of periodic acid, hold-up on the apparatus is minimized, thereby increasing the chemical yield. The use of a high atom ratio of iodine carrier to uranium (21:1) reduces the chance that fission product iodine will be adsorbed on the uranium oxide[7].

To show that no adsorption by the uranium oxide does occur in this procedure the following experiment was performed. Four samples containing atom ratios of iodine to uranium of 42:1, 84:1, 168:1 and 336:1 were irradiated. The following day (after decay of precursors) fission product iodine was separated by the fast procedure. The amount of ^{131}I and ^{133}I in each sample was determined by measurement of the 0.36-MeV and 0.54-MeV γ-ray photopeaks. Within the error of measurement (about 5%) the amount of radio-iodine collected was found to be directly proportional to the amount of ^{235}U used.

Throughout the development of this procedure, uranium peroxide ($UO_4 \cdot 2H_2O$) was used as the chemical form of the uranium. However, uranium trioxide (UO_3) also forms a clear melt with periodic acid, and it is felt that both oxides should work equally well. Uranium peroxide is easily produced from the uranyl salt, but it must be dried at a low temperature (about 100°) because with prolonged heating at higher temperatures it decomposes to form the trioxide.

The addition of activated carbon to the periodic acid improved the procedure in several ways. With activated carbon present, periodic acid breaks down more rapidly and at a lower temperature. The carbon also adsorbs a number of fission products that normally would go through the sintered-glass filter. It was found that without activated carbon about 50% of any carrier-free ruthenium present followed iodine in the separation step, while with activated carbon present the ruthenium was effectively trapped out onto the carbon and therefore removed by the sintered-glass filter. The same behavior was observed with technetium.

Graphite was found to be an effective capsule material. It could be machined easily into inert containers for the reactants. Being black and a good thermal conductor, it adsorbs heat rapidly and transfers it efficiently to the contents to start the reaction. Upon build-up of pressure from the reaction, the capsule broke open readily and released the iodine. Carbon has a low cross-section for neutrons, and if high-purity, spectrographic-grade graphite is used, few induced activities are formed in the capsule during irradiation. The thin-wall (0.5 mm), low-Z graphite absorbed only a small fraction of the γ-rays from the ^{235}U, thus making a gross γ-count of the filled capsule an easy means of checking the amount of ^{235}U in the sample before irradiation.

Decontamination factors

In order to obtain meaningful decontamination factors, the contaminant activities that were studied were always placed in a matrix of periodic acid, uranium peroxide, and activated carbon identical to that used in a typical iodine separation. As has already been mentioned it was found that some carrier-free elements were effectively trapped by the activated carbon. Therefore, when obtainable, carrier-free nuclides were used to determine decontamination factors. Table I gives the decontamination factors that were measured, and gives the amount of carrier when it was not possible to obtain carrier-free contaminant.

TABLE I

DECONTAMINATION FACTORS

Contaminant	*Weight of carrier*	*Decontamination factor*
^{113}Sn	300 μg	10^5
^{124}Sb	Carrier-free	$8 \cdot 10^3$
^{125}Te	Carrier-free	$8 \cdot 10^3$
^{82}Br	0.06 μg	11
^{99}Mo	30 μg	10^5
^{106}Ru	Carrier-free	$4 \cdot 10^3$

As was expected, the most serious contaminant turned out to be bromine. Therefore interference from short-lived fission product bromine may limit the usefulness of this procedure for making some early-time radiation measurements of fission product iodine.

For independent fission yield measurements involving the direct measurement of iodine nuclides it was sufficient to separate the iodine from the precursors Sn, Sb and Te. Decontamination factors for these were measured and found to be adequate for yield studies. Decontamination factors were not measured for the descendants of iodine, Xe, Cs and Ba; however early-time iodine spectra obtained with this procedure indicated that these elements were also effectively separated from iodine.

Exchange

Since the primary function of this iodine procedure was to make possible the determination of fission yields, it was of the greatest importance that there be chemical exchange of the carrier iodine with the fission product iodine. It was expected that shortly (<1 sec) after its formation the fission product iodine would assume one or more of its known, stable oxidation states. The distribution within these states, however, depends upon the particular process of formation and the chemical environment of the resulting iodine[8,9]. Therefore, iodine formed directly in the fission process was expected to differ from iodine formed by β-decay of tellurium. To show that exchange of carrier and fission product iodine occurred in this procedure, three separate types of experiments were performed.

It was shown that carrier-free ^{131}I in the iodide and iodate forms exchanged with carrier iodine in the periodic acid form when the latter was heated and decomposed. A solution of ^{131}I as the iodide was evaporated onto the walls of a test tube; 1 g of periodic acid was added, melted, and poured into a second test tube*. After this test tube had been counted to see how much ^{131}I was so transferred, the periodic acid was heated and the resulting iodine gas quantitatively collected in a sodium hydroxide trap. Within 5%, it was shown by this method that all of the ^{131}I tracer came over with the iodine carrier. The same experiment was conducted with ^{131}I in the iodate form with the same results.

Because it is difficult to make tracer studies which closely simulate the condition of the fission product iodine in the periodic acid matrix, it was felt that exchange could best be tested by comparing the cumulative fission yields of ^{131}I and ^{133}I measured with a standard radiochemical procedure[2] with those measured with the fast procedure. In these experiments no attempt was made to do absolute counting of the iodines. Instead γ-ray photopeak areas were used as a measure of the amounts of iodine recovered by the two procedures, and corrections were applied for chemical yield and number of fissions in each sample. Agreement within the experimental errors of the two procedures (about 5%)was obtained, showing that the same degree of exchange was achieved by both procedures.

Following the investigation of exchange by the two preceding methods, an experiment was performed using the fast radiochemical procedure to measure the independent yield of ^{133}I in thermal fission of ^{235}U, and, if possible, to verify the half-life of the ^{133}Te ground state. This work is to be published[10] and therefore will not be described in any detail in this paper. Some of the results are shown, however, since they bear upon the question of exchange.

The experiment consisted of doing rapid iodine separations at predetermined times after irradiation (from about 10 sec to 2 h) and determining the number of atoms of ^{133}I present at the times of separation. Some of the data from this experiment are shown in Fig. 3. The experimental results are shown together with the two

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* It was shown in separate experiments that less than 0.3% of the ^{131}I was extracted into CCl_4 from a water solution of this periodic acid.

theoretical curves based on the amount of ^{133}I that would be expected if the ^{133}Te ground state were to have a 1.84-min half-life or a 12.45-min half-life. This comparison was made because there have been widely conflicting reports on the half-life of the ^{133}Te ground state. Pappas[11] reported seeing a 2-min period in the β-decay of a tellurium fission product sample. The chemical procedure that was used to obtain the sample was designed to separate the ground state of ^{133}Te from its upper state, and the 2-min period that was observed in the β-decay of the sample was assigned to the ground state of ^{133}Te. A similar component (1.84 min) was observed at this Laboratory in the gross β-decay curve of a rapidly separated selenium–tellurium fission product sample, but no positive mass assignment could be made for this component. Recently, Prussin[12] measured a half-life of 12.45 ± 0.22 min for the ^{133}Te ground state and obtained all the necessary genetic data for the mass assignment. From Fig. 3 it is

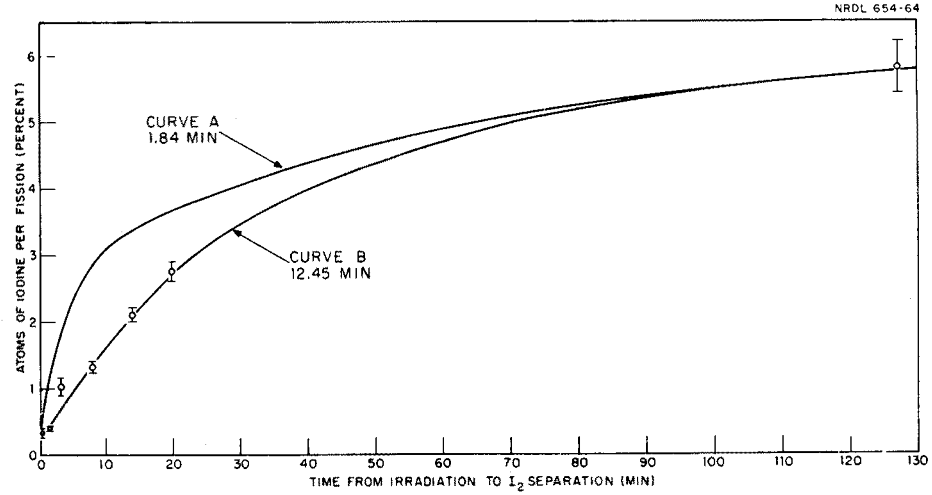

Fig. 3. Comparison of experimental and theoretical iodine-133 growth curves.

seen that our data are in good agreement with the half-life value obtained by Prussin. The ^{133}I independent and cumulative yields consistent with these data are 0.17% and 6.84% respectively. This latter value is in good agreement with the previously reported values for the cumulative yield of ^{133}I[11,13,14]. In general these data are considered to strongly support the findings of the previous experiments which indicated that exchange is achieved in the separation step.

SUMMARY

A radiochemical procedure was developed to determine fission yields and radiation characteristics of short-lived iodine fission products. Iodine was separated from other fission products of uranium in less than 10 sec after completion of irradiation. High decontamination factors of iodine from Sn, Sb, Te, Xe, Cs and Ba, and high chemical yields were obtained. The sample was prepared by dissolving uranium peroxide in molten periodic acid; the melt was cooled, ground and mixed with activated carbon. After irradiation, the periodic acid was decomposed by heat and the gaseous iodine formed was collected in carbon tetrachloride or in a cooled counting chamber. Higher temperatures could be used than in conventional aqueous systems, thus enhancing the exchange of carrier and fission product iodine.

RÉSUMÉ

Les auteurs ont développé un procédé radiochimique pour déterminer rapidement les rendements de fission et les caractéristiques de radiation d'isotopes de l'iode. L'iode est séparé d'autres produits de fission de l'uranium en moins de 10 secondes, après irradiation. L'échantillon est préparé en dissolvant le peroxyde d'uranium dans l'acide periodique fondu. Le produit de fusion est refroidi et mélangé à du charbon actif. Après irradiation, l'acide periodique est décomposé par chauffage; l'iode gazeux formé est recueilli dans le tétrachlorure de carbone ou dans une chambre de comptage refroidie.

ZUSAMMENFASSUNG

Es wird ein radiochemisches Verfahren entwickelt zur Bestimmung der Spaltausbeuten und Strahlungscharakteristiken kurzlebiger Spaltprodukte. Das Jodid wurde von anderen Spaltprodukten des Urans in weniger als 10 sec nach Ende der Bestrahlung abgetrennt. Dabei wurden hohe Dekontaminationsfaktoren des Jods von Sn, Sb, Te, Xe, Cs und Ba und hohe chemische Ausbeuten erhalten. Die Herstellung der Proben geschah durch Lösen des Uranperoxids in geschmolzener Perjodsäure. Die Schmelze wurde gekühlt, zerrieben und mit aktiviertem Kohlenstoff gemischt. Nach der Bestrahlung wurde die Perjodsäure durch Hitze zerstört und das gebildete gasförmige Jod in Tetrachlorkohlenstoff oder in einem gekühlten Zählrohr gesammelt. Es können höhere Temperaturen als bei den üblichen wässrigen Systemen verwendet werden, so dass der Austausch von Träger und Spaltproduktjod erhöht wird.

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AN AUTOMATIC ABSORPTIOMETRIC METHOD FOR THE DETERMINATION OF NITRATE

D. R. TERREY
Atomic Weapons Research Establishment, Aldermaston, Berkshire (England)
(Received May 19th, 1965)

A method was required for the determination of nitrate using the Technicon Autoanalyser continuous absorptiometric analysis system. MULLIN AND RILEY[1] have described a manual method in which the nitrate is reduced to nitrite by hydrazine, with copper(II) as a catalyst; the nitrite formed is determined by the GRIESS–ILOSVAY method, as described by RIDER AND MELLON[2]. A disadvantage of the method is that a period of 24 h is required for the reduction to reach equilibrium. PROCHAZKOVA[3] has described a modification of the procedure in which reduction is carried out for 30 min at 28°. BRITT[4] has adapted the method of PROCHAZKOVA for use with the Autoanalyser in the parts-per-billion range; his method was found to give erratic results when applied to solutions containing several parts-per-million of nitrate. The method to be described is based in part on that of PROCHAZKOVA; the procedure for determining the nitrite formed is based on the improved GRIESS–ILOSVAY method described by BENDSCHNEIDER AND ROBINSON[5] and used by CHOW AND JOHNSTONE[6] for the determination of nitrite formed from the reduction of nitrate by metallic zinc. The Autoanalyser system has been described by SKEGGS[7], and many applications have been published[8,9].

EXPERIMENTAL

The Autoanalyser manifold

The proportions of the various reagents required[3,5] were converted to relative flow rates, and an Autoanalyser manifold was set up (Fig. 1). Acetone, which is added to complex unused hydrazine after the reduction step, attacks the Tygon pump tubing, and is therefore added as a 12.5% (v/v) mixture with water. Because of the great length of the system, a considerable back-pressure is built up, and it is advisable to insert a surge suppressor (approx. 1″ of 0.01″ diameter Tygon tube) in the air line. Because of the short residence times of samples in the system, the reduction does not reach equilibrium; since all samples are processed under exactly similar conditions, this is not important.

Reduction temperature

The temperature of the heating bath was originally fixed at 50°; this was later modified to be variable between 70° and 110°. The variation in absorbance with increasing temperature was studied, using a standard solution containing 10 p.p.m. of nitrate ion. The results are shown in Table I, and clearly show the improvement

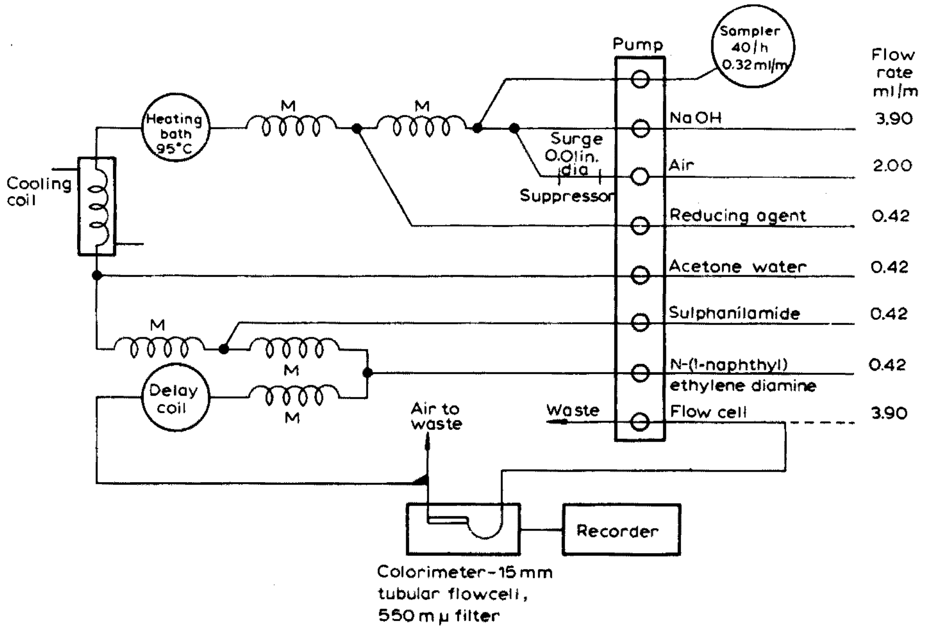

Fig. 1. Autoanalyser manifold for nitrate. All mixing coils (M) are double length.

TABLE I

EFFECT OF INCREASING REDUCTION TEMPERATURE ON ABSORBANCE

Temp. (°)	*Absorbance*	*Temp. (°)*	*Absorbance*
50	0.095	85	0.305
70	0.215	90	0.340
75	0.235	95	0.370
80	0.270		

obtained by increasing the reduction temperature; the heating bath was subsequently run at 95°.

Comparison of figures for nitrite obtained in subsequent experiments with those for equivalent amounts of nitrate indicates that approximately 80% conversion of nitrate into nitrite is achieved.

Age of reducing agent

Previous authors[1,3,4] have stated that the reducing agent must be freshly prepared each day; this was found to be unnecessary. The absorbance produced from a standard solution containing 10 p.p.m. of nitrate ion varied over the range 0.340–0.350, with a mean value of 0.345, when reducing solutions up to 10 days old were used.

Concentration of copper(II)

The effect of changing the copper(II) concentration was studied, with the results shown in Table II.

TABLE II

EFFECT OF CHANGING COPPER(II) CONCENTRATION

Cu^{2+} added (µg/ml of reducing agent)	*Absorbance (10 p.p.m. NO_3^-)*	*Cu^{2+} added (µg/ml of reducing agent)*	*Absorbance (10 p.p.m. NO_3^-)*
None	0.245	1.2	0.340
0.3	0.280	1.6	0.300
0.6	0.340	3.2	0.240
0.9	0.350		

The optimum concentration of about 1 µg Cu per ml of reducing agent corresponds to approximately 0.2 µg/ml at the appropriate stage of the Autoanalyser stream, which is in reasonable agreement with MULLIN AND RILEY's figure of 6 µg Cu^{2+} in 40 ml.

Dye formation

The nitrite formed in the reduction stage reacts with sulphanilamide in acid solution, and the diazonium salt formed is coupled with N-(1-naphthyl)ethylenediamine to give a red dye. The absorption spectrum of the dye has a broad peak with a maximum at 545 mµ; Technicon interference filters with a transmission maximum at 550 mµ are used for the absorbance determination. Sufficient hydrochloric acid is added to the sulphanilamide solution to give a pH of 1.5–2 in the solution at the coupling stage[5]. The coupling reaction is slow[5] and a delay coil has been introduced to allow time for the absorbance to reach its full value. It was observed that the N-(1-naphthyl)ethylenediamine dihydrochloride solution became discoloured after several days storage, giving a high blank absorbance. It was found that addition of 10 g/l of sodium sulphite to the reagent, followed by just sufficient hydrochloric acid to redissolve precipitated free amine, gave a stable solution, with no deleterious effect on the dye formation.

Behaviour of nitrite

The presence of nitrite in the sample results in dye formation, interfering with the nitrate determination. It has been shown that nitrite passes through the reduction stage unchanged, and that it can be determined using the same system, with the omission of the reducing agent and acetone (Fig. 2).

Nitrate in a sample containing nitrite can be determined from the difference between absorbances measured with and without reducing agent.

Reagents

AnalaR grade chemicals were used where available.

Sodium hydroxide. 1 g/l.

Reducing agent. 0.6 g of hydrazine sulphate and 6 mg of copper(II) sulphate pentahydrate per l.

Acetone. 12.5% (v/v) in water.

Sulphanilamide reagent. 1.5 g of sulphanilamide and 100 ml of concentrated hydrochloric acid per l.

N-(1-naphthyl)ethylenediamine reagent. Dissolve 2.6 g of the amine dihydrochloride in 800 ml of water, and 10 g of sodium sulphite heptahydrate, stir until dissolved.

Add just sufficient hydrochloric acid to redissolve any precipitated amine, allow to stand overnight, filter, and make up to 1 l.

Procedure

Connect the Autoanalyser manifold as shown in Fig. 1. Pump water through the system until a stable, regular pattern of air bubbles is achieved. Pump the reagents until a steady reagent blank value is indicated on the recorder. Pass the samples through the system at a rate of 40/h. The calibration should be checked daily, and standards should be included with every batch of samples.

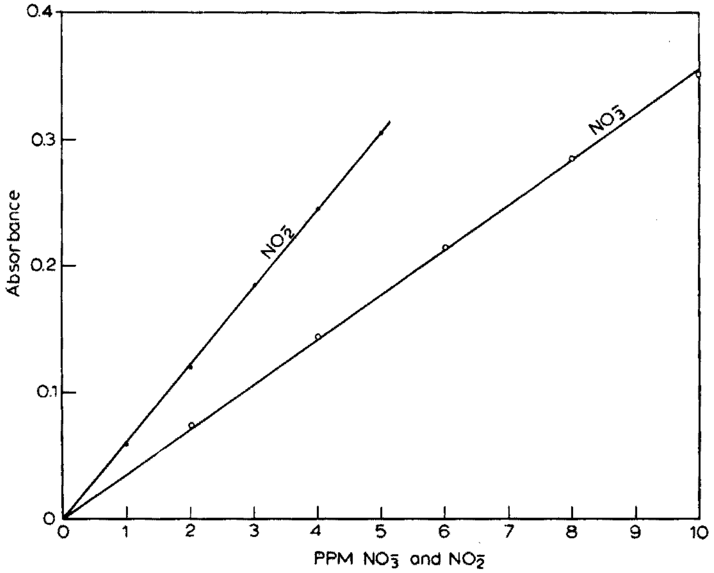

Fig. 2. Typical calibration curves.

RESULTS AND DISCUSSION

Typical results are plotted in Fig. 2, together with those for nitrite. For nitrate determination, the relative standard deviations were 2 p.p.m. ±3%, and 10 p.p.m. ± 4%.

The method described has been used successfully for the determination of nitrate in aqueous extracts from samples of various kinds. It is felt that, in view of the possible diversity of samples, their preparation is best left to the individual analyst. It should be noted, however, that metals whose hydroxides are precipitated at the pH of the reducing solution (*e.g.* Ca, Mg) will inhibit the reduction of nitrate[1].

While this paper was being prepared for publication, HENRIKSEN[10] published a description of a method which is broadly similar to that reported here. HENRIKSEN'S method is based on the work of MULLIN AND RILEY[1], and is intended primarily for sea-water samples; his system is more complex, has a longer hold-up time and a lower throughput rate than the present method. The reduction is carried out in a buffered solution, at a lower temperature, and for a longer time; the nitrite formed is determined by the method of RIDER AND MELLON[2]. The sensitivities of the two methods, allowing for differences in sample size and reagent flow rate, are very similar.

SUMMARY

A method has been developed for the determination of nitrate with the Technicon Autoanalyser in the range 2–10 p.p.m. The method depends on the reduction of nitrate to nitrite by hydrazine in alkaline solution, with copper as a catalyst. The nitrite produced diazotises sulphanilamide and the product is coupled with N-(1-naphthyl)ethylenediamine, to give a red dye, the absorbance of which is measured at 550 mμ. A relative standard deviation of 3–4% is obtained.

RÉSUMÉ

Une méthode absorptiométrique automatique, à l'aide du "Technicon Autoanalyser" a été mise au point pour le dosage des nitrates (2–10 p.p.m.). Elle consiste en une réduction du nitrate en nitrite par l'hydrazine, en solution alcaline, en présence de cuivre comme catalyseur. On procède ensuite à une diazotation avec la sulfanilamide et à une copulation avec la N-(1-naphtyl)éthylènediamine. On obtient une coloration rouge dont on mesure l'absorption à 550 mμ.

ZUSAMMENFASSUNG

Es wurde eine Methode zur Bestimmung von Nitrat mit dem Technicon-Autoanalyser im Bereich von 2–10 p.p.m. entwickelt. Die Methode beruht auf der Reduktion von Nitrat zu Nitrit durch Hydrazin in alkalischer Lösung mit Kupfer als Katalysator. Das erzeugte Nitrit diazotiert Sulfanilamid, das wiederum mit N-(1-Naphthyl)äthylendiamin kuppelt. Es ergibt sich eine rote Farbe, deren Absorption bei 550 mμ gemessen wird. Die relative Standardabweichung beträgt 3–4%.

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FRACTIONAL SUBLIMATION OF VARIOUS METAL β-DIKETONE CHELATES

EUGENE W. BERG AND FREDERICK R. HARTLAGE, JR.*
Coates Chemical Laboratories, Louisiana State University, Baton Rouge, La. 70803 (U.S.A.)
(Received May 6th, 1965)

An extensive study of the volatile characteristics of various metal β-diketone chelates has been carried on in this laboratory in the past several years. The primary objective of this study was to determine if there was any analytical significance associated with the chelate volatility.

The initial work of BERG AND TRUEMPER[1-3], and BERG AND DOWLING[4] confirmed the general volatility of the metal β diketone chelates by reporting the vapor pressure–temperature data, sublimation temperatures and molar heats of vaporization of a large number of chelates. Unfortunately, it was not possible to correlate the measured vapor pressure or sublimation temperature of a series of the chelates involving the same ligand with the molar heat of vaporization (sublimation) of the respective chelates. Neither was there any regularity noted in the magnitude of the volatility exhibited by a series of chelates of one metal with different ligands. For example, the substitution of a trifluoromethyl group for a methyl group in the ligand increased the volatility of some chelates and decreased it of others. Nevertheless, some large differences in volatilities were observed for chelates involving the same ligand and chemically similar metals. The differences were great enough to suggest that various metal chelate mixtures might be resolved by gas chromatography and/or fractional sublimation.

BERG AND HARTLAGE[5,6] have reported on a simple fractional sublimator which was very effective in resolving various mixtures of metal acetylacetonates. In light of this success it seemed appropriate to extend the fractional sublimation studies to include the metal chelates of other β-diketones. The purpose of this paper is to report on these studies.

The most promising ligands for further study were acetyltrifluoroacetone (ATA) and hexafluoroacetylacetone (HAA) because the work of TRUEMPER[1] had clearly demonstrated that in general the chelates of ATA sublimed at lower temperatures than the corresponding acetylacetonates. This suggested that the corresponding chelates of HAA might sublime at still lower temperatures. HARTLAGE's work[5] bears out this hypothesis. Among the other chelates previously studied, only the chelates of benzoylacetone (BA) and benzoyltrifluoroacetone (BTA) appeared promising for fractional sublimation studies.

The work of SIEVERS and others[7-15] which progressed simultaneously with and independently of our development of a fractional sublimation technique attests to the ease with which many of the metal β-diketone chelates can be gas-chromatographed.

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* Celanese Chemical Company (Research), Box 2768, Corpus Christi, Texas.

EXPERIMENTAL

Apparatus and procedure

A schematic diagram of, and specifications for, the fractional sublimator used in this work were reported earlier by BERG AND HARTLAGE[5,6]. Briefly, the apparatus establishes a continuous temperature gradient along a 1-m (11 mm O.D.) pyrex tube maintained at 1 mm of mercury pressure. Samples are placed in small aluminum boats in the high temperature end of the tube where they are volatilized. The gases are moved through the tube with air as a carrier and the metal chelates recrystallize on the walls of the tube in discrete and reproducible temperature zones. The chelates are recovered by cutting the tube into appropriate segments. The temperature ranges in which the individual chelates were observed to condense are discussed below.

The per cent recovery of the individual chelates was determined from the measured loss in the weight of the sample during the sublimation. Without any positive evidence that the sublimed compounds decomposed (below 200°) or recrystallized in areas other than the defined zones, it was assumed that the method gave correct values.

Synthetic mixtures of the chelates were fractionally sublimed by the same technique and each of the chelate zones was analyzed for the specific metal content. Analytical data for the separation of mixtures of Mg, Cr and Be acetyltrifluoroacetonates and Mg, Fe and Al acetyltrifluoroacetonates are described on p. 50.

Preparation of metal chelates

The exact procedure for the preparation and the description of the chelates is given by BERG AND TRUEMPER[1,2] and HARTLAGE[5]. The following general procedure was employed.

An excess of a 5% solution of the metal nitrate (sulfate in the case of beryllium), buffered with sodium acetate was added to an alcoholic solution of the ligand. If the chelate did not precipitate quickly, the solution was evaporated on a steam bath until precipitation did occur. The precipitate was collected by filtration, washed and air-dried. In most cases the crude material was recrystallized from ethanol or ethanol and water. In cases where the chelates would not dissolve in ethanol, benzene and petroleum ether were used. The pure material was dried at 70°.

Analytical methods

In determining the metal content of the chelates, the compound was decomposed with nitric acid, the residue diluted to volume with distilled water, and an aliquot taken for analysis. Iron was determined by a modified version of the 1,10-phenanthroline method; nickel with dimethylglyoxime; beryllium with *p*-nitrobenzeneazo-orcinol; aluminum with aluminon reagent; magnesium with eriochrome black T; and chromium with diphenylcarbazide.

