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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA
Vol. 28, No. 6, June 1963

THE APPLICABILITY OF THE "STRAIGHT-LINE METHOD" OF ASMUS IN THE DETERMINATION OF THE COMPOSITION OF POLYNUCLEAR COMPLEXES

The straight-line method of ASMUS was originally developed for the determination of n in mononuclear complexes of the general form AB_n ($n \geqq 1$). In the present investigation it is demonstrated that the method also can be used for determining the value of n in polynuclear complexes of the form A_mB_n ($m > 1$). The method as suggested by ASMUS, is, however, not capable of distinguishing between mono- and polynuclear species. It is further shown, that the straight-line method can be applied for the determination of the value of m.

K. S. KLAUSEN AND F. J. LANGMYHR, *Anal. Chim. Acta*, 28 (1963) 501–505

A DIFFERENTIAL THERMAL ANALYSIS STUDY OF SOME ORGANIC ACIDS. I

The differential thermal analysis curves of 25 organic acids are presented. The acids thermally decomposed to give a series of endothermic peaks which were caused by such reactions as dehydration, decarboxylation, sublimation, decomposition, and phase transitions from the solid to the liquid state. An attempt has been made to provide information which can be employed to identify the acids by a single instrumental technique.

W. W. WENDLANDT AND J. A. HOIBERG, *Anal. Chim. Acta*, 28 (1963) 506–511

SPECTROPHOTOMETRIC STUDY OF N,N'-BIS(2-SULPHOETHYL)-DITHIO-OXAMIDE AS A REAGENT FOR PALLADIUM

N,N'-bis(2-sulphoethyl)dithio-oxamide forms two water-soluble yellow chelates with palladium(II), in strong hydrochloric acid solution or in buffered weak acid solution; with excess of reagent, a 1Pd:2R complex is always obtained. The absorption maximum occurs at 425 mμ in 6 *M* hydrochloric acid and at 382 mμ in buffered weak acid solution (pH 6.6). The colour is formed more slowly in strong acid solution, but there are fewer interferences. Relatively high concentrations of Co^{2+}, Ni^{2+} and Hg^{2+} can be tolerated, as well as smaller concentrations of Ir^{3+}, Rh^{3+} and Cr^{3+}. The molar absorption coefficients are 12,860 and 10,840 respectively in 6 *M* hydrochloric acid and buffered weak acid solution. The standard deviation in both cases is 0.004 absorbance units, *i.e.* 0.033 μg of Pd.

A. GOEMINNE, M. HERMAN, Z. EECKHAUT, *Anal. Chim. Acta*, 28 (1963) 512–518

A NEW UNIVERSAL COLOUR REAGENT FOR PAPER CHROMATOGRAPHY OF CATIONS

(in German)

In an investigation of 283 organic reagents, tetrahydroxyquinone was found to be a suitable colour reagent in the paper chromatography of inorganic ions from the points of view of universality and sensitivity; all the cations (26) investigated could be located in daylight. Individual cations usually give characteristic colours so that by comparison of colours and R_F-values, absolute identification is possible.

W. Bock-Werthmann, *Anal. Chim. Acta*, 28 (1963) 519–523

APPLICATION OF THE MNF CONTROLLED DC GENERATOR TO THE SPECTRAL ANALYSIS OF IMPURITIES IN LEAD

A method for the determination of impurities in lead is described. The sample is excited by the new MNF controlled arc generator. The method is suitable for determination of the following seven impurities into the ranges of concentration shown: Sb (50–5400 p.p.m.), As (20–1000 p.p.m.), Bi (10–940 p.p.m.), Cu (1–760 p.p.m.), Zn (8–280 p.p.m.), Ag (5–160 p.p.m.) and Sn (5–1800 p.p.m.). The average square error is 3.0%.

J. L. Jiménez Seco, F. Burriel Martí, J. M. Sistiaga and A. de la Cuadra Herrera, *Anal. Chim. Acta*, 28 (1963) 524–535

THE FORMATION OF HIGHLY FLUORESCENT ZINC PHOSPHATE IN THE PRESENCE OF URANIUM AND ITS APPLICATION TO THE DIRECT FLUORIMETRY OF URANIUM IN AQUEOUS MEDIA

The formation and composition of highly fluorescent zinc phosphates in the presence of traces of uranium were investigated and a direct fluorimetric determination of uranium in aqueous media was developed, based on the formation of finely dispersed and stabilized fluorescent precipitates. The standard deviation for 20 μg of uranium in 25 ml is 5%; with the fluorimeter described, 10^{-2} μg of uranium per ml can be determined with an error of 50%. The method is very selective and can be employed for analysis of uranium in ores; it is less sensitive than conventional fluorimetry of fused alkali fluorides but is much simpler and faster. Interferences can often be eliminated by suitable masking reactions.

G. Alberti and A. Saini, *Anal. Chim. Acta*, 28 (1963) 536–542

DETERMINATION OF FLUORINE IN IRON ORE AND APATITE

A method is described for the determination of fluorine in iron ores, apatites and phosphate rocks, based on ion exchange on Dowex 2-X10 resin, and elution with strong hydrochloric acid. The determination is completed by a modified zirconium–eriochrome cyanine R spectrophotometric procedure.

Ö. S. GLASÖ, *Anal. Chim. Acta*, 28 (1963) 543–550

INVESTIGATIONS ON THE DEVELOPMENT OF A SCHEME OF SILICATE ANALYSIS BASED PRINCIPALLY ON SPECTROGRAPHIC AND ION-EXCHANGE TECHNIQUES

An attempt is made to integrate into an analytical "scheme" a series of investigations on the complete analysis of the naturally occurring silicates. Emphasis is placed on simplicity, high sensitivity (if necessary), wide element coverage, speed and satisfactory accuracy. The analytical operations involve ion exchange, solvent extraction and spectrochemical techniques. Observations are made on the following elements: Ag, Al, Au, Ba, Bi, Ca, Cd, Ce, Cs, Cu, Fe, Ga, In, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, Pb, Pd plus other elements of the platinum group, Rb, Sc, Si, Sn, Sr, Ti, Tl, V, Y, Zn and Zr.

L. H. AHRENS, R. A. EDGE AND R. R. BROOKS, *Anal. Chim. Acta*, 28 (1963) 551–573

THE OXYGEN FLASK IN QUALITATIVE ORGANIC ANALYSIS: DETECTION OF NITROGEN

(Short Communication)

A. D. CAMPBELL AND M. H. G. MUNRO, *Anal. Chim. Acta*, 28 (1963) 574–576

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(Short Communication)

G. CURTHOYS AND W. BRISLEY, *Anal. Chim. Acta*, 28 (1963) 577–579

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(Short Communication)

A. K. RAY, *Anal. Chim. Acta*, 28 (1963) 580–583

BROMINATION OF SOME 8-QUINOLINOLS

(Short Communication)

A. CORSINI AND R. P. GRAHAM, *Anal. Chim. Acta*, 28 (1963) 583–585

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o-HYDROXYACETOPHENONEOXIME AS AN ANALYTICAL REAGENT.

PART III. DETERMINATION AND SEPARATION OF PALLADIUM

(Short Communication)

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(Short Communication)

J. S. HETMAN, *Anal. Chim. Acta*, 28 (1963) 588–590

A METHOD FOR RADIOCHEMICAL SEPARATION OF MOLYBDENUM

(Short Communication)

S. M. QAIM AND F. D. S. BUTEMENT, *Anal. Chim. Acta*, 28 (1963) 591–592

THE APPLICABILITY OF THE "STRAIGHT-LINE METHOD" OF ASMUS IN THE DETERMINATION OF THE COMPOSITION OF POLYNUCLEAR COMPLEXES

K. S. KLAUSEN AND F. J. LANGMYHR

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(Received November 13th, 1962)

A new method for determining the composition of weak complexes was published recently by ASMUS[1]. He considered equilibria of the form:

$$A + nB \rightleftharpoons AB_n \tag{1}$$

and applied his method to establish the value of n. According to Asmus, n may be an integer or a fraction*.

While the applicability of the straight-line method to mononuclear systems seemed obvious, it was not clear whether it also could be used for determining the composition of polynuclear complexes.

It was therefore regarded of interest to study the applicability of the method to equilibria of the form:

$$mA + nB \rightleftharpoons A_mB_n \quad (m > 1;\, n \geqq 1) \tag{2}$$

THEORY

The theoretical considerations are based on equation (2). The designations adopted are those introduced by ASMUS[1].

Into a series of volumetric flasks of volume V a constant volume v_0 of a standard solution of A (concentration a_0) and varying volumes v of a standard solution of B (concentration b_0) are transferred. The pH is adjusted, an inert salt solution is added and the mixtures are diluted to volume. The extinctions are finally measured at a suitable wavelength.

The initial concentrations of A and B are:

$$a = a_0v_0/V \text{ and } b = b_0v/V \tag{3}$$

According to the law of mass action:

$$\frac{[A]^m[B]^n}{[A_mB_n]} = K \tag{4}$$

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* The theoretical considerations made by ASMUS[1] are based on the assumption that the coefficients before A and AB_n (equation (1)) do not differ from unity. In the summary of the same paper ASMUS, however, states that n may also be a fraction. A discrepancy was found to exist between these two statements. If n were a fraction, *e.g.* $\frac{1}{2}$, then $A + \frac{1}{2}B \rightleftharpoons AB_{\frac{1}{2}}$.

The straight-line method is based on the photometric measurement of the complex formed between A and B. In the present case the compound $AB_{\frac{1}{2}}$ has no reality, and the complex measured could therefore only be A_2B, which in turn presupposes the equilibrium $2A + B \rightleftharpoons A_2B$. It was therefore concluded that n may only assume values $\geqq 1$.

The equilibrium concentrations of the reactants are:

$$[\mathrm{A}] = a - m[\mathrm{A}_m\mathrm{B}_n] \tag{5}$$

$$[\mathrm{B}] = b - n[\mathrm{A}_m\mathrm{B}_n] = b - \frac{n}{m}(a - [\mathrm{A}]) \tag{6}$$

According to the Beer–Lambert law:

$$[\mathrm{A}_m\mathrm{B}_n] = \frac{E}{\varepsilon d} \tag{7}$$

in which E = extinction, ε = the molar extinction coefficient and d = light path in cm.

By combining equations (4), (5), and (7):

$$(a - m\frac{E}{\varepsilon d})^m[\mathrm{B}]^n = K\frac{E}{\varepsilon d} \tag{8}$$

Equation (8) can be transformed into:

$$\left[a^m - \binom{m}{1}a^{m-1}\frac{mE}{\varepsilon d} + \binom{m}{2}a^{m-2}\left(\frac{mE}{\varepsilon d}\right)^2 - \ldots + (-1)^m\left(\frac{mE}{\varepsilon d}\right)^m\right][\mathrm{B}]^n = K\frac{E}{\varepsilon d} \tag{9}$$

in which $\binom{m}{1}$, $\binom{m}{2}$ etc. are the binomial coefficients. Expression (9) can again be written, considering that $\binom{m}{1} = m$:

$$\frac{1}{[\mathrm{B}]^n} = \frac{a^m\varepsilon d}{K}\left[\frac{1}{E} + \binom{m}{2}\left(\frac{m}{a\varepsilon d}\right)^2 E - \binom{m}{3}\left(\frac{m}{a\varepsilon d}\right)^3 E^2 + \ldots \right.$$
$$\left. + (-1)^m\left(\frac{m}{a\varepsilon d}\right)^m E^{m-1}\right] - \frac{m^2a^{m-1}}{K} \tag{10}$$

By introducing equations (3), (6), and assuming, as was done by ASMUS, that $[\mathrm{A}_m\mathrm{B}_n] \ll b$:

$$\frac{1}{v^n} = \frac{a_0{}^m v_0{}^m b_0{}^n \varepsilon d}{V^{n+m}K} X_m - \frac{m^2}{K}\left(\frac{a_0v_0}{V}\right)^{m-1}\left(\frac{b_0}{V}\right)^n \tag{11}$$

in which:

$$X_m = \frac{1}{E} + \binom{m}{2}\left(\frac{m}{a\varepsilon d}\right)^2 E - \binom{m}{3}\left(\frac{m}{a\varepsilon d}\right)^3 E^2 + \ldots + (-1)^m\left(\frac{m}{a\varepsilon d}\right)^m E^{m-1} \tag{12}$$

Expressing $1/v^n$ graphically as a function of X_m for different sets of (m,n), a straight line would be expected for the set corresponding to the actual m and n of equilibrium (2).

For $m = 1$, equation (11) becomes identical with that developed by ASMUS and used by him as the basis for the construction of curves. For these mononuclear, systems the curves plotted for different values of n normally differ considerably, and the correct value of n can easily be detected.

To elucidate the applicability of the straight-line method to polynuclear systems, equation (12) was studied in more detail after making some rearrangements. To avoid the introduction of an extinction coefficient, X_m was replaced by $Y_m/\varepsilon d$. By introducing equation (7), in which $[\mathrm{A}_m\mathrm{B}_n]$ was replaced by Z, equation (12) was transformed into:

$$Y_m = \frac{1}{Z} + \binom{m}{2}\frac{m^2}{a^2}Z - \binom{m}{3}\frac{m^3}{a^3}Z^2 + \ldots + (-1)^m\frac{m^m}{a^m}Z^{m-1} \tag{13}$$

In this equation, the first fraction $1/Z$ is the dominating quantity, while the contribution from the following fractions is small, owing to the small value of Z in relation to the value of a. The consequence of this is that the form and position of the curves are determined mainly by the values of n. A straight line would thus be expected for the correct value of n, irrespective of the value of m.

The straight-line method therefore seemed applicable for the determination of n in complexes of the general form A_mB_n ($m,n \geqq 1$). It should be noted that the method as suggested by ASMUS, is not capable of distinguishing between mono- and polynuclear species.

As described above, the value of n is found experimentally by using a constant concentration of A and varying amounts of B. If a constant concentration of B and different amounts of A are applied, a straight line would be obtained for the correct value of m. If one and only one complex is predominant in the two series of solutions, the composition of this complex is given by the set (m, n). Very often, however, the composition changes in going from an excess of A to an excess of B, and in these cases the n and m values determined do not belong to the same complex.

EXPERIMENTAL

It was considered of interest to try to verify experimentally the conclusions reached in the theoretical part. For this purpose the straight-line method was applied to the system iron(III)–chrome azurol S, the reactants being designated A and B, respectively. Two series of solutions with the same pH were prepared, one with a constant concentration of iron(III) and varying concentrations of the ligand, and another with a constant amount of chrome azurol S and different amounts of iron(III). The experimental details are given in the text to Tables I and II, and the resulting curves are reproduced in Figs. 1 and 2. From Fig. 1 it is seen that a straight line was obtained for $n = 1$. The form and position of this line were not influenced by different values of m. According to ASMUS, the composition of the complex would be FeCh. By using

TABLE I

THE USE OF THE STRAIGHT-LINE METHOD FOR THE SYSTEM IRON(III)–CHROME AZUROL S

$V = 100$ ml, $a = 4 \cdot 10^{-5}$ M, $b_0 = 10^{-3}$ M, ionic strength 0.10 M (KCl), pH = 3.40, wavelength 570 mμ, 5.000-cm cells. All solutions were measured against a blank of distilled water. Ligand solution added to iron(III) solution. The calculations were based on equations (11) and (12).

Volume (in ml) of ligand standard solution	*Extinction total*	*Correction for the amount of ligand added*	*Extinction corrected*
0.10	0.132	0.036	0.096
0.13	0.166	0.047	0.119
0.15	0.197	0.054	0.143
0.17	0.218	0.061	0.157
0.21	0.257	0.076	0.181
0.25	0.309	0.091	0.218
0.33	0.384	0.120	0.264
0.40	0.430	0.146	0.284

TABLE II

THE USE OF THE STRAIGHT-LINE METHOD FOR THE SYSTEM IRON(III)–CHROME AZUROL S

$V = 100$ ml, $a_0 = 10^{-3}$ M, $b = 10^{-5}$ M, ionic strength 0.10 M (KCl), pH = 3.50, wavelength 590 mμ, 5.000-cm cells. Measured against a blank of 10^{-5} M chrome azurol S solution containing inert salt and adjusted to pH 3.50. Ligand solution added to iron(III). The calculations were based upon equations (11) and (12), and the molar extinction coefficient $\varepsilon = 0.72 \cdot 10^5$.

Volume (in ml) of iron(III) standard solution	*Extinctions*
0.10	0.048
0.12	0.065
0.15	0.104
0.20	0.156
0.25	0.228
0.33	0.344
0.50	0.540

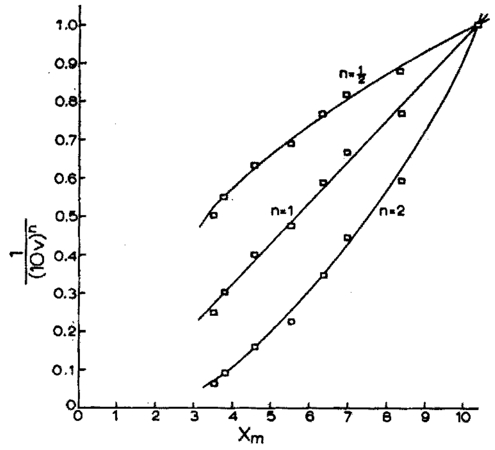

Fig. 1. The use of the straight-line method for the system iron(III)–chrome azurol S (excess of iron(III)).

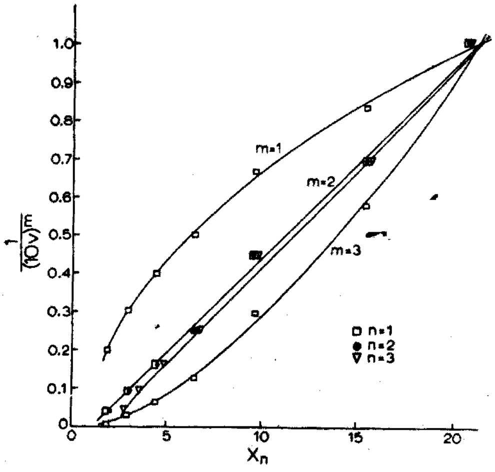

Fig. 2. The use of the straight-line method for the system iron(III)–chrome azurol S (excess of chrome azurol S).

other experimental methods, the authors found the composition to be Fe_2Ch (the results of the authors' investigations will be published later).

Fig. 2 shows a straight line for $m = 2$, indicating, according to ASMUS, the composition Fe_2Ch. From other measurements, however, the correct composition was determined by the authors to be Fe_2Ch_2.

SUMMARY

The straight-line method of ASMUS was originally developed for the determination of n in mononuclear complexes of the general form AB_n ($n \geqq 1$). In the present investigation it is demonstrated that the method also can be used for determining the value of n in polynuclear complexes of the form A_mB_n ($m > 1$). The method as suggested by ASMUS, is, however, not capable of distinguishing between mono- and polynuclear species. It is further shown, that the straight-line method can be applied for the determination of the value of m.

RÉSUMÉ

La méthode d'ASMUS ("straight-line method") appliquée primitivement à la détermination de la composition de complexes mononucléaires du type AB_n ($n \geqq 1$) peut également servir à la détermination de n dans des complexes du type A_mB_n ($m > 1$). Cependant la méthode proposée par ASMUS ne permet pas de faire la distinction entre les complexes mono- et polynucléaires. Il est ensuite démontré que cette méthode permet de déterminer la valeur de m.

ZUSAMMENFASSUNG

Die Geraden-Methode von ASMUS wurde ursprünglich für die Bestimmung von n in mononuklearen Komplexen der allgemeinen Form AB_n ($n \geqq 1$) entwickelt. Es wird gezeigt, dass diese Methode auch zur Bestimmung von n in polynuklearen Komplexen der Form A_mB_n ($m > 1$) angewandt werden kann. Die Methode, wie sie von ASMUS vorgeschlagen wurde, lässt jedoch nicht zwischen mono- und polynuklearen Verbindungen unterscheiden. Es wird ferner gezeigt, dass die Geraden-Methode auch zur Bestimmung des Wertes m verwendet werden kann.

REFERENCE

[1] E. ASMUS, *Z. Anal. Chem.*, 178 (1960) 104.

A DIFFERENTIAL THERMAL ANALYSIS STUDY OF SOME ORGANIC ACIDS. PART I

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(Received November 19th, 1962)

Although a number of organic compounds have been characterized by differential thermal analysis (DTA)[1-6], only meagre information is available on the organic acids. Previous qualitative studies have included the following acids: stearic[7]; salicylic, oxalic, tartaric, benzoic, and substituted benzoic acids[3,5]; amino acids[8]; and alginic acid[9]. More quantitative studies have been made on the phase transitions of benzoic and salicylic acids by VASSALLO AND HARDEN[10] and BARRALL AND ROGERS[11].

In an attempt to provide additional information which can be employed to "fingerprint" organic acids, a differential thermal analysis study was undertaken in the hope that it would be useful for the detection and identification of these compounds. Although the technique of DTA is essentially a qualitative one, if the number of variables are controlled, a fair degree of accuracy and precision can be obtained. To maintain controlled conditions, a commercially available DTA apparatus was employed, the Deltatherm. With this apparatus, it should be possible to establish reproducible conditions in different laboratories and thus increase the usefulness of the technique.

EXPERIMENTAL

Reagents

The highly purified oxalic, malonic, succinic, glutaric, sebacic, glycolic, DL-malic, D-tartaric, and citric acids were obtained from Professor R. C. Wilhoit, New Mexico Highlands University, Las Vegas, New Mexico. These samples were purified for heat-of-combustion studies and were of a *ca.* 99.8% purity.

The other compounds were obtained from Eastman Organic Chemicals, Rochester, N.Y.

Apparatus

The apparatus employed was the Deltatherm, manufactured by Technical Equipment Corp., Denver, Colo. Four samples were pyrolyzed per run, using a dynamic argon gas furnace atmosphere. A "sandwich"-type sample packing was employed which consisted of a 100-mg layer of previously ignited alumina, 100 mg of the organic acid, and 200 mg of alumina. The bead of the Chromel–Alumel thermocouple junction was positioned in the center of the organic acid layer. A heating rate of 10 ± 1° per min was employed on all runs.

Several of the acids were studied in the DTA–gas evolution (GE) apparatus that has previously been described[12]. About 30 mg of sample was pyrolyzed in a dynamic helium atmosphere at a heating rate of about 10° per min.

RESULTS AND DISCUSSION

The DTA thermograms are given in Figs. 1–5. The curves are exact tracings of the actual curves with the temperature indicated by the 50° markers. The DTA–GE curves are not reproduced here. Maximum peak temperatures for the acids are listed in Table I.

TABLE I

ENDOTHERMIC PEAK MAXIMA TEMPERATURES FOR THE ORGANIC ACIDS

Acid	*Curve no.*	*Peak temperatures (°)*
Oxalic dihydrate	1A	110, 120, 125, 150, 195
Malonic	1B	105, 160, 190, 290
Succinic	1C	195, 255
Glutaric	1D	75, 115, 255, 300
Citric	2A	170, 185, 210
DL-Malic	2B	150, 230, 285
D-Tartaric	2C	180, 230
Sebacic	2D	155
Glycolic	2E	85, 95, 335
Diphenylacetic	3A	155, 330
m-Methylphenoxyacetic	3B	105, 295
1-Naphthaleneacetic	3C	150, 330
2,4-Dichlorophenoxyacetic	3D	160, 175, 325
2,4,5-Trichlorophenoxyacetic	3E	175, 330
m-Chlorobenzoic	4A	165, 265
p-Chlorobenzoic	4B	260, 280
o-Chlorobenzoic	4C	145, 255
m-Iodobenzoic	4D	205, 280
p-Iodobenzoic	4E	290
p-Bromobenzoic	4F	275
2,3,5-Triiodobenzoic	5A	230, 350
p-Fluorobenzoic	5B	195, 245
p-Aminobenzoic	5C	195, 240
Fumaric	5D	310
m-Nitrobenzoic	5E	95, 165, 325, 425*

* Exothermic peak.