DISCUSSION

Several conclusions can be drawn from a close scrutiny of the sublimation recrystallization data presented in Tables I and II. First, it should be noted that the substitution of a trifluoromethyl group for a methyl group in the ligand molecule does

TABLE I

SUBLIMATION RECRYSTALLIZATION DATA FOR VARIOUS METAL β-DIKETONE CHELATES (°)
(mc = diffuse zone of microcrystals, ns = no sublimation, liq = condensed to liquid)

Metal	*Acetylacetone*[a]	*Acetyltrifluoroacetone*	*Hexafluoroacetylacetone*	*Benzoylacetone*	*Benzoyltrifluoroacetone*
Be(II)	31–15	40–20		136–116	97–71
Mg(II)	141–120	98–73	mc		liq
Ca(II)	203–167				ns
Sr(II)	ns				
Ba(II)	ns				
Al(III)	81–60	42–22		195–160	128–130
Ga(III)	92–70	74–48			115–96
In(III)	85–66				
Zn(II)	38–31	mc	mc		119–103
Cd(II)	137–117				liq
Hg(II)	75–55	ns			ns
Fe(III)	85–66	65–49		ns	liq
Co(II)	88–67	liq	mc	ns	liq
Ni(II)	111–88	95–79	mc	ns	liq
Pd(II)	94–74	79–56			133–103
Pt(II)	102–80				
Rh(III)	118–96	79–60			liq
Zr(IV)	102–77	77–62			liq
Th(IV)	116–78				
V(III)	111–94				
Cr(III)	106–80	69–50	30–20		
Mn(II)	90–70	mc	mc		liq
Cu(II)	102–82	63–50	28–16	130–95	126–101
Pb(II)		ns			

[a] From Berg and Hartlage[6].

TABLE II

SUBLIMATION RECRYSTALLIZATION ZONES FOR VARIOUS METAL ACETYLTRIFLUOROACETONATES (°)

I		*II*		*III*		*IV*	
Mg(II)	98–73	Ga(III)	74–58	Cr(III)	69–50	Al(III)	42–22
Ni(II)	95–79	Pd(II)	79–56	Cu(II)	63–50	Be(II)	40–20
		Rh(III)	79–60	Fe(III)	65–49		
		Zr(IV)	77–62				

TABLE III

SOME COMPLETE SEPARATIONS POSSIBLE WITH ACETYLTRIFLUOROACETONATES

Ga and Al	Mg and Cr	Ni and Cr	Rh and Al
Ga and Be	Mg and Cu	Ni and Cu	Rh and Be
Pd and Al	Mg and Fe	Ni and Fe	Zr and Al
Pd and Be	Mg and Al	Ni and Al	Zr and Be
	Mg and Be	Ni and Be	

indeed increase the volatility of the resulting chelates although there is an appreciable increase in the molecular weight of the chelate. This increase in volatility is observed as we compare the chelates of acetylacetone with acetyltrifluoroacetone and hexafluoroacetylacetone, and of benzoylacetone with benzoyltrifluoroacetone.

Second, that although the fluorinated ligands produce chelates more volatile than those of acetylacetone, the enhanced volatility of the ATA and HAA chelates does not appear to be advantageous for fractional sublimation purposes. The greatest *differences* in volatilities observed among the various metal chelates are among the acetylacetonates. Thus, since separation efficiency is a function of the magnitude of the *differences* in volatilities among the various chelates, the best fractional sublimation separations can be achieved with the metal acetylacetonates[6]. Only a few really good separations can be expected from the fractional sublimation of the metal acetyltrifluoroacetonates as is evident from the grouped data in Table II and Table III.

Third, the fractional sublimation of the metal chelates of HAA and BTA does not result in clearly defined recrystallization zones. The HAA chelates tend to recrystallize as microcrystals in a diffuse zone which usually extends over a major portion of the sublimation tube. This diffuse zone, as seen through a microscope, does indeed consist of minute crystals. We have no explanation for this anomalous behavior. The BTA chelates are fairly volatile but many distill rather than sublime at 1 mm pressure. Upon condensation to a liquid (rather than a solid) the chelates tend to flow down the walls of the tube and occupy a much larger portion of the sublimation tube than those chelates which sublime. Furthermore, upon cooling to room temperature the liquid chelates appear to form a glassy solid rather than a distinct crystalline form.

TABLE IV

PER CENT RECOVERY DETERMINATIONS OF SOME OF THE ACETYLTRIFLUOROACETONATES USING A TEMPERATURE GRADIENT OF 170° TO 15°

Metal	*Chelate taken (mg)*	*Chelate remaining (mg)*	*% Recovery*
Al	13.8	0.0	100.0
Be	11.6	0.0	100.0
Co	14.7	0.6	96.0
Cr	14.2	0.0	100.0
Cu	6.0	0.1	98.4
Fe	10.6	0.1	99.1
Ga	17.3	0.1	99.5
Mg	11.1	0.2	98.3
Ni	14.0	1.2	91.5
Pb	15.4	3.3	78.6
Pd	6.0	0.1	98.4
Zn	18.3	0.7	96.2
Zr	22.0	0.1	99.5

An examination of Tables IV and V shows that the chelates of ATA and HAA are sufficiently stable that they are recoverable from the sublimation apparatus in

TABLE V

PER CENT RECOVERY DETERMINATIONS OF SOME OF THE HEXAFLUOROACETYLACETONATES USING A TEMPERATURE GRADIENT OF 139° TO 15°

Metal	*Chelate taken (mg)*	*Chelate remaining (mg)*	*% Recovery*
Co	19.9	0.80	95.9
Cr	19.9	0.05	99.8
Cu	24.8	0.10	99.6
Mg	29.9	0.40	98.7
Mn	13.1	1.20	90.9
Ni	11.9	1.10	90.8
Zn	9.6	0.40	95.8

TABLE VI

ANALYTICAL DATA FOR THE SEPARATION OF MAGNESIUM, CHROMIUM AND BERYLLIUM ACETYLTRIFLUOROACETONATES

Metal taken (mg)	*Metal found in Mg fraction (mg)*	*Metal found in Cr fraction (mg)*	*Metal found in Be fraction (mg)*	*% Recovery in pure form*
No. I				
Mg 0.073	0.068	0.00	0.00	93
Cr 0.163	0.00	0.116	0.044	71
Be 0.007	0.00	0.00	0.075	—
No. II				
Mg 0.093	0.050	0.00	0.00	54
Cr 0.153	0.00	0.130	0.005	85
Be 0.072	0.00	0.00	0.068	—

No. I sublimed using temperature gradient of 170° to 15°.
No. II sublimed using temperature gradient of 139° to 15°.

TABLE VII

ANALYTICAL DATA FOR THE SEPARATION OF MAGNESIUM, IRON AND ALUMINUM ACETYLTRIFLUOROACETONATES

Metal taken (mg)	*Metal found in Mg fraction (mg)*	*Metal found in Fe fraction (mg)*	*Metal found in Al fraction (mg)*	*% Recovery in pure form*
No. I				
Mg 0.073	0.039	0.00	0.00	53
Fe 0.196	0.00	0.108	0.082	55
Al 0.078	0.00	0.00	0.076	—
No. II				
Fe 0.098		0.080	0.008	82
Al 0.056		0.00	0.057	—

No. I sublimed using temperature gradient of 139° to 15°.
No. II sublimed using temperature gradient of 100° to 15°.

near quantitative yields. This, of course, is a prime requisite for a good separation, but the non-distinct character of the recrystallized zones completely overshadows this desirable trait.

The analytical data of Tables VI and VII are typical of the separations achieved among the various metal acetyltrifluoroacetonates. The separation of mixtures of Be, Mg and Cr; Fe, Mg and Al; and Fe and Al was not quantitative and does not compare favorably with similar separations of the metal acetylacetonates reported earlier[6].

One must conclude from the collected data that, although the substitution of a trifluoromethyl group for a methyl group in the ligand molecule increases the volatility of the corresponding metal chelates, this fractional sublimation technique is more effective for separations involving the metal acetylacetonates than for the metal acetyltrifluoroacetonates, hexafluoroacetonates, benzoylacetonates and benzoyltrifluoroacetonates.

F.R.H. is indebted to Louisiana State University for a Graduate Research Assistantship which supported this study.

SUMMARY

The vacuum fractional sublimation of various metal β-diketone chelates was compared with the fractional sublimation of the metal acetylacetonates reported earlier. Characteristic recrystallization temperature zones are reported for a number of metal acetylacetonates, acetyltrifluoroacetonates, hexafluoroacetylacetonates, benzoylacetonates, and benzoyltrifluoroacetonates. The substitution of a trifluoromethyl for a methyl group in the ligand molecule increased the volatility of the corresponding metal chelates, but this increased volatility did not lead to improved separations by fractional sublimation. In particular, the hexafluoroacetylacetonates tended to recrystallize as microcrystals in diffuse zones which extended over much of the sublimation tube and the benzoyltrifluoroacetonates tended to distill rather than sublime, with the liquids flowing down the wall of the tube. The best separations were achieved among the metal acetylacetonates. The chelates studied are generally stable and can be recovered from the sublimation apparatus in near quantitative yields. Separations of mixtures of Be, Mg, and Cr; Fe, Mg and Al; and Fe and Al were studied critically. Although the separations were not complete, they compared favorably with some reported gas-chromatographic separations.

RÉSUMÉ

On a effectué une comparaison entre la sublimation fractionnée dans le vide de divers chélates métal–β-dicétones et celle d'acétylacétonates métalliques. Les zones de température de recristallisation caractéristiques sont données pour un certain nombre d'acétylacétonates, acétyltrifluoroacétonates, hexafluoroacétylacétonates, benzoylacétonates et benzoyltrifluoroacétonates. La substitution d'un groupe trifluorométhyl à un groupe méthyl dans la molécule de "ligand" augmente la volatilité du chélate métallique correspondant, mais n'améliore pas la séparation par sublimation fractionnée. Les séparations les meilleures sont obtenues avec les acétylacétonates. On a examiné en particulier les séparations suivantes: Be, Mg et Cr; Fe, Mg et Al; Fe et Al. Bien que ces séparations ne soient pas complètes, elles peuvent se comparer avantageusement à celles de certaines séparations par chromatographie gazeuse.

ZUSAMMENFASSUNG

Die fraktionierte Sublimation verschiedener Metall-β-Diketonchelate im Vakuum wurde mit früher veröffentlichten Werten, die ohne Vakuum erhalten wurden, verglichen. Für eine Anzahl von Metall–Acetylacetonaten, –Acetyltrifluoroacetonaten, –Hexafluoroacetylacetonaten –Benzoylacetonaten und –Benzoyltrifluoroacetonaten ergaben sich charakteristische Temperaturzonen für die Kristallisation. Die Substitution von Trifluoromethyl an Stelle einer Methylgruppe steigerte die Flüchtigkeit der entsprechenden Metallchelate, führte jedoch nicht zu verbesserten Trennungen bei der fraktionierten Sublimation. Die Hexafluoroacetylacetonate rekristallisieren als Mikrokristalle in Diffusionszonen, die sich über einen grossen Teil der Sublimationsröhre erstrecken. Die Benzoyltrifluoroacetonate neigen mehr zur Destillation als zur Sublimation. Die besten Trennungen wurden mit den Acetylacetonaten erzielt. Die untersuchten Chelate sind im allgemeinen stabil und können aus der Sublimationsapparatur nahezu quantitativ zurückgewonnen werden. Die Trennung von Mischungen aus Be, Mg und Cr; Fe, Mg und Al; und Fe und Al wurden kritisch untersucht. Obgleich die Trennungen nicht vollständig waren, sind sie günstiger als gaschromatographische Trennungen, über die berichtet wurde.

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A NEW REACTION FOR THE IDENTIFICATION AND DETERMINATION OF PERCHLORATE

PART I. DETECTION OF PERCHLORATE

PASCHOAL SENISE

Departamento de Química, Faculdade de Filosofia, Ciências e Letras, Universidade de São Paulo, São Paulo (Brazil)

(Received June 24th, 1965)

Several cations react with pyridine and certain anions, mainly halides and pseudohalides, to form complexes which can be extracted into organic solvents, particularly chloroform. This property has found analytical application for the detection and determination of different cations[1-3] as well as for the detection of certain anions[1,2]. Among these compounds, copper(II) complexes and especially the copper(II) pyridine thiocyanate $Cu(SCN)_2(py)_2$, reported for the first time by SPACU[4], have been widely employed.

It seemed interesting to investigate the possibility of attaining higher selectivity with regard to extractability into organic solvents by substituting other amines for pyridine and azide for thiocyanate.

A thorough study has shown that from solutions of copper(II) ions containing azide and excess of 2,2'-dipyridyl a yellow extract is obtained with some solvents when certain anions are present in the aqueous phase. Among these anions, perchlorate was found to be responsible for the extractability into several solvents including methyl isobutyl ketone.

On the basis of this observation both a test for the identification of perchlorate and a spectrophotometric method of determination were developed. In this paper the detection test is reported.

EXPERIMENTAL

Preliminary studies

A series of experiments was first run with copper sulfate solutions containing azide ions and excess dipyridyl both in the presence and in the absence of minute amounts of perchlorate. These solutions were shaken with a number of different types of organic solvent and the extraction was evaluated by the yellow color of the extract.

It was observed that hydrocarbons were completely ineffective as extractants while the acyclic alcohols with less than 7 atoms in the carbon chain always provided a yellow extract regardless of the presence of perchlorate in the aqueous layer, the same being true for cyclopentanol and cyclohexanol. Most of the ethers and esters tested were found to be poor extractants, but with several ketones the organic layer appeared yellow when perchlorate was present in the aqueous solution whereas it was colorless in the absence of perchlorate. Chloroform showed the same behavior. The final selection of the solvent, however, was made after performing a number of experiments in the presence of other anions. It was found, for instance, that when large amounts of chlorate or nitrate were present the chloroform extract appeared slightly yellow while this apparently did not occur with several ketones. For this reason and because among the ketones tested methyl isobutyl ketone was the one easily available, this solvent was chosen for the test.

The influence of pH, concentration of copper and azide ions as well as of dipyridyl was investigated systematically during the quantitative study which led to the spectrophotometric method and will be reported at a later date. The results of this study, however, were taken into consideration in order to establish the final conditions of the procedure for the qualitative test. Thus, as it was considered that a certain control of pH was advisable and that a large excess of dipyridyl should always be kept in solution, it was decided to work with a buffered reagent and to employ a solution of 2,2'-dipyridyl in methyl isobutyl ketone instead of the pure solvent as extractant.

Reagents

Copper-2,2'-dipyridyl. Dissolve 0.3 g of 2,2'-dipyridyl in 2.5 ml of a 0.15 *M* solution of copper sulfate by careful heating in a water bath at 50–60°. Add 2.5 ml of a 0.10 *M* solution of sodium azide and bring to a final volume of 10 ml with an acetate buffer of pH 5.1 (final pH 5.2–5.4)*. Keep under diffuse light.

Solvent. Use a recently prepared solution of 2,2'-dipyridyl in methyl isobutyl ketone (15–20 mg/ml). Keep in the dark.

Procedure

To a drop of the sample solution (pH 4–9) in a microtube, add a drop of the reagent and 3 drops of solvent. Shake vigorously and allow the phases to separate. A yellow color appears in the organic layer if perchlorate is present. Compare with a blank run in parallel. Limit of identification: 3 μg ClO_4^-. Limit of dilution: 1:10,000.

Interference study

The influence of foreign anions was studied by carrying out the recommended procedure and taking in every case a drop of solution containing 5 μg of ClO_4^- and a much higher amount of the ion studied. In parallel, another series of experiments was run with the same amount of the foreign ion and no perchlorate present. The following ions were found not to interfere when 1000 μg of each were taken: F^-, Cl^-, Br^-, ClO_3^-, BrO_3^-, IO_3^-, NO_3^-, SO_4^{2-}, HSO_3^-, PO_4^{3-}, CO_3^{2-}, CH_3COO^-. No interference was observed in further experiments carried out with 500 μg of SeO_4^{2-}, SeO_3^{2-}, TeO_3^{2-}, HPO_3^{2-}, $H_2PO_2^-$, $HAsO_4^{2-}$, AsO_2^-, MoO_4^{2-}, WO_4^{2-}, CrO_4^{2-}, $C_2O_4^{2-}$ and $B_4O_7^{2-}$. On account of the low solubility of sodium tellurate the test with this salt was performed with 300 μg TeO_4^{2-} and no interference was observed. In the experiments carried out with tungstate and chromate the formation of a precipitate was noticed but this did not affect the test.

Special attention was paid to the effect of chloride, chlorate and nitrate ions. Experiments in these cases were repeatedly performed with solutions containing the

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* A small amount of dipyridyl remains undissolved and is slowly absorbed by the solution.

minimum amount of perchlorate detectable by the proposed procedure. It was thus found that 5,000 μg of chloride did not interfere in the identification of 3 μg of perchlorate. With regard to chlorate and nitrate it should be noted that when the test was carried out with a solution containing no perchlorate and 1,000 μg of chlorate or nitrate an extremely feeble coloration appeared in the organic phase. Nevertheless 3 μg of perchlorate could still be unequivocally detected, by simple comparison with a blank run with a solution containing the amount of chlorate or nitrate referred to above.

Perrhenate and periodate behave exactly as perchlorate thus interfering in the test.

Iodide and thiocyanate also interfere because both form colored extractable compounds with copper ions and dipyridyl.

Thiosulfate, in large amount, may replace azide allowing the extraction of an olive green product when perchlorate is present.

Perrhenate was eliminated by previous precipitation as Re_2S_7, as described by GEILMANN AND BODE[5], *i.e.*, by boiling with thiosulfate a few milliliters of the sample solution, approximately 6 *N* in sulphuric acid. The excess thiosulfate was destroyed by treatment with perhydrol.

Preliminary elimination of the other interfering anions can be easily performed with the help of well known reactions. Procedures were worked out on a drop scale and are given below. These procedures were found suitable for the elimination of 300 μg IO_4^-, 2000 μg I^-, 1000 μg SCN^- and 1000 μg $S_2O_3^{2-}$, respectively. Periodate was reduced to iodate by arsenite in the presence of excess hydrogen carbonate; iodide was oxidized to iodine by iodate in acid medium; thiocyanate and thiosulfate were destroyed by oxidation with bromine.

Procedure for the elimination of some interfering anions

Periodate. To a drop of the sample solution in a microtube, add a drop of a saturated solution of sodium hydrogen carbonate and a drop of a 0.1 *N* sodium arsenite solution. Mix and let stand for 2–3 min. Add a drop of 1 *N* sulfuric acid. Take a drop of the resulting solution to perform the test as described.

Iodide. To a drop of the sample solution in a microtube, add 1 ml of chloroform and a drop of a 0.1 *M* solution of sodium iodate approximately 1 *N* in sulfuric acid. Shake well, add a drop of a saturated solution of sodium hydrogen carbonate, mix and centrifuge. Use a drop of the aqueous phase to perform the test.

Thiocyanate. To a drop of the sample solution in a microtube, add drop by drop and under continuous shaking a chloroform solution of bromine until the organic layer appears slightly colored. Let stand for 5 min and add a drop of 3 *N* sodium hydroxide followed by a drop of a saturated solution of sodium acetate. Take a drop of the aqueous phase to carry out the test.

Thiosulfate. Proceed as described for thiocyanate but omit the addition of sodium hydroxide after accomplishing the oxidation with bromine.

Certain ions that react with azide in the conditions of the test, *e.g.* permanganate, persulfate and nitrite, should obviously be absent as well as ions that react with copper(II), *e.g.* sulfide, ferrocyanide and ferricyanide. Cyanide and cyanate, in large amounts, inhibit the test and should also be previously removed. Vanadate forms a precipitate with the copper–dipyridyl complex but can be removed by a previous precipitation with barium acetate.

With regard to cations it was observed that the colored compounds formed by iron(II), iron(III), cobalt or nickel with 2,2′-dipyridyl and azide ions are not extracted by methyl isobutyl ketone, no color being observed in the organic layer either in the presence or in the absence of perchlorate. These metal ions, however, compete with copper in the reaction with dipyridyl and azide thus decreasing somewhat the sensitivity of the test. The same is true for other ions that form colorless or slightly colored complexes, such as cadmium, zinc and manganese. Some other cations consume azide by precipitation or complexation, *e.g.* silver, lead or mercury. All these cations may be previously precipitated by boiling the sample solution with sodium carbonate or may be removed with the help of ion-exchange resins.

Test sensitivity improvement by means of the ring oven technique

With the intention of enhancing the sensitivity of the test, the indirect detection of perchlorate was tried through the identification of the extracted copper. Best results were obtained for this purpose by making use of the WEISZ ring oven technique[6], after extracting the copper compound with a larger volume of solvent and back-extracting it to the aqueous phase. The application of this technique, however, decreased considerably the tolerable amount of chlorate and nitrate, the limit being lowered to 30 μg and 100 μg for chlorate and nitrate, respectively. Larger amounts of these ions should thus be previously removed. Reduction in alkaline medium with Devarda alloy was found to be efficient for this purpose.

Chloride and bromide even in amounts of 1000 μg, were found not to interfere and with regard to all the other ions studied the same general behavior as reported above was observed.

PROCEDURE

To a drop of the sample solution (pH 4–9) in a microtube, add a drop of the reagent and 9 drops of solvent (about 0.3 ml). Shake vigorously and centrifuge for a few seconds. Remove the organic layer, transferring it to another microtube with the help of a capillary dropping pipette. Add to the extract a drop of a 0.15 *N* sodium hydroxide solution, shake vigorously and centrifuge. Remove the organic phase and discard it.

Carefully transfer the alkaline solution to a disk of filter paper on the hot ring oven, with the help of a capillary dropping pipette. Wash the spot 10 times with 5 μl of 0.1 *N* hydrochloric acid each time. After complete vaporization has occurred remove the paper, spray it with an alcoholic 1% solution of dithiooxamide and fume over ammonia. Rinse the paper with distilled water and dry it at 100–105°. Compare the green to black ring with a blank run exactly in the same manner.

Limit of identification: 0.15 μg ClO_4^- (S & S no. 589^2 paper). Limit of dilution: 1:200,000.

If chlorate or nitrate are present proceed as follows.

Chlorate and, or, nitrate present. To two drops of the sample solution in a microtube kept under cold water, add 2 drops of a 30% sodium hydroxide solution and, approximately, 2 mg of Devarda alloy. Let stand for about an hour. Add a drop of 11 *N* sulfuric acid and a drop of 3 *N* acetic acid. Centrifuge and take a drop of the supernatant solution to perform the test as described.

DISCUSSION

It was found that the composition of the extracted product, responsible for the color of the organic phase, corresponds to the formula $Cu(dipy)_2N_3ClO_4$. The compound was isolated and analysed; its preparation and properties will be described later.

It may be interesting to note that if 2,2′-dipyridyl is replaced by 1,10-phenanthroline, the same general behavior is observed when methyl isobutyl ketone is used as solvent, but the sensitivity of the test decreases somewhat.

As referred to above, perrhenate ions behave exactly as perchlorate in the reaction described and this property can thus be used as a means for detecting perrhenate. A test of identification is actually being developed in our laboratory, with the particular aim of detecting rhenium in molybdenites.

The author is indebted to Dr. L. SANT'AGOSTINO and to Mr. J. A. GARCIA SANCHES for technical help given in the course of this study and to Fundação de Amparo à Pesquisa do Estado de São Paulo for financial support.

SUMMARY

Perchlorate is extracted into methyl isobutyl ketone from aqueous solutions of copper(II) ions containing azide ions and an excess of 2,2′-dipyridyl. The yellow color of the organic phase can be used for the detection of perchlorate. A procedure is given which allows the identification of 3 μg of perchlorate. Considerably larger amounts of nitrate, chlorate, chloride and several other anions can be tolerated. By performing the test with the help of the WEISZ ring oven technique, a limit of identification of 0.15 μg of perchlorate can be attained.

RÉSUMÉ

Une nouvelle réaction est proposée pour l'identification des perchlorates. On procède à une extraction dans la méthylisobutylcétone à partir de solutions aqueuses de cuivre(II), renfermant un azoture et un excès de 2,2′-dipyridyle. Une coloration jaune de la phase organique indique la présence de perchlorate (limite d'identification: 3 μg). De relativement grandes quantités de nitrate, chlorate, chlorure et de nombreux autres anions ne gênent pas. En appliquant la technique de WEISZ ("ring oven technique"), on arrive à une limite d'identification de 0.15 μg.

ZUSAMMENFASSUNG

Perchlorat lässt sich mit Methylisobutylketon aus wässrigen Lösungen, die Kupfer(II)-Ionen, Azidionen und einen Überschuss von 2,2′-Dipyridyl enthalten, extrahieren. Die dabei entstehende gelbe Farbe der organischen Phase kann als Nachweis verwendet werden. Es wird ein Verfahren angegeben, das den Nachweis von 3 μg Perchlorat erlaubt. Beträchtlich grössere Gehalte von Nitrat, Chlorat, Chlorid und verschiedener anderer Anionen sind zulässig. Mit der WEISSschen Ringofentechnik kann eine Nachweisgrenze von 0.15 μg Perchlorat erreicht werden.

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Anal. Chim. Acta, 34 (1966) 53–58

SEPARATION AND MEASUREMENT OF CESIUM-137 IN PRECIPITATION*

J. E. JOHNSON, D. W. WILSON, G. M. WARD AND R. D. THOMPSON**
Animal Science Department, Colorado State University, Fort Collins, Colo. (U.S.A.)
(Received May 17th, 1965)

Cesium-137 is a γ-ray emitting nuclide produced in high fission yield by decay of ^{137}Xe following a nuclear detonation. The relatively long half-life of 30 years and the chemical similarity to potassium has warranted studies of fallout ^{137}Cs and its potential biological consequences.

The value of precipitation monitoring of fallout ^{137}Cs is largely to predict its concentration in subsequent steps in the food chain and the resulting body burdens of this nuclide in man. It has been shown[1] that dairy products and meat account for 75–80% of the human intake of ^{137}Cs. This pathway is initiated by direct foliar absorption of ^{137}Cs in environmental precipitation samples. In a period when recently formed nuclear debris is present in rain the accuracy of γ-ray spectrometric determinations of ^{137}Cs is low due to the complexity of the gross γ-ray spectrum. The presence of several high fission yield γ-ray emitting nuclides, notably Zr–^{95}Nb, ^{103,106}Ru, ^{125}Sb and ^{144}Ce, results in enough interference from both photoelectric and Compton contributions to make direct quantitative spectral analysis for ^{137}Cs an impossibility. The alternatives to immediate γ-ray analysis are either to store the rain sample until sufficient time has elapsed for decay of the Zr–^{95}Nb, the major contributor, or, preferably, to separate the ^{137}Cs by a chemical method.

The ion-exchange technique for collection of fallout in rainwater has been applied extensively and has the advantage of efficiently concentrating the radioactivity from a large volume of rain. BONI[2] reported on the efficiency of collection and the breakthrough point for fallout cations when the ion-exchange collection method was used.

Selective elution methods for obtaining specific radionuclides from the resin have not been reported in connection with rainwater analysis; however, elution of ^{137}Cs from a cation-exchange resin with ammonium chloride has been investigated by WISH[3], and MATHERS AND HOELKE[4] have reported a selective elution procedure to separate a number of elements from a fission product mixture; ^{137}Cs lends itself well to selective elution from a cation-exchange resin because of its low retention coefficient on the resin. This property is a good basis for separating ^{137}Cs from many interfering γ-ray emitters since, in general, these cations are polyvalent and consequently are more tightly bound to the resin.

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* This work was supported by contract AT(11-1)-1171 with the U.S. Atomic Energy Commission. Published with the approval of the Director of the Colorado Agricultural Experiment Station as Scientific Series Paper No. 1008.

** Chemistry Department, Colorado State University.

EXPERIMENTAL

Three fiberglass funnels located 5 ft. above ground with a catch area of 61.9 sq. ft. each were used as precipitation collectors. The amount of precipitation was determined from the volume of water collected by the funnels as well as by a rain gauge. At two of the sampling sites the collected precipitation was allowed to pass by gravity through an 80-ml resin bed of Dowex 50W-X12 (100–200 mesh, H^+ form). The resin columns were 28 × 3.8 cm polyethylene cylinders with threaded ends. The upper end, threaded to the funnel, contained a glass wool plug for coarse sediment collection. At the third site, the precipitation was collected in a 55-l polyethylene bottle and the entire collection taken to the laboratory for ion-exchange recovery of ^{137}Cs.

The columns were brought to the laboratory immediately following a rain after all the water had passed through them. Elution of the column was carried out with 1 l of 0.5 *M* ammonium nitrate at a flow rate of 5–10 ml/min. The eluant was collected in a 1-l polyethylene bottle and counted with a γ-ray spectrometer. Following elution, the sediment and glass wool mat were placed on a BM-2133 air filter pad and the mass spread evenly over the pad with a Nalgene spatula after wetting the mass with 40% hydrofluoric acid solution to dissolve the glass wool. The pad and contents were dried and enveloped for counting by γ-ray spectrometry.

The eluant was counted for 120 min in a 1-l polyethylene bottle placed lengthwise on a 4-in. thick by 8-in. diameter NaI (Tl) crystal. The crystal was shielded from background activity by a 5-in. thick steel-walled chamber and the output of the detector was fed to a 400-channel pulse-height analyzer. The system was calibrated by comparison with a standard of cesium-137 chloride plus carrier in the same geometry. Contributions of other γ-ray emitters possibly present in the eluant were subtracted from the apparent ^{137}Cs count by means of a computer-programmed spectrum stripping equation. This equation was generated from 7 simultaneous equations in 7 unknowns where the unknowns were the true amounts of the 7 nuclides in the sample and the constants were empirical Compton ratios determined by counting samples of each nuclide in the eluant geometry.

The sensitivity of detection was 50 picocuries, at the 95% confidence interval, per total rain sample in the eluant geometry and the counting yield was 17.2 counts per 120 min per picocurie. Recovery of ^{137}Cs from solutions spiked with both cesium-137 chloride and zirconium–niobium-95 oxalate was 95 ± 5%.

RESULTS AND DISCUSSION

The γ-ray spectrum resulting from each step in the procedure was studied to observe the behavior of the various fallout nuclides in rainwater. The original purpose of adopting the method of elution with 0.5 *M* ammonium nitrate was to separate Zr–^{95}Nb from ^{137}Cs. This separation was evident from a comparison of the γ-ray spectra of the resin column containing the total cation activity and the eluant fraction of a May, 1963, rainwater sample (Fig. 1)*. The spectrum of the resin column contained peaks identified as those due to the presence of Ce–^{144}Pr, ^{103,106}Ru

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* The column and the eluant bottle presented widely different counting geometries and the counting sensitivities were, therefore, not the same for both spectra.

and Zr–^{95}Nb. From this spectrum there was no indication that the precipitation sample contained ^{137}Cs. The γ-ray spectrum of the eluant, however, contained a relatively large photopeak due to ^{137}Cs and the actual ^{137}Cs activity could be determined by spectrum stripping, taking into account the contribution of the other γ-ray emitters to the area under the ^{137}Cs, 662 keV, absorption peak.

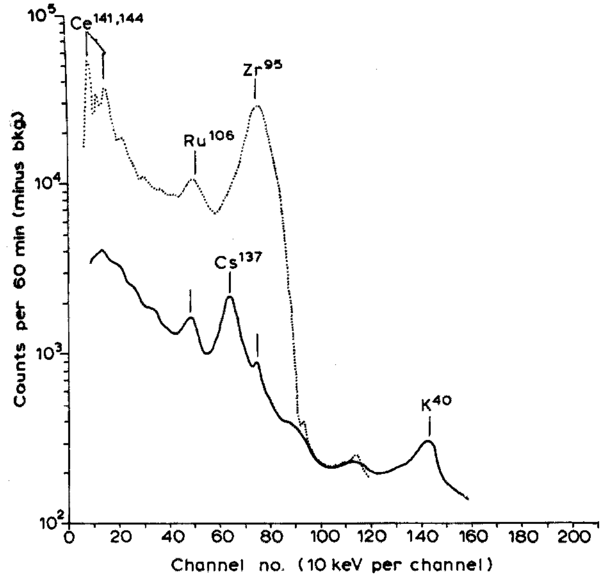

Fig. 1. γ-Ray spectrum of cation-exchange column containing precipitation sample collected 7/8/62 prior to elution and spectrum of ammonium nitrate eluant fraction: ---, column; —, eluant.

Zr–^{95}Nb was not found in the present fallout but the method presented has not been discarded since it afforded other separations useful in reducing the complexity of the γ-ray spectrum of rain samples as well as concentrating the activity in the rain sample. The resin columns usually contained ^{144}Ce–Pr, ^{125}Sb, ^{106}Ru and ^{54}Mn as well as ^{137}Cs; ^{54}Mn is an activation product and presumably added to certain nuclear tests as a tracer. The eluant contained only ^{106}Ru, ^{125}Sb and ^{137}Cs.

The retention of ^{137}Cs by the resin bed was 100% at the flow rates of ammonium nitrate studied up to 12 ml/min. As the flow rate was increased from 1.4 to 9.0 ml/min the ^{95}Zr retention decreased from 50 to about 20%. Ammonium nitrate was the only eluant tried that allowed separation of the ^{137}Cs from ^{95}Zr. The optimum concentration that would elute 100% of the ^{137}Cs in a 1-l volume was found to be 0.5 *M*.

The absolute recovery, however, was a function of the amount and type of sediment contained in the sample. The sediment was primarily wind-blown dust that settled in the rain funnels, although some may have been brought down by the precipitation. In Northern Colorado, winds and ground dust storms often precede summer rains and it is impractical to maintain collecting funnels free of sediment at the time of rain. For analysis, the sediment was collected by the glass wool plug at the top of the column and leached by the ammonium nitrate elution volume. After elution it was found that the plugs contained up to 30% of the total ^{137}Cs activity.

This was probably due to soil particles capable of removing ^{137}Cs from solution irreversibly with respect to ammonium nitrate elution.

To study the effect of sediment on recovery, standard cesium-137 chloride solutions were added to samples of subsoil, surface soil, and actual sediment collected by washing down the funnels with distilled water prior to a rain. These soil solutions were allowed to stand for several days and then passed through ion-exchange columns and eluted as described above. Approximately 75% of the added ^{137}Cs activity was bound irreversibly by the subsoil and surface soil samples. However, the sediment collected from the funnels gave up essentially 100% of the added activity indicating no loss to the soil particles. The loose, easily blown dust that settled on the funnels was found to be very high in silt which did not have the platy structure of local montmorillonite clay soils and as a result nearly all of the ^{137}Cs was exchangeable. Clay matrices have often been noted to bind ^{137}Cs very tenaciously and it can be removed only by sodium carbonate fusion[5] or sodium hydroxide digestion techniques[6]. The ^{137}Cs in the residue can be assumed to have originated in the rain water and not the sediment per se as the ^{137}Cs concentration of a few grams of top soil was small compared to the total ^{137}Cs activity in the precipitation.

It was noted in the experiment that even the silt–^{137}CsCl suspension, when counted after standing several hours, gave higher apparent activity than that added. This indicated that the soil colloid on settling carried much of the ^{137}Cs activity with it, and resulted in an improved counting efficiency. This is important to recognize, since any residue left in collecting funnels or jugs, even though predominantly silt, may retain by adsorption large amounts of fission product activity. The collecting funnels should be washed down with water immediately after each rain and the sediment carefully collected and washed on to the ion-exchange column.

Although trials indicated that under our conditions, nearly 100% removal of the ^{137}Cs adsorbed on the sediment was achieved, the percentage of clay is apt to vary and appreciable amounts of ^{137}Cs can be lost.

The glass wool plug will also contain interfering fission product activity which must be allowed to decay until reliable counting estimates of any ^{137}Cs activity can be made. If any is present it is added to the elution activity to obtain the total deposition of ^{137}Cs per rainfall.

SUMMARY

In rainwater samples containing fallout debris of recent origin, the ^{137}Cs absorption peak in a γ-ray scintillation spectrum contained, and was often completely obscured by, contributions from other γ-ray emitting radionuclides, so that the ^{137}Cs activity could not be determined directly. Precipitation samples were collected with rain funnels and passed through Dowex 50W-X12 cation-exchange columns. The ^{137}Cs was selectively eluted with 0.5 M ammonium nitrate. The absolute recovery of ^{137}Cs was complicated by the presence of airborne sediments that were invariably collected with the sample and could irreversibly fix ^{137}Cs from the rainwater.

RÉSUMÉ

Les auteurs ont effectué une séparation et une mesure de césium-137 dans de échantillons d'eau de pluie, renfermant des débris de retombée d'origine récente. Les échantillons recueillis sont traités par une résine Dowex 50W-X12 (échange de cations); ^{137}Cs est élué sélectivement au moyen de nitrate d'ammonium 0.5 *M*. Le rendement absolu cependant dépend de la teneur et du type de sédiment contenu dans l'échantillon.

ZUSAMMENFASSUNG

In Regenwasserproben, die Fallout jüngsten Ursprungs enthalten, konnte häufig die ^{137}Cs-Aktivität nicht direkt bestimmt werden, da andere gammastrahlende Radionuklide störten. Die Proben wurden auf einen Dowex-50W-X12-Kationenaustauscher gegeben und das ^{137}Cs selektiv mit 0.5 *M* Ammoniumnitrat eluiert. Die Rückgewinnung des ^{137}Cs wurde durch die Gegenwart von Sedimenten aus der Luft erschwert, die ungleichmässig mit der Probe gesammelt wurden und ^{137}Cs festhielten.

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ÉTUDE DES FACTEURS INTERVENANT DANS LE DOSAGE DE TRACES DE CADMIUM PAR POLAROGRAPHIE AVEC REDISSOLUTION ANODIQUE (OU POLAROGRAPHIE INVERSE; ANODIC STRIPPING)

ED. MARTIN, D. MONNIER ET W. HAERDI
Laboratoires de Chimie Minérale et Analytique, Université de Genève (Suisse)

(Reçu le 24 novembre 1964)

Dans le cas de l'analyse des traces de métaux donnant des amalgames avec le mercure, la polarographie présente plusieurs avantages: sensibilité, précision, risques de contamination réduits, simplicité.

Quelques problèmes d'analyses de traces ont déjà été résolus par cette méthode tels que le dosage des traces dans les acides concentrés[1,2], dans le zinc métallique et le sulfure de zinc[3], dans l'aluminium de grande pureté[4,5] et dans l'eau de la Mer Morte[6,7].

Une étude bibliographique attentive portant à la fois sur les applications pratiques de la polarographie inverse[1-14], sur ses aspects théoriques et ses limites[11-14] nous a montré la nécessité d'effectuer une étude systématique des facteurs qui interviennent dans cette méthode afin d'en développer son champ d'application et de la rendre aussi sensible et précise que possible.

Cette méthode consiste à réduire, sur une goutte de mercure suspendue et de surface bien déterminée, l'ion à doser. On concentre ainsi cet élément. Puis, en appliquant à cette électrode un potentiel de moins en moins négatif, on remet une partie du métal amalgamé en solution. On obtient ainsi une courbe potentiel–courant dont le maximum est proportionnel à la concentration du métal dans la solution.

PARTIE EXPÉRIMENTALE

Solutions, réactifs, appareillage

Electrolyte de base: chlorure de potassium p.a. en solution 0.1 *N* dans de l'eau bidistillée.

Solution standard de cadmium: 100 µg de Cd/ml dans KCl 0.1 *N* (en partant de l'acétate de cadmium p.a. Merck).

La cellule et ses constituants: la cellule d'électrolyse thermostatisée Metrohm d'un volume de 60 ml est constituée de deux parties reliées au moyen d'un rodage; la partie supérieure comporte cinq ouvertures rodées. L'électrode à goutte de mercure pendante (Hanging Mercury Drop Electrode ou H.M.D.E.) est introduite dans l'ouverture centrale, les autres sont destinées à recevoir l'électrode au chlorure d'argent saturée, le tube d'arrivée de l'azote, le tube d'évacuation de ce gaz. Dans la 5^{me} ouverture on peut introduire une électrode supplémentaire pour contrôler le potentiel par exemple. La solution est agitée au moyen d'un agitateur magnétique.

Le système d'arrivée de l'azote dans la cellule est constitué de deux tubes concentriques dont le plus long, central, pénètre dans la solution et permet d'éliminer l'oxygène avant l'électrolyse. Au cours de la détermination, l'azote passe par le tube extérieur, sans barboter dans la solution.

L'électrode de référence est une électrode au chlorure d'argent saturée. Elle est reliée à la solution au moyen d'un tube, renfermant une solution de chlorure de potassium saturée, dont l'extrémité est constituée par un disque de verre fritté très fin. L'électrode à goutte de mercure pendante (H.M.D.E.) est constituée d'un capillaire et du microdoseur Metrohm E 410. Ce dispositif permet de former des gouttes de mercure de dimension déterminée et reproductibles.

Polarographe enregistreur Metrohm du type E 261 R.

Mode opératoire

La cellule d'électrolyse est rincée avec de l'acide nitrique 1:1, avec de l'eau distillée et enfin avec de l'eau bidistillée. La solution est introduite dans la cellule et l'on chasse l'oxygène dissous en faisant barboter de l'azote (99.99%) dans la solution pendant 15 min. Pendant toute cette opération la solution est agitée au moyen d'un agitateur magnétique. Au cours de la détermination on fait passer l'azote dans la cellule au-dessus de la solution. On amène alors au moyen de la vis micrométrique du microdoseur le mercure jusqu'à l'extrémité du capillaire, puis on forme une goutte de mercure de dimensions déterminées par un déplacement approprié de la vis micrométrique. L'électrolyse est alors effectuée à un potentiel et une température déterminés et pendant un temps qui dépend de la concentration en cadmium. On choisit la sensibilité en fonction de la concentration du cadmium dans la solution et le temps est d'autant plus long que la concentration de cadmium dans la solution est plus faible. On ramène ensuite le potentiel vers des valeurs moins négatives à vitesse constante (1 V/min) et la courbe potentiel–courant qui en résulte est enregistrée. Elle présente un maximum qui est proportionnel à la concentration du cadmium dans la solution et que nous mesurons comme indiqué à la Fig. 1.

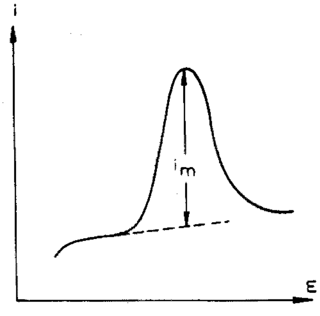


Fig. 1. Détermination graphique de i_m.

Etude analytique

Nous avons examiné l'influence des facteurs suivants sur la sensibilité et la reproductibilité de la méthode (c.à.d. sur la valeur de i_m):
1) potentiel d'électrolyse, 2) durée de l'électrolyse, 3) oxygène dissous, 4) volume de la solution, 5) température, 6) surface des gouttes, 7) concentration de cadmium, 8) agitation de la solution.

1) *Influence du potentiel d'électrolyse.* Conditions de travail: potentiel d'élec-

trolyse compris entre −1 V et −0.20 V; température: 20°; surface des gouttes de mercure: 1.38 mm²; durée de l'électrolyse: 3 min en agitant la solution puis 1 min sans agitation; vitesse de balayage anodique: 1 V/min; volume de la solution: 50 ml; concentration Cd^{2+}: 0.1 µg/ml; dégazage: 15 min.

TABLEAU I

INTERDÉPENDANCE DU COURANT MAXIMUM ET DU POTENTIEL D'ÉLECTROLYSE

Potentiel d'électrolyse (V)	*Courant maximum (A)*	*Potentiel d'électrolyse (V)*	*Courant maximum (A)*
−1.0	$3.7 \cdot 10^{-7}$	−0.50	$9 \cdot 10^{-9}$
−0.90	$3.3 \cdot 10^{-7}$	−0.40	$7 \cdot 10^{-9}$
−0.80	$3.2 \cdot 10^{-7}$	−0.30	$6 \cdot 10^{-9}$
−0.70	$3.2 \cdot 10^{-7}$	−0.20	$6 \cdot 10^{-9}$
−0.60	$1.6 \cdot 10^{-7}$		

Entre −1.0 et − 0.70 V, l'intensité est maximum et constante. Il faut donc travailler dans ce domaine de potentiel si l'on veut avoir une sensibilité et une précision aussi élevée que possible.

2) *Influence du temps d'électrolyse.* Conditions de travail: les mêmes que sous 1), sauf en ce qui concerne le potentiel d'électrolyse qui est constant et égal à −1.0 V. Les résultats sont donnés dans la Fig. 2.

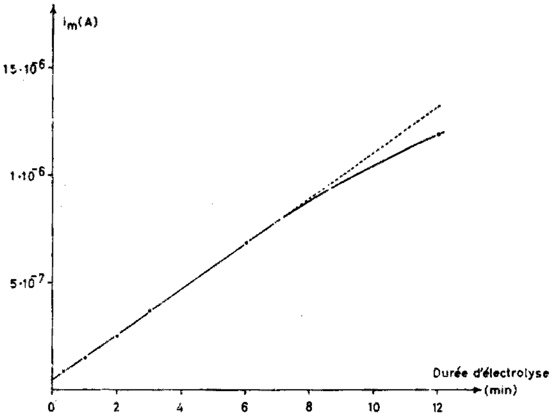


Fig. 2. Influence du temps d'électrolyse.

On constate que le courant maximum i_m dépend de la durée de l'électrolyse. Sur le graphique (Fig. 2) nous avons représenté la variation du courant maximum en fonction de la durée d'électrolyse. La courbe représentative montre que pour des durées d'électrolyse inférieures à 6 minutes le courant maximum est directement proportionnel à la durée d'électrolyse.

3) *Influence de l'oxygène.* Nous avons étudié l'effet de l'oxygène dissous sur le courant maximum i_m et son élimination par barbotage d'azote. Conditions de travail identiques à 1), sauf en ce qui concerne la durée d'électrolyse qui est de 3+1 min et la durée de dégazage qui est variable.

La présence d'oxygène (*cf.* Tab. II) dissous provoque une augmentation du courant maximum; cet effet gênant peut être supprimé par barbotage d'azote dans la solution pendant une durée suffisante (10 min environ). Un passage plus prolongé de l'azote ne modifie plus l'intensité du courant maximum. Nous avons d'autre part tenté d'éliminer l'oxygène dissous au moyen de quelques gouttes d'une solution saturée de sulfite de sodium, mais cette élimination n'est pas complète.

4) *Influence du volume de la solution.* Conditions de travail comme pour 3), sauf en ce qui concerne la durée du barbotage de l'azote qui est de 15 min et le volume de la solution qui est variable. On observe (Tableau III) une variation sensible de i_m avec le volume de la solution dont il faut tenir compte lors de l'élaboration des méthodes analytiques.

TABLEAU II

COURANT MAXIMUM EN FONCTION DE LA DURÉE DU BARBOTAGE DE N_2

Durée du barbotage d'azote (min)	*Courant maximum (A)*
0	$6.2 \cdot 10^{-7}$
5	$5.0 \cdot 10^{-7}$
10	$5.2 \cdot 10^{-7}$
15	$5.2 \cdot 10^{-7}$

TABLEAU III

VARIATIONS DU COURANT MAXIMUM D'APRÈS LE VOLUME DE SOLUTION

Volume de solution (ml)	*Courant maximum (A)*
35	$4.7 \cdot 10^{-7}$
40	$4.5 \cdot 10^{-7}$
45	$4.4 \cdot 10^{-7}$
50	$4.0 \cdot 10^{-7}$

5) *Influence de la température.* Conditions comme pour 4), sauf en ce qui concerne la température. Les résultats sont donnés dans le Tableau IV.

Dans l'intervalle de température étudiée l'intensité du courant maximum est en première approximation proportionnelle à la température. La courbe représentative de la variation du courant maximum en fonction de la température est une droite de pente égale à $1.57 \cdot 10^{-8}$ A/°C. Cet effet est plus élevé qu'en polarographie.

La température a une influence marquée sur l'intensité du courant maximum et plus élevée qu'en polarographie. Il est, par conséquent, indispensable de travailler à température constante si l'on veut obtenir des résultats reproductibles.

6) *Influence de la surface de la goutte de mercure.* Conditions de travail identiques à 5), sauf qu'on travaille à la température constante de 20° et qu'on fait varier la surface de la goutte.

On constate que pour des surfaces comprises entre 0.86 et 2.22 mm^2, le courant maximum est proportionnel à la surface de la goutte (Tableau V).

7) *Influence de la concentration du cadmium courbe d'étalonnage.* Conditions de travail comme en 6), sauf en ce qui concerne la concentration du cadmium et la surface de la goutte qui est constante et de 1.38 mm^2.

TABLEAU IV

INFLUENCE DE LA TEMPÉRATURE SUR LE COURANT MAXIMUM

Température (°)	*Courant maximum (A)*	*Température (°)*	*Courant maximum (A)*
20	$3.4 \cdot 10^{-7}$	40	$6.1 \cdot 10^{-7}$
25	$4.0 \cdot 10^{-7}$	45	$7.0 \cdot 10^{-7}$
30	$5.2 \cdot 10^{-7}$	50	$8.0 \cdot 10^{-7}$
35	$5.9 \cdot 10^{-7}$	60	$9.7 \cdot 10^{-7}$

TABLEAU V

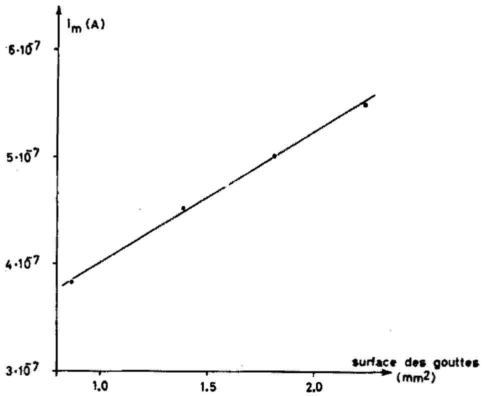
CORRÉLATION ENTRE LA SURFACE DES GOUTTES DE Hg ET LE COURANT MAXIMUM

Surface des gouttes de Hg (mm^2)	*Courant maximum (A)*
0.86	$3.8 \cdot 10^{-7}$
1.38	$4.5 \cdot 10^{-7}$
1.80	$5.0 \cdot 10^{-7}$
2.22	$5.5 \cdot 10^{-7}$

TABLEAU VI

INFLUENCE DE LA CONCENTRATION DE Cd^{2+} SUR LE COURANT MAXIMUM

Concentration Cd^{2+} (µg/ml)	*Courant maximum (A)*	*Ecart extrême (A)*	*Ecart extrême (%)*
0.001	$5.2 \cdot 10^{-9}$	$\pm 0.08 \cdot 10^{-9}$	±1.8
0.005	$2.26 \cdot 10^{-8}$	$\pm 0.01 \cdot 10^{-8}$	±0.4
0.01	$5.28 \cdot 10^{-8}$	$\pm 0.03 \cdot 10^{-8}$	±0.6
0.02	$8.93 \cdot 10^{-8}$	$\pm 0.2 \cdot 10^{-8}$	±2.2
0.05	$2.17 \cdot 10^{-7}$	$\pm 0.05 \cdot 10^{-7}$	±2.3
0.08	$3.63 \cdot 10^{-7}$	$\pm 0.03 \cdot 10^{-7}$	±0.8
0.1	$4.49 \cdot 10^{-7}$	$\pm 0.04 \cdot 10^{-7}$	±0.9



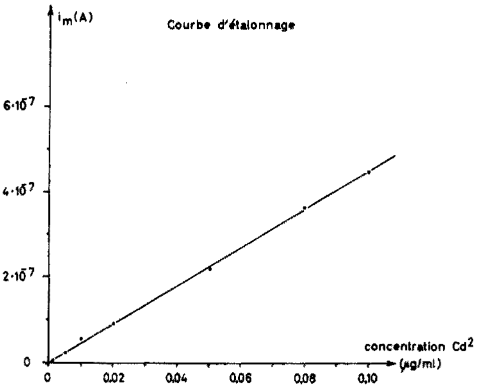


Fig. 3. Influence de la surface des gouttes.

Fig. 4. Courbe d'étalonnage.

Sur chaque solution nous avons effectué trois déterminations complètes. Dans le Tableau VI nous donnons pour chaque solution la valeur moyenne du courant maximum et l'écart entre cette valeur et la valeur extrême.

8) Influence de l'agitation de la solution. Conditions de travail identiques à 7), sauf qu'on maintient constante à 0.1 μg/ml la concentration de cadmium et qu'on fait varier la vitesse de l'agitation électromagnétique.

Dans un premier essai l'électrolyse a été effectuée pendant une durée de 4 min dont 3 min avec agitation de la solution et 1 min sans agitation, sous ces conditions, l'intensité du courant maximum était de $3.3 \cdot 10^{-7}$ A. Dans un deuxième essai l'électrolyse a été effectuée pendant une durée de 4 min sans agitation. Les autres conditions restant inchangées nous avons mesuré une intensité de courant maximum de $3.4 \cdot 10^{-8}$. Le courant maximum est donc en première approximation 10 fois plus intense lorsque l'électrolyse est effectuée avec agitation de la solution.

CONCLUSIONS ET REMARQUES

Afin d'obtenir des résultats reproductibles il faut maintenir certains facteurs constants:

1. le dispositif d'agitation magnétique s'échauffe notablement ce qui entraîne une variation de la température de la solution. Il est donc préférable, si on veut des résultats très précis, d'utiliser une cellule thermostatisée.
2. il faut opérer sur des volumes de solution constants et avec le même système et la même vitesse d'agitation.
3. pour un dosage déterminé la durée d'électrolyse doit être constante.
4. avant d'effectuer la redissolution anodique il faut laisser reposer la solution quelques minutes après agitation, et maintenir les électrodes sous tension.

En travaillant dans ces conditions la reproductibilité est très bonne comme le montrent les valeurs obtenues pour la courbe d'étalonnage. Signalons que chaque résultat est obtenu avec une goutte de même surface, formée dans les mêmes conditions avec le microdoseur. L'écart extrême maximum obtenu dans l'établissement de la courbe d'étalonnage est inférieur à l'écart dû au microdoseur et à diverses opérations analytiques exigées par ce dosage.

Remarques. Dans les essais effectués, même dans le cas d'ultra-traces, nous n'avons pas été gêné par des contaminations, ni par l'adsorption sur les parois des récipients, même pour des concentrations de cadmium de l'ordre de 10^{-9} g/ml. Du reste notre choix pour cette étude systématique s'est porté sur le cadmium car cet élément présente tous les avantages, tant en ce qui concerne l'amalgame formé que les contaminations par l'eau, les réactifs et l'atmosphère qui sont pratiquement nulles.

Signalons encore que des perturbations se sont produites dans la formation des gouttes de mercure au moyen du microdoseur. Après une durée d'utilisation plus ou moins longue, la goutte se détache du tube sans raison apparente. En fait on observe dans le capillaire la présence de débris de caoutchouc provenant du filtre d'étanchéité placé entre le capillaire et le microdoseur. C'est pourquoi nous avons remplacé ce joint par une rondelle de téflon. Le phénomène observé ne se produit alors qu'après une utilisation prolongée du capillaire. Dans ce cas il faut le laver à l'alcool puis à l'éther et enfin le siliconer à nouveau avec une solution à 10% de rhodorsil dans du *n*-hexane.

Nous remercions le Fonds National Suisse grâce auquel nous avons pu entreprendre ce travail.

RÉSUMÉ

Une étude systématique des facteurs intervenant dans le détermination des traces de cadmium par polarographie avec redissolution anodique (anodic stripping) à une électrode à goutte de mercure pendante a été effectuée. Elle a permis de définir et de développer le champ d'application de cette méthode et de la rendre aussi sensible et précise que possible.

SUMMARY

A systematic study of the factors influencing the determination of traces of cadmium by anodic stripping at a hanging mercury drop electrode has been made. The limits of application of the method have been widened and the studies have allowed the method to be made as sensitive and accurate as possible.

ZUSAMMENFASSUNG

Beschreibung einer systematischen Untersuchung über die Faktoren welche die Bestimmung von Spuren von Cadmium anodischen stripping Methode am hängendem Quecksilbertropfen beeinflussen. Der Anwendungsbereich und die Grenzen des Methode konnten erweitert und festgelegt werden. Die Methode ist sehr genau und empfindlich.

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SPEKTROFOTOMETRISCHE BESTIMMUNG VON CALCIUMSPUREN NACH IHRER ABTRENNUNG AUS KONZENTRIERTEN LITHIUMCHLORID-LÖSUNGEN MITTELS KATIONENAUSTAUSCH

JÜRGEN BOSHOLM
Institut für Anwendung radioaktiver Isotope, Technische Universität, Dresden (Deutschland)

(Eingegangen den 23. April, 1965)

Der spektrofotometrische Nachweis von Spurenelementen wird in den meisten Fällen durch die Anwesenheit des Hauptbestandteiles gestört. Oft kann dieser Einfluss durch eine entsprechende Verdünnung ausgeschaltet werden. Das geschieht jedoch auf Kosten der Empfindlichkeit der Bestimmung. Deshalb ist vielfach vor der eigentlichen Messung eine Abreicherung der Matrix bzw. eine Anreicherung der Spuren erforderlich.

Dies trifft auch für die spektrofotometrische Calciumbestimmung mit Cresolphthalexon in Lithiumsalzen zu: in konzentrierten Lösungen verhindert der hohe Lithiumgehalt die Bildung des gefärbten Komplexes, während bei Verdünnung die Nachweisgrenze für Calcium unterschritten wird.

Sehr elegant sind in solchen Fällen Analysenmethoden, die Nachweis und Konzentrierung der Spur bzw. Abtrennung des Hauptbestandteiles in einem Schritt vereinen, wie dies z.B. bei extraktions-fotometrischen Verfahren geschieht. Calciumionen bilden mit 8-Oxychinolin einen Komplex, der in Gegenwart von Butylamin extrahiert werden kann und sich gleichzeitig zur spektrofotometrischen Messung eignet. Wie eigene Versuche ergaben, nimmt jedoch das Verteilungsverhältnis von Calcium mit sinkender Calciumkonzentration und steigendem Lithiumgehalt der Lösung stark ab, was eine Anwendung bei geringen Calciummengen ausschliesst[1].