In general, only endothermic peaks were observed for the acids, indicating the absence of oxidation reactions which were prevented by the argon gas atmosphere. The endothermic peaks were caused by such reactions as dehydration, decarboxylation, sublimation, decomposition, and phase transitions from the solid to the liquid state. The maximum peak temperatures for phase transitions were 10 to 30° higher than the reported fusion temperatures. However, due to the dynamic nature of the system, this was expected. Such behavior has previously been discussed in detail[10].

The only hydrated organic acid studied was oxalic acid dihydrate (Fig. 1A). A rather broad peak at about 110°, followed by the two sharp peaks at 120° and 125°, respectively, were caused by the dehydration reaction. This was also confirmed by the GE curve on this compound. The 195° peak was due to several reactions: (*a*) fusion of the acid (m.p. 189°), and (*b*) decomposition of the anhydrous acid to water, carbon dioxide, and carbon monoxide. Again, this was confirmed by the GE curve.

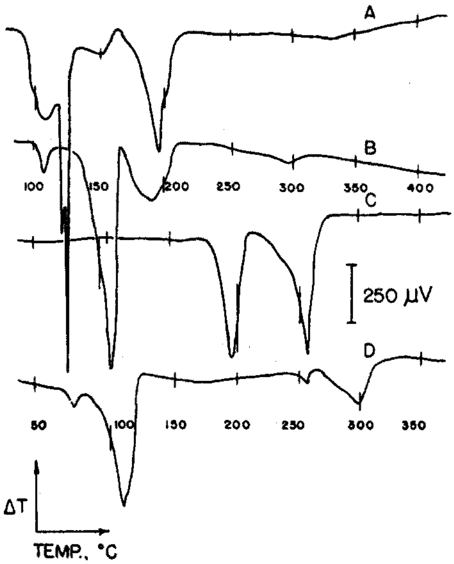
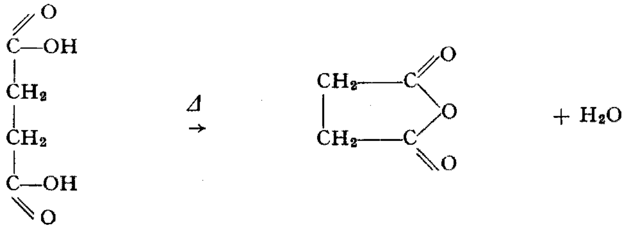


Fig. 1. DTA curves of organic acids. A, oxalic acid dihydrate; B, malonic acid; C, succinic acid; D, glutaric acid.

Malonic acid (Fig. 1B) exhibited a phase transition at about 105° as shown by the endothermic peak at this temperature. The 160° peak was caused by the fusion of the acid (m.p. 135.6°) followed by another peak at 190° which was probably caused by the decomposition of the acid to give acetic acid and carbon dioxide. The GE curve indicated that a gaseous component was evolved during the 190° peak but not during the 160° peak.

Succinic acid (Fig. 1C) gave two peaks, at 195° and 255°, respectively. The first peak was caused by the fusion of the acid (m.p. 181°) while the second peak was probably due to anhydride formation such as:



Because of the dynamic nature of the system, the anhydride probably decomposed as rapidly as it was formed.

Glutaric acid (Fig. 1D) had a small peak at 75° followed by a larger one at 115°. The 75° peak may be due to a phase transition since no GE peak was observed at this temperature. The 115° peak is definitely caused by the fusion of the acid (m.p. 98°). Again there is the possibility of anhydride formation and subsequent decomposition as indicated by the 255° and 300° peaks.

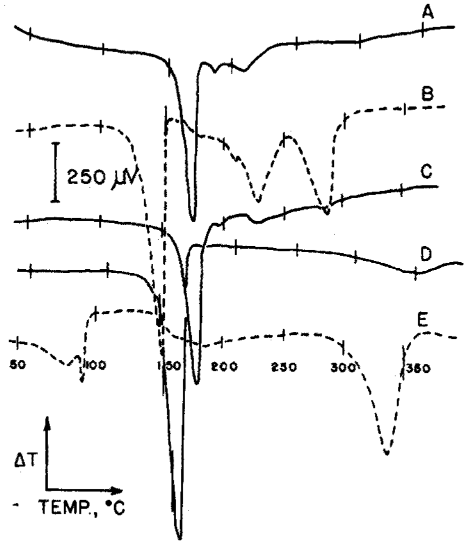


Fig. 2. DTA curves of organic acids. A, citric acid; B, DL-malic acid; C, D-tartaric acid; D, sebacic acid; E, glycolic acid.

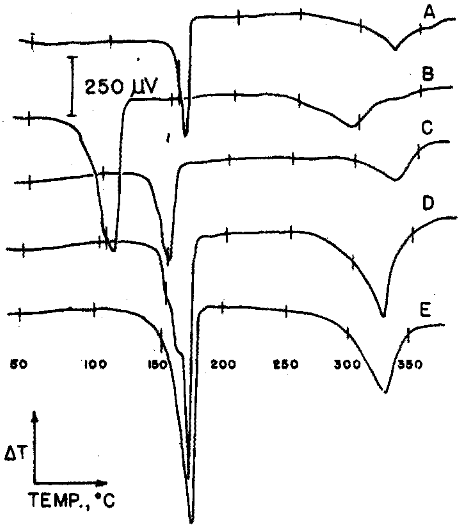


Fig. 3. DTA curves of organic acids. A, diphenylacetic acid; B, *m*-methylphenoxyacetic acid; C, 1-naphthaleneacetic acid; D, 2,4-dichlorophenoxyacetic acid; E, 2,4,5-trichlorophenoxyacetic acid.

The remaining dicarboxylic acids are given in Fig. 2. The first peak in each curve was caused by the fusion of the acid while the remainder of the peaks were caused by the decomposition of the liquid acids. The most stable of the dicarboxylic acids, based on peak maxima temperatures, was glycolic acid.

A number of substituted acetic acids are given in Fig. 3. Diphenyl- and 1-naphthaleneacetic acids (curves A and C, respectively) exhibited similar curves, differing by only 5° on the first peak temperature. The introduction of another chlorine atom into 2,4-dichlorophenoxyacetic acid did not change the curve very much. The 2,4-dichloro acid (curve D) had a shoulder peak at about 160° which was absent from the curve (curve E) of the 2,4,5-trichloro acid.

The changes in the curves caused by the position of the halogen atom in some of the isomeric chloro-, bromo-, and iodobenzoic acids are illustrated in Figs. 4 and 5. The three chlorobenzoic acids, *m*-chloro-, *p*-chloro-, and *o*-chloro- (Fig. 4, curves A, B, and C, respectively) gave three entirely different curves. Likewise, there was a pronounced difference between the curves for *m*-iodo- and *p*-iodobenzoic acids (Fig. 4, curves D and E, respectively). The curves obtained for the isomeric acids containing different halogens do not show as great a change. Thus, the *p*-chloro-, *p*-bromo-, and *p*-iodobenzoic acids (Fig. 4, curves B, E, and F, respectively) all gave peaks in the 200–300° range. However, *p*-chlorobenzoic acid had two peaks, *p*-iodobenzoic acid had a shoulder peak, and *p*-bromobenzoic acid had a single broad peak. *p*-Fluorobenzoic acid (Fig. 5, curve B) gave two peaks but at lower temperatures than the other three acids.

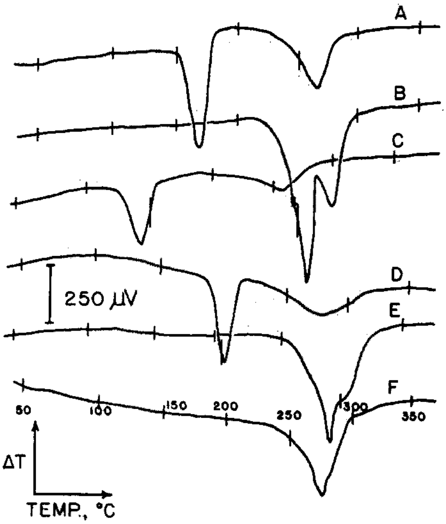


Fig. 4. DTA curves of organic acids. A, *m*-chlorobenzoic acid; B, *p*-chlorobenzoic acid; C, *o*-chlorobenzoic acid; D, *m*-iodobenzoic acid; E, *p*-iodobenzoic acid; F, *p*-bromobenzoic acid.

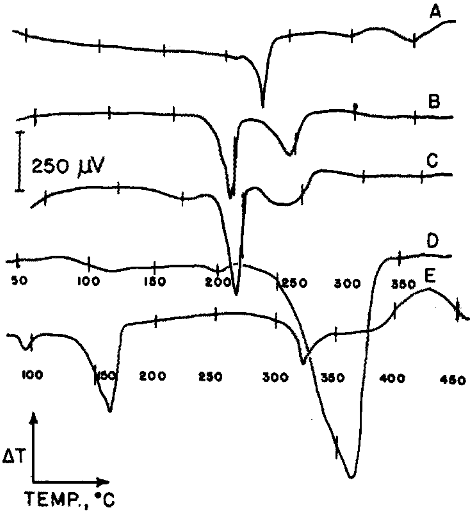


Fig. 5. DTA curves of organic acids. A, 2,3,5-triiodobenzoic acid; B, *p*-fluorobenzoic acid; C, *p*-aminobenzoic acid; D, fumaric acid; E, *m*-nitrobenzoic acid.

Only one of the acids studied gave an exothermic peak as well as endothermic peaks. This compound was *m*-nitrobenzoic acid (Fig. 5, curve E) which gave a broad exothermic peak centered at about 425°.

The large endothermic peak of fumaric acid (Fig. 5, curve D) was of interest. This acid gave by far the largest endothermic decomposition peak.

From the various curves presented here, it can be seen that DTA shows promise as a useful technique for the identification of organic acids. Of course, the curve itself is not unequivocal proof of a particular acid but it is, in many cases, a rapid method for the identification of the compound. Further studies are needed in order to determine the changes in peak temperature with the purity of the acid. By DTA, it may be possible to ascertain the purity, within certain limits, of the organic acids. Such a technique would be extremely useful from a quality control standpoint.

It is a pleasure to acknowledge the help of Dr. R. C. WILHOIT who supplied some of the organic acids.

SUMMARY

The differential thermal analysis curves of 25 organic acids are presented. The acids thermally decomposed to give a series of endothermic peaks which were caused by such reactions as dehydration, decarboxylation, sublimation, decomposition, and phase transitions from the solid to the liquid state. An attempt has been made to provide information which can be employed to identify the acids by a single instrumental technique.

RÉSUMÉ

Les auteurs présentent les courbes d'analyse thermique différentielle de 25 acides organiques. Les acides sont décomposés thermiquement en donnant une série de pics endothermiques, dus à des réactions telles que déshydratation, décarboxylation, sublimation, décomposition et passage de l'état solide à l'état liquide.

ZUSAMMENFASSUNG

Es werden die Kurven der Differential-Thermoanalysen von 25 organischen Säuren gegeben. Bei der thermischen Zersetzung wurde eine Anzahl von endothermischen ,,peaks" beobachtet, die auf Reaktionen wie Dehydratisierung, Dekarboxylierung, Sublimation, Zersetzung und Phasenänderung (fest — flüssig) zurückgeführt werden.

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SPECTROPHOTOMETRIC STUDY OF N,N'-BIS(2-SULPHOETHYL)-DITHIO-OXAMIDE AS A REAGENT FOR PALLADIUM

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In recent investigations several substituted dithio-oxamides[1-5] have been proposed as reagents for palladium. JACOBS AND YOE[6] have examined the complex formation of N,N'-bis(2-sulphoethyl)dithio-oxamide with copper(II), cobalt(II) and nickel(II).

It has been found that this reagent forms different yellow, water-soluble chelates with palladium(II). The color sensitivity and stability of some of these chelates, formed between 1 mole of palladium and 2 moles of the reagent, compare favourably with those of several reactions with other substituted dithio-oxamides. The reaction can be carried out in strong hydrochloric solution as well as in buffered weak acid solution, and does not require strict control of variables. The reagent has the further advantage of being water-soluble.

In this paper the spectrophotometric determination of palladium with the above reagent is studied.

EXPERIMENTAL

Apparatus

Absorbance curves were recorded with a Beckman Model DK1 spectrophotometer. Matched silica cells of 1 cm light path were used. Absorbances at a definite wavelength were measured with a Hilger Uvispek spectrophotometer.

Reagents

Standard palladium solution. This was prepared by dissolving 4 g of palladium(II) chloride (Carlo Erba, R. P.) in 200 ml of distilled water, with sufficient hydrochloric acid to give a final solution about 0.9 *M* in the acid. The palladium content was determined gravimetrically by precipitation with dimethylglyoxime. The standard solution contained 11.74 mg of palladium per ml. Working solutions were prepared as needed, by volumetric dilution of this stock solution.

Reagent solution. A 0.02 *M* solution of N,N'-bis(2-sulphoethyl)dithio-oxamide diammonium salt was prepared by dissolving 7.410 g in 1000 ml of distilled water. The stock solution is stable for at least 2 months. All other solutions were made by diluting this standard solution.

Buffer solutions. Buffer solutions according to Sørensen were made by mixing adequate amounts of a 0.1 *M* citric acid solution with a 0.2 *M* solution of sodium dihydrogen phosphate as given by KORDATZKI[7].

Solutions of foreign ions. Stock solutions containing 1 mg per ml of the ion were prepared from nitrates or chlorides of the metal.

Complex formation between palladium(II) and N,N-bis-(2-sulphoethyl)dithio-oxamide

Absorbance curves obtained in strong hydrochloric acid solution (6 *M*) are shown in Fig. 1. The reagent shows an absorption maximum at 302 mμ and a negligible extinction above 400 mμ. Sharp maxima at 386 mμ and 280 mμ are found when 1 mole of palladium(II) is added to 1 mole of reagent. For an 1:2 ratio a flat maximum occurs at 425 mμ and a sharp one at 283 mμ. The curves obtained in a buffered weak acid solution at pH 6.6 are represented in Fig. 2. In this solution the maxima are shifted to the UV region. For an 1:1 ratio of the metal and ligand, the maximum is found at 275 mμ; for one mole of Pd with 2 moles of reagent, a flat maximum occurs at 382 mμ and a second very pronounced maximum at 281 mμ. The composition of the complex formed was established by the continuous variations method of JOB as modified by VOSBURG AND COOPER[8] and the mole ratio method of YOE AND JONES[9]. In strong acid solution, absorbance measurements were made at 425 mμ and 386 mμ. It can be seen from Figs. 3 and 4 that two complexes are formed, the first corre-

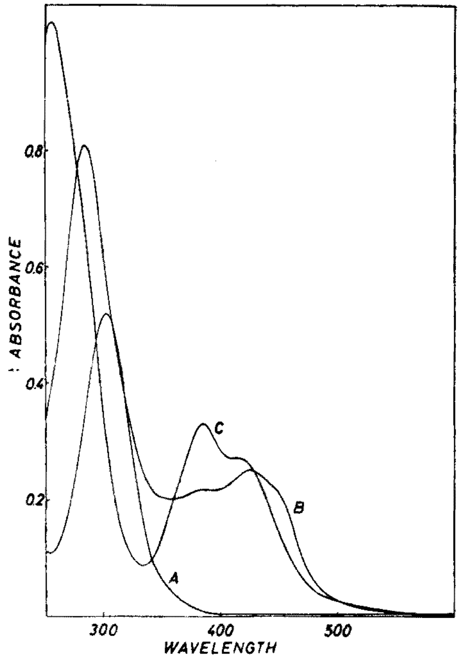

Fig. 1. Absorbance curves for Pd–reagent mixtures in strong hydrochloric acid solution. A, reagent $5 \cdot 10^{-5}$ *M*; B, reagent $5 \cdot 10^{-5}$ *M*–Pd Cl_2 $2.5 \cdot 10^{-5}$ *M*; C, reagent $5 \cdot 10^{-5}$ *M*–PdCl_2 $5 \cdot 10^{-5}$ *M*.

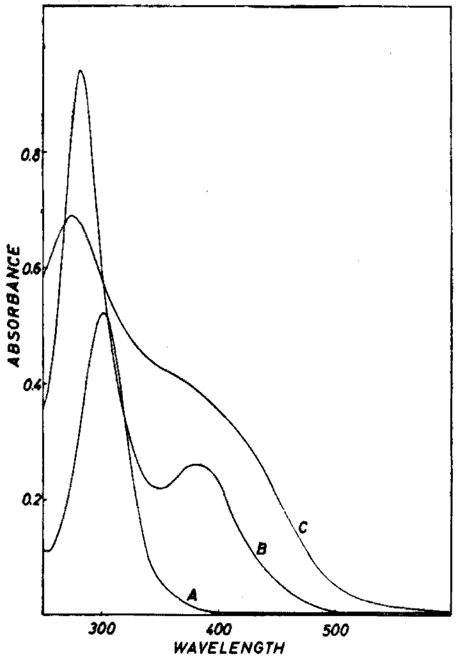

Fig. 2. Absorbance curves for Pd–reagent mixtures at pH = 6.6. A, reagent $5 \cdot 10^{-5}$ *M*; B, reagent $5 \cdot 10^{-5}$ *M*–Pd Cl_2 $2.5 \cdot 10^{-5}$ *M*; C, reagent $5 \cdot 10^{-5}$ *M*–Pd Cl_2 $5 \cdot 10^{-5}$ *M*.

sponding to a ratio 1Pd:1R, the second to a ratio 1Pd:2R in the presence of excess reagent.

In buffered weak acid solution, measurements were made at 382 mμ and 350 mμ. Figs. 5 and 6 show that also in this medium the two complexes 1Pd:1R and 1Pd:2R are formed. It can be shown that the 1:2 complex is the most stable and is formed always in the presence of excess reagent. It is therefore the most suitable for the spectrophotometric determination of palladium.

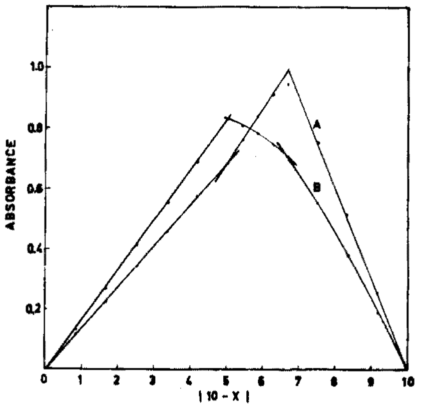

Fig. 3. Continuous variations method. A, $\lambda = 425$ mμ; B, $\lambda = 386$ mμ.

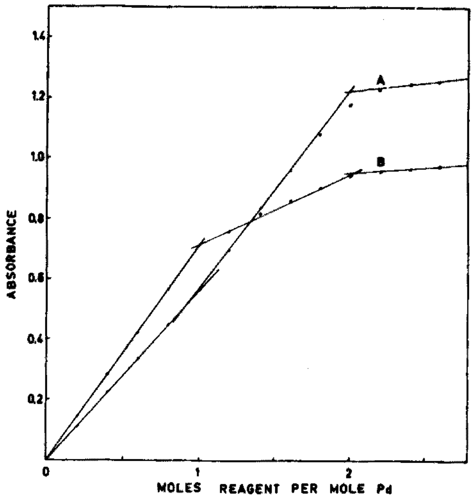

Fig. 4. Mole ratio method. A, $\lambda = 425$ mμ; B, $\lambda = 386$ mμ.

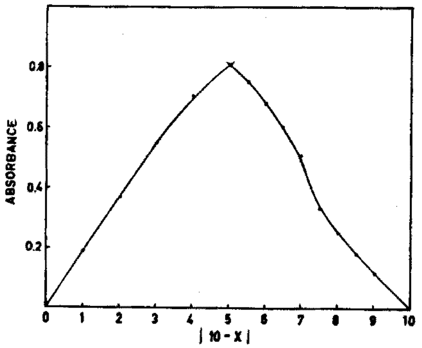

Fig. 5. Continuous variations method at pH 6.6 and 350 mμ.

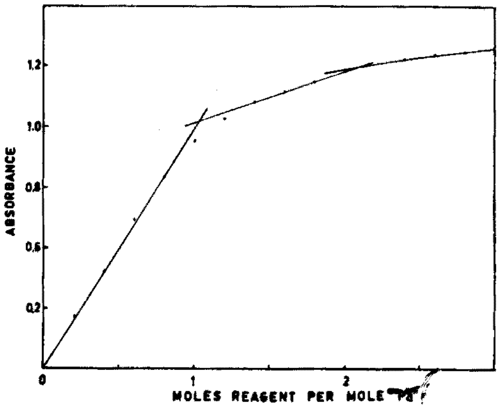

Fig. 6. Mole ratio method at pH 6.6 and 382 mμ.

(A) Determination of palladium in strong hydrochloric acid solution

The absorbance curve (Fig. 1) shows a maximum at 425 mμ. As the reagent solution has a slight extinction at this wavelength all absorbances were measured against a reagent blank of the same acidity.

Effect of hydrochloric acid concentration. In order to examine the effect of acid concentration, different samples were prepared, each containing 5 ml of $5 \cdot 10^{-4}$ *M* reagent and 2.5 ml of $5 \cdot 10^{-4}$ *M* $PdCl_2$ and different amounts of a 10 *M* hydrochloric acid solution. The samples were diluted to 50 ml with twice-distilled water, the final concentration of acid being varied from 0.5 to 8 *M*.

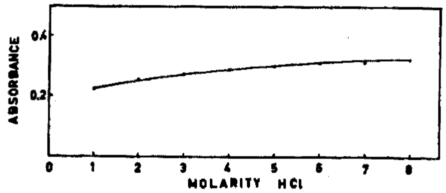

Fig. 7. Effect of hydrochloric acid concentration on Pd complex at 425 mμ.

Fig. 7 shows that the absorbance does not rise remarkably above a hydrochloric acid concentration of 5 *M*. For practical reasons, a final concentration of 6 *M* was chosen.

Effect of reagent concentration. Samples were prepared containing 5 ml of $5 \cdot 10^{-4}$ *M* $PdCl_2$, 30 ml of 10 *M* hydrochloric acid, different amounts of reagent solution, and distilled water up to 50 ml. The final concentrations of the reagent and the corresponding absorbances are given in Table I. It can be seen that for constant absorbances, a four-fold or greater excess of reagent is required.

TABLE I

EFFECT OF REAGENT CONCENTRATION

Pd concn. $5 \cdot 10^{-5}$ *M*

Final reagent concn.	*Absorbance (425 mμ)*
$1.0 \cdot 10^{-4}$	0.597
$1.5 \cdot 10^{-4}$	0.637
$2.0 \cdot 10^{-4}$	0.642
$4.0 \cdot 10^{-4}$	0.643
$12.0 \cdot 10^{-4}$	0.644
$20.0 \cdot 10^{-4}$	0.643

Effect of time on colour formation. Maximum absorbance is reached after 30 min, and remains constant for 30 min. After this time the absorbance decreases very slowly. This can be seen from Table II where the absorbances are noted, measured after different times against a reagent blank.

Conformity to Beer's law and sensitivity. Beer's law was examined using a series of samples with a reagent concentration of $2 \cdot 10^{-3}$ *M*, and was found to be obeyed over the range 1 to 12 μg per ml. The average molar extinction coefficient was found to be $\varepsilon = 12{,}860$ with a mean deviation of 0.44%.