Es wurde deshalb versucht, das Calcium vor seiner spektrofotometrischen Bestimmung vom Lithiumchlorid abzutrennen. Dies kann unter gleichen Bedingungen mit dem bereits zur Isolierung von Magnesium- und Aluminiumspuren beschriebenen Ionenaustauschverfahren unter Verwendung eines stark sauren Kationenaustauschers (Wofatit KPS) geschehen[2]. Nachteilig, vor allem bei geringen Calciumgehalten und für eine weitere Verwendung des gleichzeitig gereinigten Lithiumsalzes, wirkt sich die zur Chromatografie erforderliche starke Verdünnung des Analysenmaterials aus. Aus diesem Grunde wurde versucht, unter Benutzung eines anderen Kationenaustauschers die gleichen Trennfaktoren ($\beta_{Ca/Li}$) bei höheren Salzkonzentrationen zu erreichen. Hierzu eignen sich schwach saure Austauscher mit Carboxylgruppen, die eine hohe Affinität gegenüber zwei- und mehrwertigen Ionen besitzen.

EXPERIMENTELLES

Ionenaustausch

Die Untersuchungen wurden mit dem schwach sauren Kationenaustauscher

Wofatit CP durchgeführt. Das Harz hatte einen Korndurchmesser von 0.2–0.3 mm und wurde in der Li^+-Form eingesetzt, da in der H^+-Form auch aus neutralen Lösungen kein Austausch erfolgt. Die Arbeitstemperatur betrug *ca.* 25°. Die benutzten Lösungen reagierten neutral (pH 5–7).

Zur Bestimmung von Verteilungsverhältnissen aus Gleichgewichtsversuchen wurden 0.1 g lufttrockenes Harz mit 2 ml wässriger Lösung verschiedener LiCl-Konzentration 2 Stunden geschüttelt und anschliessend die Verteilung des in Spuren zugesetzten Kations zwischen den beiden Phasen bestimmt: Natrium, Cäsium und Calcium radiometrisch unter Verwendung der Isotope ^{22}Na, ^{137}Cs und ^{45}Ca; Lithium, Magnesium und Aluminium spektrofotometrisch nach bekannten Methoden[3].

Die für Elutionsversuche benutzten Säulen hatten einen Durchmesser von 0.5 bzw. 1.0 cm bei 10 cm Länge. Die entsprechenden Harzeinwaagen betrugen 0.4 bzw. 2.0 g Wofatit CP. Es wurde mit einer Flussrate von 1 ml/cm^2 min eluiert.

Spektrofotometrie

Cresolphthalexon (*o*-Cresolphthalein-α,α'-di(imino)diessigsäure) bildet im schwach alkalischen Medium mit Calciumionen einen violett gefärbten Komplex, der zur quantitativen Calciumbestimmung geeignet ist[4]. Zu diesem Zweck wurde die neutrale Probelösung in einen 10-ml Masskolben überführt, 2.5 ml Pufferlösung und 1 ml der Reagenzlösung zugesetzt, mit Wasser bis zur Marke aufgefüllt und die Extinktion in 1-cm Küvetten mit einem lichtelektrischen Spektrofotometer (UVISPEK, Hilger & Watts, London) bei 567 mμ gemessen. Die gleiche Lösung ohne Calciumionen diente als Blindlösung.

Die Pufferlösung hatte den pH 10.15 und wurde durch Lösen von 0.75 g NH_4Cl zu 100 ml mit verdünntem Ammoniak hergestellt. Als Reagenzlösung wurde eine 0.03%ige Lösung von Cresolphthalexon in einem Puffer/Wasser-Gemisch (28 Teile Puffer, 72 Teile Wasser) verwendet.

ERGEBNISSE

Ionenaustausch

Zur Auswahl günstiger Elutionsbedingungen für die Trennung ist die Kenntnis der Verteilungsverhältnisse (K_D) entscheidend. In Fig. 1 sind die K_D-Werte von Calcium und einigen anderen in diesem Zusammenhang interessierenden Kationen, wie sie aus Gleichgewichtsversuchen zwischen Wofatit CP und einer wässrigen Lösung erhalten wurden, in Abhängigkeit von der LiCl-Konzentration dargestellt. Drei aus Elutionsversuchen ermittelte Werte für Calcium stimmen mit diesen gut überein.

Während zwischen den Alkalimetallen nur ein sehr geringer Unterschied in den Verteilungsverhältnissen besteht, tritt ein grosser Sprung zwischen den ein- und mehrwertigen Kationen auf. Wie die Darstellung der Trennfaktoren $\beta_{Ca/Li}$ in Abhängigkeit von der LiCl-Konzentration für die beiden Harze Wofatit KPS und Wofatit CP in Fig. 2 zeigt, erhält man für Wofatit CP neben wesentlich höheren Werten auch einen geringeren Einfluss der LiCl-Konzentration, so dass sich dieser Austauscher besonders zur Abtrennung mehrwertiger Kationen aus konzentrierten Lösungen der Alkalihalogenide eignet.

Für die chromatografische Abtrennung der mehrwertigen Elemente aus 1 g Lithium erhält man bei Einsatz einer 1–2 *M* LiCl-Lösung ein günstiges Verhältnis von

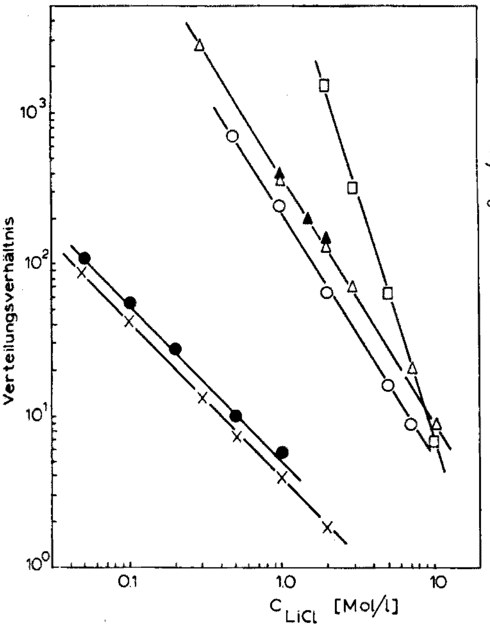

Fig. 1. Verteilungsverhältnisse zwischen Wofatit CP und wässriger Lösung in Abhängigkeit von der LiCl-Konzentration. × Na, ● Cs, ○ Mg, △ Ca (▲ Elutionsversuche), □ Al.

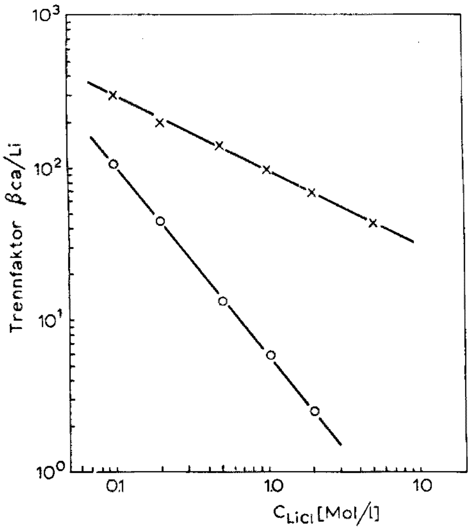

Fig. 2. Trennfaktoren $\beta_{Ca/Li}$ in Abhängigkeit von der LiCl-Konzentration bei Wofatit KPS und Wofatit CP. ○ Wofatit KPS, × Wofatit CP.

Harz- und Flüssigkeitsvolumen. Höhere LiCl-Konzentrationen erfordern grössere Harzeinwaagen und für verdünntere Lösungen ergeben sich wesentlich längere Versuchszeiten. Bei einer Säuleneinfüllung von 2 g Harz und einem Verteilungsverhältnis $K_{D(Ca)} = 300$ ergibt sich nach:

$$K_D = (V - V_0)/m$$

(V = Flüssigkeitsvolumen bis zur Elution des Peakmaximums, V_0 = freies Säulenvolumen, m = Harzeinwaage)
bis zur Elution des Peakmaximums ein Volumen von 600 ml. D.h. bei Verwendung solch einer Säule werden die Calciumionen aus 100 ml einer 1.44 M LiCl-Lösung (entspricht einer Lithiummenge von 1 g) sicher zurückgehalten. Modellversuche unter Zusatz von ^{45}Ca bestätigten dies und ergaben Calciumausbeute über 99% (siehe Fig. 3).

Die Elution des Calciums von der Säule kann mit verdünnter Säure durchgeführt werden. Dabei werden alle eingetauschten Elemente durch Wasserstoffionen ersetzt. Während zunächst das eingetauschte Lithium eluiert wird, erscheinen anschliessend die Calciumionen im Ausfluss. Es findet eine Verdrängungschromatografie statt und ein Überschneiden der einzelnen Fraktionen lässt sich nicht vermeiden.

Zur vollständigen Elution benötigt man eine Säuremenge, die unabhängig von ihrer Konzentration nur wenig über der Kapazität des Harzes liegt. So werden z.B. bei einer Kapazität der Säule von 4 mVal zur Elution 22 ml einer 0.2 N HCl, d.h. 4.4 mVal Säure gebraucht.

Um die Calciumionen und andere mehrwertige Spurenelemente quantitativ von

Lithium zu trennen, ist ein anderes Elutionsmittel erforderlich. Seine Affinität zum Austauscher muss zwischen der von Lithium und Calcium liegen. Das ist bei Ammoniumchlorid der Fall, welches stärker als Lithium und schwächer als Calcium absorbiert wird.

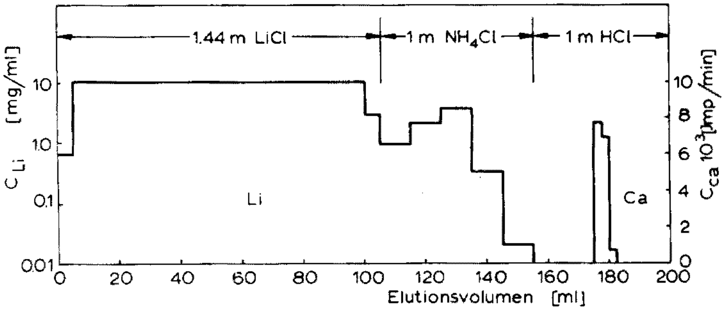

Fig. 3. Modelltrennung von Calcium und Lithium. Säule: 2 g Wofatit CP in der Li^+-Form; Speiselösung: 1.44 M LiCl und $7.7 \cdot 10^{-5}$ M $CaCl_2$.

Die aus Gleichgewichtsversuchen ermittelten Verteilungsverhältnisse betragen in Gegenwart einer 1 M NH_4Cl-Lösung $K_{D(Ca)} = 200$ und $K_{D(Li)} = 2$, so dass bei Übergabe der Lösung zunächst nur Lithium verdrängt wird. Die Elution des Calciums erfolgt anschliessend mit verdünnter Salzsäure.

Vom Ammoniumchlorid kann die Calciumfraktion durch Abrauchen befreit werden. Versuche mit ^{45}Ca und Trägermengen von 0.1–10 mg Calcium ergaben Verluste unter 1% Calcium.

Spektrofotometrie

Die Eichkurve verläuft unter den angegebenen Bedingungen bis zu einem Gehalt von über 15 μg Ca/Probe linear. Die Empfindlichkeit ergab sich für log $I_0/I = 0.001$ zu 0.002 μg Ca/cm² ($E_{molar} = 19.300$ l/Mol cm).

Die Reagenzlösung ist nur wenige Tage beständig. Bereits 3 Tage nach ihrer Herstellung tritt bei der Benutzung eine merkliche Erniedrigung der gemessenen Extinktionswerte ein, und zwar unabhängig vom Calciumgehalt. Die Extinktion des gefärbten Komplexes wurde über eine Zeit von 6 Stunden verfolgt, wobei keine merkliche Änderung der Messwerte nachzuweisen war.

Als Standardabweichung beim Nachweis von 3 μg Calcium ergab sich aus 10 Proben ein Wert von ±0.10 μg Calcium, das entspricht einer Varianz von 3.3%.

Die Nachweisgrenze (x_{Ca}) ergibt sich aus der Standardabweichung (s_{Ca}) der Blindlösung[5]. Zu ihrer Bestimmung wurde die Extinktion von 10 Blindlösungen gegen Wasser gemessen. Aus der gefundenen Standardabweichung von ±0.07 μg Calcium ergibt sich nach:

$$x_{Ca} = 3\sqrt{2}\, s_{Ca}$$

für die Nachweisgrenze ein Wert von 0.3 μg Ca/Probe.

Die Gegenwart anderer Ionen hat einen unterschiedlichen Einfluss auf die Calciumbestimmung. So ergaben sich für 3 μg Calcium bei Anwesenheit verschiedener

Mengen Li^+-, Mg^{2+}-, Al^{3+}- bzw. Fe^{3+}-Ionen die in Fig. 4 dargestellten Abweichungen auf die Extinktion. Während Mengen unter 10 µg Aluminium und Eisen noch keine Änderung bewirken, verfälscht bereits 1 µg Magnesium das Resultat. Sie lassen sich jedoch bis zu Mengen von 5 µg Magnesium kompensieren, wenn in Probe und Blindlösung gleiche Magnesiumgehalte vorliegen. Lithium stört den Nachweis über 0.5 mg Li/Probe. Durch Zugabe zur Blindlösung lassen sich noch Gehalte bis zu 5 mg Lithium kompensieren. Grössere Mengen müssen zuvor abgetrennt werden.

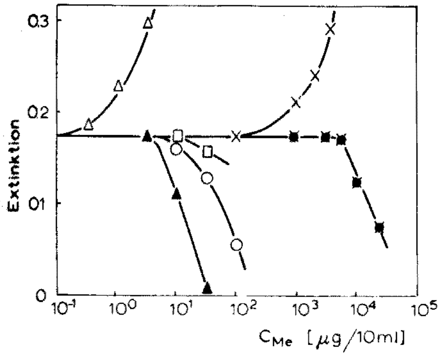

Fig. 4. Einfluss verschiedener Kationen auf die Extinktion des Komplexes Calcium–Cresolphthalexon. × Li, ✖ Li kompensiert, △ Mg, ▲ Mg kompensiert, ○ Al, □ Fe.

VORSCHRIFT

Die 1 g Lithium entsprechende Menge eines Lithiumsalzes wird mit Wasser zu einem Volumen von 100 ml gelöst, wobei die Lösung neutral reagieren soll. Diese Lösung lässt man über eine mit 2 g Wofatit CP (Li^+-Form) gefüllte Säule fliessen und wäscht mit 5 ml Wasser nach. Dann verdrängt man mit 50 ml einer 1 *M* NH_4Cl-Lösung die eingetauschten Lithiumionen, wäscht wiederum mit 5 ml Wasser und eluiert das Calcium mit 10 ml einer 1 *N* HCl. Nach dem Abrauchen des Ammoniumchlorids kann das Calcium spektrofotometrisch mit Cresolphthalexon bestimmt werden. Unter diesen Bedingungen lassen sich noch 10^{-4}% Calcium nachweisen. Bei höheren Calciumgehalten kann man von entsprechend niedrigeren Lithiumeinwaagen ausgehen und kleinere Säulen zur Abtrennung benutzen.

ANALYSEN

Das Ergebnis einer nach dieser Vorschrift durchgeführten Modelltrennung mit gereinigtem Lithiumchlorid (unter 10^{-4}% Ca) als Ausgangsmaterial und Zusatz von 4 µCi ^{45}Ca (spezifische Aktivität 0.15 g Ca/mCi) ist in Fig. 3 dargestellt. Während der Übergabe der 100 ml 1.44 *M* LiCl-Lösung herrscht im Eluat die gleiche Lithiumkonzentration wie in der Speiselösung. Sie sinkt beim Waschen mit 1 *M* NH_4Cl-Lösung bis auf Gehalte unter 0.05 mg Li/ml ab. In diesen Fraktionen war keine Ca-Aktivität nachzuweisen. Bei einer Ausgangsaktivität von 10,000 Imp./min ^{45}Ca/ml wurde also ein Abreicherungsfaktor von über $2 \cdot 10^3$ erreicht.

Anschliessend wurde das Calcium mit 1 *N* Salzsäure als schmaler Peak eluiert. Die Calciumausbeute betrug 99% und kann als quantitativ angesehen werden. Es gelang also eine Trennung von Calcium und Lithium bei einem Molverhältnis von 10^4.

Als Beispiel für die Anwendung der beschriebenen Methode soll das Ergebnis der Analyse eines LiCl-Präparates ("reinst", VEB Fluorwerke Dohna) angeführt werden (Tabelle I). Ausser dem Calciumgehalt sind zum Vergleich die nach anderen Vorschriften spektrofotometrisch bestimmten Gehalte an Magnesium und Aluminium mit Titangelb bzw. Alizarin S[2], Eisen mit Phenanthrolin[3], Mangan als Permanganat nach Mitfällung an Eisenhydroxid[3] und der Summe der Schwermetalle als Kupfer mit Diäthyldithiocarbamat[6] angegeben. Während die Konzentration der meisten Verunreinigungen im p.p.m.-Bereich liegt, wird für Calcium ein relativ hoher Gehalt von 0.2% gefunden.

Da die meisten Anionen das Verteilungsverhältnis des Calciums nur unwesentlich beeinflussen, können auch Salze mit anderen Anionen analysiert werden. So wurden z.B. beim Einsatz von Lithiumhydroxid besonders günstige Werte erhalten. Aufgrund der wenig unterschiedlichen Verteilungsverhältnisse kann man die beschriebene Methode ebenfalls zur Bestimmung des Calciums in anderen Alkalimetallen anwenden.

TABELLE I

SPEKTROFOTOMETRISCH BESTIMMTE VERUNREINIGUNGEN IN LITHIUMCHLORID

(Angaben in Gewichtsprozent; M = Mittelwert mit Standardabweichung)

Nr.	*Ca* *(%)*	*Mg* · 10^3 *(%)*	*Al* · 10^3 *(%)*
1	0.183	0.96	1.50
2	0.180	1.08	1.60
3	0.179	0.91	1.05
4	0.174	1.10	1.65
5	0.183	1.08	1.05
M	(0.180 ± 0.002)%	(1.03 ± 0.04) · 10^{-3}%	(1.37 ± 0.13) · 10^{-3}%

Nr.	*Fe* · 10^4 *(%)*	*Mn* · 10^4 *(%)*	*Me*[a] · 10^3 *(%)*
1	2.73	1.34	2.64
2	2.78	1.54	2.68
3	2.84	1.73	3.01
4	2.78	1.40	2.97
5	3.01	1.77	2.86
M	(2.83 ± 0.05) · 10^{-4}%	(1.56 ± 0.09) · 10^{-4}%	(2.86 ± 0.06) · 10^{-3}%

[a] Summe der Schwermetalle als Kupfer, ohne Eisen und Mangan.

ZUSAMMENFASSUNG

Calcium wurde aus 1–2 *M* LiCl-Lösung mit Hilfe des schwach sauren Kationenaustauschers Wofatit CP abgetrennt. Die quantitative Trennung von Calcium und Lithium gelang durch Waschen der Säule mit 1 *M* NH$_4$Cl-Lösung. Nach Elution des Calciums mit verdünnter Salzsäure wurde das Ammoniumchlorid abgeraucht. Der Rückstand wurde aufgenommen und nach Zugabe von Pufferlösung und Cresolphthalexon die Extinktion bei 567 mμ gemessen. Die Empfindlichkeit betrug 0.002 μg

Ca/cm^2, die Nachweisgrenze bei Einsatz von 1 g Lithium $10^{-4}\%$ Calcium. Die Eichkurve verlief bis über 15 μg Ca linear.

SUMMARY

Calcium was separated from 1–2 *M* solutions of lithium chloride by means of Wofatit CP cation exchanger. Calcium was quantitatively separated from lithium by elution with 1 *M* ammonium chloride. Calcium was eluted with hydrochloric acid and, eventually, measured spectrophotometrically at 567 mμ after addition of buffer and cresolphthalexone. The sensitivity was found to be 0.002 μg Ca/cm^2 and Beer's law was obeyed up to 15 μg Ca. With 1 g of lithium, the limit of determination was $10^{-4}\%$ Ca.

RÉSUMÉ

L'auteur propose une méthode de séparation du calcium d'avec le lithium, au moyen de Wofatite CP comme échangeur de cations. Le calcium est séparé quantitativement par élution avec NH_4Cl 1 *M*, puis élué à l'aide d'acide chlorhydrique. Il peut finalement être dosé spectrophotométriquement à 567 mμ, après addition d'un tampon et de crésolphtalexone. Sensibilité 0.002 μg Ca/cm^2; la loi de Beer s'applique jusqu'à 15 μg Ca. Limite d'identification: $10^{-4}\%$ de calcium en présence d'un gramme de lithium.

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GRAVIMETRIC DETERMINATION OF ZIRCONIUM WITH A NEW AZOPYRAZOLONE DERIVATIVE

G. POPA, G. BAIULESCU, C. GREFF AND S. MOLDOVEANU
Laboratory of Analytical Chemistry, Faculty of Science, University of Bucharest, Bucharest (Rumania

(Received April 12th, 1965)

The successful use of some azopyrazolone derivatives such as tartrazine[1] and flavazine L[2] in the determination of zirconium(IV) by precipitation and ignition to the oxide or by direct weighing of the precipitate[1,3,4] suggested that an examination of the use of some analogous compounds in the determination of zirconium(IV) might be profitable. Of various compounds tested, the disodium salt of 3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-ylazo-2'-(6',8'-naphthalenedisulfonic acid) obtained by the coupling of 3-methyl-1-phenyl-5-pyrazolone with diazotized 2-amino-6,8-naphthalenedisulfonic acid (amino-G acid) was found to be a good precipitation reagent for zirconium(IV).

The new compound is less selective than G-acid[5], but the precipitate is of definite composition and can be weighed directly.

EXPERIMENTAL

Reagents and apparatus

Zirconium(IV) solution. The solution contained 2.02 mg Zr/ml, obtained by dissolving $ZrO(NO_3)_2 \cdot 2H_2O$ in 1% (v/v) nitric acid.

Precipitation reagent. The disodium salt of 3-methyl-5-oxo-1-phenyl-2-pyrazolin-4-ylazo-2'-(6',8'-naphthalenedisulfonic acid) was synthesized as follows: 16.25 g of the monosodium salt of amino-G acid was dissolved in a solution of 2.65 g of anhydrous sodium carbonate in 100 ml of water; 3.7 g of sodium nitrite was added to the solution. The mixture was slowly poured into a beaker containing 15 ml of concentrated hydrochloric acid and 60 g of crushed ice. After 15 min, the free nitrous acid was removed with a concentrated urea solution and then 8.7 g of 3-methyl-1-phenyl-5-pyrazolone dissolved in a cooled solution of 2.2 g of sodium hydroxide in 50 ml of water was added. The mixture was set aside for 1 h with occasional stirring and then heated to 90°; 6 g of anhydrous sodium carbonate was added and the solution was saturated with sodium chloride. The precipitate was twice recrystallized from a water–dioxane mixture and then washed with cold ethanol and ether. The yield after recrystallization was 70%.

For precipitation an aqueous 1% solution of the reagent was used. The thermograms were recorded on an Erdey derivatograph MOM (Metrimpex, Budapest) with a heating speed of 10° per min.

Procedure

A sample containing 2.5–20 mg of zirconium(IV) was diluted with water to *ca.* 50 ml and heated to *ca.* 60°, after the pH of the mixture had been adjusted to 1–1.5. An excess of the reagent solution was then added and the obtained precipitate was left to deposit.

The solution could be filtered through filter paper and the precipitate ignited to ZrO_2 but it was preferable to filter through a G4 crucible. The precipitate was then washed with water until the filtrate became light yellow and dried at 105°; alternatively, it was washed with propanone and ether and dried *in vacuo*.

RESULTS AND DISCUSSION

Effect of pH on precipitation

For this study, zirconium(IV) was precipitated at different acidities and the samples were ignited to ZrO_2. The results (Table I) indicated that the precipitation was quantitative when the pH was greater than 0.6.

TABLE I

EFFECT OF pH ON PRECIPITATION

(Zr present 0.0202 g)

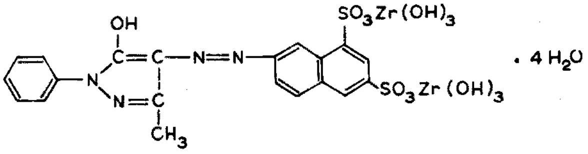
Sample no.	*Weighed ZrO_2 (g)*	*Zr found (g)*	*Difference (g)*	*HCl concn. (N)*	*pH*
1	0.0272	0.0201^{4}	-0.0000^{6}	—	1.6
2	0.0275	0.0203^{5}	$+0.0001^{5}$	—	1.3
3	0.0270	0.0199^{9}	-0.0001^{1}	0.25	0.6
4	0.0260	0.0197^{5}	-0.0004^{5}	0.5	0.3
5	0.0242	0.0179^{2}	-0.0022^{8}	1	—
6	0.0068	0.0050^{3}	-0.0151^{7}	2	—

Study of selectivity

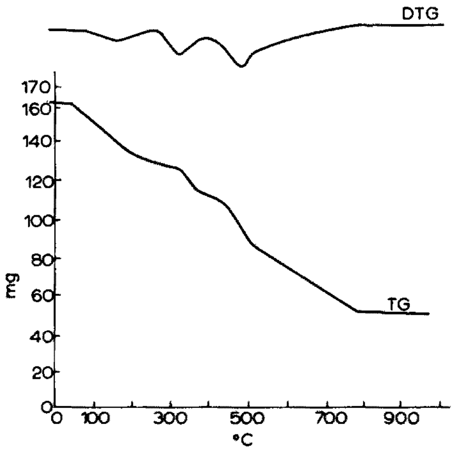
Qualitative tests were made with 45 ions and it was observed that the following ions did not precipitate at pH 1: Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Cu^{2+}, Ag^+, Au^{3+}, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Sc^{3+}, Y^{3+}, La^{3+}, Ce^{4+}, Al^{3+}, Ga^{3+}, In^{3+}, Tl^+, Ti^{4+}, GeO_3^{2-}, Sn^{2+}, Pb^{2+}, VO_3^-, Cr^{3+}, MoO_4^{2-}, WO_4^{2-}, UO_2^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Pt^{4+}. Mercury(I) formed a yellow precipitate soluble in nitric acid. Thorium(IV) and bismuth(III) formed yellow precipitates soluble in dilute nitric acid. Hafnium gave a yellow precipitate in the same way as zirconium. Barium gave a yellow precipitate soluble in warm water, whereas palladium(II) formed only a brown colour. Fluoride, sulfate, citrate, tartrate and oxalate ions masked the reaction.

Direct weighing of the precipitate

Thermogravimetric analyses were carried out on precipitates washed with propanone and ether and dried *in vacuo*. The thermogram (Fig. 1) showed that the compound contained 6 molecules of water. The experimental conversion factor was found to be 0.2164, corresponding to a molecular weight of 843.03. The probable formula of the compound is therefore:



It is obvious from these results that the precipitate could be utilized for the determination of zirconium(IV) by direct weighing of the precipitate after being washed with propanone and ether and dried *in vacuo.*



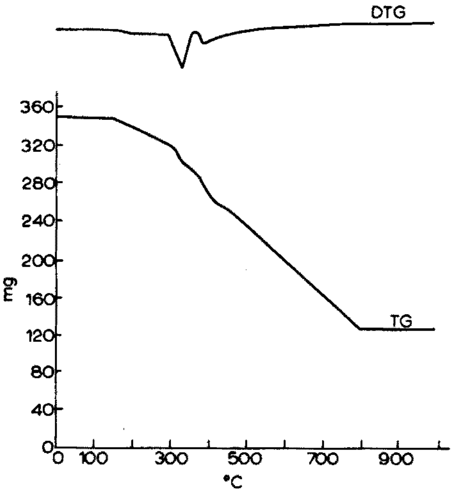


Fig. 1. Thermogram of the precipitate washed with propanone and ether.

Fig. 2. Thermogram of the precipitate dried at 105°.

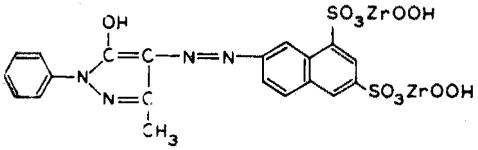
TABLE II

DETERMINATION OF ZIRCONIUM BY DIRECT WEIGHING OF THE HEXAHYDRATE

Sample no.	*Zr present (mg)*	*Weight of precipitate (mg)*	*Zr found (mg)*	*Difference (mg)*
1	5.0^{5}	23.8	5.1^{5}	+0.1
2	5.0^{5}	23.2	5.0^{2}	-0.0^{3}
3	10.1	47.0	10.1^{7}	$+0.0^{7}$
4	10.1	46.4	10.0^{4}	-0.0^{6}
5	15.1^{5}	70.5	15.2^{6}	$+0.1^{1}$
6	15.1^{5}	70.7	15.3	$+0.1^{5}$
7	20.2	94.0	20.3^{4}	$+0.1^{4}$
8	20.2	93.0	20.1^{3}	-0.0^{7}

The results obtained for a number of samples with various zirconium contents are given in Table II.

When the compound is heated at 105° for 1 h, it loses 6 molecules of water, probably changing into:



A thermogram of the compound washed with water and dried at 105° showed that the compound was thermally stable up to 150° (Fig. 2). This made possible the direct weighing of the precipitate washed with water and dried at 105° for the gravimetric determination of zirconium. Results obtained in this way in a number of samples with zirconium contents of 2.5 to 20 mg are given in Table III. The compound dried at 105° very slowly regained 4 molecules of water but this had no deleterious effect on the gravimetric application. The increase in weight of 0.3493 g of compound dried at 105° plotted against time is given in Fig. 3. The increase in weight in the first hour was only *ca.* 0.2%.

TABLE III

DETERMINATION OF ZIRCONIUM BY DIRECT WEIGHING OF THE ANHYDROUS SALT

Sample no.	*Zr present (mg)*	*Weight of precipitate (mg)*	*Zr found (mg)*	*Difference (mg)*
1	2.5^{3}	10.5	2.6^{1}	$+0.0^{8}$
2	2.5^{3}	10.2	2.5^{3}	—
3	5.0^{5}	20.6	5.2^{0}	$+0.1^{5}$
4	10.1	41.1	10.2^{0}	$+0.1^{0}$
5	10.1	40.8	10.1^{3}	$+0.0^{3}$
6	15.1^{5}	60.9	15.1^{2}	-0.0^{5}
7	20.2	81.0	20.1^{0}	-0.1^{0}
8	20.2	81.2	20.1^{5}	-0.0^{5}

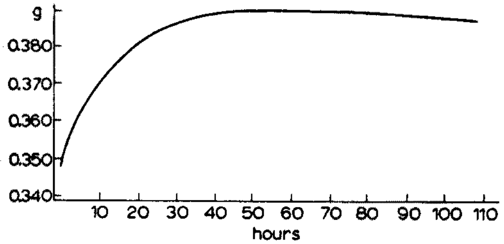


Fig. 3. Slow increase of weight of dried precipitate.

CONCLUSIONS

The new gravimetric reagent for zirconium(IV) allows the direct weighing of the precipitate, either after washing with propanone and ether and drying *in vacuo*, or after washing with water and drying at 105°. The reagent is quite selective, though less so than the G-acid previously recommended[5]; with the latter reagent only titanium and hafnium interfered. However, the precipitate formed with G-acid cannot be weighed directly because it is not of constant, well-defined composition, and, since titanium frequently occurs together with zirconium, the use of the new reagent seems preferable on all grounds.

The method is also faster and simpler than that with mandelic acid[6], *p*-chloromandelic acid or *p*-bromomandelic acid[7,8].

The authors express their grateful thanks to E. SEGAL and D. FATU for experimental assistance.

SUMMARY

3-Methyl-5-oxo-1-phenyl-2-pyrazolin-4-ylazo-2′-(6′,8′-naphthalenedisulfonic acid) (disodium salt) is proposed as a new reagent for the gravimetric determination of zirconium. The precipitate formed at pH 1–1.5 can be weighed directly and there are few interferences.

RÉSUMÉ

Un nouveau dérivé de l'azopyrazolone est proposé pour le dosage gravimétrique du zirconium. Le précipité formé au pH 1–1.5 peut être pesé directement. On observe peu d'interférences.

ZUSAMMENFASSUNG

Es wird ein neues Derivat des Azopyrazolons als gravimetrisches Reagenz für die Bestimmung von Zirkonium vorgeschlagen. Der beim pH-Wert 1–1.5 gebildete Niederschlag kann direkt gewogen werden. Es treten wenig Störungen auf.

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GAS CHROMATOGRAPHIC FRACTIONATION AS A SUPPLEMENT AND REPLACEMENT FOR LABORATORY DISTILLATION

A. B. CAREL AND GERALD PERKINS, JR.
Research and Development Department, Continental Oil Company, Ponca City, Okla. (U.S.A.)

(Received May 21st, 1965)

Gas chromatography is recognized primarily as a method of analysis. Its analytical capabilities have satisfied a universal need and have been universally applied. Its application to practical large-scale fractionation, on the other hand, has lagged. This is not to imply that its promise as a method of separation has been overlooked. Everyone is aware that the area of "preparative gas chromatography" is quite active. But requirements for separation and purification are, in most cases, more narrowly limited than analytical needs and much of the work in applied preparative chromatography has led to instruments designed for special purposes. Biochemists are often happy with the preparation of milligram quantities of material from very small complex samples. Organic chemists would sometimes welcome liter quantities of highly pure reagents. Some industries are hoping to obtain commercial quantities of specialized products economically by gas chromatography. Behind this diversity of desires stands the unifying concept of *recovering* one or more purified components of a sample by means of gas chromatography, but techniques and instruments usually diverge accordingly as desires for the quantity of product and as the availability and cost of sample vary. Generally, one or more of the qualities of high resolution, large throughput, economy and convenience are sacrificed in order to enhance the others.

A distillation facility designed to provide service for a research and development laboratory meets such a variety of assignments that it routinely encounters small and large, simple and complex samples from which must be prepared small or large, moderately or highly pure fractions of major or minor components and always as rapidly and cheaply as possible. For chromatographic fractionation to prove routinely useful requires an instrument which can provide great versatility with a minimum of trouble and expense. The following account describes the design and application of a suitable instrument and the emergence of a new dimension in large-scale laboratory fractionation.

EXPERIMENTAL

Apparatus

Figures 1a and b show a block diagram of the complete apparatus and a photograph of the operating assembly. The overall design follows conventional patterns and only certain details need explanation.

The injection devices are not essentially novel but consist merely of pressurized

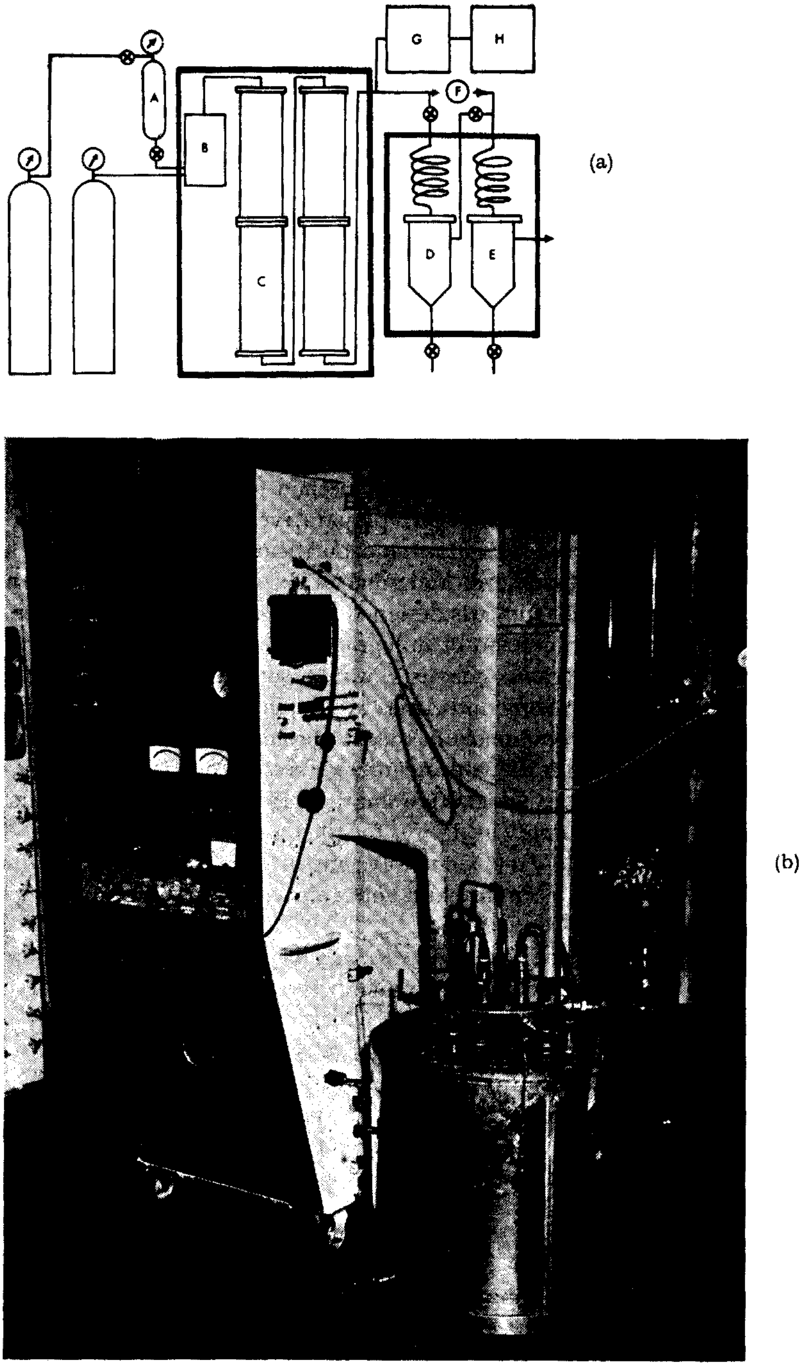
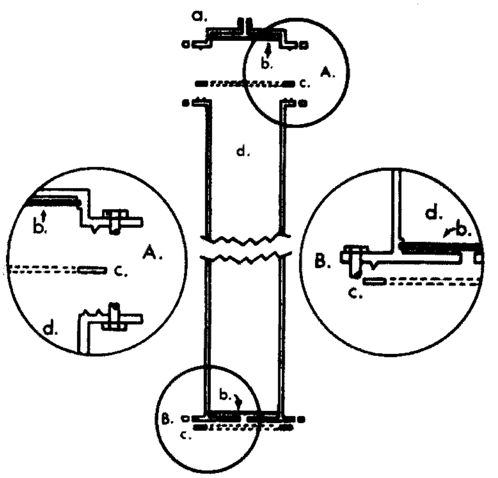


Fig. 1. Preparative chromatograph. (a) Block diagram of apparatus: A, sample injector; B, vaporizer; C, column section; D, component trap; E, scrubber trap; F, position of trap manifold; G, detector; H, recorder. Heavy lines indicate column oven and trap cooling-bath. (b) Assembled apparatus.

chambers of various volumes. For convenience they can be built to provide any of a number of standard methods of charging and discharging a desired volume in any given time. The chambers may be quickly and conveniently exchanged by means of standard fittings and may be replaced by a septum for conventional syringe injection. Single-injection sample volumes normally range from 1 ml to about 200 ml, although amounts greater and less has been used in special cases. The rate of injection may vary from instantaneous syringe injections of small samples to about 100 ml/min for the large samples.

The sample vaporizer currently employed is also not novel but simply heats the incoming carrier gas and injected sample as is usually done in gas chromatographs by a process which may be accurately described as "by brute force". The vaporizer design can and should be improved and this is discussed presently.

The columns* were developed in our laboratory and were designed to give good resolution for extremely large samples. This allows the use of short column lengths in most applications, with a correspondingly short in-column residence time. The most recent design of column and appurtenances is now being built and marketed by F & M Scientific Corporation (Avondale, Pennsylvania) and a complete description is available in their advertising literature. For the work reported in this paper, that portion of the column which contains the packing and which requires the ordinary handling and manipulation associated with columns was constructed as shown in Fig. 2. The usual section was 4 in. in diameter and about 2 ft. long. At times a 6-in. diameter was employed and these sections were about 18 in. in length. Essentially, the section consists of an unrestricted length of stainless steel tubing closed near the bottom by a porous, stainless steel disc which supports the packing, and an offset stainless steel end plate, which completes the gas-tight enclosure of the end



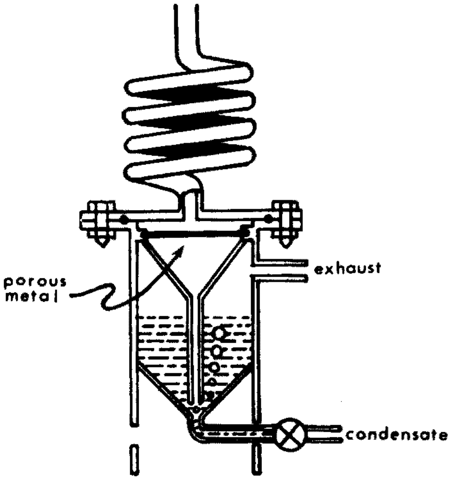


Fig. 2. Design of preparative column section. (a) column diffuser head; (b) porous metal plates; (c) aluminum gasket; (d) packing chamber. Inserts A and B are enlarged to show details of gasket seal and mixing chamber.

Fig. 3. Design of large traps.

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* Patents applied for.

and which is pierced by a central exhaust orifice. This arrangement incidentally produces a very thin mixing chamber at the section terminus. The top and bottom of the section are equipped with grooved flanges about the circumference so that other sections, or covers, or the intake and exhaust chambers may be attached by bolting the flanges together with a thin aluminum gasket pressed between. Such connections are leakproof at temperatures and pressures in excess of 250° and 120 psig, respectively. When sections are stacked vertically they are simply bolted together. When vertical stacks are placed side by side, a circular cover plate equipped with centrally located, threaded fittings is attached to the top of one stack and connected with a length of small-diameter tubing to the bottom of the preceding stack. This cover plate is similar to the one placed at the head of the column and also contains a porous metal plate. Its construction is shown in Fig. 2.

Trap design is of considerable importance since an extraordinary range of sample volumes must be accommodated. The large samples lend themselves to recovery of trace components and so, even within one sample, component volumes may vary over quite a wide range. Small component volumes are not accompanied by a corresponding decrease in carrier gas volume and, as a consequence, small traps are doubly inadequate. A type of trap* which seems to give excellent recoveries is shown in Fig. 3. Several modifications are useful. Essentially, the trap provides a large condensing surface of reasonably good thermal conductivity. This surface can be maintained at any chosen temperature by means of an external bath. Usually the temperature is best kept significantly above the components' freezing point so that the combination of moderate temperature gradient and low gas velocity very effectively precipitates the condensed material from the vapor phase. These features are realized through the use of metal surfaces throughout, high surface area being obtained with the use of porous stainless steel plates. Finally, the bottom of the trap is tapered sharply to collect even very small volumes. When the volume is so small that an inordinate percentage is held up in the porous steel, this member is rinsed with some low boiling liquid which may be readily separated from the recovered product. The rinse is done by injecting the liquid into the unit and recovering it in the trap.

The traps are arranged along a manifold, circular in the design shown in the photograph of Fig. 1, with a suitable valving arrangement. Depending upon the degree of convenience desired and the acceptable level of expense, the valving may vary from completely manual to completely automatic. The final effluent at all times passes through a last trap which removes any condensable material which has escaped prior traps or which has been intentionally bypassed around the other traps. A back-pressure regulator is provided at the flow terminus and is indispensable for providing proper flow to the detectors.

Two detectors were provided. Nitrogen is commonly employed as the carrier gas and is not recirculated. Other inexpensive carrier gases may also be used. At times, anomalous thermal conductivity signals result from the use of nitrogen and, at these times, the proper choice of cut point may be difficult to determine from an inspection of the recorder trace. With experience this is seldom true but, to avoid delay with unfamiliar samples or with inexperienced operators, both a hydrogen

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* Patents applied for.

flame ionization detector and a thermal conductivity detector were included in the design. The sample input to the detectors is taken via capillary line from the main stream flow at a point between the column exit and the trap manifold. The incorporation of these detectors involves no novel feature and will not be described.

As indicated in Fig. 1, the columns and associated plumbing are enclosed within an oven. This oven is heated by a current of air, drawn from the oven head space by two squirrel-cage blowers, discharged at 700 cu. ft./min behind a baffle and across two 3000-W Nichrome-ribbon heaters and then circulated to the bottom of the column chamber. The columns are supported in a vertical position on a steel rack; 4-ft. vertical sections, consisting of two 2-ft. units, are mounted side by side when greater length is desired. The oven will accommodate 30 ft. of 4-in. column or 16 ft. of 6-in. column. The oven has interior dimensions of approximately 1.5 × 5.0 × 3.0 ft. and the column chamber is about 1.5 × 5.0 × 1.75 ft. Manual programming is possible but has not been found necessary.

Materials and operation

The instrument was designed to give maximum resolution, throughput, recovery and convenience of operation with minimum cost, insofar as our current knowledge was capable. Resolution and capacity will be considered further in the discussion. Let it suffice to say here that, without overload, HETP values as low as 1.5 mm may be calculated from the detector trace. This is not the most basic criterion for performance, however, since the passage of material through the detector does not necessarily occurs in the same manner as the passage of components from column to trap. It happens that the detector signal more nearly reflects the history of the sample in its route along the capillary connection to the mainstream. The design of this line, its placement and the pressure maintained at its head all have a marked influence on the final chromatogram. Thus, the quantity and purity of recovered product must be the basic test of efficiency and the chromatogram should merely serve as a guide for making adjustments and choosing cut points. Purity and recovery values are most meaningful when associated with specific separations, and some case histories will be presented shortly. Generally, no recovery after a single pass has ever been less than 70% of the amount of component present in the sample (as determined by separate analysis) and recovery values for well resolved components present in greater than trace quantity were usually better than 90% after a single pass.

Convenience and cost of operation are not unrelated. Over an extended period the most expensive material items in preparative gas chromatography are usually the column packing and carrier gas. The other most expensive accountable item is labor. In our work, minimization of time, cost and inconvenience has been given considerable attention. A brief discussion will be informative.

A variety of column supports has been used. Some were identical to those employed in analytical chromatography. But commercially available supports are very expensive even when purchased in large lots and they were used only when substitutes proved unsuccessful or where comparisons were to be made. The most successful cheap support proved to be ungraded, raw Celite 545 (Johns-Manville Company). Particle sizes from 35 to more than 120 mesh were variously used with good results. Generally, it was found that better separations were obtained with the smaller particle sizes and the narrower mesh ranges. In the early days of gas chromatography many supports were evaluated and these studies are available in the literature. Much of the information given by PURNELL[1] for analytical columns was found to be applicable to preparative columns. Some of our own results are shown in Fig. 4; in the case shown, Chromosorb W provided lower HETP values for small injection volumes while raw, ungraded Celite proved much more efficient for large injection volumes. This represented but one case but our experience has been that a cheap material is usually available to do any job possible with an expensive support. Chromosorb W costs about 500 times more than raw Celite.

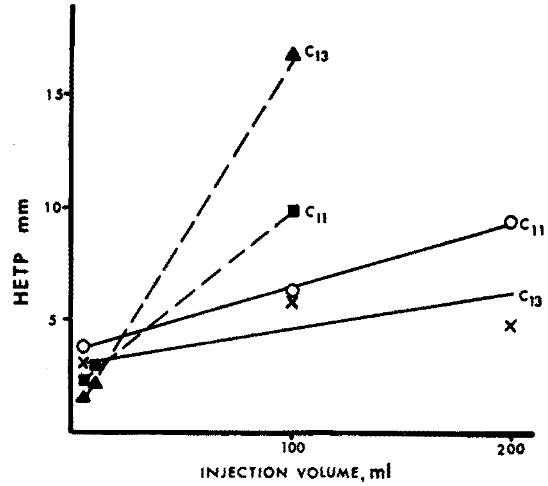

Fig. 4. Comparison of raw Celite and Chromosorb W: dashed line = Chromosorb W coated with Apiezon L, solutes, *n*-tridecane ▲ and *n*-undecane ■ ; solid line = raw Celite coated with Apiezon L, solutes, *n*-tridecane × and *n*-undecane ○.

Those partitioning agents must of necessity be chosen which will accomplish the required separation. Some common and often-recommended materials are quite cheap. Others are very expensive. Apiezon L, which has an exceptional capacity and allows very high throughput, is among the more expensive materials, whereas various very cheap asphaltic petroleum fractions can be used in a wide variety of applications. Polyethylene, of course, is quite cheap but of low capacity. For polar columns of reasonable capacity and thermal stability, Carbowax and Resoflex (LAC-4-R-886) are excellent and of only moderate cost; Resoflex 886 is about 30 times as expensive as Carbowax 20M. With dioctyl phthalate, not quite so thermally stable, cost would be further greatly reduced.

Costs of suitably coated column packing vary from about $100 per ft. when traditional materials are used to about $0.10 per ft. when some effort is put into a search for suitable materials of low cost. A great variety of cheap column packings is not expensive or inconvenient to keep on hand since column sections may be emptied and refilled quickly and easily and it is then not required that packed columns be kept in storage.

To fill a column section, the previously prepared packing is simply scooped into the open end of the section and the section is jarred gently and casually to settle the packing so that a maximum amount may be added. No elaborate settling procedure is recommended so that the packing is given no opportunity to become stratified or size graded, with resulting increase in HETP. Each section is filled to within an inch of the top, pressurized briefly with nitrogen to 30 psig, topped off with additional packing and then capped for storage or attached to another section. No further attention is accorded the packing procedure and this is an important feature of the column's usefulness. Since so little time and effort is needed for packing the column sections they may be filled just prior to use and emptied immediately thereafter, the packing being returned to bulk storage. Whenever a column has been used for an extended period it suffers a loss of efficiency due to stripping and channeling within the topmost section. This section may then be removed, emptied, and refilled after the packing is thoroughly remixed. It is not necessary to recoat the support. The remixing restores the section to its original efficiency so that either the stripped support is recoated *in situ* during operation or the stripping is only of secondary importance as compared to the channeling. We have never had to discard or recoat any packing. Some materials have been in constant use since early 1962 with no decrease in utility. As a result, a wide selection of partitioning agents may be gradually built up.

Helium is an expensive carrier gas. With no provision for reuse its cost is completely prohibitive. Recirculation of carrier gas is undesirable because of the added space required, the maintenance of additional equipment, the increased expense of the instrument, the added cost of coolant and the difficulty arising from inefficient cleanup of the recirculated gas. Consequently, nitrogen is preferred as carrier gas. For comparative purposes helium was used in most of the applications described later so that the resulting chromatograms would bear a closer visual relationship to those encountered in analytical chromatography. The same separations can be and are normally made with nitrogen as the carrier gas and nitrogen has generally provided greater efficiency for the larger injection volumes (*ca.* 100–200 ml) than has helium. The nitrogen is not recirculated but is exhausted to a fume hood after passage through the final scrubber trap.

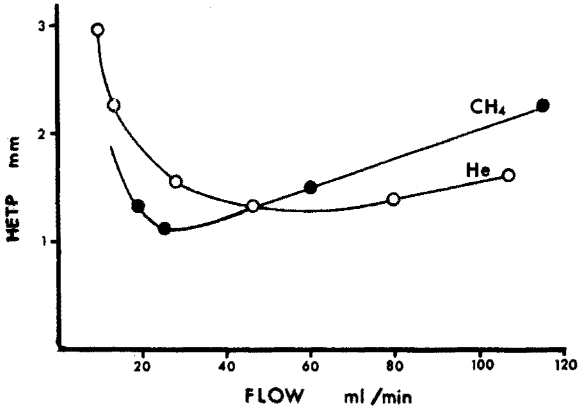

Fig. 5. Comparison of methane and helium.

For some applications methane has proved quite effective. In fact, as shown in Fig. 5, methane was capable of providing a smaller HETP than helium, although at a slightly lower flow rate than was optimum for helium. For our purposes very pure methane was available at small cost but, where this is not the case, natural gas should prove adequate for many separations. The inherent dangers of this substance must be held in mind. And the same is true of hydrogen, another cheap gas. Other possible gases are carbon dioxide and mixtures of nitrogen and hydrogen.

A typical carrier gas flow rate is about 10 l/min at standard conditions. The cost of nitrogen is thus about one cent per minute. A typical separation requires about 25 min. Assuming an average injection size of 20 g and a single component of interest, present at a concentration of 10%, the cost of carrier gas would be about 15 cents per g of recovered component. A simple purification of a major component (*ca.* 99%) from a large injection (200 g) would involve a cost of about $0.0013/g whereas separation of a minor component (*ca.* 0.05%) from a complex sample requiring small injection size (1 g) would involve a cost of about $500/g. This latter cost shows why chromatography is properly a supplement of distillation and not a general replacement for it. These costs are based upon 100% recovery and a single passage through the instrument.

A fractionation is usually preceded by an inspection of the sample with an analytical chromatograph. This analysis is used to select proper operating conditions and proper cut points. For this reason the analytical column and the preparative column should be made from an identical batch of packing. A very small injection (*ca.* 1 ml) is used so that the resulting chromatogram will be as nearly identical as possible to the analytical chromatogram. The pilot run is indispensable to show that all is operating properly. In many cases, the entire sample is separated in one injection and faulty performance of the system could lose or destroy the sample. When the composition of a sample is known approximately, the analytical separation may be omitted and the pilot run used to establish cut points. When conditions are considered proper the first large injection is made.

The greatest throughput is obtained by overloading the column to some extent. How much overload can be accommodated is dependent upon the degree of resolution and the purity and percent recovery desired. These things are best judged from experience. For columns of reasonable capacity, samples up to 50 g may be injected with only small loss of resolution. As stated, single injections of volumes as large as 200 ml have been made, without peak overlap. Since good recoveries of high purity material can be made from unresolved peaks, a practical separation could be accomplished with much larger sample size provided the vaporizer was not overloaded.

Cuts are made by passing the column effluent into the appropriate trap. The stripped carrier gas is discarded. Condensation of the various components is best accomplished at the highest temperature possible so, during the fractionation of a sample of wide boiling range, the bath liquid surrounding the traps should be heated to progressively higher temperatures. For the present purposes, for which chromatography was supplemented by distillation and *vice versa*, samples of wide boiling range were first fractionated by distillation, so no examples of the use of temperature-programmed traps are presented.

RESULTS

To illustrate the performance of the preparative chromatograph and to show its integration into a distillation facility, the following 5 specific examples show a variety of applications:

Case 1

The sample was a commercially available mixture of oxo alcohols, C_{11} through C_{15}, which contained significant quantities of material other than normal alcohols. The analytical chromatographic trace (Fig. 6) showed this non-normal material to be concentrated in what appeared to be a homologous series of compounds falling between the normal alcohols. Samples of these intermediate compounds were needed for identification. An approximate analysis of the starting material is given in Table I.

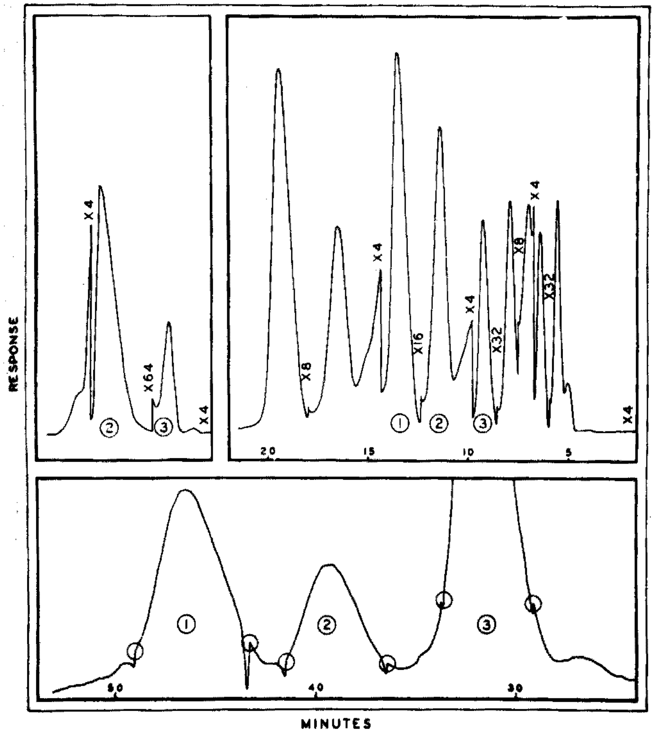

Fig. 6. Isolation of impurity from alcohols. (1) n-tetradecanol, (2) 2-methyltridecanol, (3) n-tridecanol. Analytical trace of charge stock, upper right; preparative trace, bottom (the circles indicate cut points); analytical trace of product, upper left.