This corresponds to a sensitivity of 0.0083 μg/ml as defined by SANDELL[10].

Recommended procedure and standard deviation. To the sample, containing 1 to 10 µg of palladium, 30 ml of 10 *M* hydrochloric acid is added, followed by 5 ml of $2 \cdot 10^{-2}$ *M* reagent solution. The sample is diluted to 50 ml with twice-distilled water, and the absorbance is measured after 30 min at 425 mµ against a reagent blank containing the same concentration of acid.

TABLE II

STABILITY OF COLOUR

Time (min)	*Absorbance*
6	0.640
10	0.645
15	0.648
30	0.649
60	0.649
90	0.647
120	0.646
150	0.643
180	0.639

TABLE III

EFFECT OF FOREIGN IONS

Amount of Pd in the reference solution: 267 µg

Foreign ion (X)	*Ratio X:Pd*	*Palladium found (µg)*	*% Error*
Pt^{4+}	0.2	272	+ 1.9
Rh^{3+}	5.0	280	+ 4.8
Ir^{3+}	7.5	276	+ 3.3
Ru^{3+}	0.4	273	+ 2.2
Au^{3+}	0.8	271	+ 1.5
Co^{2+}	153.0	260	— 2.7
Fe^{3+}	0.2	272	+ 1.9
Ni^{2+}	38.0	271	+ 1.5
Cr^{3+}	3.8	271	+ 1.5
Cu^{2+}	0.16	278	+ 3.8
Hg^{2+}	191.0	267	0
Nitrate	280.0	268	+ 0.4
Sulphate	280.0	268	+ 0.4

Ten samples were measured in this way. The standard deviation was 0.004 absorption units, which corresponds to 0.033 µg of palladium per ml.

Effect of foreign ions. To test the influence of foreign ions on the colour, samples were prepared containing 5 ml of $2 \cdot 10^{-3}$ *M* reagent, 30 ml of 10 *M* hydrochloric acid and 267 µg of palladium. Varying amounts of suitable solutions of the diverse ions were added individually, and the solutions were diluted to 50 ml.

Table III gives the palladium concentration found, and the percentage error for different ratios of foreign ion to palladium. Cu^{2+}, Pt^{4+}, Ru^{3+}, Fe^{3+}, and Au^{3+} interfere badly. Less interfering are Rh^{3+}, Ir^{3+} and Cr^{3+}, while Ni^{2+}, Co^{2+}, Hg^{2+}, nitrate and sulphate ions can be present in a fifty-fold excess without great interference.

(B) Determination of palladium in buffered weak acid solution

In buffered weak acid solution the absorbance curve (Fig. 2) shows a maximum at 382 mμ. As the reagent blank shows an extinction of 0.549 at this wavelength, all measurements are carried out against a reagent blank in the same buffer solution at 392 mμ where the extinction is lower.

Effect of pH and color stability. In the presence of excess reagent, the absorbance remains practically constant in the pH range from 3 to 8. Therefore strict control of acidity is not required, and all measurements are made in a sodium phosphate–citric acid buffer at pH 6.6. At this value maximum absorbance is reached in less than 10 min. The color intensity remains constant for at least 5 h.

Conformity to Beer's law and sensitivity. Beer's law is obeyed over the range 0.5 to 8.5 μg Pd per ml. An average molar extinction coefficient $\varepsilon = 10,840$ was found with a mean deviation of 0.35%. The corresponding sensitivity, as defined by SANDELL, is 0.0098 μg per ml.

Recommended procedure and standard deviation. To the sample, containing 1 to 8 μg of palladium, 20 ml of the buffer pH 6.6 is added, followed by 5 ml of $2 \cdot 10^{-2}$ *M* reagent solution. The sample is diluted to 50 ml with twice-distilled water, and the absorbance is measured at 392 mμ against a reagent blank containing the same buffer.

Ten samples were measured in this way. The standard deviation was 0.004 absorption units, corresponding to 0.039 μg of Pd.

Effect of foreign ions. The effect of foreign ions was studied as described above. The results are summarized in Table IV. It can be seen that the interference at pH 6.6

TABLE IV

EFFECT OF FOREIGN IONS

Amount of Pd in the reference solution: 267 μg

Foreign ion (X)	*Ratio X:Pd*	*Palladium found (μg)*	*% Error*
Pt^{4+}	1.1	270	+ 1.1
Rh^{3+}	1.8	270	+ 1.1
Ir^{3+}	1.5	270	+ 1.1
Ru^{3+}	0.1	276	+ 3.4
Au^{3+}	1.5	271	+ 1.5
Co^{2+}	0.4	273	+ 2.2
Fe^{3+}	0.4	284	+ 6.3
Ni^{2+}	1.0	270	+ 1.1
Cr^{3+}	3.7	270	+ 1.1
Cu^{2+}	0.2	272	+ 1.9
Hg^{2+}	3.2	278	+ 4.1
Nitrate	300.0		<1
Sulphate	300.0		<1

of most cations is greater than for the reaction in strong acid solution. Therefore the latter medium must be preferred for practical applications, although the rate of colour formation is less.

SUMMARY

N,N′-bis(2-Sulphoethyl)dithio-oxamide forms two water-soluble yellow chelates with palladium(II), in strong hydrochloric acid solution or in buffered weak acid solution; with excess of reagent, a 1Pd:2R complex is always obtained. The absorption maximum occurs at 425 mμ in 6 *M* hydrochloric acid and at 382 mμ in buffered weak acid solution (pH 6.6). The colour is formed more slowly in strong acid solution, but there are fewer interferences. Relatively high concentrations of Co^{2+}, Ni^{2+} and Hg^{2+} can be tolerated, as well as smaller concentrations of Ir^{3+}, Rh^{3+} and Cr^{3+}. The molar absorption coefficients are 12,860 and 10,840 respectively in 6 *M* hydrochloric acid and buffered weak acid solution. The standard deviation in both cases is 0.004 absorbance units, *i.e.* respectively 0.033 and 0.039 μg of Pd.

RÉSUMÉ

Le N,N′-bis(2-sulphoethyl)dithio-oxamide forme avec le palladium aussi bien en milieu acide chlorhydrique concentré (6 *M* HCl) qu'en solution tampon de pH 6.6 deux complexes jaunes, solubles dans l'eau. En présence d'un excès de réactif on obtient toujours le complexe 1Pd:2R. Ce dernier complexe montre un maximum d'absorption à 425 mμ en 6 *M* HCl et à 382 mμ en solution tampon de pH 6.6. Les coefficients d'absorption sont respectivement 12,860 et 10,840.

ZUSAMMENFASSUNG

N,N′-bis(2-Sulphoethyl)dithio-oxamide bildet mit Palladium sowohl in stark salzsaurem Medium (6 *M* HCl) wie in einer schwach sauren Pufferlösung zwei wasserlösliche, gelb gefärbte Komplexe. Mit einem Übermasz Reagenz bekommt man immer den Komplex 1Pd:2R, der ein Absorptionsmaximum hat bei 425 mμ in HCl Medium und bei 382 mμ in einer schwach sauren Pufferlösung. Der molare Extinktionskoeffizient ist respektiv 12,860 und 10,840.

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EIN NEUES UNIVERSELLES ENTWICKLUNGSREAGENZ FÜR DIE PAPIERCHROMATOGRAPHIE VON KATIONEN

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(Eingegangen den 25. November, 1962)

Bei der Prüfung papierchromatographischer Methoden zur Anwendung auf die Aktivierungsanalyse zeigte sich der Mangel eines Reagenzes, das alle gebräuchlichen Kationen mit ausreichender Empfindlichkeit und ohne Komplikationen auf dem Papier anfärbt. Dieses Reagenz muss also Eigenschaften besitzen, die bei den in der anorganischen Chemie verwendeten organischen Reagenzien bisher nicht angestrebt wurden. Es sollte nämlich so wenig wie möglich spezifisch sein, *d.h.* es sollte mit möglichst *allen* Elementen eine intensive Färbung geben, um deren Flecke auf dem Papierchromatogramm zu lokalisieren. Die bisher vorgeschlagenen Farbreagenzien (siehe *Diskussion*) erfüllen diese Bedingung mehr oder weniger unvollständig.

Zur Gewinnung exakter Vergleichswerte wurden die gebräuchlichsten Kationen auf Chromatographiepapier mit 283 käuflichen organischen Reagenzien angefärbt und die Intensität der entstandenen Farbstoffe mit Hilfe einer automatischen Apparatur gemessen*. Bei dieser Untersuchung fielen *u.a.* die Eigenschaften des Tetrahydroxychinons auf, das bisher nur zur Bestimmung des Bariums verwendet wurde[1–4]. Wir prüften die Färbebedingungen dieser Verbindung auf Kationen und Anionen und bestimmten die Empfindlichkeit des Nachweises von den gebräuchlichsten 26 Kationen mit Tetrahydroxychinon unter den Bedingungen, wie sie bei der Papierchromatographie anorganischer Ionen vorliegen.

Anfärbung

Reagenzlösung. 200 mg Tetrahydroxychinon p.a. (Firma Merck, Darmstadt) wird in 100 ml Äthanol unter leichtem Erwärmen gelöst.

Mit Hilfe einer Sprühvorrichtung beliebiger Konstruktion besprüht man das *vollständig* getrocknete Chromatogramm gleichmässig mit der Reagenzlösung. Eine sorgfältige Trocknung des Chromatogramms vor dem Besprühen ist unbedingt notwendig, weil sonst das Chromatogramm eine dunkelbraune Färbung annimmt, die eine Wiederholung des Versuchs notwendig macht. Nach dem Besprühen mit der Reagenzlösung ist wieder die vollständige Verdunstung des Äthanols abzuwarten und dann das Chromatogramm über einer Schale mit konzentriertem Ammoniak zu dämpfen. Es ist nicht empfehlenswert, das Chromatogramm in einem geschlossenen Behälter stundenlang NH_3-Dampf auszusetzen. In der Regel ist die Anfärbung der

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* Eine Veröffentlichung der gesamten Ergebnisse dieser Untersuchung ist in Vorbereitung.

Kationen unmittelbar nach dem Dämpfen am stärksten. Nach längerer Lagerzeit verblassen die Farben etwas. Ein erneutes Besprühen mit dem Reagenz und erneutes Dämpfen lässt die Farben wieder erscheinen. Die Regeneration der Farben, indem man nur den Dämpfungsvorgang wiederholt, ist nicht ausreichend.

Empfindlichkeitsmessung. Die Empfindlichkeit der Farbreaktion wurde nicht durch Anfärbung aufgetropfter Salzlösungen auf Filtrierpapier geprüft, sondern es wurde ein echtes Chromatogramm mit abnehmenden Konzentrationen angefertigt und anschliessend mit dem Reagenz entwickelt. Dadurch wurde das Vortäuschen einer erhöhten Empfindlichkeit durch Anfärben der Anionen vermieden. Ausserdem ist die nunmehr erhaltene Empfindlichkeit realistischer, da bei der Papierchromatographie die Substanz immer etwas auseinandergezogen wird. Als Chromatographiepapier wählten wir das Papier Nr. 2040 a der Firma Schleicher und Schüll aus, das durch Waschen mit Säure von der Firma nachgereinigt war. Die Salzlösungen wurden mit geeichten Platinösen oder Glaskapillaren aufgetragen.

Als Steigflüssigkeit benutzten wir Butanol/5 N HNO_3 im Volumenverhältnis 7:1, die den besten Trenneffekt für möglichst viele der von uns untersuchten Kationen ergab.

Die Salzlösungen wurden nacheinander immer auf das Doppelte verdünnt, so dass 16 Konzentrationen vorlagen von $M/1$ bis $M/32768$. Es wurden also von jeder Salzlösung 16 verschiedene Konzentrationen geprüft, wenn die Löslichkeit keine obere Grenze setzte.

Volumeneichung

Zur Empfindlichkeitsbestimmung war das Volumen der Lösung zu ermitteln, das nötig ist, um einen Fleck mit bestimmtem Radius zu erzeugen. Zu diesem Zweck wurde auf dem gleichen Chromatographiepapier eine gefärbte Wassermenge aufgetropft und der mittlere Radius ausgemessen. Das zugehörige Volumen wurde durch Wägung bestimmt. Der Fehler, der durch Verdunstung während der Wägung auftritt, konnte vernachlässigt werden.

Wie zu erwarten, war das Volumen der aufgetropften Lösung proportional dem Quadrat der zugehörigen Radien (Tabelle I). Um einen Fleck mit dem Durchmesser von 3 mm auf dem Papier 2040 a (siehe oben) zu erzeugen, waren 3.6 µl Lösung erforderlich.

Anionen

Da sich auf einem fertigen Chromatogramm in der Regel die Anionen nicht an der

TABELLE I

VOLUMENEICHUNG

Volumen (µl)	*Mittlerer Radius, r (mm)*	*r^2 (mm^2)*
2.6	1.3	1.7
4.0	1.6	2.6
4.9	1.7	2.9
6.3	2.0	4.0
8.6	2.3	5.3
12.9	2.8	7.8
14.2	3.1	9.6
20.4	3.5	12.2

gleichen Stelle wie die dazugehörigen Kationen befinden, würde eine gleichzeitige Anfärbung der Anionen die Anzahl der Flecken unnötig erhöhen. Vorteilhafterweise färbt Tetrahydroxychinon von den gebräuchlichen Anionen nur Oxalat- und Sulfationen an. Die von uns getesteten Kationen wurden deshalb in Form ihrer Nitrate, Chloride oder Acetate aufgetragen. Auch bei unbekannten Substanzen ist eine Störung durch Anfärbung von Anionen bei entsprechender Auswahl der lösenden Säuren leicht zu vermeiden.

ERGEBNISSE

Die Empfindlichkeitsangaben (Tabelle II) beziehen sich auf das Gewicht des jeweiligen Elements, das nach der chromatographischen Trennung auf dem Papier eine im Tageslicht gerade noch sichtbare Farbreaktion auslöst. Dabei wurde ein Durchmesser des Ausgangsflecks von 3 mm zugrunde gelegt. Die Empfindlichkeit der Methode wurde für eine Betrachtung der Anfärbung innerhalb von 5 Minuten und nach *ca.* 1 Stunde berechnet.

TABELLE II

ANFÄRBUNGSEMPFINDLICHKEIT

Element	*Empfindlichkeit, nach < 5 min (µg)*	*Empfindlichkeit, nach ca. 1 Std. (µg)*
Li	0.3	0.6
Na	—*	1.0
K	—*	4.0
Rb	—*	10.0
Cs	—*	10.0
Be	0.1	0.1
Mg	0.07	0.1
Ca	0.03	0.2
Sr	0.06	0.03
Ba	0.05	0.01
Al	0.2	0.3
Sn	0.08	0.08
Pb	0.04	0.3
Sb	0.04	0.7
Bi	0.07	0.2
Cu	0.003	0.2
Zn	0.1	0.4
Cd	0.08	0.5
Hg	5.0	20.0
Y	0.1	0.06
La	0.05	2.0
Cr	0.07	0.3
Mn	0.005	0.08
Fe	0.04	0.01
Co	0.02	0.08
Ni	0.01	1.0

* Der Farbstoff bildet sich erst nach einiger Zeit.

Anfärbung durch Substanzen ähnlicher Konstitution

Bei Prüfung einiger organischer Reagenzien, die eine ähnliche Konstitution wie das Tetrahydroxychinon besitzen, erwiesen sich sämtliche Verbindungen als weniger geeignet. Die Anfärbungen durch *Kaliumrhodizonat* zeigten bei vielen Kationen einen ähnlichen Farbton wie die durch Tetrahydroxychinon, unterschieden sich aber wesentlich in der Intensität. Auffällig ist besonders die geringere Empfindlichkeit des Kaliumrhodizonats bei den Schwermetallen. Auch bei *Chloranilsäure* waren bei einzelnen Kationen gewisse Parallelen gegenüber dem Färbeverhalten des Tetrahydroxychinons zu entdecken, es überwiegen jedoch Abweichungen in bezug auf Farbtiefe und oft im Farbton. Die Universalität ist auch geringer. Wie zu erwarten war, verhält sich *Hydrochinon* ganz anders als Tetrahydroxychinon. Nur mit relativ wenigen Kationen erhält man dunkelgraue Anfärbungen, wie sie im allgemeinen von organischen Reduktionsmitteln induziert werden.

DISKUSSION

Für die Lokalisierung anorganischer Verbindungen auf Papierchromatogrammen wurden zahlreiche Möglichkeiten vorgeschlagen. Neben physikalischen Methoden (Strahlenabsorption, Leitfähigkeitsmessungen, usw.) haben Färbereagenzien eine grosse Bedeutung erlangt. Da anorganische Verbindungen (*z.B.* H_2S) nur eine relativ kleine Anzahl von Kationen anfärben, werden schon seit längerer Zeit mit Vorteil organische Substanzen verwendet.

8-Hydroxychinolin und Kojisäure verwendeten POLLARD, MCOMIE UND ELBEIH[5] als Fluoreszenzreagenzien. Nach dem Besprühen des Chromatogramms betrachteten sie es im ultravioletten Licht.

Eine Mischung beider Substanzen wird in Monographien über Chromatographie[6-8] als bestes Universalreagenz beschrieben.

Dieses Reagenz, wie auch alle anderen, die zur Lokalisation von Kationen vorgeschlagen wurden[9-17], zeigte sich in bezug auf Universalität und oft auch Empfindlichkeit dem oben beschriebenen unterlegen.

Mein Dank gilt allen, die an dieser Untersuchung mitgewirkt haben, insbesondere Frau H. ALEX.

ZUSAMMENFASSUNG

Nach systematischen Untersuchungen an 283 käuflichen organischen Reagenzien erwies sich Tetrahydroxychinon als ein Färbereagenz für die Papierchromatographie anorganischer Ionen, das die Bedingungen, die an ein solches Reagenz gestellt werden, Universalität und Empfindlichkeit, in hohem Masse erfüllt. Mit diesem Reagenz liessen sich sämtliche von uns untersuchten Kationen (26) mit einer meist recht hohen Empfindlichkeit auf Papierchromatogrammen lokalisieren. Alle entstandenen Farbflecke sind im Tageslicht sichtbar. Damit ist in vielen Fällen durch Farbvergleich mit einer synthetischen Probe und dem R_F-Wert eine sichere Identifizierung des Kations möglich.

SUMMARY

In an investigation of 283 organic reagents, tetrahydroxyquinone was found to be a suitable colour reagent in the paper chromatography of inorganic ions from the points of view of universality and sensitivity; all the cations (26) investigated could be located in daylight. Individual cations usually give characteristic colours so that by comparison of colours and R_F-values, absolute identification is possible.

RÉSUMÉ

L'auteur propose un nouveau réactif coloré universel pour la chromatographie sur papier des cations: la tétrahydroxyquinone, choisie parmi 283 réactifs organiques. Tous les cations (26) ont pu ainsi être localisés. Toutes les zones colorées sont visibles en lumière du jour.

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APPLICATION OF THE MNF CONTROLLED DC GENERATOR TO THE SPECTRAL ANALYSIS OF IMPURITIES IN LEAD

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In the analysis of lead with a low content of impurities, the use of the MNF controlled DC generator as an excitation source is advantageous. This device has already been described[1,2] but it seems appropriate to summarize its characteristics here. The MNF arc generator was designed with the idea of developing an excitation source which would retain the inherent sensitivity characteristics of arc excitation, but would also allow one to avoid the errors involved, which are reflected in an insufficient reproducibility of results. A detailed study of commercial arc sources led us to the conclusion that this lack of reproducibility was due to the following three causes.

(*1*) The use, in the majority of excitation sources, of alternating current arcs in order to obtain those pauses which are necessary to prevent overheating of electrodes.

(*2*) Neglect of failures in arc burning so that different actual ignition times may be obtained for two identical exposure periods.

(*3*) Preliminary programming of pauses and burning periods, so that if failures in arc burning are recorded during the ignition period, the electrode temperature is not constant during these periods.

We therefore designed (Fig. 1) an excitation source which avoids these disadvantages by means of the following devices:

(*a*) A special rectification system which can produce intermittent direct current and thus obviates the alternate polarity in the electrodes.

(*b*) Control of the exposure period, not in terms of time (classical device) but in terms of the energy employed. This energy is measured by counting the intermittent current impulses, which flow through the electrodes (analytical gap), and is obtained by the emission of voltage impulses to an electronic counter by a fixed resistance inserted in series with the electrodes.

(*c*) Electrode cooling pauses are not previously programmed, but are produced when a special electronic device establishes that the electrode temperature has reached an empirically pre-established limit.

In this way, high current intensities can be employed in the discharge while, at the same time, no electrode melting can take place.

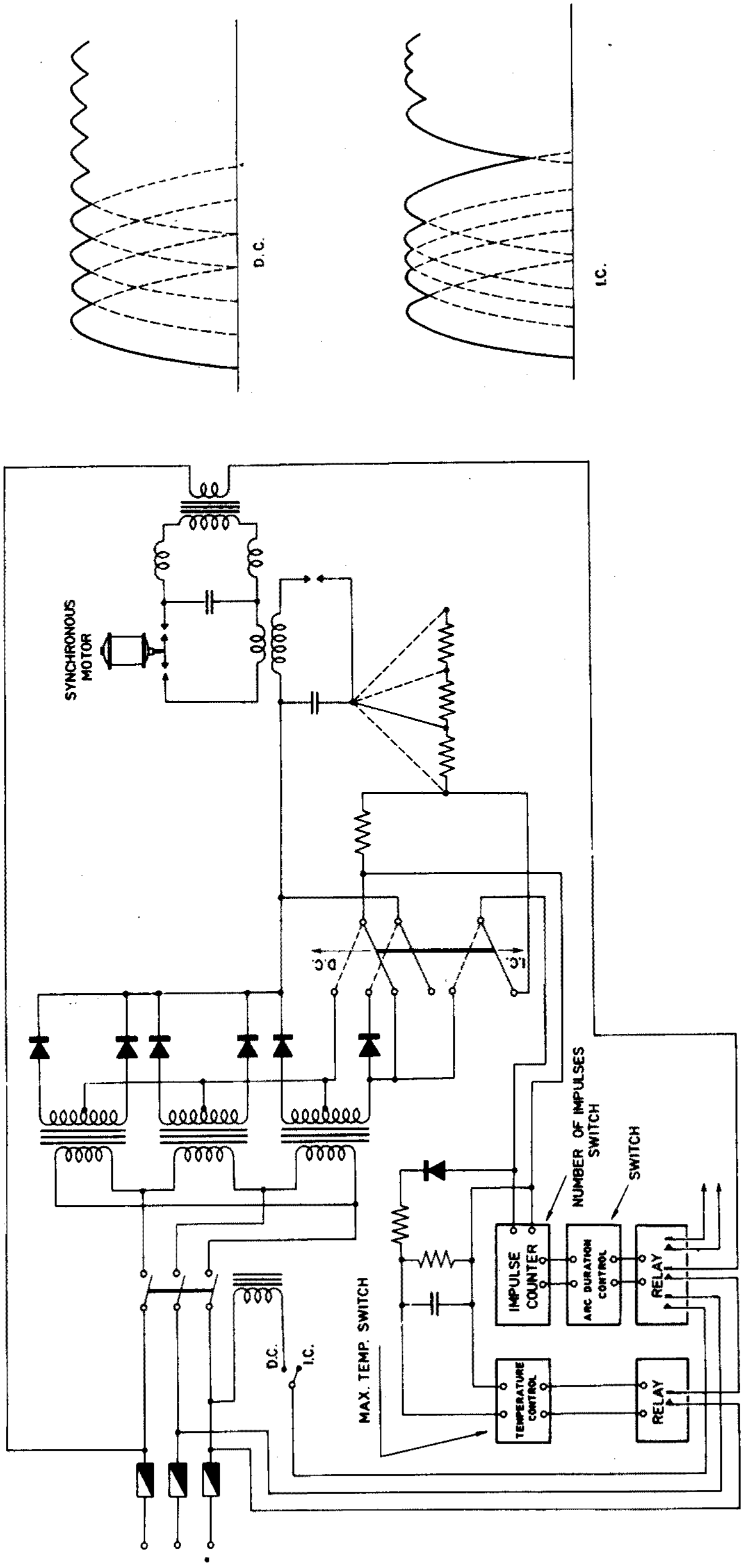

Fig. 1. Simplified scheme of the MNF arc generator.