TABLE I

ANALYSIS OF ALCOHOL MIXTURE

Component	*% of mixture*	*Purity obtained*
n-C_{12} Alcohol and lighter	17	—
Intermediate compound	6	95.0
n-C_{13} Alcohol	20	99.4
Intermediate compound	4	98.5
n-C_{14} Alcohol	30	99.2
n-C_{15} Alcohol and heavier	23	—

Distillation was attempted first. A spinning band column of 30 plates, 8 mm in diameter, was operated at reflux ratios from 40/1 to 120/1. After 24 h of operation no fraction contained any component in a purity greater than 75%. At this juncture, the most likely cuts were combined, giving 4 fractions varying in volume from 10 ml to 13 ml with a combined total of 45 ml.

These 4 fractions were sequentially injected into the preparative chromatograph, each fraction comprising a single injection. A 6-ft. column of 4-in. diameter was employed and was packed with 25% Apiezon L on a mixture of 60–100 mesh untreated Celite and 80–100 mesh Chromosorb W. Helium was the carrier gas. From the 4 injections, essentially pure components were recovered (Table I). A total time of 4 h was required for the chromatographic separation. All components were recovered in amounts greater than 75% as calculated from the original chromatographic analysis. Figure 6 shows the pertinent chromatograms for the separation of the impurity (proved to be 2-methyltridecanol) lying between *n*-tridecanol and *n*-tetradecanol.

Case 2

The sample originated with API Research Project No. 58A, Oklahoma State University, and was submitted by Dr. E. J. EISENBRAUN. It consisted of a mixture of three isomers of *o*-tetramethylindane (TMI): 1,1,5,6-TMI; 1,1,4,5-TMI and 1,1,6,7-TMI. A chromatographic analysis of the original sample (Fig. 7a) gave the approximate analysis shown in Table II.

Distillation was attempted first. A column of 80 plates, 1 in. in diameter, was operated at a pressure of 20 mm Hg and a reflux ratio of 60/1; 400 ml of sample were charged and 5% cuts were made until 85% of the charge had been taken overhead. The column was operated continuously until 85% was recovered. A total time of 77 h was consumed, 32 of which were used in taking over the product and 40 of which were given to total reflux. The temperature range was less than 5°. Isomers A and C were obtained in no cut in greater than 85% purity. Isomer B was never present in greater than 40% purity.

Preparative chromatography was employed. For isomers A and C the original sample was injected. For isomer B, a composite of distillation cuts was used. This composite contained less than 2% of isomer A. The column was 4 in. in diameter and 12 ft. long. It was packed with 25% LAC-4-R-886 on acid-washed Chromosorb W, 80–100 mesh. Helium was the carrier gas. Injections (5 ml) were made at 15-min intervals until 50 ml had been passed through. Two passes were required to obtain the A and C isomers in high purity. The B isomer required 3 passes. Recovery was about 80% on each pass. Recovery and purity data are given in Table II.

TABLE II

ANALYSIS OF TETRAMETHYLINDANES

Isomer	*Original % concentration*	*Purity after recovery*	*% Recovery*
1,1,5,6-TMI (A)	46	100	64
1,1,4,5-TMI (B)	16	100	51
1,1,6,7-TMI (C)	38	99.9	64

In this instance, the prior distillation did not succeed in concentrating isomer B significantly but it did separate isomers A and B almost completely so that the subsequent chromatographic fractionation of isomer B was made much simpler. Pertinent chromatograms are shown in Fig. 7.

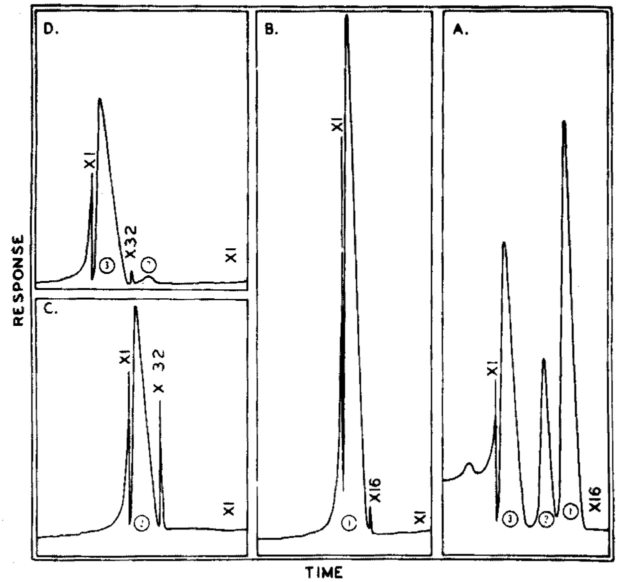

Fig. 7. Separation of tetramethylindanes. (A) analytical trace of charge stock: (1) 1,1,5,6-tetramethylindane (TMI), (2) 1,1,4,5-TMI, (3) 1,1,6,7-TMI; (B), (C) and (D) analytical traces of individual products.

Case 3

Two samples are considered here because the purpose of the separations was similar while the size of the injection differed materially. Sample I was research-grade neopentane which had produced unpredicted results in a study of reaction kinetics. It was found that about 200 p.p.m. of propane were present in the material and about 1 p.p.m. of some unknown contaminant. It was desired that enough material, free of these impurities, be collected to allow a new series of experiments. Sample II was ostensibly pure *n*-decane which was to be used as solvent for the preparation of very dilute standard solutions of *n*-heptane. These were used in studies of the response of various types of hydrogen flame ionization detectors. No decane could be found which was free of chromatographic interference at high sensitivities in the region of *n*-heptane elution. The best available contained about 175 p.p.m. impurities in this region. It was required that 200 ml of this material be stripped of pertinent impurities.

Distillation was not attempted in either case because of the predictably longer time required. Sample I was fractionated with a 6-ft. × 4-in. column of 25% dioctylphthalate on raw Celite. Five injections of about 25 g each were made. Total time required was 30 min. The recovery was better than 75% and no detectable impurities were present in the recovered product. Figure 8 presents the analytical chromatographic traces of the charge and product and the preparative trace used for selecting cut points.

Sample II was fractionated with a 6-ft. × 4-in. column of 25% Apiezon L on a mixture of Celite and Chromosorb W. This mixture of supports was a matter of expediency to use material on hand and had no significant relationship to efficiency. Two injections of 100 ml each were made. Total time required was 36 min. Recovery was 96% and the purified product contained no detectable impurities in the critical region. Chromatograms are shown in Fig. 8.

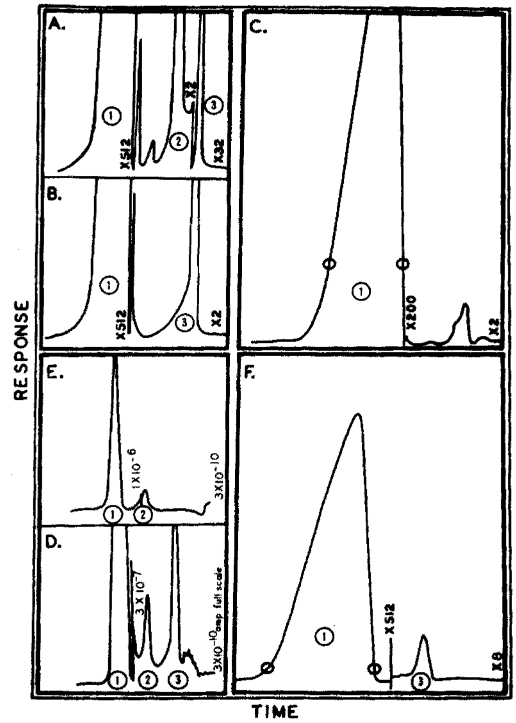

Fig. 8. Purification of neopentane and *n*-decane. (A) analytical trace of charge stock for purification of neopentane: (1) neopentane, (2) propane, (3) air; (B) analytical trace of purified product; (C) preparative trace; (D) analytical trace of charge stock for purification of *n*-decane: (1) *n*-decane, (2) *n*-nonane, (3) *n*-heptane; (E) analytical trace of purified product; (F) preparative trace— that portion of the peak between the circles was collected.

Case 4

Here again, two similar samples are considered. Sample I was received from API Research Project No. 58A and consisted of a mixture of *trans–trans* and *cis–trans* 3-methylcyclopentane-1,2-dicarboxylic acid dimethyl ester. Sample II was submitted by Dr. H. G. HECHT, Texas Technological College, and consisted of the *cis* and *trans* isomers of 1,4-dichlorobutene-2. The compositions of both samples, as determined by chromatographic analysis, are given in Table III.

Sample I was fractionated with a 6-ft. × 4-in. column of 25% Apiezon L on a mixture of Celite and Chromosorb W with helium as carrier gas. Four injections of 20 ml each were made. Total time required was about 2 h. Better than 70% recovery was achieved. Product purity is shown in Table III. If greater purity had been necessary another pass would have rendered both isomers essentially completely pure. Recovery would have dropped to about 50% however.

Sample II was separated with a 12-ft. × 4-in. column of 25% LAC-4-R-886 on 80–100 mesh, acid-washed Chromosorb W. Helium was used as carrier gas. Four injections of 5 ml each were made and the total time required was 92 min. Purity and recovery data are given in Table III.

TABLE III

ANALYSIS OF GEOMETRIC ISOMERS

Component	*% of sample*	*% Final purity*	*% Recovery*
Sample I			
Light ends	5	—	—
Trans–trans isomer	50	99.7	>70
Cis–trans isomer	41	97.5	>70
Heavy ends	4	—	—
Sample II			
Light ends	10	—	—
Cis isomer	7	—	—
Trans isomer	82	99.9	88.4
Heavy ends	1	—	—

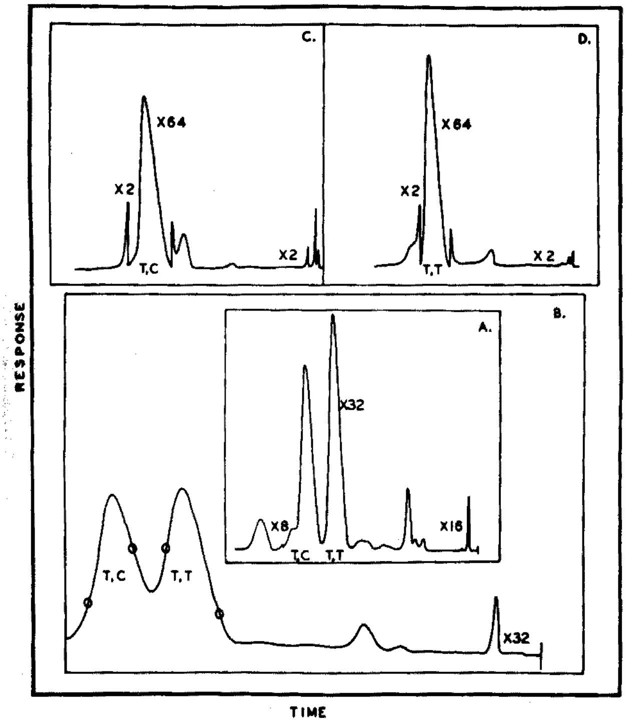

Fig. 9. Separation of isomers of dicarboxylic acid esters. (A) analytical trace of charge stock of a mixture of *trans–trans* (T,T) and *trans–cis* (T,C) 3-methylcyclopentane-1,2-dicarboxylic acid dimethyl ester; (B) preparative trace; (C) and (D) analytical traces of separated isomers. The region between the circles in (B) is the portion of the peaks collected in the traps.

Distillation was not attempted with either of these samples since they were the products of prior distillations and further distillation would have required much more time than the chromatographic fractionation. Chromatograms are shown in Figs. 9 and 10.

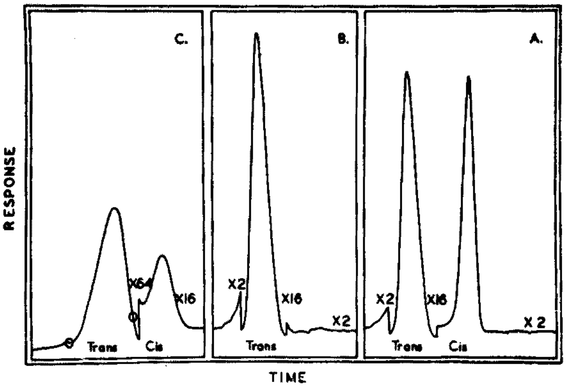

Fig. 10. Separation of 1,4-dichlorobutene-2 isomers. (A) analytical trace of charge stock; (B) analytical trace of purified *trans* isomer; (C) preparative trace—that portion of the peak between the circles was collected.

Case 5

This case is included to show the use of nitrogen as carrier gas. The sample was predominantly a mixture of C_6 and C_8 olefins, but a significant amount (*ca.* 1.3%) of some unknown impurity was present. Enough of the impurity was needed to effect identification. A single injection of 80 ml gave more than 1 ml of recovered product (> 94% recovery) whose purity was in excess of 98%. The time required was about 30 min. The column was 6 ft. x 4 in. and was packed with 25% asphalt on raw Celite. Nitrogen was the carrier gas. Figure 11 shows the preparative chromatogram.

The original sample in this case was a distillation cut of 14% of original charge

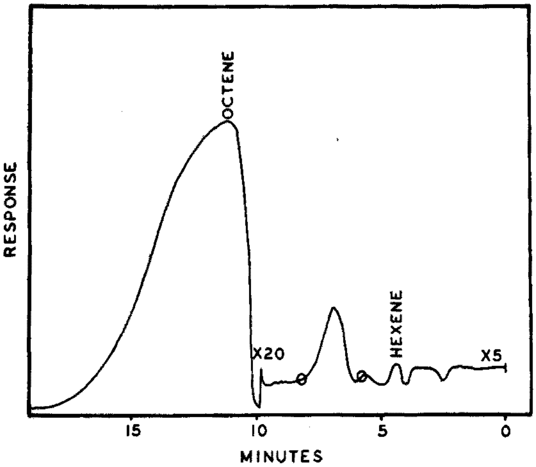

Fig. 11. Preparative separation with nitrogen carrier gas and thermal conductivity detector.

stock, so that the 1.3% impurity had already been concentrated nearly ten-fold. Further distillation was considered impractical from the point of view of time.

It may be seen from the figure that the hydrocarbons of lower molecular weight do not give conventional chromatographic peaks with nitrogen carrier gas and a thermal conductivity detector. This is a well known phenomenon. The anomalies are not present with a hydrogen flame ionization detector.

DISCUSSION

Gas chromatographic fractionation has a definite place in a distillation laboratory and current technology is adequate to provide a practical instrument for the purpose. Chromatography is most logically needed: (*a*) when it will save time, (*b*) when it will accomplish otherwise impossible separations, and (*c*) when it will decrease expense. These requirements are not distinct and unrelated.

Almost without fail, proponents of distillation will maintain that distillation can accomplish any separation possible with large-scale chromatography. It cannot be denied that special techniques of azeotropic and extractive distillation make use of the same physical properties which are effective in chromatographic separations. To utilize these special techniques, however, requires that each different sample be handled as a special case, with a considerable amount of work necessary to establish proper conditions. A research laboratory distillation facility deals with a large number of dissimilar samples. It has become apparent in our work that, whenever boiling point separation is not sufficient to allow fractional distillation, chromatographic separation is to be preferred. Conditions may be established in a short time with an analytical chromatograph and with very small samples and the actual fractionation can almost always be accomplished in less time than a distillation. So, considering the time element, certain separations may be considered as impossible for practical distillation and most of these may be done by chromatography.

The element of expense is the limiting condition for the use of chromatography and is the factor which relegates chromatography to the role of a distillation supplement. The expense of the instrument and associated equipment is not relatively great but the operating expense for the recovery of large quantities of trace components is prohibitive without the use of distillation for concentrating the sample. In general, the expense of treating really large sample volumes (*i.e.* several gallons) is significantly greater for chromatography than for distillation. Distillation is also useful in minor roles. The incompatibility of some samples for the partitioning agent makes removal of offending components imperative. This is usually accomplished by distillation. Very often, especially with new columns, the chromatographic product is contaminated with high boiling materials eluted from the substrate. These can be removed by adsorbents but it is more often conveniently done by distillation. Finally, high boiling and relatively non-volatile constituents which normally remain in the column may be initially removed by distillation, although it is not impractical to regenerate periodically the packing from the topmost column section since it may be conveniently removed for this purpose.

Distillation and chromatographic fractionation work very well together and have become so well integrated in our work that a ratio of about 1 chromatograph for every 5 distillation columns is employed.

Some reassurance is needed in the matter of instruments. As stated before, most of those engaged in preparative chromatography have been interested in rather specialized objectives—maximum resolution and efficiency, maximum throughput, theory, etc. No one has stopped to put together the simplest instrument which would accomplish a compromise of features applicable and acceptable in a distillation laboratory. Those commercial preparative instruments which have appeared are generally acknowledged to be analytical instruments designed to recover analytically useful quantities of material but not suited for quickly providing large-scale solvents, purified reactants, pilot-scale separations, etc.

Papers by BAYER AND WITSCH[2] and by HUYTEN *et al*[3]. described sufficient conditions for obtaining an adequate column efficiency with large columns. Much more recently GIDDINGS[4] has given a comprehensive account of the characteristics of large columns with some implications for the practical optimization of operation. Most attempts to realize good column efficiency have concentrated on achieving a more nearly uniform temperature within the column and a minimum degree of packing irregularity (particle size, loading, density, etc.). This has resulted either in the utilization of smaller bores, with the resulting small throughput amplified by automated, repetitive injections[5,6] or in odd geometries involving mixing washers[7,8], increased heat exchange surface[9,10], multiple columns, etc., all of which greatly increase the difficulty of packing and the inconvenience of handling, or, finally, in elaborate attention to packing[11] with its increased time, expense and inconvenience.

The column described in the present work was not designed for extreme efficiency but for acceptable efficiency with acceptable convenience. Irregularities in packing are minimized by a design which simplifies the packing procedure to the point that an entirely random distribution of packing is more nearly achieved. Happily, a simplified procedure is synonymous with increased convenience. Considerable attention was also given to increased heat exchange with minimum wall area and the materials of construction and geometry, particularly of the head spaces, accomplish this quite well. The sectional design, while primarily for convenience, may also help the efficiency through periodic remixing, although AMY *et al.*[7] have not found it so and our experiments have not demonstrated the magnitude of improvement.

Column efficiency as measured by the HETP is only one consideration. This usually varies for different solutes and, whenever the partition coefficient is not constant (*i.e.* for large samples), for different concentrations of the same solute. High throughput with concurrent efficient recovery of acceptably pure product depends equally on such other things as vaporizer design, capacity of the partitioning agent, trap design, fractionating procedures and the particular requirements of the sample at hand. Preparative columns are generally operated so that the column is overloaded for some or all of the sample components. It is important to find partitioning agents which will give the best efficiency under these conditions. This is particularly true for polar partitioning liquids which generally overload easily. Ordinarily, only the pilot run in large-scale preparative chromatography will give a trace comparable to the analytical trace. The actual separation will be made from components which overlap to some precalculated optimum extent. The concentration profile of eluted components will correspond most nearly to the results expected of a combination of frontal and elution analysis. Under these conditions special attention must be paid to the optimization of the fractionating procedure. This will always involve a compromise of recovery, purity and throughput. Some discussion of the principles involved has been given by REILLEY *et al.*[12], PRETORIUS *et al.*[13–15] and SAWYER AND PURNELL[16].

It has been recognized by SAWYER AND PURNELL[16] and verified by our experience that the design of the vaporizer is as important as that of the column. Here again, the design which has been described is adequate, consistent with expense, but currently constitutes the limiting factor influencing injection sample size. The design can be improved and is presently receiving paramount attention in our work, but the task is difficult.

Finally, it must be emphasized that much of the discontent with large-scale preparative chromatography arises from dissatisfaction with the recorded chromatogram. This visual record is a product of the detector. In large-scale work the detector scans only a very small fraction of the column effluent and very often produces an anomalous signal due almost wholly to the environment of the splitter and connecting lines. Proper geometric design and back-pressure regulation in these areas will often disclose that excellent results are being obtained at the traps.

In conclusion, we have employed chromatographic fractionation in our distillation laboratory for more than 5 years and presently consider it indispensable.

SUMMARY

A preparative gas chromatograph which accommodates sample injection volumes of <1 ml–>200 ml is described. Traps adequate for the quantitative recovery of a similar range of component volumes are also described. Materials, costs and details of operation are discussed. A diverse set of case histories is presented to show that such an instrument is entirely capable of supplementing and replacing normal distillations.

RÉSUMÉ

On décrit une chromatographe gazeuse permettant une injection de volume d'échantillon <1 ml–>200 ml. Une discussion est donnée au sujet du matériel, du prix et des détails des opérations. Divers exemples montrent qu'un tel appareil est entièrement capable de compléter des distillations normales.

ZUSAMMENFASSUNG

Ein präparativer Gaschromatograph für Proben zwischen 1 ml und 200 ml wird beschrieben. Angemessene Auffänger für die quantitative Rückgewinnung Komponenten ähnlichen Bereichs werden beschrieben und der Materialbedarf, die Kosten und Einzelheiten des Verfahrens diskutiert. Es wird gezeigt, dass ein solches Instrument im Stande ist normale Destillationen zu vervollständigen und zu ersetzen.

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SHORT COMMUNICATIONS

Gas-volumetric determinations by means of hypodermic syringes: the determination of hypophosphite

Gas-volumetric methods of analysis are procedures based on the measurement of the volume of a gas evolved in a stoichiometric chemical reaction. Although the reaction itself is often rapid, simple, and specific, the equipment required is usually so cumbersome, expensive, and complicated, that the use of such procedures tends to be avoided. These difficulties can sometimes be circumvented by using a conventional large-capacity hypodermic syringe as both a reaction vessel and measuring burette for gas-volumetric analysis. After the reaction has been allowed to proceed, the volume of gas evolved is obtained directly without critical manipulations or equilibrations. This technique has been applied to a method for the analysis of hypophosphite solutions, with only simple laboratory equipment. The accuracy was found to be adequate for process control work. Although this technique is illustrated here by its application to the determination of hypophosphite, it appears to be general in scope and capable of use in many gas-volumetric procedures.

The use of hypophosphite as a reducing agent in electroless plating baths created a need for a fast and simple, yet reasonably accurate method for its determination. None of the existing chemical methods met these requirements. There are no direct oxidimetric methods for measuring hypophosphite because invariably its reactions with oxidants are slow. Those methods reported in the literature using cerium(IV)[1,2], iodine[3,4], bromate[5], persulfate[6] and permanganate[7] involve back-titration of the excess reagent, usually after a lengthy reaction time. The colorimetric methods reported[8-11] are based on the formation of the heteropoly blue complexes and are not selective when other phosphorus species are present.

A gas-volumetric method, based on the catalytic evolution of hydrogen gas, has been used for the determination of hypophosphite in electroless nickel plating baths[12,13]. A small amount of palladium black in an acid solution of hypophosphite acts as a catalyst for the reduction of water to hydrogen, with the simultaneous oxidation of hypophosphite to phosphite. In one procedure[12], the hydrogen evolved is burned and the flame temperature is related to the quantity of hypophosphite in solution; however, in other procedures[13], the hydrogen is measured in a conventional gas burette.

The procedure described here employs the chemistry just named, but eliminates the need for elaborate gas-volumetric measuring equipment through the use of a hypodermic syringe. Since the reaction of hypophosphite with water proceeds only at higher temperatures, the sample and the catalyst can be mixed with negligible reaction at room temperature. This permits the mixture to be drawn into the syringe, the excess air to be expelled, and the reaction volume to be adjusted to the desired level, without significant evolution of hydrogen. The syringe is then capped and heated in a boiling-water bath for 10 min to allow the evolution of hydrogen to proceed to completion. After the syringe has been cooled, the volume of generated gas which is proportional to the amount of hypophosphite in the sample is read directly from the volume calibrations on the syringe. Only 15 min per analysis is required; by using 3 syringes, a dozen analyses can be completed within an hour.

Reagents

The catalyst solution contains 166 mg of palladium chloride plus 2 ml of concentrated hydrochloric acid in 100 ml of water. The sulfuric acid and sodium hypophosphite monohydrate used were reagent grade. A conventional 30-ml glass syringe was modified to take a stopper to keep it gastight during the reaction and measurement steps. Figure 1 shows a photograph of the syringe disassembled, as well as in use.

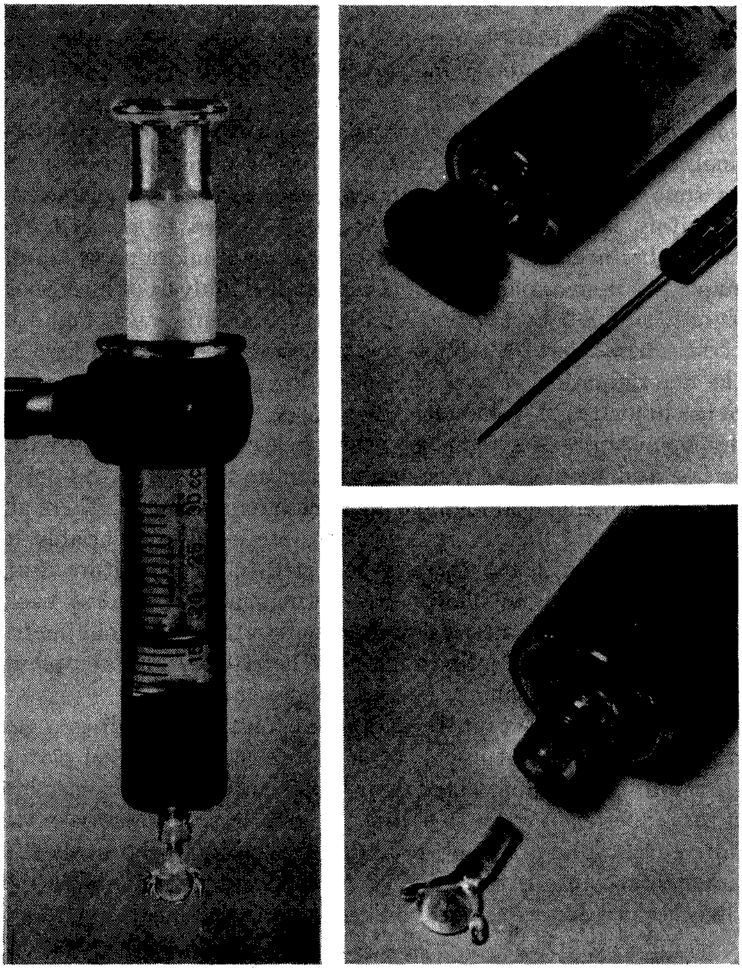


Fig. 1. Syringe adapted for gas-volumetric measurements of hypophosphite.

Procedure

The sample solution (25 ml) containing 1–7 g of sodium hypophosphite monohydrate per l is pipetted into a 100-ml beaker; 8 drops of concentrated sulfuric acid and 8 drops of the palladium chloride catalyst solution are added and mixed. Without undue delay, approximately 12 ml of this solution is drawn into the syringe. The syringe is inverted and the liquid level is adjusted until the plunger is exactly even with the 10-ml graduation. At this point, the syringe is capped and lowered, tip down, into a beaker of boiling water. The syringe is clamped in a position such that the level of the boiling water is approximately the same as the solution level within the syringe. The evolution of hydrogen is preceded by the precipitation of palladium black. After 10 min of heating, the syringe is cooled to room temperature. For maximum precision, the syringe should be cooled in a thermostatted water bath controlled to $\pm 1^\circ$. Once the syringe plunger is riding freely, the volume of gas is measured by using the calibration marks on the syringe. The gas volume is then related to the hypophosphite concentration *via* a calibration curve prepared by the identical procedure. Each syringe must be calibrated.

Discussion

As expected, it was found that the volume of hydrogen evolved is linearly proportional to the hypophosphite concentration in the range of 1–7 g per l of the monohydrate salt (Fig. 2). It is presumed that appreciably higher concentrations may be analyzed by making appropriate dilutions.

The use of all-glass syringes with non-metal caps is necessary. When sealed metal needles were used to cap the syringe, high results were obtained owing to attack of the metal by the acid solution. Either a glass cap or a rubber septum provides a tight-fitting seal, as shown in the inserts of Fig. 1. A male glass plug was ground to fit the opening of a syringe from which a metal Luer–Lok fitting had previously been removed. This type of closure was used for most of these experiments. Syringes of this type may also be sealed by using Arthur H. Thomas No. 2330 Rubber Stoppers for Vaccine Bottles.

Several reaction parameters were studied. The rate of the reaction was found to depend on pH. Figure 2 shows that the evolution of hydrogen proceeds at a maximum rate below pH 3, whereas, above pH 5, the reaction is so slow that heating times considerably in excess of 10 min are required for complete reaction.

Palladium chloride is employed as a catalyst; it acts as an initiator by reacting with hypophosphite to form phosphite and metallic palladium according to the following reaction:

$$Pd^{2+} + H_2PO_2^- + H_2O \rightarrow Pd^0 + H_2PO_3^- + 2\ H^+$$

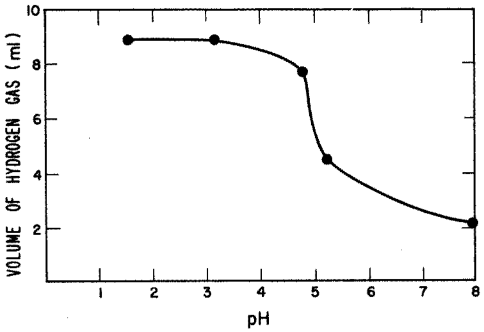
The amount of hypophosphite consumed by this reaction, which does not produce hydrogen gas, is small compared to the amount involved in the main catalytic reaction:

$$H_2PO_2^- + H_2O \xrightarrow{Pd} H_2PO_3^- + H_2\uparrow$$

Since palladium serves as a catalyst, the reaction velocity is dependent upon its concentration, as is illustrated in Fig. 3. Eight drops (*ca.* 0.4 ml) of the catalyst solution per 25 ml of sample appears to provide a rapid and acceptable rate of reaction at elevated temperatures. With this concentration of catalyst, the reaction at room temperature is imperceptible. No loss of hydrogen gas is observed within 5 min after the addition of the catalyst and acid, which allows ample time for filling, leveling, and capping of the syringe.

As an indication of precision, the standard deviation (1 σ) for this procedure based on 7 analyses was found to be 0.1 g per l at a level of 3 g per l of sodium hypophosphite. Other phosphorus species such as phosphite and phosphate were found not to interfere.

This novel use of a syringe both as a reaction vessel and as a gas burette should be applicable to other analytical methods where gas-volumetric measurements are made, such as the Zerewitinov determination of reactive hydrogen, metal hydride analysis, and metal-catalyzed peroxide reactions. This technique can also be used with rapid reactions or those that occur at room temperature. If a rubber septum is used to seal the measuring syringe containing the sample solution, the catalyst or reagent can be introduced by means of a second, smaller syringe. Refined narrow-bore syringes would undoubtedly provide even better precision and accuracy.



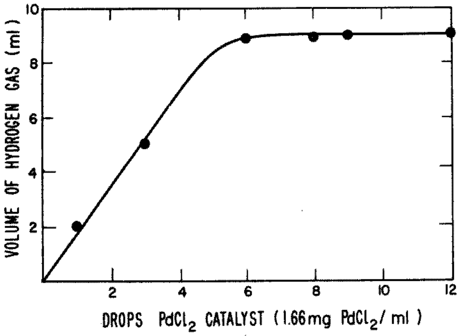


Fig. 2. Effect of pH. 3.0 g $NaH_2PO_2 \cdot H_2O$ per l; heating time: 10 min; 8 drops of catalyst solution in 25 ml.

Fig. 3. Effect of catalyst concentration. 3.0 g $NaH_2PO_2 \cdot H_2O$ per l; heating time: 10 min.

Research Laboratories,
Eastman Kodak Company,
Rochester, N. Y. 14650 (U.S.A.)

T. N. Tischer
A. D. Baitsholts
E. P. Przybylowicz

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(Received May 28th, 1965)

Detection of volatile carbon-14 labeled compounds by a modified gas chromatography–ionization chamber technique

During the last few years gas chromatography has become an important analytical tool in organic analysis. At the same time ^{14}C-labeled compounds have become increasingly available. The combination of these 2 important developments provides a very powerful method for the study of reaction kinetics of organic systems.

One of the methods which has been employed for the radio-assay of volatile labeled compounds involves a gas chromatography–ionization chamber technique. With this technique simultaneous detection of mass and radioactivity is accomplished by directing the effluent stream from the chromatograph through a thermal conductivity cell and then a flow ionization chamber. WILZBACH AND RIESZ[1,2] have used this technique for the separation and radio-assay of tritium-labeled compounds. NYSTROM[3] used a modified WILZBACH type ionization chamber which could be heated to 100° for separating and detecting a variety of tritium- and ^{14}C-labeled compounds. TOLBERT[4,5] has built ionization chambers which can be used up to 225°. Improved chambers have been described by DOBBS[6] and by MASON *et al.*[7] which are operable up to 240°. CACACE[8] has developed a system which has the advantage that it operates at room temperature. With a sensitive detector such as a vibrating-reed electrometer the limit of detection of all the mentioned gas chromatography–ionization chamber devices is of the order of 10^{-7}–10^{-9} curie of tritium or ^{14}C in a single peak.

It is possible to increase the sensitivity to a limit of approximately 10^{-11} curie of ^{14}C by a simple modification of the usual gas chromatography–ionization chamber technique. The radioactive compounds are separated by preparative gas chromatography, but instead of simultaneously counting with a flow ionization chamber, the compounds are trapped out as they elute from the gas chromatographic column, and then are subsequently transferred to a static ionization chamber where entire separated fractions are counted.

Reported in this paper are specific activities of the oxidation products of ^{14}C-labeled propylene. These data were obtained by the modified gas chromatrography–ionization chamber technique which is described in some detail. A particularly important feature of the technique is that it is possible to use the ionization chamber at room temperature for volatile liquid compounds.

Materials

Propylene-3-^{14}C with a specific activity of 1 mc/mmole was obtained from Research Specialties, Inc., Richmond, California. The material was freed of radioactive impurities by passing the entire sample through a preparative gas chromatographic column, collecting only the propylene fraction. Research grade Phillips propylene of 99.5% purity was used to dilute the radioactive propylene to a specific activity of approximately 0.25 μc/mmole. Linde tank oxygen of 99.9% purity was used as the oxidizing agent.

Apparatus and procedure

The labeled products were formed by the high temperature oxidation of propylene-3-^{14}C which was carried out in an electrically heated fused quartz flow reactor. Because of the increased sensitivity of the modified gas chromatography–

ionization chamber technique, it was possible to carry out the experiments with radioactive propylene which had been diluted with a large excess of ordinary propylene. Since total product recovery was not necessary with the diluted radioactive propylene, evacuated 1-l flasks were used for the collection of small portions of the product stream, while the major portion was vented to the atmosphere.

The procedure involved in the application of the modified gas chromatography–ionization chamber technique to the specific activity determinations of the labeled oxidation products was as follows. Approximately 100 ml (NTP) of the product gas sample was separated into individual components by preparative gas chromatography. A column containing 20% β, β'-oxydipropionitrile on Chromosorb was used for the separation. As the radioactive components were eluted from the chromatographic column they were collected at −195° in copper gauze-packed traps which were connected to a vacuum line. After separation and collection of individual components was completed, arbitrary volumes of counting gas (argon) were introduced into each of the traps containing the radioactive materials. A series of homogeneous gas mixtures of argon and each of the radioactive compounds was formed by allowing the closed traps to warm up to room temperature. Next, each of the mixtures was transferred, in turn, into the ionization chamber by means of a Toepler pump and the chamber was brought to atmospheric pressure with a further addition of argon. Finally, the radioactivity of each mixture was determined with an Applied Physics Corp. vibrating-reed electrometer. After the radioactivity assay had been made, an aliquot of each sample was withdrawn from the ionization chamber and introduced into the gas chromatograph. A knowledge of the peak area obtained and the volume of the precalibrated ionization chamber (287 ml) together with the previously determined radioactivity allowed a determination to be made of the specific activity of the radioactive species.

Results and discussion

The data obtained from some products of propylene-3-^{14}C oxidation are given in Table I. The specific activities given in column 4 are calculated from the values of the ionization chamber current in column 2 and the size of sample in mmol, calculated from chromatographic peak areas and given in column 3. No attempt was made to place the specific activity values on an absolute basis (curie/mmol), since the data are used only for comparative purposes (1 μc $\sim 4 \cdot 10^{-12}$ A). Thus, in column 5 are given values of the "relative specific activity" which is defined as the specific activity relative to propylene.

TABLE I

SPECIFIC ACTIVITIES FOR PROPYLENE-3-^{14}C OXIDATION PRODUCTS

(Reaction temperature = 625°; feed composition: 70% $^{14}CH_3CH{=}CH_2$, 30% O_2)

Component	*Ion current ($A \cdot 10^{14}$)*	*Mmol*	*Specific activity ($A/mmol$) $\cdot 10^{13}$*	*Relative specific activity*
Propylene oxide	1.64	0.0199	8.26	1.08
Acrolein	4.34	0.0615	7.05	0.92
Propionaldehyde	1.11	0.0134	8.26	1.08
Biallyl	7.55	0.0452	16.70	2.18
Propylene	46.59	0.609	7.64	1.00

From the viewpoint of reaction mechanism, there is reason to believe that the products propylene oxide, acrolein and propionaldehyde retain the carbon skeleton of propylene[9]. If this is assumed to be the case, then the relative specific activities of these 3 compounds should be equal to unity. As is evident from the Table, each of the experimental values deviate from unity only by approximately 8%. If account is taken of the errors in the ion current measurement (*ca.* 1%) and the errors in the chromatographic determinations of the quantities of material assayed (*ca.* 4–5%) and the difficulties in handling small quantities of material, a deviation of 8% does not seem unreasonable.

In a similar manner, if it is assumed that biallyl is formed by the recombination of 2 allyl radicals, then the relative specific activity should be twice that of propylene, *i.e.* 2. The experimental value of 2.18 deviates from the theoretical value by 9%, which again is not unreasonable.

There are several important advantages of the modified gas chromatography–ionization chamber technique for the determination of specific activities of volatile organic compounds.

(*1*) The technique is very sensitive, since as little as 10^{-11} curie of radioactivity can be determined with great accuracy. Because of the extreme sensitivity starting materials of very low specific activity can be used. The accuracy of the counting measurements can be improved even further by long countings and repeat determinations since a static ionization chamber is employed instead of the usual flow ionization chamber.

(*2*) The ionization chamber can be operated at room temperature as long as the partial pressure of the volatile compound does not exceed its vapor pressure.

(*3*) The radioactive compounds can be recovered for further examination, if necessary, since the compounds need not be converted to carbon dioxide before counting.

(*4*) The specific activity data are not affected by small handling losses, if any occur, since a gas chromatographic determination of the quantity of radioactive compound actually present in the ionization chamber is made immediately after the sample is counted.

Union Carbide Corporation, Olefin Division,
South Charleston,
West Virginia (U.S.A.)

E. RODERICK WHITE*
HUBERT G. DAVIS

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(Received May 10th, 1965)

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* Present address: Nuclear Science and Engineering Corp., Pittsburgh, Pa., 15236.

An ion-exchange method for the detection of esters

The difficulties inherent in developing a method for the detection of esters have been recently reviewed[1]. WEST AND QURESHI[1] developed a method in which the esters are hydrolyzed enzymatically and subsequently detected with methyl red. This method is fast, selective and reliable, but benzaldehyde, nitrobenzene and bromobenzene interfere, acid esters give only a weak response, and the test cannot be applied to esters of inorganic acids. In addition to enzymes, ion-exchange resins also offer possibilities for the hydrolysis of esters. Although they are not as specific as enzymes, ion exchangers are more stable, easier to handle and more versatile in their action. An ion-exchange method for the detection of esters should therefore be simpler and more generally applicable.

Reagents

Esters. Reagent-grade esters were used without further purification.

Resins. Dowex 1-X8 (20–50 mesh) and Amberlite IR-120 resins were used after the usual regeneration and conversion to OH^- and H^+ forms respectively.

Test solutions. Liquids for ester tests were used as aqueous 5% solutions or emulsions. Solids were dissolved in water to give solutions containing 1 g/l.

Methyl red. The reagent was prepared by dissolving 1 g in 600 ml of ethanol and diluted to 1 l with water. The solution was filtered if necessary.

Procedure

Shake a few ml of the test solution or emulsion for 2 min with small quantities of wet exchanger in the OH^- form. Filter through a glass wool plug and test a drop of the filtrate with methyl red. If a red color is obtained, repeat the process until the filtrate (one drop) gives a yellow color with the indicator. Then divide the filtrate into two parts. Set one part (A; a few drops) aside for comparison and heat the other part (B) with 0.20–0.30 g of dry cation exchanger in the H^+ form over a boiling water bath; shake for a few sec and filter through a dry glass wool plug. Add a drop of methyl red to this filtrate and also to the portion A. If the color in portion B is pink, when compared with portion A, an ester is indicated. This comparison is necessary in the case of esters of aromatic and inorganic acids which give a light pink color. Esters of aliphatic acids give a deeper color and comparison is not necessary. It is important for the success of the experiment that fresh glass wool be used for each test.

Results

Study of interferences. The ester test was performed with pure samples of different types of organic compounds. The following compounds gave a negative ester test.

(a) *Alcohols.* Methyl, ethyl, isopropyl, isobutyl, benzyl, cyclohexanol, ethylene glycol and glycerine.

(b) *Ketones.* Methyl, ethyl, methyl isopropyl, acetone, acetophenone, acetylacetone and cyclohexanone.

(c) *Aldehydes.* Acetaldehyde, benzaldehyde, chloral hydrate, crotonaldehyde and formaldehyde.

(d) *Ethers.* Isopropyl ether and dioxan.

(e) *Acids.* Acetic, propionic, oxalic, trichloroacetic and benzoic.

(f) *Hydrocarbons.* Benzene, hexane, toluene.

(g) *Halogen compounds.* Bromobenzene, ethylene bromide, ethylene dibromide, chloroform, carbon tetrachloride and chlorobenzene.

(h) *Nitrogen compounds.* Urea, nitrobenzene, aniline, diethylamine and pyridine.

(i) *Carbohydrates.* Sucrose, lactose and glucose.

(j) *Sulphur compounds.* Thiourea.

Formamide and acetamide gave positive tests.

Reaction with different esters and applications. In order to test the versatility of this reaction the ester test was repeated with numerous esters available. The following esters gave a positive test: ethyl acetate, cyanoacetate, acetoacetate, acetone dicarboxylate, α-bromo-*n*-butyrate, benzoate, oxalate, nitrate, and phthalate; diethyl malonate and oxalate; methyl acetate and benzoate; dimethyl sulphate; *n*-propyl acetate; monobromoethyl acetate, *n*-butyl acetate, tributyl phosphate and benzoamyl ester. Methyl salicylate, benzylbenzoate and ethyl carbonate gave negative tests.

Esters must sometimes be detected in the presence of other substances. In order to test the utility of this method, various synthetic mixtures were prepared. The results are summarized in Table I. Ethyl acetate was taken as a representative ester.

TABLE I

DETECTION OF ESTERS IN A MIXTURE BY THE ION-EXCHANGE METHOD

Composition of the mixture		*Remarks*
1. Ethyl acetate–ethanol	(1 : 1)	Positive
2. Ethyl acetate–dioxan	(1 : 1)	Positive
3. Ethyl acetate–sucrose	(1 : 1)	Positive
4. Ethyl acetate–acetaldehyde	(1 : 1)	Positive
5. Ethyl acetate–ethylene glycol	(1 : 1)	Positive
6. Ethyl acetate–bromobenzene	(1 : 1)	Positive, observe upper layer
7. Ethyl acetate–nitrobenzene	(1 : 1)	Positive, observe upper layer
8. Ethyl acetate–chloroform	(2 : 1)	Positive, observe upper layer
9. Ethyl acetate–carbon tetrachloride	(2 : 1)	Positive, observe upper layer
10. Ethyl acetate–benzene	(1 : 1)	Positive, observe lower layer
11. Ethyl acetate–toluene	(1 : 1)	Positive, observe lower layer

If a positive ester test is obtained, esters or amides may be present. To distinguish between the two, the pH of the test solution is roughly determined with pH paper; 3 ml of the test solution are then warmed at 40–45° with wet (about 0.3 g) Dowex 1-X8 in the OH^- form. The contents are then filtered through glass wool and the pH of the solution is again determined. In the case of an ester there is no significant change in pH, while in the case of an amide the solution becomes distinctly basic.

It is useful to compare the ion-exchange method with the hydroxamic acid[2] and enzymatic[1] tests. The more important points are summarized in Table II.

Discussion

The results show that ion exchange offers a useful method for the detection of esters. The principle of the method is simple: ion exchangers hydrolyze esters more effectively than does acid[3], and no new ions are introduced into the solution.

TABLE II

COMPARISON OF THE ION-EXCHANGE METHOD FOR THE DETECTION OF ESTERS WITH THE HYDROXAMIC ACID AND ENZYMATIC METHODS

Basis of comparison	*Hydroxamic acid test*	*Enzymatic test*	*Ion-exchange test*
Number of tests usually performed	Three tests are recommended	One test	One test
Effect of time	Best to note the color within 5 min. The color may diminish with time	Note the color after 5 min. The color becomes more intense with time	Color produced immediately. No effect of time
Test with esters of inorganic acids	Negative	Negative	Positive
Test with chloral hydrate	Positive	Negative	Negative
Test with chloroform	Positive	Negative	Negative
Test with formaldehyde and benzaldehyde	Weakly positive	Negative	Negative
Most amides	Positive	Negative	Positive
Acid esters	Weakly response	Weakly response	Definitely positive

$$CH_3COOC_2H_5 + H_2O \xrightarrow{RH^+} CH_3COOH + C_2H_5OH$$

The ion exchanger is easily removed from the solution by filtering through a glass wool plug. The consequent decrease in pH is readily detected with an indicator such as methyl red. Most esters are partially hydrolyzed on keeping and hence have an acid reaction; to overcome this difficulty the ester solution is first shaken with a small quantity of anion-exchange resin. Small portions of the resin are taken and the reaction is carried out in the cold, so that neutralization of the excess acid occurs without any significant hydrolysis of the ester. The use of the anion-exchange resin has the advantage of not introducing new cations; in the hydrolysis step, cations would exchange with hydrogen ions of the resin and a false positive test would be obtained.

The method is more versatile than the hydroxamic acid and enzymatic methods. For instance it gives positive tests with inorganic esters like ethyl nitrate and tributyl phosphate. The method fails with ethyl carbonate because methyl red is not able to detect the small change in pH resulting from the hydrolysis of ethyl carbonate. Considering that ion exchangers in the hydrogen form generally catalyze hydrolysis, it is surprising that interference in this test is almost insignificant.

Aldehydes, ketones and acid chlorides do not interfere, hence this method can be used with great advantage where a fast, simple and selective method is required for the detection of esters. The method was tried with about 40 unknowns and in almost all cases the esters were correctly detected. Only acetylacetone gave an erroneous positive test. Methyl salicylate was not detected reliably, the test being sometimes positive and sometimes negative. Benzyl benzoate proved very difficult to hydrolyze and did not respond to the ester test.

The main interference is caused by amides which are hydrolyzed by the cation-exchange resins and cause a significant release of H^+ ions, through the exchange of ammonium ion.

Anion-exchange resins (OH^- form) distinguish neatly between an ester and an amide.

An ester solution exhibits a neutral reaction while an amide gives an alkaline response.

$$CH_3COOC_2H_5 + ROH + H_2O \rightleftharpoons CH_3COOR + H_2O + C_2H_5OH$$

$$CH_3CONH_2 + ROH^- + H_2O \rightleftharpoons CH_3COOR + NH_4OH$$

The ion-exchange method is fairly sensitive. Under the above conditions, only 2 ml of 0.1% ethyl acetate solution are required for the test. The method is less sensitive for esters of inorganic acids; 2% tributyl phosphate and 5% ethyl nitrate are required. It should be possible to modify this test so as to increase its sensitivity and to use different ion-exchange resins to classify the esters themselves.

The authors express their sincere gratitude to Dr. PHILIP W. WEST who first suggested the use of ion-exchange resins for the detection of esters. They are also grateful to Dr. A. R. KIDWAI, Head of the Department of Chemistry for his interest in the work and for research facilities. The financial assistance given to one of us (S.Z.Q.) by the Government of India is gratefully acknowledged.

Prince of Wales Chemical Laboratories,
Aligarh Muslim University,
Aligarh (India)

MOHSIN QURESHI
SAIDUL ZAFAR QURESHI

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(Received August 1st, 1964)

Investigations on tests for phosphate and silicate by the ring-oven method

In the course of investigations on the application of ring-oven methods to the analysis of mineral samples containing silicate and phosphate, difficulties were encountered in applying the well-known molybdate–benzidine test[1]. In this very sensitive test, not only molybdenum blue, but also the far more brilliant benzidine blue are formed. Arsenate and germanate give analogous reactions; fluoride and oxalate interfere with the phosphate test by forming stable complexes with molybdenum, while the less stable molybdenum–tartrate complex allows only phosphate to react and prevents the formation of silicomolybdate[1].

WEISZ[2] has described a ring-oven procedure for phosphate without comment on possible interferences. The ring is sprayed with ammonium molybdate solution and dried successively 3 times, sprayed with benzidine acetate reagent solution and developed over ammonia. MUSIL *et al.*[3] used this procedure in presence of arsenate, which reacts too slowly in the cold to interfere even when present in large excess. The use of the molybdate–benzidine test for the detection of silicate after sodium carbonate fusion is mentioned by WEISZ[4], but no procedure is described. FEIGL[5] describes a spot-test procedure for the detection of phosphate in presence of silicate, based on the masking action of tartrate. This test is designed for use on filter paper and lends itself for use on the ring oven.

So far, no simple straightforward test for silicate in presence of phosphate is available. FEIGL recommends the preliminary precipitation of ammonium phosphomolybdate; soluble ammonium silicomolybdate remains in solution and can be detected in presence of oxalate which decomposes the small amount of phosphomolybdate still present.

Phosphomolybdic and silicomolybdic acids are formed only in acidic solution. Phosphate, assumed to be present as orthophosphate, reacts instantaneously in cold solution, but silicate requires a prolonged time and elevated temperature. The formation of phosphomolybdate is retarded by the presence of tartaric or citric acid. The equilibrium

$$H_3PO_4 + 12\ MoO_3 \rightleftharpoons H_3P(Mo_3O_{10})_4$$

must respond with extreme sensitivity to a reduction of the concentration of available molybdate due to complexing with the organic ions. It was found necessary to use a longer time and elevated temperatures to obtain the full sensitivity of the test when tartaric or citric acid was present. Oxalic acid, when present in excess, was found to prevent the formation of polymolybdate for phosphate and silicate.

The proposed procedure involves 4 steps: (*1*) formation of a ring containing phosphate or silicate; (*2*) formation of phosphomolybdate or silicomolybdate; (*3*) application of benzidine reagent; and (*4*) performance of the redox reaction yielding molybdenum blue and benzidine blue, by pH adjustment.

Good results were obtained using the ring-oven procedure for the detection of phosphate given by WEISZ. For routine use, however, it seemed more convenient to eliminate the need to spray a highly corrosive reagent and to reduce the operating time by omitting successive dryings.

The application of the same procedure for the detection of silicate was not successful. Very diffuse, pale rings were obtained when 10 μg of silicate was treated for a long time at elevated temperature.

The procedure adopted finally consisted of applying the ammonium molybdate–nitric acid reagent first to the centre of a filter paper disc; the sample solution was then added so that polymolybdate formation started. With phosphate, immediate washing with silicate-free ammonia solution was satisfactory, but with silicate 2 min were necessary for silicomolybdate to form. It was found that silicate ion alone could be washed to the ring completely by means of sodium hydroxide but not by ammonia solution. Clean strong rings were obtained when at least the major portion of silicate was converted to silicomolybdate. Far less intense rings were obtained when silicate was applied before the ammonium molybdate reagent, possibly because the acidic molybdate solution provided better conditioning of the cellulose fibers than the alkaline silicate solution.

Experiments on the best way of applying the benzidine acetate reagent showed that sucking of the reagent solution from the centre of the filter paper gave results far superior to spraying or bathing. The migration of the benzidine solution swept all unnecessary excess reagent, free nitric acid and ammonium nitrate beyond the ring. The presence of all these compounds exerted a favourable influence on the formation of the polymolybdate complex. The conditions for the subsequent redox reaction, however, would be improved by the absence of strong acid and nitrate ion.

The redox reaction between phospho- or silicomolybdate and benzidine does not start until the pH is raised to above 5 (for phosphomolybdate) or 8 (for silicomolybdate). FEIGL recommends either fuming over ammonia or application of sodium acetate. The blue color develops slowly when the ring is exposed to ammonia vapours, depending on the neutralisation of free acids originally present in the ring; as soon as the buffer capacity of the ammonium acetate–acetic acid is exhausted, the pH rises quickly, resulting in fading of the bright blue color to an insignificant gray. It proved difficult to stop fuming at just the right time, so that the reproducibility was poor and unsuitable for semiquantitative estimation.

When sodium acetate was applied by spraying, it was difficult to reach the required range above pH 8. Bathing of the ring in sodium acetate solution would provide the required pH range, but the solubility of benzidine phosphomolybdate, or of the more soluble benzidine silicomolybdate, reduced the sensitivity of the test, as the precipitates dissolved off the ring before reaction.

Satisfactory results were obtained when the pH adjustment was performed by using saturated borax solution; the required pH of about 9 was easily reached and maintained. Consistently reliable results were obtained with good reproducibility and sensitivity.

Apparatus

Ring oven with accessories[2]. Filter paper discs, 5.5 cm diameter, Whatman No. 41, 42 or Schleicher and Schüll 589[2], white ribbon, or similar.

Reagents

Ammonium molybdate–nitric acid solution. Dissolve 10 g of ammonium molybdate in 80 ml of cold water. Pour the solution into 20 ml of nitric acid (d 1.42).

Ammonia solution, silicate-free. Prepare by isothermal distillation. Place a polythene beaker, filled with freshly boiled distilled water from a quartz still, in an empty desiccator, together with another beaker or dish containing at least twice the amount of concentrated ammonia solution. Keep the desiccator closed for some time, depending on the required concentration.

Benzidine acetate solution. Dissolve 50 mg of benzidine in 100 ml of 10% (v/v) acetic acid. The solution keeps about 1 week.

Ammonium molybdate–tartrate solution. Prepare by dissolving 15 g of tartaric acid in 100 ml of the ammonium molybdate–nitric acid solution mentioned above. Prepare the citrate and oxalate solutions analogously.

Standard phosphate solution (10 mg P_2O_5/ml). Dissolve 5.047 g of disodium hydrogen orthophosphate dodecahydrate in water to give 100 ml.

Standard silicate solution (10 mg SiO_2/ml). Fuse 1.003 g of silica (99.7% pure) with 2.5 g of anhydrous sodium carbonate and 3 g of potassium carbonate. Cool and dissolve the melt in water to give 100 ml.

General procedure

Apply 5–10 μl of ammonium molybdate–nitric acid solution to the centre of a filter paper disc by means of a capillary pipette. Apply the sample solution. Wait for 2 min in the case of silicate. Wash to the ring using silicate-free 0.5 *N* ammonia solution, applied in about 20 5-μl portions. Acidify by exposing the filter to the vapours of cold concentrated nitric acid, and dry. Feed about 25 μl of benzidine solution to the centre of the filter, by slow suction from a 0.1-ml Ostwald–Folin pipette, without any flooding. Apply a saturated solution of borax in water until the bright blue color of the ring is fully developed. Limit of identification: 0.05 μg P_2O_5 or SiO_2.

Procedure for phosphate in presence of silicate. Apply 5–10 μl of ammonium molybdate–tartaric acid solution to the centre of a filter paper disc. Apply the sample solution and expose the filter to steam for 30 sec. Place the filter on the ring oven and start washing to the ring as described above. Limit of identification: 0.1 μg P_2O_5 in presence of 50 μg SiO_2

Procedure for differential detection of both phosphate and silicate in presence of each other. Mark the centre of a filter paper disc and draw a semicircular line of 8 mm radius, using a soft pencil. Apply a 5-μl drop of ammonium molybdate to the centre of the filter paper disc, and apply tartaric acid solution along the semicircle, using a narrow capillary to draw a narrow line. The tartaric acid solution must not spread into the central region. Apply the sample solution to the centre of the filter. Place the filter on the ring oven and start washing after 2 min with silicate-free ammonia solution as described in the general procedure. Phosphate only will be indicated beyond the marked semicircle. The other half of the ring shows phosphate plus silicate.

The application of this differential procedure is limited to up to a ratio of $P_2O_5:SiO_2 = 3:1$, which still gives a significantly stronger test for the sum than for P_2O_5 alone. Smaller ratios of $P_2O_5:SiO_2$ offer no difficulties, although the sensitivity is slightly reduced. 0.5 μg P_2O_5 in presence of 50 μg SiO_2 can still be detected.

Further investigations on the semiquantitative application of these tests are in progress.

This work was carried out under the cultural agreement between Austria and the United Arab Republic. All authorities concerned are thanked for their cooperation and assistance.

Microanalytical Chemistry Unit,
National Research Centre,
Dokki, Cairo (Egypt)

Y. A. GAWARGIOUS
L. J. OTTENDORFER*
S. W. BISHARA

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(Received May 21st, 1965)

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* Permanent address: Institut für analytische Chemie und Mikrochemie, Technische Hochschule Wien (Austria).