EXPERIMENTAL

Analyses were carried out with a Fuess 110 M model medium dispersion quartz spectrograph. Ilford photographic plates of Ordinary type emulsion were employed unless otherwise mentioned. Development and fixing were carried out by recommended techniques according to the type of emulsion used[3]. The temperature for all these operations was 20°.

The electric parameter values were normally 225 V and 15 A. Except in the sensitivity and pre-ignition tests lead rod electrodes 8 mm in diameter with an impurity content of 160 p.p.m. Bi, 10 p.p.m. Cd, 20 p.p.m. Cu and 35 p.p.m. Ag were used; with the excitation technique employed, other impurities were not detectable. The counter-electrodes were high-purity JM-2B (Johnson–Matthey) graphite rods 6 mm in diameter and ending in a 90° bevelled point. The distance between the electrodes was 4 mm and the metal was employed as the cathode, except in the experiments carried out to establish the best polarity.

RESULTS AND DISCUSSION

Polarity

It was observed experimentally that when the metallic electrode was employed as the cathode and the graphite electrode as the anode, the sensitivity obtained for the different impurities studied was greater than when the polarity was reversed. Moreover, the reproducibility of results was better (Table I); a comparison of the results obtained by photometry of the 3220 lead, 3067 bismuth and 2288 cadmium lines, shows that when the polarity was changed, the reproducibility of the results decreased considerably.

TABLE I

EFFECT OF POLARITY ON RESULTS

Analytical line	*Electrode shape and diameter*	*Average transmission referred to a 500 "fog" value*	*Mean square error (%)*	*Analytical line*	*Electrode shape and diameter*	*Average transmission referred to a 500 "fog" value*	*Mean square error (%)*
Cadmium	A[a]	285	4.25	Silver	A	—[c]	—
2288	B[b]	353	3.15	3280	B	59	1.7
Bismuth	A	305	11.8	Lead	A	101	15.5
3067	B	66	4.0	3220	B	35	4.0
Silver	A	—	—	Bismuth	A	—[c]	—
3382	B	86	3.5	2898	B	327	1.66

[a] A = Metal electrode as anode.

[b] B = Metal electrode as cathode.

[c] Not detected: readings were about the same as the "fog" value.

When the metallic electrode was employed as the anode, the sensitivity diminished to such an extent that photometry was practically impossible for the 3383 and 3280 silver, 3247 and 3274 copper and 2898 bismuth lines, because the values obtained were close to that of the background of the corresponding region. The so-called cyanogen bands were rather intense, preventing the photometry of any impurity element with analytical lines in the region of the spectrum in which they appeared.

It was also found that the reproducibility was better when the test electrode lay in the lower portion of the arc.

In view of these results the metallic electrode was always used as the cathode and was located in the lower part of the arc for all later work.

Preburn period

Electrodes of 6 mm diameter containing Cd, Bi, Ag, Cu, As and Sb as impurities were employed in the study of the influence of preburning. Figure 2 shows that the optical densities of the different lines measured remained unchanged so long as the number of exposure impulses (in these experiments this number was 154 ± 1) remained the same, even when the number of preburning impulses was variable; thus, the preburning factor had no influence whatsoever on lead and it was therefore omitted in later work. The values of the optical densities corresponding to points "a" and "o" in the abscissa of Fig. 2 were obtained in experiments carried out without any previous pre-ignition impulse. In the experiments corresponding to point "a", the spectrograph shutter was opened by hand one second before the electrode excitation was started, in order to avoid any possible delay in the shutter opening attributable to the inertia of the system when the shutter was operated by a relay; on the other hand, for the values corresponding to point "o", this shutter was electrically operated by a relay at the very moment of starting the experiment. In this way, it was confirmed that there was no delay in the opening of the shutter when it was electrically operated.

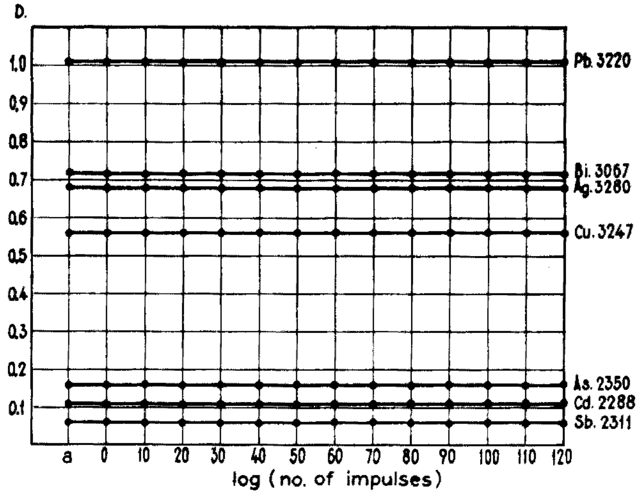

Fig. 2. Effect of number of preburn impulses.

Exposure period (number of impulses).

The different curves shown in Fig. 3 are the same as the blackening curves of a photographic emulsion; *i.e.* they comprise a linear region in which proportionality exists between the energy received and the blackening obtained, and two curved zones. The first of these, located in the inferior part corresponding to feeble blacken-

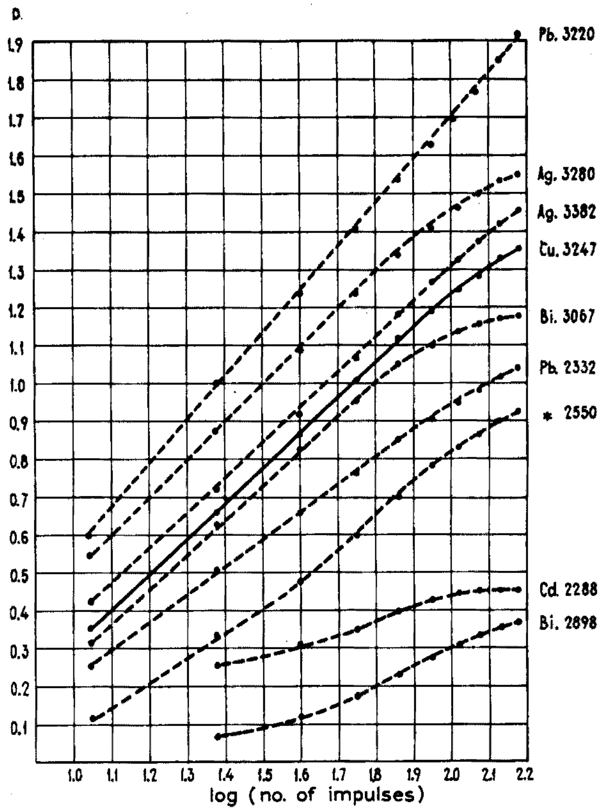

Fig. 3. Effect of 'exposure' period.

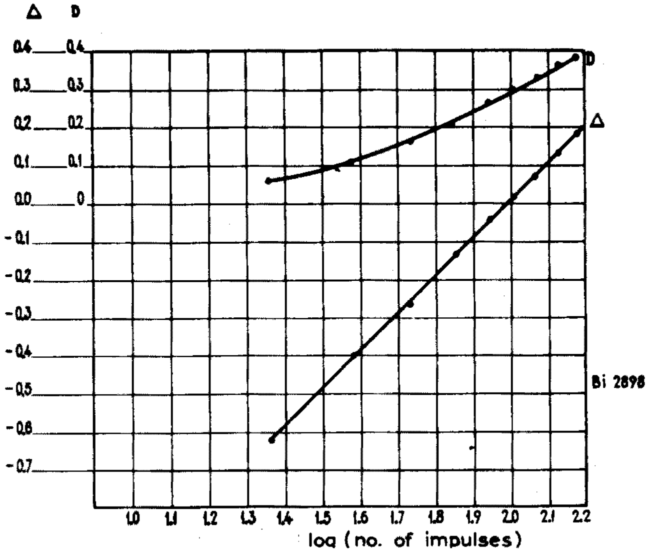

Fig. 4. Employing Seidel's transformate.

ings can be used by means of Seidel's transformate, as may be seen in Fig. 4. The second, which appears in the higher portion corresponding to the intense blackening region, is of no importance in analytical determinations. It can thus be inferred that the number of impulses which must be applied in each case is established by the concentration of the impurity in the base element and by the wavelength employed in its determination. It is, therefore, necessary to operate within the area of linearity and to select the appropriate wavelength.

Electrode temperature

The temperature control in the MNF source is based on the charge–discharge phenomena taking place in a capacitor (see Fig. 1) fed by a voltage which is proportional to the arc current. For a definite current intensity, the electrode temperature increases parabolically with time, until an asymptotic value is reached at which the energy supplied is equal to the heat dissipated by radiation from the electrode.

Both these curves have the same shape as the charge and discharge curves of a capacitor. Therefore, if appropriate values are chosen for the "c" and "k" parameters, a sufficient degree of precision can be obtained by taking the difference in the potential of the armatures of the capacitor, fed by a voltage which is proportional to the arc temperature, as a measure of the electrode temperature.

The electronic system for the temperature control interrupts the arc when the voltage difference in the condenser reaches a pre-established value equivalent to the highest temperature that the electrode can stand without melting. This voltage difference operates a measuring device graduated in an arbitrary scale of 0–100. These arbitrary values are shown in the abscissa of Fig. 5; the value for which a

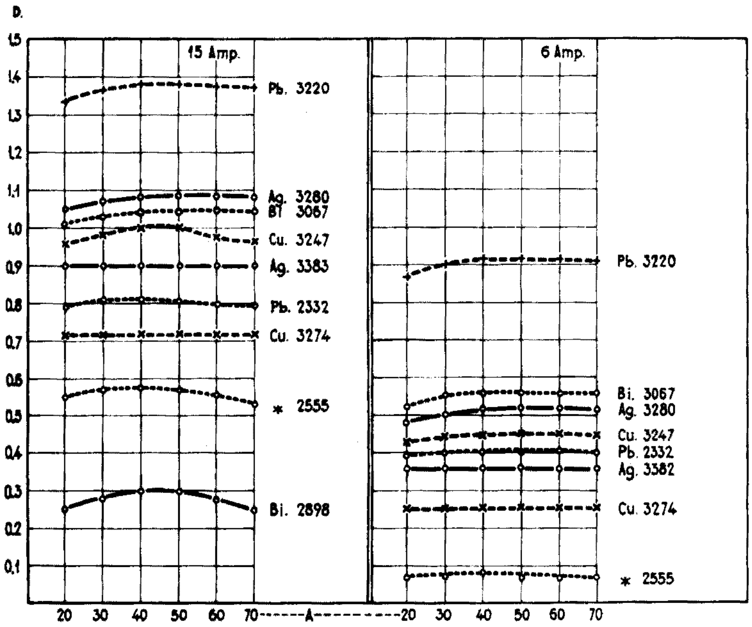

Fig. 5. Effect of electrode temperature.
(A) Position of the temperature control. (*) Background.

definite number of impulses (in this experiment 154 ± 1) can be produced without melting the electrode, must be empirically established for each type of electrode, varying with its nature, shape and size. It should be noted that for a greater numerical value in this temperature scale, the time during which a definite number of impulses is recorded is conversely shorter. Thus, the smaller number of pauses recorded during the process determines that the temperature attained by the electrode is higher. Because of this, temperature values lying close to the melting point temperature are to be recommended, for this results in a decrease of exposure times.

Influence of electrode size and shape on reproducibility of results

In order to show how the size and shape of the electrode affected the reproducibility of the results, several plates were obtained with definite fixed values for each of the parameters discussed above, but with lead electrodes of different shapes and sizes. Ingots 100 mm long, 10 mm wide and 10 mm thick, and rods of 6–8 mm diameter were employed.

TABLE II

EFFECT OF ELECTRODE SHAPE AND SIZE ON REPRODUCIBILITY

Analytical line	*Electrode shape and diameter*	*Average transmission referred to a 1000 "fog" value*	*General mean value*	*Mean square error referred to the partial mean value (%)*	*Mean square error referred to the general mean value (%)*
Cu 3274	A[a]	124	122	3.30	3.15
	B[b]	120		2.19	
	C[c]	121		3.40	
Cd 2288	A	460	492	2.00	6.15
	B	487		1.29	
	C	529		1.50	
Pb 2332	A	108	111	3.65	3.25
	B	114		1.82	
	C	112		1.76	
Ag 3280	A	62	60	1.90	3.41
	B	59		1.90	
	C	60		3.90	
Bi 2898	A	436	431	3.45	3.55
	B	426		3.05	
	C	432		4.40	
Bi 3067	A	65	65	2.00	2.88
	B	65		2.95	
	C	65		3.69	

[a] A = Rod 8.0 mm diameter.
[b] B = Rod 6.5 mm diameter.
[c] C = Ingot 100 × 10 × 10 mm.

The results obtained by photometry of the lines corresponding to 42 spectrograms on the same plate are shown in Table II; these indicate that the precision of this controlled excitation method is excellent; for, even though the "internal standard" technique was not employed in the photometric operations, when electrodes of a definite shape, either cylinders or small ingots, were used, the maximum mean square error was 3.5%.

From experience gained in a large number of determinations, we believe that this error can be ascribed to the photometric system rather than to the excitation method employed. Consequently if the "internal standard" technique were used, the errors caused by photometry would be multiplied without the possible small dispersion caused by excitation being corrected.

Sensitivity limit

In order to establish the limit of sensitivity of this method several tests were carried out under the optimum conditions mentioned above as regards photographic emulsion, polarity, separation, type and shape of the counter-electrode and electrical parameters; 153 ± 1 impulses were applied. As electrodes, standard spectral analysis lead samples supplied by the Bunddsenstalt für Material Prüfung (BAM, Berlin–Dahlem) were employed in 6-mm diameter rods. Other Spanish or German lead samples, whose composition was established by colorimetric methods, were also used.

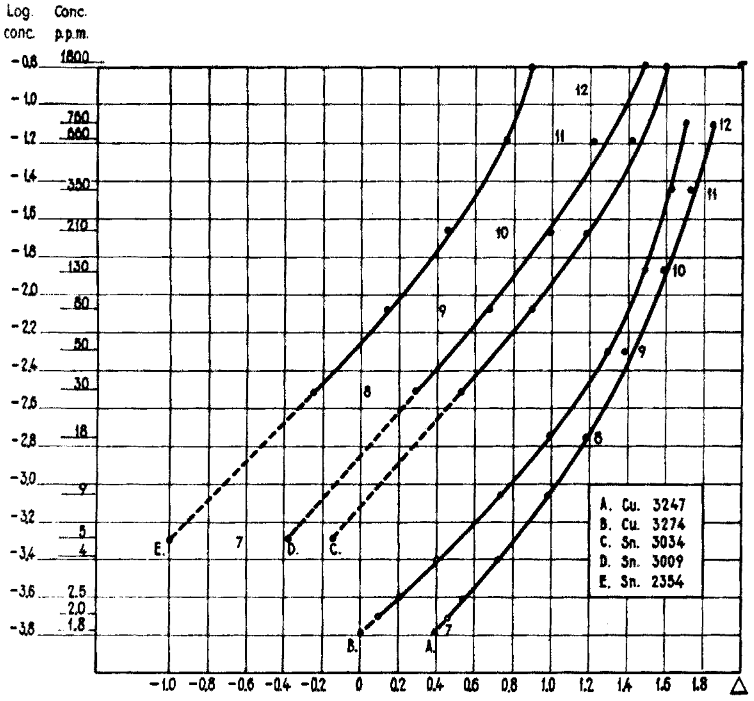

Fig. 6. Curves obtained with Ilford no. 30 Ordinary plate. Logarithm of impurity concentration *vs.* Δ. Cu step-filter — 50% transmission, Sn step-filter — 100% transmission.

Fig. 6 shows the logarithm of the impurity concentrations plotted against the function. In these curves the shaded circles correspond to the values given by the supplier except for the values of points 7 and 8 which were found by means of the present excitation technique. The open circles correspond to values determined by colorimetric and polarographic analysis in Spanish and German lead samples which we have compared.

From curves A and B (Fig. 6) it is clear that the copper content given by BAM for sample no. 8 (30 p.p.m.) was wrong and that the correct value was 18 p.p.m.; moreover sample no. 7, whose copper content was not included in its specifications, actually contained 1.9 p.p.m.

A step-filter* was used in order to obtain, for the higher copper concentrations, line blackenings which could be photometered within the appropriate limits.

Extrapolation (with the possible error involved, which, however, was unavoidable owing to a lack of standards containing sufficiently low amounts of tin) of curves C, D and E (Fig. 6) gave a result of 5 p.p.m. Sn for the BAM no. 7 sample; this content was not indicated in the specification.

Calibration curves

With the lead standard samples supplied by BAM (6-mm diameter rods) and different types of photographic emulsions (Ilford Ordinary no. 30, Ilford Thin Halftone and Ilford Long Grand Spectrum) but with the same conditions of polarity, counter-electrode type and shape, separation, electrical parameters and impulse

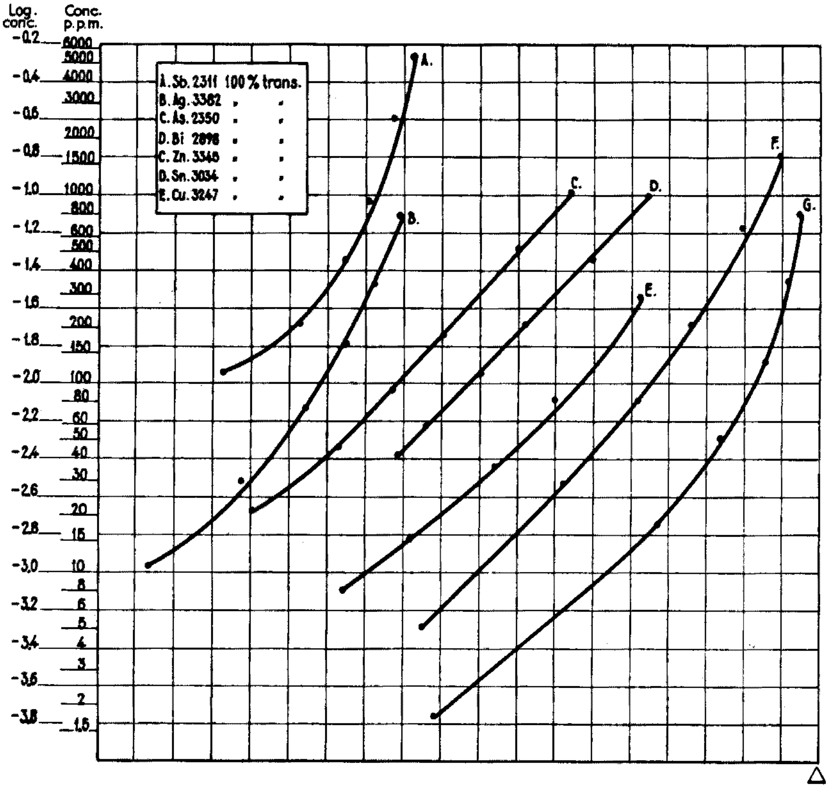

Fig. 7. Curves obtained with Ilford no. 30 Ordinary plate.

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* The one employed consisted of plane parallel quartz plates with a platinum deposit which with only one illumination gave a degraded spectrum corresponding to 100, 50, 25, 6 and 3% of transmission.

number, several plates were obtained. The multi-step filter was employed in the case of some spectra, in order to include the blackening values of certain lines within the limits suitable for their photometry.

On the basis of the spectrograms obtained, the different curves shown in Figs. 7 and 8 were drawn, and the most suitable filter scale and line were selected for each element.

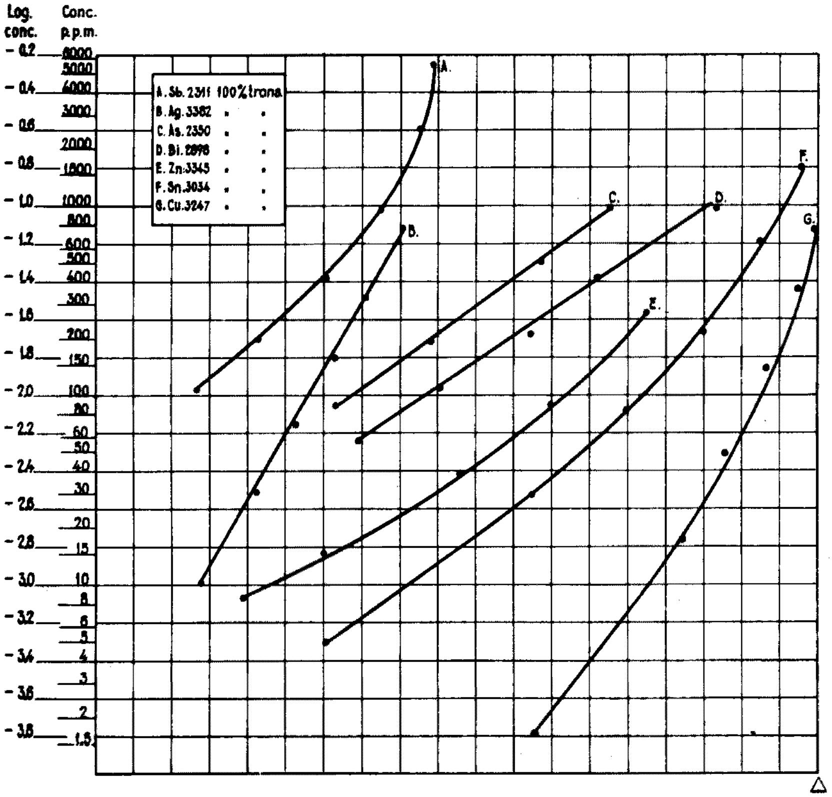

Fig. 8. Curves obtained with Ilford Thin Halftone emulsion plate.

In the ultraviolet region the Ilford Long Grand Spectrum plates had no advantages over the above-mentioned plates from the viewpoints of sensitivity and contrast.

The curves obtained indicate that for elements such as antimony, arsenic and zinc, it is better to operate with fast emulsions in order to obtain very high blackenings for the higher impurity concentration lines. This causes greater difficulties in obtaining correct photometry, hence it is necessary to employ the multi-step filter or, as we have shown before, its equivalent: modification of the number of impulses.

The Ilford Thin Halftone emulsion allows a greater contrast, which is reflected in a smoother value of the slopes of the curves. This decreases the errors in determination but, on the other hand, it causes a loss of sensitivity.

COMPARISON OF RES

Analysed elements	*7*				*8*				*9*			
	A				*A*				*A*			
	B	*C*	*D*	*E*	*B*	*C*	*D*	*E*	*B*	*C*	*D*	
Bi	100	99	100	106	25	< 50	< 40	26	50	49	49	
Fe	10	11	—	—	10	11	—	—	10	11	—	
Cu	5	5.3	5	4.9	3	3.1	3	2.9	45	40	45	
Sb	< 1	< 1	<110	< 20	3	2.9	<110	< 20	< 1	< 1	<110	<
Sn	< 10	—	< 5	1.2	< 10	—	< 5	< 1.2	< 10	—	< 5	<
Zn	9	10	8.5	—	8.5	8	8	—	7	7	< 8	
Cd	—	1	—	< 2.5	—	2.7	—	2.5	—	1	—	<
As	< 1	—	< 20	< 20	1	—	< 20	< 20	2	—	< 20	<
Ag	7	—	< 10	8	—	—	< 10	9.5	9	—	< 10	

Analysed elements	*G–3*				*G–1*				*4*			
	A				*A*				*A*			
	B	*C*	*D*	*E*	*B*	*C*	*D*	*E*	*B*	*C*	*D*	
Bi	60	60	60	59	75	74	74	75	230	230	228	≫
Fe	4	4	—	—	7	6	—	—	14	13	—	
Cu	5	5	5	5.1	680	>100	680	≫ 80	6	6.5	6	
Sb	40	39	<110	40	5	—	<110	< 20	1	1	<110	<
Sn	< 10	—	< 5	< 1.2	< 10	—	< 5	< 1.2	< 10	—	< 5	<
Zn	—	—	< 8	—	—	—	< 8	—	< 1	< 1	< 8	
Cd	—	< 1	—	< 2.5	—	—	—	< 2.5	—	< 1	—	<
As	10	—	< 20	< 20	10	—	< 20	< 20	< 1	—	< 20	<
Ag	13	—	13	14	15	—	14	15	13	—	13	

[a] (A) Contents in p.p.m. obtained by
(B) Chemical analysis
(C) Polarographic analysis
(D) Spectral analysis; metallic electrodes
(E) Spectral analysis, salt method.
(>) The impurity is more concentrated than indicated, but not measurable with the standards employed.
(—) The impurity was not determined by this technique.
(<) If present, the impurity has a concentration below that indicated.
Sample numbers *7*, *8*, *9*, *20*, *10*, *12*, *G–3*, *G–1* and *G–2* and *R* were Spanish lead.
Sample numbers *4* and *13* were German lead.

Comparison of results

Table III shows the results obtained in the determination of the impurity content of several Spanish and German lead samples by different analytical techniques: polarography, colorimetry and spectrography. The large degree of agreement in the results obtained shows the correctness of spectral analysis with a controlled arc excitation source. Its advantage over other methods lies in its greater speed.

DIFFERENT METHODS[a]

20				*10*				*12*			
A				*A*				*A*			
B	*C*	*D*	*E*	*B*	*C*	*D*	*E*	*B*	*C*	*D*	*E*
60	158	160	159	50	49	50	50	10	< 50	< 40	10
16	15	—	—	12	11	—	—	14	15	—	—
20	21	20	21	35	35	38	37	60	58	55	57
—	—	<110	< 20	< 1	< 1	<110	< 20	80	79	<110	78
10	—	< 5	< 1.2	< 10	—	< 5	< 1.2	10	—	< 5	< 1.2
6	5.9	< 8	—	5.5	6	< 8	—	< 1	< 1	< 8	—
—	10	—	10	—	1	—	< 2.5	—	< 1	—	< 2.5
4	—	< 20	< 20	7	—	< 20	< 20	52	—	< 20	< 20
—	—	35	35	11	—	10	11	—	—	< 10	8

13				*G–2*				*R*			
A				*A*				*A*			
B	*C*	*D*	*E*	*B*	*C*	*D*	*E*	*B*	*C*	*D*	*E*
50	49	50	50	60	59	60	61	100	98	100	99
12	11	—	—	5	4.9	—	—	16	15	—	—
3	2.5	2.5	2.7	8	8	7.5	8	5	5	4.5	4.9
1	< 1	<110	< 20	5	5	<110	< 20	35	36	<110	34
10	—	< 5	< 1.2	< 10	—	< 5	< 1.2	< 10	—	< 5	< 1.2
—	8	8	—	4.5	5	< 8	—	6	7	< 8	—
—	< 1	—	< 2.5	—	1	—	< 2.5	—	1	—	< 2.5
1	—	< 20	< 20	10	—	< 20	< 20	4	—	< 20	< 20
11	—	10	11	11	—	11	10.5	9	—	9	8.9

SUMMARY

A method for the determination of impurities in lead is described. The sample is excited by the new MNF controlled arc generator. The method is suitable for determination of the following seven impurities into the ranges of concentration shown: Sb (50–5400 p.p.m.), As (20–1000 p.p.m.), Bi (10–940 p.p.m.), Cu (1–760 p.p.m.), Zn (8–280 p.p.m.), Ag (5–160 p.p.m.) and Sn (5–1800 p.p.m.). The average square error is 3.0%.

RÉSUMÉ

Une méthode spectrographique est décrite pour le dosage des impuretés dans le plomb, utilisant le nouveau générateur à arc contrôlé ("MNF"). On peut ainsi doser les sept impuretés suivantes: Sb (de 50 à 5400 p.p.m.), As (de 20 à 1000 p.p.m.), Bi (de 10 à 940 p.p.m.), Cu (de 1 à 760 p.p.m.), Zn (de 8 à 280 p.p.m.), Ag (de 5 à 160 p.p.m.) et Sn (de 5 à 1800 p.p.m.).

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung der Verunreinigungen in Blei, unter Verwendung eines neuartigen Funken generators. Es können damit erfasst werden: Sb (50–5400 p.p.m.), As (20–1000 p.p.m.), Bi (10–940 p.p.m.), Cu (1–760 p.p.m.), Zn (8–280 p.p.m.), Ag (5–160 p.p.m.) und Sn (5–1800 p.p.m.).

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THE FORMATION OF HIGHLY FLUORESCENT ZINC PHOSPHATE IN THE PRESENCE OF URANIUM AND ITS APPLICATION TO THE DIRECT FLUORIMETRY OF URANIUM IN AQUEOUS MEDIA

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In a previous paper[1] we have shown that traces of uranium produce an intense fluorescence when a solution of sodium orthophosphate is added to a solution of zinc acetate. This fluorescence has been used to detect uranium on paper with high sensitivity (detection limit 10^{-3} μg) and selectivity as well as for a rapid determination of uranium in natural waters[2].

In the present paper, the conditions of formation and the composition of this fluorescent compound are described. We have also examined the possibility of forming this compound directly in aqueous solution as a finely dispersed precipitate and measuring the fluorescence of suspensions stabilised with agar or gelatin with a suitable fluorimeter.

EXPERIMENTAL

Reagents and apparatus

All reagents employed were Merck chemicals (Reagenzien pro analysi). The Bacto Agar was a product of Difco Laboratories Inc., Detroit. A suitable fluorimeter, schematically represented in Fig. 1, was constructed for measuring the intensity of the fluorescence.

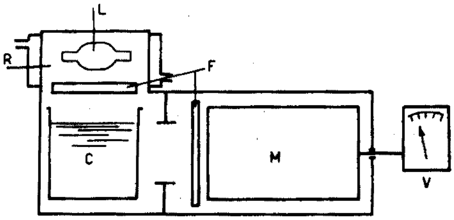

Fig. 1. Layout (schematic) of the fluorimeter employed. L, UV Lamp (Hanau M.B.H.); R, Lamp housing cooled with water; F, Filters (Corning No. 5860 and 3484); C, Pyrex cell (25 ml); M, Photomultiplier tube (1 P21); V, Vacuum tube voltmeter.

Formation and composition of the fluorescent precipitates

Highly fluorescent precipitates can be obtained in the presence of uranium by adding a zinc salt to acidic solutions (pH 4–6) of ammonium, sodium or potassium phosphate, or to buffer solutions of the KH_2PO_4–Na_2HPO_4 type.

The precipitates always contain zinc, phosphate, water and varying amounts of the alkali cation present in the solution. If, for example, the precipitation is carried out with an ammonium monohydrogen phosphate solution at pH 6, a precipitate containing ammonium is obtained (zinc ammonium phosphate[3,4]); with Na_2HPO_4–NaH_2PO_4 buffer solution, a precipitate containing sodium is obtained. Chemical analysis (see Table I) showed that the precipitate obtained at pH 5 has the ratio $Zn:PO_4:Na:H_2O$ = 1.01 : 1.01 : 0.50 : 0.91.

TABLE I

COMPOSITION OF THE PRECIPITATE

(obtained with Na_2HPO_4–NaH_2PO_4 buffer at pH 5 and dried at 110°)

Constituent	*Method employed*	*Number of analyses*	*Average (%)*
Zinc	Titration with ferrocyanide	6	34.3
	Precipitation with oxine	4	34.2
Phosphate	Gravimetric as magnesium salt and as	3	49.9
	phosphomolybdate	3	50.5
Sodium	Titration with zinc uranyl acetate	3	6.0
	Radiometric method with ^{22}Na	2	5.9
Water	Karl Fischer	2	8.5

The intensity of the fluorescence of the various precipitates is practically the same irrespective of the kind and amount of the alkali ion present. However, appreciable variations in the intensity of the fluorescence can be obtained by varying the pH of the precipitation. In order to obtain a reproducible fluorescence it is best, therefore, to carry out precipitation in a buffered medium. In this work, when not otherwise specified, the fluorescent precipitate was obtained by adding zinc acetate to a buffer solution containing Na_2HPO_4–NaH_2PO_4 and traces of uranium, and had the analysis given above.

An attempt was also made to establish whether the zinc could be replaced by other elements forming insoluble phosphates. Highly fluorescent precipitates can be obtained only with cadmium(II), beryllium(II), thorium(IV) and aluminum(III), but the intensity of fluorescence of these is appreciably lower than that obtained with zinc(II).

Fig. 2 shows the intensity of the fluorescence of the precipitate as a function of the pH, the optimum lying at about pH 5. Below pH 2.4, no precipitate is formed, while, above pH 5, the fluorescence of the precipitate rapidly decreases. Determination of the amounts of uranium remaining in solution after precipitation at various pH values showed that at pH 5 virtually no uranium is present in solution, while at pH 12 about 90% remains unprecipitated.

In order to determine the effect produced by the concentration of phosphates present in the solution, the variation in the fluorescence of the precipitate (at pH 5) was studied with increasing concentrations of phosphates. Starting with a solution containing 40 μg of uranium, the intensity of the fluorescence of the precipitate (formed with 1 ml of 1 *M* zinc acetate) increases very rapidly as the concentration of the buffer increases up to about 0.02 *M* and then remains constant up to at least 0.8 *M*. While it is possible to obtain the highest intensities even with very dilute buffers, high phosphate concentrations are preferable because it is easier to maintain the optimum pH even when acidic or alkaline solutions containing uranium are used.

The amount of uranium present in the precipitate depends on the concentration of the uranium in the solution. Figure 3 shows the relative intensities of the fluorescence as a function of the amount of uranium present in 25 ml of solution. Curves a, b and c represent precipitates formed respectively with 0.5, 1 and 2 ml of 1 *M* zinc acetate solution. The intensity of the fluorescence is proportional to the amount of uranium present only for small amounts of uranium in the precipitate. With starting amounts respectively of 140, 220 and 370 μg of uranium, the intensity of the fluorescence is virtually constant (saturation). This maximum of fluorescence is reached when the atomic ratio of uranium to zinc in the precipitate (by gravimetry) is about 1000:1; thus, when more than this amount of uranium is present the fluorescence does not increase further.

Fig. 2. Relative intensity of fluorescence plotted against pH.

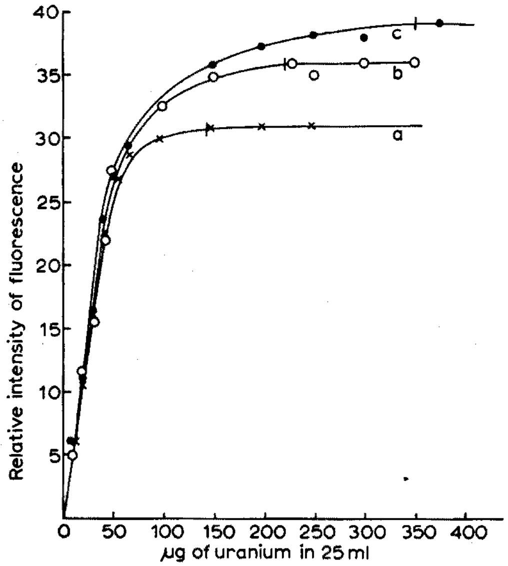

Fig. 3. Relative intensity of fluorescence plotted against the amount of uranium in 25 ml of solution. Conditions: (a) 0.5 ml 1 *M* zinc acetate, (b) 1 ml 1 *M* zinc acetate, (c) 2 ml 1 *M* zinc acetate.

Thermoquenching

As the temperature rises, the intensity of the fluorescence of the compound remains practically constant up to 127°, thereafter falling off progressively up to 177°. Above 177° only a faint luminescence remains, and even this disappears entirely at 307°. At about 850° the precipitate fuses. Cooling produces a vitreous substance that is fluorescent under UV light.

Determination of uranium by fluorimetry

Figure 4 shows the standard curve for 21 ml of NaH_2PO_4-Na_2HPO_4 buffer, 1 ml of 0.1 *N* nitric acid solution containing varying amounts of uranium, 2 ml of Bacto Agar solution and 1 ml of 1 *M* zinc acetate. The Bacto Agar was chosen because of all the colloid-protecting substances tested (gelatin, methylcellulose, carboxymethylcellulose and BTC 2125), it gave the best results in stabilizing the dispersion. The conditions under which the precipitate is obtained (temperature, stirring, etc.) must be strictly controlled.

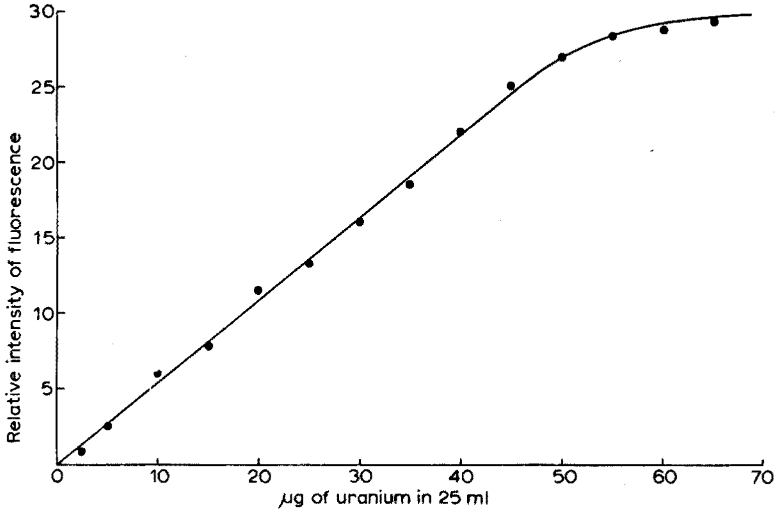

Fig. 4. Relative intensities of fluorescence plotted against the amount of uranium in 25 ml of solution. Conditions: 21 ml of NaH_2PO_4-Na_2HPO_4 (pH 5) buffer + 1 ml of 0.1 *N* HNO_3 containing the uranium + 2 ml of Bacto Agar solution + 1 ml of 1 *M* zinc acetate.

From the curve in Fig. 4 it can be seen that under the conditions indicated, the intensity of the fluorescence is proportional to the amount of uranium present only up to 50 µg of uranium in 25 ml of solution.

The estimated standard deviation of the relative error for 18 different solutions each containing 20 µg of uranium was found to be 5%. With the fluorimeter described above, 10^{-2} µg of uranium per ml can be determined with an error of 50%.

Interferences

Many substances, even when present in small amounts, appreciably quench the fluorescence of the precipitate. Table II shows the amounts of inorganic ions which produce a 50% quenching of the fluorescence of a precipitate containing 10 μg of uranium.

As with fluorimetry of uranium in fused alkali fluorides[5], the percentage of quenching is not governed by the concentration ratio of uranium to the interfering element, but only by the concentration of the latter (Fig. 5). The only difference is that for ions which form highly insoluble phosphates, the concentration cannot increase beyond the value at which a precipitate is formed in the buffer employed. Since aqueous solutions are used, it is possible to reduce the effective concentration of many ions by adding appropriate complexing agents; for example, sodium fluoride completely eliminates the interferences of iron(II), iron(III), lead(II) and cerium(IV).

Application of the method to the analysis of uranium-containing minerals

A mineral sample (1–2 g) is decomposed with nitric acid or nitric–hydrofluoric acid (depending on the type of mineral), and the solution is evaporated to dryness, dissolved in 0.5 *N* nitric acid and diluted to volume in a 25-ml flask (for materials with a low uranium content a 10-ml flask is better). To 5 ml of the solution are added 9.5 g of aluminium nitrate, which is dissolved by heating on a water bath. The solution is cooled and extracted twice with 5 ml portions of ethyl acetate. The

TABLE II

THE AMOUNT OF VARIOUS IONS IN 25 ml OF BUFFER WHICH QUENCH THE FLUORESCENCE OF 10 μg U(VI) BY 50%

Quenching ion	*Amount of ion (μg)*	*Quenching ion*	*Amount of ion (μg)*	*Quenching ion*	*Amount of ion (μg)*
SO_4^{2-}	>1000	Cd^{2+}	1000	Co^{2+}	15
NO_3^-	>1000	Tl^+	550	Cu^{2+}	10
F^-	>1000	Zr^{4+}	500	Ni^{2+}	10
Cl^-	>1000	Th^{4+}	500	Hg^{2+}	10
SiO_2 as Na_2SiO_3	>1000	Sn^{4+}	200	Pb^{2+}	10
Alkali metals	>1000	Sn^{2+}	150	Fe^{2+}	8
Alkaline earths	>1000	Be^{2+}	100	Bi^{3+}	5
V as VO_3^-	1000	Ag^+	35	Ce^{4+}	5
La^{3+}	1000	Ti^{3+}	25	Mn^{2+}	3
Al^{3+}	1000	Hg_2^{2+}	25	Fe^{3+}	1
				Cr^{3+}	1

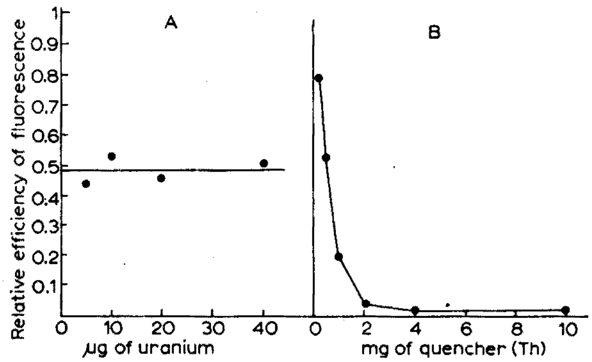

Fig. 5. (A) Relation between quenching and the concentration of uranium (uranium added with a constant amount of Be(II) quencher (100 μg)). (B) Variation of quenching with the concentration of the quencher (Th).

organic phase is then extracted three times with 10 ml portions of 0.01 *N* nitric acid (stirring each time for 5 min). Depending on the uranium content 5 to 20 ml of the solution are taken for the fluorimetric determination.

Values obtained by adding known quantities of uranium to solutions obtained from ores from the Canale Monterano area are given in Table III. Fluorimetric analysis of the precipitate in all cases gave low values, probably because some uranium was lost in the various extraction processes.

Subsequently, several specimens from the same Canale Monterano area were analysed. These samples were also analysed by fluorimetry with sodium fluoride–sodium potassium carbonate[5], and the results were in reasonable agreement. In this case, again, the dispersion fluorimetric method gave values slightly lower than those obtained by conventional fluorimetry (Table IV).

At the present time, attempts are being made to measure the fluorescence directly by means of a commercial spectrophotofluorimeter (Aminco–Bowman), and to determine the uranium by collecting the precipitate and measuring the fluorescence intensity with a commercial fluorimeter designed for uranium fluorimetry (G.M. Jarrel Ash).

TABLE III

ANALYSIS OF ORE SAMPLES WITH KNOWN AMOUNTS OF URANIUM ADDED

Number of sample	*Uranium in 10 ml of solution determined by conventional fluorimetry* (μg)*	*Uranium added (μg)*	*Calculated uranium (μg)*	*Uranium found (proposed method) (μg)*
1	33·1	—	33·1	33
1	33·1	50	83·1	77
1	33·1	100	133·1	124
1	33·1	200	233·1	233
1	33·1	250	283.1	266
2	32.1	—	32.1	31
2	32.1	50	82.1	79
2	32.1	100	132.1	121
2	32.1	200	232.1	224
2	32.1	250	282.1	266

The solutions were obtained by dissolving minerals containing uranium with HNO_3–HF.

TABLE IV

ANALYSIS OF ORES BY BOTH METHODS

Number of sample	*U (p.p.m.)*	
	Conventional fluorimetry	*Proposed method*
1	121	120
2	110	109
3	160	164
4	110	104
5	182	179
6	101	100
7	123	122

DISCUSSION

The results show the feasibility of a direct determination of uranium in aqueous media by fluorimetric analysis of highly fluorescent dispersions. While the method described is at present less sensitive than conventional fluorimetry, it can be employed for ores of low uranium content because relatively large volumes of solution can be taken for the determination. For example, a specimen containing 5 p.p.m. of uranium may be analyzed by dissolving 1 g and diluting it to a volume of 15–20 ml. After interferences have been separated, the entire solution (which contains 5 μg of uranium) can be employed to form the fluorescent dispersion.

In contrast to the fusion method, the method based on the formation of the fluorescent dispersion allows many interferences to be eliminated with suitable masking agents. In certain cases, therefore, the method may be employed directly without previous separation of the uranium. The precipitation method offers another advantage in that it is possible to carry out fluorimetric determinations without resorting to the high temperature fusion necessary in the classical method.

The method described, therefore, does not completely replace conventional fluorimetry if a very high sensitivity is needed, yet it offers advantages in many specific cases on account of its simplicity and rapidity, and especially when it is possible to eliminate interferences by adding appropriate complexing agents.

SUMMARY

The formation and composition of highly fluorescent zinc phosphates in the presence of traces of uranium were investigated and a direct fluorimetric determination of uranium in aqueous media was developed, based on the formation of finely dispersed and stabilized fluorescent precipitates. The standard deviation for 20 μg of uranium in 25 ml is 5%; with the fluorimeter described, 10^{-2} μg of uranium per ml can be determined with an error of 50%. The method is very selective and can be employed for analysis of uranium in ores; it is less sensitive than conventional fluorimetry of fused alkali fluorides but is much simpler and faster. Interferences can often be eliminated by suitable masking reactions.

RÉSUMÉ

Les auteurs ont effectué une étude sur la formation et la composition de phosphates de zinc très fluorescents, en présence de traces d'uranium. Ils ont développé une méthode de dosage fluorimétrique direct, basée sur la formation de précipités finement dispersés et stabilisés. Cette méthode est très sélective et peut être utilisée pour le dosage de l'uranium dans les minerais. Elle est moins sensible que la méthode fluorimétrique conventionnelle, aux fluorures alcalins fondus; mais elle est plus simple et plus rapide.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Herstellung und Zusammensetzung uranhaltiger, stark fluoreszierender Zinkphosphate. Es wurde eine Methode entwickelt zur direkten fluorometrischen Bestimmung von Uran, die auf der Bildung von fein verteilten, stabilisierten Niederschlägen beruht. Die Methode ist spezifisch und kann zur Uranbestimmung in Erzen angewandt werden. Sie ist weniger empfindlich als die konventionelle Methode, aber einfacher und rascher.

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DETERMINATION OF FLUORINE IN IRON ORE AND APATITE

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The determination of fluorine in different materials, such as ores, slags, dusts, etc., is of ever-increasing importance. The conventional method involves distillation of fluorine as suggested by WILLARD AND WINTER[1], followed by titration with standard thorium nitrate solution in the presence of alizarin red S indicator. The disadvantages of this method are well known[2,3]; small quantities of other acids may be distilled and interfere with the titration, and large quantities of aluminium, iron and amorphous silica prevent quantitative distillation. The determination of fluorine in phosphate ores containing large quantities of iron and aluminium is rendered difficult not only by the presence of elements which interfere in the titration, but also by incomplete recovery of the fluorine during distillation. Accordingly, in the present work, distillation was avoided and an ion-exchange method was preferred for the separation of fluoride.