Ultramicrocoulometric titration of chromium(VI)

OELSEN AND GOBBELS[1] first described the use of electrically generated iron(II) for coulometric titrations. COOKE AND FURMAN[2] extended the use of this reagent to the titration of chromium(VI). They titrated 1–9 mg of chromium with an average error of about 1%. MEITES[3] applied this titration to microgram quantities of chromium using a millicoulometer; in the titration of 0.14 μeq., the error was less than 1%; with 0.005 μeq., the average error was 6%.

The present paper describes the coulometric titration of nanogram amounts of chromium(VI) using a sensitive amperometric end-point detection[4]. As little as 4 ng of chromium(VI) were determined with a mean error of 3.7%.

Reagents

Reagent-grade chemicals were used throughout. Standard solutions of chromium(VI) were prepared from primary standard potassium dichromate. Water used to prepare these solutions was distilled through an American Sterilizer Company Spanish Dungeon triple still and then deionized by a mixed bed ion-exchange column containing Amberlite IRC120 and Amberlite IRA400 resins. For very dilute solutions of chromium(VI) ($< 10^{-3}$ N), the water was finally distilled in all-glass apparatus from alkaline permanganate solution. Chromium solutions less than 0.01 N were prepared fresh daily.

Oxygen was removed from solutions by bubbling for 15 min with "Seaford" nitrogen (Southern Oxygen Company). The nitrogen was passed through solutions of chromium(II) sulfate, potassium dichromate, potassium permanganate, and the generating electrolyte before passage into the cell.

The generating electrolyte consisted of 7 parts (v/v) of 0.6 M iron(III) in 2 M sulfuric acid and 1 part of 85% phosphoric acid; iron(III) sulfate or iron(III) ammonium sulfate could be used.

Apparatus

Micropipettes (5, 50, 100 μl) were calibrated coulometrically[5] with a precision of 0.2% or better.

Titrations were performed with a ChrisFeld Microcoulometric Quantalyzer, Model 6 (ChrisFeld Precision Instruments Corp., Beltsville, Md.). The accuracy of the generation currents supplied by this instrument was checked by measuring the IR drop across a standard resistor (±0.002%; Electro Scientific Industries, Portland, Oreg.) and was found to be better than 0.1% at all values. Potential measurements were made with a Leeds and Northrup Potentiometer, No. 8687.

Titrations were performed in a 50-ml beaker. The auxiliary electrode was 1 cm² of platinum foil isolated by placing in a glass tube fitted with a sintered glass frit end. The generating electrode was a 2 cm² platinum foil and the indicating electrode was a 1 cm² platinum foil. A saturated calomel electrode (S.C.E.) served as reference electrode. Solutions were stirred with a magnetic stirrer equipped with a synchronous motor.

Amperometric currents were recorded automatically on a Sargent Polarograph, Model FS. The potential impressed between the indicating electrode and the S.C.E. (+0.90 V) was supplied by this polarograph.

Procedure

The generating electrolyte (30 ml) was added to a 50-ml cell and the solution was deoxygenated by bubbling with nitrogen for 15 min. Then chromium(VI) was added until the amperometric current due to iron(II) impurities decreased to a small, constant value. The sensitive amperometric system similar to that previously reported[4] was used to detect the end-point as follows. The solution was pretitrated at 96.5 μA until an end-point break just occurred. The generation was stopped and the recorder pen was adjusted to the top of the chart paper. Then the generation was continued at either 96.5 μA or 9.65 μA; the linearly increasing amperometric current was recorded until a sufficient amount of iron(II) had been generated to be in excess of the sample to be added. The generation was stopped and the recorder was allowed to continue recording of the amperometric current. The sample was added and the current decrease (due to depletion of iron(II)) was recorded until the current had leveled off to a straight line again. The sample titration value was determined by measuring the decrease in current and then calculating the time-equivalent in sec from the slope of the titration curve (before sample addition).

Results and discussion

Typical titration curves of 80-ng and 4-ng samples are shown in Figs. 1 and 2. The pen response of the Model FS polarograph is 1-sec full scale. Therefore, the current decreases rapidly when the sample is added. The noise level in Fig. 1 is greater than that in Fig. 2 even though the recorder sensitivity is lower. The noise

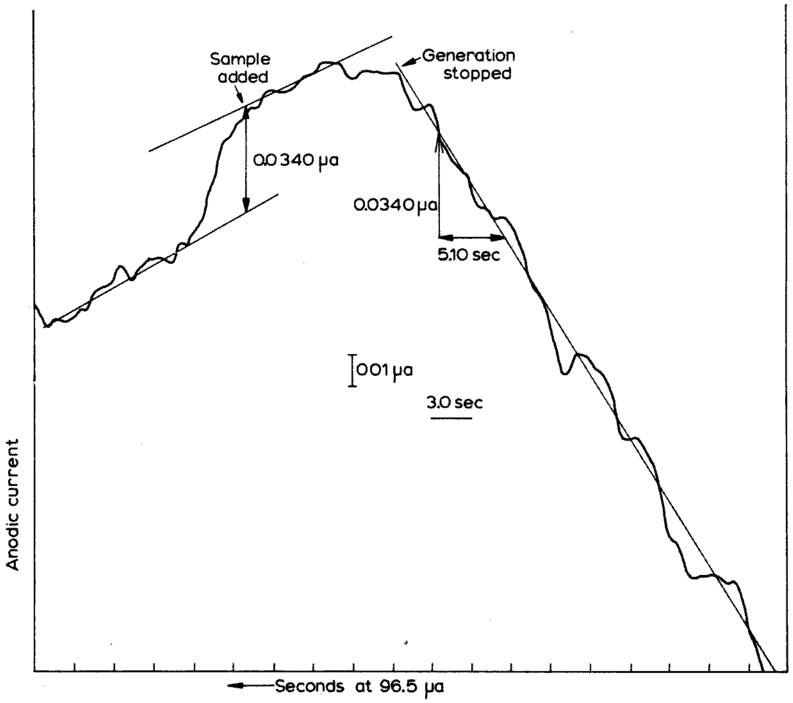

Fig. 1. Titration curve of 86.6 ng of chromium at 96.5 μA. Theoretical end-point is 5.06 sec. Solution volume, 30 ml.

(principally stirring) in Fig. 2 was decreased by filtering with a resonant choke-capacitor filter. The disadvantage of this filter is the slower response of the recorder and, therefore, slower attainment of recorder pen equilibrium. For this reason, the filter was not used unless noise was excessive.

At lower sensitivities of the polarograph (higher generating rates), the amperometric current, after stopping the generation, decreased slightly with time, in a linear fashion (Fig. 1). This is probably due to slight depletion of the iron(II) by any of several mechanisms: first, a small amount of iron is utilized at the indicating electrode; secondly, small iron losses might occur by adsorption on the walls of the vessel or on the platinum electrodes dipping in the solution; thirdly, and probably most important, there are probably losses due to oxidation of iron(II) since it is difficult to remove the last traces of oxygen from solution. This caused no problem as long as the current–time lines before and after adding the sample were approximately parallel.

At the higher sensitivities of the polarograph (lower generating currents), the amperometric current appeared to continue to increase slightly after generation had stopped (Fig. 2). This is probably due to instrument drift since the amplifier is operating at full sensitivity and also the slow pen response resulting from the time constant of the noise filter. The current, thus, appears not to decrease when the sample is added, but levels off momentarily.

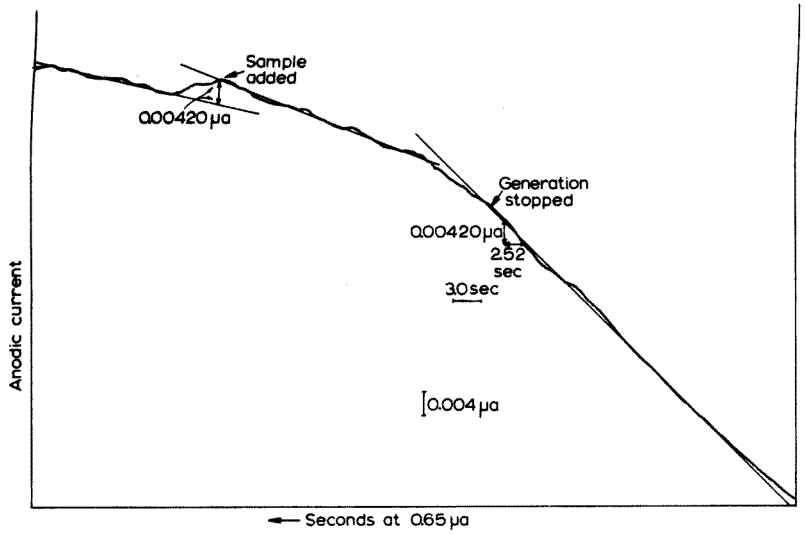

Fig. 2. Titration curve of 4.32 ng of chromium at 9.65 μA. Theoretical end-point is 2.50 sec. Solution volume, 30 ml.

The current depletion due to the sample was in all cases measured at the point at which the sample was added. This is illustrated in both Figs. 1 and 2. A series of curves was recorded and given to impartial observers for calculation to check on any unintentional bias which might have occurred in extrapolating the "noisy" curves. The results of a series of 10 identical runs showed a precision within 1%.

TABLE I

TITRATION OF NANOGRAM AMOUNTS OF CHROMIUM

(All titrations were performed in a volume of 30 ml. Generating current was 96.5 μA)

Cr taken (ng)		*Cr found (ng)*	*Relative error (%)*	*Theor. end-point (sec)*	*Sensitivity of polarograph (μA/mm)*
825		807	−2.2	49.7	0.01
825		836	1.3	49.7	0.01
825		846	2.5	49.7	0.01
825		834	1.1	49.7	0.01
825		834	1.1	49.7	0.01
	Ave. std. devn. = ± 16 ng	831	± 1.6		
	Mean error = + 0.73%				
86.6		86.2	−0.35	5.06	0.01
86.6		89.3	3.8	5.06	0.01
86.6		84.2	−2.8	5.06	0.01
86.6		86.2	−0.35	5.06	0.01
	Ave. std. devn. = ± 2.4 ng	86.5	± 1.8		
	Mean error = − 0.12%				
86.6		83.2	−2.7	5.06	0.001
86.6		88.3	2.0	5.06	0.001
86.6		85.3	−1.5	5.06	0.001
86.6		87.3	0.81	5.06	0.001
86.6		86.3	−0.35	5.06	0.001
86.6		87.3	0.81	5.06	0.001
	Ave. std. devn. = ± 1.5 ng	86.3	± 1.4		
	Mean error = − 0.35%				
41.2		40.8	−0.97	2.49	0.001
41.2		38.7	−6.1	2.49	0.001
41.2		40.8	−0.97	2.49	0.001
41.2		39.8	−3.4	2.49	0.001
41.2		39.6	−3.9	2.49	0.001
	Ave. std. devn. = ± 1.7 ng	39.9	± 3.1		
	Mean error = − 3.2%				
17.3		14.4	−16	1.01	0.001
17.3		17.5	−1.1	1.01	0.001
17.3		15.4	−11	1.01	0.001
17.3		15.4	−11	1.01	0.001
17.3		16.4	−5.2	1.01	0.001
17.3		15.4	−11	1.01	0.001
17.3		10.3	−40	1.01	0.001
	Ave. std. devn. = 3.3 ng	14.9	±14		
	Mean error = − 14%				
4.32[a]		4.25	−1.6	2.50	0.0004
4.32[a]		4.46	3.2	2.50	0.0004
4.32[a]		4.15	−3.9	2.50	0.0004
4.32[a]		4.76	10	2.50	0.0004
4.32[a]		4.65	5.6	2.50	0.0004
4.32[a]		4.76	10	2.50	0.0004
	Ave. std. devn. = ± 0.31 ng	4.49	± 5.7		
	Mean error = + 3.9%				

[a] Generating current was 9.65 μA.

Recoveries of nanogram samples of chromium were very satisfactory (Table I). Even when the end-point value was only 1 sec or less, results were within *ca.* 15% (96.5 μA generating current). More accurate results were obtained if a lower generating current was employed with a correspondingly longer titration time. The extreme sensitivity of this method is evident in the titration of 4 ng of chromium in a volume of 30 ml with an end-point of 2.5 sec using 9.65 μA generating current. In a series of 6 titrations, the mean error was 3.9% and the average relative error was 5.7%.

If the sample volume is appreciable, a blank correction should be made by adding the same volume of blank reagents.

The authors gratefully acknowledge the technical assistance of Miss ARLIEN L. STEINER.

Division of Biochemistry,
Walter Reed Army Institute of Research,
Walter Reed Army Medical Center,
Washington, D. C., 20012 (U.S.A.)

GARY D. CHRISTIAN
FREDRIC J. FELDMAN

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(Received May 10th, 1965)

Rapid isolation of radio-silver and certain other radio-elements from solution. Application to a search for ^{121}Ag in ^{235}U fission

A previous investigation[1] related to a general study of the nuclear charge distribution in near-symmetric fission suggested the possibility that short-lived ^{121}Ag forms in the thermal neutron irradiation of ^{235}U. For exploring this possibility a rapid procedure for the separation of silver from a freshly irradiated solution was required. Evaluation of the existence of ^{121}Ag would depend upon the measurement of the quantity of ^{121}Sn (half-life of 27.5 h) growing from separated silver for various intervals between the time of irradiation and the time of silver separation. Therefore, the procedure demanded the separation of silver from tin as well as from the intervening decay product elements, cadmium and indium.

This note describes a very rapid method for the separation of silver from the descendant chain elements. It is based upon the well-known reduction of ionic silver by metallic copper. The results of the search for ^{121}Ag are reported. Also the behavior of a variety of other elements in this separation is given. The latter information may provide the basis for wider application of the separation procedure.

Chemicals and radioactivities

Copper powder, purified grade, was supplied by the J. T. Baker Chemical Company (Lot No. 29,981). Other chemicals used were of reagent-grade quality.

Radioactive tracers were obtained from the Oak Ridge National Laboratory and Nuclear Science and Engineering Corporation. Their purity was established by γ-ray spectroscopy.

Filtration apparatus

The filtration apparatus was adapted from a commercially available filter tower (Tracerlab Division of Laboratory for Electronics). A disc (7/8 in. diameter) of 10 μ pore size stainless steel mesh (Chas. Lowe Co., San Francisco) replaced the existing porous steel disc. The wire mesh supported 1 g of copper powder. The powder was washed several min before use with 10 ml of 1.6 N nitric acid. The tower was connected to a suction flask and the filtration rate was 30 ml/sec.

Procedure

A preliminary study of the distribution of silver, cadmium, indium, and tin between copper bed and filtrate was carried out under conditions that approximated those which were to exist in the irradiation experiments. Fifteen milliliters of 4 N nitric acid containing 100 mg of uranium and 10^6 c.p.m. each of ^{110}Ag, ^{109}Cd, ^{114}In, or ^{113}Sn were rapidly filtered through a copper bed which was then immediately washed with 5 ml of 1.6 N nitric acid. The copper was dissolved in concentrated nitric acid and then brought to a definite volume. One day after separation, the γ-ray activity of this solution was compared with that of a similarly prepared standard (including the same amount of copper).

In the ^{121}Ag experiments, a pneumatically driven sample carrier (rabbit), loaded with 100 mg ^{235}U in 0.6 ml 4 N nitric acid, was irradiated at the Vallecitos Nuclear Test Reactor (NTR) for 10 sec in a flux of 10^{12} neutrons/cm^2/sec. At the end of the irradiation the rabbit was pneumatically transferred in about 1 sec a distance of 50 ft. to the mobile laboratory. The irradiated solution was transferred by suction to a tube containing 10 ml of 4 N nitric acid, and the rabbit was washed with 5 ml of 4 N nitric acid. The combined solution was passed through the copper powder in the filtration apparatus at a definite time with reference to the end of the irradiation. Passage of the solution through the copper was accomplished in about 0.5 sec. The copper bed was washed immediately with 5 ml of 1.6 N nitric acid.

Copper and supporting stainless steel mesh were transferred to a centrifuge tube which contained a known volume of standardized tin carrier. Several hours after irradiation concentrated nitric acid was added dropwise to dissolve the copper and 10 ml of saturated ammonium chloride solution were added to the solution. The solution was adjusted to pH 8 with ammonia solution, and the precipitate which formed was collected by centrifugation. To the precipitate of tin hydroxide were added 10 ml of concentrated ammonia, and the mixture was stirred thoroughly to solubilize residual copper precipitate. The mixture was centrifuged, and after the excess supernatant liquid was decanted, 1 ml of concentrated hydrochloric acid was added to the precipitate. Analysis of the resultant solution for ^{121}Sn by the radiochemical procedure of COWAN[2] was begun several hours after the irradiation.

For the other radio-elements studied (see Table I), 10^6 c.p.m. of the respective radioactivity in 10 ml of 4 N nitric acid was filtered through the bed, and the bed was then immediately washed with 20 ml 1.6 N nitric acid. The bed was dissolved and radiochemically analyzed as described above in the preliminary study.

TABLE I

QUANTITY OF RADIOACTIVITY RETAINED BY COPPER BED

Radioactivity	*Retained on copper (%)*	*Radioactivity*	*Retained on copper (%)*
^{110m}Ag	98.3 ± 1.2[a]	^{114m}In	0.06 ± 0.02
^{109}Pd	85.0 ± 6.5	^{99m}Tc	0.05 ± 0.02
^{203}Hg	74.4 ± 5.6	^{85}Sr	0.04 ± 0.01
^{195}Au	72.5 ± 3.0	^{65}Zn	0.04 ± 0.02
^{131}I(I$^-$)	33.3 ± 1.0	^{113}Sn(IV)	0.03 ± 0.01
^{125}Te(IV)	7.2 ± 0.08	^{68}Ge	0.02 ± 0.00
^{106}Ru(III)	6.8 ± 0.2	^{99}Mo	0.01 ± 0.00
^{75}Se(IV)	5.3 ± 1.3	^{86}Rb	0.01 ± 0.00
^{95}Zr	0.68 ± 0.18	^{133m}Ba	< 0.01
^{77}As(III)	0.60 ± 0.00	^{60}Co(II)	< 0.01
^{95}Nb	0.09 ± 0.01	^{144}Ce(III)	< 0.01
^{44}Ti	0.08 ± 0.07	^{54}Mn(II)	< 0.01
^{125}Sb(III)	0.08 ± 0.03	^{91}Y	< 0.01
^{109}Cd	0.06 ± 0.02	^{204}Tl(I)	< 0.01

[a] For silver, cadmium, indium and tin the standard deviations are based upon at least 4 determinations. The errors for the other radio-elements are the average deviation of 2 determinations from the mean.

Results and discussion

Preliminary experiments indicated that silver was essentially quantitatively reduced and deposited on the copper bed; the retention of cadmium, indium, and tin was less than 0.1% (Table 1). The procedure could therefore be used reliably to study the formation of ^{121}Ag in fission.

In the search for ^{121}Ag 12 irradiations were performed and separations were made in the interval of 3.5 to 60 sec after the end of fission. ^{121}Sn was undetected even in the shortest time of separation. Therefore, either the half-life of ^{121}Ag is considerably less than several seconds or its fission yield is inordinately low.

The retention at the tracer level of various other radio-nuclides by the copper bed is shown in Table I. Of the 28 elements studied, only palladium, silver, gold and mercury were deposited in excess of 70%. Selenium, ruthenium, tellurium and iodine were partly retained by copper to the extent of 5–33%. Of the remaining 20 metals, with two exceptions, substantially less than 0.1% of the radio-nuclide adhered to the filter. The selectivity inherent in the process may provide for the isolation of certain few elements to the exclusion of a significant number of other elements. It seems probable that even greater selectivity may be achieved by modification of the pH and by the action of complexing agents.

Comparison of the oxidation potentials for the electrode half-reactions of these elements with the half-reaction for copper[3] clearly accounts for the results obtained. Where the oxidation potential for the element is more negative than the potential for copper, appreciable reduction and removal from solution occurs. When the potential is more positive only a negligible fraction of the element is retained by the filter.

It is noteworthy that the kinetics of the oxidation–reduction reaction are extremely rapid. For silver, for example, the reaction is complete within the time required for the solution to pass through the copper filter bed (about 1/2 sec).

Current investigation is concerned with the use of this process to remove silver and palladium separately from solution. Because of its inherent speed such a procedure should afford characterization of the half-lives and yields of short-lived species of these two elements in the region of symmetric fission.

U.S. Naval Radiological Defense Laboratory,
San Francisco,
California, 94135 (U.S.A.)

HERBERT V. WEISS
WILLIAM L. REICHERT

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(Received May 22nd, 1965)

Anal. Chim. Acta, 34 (1966) 119–122

BOOK REVIEWS

Reagents & Reactions for Qualitative Inorganic Analysis, Fifth Report, Analytical Chemistry Division, International Union of Pure & Applied Chemistry, Butterworths, London, 1964, x + 88 pp., price 32s 6d.

This reprint of the report by the Commission on Analytical Reactions was first published in the IUPAC journal, Pure & Applied Chemistry, 8 (1964) No. 1. It contains descriptions of 80 qualitative tests for 49 cations and anions which have been thoroughly examined by the members of the Commission. The limit of identification and the limitations of each test are included in the general descriptions.

The previous Report in this series appeared in 1948, and few copies of this, and even fewer of the earlier Reports, are now available. For these reasons, some of the earlier work has been re-checked and where suitable it has been included with the new material. For most of the ions examined alternative tests are offered. In general, drop reaction tests on spot plate or paper are used, but crystal tests are also included where the characteristics of the crystals are suitably defined (and where alternative colour reactions are not acceptable).

Whilst it is to be hoped that another 16 years will not elapse before the Sixth Report is made available, the authoritative nature of the present report should enable it to hold its own for many years. This reprint, now conveniently published in book form, and at a reasonable price, provides an undisputed source of qualitative inorganic tests which most analytical chemists will welcome.

W. I. STEPHEN (Birmingham)

EARLE R. CALEY, *Analysis of Ancient Metals*, International Series of Monographs on Analytical Chemistry, Vol. 19, Pergamon Press, Oxford, 1964, xii + 173 pp., price 70 s.

The investigation of the chemical composition of ancient materials has a long history, since it dates back to the pioneer work of KLAPROTH in the eighteenth century. However it is only in comparatively recent times that systematic analyses have been carried out on an increasing scale. This has come about because it has been realised that the analytical examination of ancient materials can provide information which will help to solve various problems of interest to the archaeologist. In this field the analysis of ancient metals and their corrosion products has attracted particular attention, because metal objects are of great cultural significance to the archaeologist.

The author of this monograph is a recognised authority on the examination of ancient materials, who is familiar with the practical problems involved, and with the pitfalls which have to be avoided, if reliable analyses are to be obtained. It is for this reason that the two opening chapters are devoted to the question of the heterogeneity of ancient metals and the problem of sampling, and to the preliminary observations which should be made on the objects themselves prior to analysis. This information is of vital importance to any chemist who may wish to analyse ancient metal objects. In the following chapters there is a critical and selective description of the methods to be employed for the analysis of the metals likely to occur in ancient metal objects. The recommended procedures—based on the author's own extensive experience—are described in full detail, since this monograph is intended as practical guide to the identification and analysis of ancient metals and their corrosion products. However, in addition, typical results of analyses covering a wide range of metal objects are included, and the significance of these from the archaeological point of view is discussed in a fascinating fashion, which adds greatly to the interest of this book. Numerous references are included at the end of each chapter, and these are of great bibliographical value, as the literature on this subject is very widely scattered. This monograph can be unreservedly recommended as an authoritative account of a specialised field of analytical chemistry, in which the chemist adapts his skills to meet the needs of the archaeologist.

A. E. WERNER (London)

Anal. Chim. Acta, 34 (1966) 123

JOZEF MIKA, *Metallurgische Analysen*, Akadémiai Kiadó, Budapest, 1964, 843 S., Preis Ganzleinen $ 12.00.

This work is a completely revised German edition of the Hungarian version entitled *Huttenmännische Analysen*, which appeared in 1958. The contents are briefly described in the subtitle, *Chemische Untersuchungsmethoden der technisch wichtigen Metallen, Legierungen und Erze.* Indeed, this book is not a complete review of technical analyses, for only analytical procedures of the most important metals, alloys and ores are treated. However, an essential difference from the many other available books dealing with technical analyses lies in the fact that not only are the analytical procedures given but that also the theoretical background of the methods

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is explained; the application range, the advantages and even the possible errors are also discussed. In this monograph the author has collected the most frequently used methods which can be extended to many other problems if some small modifications are made. This enables the practising analytical chemist to make use of these methods for his own particular requirements.

The procedures described cover the field of titrimetric, gravimetric, photometric, potentiometric, electrolytic and polarographic methods. It is a pity, however, that no attention is given to recently developed techniques such as ion exchange, extraction and masking; the author considers that at present there is insufficient experience at our disposal to ascertain if these rapid separation methods fulfil our requirements. The procedures are treated in a very clear and easily understandable way, and are often illustrated with valuable figures.

Because of the very simple classification it is possible to find almost instantaneously a procedure for the determination of each common element in different matrices. The text is divided into two main sections: part I deals with the analysis of the most important metals (Fe, Al, Mg, Cu, Pb, Sn, Zn, Ag) and their alloys. The determinations of an element in a matrix are generally preceded by a qualitative spot test. Part II deals with the ore analysis of the earlier mentioned elements; major and minor constituents are dealt with. Special attention is given to the technical analyses of bauxite, magnesite and dolomite.

Although there is a lack of literature references, this monograph will undoubtedly prove very convenient for the analyst. The discussions about precision, analysis time, and utility in different fields will be particularly appreciated.

R. DAMS (Ghent)

Anal. Chim. Acta, 34 (1966) 123–124

ERRATUM

The determination of active oxygen and iron(II) in oxide compounds, G. W. VAN OOSTERHOUT AND J. VISSER, *Anal. Chim. Acta*, 33 (1965) 330.

On p. 332, line 21 should read:

The ferrite contains: $\frac{(V-V_0)\cdot t\cdot 55.85}{a}\cdot 100 = \%$ divalent iron.

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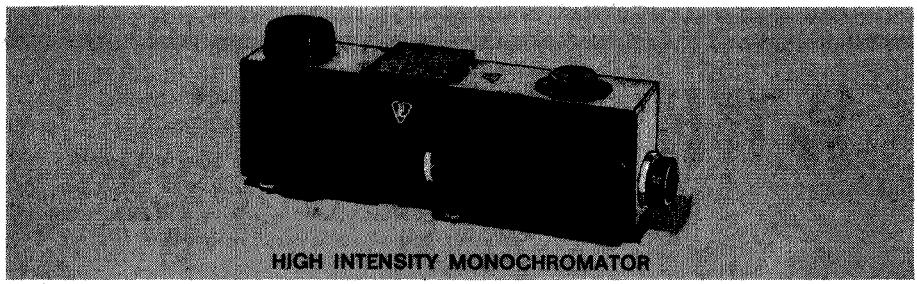

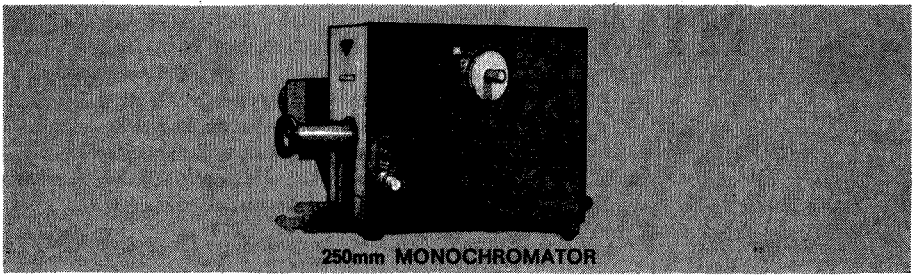

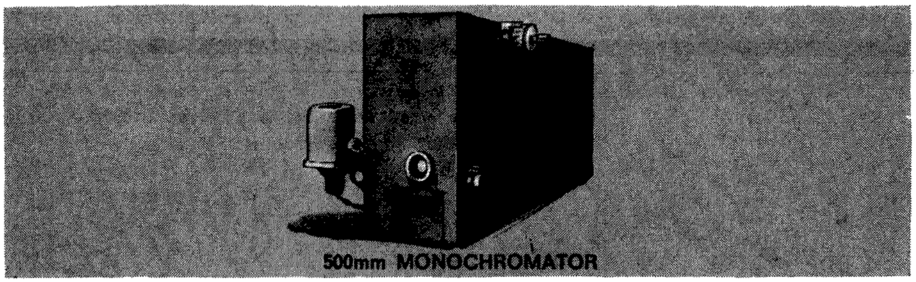

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edited by S. Coffey, M.Sc. (London), D.Sc. (Leyden). Formerly of I.C.I. Dyestuffs Division, Blackley, Manchester. Assisted by an Advisory Board of prominent scientists.

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