Much information is available regarding the behaviour of metals with anion exchangers in different media, and especially in hydrochloric acid solutions. KRAUS AND NELSON[4] have given a behaviour pattern for most of the metals in the Periodic Table. NEWMAN[5] describes the separation of fluoride from interfering elements with an anion exchanger and EDTA as complex former. FUNASAKA *et al.*[6] separate fluoride from phosphate ions with 0.1 M sodium hydroxide as eluant. Various other procedures are available[3]. In the present work an anion-exchange method for the separation of fluoride from ions such as Fe^{3+}, Hf^{4+}, Ti^{4+}, Mn^{2+}, SO_4^{2-} and to a certain extent PO_4^{3-}, was developed.

A modification of MEGREGIAN's[7] spectrophotometric method for fluoride was selected from the many procedures available, as most suitable for the completion of the determination. Since its introduction in 1954, this technique has gained widespread recognition.

Spectrophotometric method for fluoride

MEGREGIAN's method is based on the bleaching effect of fluoride on the zirconium–eriochrome cyanine R complex; the effect of interfering substances, such as aluminium and phosphorus, can be reduced by increasing the acidity of the reaction solution, but the sensitivity decreases with increasing acidity[7]. However, in the present case, a certain loss in sensitivity could be tolerated and the procedure was therefore examined at higher hydrochloric acid concentrations than those used by MEGREGIAN. Fig. 1 shows the optical density as a function of wavelength for the bleaching effect of fluoride on the Zr–E.C.R. complex, and Fig. 2 shows the linear relationship between the fluoride concentration and the optical density at 532 mμ at a hydrochloric acid concentration of 1.4 M and a temperature of 25°.

In order to obtain a better understanding of the effect of interferences, samples containing varying quantities of fluoride and 0.5 mg Al^{3+}/50 ml were analysed at different degrees of acidity (Table I). Table II shows samples containing different quantities of phosphorus (as phosphate) analysed at varying degrees of acidity. For ore and mineral phosphates, for which the method was developed, aluminium exists in the form of aluminium oxide which is largely insoluble in hydrochloric acid. Some of the oxide goes into solution but, as shown in Table I, quantities up to 0.5 mg Al^{3+}/50 ml of sample have no effect, provided that the sample is allowed to stand 1 h before measuring. Zirconium displaces the equilibrium

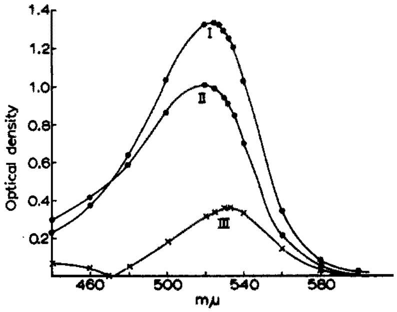

Fig. 1. Effect of fluoride on the absorption spectrum of zirconium–eriochrome cyanine R complex. I, Reagents A and B; II, Reagents A and B + 10 μg F^- diluted to 50 ml; III, Difference between I and II.

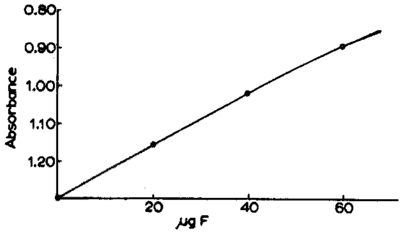

Fig. 2. Standard curve for fluoride at 532 mμ.

TABLE I

EFFECT OF ALUMINIUM ON THE DETERMINATION

HCl in test solution (M)	*μg F^- added*	*μg Al^{3+} added*	*μg F^- found*		
			Measured immediately	*Measured after 1 h*	*Measured after 4 h*
0.86	0	500	0	0	0
0.86	20	500	14.4	18	18.8
0.86	40	500	26.0	37.6	37.6
0.86	60	500	37.2	54.0	54.8
1.23	0	500	0	0	0
1.23	20	500	20	20	20
1.23	40	500	36	40	39
1.23	60	500	50	59	60

$$(AlF_6)^{3-} + Zr^{4+} \rightleftharpoons (ZrF_6)^{2-} + Al^{3+}$$

to the right and after a time the effect of aluminium is not noticeable.

TABLE II

EFFECT OF PHOSPHATE ON THE DETERMINATION

HCl in test solution (M)	*μg F^- added*	*μg P^{5+} added*	*μg F^- found*			
			Measured immediately	*Measured after 1 h*	*Measured after 2 h*	*Measured after 4 h*
0.86	50	200	50	50	50.5	52
0.86	50	270	67	69	74	>100
0.86	50	350	78	>100	—	—
0.86	20	200	26	27	30	31
0.86	20	280	55	59	64	72
0.86	20	350	80	>100	—	—
1.23	50	200	50	50	50.2	50
1.23	50	280	50	50	50	52
1.23	50	350	50	50.8	55	60
1.23	20	200	20	20	20	20
1.23	20	280	20	20.2	20	21
1.23	20	350	20	20	21	26

Phosphate also interferes in the procedure by forming a precipitate with the zirconium ion. However, by increasing the acidity of the reaction solution the interference can be reduced. If the phosphorus content is $\leq$ 0.3 mg/50 ml, no interference occurs; there is no difficulty involved in maintaining the quantity of phosphorus below the maximum limit, for samples containing large quantities of phosphorus usually contain relatively large quantities of fluorine. If fluorine is present in the form of, *e.g.* calcium fluoride, there is no problem.

Dissolution of the sample

Experiments made with different digestion times for samples containing fluorine and calcium, and with fluorine and silica, showed that the solution can be heated during dissolution, but boiling should be avoided as fluoride begins to be lost as fluorosilicic acid after about 30 sec.

Separation with Dowex 2-X10

It is known that the adsorbability of the fluoride ion is the least of the monovalent anions, and that the polyvalent ions are usually more strongly adsorbed than monovalent ions. Thus the fluoride ion should be eluted first from an anion exchanger. If the ion-exchange resin used is in the chloride form, the stability of which lies between those of fluoride and phosphate, an eluant containing chloride should elute fluoride quantitatively while the phosphate remains on the column. In addition to the ionic form of the exchanger, factors which influence this separation are the length of the column and the concentration of the eluant. The particle size is also important: the smaller the particle size, the more rapid the elution.

It was shown that the elution volume necessary for complete elution of fluoride increases as the concentration of the eluant decreases. In elution with 100 ml of 10 *M* hydrochloric acid, approximately 20% of the phosphorus content remains on the resin after quantitative elution of fluoride. An increase in the length of the column from 18 to 24 cm, with otherwise unchanged conditions, produces little or no alteration of the separation factor. Good separation of fluoride from phosphate with 1–2 *M* hydrochloric acid should be achieved, but when the acidity of the eluant is decreased, a rapid reduction of the distribution coefficient for Fe^{3+}, Ti^{4+}, Mn^{2+} and Hf^{4+} occurs. At the same time, precipitation of calcium fluoride may take place in this environment. Since quantitative separation of fluoride from phosphate is not essential in the present method, no further experiments were carried out.

Tests showed that no fluoride was lost in the effluent and that fluoride could be recovered quantitatively in the first 100 ml of eluate (Table III).

TABLE III

ELUTION DATA FOR FLUORIDE WITH 10 *M* HCl

Fluorine added: 10.0 mg. Temp. 25°. Rate of elution: 1–2 ml/min.

Resin used	*mg F^- found in the effluent (50 ml)*	*mg F^- found in the eluate*	*Fractions of eluate (ml)*
Dowex 1–X10 (200–400 mesh)	0.03	2.36	25
		4.44	50
		2.48	75
		0.72	100
		0.00	125
		F^- = 10.00 mg	
Dowex 2–X10 (200–400 mesh)	0.00	2.16	25
		4.04	50
		2.76	75
		1.12	100
		0.00	125
		F^- = 10.08 mg	

EXPERIMENTAL

Apparatus

The optical measurements were made in 1 cm cells with a Beckman DU spectrophotometer. The glass ion-exchange columns had an internal diameter of 2.3 cm.

Reagents

10 M Hydrochloric acid. 1,000 ml of concentrated acid (d. 1.19) diluted with distilled water to 1,250 ml.

Reagent A. Eriochrome cyanine R (E.C.R.), 1.800 g dissolved in distilled water and diluted with distilled water to 1 l.

Reagent B. 0.265 g of zirconium chloride ($ZrOCl_2$), dissolved in 10 ml of distilled water and diluted with concentrated hydrochloric acid to 1 l.

Reference solution. 10 ml of reagent A added to 100.0 ml of distilled water and 10.0 ml of concentrated hydrochloric acid.

Dowex 2-X10 resin. Capacity (total): 3.0 ± 0.3 meq per dry g. Moisture: 30–36% by weight. Particle size: 200–400 mesh (dry).

Preparation of column

Weigh *ca.* 50 g of wet Dowex 2-X10 resin in the chloride form into a beaker and mix with about 50 ml of distilled water. Transfer the suspension to the column, and allow to settle. Wash with 100 ml of distilled water and finally treat with 75 ml of 10 *M* hydrochloric acid. The height of the column should be 18.5 cm (± 0.5 cm).

After each analysis, remove 2–3 cm from the top of the column (the adsorbed iron is here) and wash the column two or three times with distilled water. Make up to 18.5 cm (± 0.5 cm) with resin. Before use, pass through *ca.* 75 ml of the eluant.

Procedure

For iron ores, weigh 0.2–1.0 g of finely ground sample into a 250-ml beaker. For apatite concentrates, weigh 0.1–0.5 g of the sample so that the phosphorus content is $\leq$ 0.3 mg/50 ml of the final solution. Add 50 ml of concentrated hydrochloric acid and warm gently with occasional shaking until all soluble material has dissolved (0.5–1 h); do not boil.

Transfer the sample solution to the ion-exchange column, conditioned with 10 *M* acid, and pass through the resin bed. Reject the effluent. Elute fluoride with 25 ml portions of the 10 *M* acid, allowing each portion to reach the top of the bed before the next addition. Collect 100 ml of eluate in a 100-ml measuring flask. Transfer the solution to a 500-ml measuring flask and dilute with distilled water to the mark. Transfer 5.0 ml of this solution to a 50-ml measuring flask together with 5.0 ml portions of reagents A and B. Dilute with distilled water to the mark and shake well. This solution should contain not more than 0.06 mg of fluoride.

Ensure that the solution is at the correct temperature (24–26°). Adjust the zero reading at 532 mμ with the aid of the reference solution, and measure the absorbance. For iron ore samples, measure 1 h after the mixing of the reagents. For apatite concentrates, measure the absorbance immediately.

In parallel with each test series, run a series of standard determinations: to 0, 5, 10 and 15 ml portions of standard fluoride solutions (containing 0, 20, 40 and 60 μg of fluoride respectively) add 10 ml of 1 *M* hydrochloric acid and reagents A and B as above and complete the determinations as described above.

DISCUSSION AND RESULTS

The quantity of hydrochloric acid added to the standard samples as compensation for the quantity of acid to be found in 5.0 ml of test solution after the ion exchange, can vary by 0.5 ml without affecting the total colour of the system. The equilibrium of the colour complex varies with the temperature, but is maintained constant within the 24–26° range. Table IV shows the results of ion exchange and elution of fluoride in the presence of different anions and cations. The materials were dissolved in 50 ml of concentrated hydrochloric acid and ion exchange and elution were applied as described above at a temperature of 25°.

The values obtained by different distillation processes and by the proposed method are shown in Tables V, VI and VII. These results show that the method is satisfactory for the analysis of apatite concentrates, mineral phosphates and iron ores. Dowex 1-X10 can replace the Dowex 2-X10 resin with equally satisfactory results but the latter is cheaper and allows a faster rate of elution.

TABLE IV

ELUTION OF FLUORINE IN THE PRESENCE OF OTHER IONS

Cation	*Anion*	*Added as*	*Quantity cation (mg)*	*Quantity anion (mg)*	*Quantity F^- added (mg)*	*Quantity F^- found (mg)*	
						Measured immediately	*Measured after 2 h*
Ti^{4+}	Cl^-	$TiCl_4$	3	2.2	6.00	5.96	5.96
Ti^{4+}	Cl^-		5	4.4	6.00	6.00	6.00
Al^{3+}	Cl^-	$AlCl_3 \cdot H_2O$	5	2.1	6.00	5.80	6.00
Al^{3+}	Cl^-	$AlCl_3 \cdot H_2O$	10	4.4	6.00	5.78	6.00
Na^+	Cl^-	NaCl	10	6.1	6.00	6.00	6.00
K^+	Cl^-	KCl	10	5.3	6.00	5.98	5.97
Fe^{2+}	—	Fe(met)	7	—	6.00	6.00	6.00
Fe^{2+}	—		70	—	6.00	6.00	6.02
Cu^{2+}	SO_4^{2-}	$CuSO_4$	1.2	1.8	6.00	6.00	6.00
Cu^{2+}	SO_4^{2-}	$CuSO_4$	4.8	7.2	6.00	6.00	6.00
Mn^{2+}	SO_4^{2-}	$MnSO_4$	1.8	3	6.00	—	6.00
Mn^{2+}	SO_4^{2-}	$MnSO_4$	18	30	6.00	—	6.72
Fe^{3+}	O^{2-}	Fe_2O_3	500	—	6.00	5.98	6.00
Ca^{2+}	Cl^-	$CaCl_2$	20	30			
Fe^{3+}	O^{2-}	Fe_2O_3	500	—	6.00	5.94	5.94
Ca^{2+}	Cl^-	$CaCl_2$	40	60			
Na^+	SiO_3^{2-}	Na_2SiO_3	38	62			
NH_4^+	VO_3^-	NH_4VO_3	0.8	4.2	6.00	6.02	6.00
NH_4^+	VO_3^-	NH_4VO_3	8.0	42	6.00	5.00	6.00

TABLE V

ANALYSIS OF APATITE CONCENTRATES

Sample no.	*% F (dist. at 130°, titrimetry)*	*% F (dist. at 160°, photometry)*	*% F (Ion exch., photometry)*	*% P in sample*	*Sample for ion exchange (g)*
1	0.63	0.48	0.526	3.7	0.5
1			0.528		0.5
1			0.536		0.5
2	1.98	1.91	1.85	11.8	0.2
2			1.85		0.2
2			1.85		0.2
3	2.70	2.72	2.68	16.5	0.2
3			2.68		0.2
3			2.76		0.1
3			2.68		0.1
4	2.43	2.00	2.16	13.5	0.2
4			2.13		0.2
4			2.12		0.2
5	4.15	3.51	3.54	15.2	0.1

TABLE VI

ANALYSIS OF MINERAL PHOSPHATE

Sample	*% F (dist. at 130°, titrimetry)*	*% F (Ion exchange[5])*	*% F (dist. at 160°, photometry)*	*% F (Ion exch., photometry)*	*% P in sample*	*Sample for ion exchange (g)*
Phosphate Rock "Florida"	3.92	4.08	3.87	3.92	15.0	0.1
		3.87		3.92		0.1
		3.80		3.92		0.1
				3.94		0.1
Phosphate Rock "Tennessee"	3.47		3.43	3.48	13.7	0.1
	3.56	3.62		3.48		0.1
	3.50	3.52		3.48		0.1
	3.63	3.48		3.48		0.1

TABLE VII

ANALYSIS OF IRON ORES

Ore sample	*% F (dist. at 130°, titrimetry*	*% F (dist. at 160°, photometry)*	*% F (Ion exch., photometry)*	*% P in sample*	*Sample for ion exchange (g)*
Haukivaara	0.74	0.58	0.600	3.2	0.5
Haukivaara			0.592		0.5
Haukivaara			0.600		0.5
Haukivaara			0.600		0.5
Leveäniemi	0.29	0.18	0.228	2.3	1.0
Leveäniemi			0.228		1.0
Leveäniemi			0.228		1.0
Leveäniemi			0.220		1.0
Nokutusvaara	1.93	1.76	1.73	9.85	0.2
Nokutusvaara			1.73		0.2
Nokutusvaara			1.76		0.2
Nokutusvaara			1.73		0.2
Lu-D^{1}	0.14	0.068	0.044	0.12	1.0
Lu-D^{1}			0.046		1.0
Lu-D^{1}			0.046		1.0
Kuj-D^{3}	0.34	0.28	0.276	1.91	1.0
Kuj-D^{3}			0.288		1.0
Kuj-D^{3}			0.276		1.0
Kuj-D^{3}			0.276		1.0
KR	0.69	0.82	0.808	4.69	0.5
KR			0.808		0.5
KR			0.808		0.5
KR			0.824		0.5
Nup-R	0.80	0.72	0.724	4.19	0.5
Nup-R			0.736		0.5
Nup-R			0.736		0.5
Nup-R			0.736		0.5
Kip-D^{5}	0.36	0.48	0.456	2.04	1.0
Kip-D^{5}			0.456		1.0
Kip-D^{5}			0.456		1.0
Kip-D^{5}			0.456		1.0

The author wishes to express his sincere thanks to S. STRÖM of this laboratory for her assistance in making the experimental measurements.

SUMMARY

A method is described for the determination of fluorine in iron ores, apatites and phosphate rocks, based on ion exchange on Dowex 2-X10 resin, and elution with strong hydrochloric acid. The determination is completed by a modified zirconium–eriochrome cyanine R spectrophotometric procedure.

RÉSUMÉ

Une méthode est décrite pour le dosage du fluor dans les minerais ferreux, apatites et roches phosphatées. Elle s'effectue à l'aide d'un échangeur d'ions (résine Dowex 2-X10) avec élution au moyen d'acide chlorhydrique conc. Le fluor est finalement dosé par spectrophotométrie, en utilisant le réactif zirconium–ériochrome cyanine R.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von Fluor in Eisenerzen, Apatiten und Phosphatgesteinen mit Dowex 2-X10 Austauscherharz und starker Salzsäure als Eluierungsmittel. Die eigentliche Bestimmung erfolgt spektrophotometrisch nach einem modifizierten Zirkonium–Eriochromcyanin-R Verfahren.

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INVESTIGATIONS ON THE DEVELOPMENT OF A SCHEME OF SILICATE ANALYSIS BASED PRINCIPALLY ON SPECTROGRAPHIC AND ION EXCHANGE TECHNIQUES

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Naturally occurring silicates are analytically among the most complex substances known. Aside from the abundant elements, Na, K, Mg, Ca, Al, Si, Fe, O and to a lesser extent Mn and Ti, which together make up more than 99% of the earth's crust, they contain in varying amounts virtually all the rarer elements. A complete silicate analysis is usually extremely tedious and the present paper describes work which has been done towards developing a scheme designed mainly to facilitate the reasonably complete analysis of the common silicates such as granite, basalt, ultramafics, syenite, shale, soil and the common meteorites. Particular emphasis is placed on simplicity, high sensitivity (where necessary), wide element coverage, speed and satisfactory accuracy; hence, spectrochemical methods, ion exchange and, to some extent, solvent extraction have been given particular attention.

The principal advantages of concentrating or separating elements by ion exchange are simplicity and speed; for trace element work in particular, whole groups of elements may be concentrated and estimated in a single operation. Moreover, the few reagents — principally mineral acids — required can be readily purified, so that reagent impurity is not a serious source of error. Lead is an exception to this general statement[1-4]. However, the prevention of contamination is of prime importance in trace analysis, thus the purity of each reagent batch was tested spectrochemically. Large volumes of reagents were taken to dryness and examined spectrochemically; ion-exchange resins were examined by arcing the ash from 5 g of resin; and blank tests were made in all cases.

Hydrochloric acid is a particularly useful eluant. It is easily handled and obtainable in high purity and does not give rise to excessive bulk — which is important if a spectrochemical determination is to be carried out — in contrast to some organic eluants, *e.g.* citric acid and EDTA. In addition the chlorides of all elements are volatile when excited in the DC arc so that spectrochemical analysis is usually facilitated.

In a critical account of the present status of classical chemical analysis as applied to geological materials, VINCENT[5] forecasted that such methods would soon "be

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largely replaced by separation based upon chromatography or ion exchange, which could do much to reduce the personal factors involved".

Attempts to develop ion-exchange enrichment and separation techniques coupled with quantitative spectrochemical techniques for estimating several elements in rocks, meteorites and minerals have been described by Edge, Brooks, Ahrens *et al.*[1–4,6–10]. These investigations were mainly concerned with the so-called trace metals, but Edge[1] has described ion-exchange investigations for abundant elements as well. Ion-exchange separations have been used by other workers[11–13] for the analysis of major elements in silicates. Welford *et al.*[14] have developed a scheme based on anion- and cation-exchange separations for estimating Sr, Ba, Ce, Cs, Y, Zr, Nb and W in fallout samples containing bulk Si, Fe and Ca; and Jarman and Matic[15] describe a scheme in which anion exchange and solvent extraction are used for the rapid quantitative analysis of uranium ore acid leach solutions.

Other concentration procedures may be used; for example, indium and thallium can be concentrated from a silicate rock solution by ether extraction of their iodo-complexes and thereafter determined spectrochemically[16,17] (see p. 560). A tributylphosphate (TBP) solvent extraction–spectrochemical procedure has been used[18] for the estimation of molybdenum in granites and related rocks (see p. 561). The idea of developing a *trace metal* scheme based on concentration by ion-exchange and spectrochemical estimations, has been briefly outlined[19].

In the present paper, attention is given to both abundant and trace elements. Though a complete scheme for all elements cannot yet be provided, detailed information is available on many elements and certain 'group' operations, and part of the main problem will be to fit such operations into a comparatively simple analytical scheme.

The list below includes all elements (arranged alphabetically) on which at least some observations have been made and which will be considered in the present paper. Elements which are normally classed as abundant in the earth's crust are boxed.

Ag $\boxed{\text{Al}}$ Au Ba Bi $\boxed{\text{Ca}}$ Cd Ce
Cr Cs Cu $\boxed{\text{Fe}}$ Ga In $\boxed{\text{K}}$ La
Li $\boxed{\text{Mg}}$ $\boxed{\text{Mn}}$ Mo $\boxed{\text{Na}}$ Nd Ni Pb
Pd (+ Pt etc.) Rb Sc $\boxed{\text{Si}}$ Sn Sr $\boxed{\text{Ti}}$
Tl V Y Zn and Zr

Spectrochemical methods of direct DC arc excitation of powders have been extensively used to provide abundance data on several elements — usually those present at low (1–50 p.p.m.) but not extremely low concentrations — in silicate rocks and minerals. Various DC arc methods have been used (see Ahrens and Taylor[20]) and details of these excitation techniques are not considered here; the elements which can usually be determined are listed in Table I. In an over-all scheme of silicate analysis as envisaged here, the direct excitation techniques would comprise one step and for some elements could be used as a check determination (see p. 567). Elements which are bracketed in Table I are quite often just below detection limit concentrations. With the exception of one of the detection limits of zinc, all the detection limits fall within the range 0.5–10 p.p.m.

TABLE I

"TRACE" METALS USUALLY DETECTABLE IN COMMON SILICATE ROCKS (IGNEOUS, METAMORPHIC AND SEDIMENTARY) BY SPECTROCHEMICAL METHODS OF DC ARC EXCITATION[a]

Element	*Detection limit (p.p.m.)*	*Crustal abundance (p.p.m.)*	*Element*	*Detection limit (p.p.m.)*	*Crustal abundance (p.p.m.)*
(Ag)	0.5	0.08	Ni	5	35
(B)	10	3	Pb	5	15
Ba	5	10000	Rb	1	115
Bi	20	0.2	Sc	2	20
Co	10	20	(Sn)	10	2
Cr	1	100	Sr	5	450
(Cs)	2	5	(Tl)	1	1.3
Cu	0.5	55	V	5	120
Ga	3	19	Y	10	28
La	10	18	(Zn)	100 3^{b}	40
Li	0.5	32			
Mo	5	1	Zr	10	156
Nd	10	24			

[a] Approximate detection limits and estimated crustal abundances are from AHRENS AND TAYLOR[20].
[b] See AHRENS AND TAYLOR[20], p. 75.

DISCUSSION OF PROPOSED SCHEME

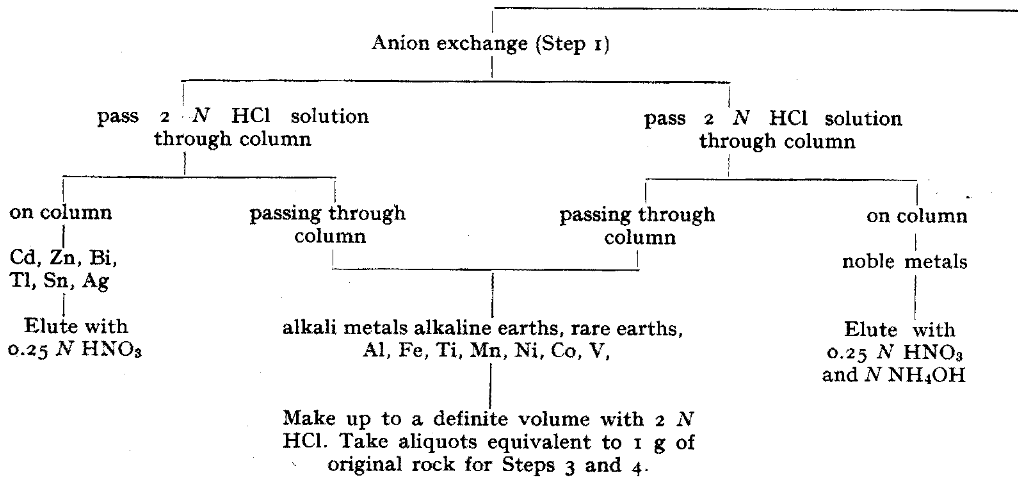
The proposed scheme is shown diagrammatically in Fig. 1. A common dissolution procedure with HF–aqua regia–H_2SO_4 is followed by division of the solution into aliquots, one for each "step". The scheme was worked out and tested with separate samples and dissolution procedures for each group, but no significant differences should arise from the use of a single starting solution. The accuracy of the estimations is improved if naturally occurring silicates similar in composition to the unknowns are available; we have made particular use of the reference rocks, granite G-1 and diabase W-1, and the collected data on these two rocks[21,22].

Notes on the dissolution of silicates

Only acid dissolution procedures were used in these investigations. Fluxes such as sodium bisulphate, carbonate and peroxide or potassium fluoride, were not employed because the additional cations introduced would reduce the capacity of the cation-exchange columns. Moreover, fluxes as well as sinters tend to introduce impurities and it is difficult to make satisfactory blank corrections when solid reagents are used.

For the cation-exchange procedures (Step 4) and the anion-exchange separation in 11.3 N hydrochloric acid solution (Step 3), mixed hydrofluoric and perchloric acids were used for the dissolution of silicate powders; these mixed acids have been used extensively in the estimation of the alkali metals[23-27], and CHAPMAN *et al.*[28] found no loss by volatilization of the alkali metals, alkaline earths, La, Zn, Sn, Pb, Cd, Ag, Bi, Ti, V, Co, Ni and Mo by such treatment, although appreciable quantities of Si, B, Ge, As, Sb, Cr, Se, Os, Ru, Re and Mn are volatilized.

Although sulphuric acid can be used in place of perchloric acid in the sample dissolution (for example, for estimation of Mo in granitic rocks after TBP extraction, p. 561), the latter acid is preferable for the decomposition of materials relatively rich in Ca, Sr, Ba and Pb since soluble perchlorates are produced. Insoluble sulphates of


Anion exchange (Step 1)
pass 2 N HCl solution through column
pass 2 N HCl solution through column
on column
Cd, Zn, Bi, Tl, Sn, Ag
Elute with 0.25 N HNO3
passing through column
passing through column
alkali metals alkaline earths, rare earths, Al, Fe, Ti, Mn, Ni, Co, V,
Make up to a definite volume with 2 N HCl. Take aliquots equivalent to 1 g of original rock for Steps 3 and 4.
on column
noble metals
Elute with 0.25 N HNO3 and N NH4OH

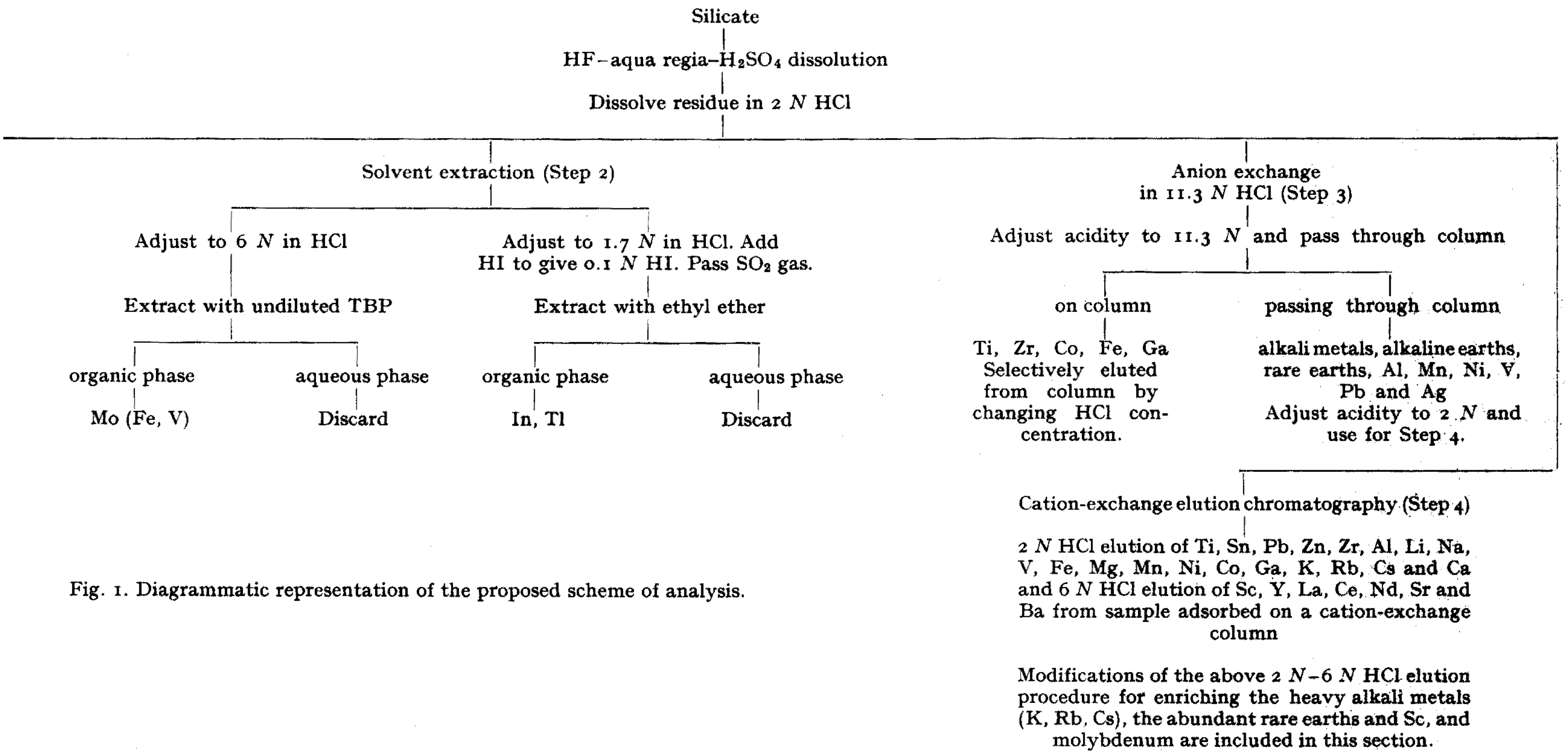


Fig. 1. Diagrammatic representation of the proposed scheme of analysis.

the above elements would clog the interstices of the ion-exchange resin. Perchloric acid cannot be used for the dissolution of the silicate powders if the 2 N HCl anion-exchange procedure (Step 1) is to be employed, because perchlorate markedly depresses the adsorption from HCl media of such elements as zinc and thallium[29,30].

Details of the hydrofluoric–perchloric acid dissolution procedure are as follows.

Procedure. Moisten 1 g of rock powder (100 mesh) with deionized water in a platinum basin and treat with 15 ml of hydrofluoric acid (40%) and 1 ml of perchloric acid (70%); after slow evaporation, add 10 ml HF and 1 ml $HClO_4$ and continue evaporation until the evolution of copious $HClO_4$ fumes has ceased. Add 10 ml of 2 N HCl and warm for 2 min while stirring. Decant the HCl into a 50-ml polythene bottle. Treat the residue with 10 ml HF and 1 ml $HClO_4$ and take slowly to dryness. When cool, add 6 ml of 2 N HCl, warm and stir for 2 min and decant into the same polythene bottle. Fume any undecomposed material with 1 ml $HClO_4$. The resultant residue usually dissolves completely in 2–3 ml of 2 N HCl. On completion of the dissolution procedure, wash the platinum dish with 2 ml HCl and add the washings to the polythene bottle. The dissolution of chondrites is described on p. 569.

For the procedures involving enrichment through anionic chloro-complex formation (Step 1) and the estimation of indium and thallium after solvent extraction (Step 2), a HF–aqua regia–H_2SO_4 dissolution procedure[31] was employed. If greater or lesser quantities than those given below are required, pro rata volumes of reagents must be used.

Procedure. Weigh 40 g of finely powdered rock sample (100 mesh or finer) into a 150-ml 'Teflon' beaker. Add 10 ml of aqua regia and stir to a paste with a 'Teflon' rod. Very cautiously add 50 ml of hydrofluoric acid (40%) in small amounts each about 3 ml. This is a hazardous operation and care must be exercised to avoid frothing. Add a further 40 ml of aqua regia and take to dryness in a water bath. Because of the low heat conductance of 'Teflon', the beaker should actually be immersed in the water bath with the top protruding about 1/4″ above the top of the bath. When the sample is dry (usually after about 24 h) add 50 ml of hydrochloric acid (s.g. 1.18) and transfer the contents to a 250-ml borosilicate glass beaker. Add 150 ml of water, boil for 5 min, allow to settle for 30 min and pour off the supernatant solution. Transfer the residue back to the 'Teflon' beaker and again add 50 ml of hydrofluoric acid and 50 ml of aqua regia. (The caution noted above in adding reagents is not necessary in this step.) Again take to dryness in the water bath and combine the residue with the original decanted liquid. Add 50 ml of sulphuric acid (s.g. 1.82) to the solution and fume to dryness to remove excess fluoride. (This step is carried out in a vitreosil dish; traces of fluoride combine with the silicon of the dish and are evaporated.) Add about 200 ml of 2 N hydrochloric acid and 1 ml of bromine to the residue. Boil for 5 min and add sufficient 2 N hydrochloric acid to adjust the total volume to about 1200–1300 ml.

A clear solution should be obtained when most rock types are treated as above. Some rocks may, however, not dissolve completely in which case the sediment should be separated from the supernatant liquid and fumed with 10–15 ml of sulphuric acid; the residue should then be added to the decanted liquid and after boiling dissolution should be complete.

This dissolution procedure is recommended for the integrated scheme, though certain elements may be lost through volatilization.

According to LUNDELL *et al.*[32], osmium is volatilized from hot aqua regia solution and gold is volatilized to some extent if the aqua regia solution is rapidly evaporated to dryness or if such solutions are treated with sulphuric acid and evaporated to copious fumes. No volatilization of gold occurs if the aqua regia solution is first treated with 70% perchloric acid and then evaporated to copious fumes of perchloric acid. Other elements which are lost when fuming with sulphuric acid are rhenium[33] and osmium[34].

STEP I. PROCEDURES INVOLVING ENRICHMENT THROUGH ANIONIC CHLORO-COMPLEX FORMATION

The estimation of Cd, Zn, Sn, Tl, Bi, Ag and certain other elements

The procedure is based on the formation of stable anionic chloro-complexes by certain 18-electron and *d*-type transition metals. Their adsorption on basic exchange resins has been investigated particularly by KRAUS AND NELSON[35,36] and JENTZSCH AND FROTSCHER[37], who measured the distribution coefficients of several elements on the strongly basic exchanger Dowex 1, and showed that whereas some elements form anionic chloro-complexes over an extensive HCl normality range (*e.g.* from 0.1 N to 12 N, Bi forms complexes $[BiCl_4]^-$, $[BiCl_5]^{2-}$, and $[BiCl_6]^{3-}$) others form complexes only over a restricted range. At a normality of 2 N the elements shown in Table II, arranged in order of decreasing magnitude of distribution coefficients, form anionic chloro-complexes.

TABLE II

LOG VOLUME DISTRIBUTION COEFFICIENTS OF ELEMENTS WHICH FORM ANIONIC CHLORO-COMPLEXES IN 2 N HCl[35,36]

Element	*log D_v*	*Element*	*log D_v*	*Element*	*log D_v*
Au(III)	6.0	Cd(II)	3.1	Pb(II)	1.5
Tl(III)	5.0	Zn(II)	3.0	Nb(V)	1.3
Os(III)	3.8	Re(VII)	2.8	Mo(VI)	1.2
Ir(IV)	3.8	Sn(II)	2.7	Fe(III)	1.0
Bi(III)	3.5	Ru(IV)	2.6	Ta(V)	1.0
Pt(IV)	3.4	Pd(II)	2.5	U(VI)	1.0
Sn(IV)	3.2	Ag(I)	2.0	In(III)	1.0
Sb(III)	3.2	Cu(I)	2.0		

Of the abundant elements (O, Si, Fe, Al, Na, K, Ca, Mg, Mn and Ti) which together form 99% of the earth's crust, only iron forms an anionic chloro-complex; this complex, $[FeCl_4]^-$, is weak (log $D_v = 1.0$), and can be easily separated (see below) from the stronger complexes. This is very fortunate because iron is a major constituent of many minerals and rocks and must be separated in order to achieve an effective enrichment of the other metals; also, the spectrum of iron is complex and its concentration must be reduced to a very low level because of possible interference. Interference of Fe 3067.2 Å with Bi 3067.7 Å is a good example[3].

With the exception of iron, the concentrations of most of the elements listed in Table II in rocks, soils, minerals and meteorites are usually below their spectrochemical detection limits (see EDGE *et al.*[6]). If, however, the trace elements can be adsorbed selectively from a hydrochloric acid solution of a comparatively large quantity (5–10 g) of rock — elements having log D_v's $\geqq 2$ are quantitatively adsorbed from 2 N HCl onto strong base anion-exchange resins[37] — then subsequent elution may yield a product in which the concentrations of these elements are above their spectrochemical detection limits, so that they can be determined. This is the basis of the procedures described below. The sensitivity of the combined procedure can be increased by using larger samples until a limit is imposed by practical considerations such as reagent blanks and the degree of adsorption of the elements on to the resin.

Zn, Cd, Bi, Tl and Sn may be estimated in most common silicate rocks by means of the above procedure[2,3,17]. The concentrations of Au, Os, Ir, Pt, Ru, Pd and Re are invariably so low that they cannot be detected in silicate rocks and minerals by this procedure unless a very large sample is taken[7]. They have accordingly been omitted from the procedure described below and are dealt with later (p. 559).

NISHIMURA AND SANDELL[38] have determined zinc in meteorites (irons and chondrites) by the above enrichment procedure combined with colorimetric analysis.

Procedure for Cd, Zn, Sn, Tl and Bi. Treat a 2 N HCl aliquot, equivalent to 5 g of original rock, with bromine to ensure that all the thallium is in the trivalent state, because only thallium(III) forms stable anionic chloro-complexes. Boil out the excess of bromine, cool and pass the solution through a 20 cm $\times$ 1 cm^2 column of Amberlite IRA 400 (8X, 100–200 mesh, chloride form) at a flow-rate of 30 ml/h. Wash the column previously with 2–3 column volumes of 2 N HCl. Elute with 2 l of 0.25 N nitric acid. Fig. 2 shows the elution curves for a 20-g specimen of Cape granite[6]. The first 100 ml contain most of the iron and trace metals (In, for example) whose anionic chloro-complexes have comparatively low D_v values; this fraction may be discarded. Collect the 100–2000 ml fraction and take to dryness in an evaporating dish to which some sodium chloride solution, sufficient to provide a sodium chloride residue of 15 mg, has been added. The purpose of the sodium chloride is threefold:

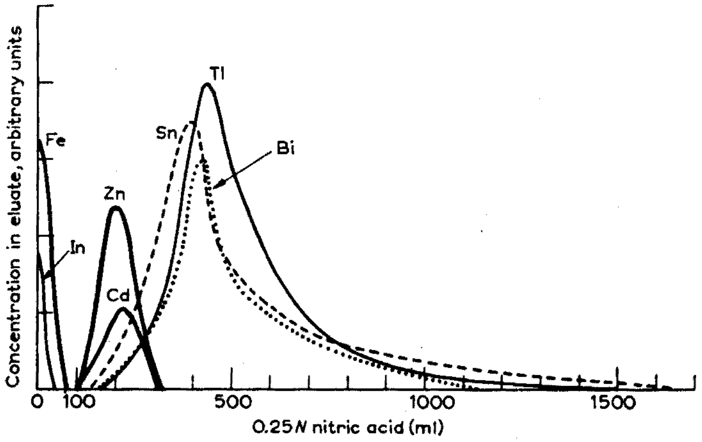


Fig. 2. The elution of trace amounts of Zn, Cd, Tl, Bi, In and Sn from 20 g Cape Granite with 0.25 N nitric acid.

(*1*) To provide a matrix which will ensure a spectrum comparatively free from

CN bands, which otherwise interfere excessively with Tl 3775 Å (see, *e.g.* AHRENS AND TAYLOR[20]).

(2) To provide bulk in which to collect the effluent residue which is otherwise inconveniently small to handle for spectrochemical analysis.

(3) To provide a matrix with a uniform composition for spectrochemical analysis.

Load the residue into a graphite anode (3.2 mm I.D. × 5 mm deep) and arc at 6 A until the Na "D" colour begins to wane, usually after about 1.5 min. The small quantity of iron which is normally present emits its most intense spectrum after the distillation of sodium has subsided, which is fortunate in that iron interference with Bi 3067 Å is kept to a minimum. It is imperative not to overexpose, otherwise CN emission interferes excessively with Tl 3775 Å.

Notes on the estimation of silver. We have not yet attempted to determine silver. As the magnitude of log D_v for the silver anionic chloro-complex in 2 *N* HCl is quite high (2.0; see Table II), silver should appear more or less quantitatively in the 100–2000 ml nitric acid fraction. A spectrochemical examination of the silver line intensities in the residue of the 0–100 ml and 100–2000 ml fractions from several rocks shows quite clearly that only a very small proportion of silver is present in the 0–100 ml fraction and that the major proportion (90–95%) is in the larger fraction. There is little doubt therefore that the general procedure outlined above could be applied to the estimation of silver. This possibility enhances the value of the outlined procedure considerably because very little information is available on the geochemistry of silver and very few workers undertaking trace element analyses ever report silver; its determination invariably involves a separate procedure.

HAMAGUCHI AND KURODA[39,40] have estimated silver by means of the following precipitation enrichment-spectrochemical procedure: 1 g of sample is decomposed with hydrofluoric and perchloric acids, stannous chloride is added to a 2 *N* HCl solution of the sample and the precipitated silver is collected with tellurium. Silver is estimated spectrochemically using indium as the internal standard.

Observations on the noble metals (Au, Pt, Pd, Ir, Ru, Rh, Os and Re)

Some previous studies of these metals are available[2,7]; BEAMISH[41] has critically reviewed methods for isolating and separating the platinum metals. These elements form strong anionic chloro-complexes (Table II; the value of the volume distribution coefficient of Rh(IV) in 2 *N* HCl is unknown, but said to be high[35]) and in principle may be estimated by means of the above procedure. Because of their rarity, however, none is spectrochemically detectable in the residues from 5 g quantities of rock; far larger quantities must be used. The volatilization of Os, Ru, Re and Au during the dissolution of silicate powders was noted on p. 556.

The column behaviour of the noble metals and rhenium was observed by adsorbing a 2 *N* HCl solution containing 1000 p.p.m. Re, 500 p.p.m. each of Ir, Pt and Os and 100 p.p.m. each of Pd, Ru, Rh and Au on to a 20 cm long × 1 cm^2 column of Amberlite IRA 400 (8X, 100–200 mesh, chloride form) resin, washing with a further quantity of 2 *N* HCl and then eluting the adsorbed ions at a flow-rate of 50 ml/h. In addition to elution with 0.25 *N* nitric acid, 1 *N* ammonia as an eluant was also investigated because many of the noble metals form stable complex ammines (see MCNEVIN AND CRUMMETT[42]). Some elution curves are shown in Fig. 3.

By means of elution with 0.25 *N* nitric acid and 1 *N* ammonia, Au, Pt, Pd, Ir, Rh and Ru have been detected[7] in a hortonolite dunite (ex Merensky Reef) and Au and Pt in Cape Granite[6]. Sample weights of 150 g and 200 g respectively, were employed. To handle such large quantities of rock and to avoid noble metal contamination, 'Teflon' beakers were used (see also p. 556).

A procedure which could perhaps fit into the analytical scheme described here is that of HAHN–WEINHEIMER[43,44], who enriched the noble metals, except gold, from a solution of silicate rock by means of complex formation with 2-quinolineselenol which may be extracted with chloroform; the metals were finally determined spectrochemically.

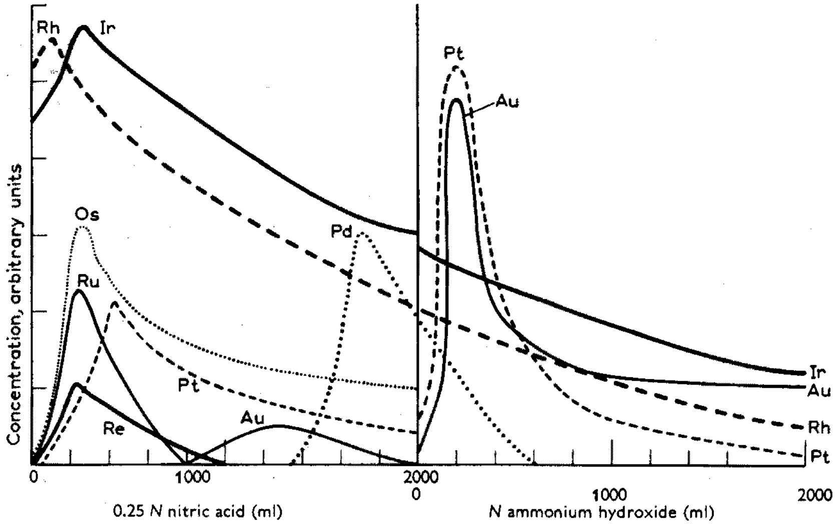


Fig. 3. The elution of the noble metals and Re with 0.25 N HNO_3–N NH_4OH.

STEP 2. PROCEDURES INVOLVING SOLVENT EXTRACTION

Estimation of indium and thallium

The procedure is based on the formation of iodo-complexes of indium and thallium which may be quantitatively extracted into ethyl ether from a dilute hydrochloric acid solution containing hydriodic acid[16,17].

If indium and thallium are to be determined in addition to the other elements involved in the scheme, a 15% (1.7 N) hydrochloric acid solution is prepared from the original solution equivalent to about 2 g of sample. The solution volume should be about 20 ml.

Procedure. Add sufficient hydriodic acid (s.g. 1.7) to each solution to give a 1 N HI solution. Pass sulphur dioxide through the solution until the iodine colour has disappeared; this also reduces thallium(III) to the monovalent state. (Note: for the formation of stable anionic chloro-complexes (Step 1) thallium(III) is necessary, whereas thallium(I) is required for the formation of stable iodo-complexes.) Extract the iodo-complexes of indium and thallium with an equal volume of pre-equilibrated (1.7 N HCl) ethyl ether in a 1 l separating funnel. Evaporate the ether extract to dryness and add a further 50 ml of 1.7 N HCl followed by the requisite amount of hydriodic acid.

After treatment with sulphur dioxide, again extract indium and thallium with an equal volume of ether. (The double extraction is necessary to separate indium and thallium from traces of other interfering elements, particularly iron, and also to remove any traces of sulphuric acid remaining from the sulphation stage, which would make it difficult to obtain a satisfactorily dry and compact residue for packing into the electrodes for spectrochemical analysis.) The subsequent handling of the second ethereal residue depends on whether a spectrochemical or another method (*e.g.* polarographic) is used for the estimation; if a spectrochemical method is to be used, proceed as follows: evaporate the ethereal extract to dryness in a 50-ml porcelain basin containing 20 mg NaCl and remove iodine with a few ml of nitric acid. Load the dry residue into graphite anodes (3.2 mm I.D. × 5 mm deep) and arc at 7 A in the wavelength range 2750–4680 Å. Prepare working curves from standards containing 0.02, 0.04, 0.10, 0.20, 0.60 and 2.0 μg In and Tl in 20 mg of NaCl. Each standard, and unknown, contained 10 μg Bi as internal standard.

Notes. The detection limits which may be reached if the equivalent of 3–5 g of rock is taken, are about 0.02 p.p.m. for indium and a little more (approximately 0.02–0.04 p.p.m.) for thallium. As these detection limits are low, it is possible to estimate the two metals in most silicate rocks; thallium in ultramafic rocks is a probable exception. The thallium sensitivity is about the same as that attainable in the procedure outlined in Step 2. If thallium is determined in both Steps 1 and 2, one result may serve as a check against the other.

Estimation of molybdenum in granitic and related rocks after TBP solvent extraction

The procedure is based on the extraction of molybdenum by TBP from 6 *N* hydrochloric acid[18].

Procedure. Digest 1 g of rock as described on p. 556, but substituting sulphuric acid (s.g. 1.82) and 6 *N* hydrochloric acid for the acids used in the previous procedure. Transfer the resultant 6 *N* HCl solution (20–25 ml) to a 100-ml separating funnel and extract with 25 ml of undiluted TBP (commercial grade) previously equilibrated with 6 *N* HCl. After equilibration for 2 min, allow the layers to separate and run off the aqueous layer. Strip molybdenum from the TBP phase by shaking with 5 separate 10-ml portions of deionized water for 1 min each time. Since emulsions were formed during stripping, centrifugation was employed for phase separations.

Combine the water washings and evaporate to near dryness in an 80-ml porcelain basin. Add 20 mg of carbon powder containing 0.2% $(NH_3)_4Pd(NO_3)_2$ and evaporate to dryness. Load the resultant residue (containing iron and vanadium in addition to molybdenum), in a graphite anode (2.4 mm I.D. × 5 mm deep) and arc to completion at 7 A; the analysis pair were Mo 3170.3 Å and Pd 3421.2 Å. A working curve may be prepared with the aid of the standard granite G-1[1,22] carried through the same column and spectrochemical procedure as the rock samples.

STEP 3. ANION-EXCHANGE SEPARATION IN 11.3 *N* HCl SOLUTION

The anion-exchange procedures described above were carried out in 2 *N* HCl. Certain advantages of concentration and separation may be found at other normalities. If 11.3 *N* hydrochloric acid is used, some elements (*e.g.* Fe, Ti, Zr, Co and Ga) which at low normalities form no, or relatively weak, anionic chloro-complexes, form very strong complexes (log D_v Fe(III)$=4$; log D_v Ti(IV)$=3$; log D_v Co(II)$=2$; log D_v Ga-

(III)=4)[35,36] which are quantitatively held on the exchanger. For example, we have mentioned (p. 557) the desirability of removing most of the iron, but this is not possible in 2 *N* HCl because the complex formation is not complete at this normality (log D_v = 1.0). In 11.3 *N* HCl, however, the complex is fully developed (log D_v = 4.3) and $[FeCl_4]^-$ is quantitatively held by the exchanger.

The procedure described below is based on the work of KRAUS *et al.*[35,36]. It was clear from their work that certain ions, such as alkali metals, alkaline earths, rare earths, aluminium, nickel and some other metals were not adsorbed by the resin from 11.3 *N* HCl and therefore could be collected as a separate fraction. Ions such as iron were retained by the resin and could be eluted selectively by changing the concentration of the HCl eluant. In this way it is possible to obtain the following four fractions.

Fraction	*HCl eluant concentration (N)*	*Elements eluted*
(a)	11.3	alkali metals, alkaline earths, rare earths, Al, V, Ni, Pb, Mn and Ag
(b)	8	Ti and Zr
(c)	4	Co
(d)	1	Fe and Ga

Final elution of the column with 0.25 *N* nitric acid did not reveal the presence of thallium(III), tin(II, IV) or zinc(II) (elements adsorbed by anion exchangers from 11.3 *N* HCl and which are difficult to remove in chloride media[35,36]). In the above investigations perchloric–hydrofluoric acid was employed for sample dissolution. The suppression of anion-exchange adsorption of zinc(II) and thallium(III) by perchlorate anion is well known[29,30].

Notes on certain elements

Iron is a major constituent in ultrabasic and basic rocks, mafic minerals and chondrite meteorites and the bulk must be removed if the concentration of certain trace elements is to be brought within the detection limits of the analytical technique, the estimation of Cs in chondrites and basic rocks is an example[4] (*cf.* p. 569). Anion exchange in 11.3 *N* HCl may be used to great advantage to remove iron.

Perhaps the least satisfactory estimation in a classical silicate analysis is that of aluminium by difference in the precipitate formed with ammonium hydroxide. Various procedures have been described for the separation of aluminium from the R_2O_3 group of elements. MILNER AND WOODHEAD[45] used a cupferron extraction for the removal of Fe, Ti and Zr before the aluminium determination. From our experiments it seems likely that aluminium could be separated from other R_2O_3 elements by anion exchange in 11.3 *N* HCl and then estimated by any of the conventional procedures. Any platinum that might accompany these elements would be adsorbed on the resin together with Fe, Zr and Ti from 11.3 *N* HCl[35,36].

Anion exchange in 11.3 *N* HCl provides a rapid group separation of Al, Ca and Mg from Fe and Ti. LEWIS *et al.*[46] separated Al, Ca and Mg from Fe and Ti by anion exchange in 10 *N* HCl, and selectively titrated Al, Ca and Mg with EDTA; the method has been applied successfully to the analysis of slag and sinter. JARMAN AND MATIC[15] used a similar procedure for separating Al, Ca, Mn and Ni from Fe, Co, Zn and Cd in uranium ore acid leach solutions.

Manganese(II) may be separated from all other elements in fraction (a) above by adsorption on a long column containing a resin of high cross-linkage and fine particle size (200–400 mesh) with 12 *N* HCl for the sorption step[46].

Iron may be determined titrimetrically[5] in a suitable aliquot of fraction (d) by reduction to iron(II) and titration with an oxidant.

Titanium may be determined spectrophotometrically[23] as the peroxy complex in a suitable aliquot of fraction (b).

It is unlikely that zirconium, cobalt and gallium would be estimated by means of the anion exchange (in 11.3 *N* HCl)–spectrochemical procedure because these elements can normally be estimated spectrochemically by direct DC arc excitation[20,47]. In ultrabasic rocks, however, the zirconium concentration is likely to fall below the spectrochemical detection limit, thus the anion exchange–spectrochemical procedure could be useful. Another application could be the determination of cobalt in granites, where its concentration is sometimes below direct DC arc excitation limits.

If Zr, Co and Ga were estimated routinely by the anion exchange (in 11.3 *N* HCl)–spectrochemical procedure, the results would serve to check the direct excitation method.

Procedure

Obtain a 20 ml 11.3 *N* HCl solution either (*1*) by adding hydrochloric acid (s.g. 1.18) to the residue obtained by evaporating an aliquot equivalent to 1 g from the original 2 *N* HCl solution, or (*2*) by digesting 1 g of rock powder with $HF–HClO_4$ and taking the residue up in 20 ml of 11.3 *N* HCl. Soak this solution into a 22 × 1.9 cm column of Amberlite IRA 400 (8X, 100–200 mesh, chloride form) at a flow-rate of 0.25 ml/min. (Before the sorption, wash the column with 2–3 column volumes of 11.3 *N* HCl.) Elute with 120 ml volumes of 11.3, 8, 4 and 1 *N* HCl, at a flow-rate of 1 ml/min.

The 11.3 *N* HCl effluent may be evaporated to *ca.* 5 ml for use in cation-exchange elution chromatography (Step 4, see below).

STEP 4. THE USE OF CATION-EXCHANGE ELUTION CHROMATOGRAPHY

Concentration or separation has so far been achieved either through anion-exchange techniques or by means of solvent extraction. In the procedures which follow, cation-exchange elution chromatography is mainly used[1,4,9], with emphasis on certain trace metals, notably Cs, the abundant rare earths (Ce, La, Nd plus Y), Sc, Mo, Sn and Ga; some observations are also made on Li, Na, K, Rb, Mg, Ca, Sr, Ba, Mn, Fe, Ni, Co, Ti, Zr, Zn, Pb and Al, several of which (Na, K, Mg, Ca, Mn, Al, Ti and Fe) are abundant.

Several studies were undertaken to ascertain the sequence of movement of ions through the cation-exchange columns under different experimental conditions. Not all of these sequence investigations have been incorporated into the proposed scheme, but the main results are given in Table III for the sake of general utility; further information is available[1].

Elements which form stable anionic complexes (Ti, Zr, Al* as fluoro-complexes,

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* Al is, however, not eluted entirely as fluoroaluminate, the balance of this element being eluted as Al^{3+}.

and Zn, Sn and Pb as chloro-complexes) pass through the column first, followed by elements which form less stable chloro-complexes, *e.g.* Fe, Co and Ga, and those which show no tendency to anionic fluoro- or chloro-complex formation, *e.g.* alkali metals, alkaline earths and rare earths. Within each cationic charge group, the order of elution usually follows that of the radius of the hydrated ions *e.g.* in the alkali metals, the order is $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. The above pattern of elution behaviour may be disturbed by disruption of the hydrated shells of cations (dehydration; *e.g.*, with the 6 *N* HCl eluant, the position of Cs with respect to K and Rb is reversed; the partial dehydration of the alkali metal ions brings about a reversal of their affinities for the sulphonic acid groups of the resin) and anionic chloro-complex formation (*e.g.*, the earlier elution of Co and Ga with 6 *N* HCl is due to increased anionic chloro-complex formation leading to a displacement of the ion-exchange equilibria).

TABLE III

THE SEQUENCE FOR THE MOVEMENT OF MAJOR AND TRACE CONSTITUENTS OF COMMON SILICATES THROUGH CATION-EXCHANGE COLUMNS ON ELUTION WITH VARIOUS CONCENTRATIONS OF HCl ELUANT[a]

1 N HCl	*Ti* *Al* Sn Pb Zr	Li Zn	*Na*	V Be	*Mg*	*K* Rb	Cs	*Mn*	Ni Co					
	Elution not carried any further. Fe, Ga, Ca, Sr, Ba, rare earths and most of the Al still on the column.													
2 N HCl	*Ti* *Al* Zr Zn Pb Sn	Li	V	*Na* *Fe*	*Mg* *Mn*	Ni Co	*K* Rb	Cs	Ga	*Ca*	Sr	Y	Ba	La
2.5 N HCl	*Ti* *Al* Zr Zn Pb Sn	Mo	Li V *Fe*	*Na* *Mg* *Mn*	Ni Co	*K* Rb Ga	Cs	*Ca*	Sr	Y	Nd	Ba	La	
3 N HCl	*Ti* *Al* Sn Pb Zn Zr	*Fe* Mo	Li V	*Mg* *Na* *Mn*	Ni Co	Ga	*K* Rb	Cs	*Ca*	Sr	Y	Nd	Ba	La
6 N HCl	*Ti* *Al* Sn Pb Zn Zr	*Fe* Ga	*Mn* V Co	*Mg* *Na* Li Ni	Cs	*K* Rb	*Ca*	Y	Sr	Nd	La	Ba		

[a] Major constituents are italicized in the above elution sequences.

The elution behaviour of alkali metals[48], alkaline earths[48–52], rare earths[53], Mn, Fe, Ni and Zn[54] from Dowex 50 cation-exchange columns with a wide range of hydrochloric acid concentrations has been investigated in detail.

Although operating conditions can be selected for separating solutes completely from one another[55], it must be emphasized that in trace element investigations, it is necessary only to concentrate the trace constituents to within their spectrographic detection limits.

The sample for cation-exchange elution chromatography may be

(*1*) An aliquot, equivalent to 1 g of original rock, of the 2 *N* HCl effluent after anion-exchange removal of Tl, Sn, In, Cd, Bi and other anionic chloro-complexes stable in 2 *N* HCl (Step 1),

(*2*) the 2 *N* HCl solution obtained from a separate attack of 1 g silicate material,

(*3*) the 11.3 *N* HCl effluent (after adjustment of volume and acidity) from the anion-exchange removal of Fe, Ti, Zr, Co and Ga (Step 3).

In all cases the sample volume should be 15–25 ml and the acidity 2 *N*.

Cation-exchange enrichment procedure

Soak the 2 *N* HCl solution of rock sample into the top of a 38 × 1.7 cm column of Dowex 50 (8X, 200–400 mesh, H-form) resin at a flow-rate not exceeding 0.25 ml/min. Wash the column previously with 2–3 column volumes of 2 *N* HCl. Commence elution with 2 *N* HCl at a flow-rate of 15 ml/h. An arrangement described by EDGE[56] is used to obtain the slow, steady flow-rate required.

Figs. 4 and 5 show the relative elution positions of the major and some trace constituents from the standard granite G-1[21,22] and standard diabase W-1[21,22] under the above conditions. It must be emphasized that the elution curves in Figs. 4 and 5 show only the relative elution positions of the various elements; the absolute positions may vary with rock type and between apparently similar batches of resin; it is essential

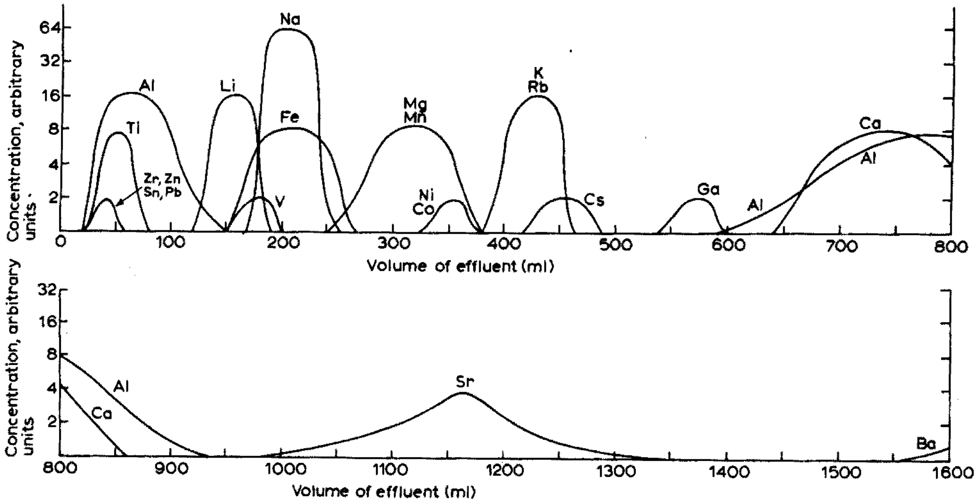

Fig. 4. The 2 *N* HCl elution of major and some trace constituents of 1 g granite G-1.

therefore to construct a separate elution curve for each rock type and resin batch.

The discussions which follow refer mainly to common acid and basic rocks unless otherwise stated.

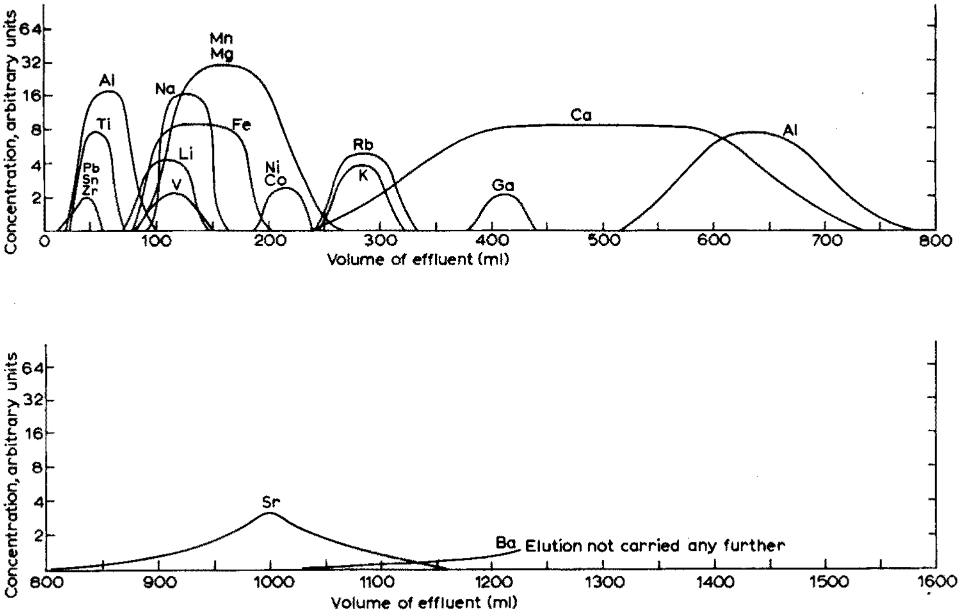

Fig. 5. The 2 *N* HCl elution of major and some trace constituents of 1 g diabase W-1.

Notes on the determination of different elements

(1) Ti, Sn, Pb, Zn and Zr; Al; Li and Na; V; Fe; Mg; Ni and Co; Ga; Mo

Titanium, tin, lead, zinc and zirconium. These elements together with some aluminium, appear first in the effluent on elution with 2 *N* HCl of granites and basic rocks.

Titanium may be determined in Step 3 but can be determined here also after complex formation with hydrogen peroxide[23]. The estimation is carried out in the 0–80 ml fraction. In certain spectrochemical procedures, titanium may serve together with iron and sodium or potassium as a variable internal standard[20]. Titanium is a useful internal standard for estimating zirconium and the abundant rare earth elements in the direct DC arc excitation step referred to on p. 552.

Tin, zinc and lead may be determined in Step 1 or here. For granites and basic rocks, the 0–80 ml 2 *N* HCl fraction is collected.

Spectrochemical procedure for tin. Add 2 ml of 0.001% indium internal standard solution (prepared from C.P. $InCl_3$) and 5 ml of sulphuric acid (s.g. 1.82) to the "Titanium fraction" in a 150-ml silica evaporating basin. (Sulphuric acid is added to prevent loss of tin(IV); tin(II) is readily oxidised to tin(IV) by air and by strong HCl[57].) Load the resultant residue (*ca.* 250 mg) into four graphite anodes (3.2 mm I.D. × 5 mm deep). The residue may tend to extrude after a few seconds of arcing, but a satisfactory burn may be obtained by pre-heating the loaded electrode in a Bunsen flame for about 15 sec; any extruded material is repacked into the electrode before arcing. (On heating, tin (MELLOR[58]) and indium (SEWARD[59]) sulphates are converted to their oxides, the melting points of which are 1127° and 850° respectively[60], hence loss of these metals should be negligible.) In the arcing procedure, each sample is arced for 15 sec at 3 A. The analysis pair is Sn 3175 Å and In 3526 Å.

Details of the zinc and lead estimations have not been worked out; indium would be a suitable internal standard for the spectrochemical estimation of these two elements[20].

Although zirconium could probably be determined in the 0–80 ml 2 *N* HCl fraction (titanium would be a suitable internal standard[20]), such a procedure would find little application, since zirconium may be estimated in almost all silicate rocks with the exception of some ultramafics by direct DC arc excitation[20].

Aluminium. Aluminium is scattered throughout various effluent fractions (AlF_6^{3-} in the early and Al^{3+} in the latter fractions) and because of this dispersion throughout the fractions, aluminium should be estimated in a separate operation. An aliquot of the original 2 *N* HCl solution equivalent to 0.5 g of silicate is diluted to the mark in a 500-ml graduated flask and aluminium may be determined directly by the method of RILEY[23]; iron is complexed as the dipyridyl complex and aluminium is extracted at pH 5 with 8-hydroxyquinoline in chloroform; the absorptivity of the aluminium complex is measured at 410 mμ.

Lithium and sodium. Lithium and sodium may be estimated in the 100–260 ml 2 *N* HCl fraction from granites and the 80–160 ml 2 *N* HCl fraction from basic rocks.

Sodium may be determined flame-photometrically[5] and may then serve as a variable internal standard for estimating lithium either in the same fraction, or of lithium, potassium, rubidium and caesium by direct excitation procedures[20,47]. The use of an enrichment procedure is of little value for lithium since lithium may be estimated in almost any type of rock and in nearly every silicate mineral by direct DC arc excitation of powders[20].

Vanadium. Vanadium could be determined in the 150–200 ml 2 *N* HCl fraction from granites or the 80–150 ml fraction from basic rocks (Pd added as $(NH_4)_2Pd(NO_3)_4$ would be a suitable internal standard) but such a procedure is scarcely worthwhile, since vanadium can be estimated in almost all silicate rocks by direct DC arc excitation[20]. Basic rock types usually contain more vanadium than granites where the vanadium content borders on the detection limit (5 p.p.m.).

Iron. This abundant element may be determined in a suitable aliquot of the 150–270 ml 2 *N* HCl fraction from granites or the 80–200 ml fraction from basic rocks. Various procedures may be employed (titrimetric[5], gravimetric[5] and colorimetric[23]), but the titrimetric methods are perhaps the most satisfactory.

Magnesium. This abundant element may be determined in the 250–380 ml 2 *N* HCl fraction from granites or the 80–260 ml fraction from basic rocks by means of EDTA[5] in the presence of triethanolamine to complex any manganese.

Manganese. Manganese may be determined in the 250–380 ml 2 *N* HCl fraction from granites or the 80–260 ml fraction from basic rocks; a spectrophotometric estimation is suitable after oxidation to permanganate with persulphate[23]. The HF–$HClO_4$ dissolution procedure is not suitable in this case (see p. 553), but the HF–aqua regia–H_2SO_4 method[31] (p. 556) is applicable.

Nickel and cobalt. Nickel and cobalt could be determined in the 330–380 ml fraction from granites or the 180–240 ml fraction from basic rocks; however, an enrichment procedure is of little value because these elements may be estimated in almost all silicate rocks, with the exception of some acid rocks, by direct DC arc excitation[20].

Gallium. The use of an enrichment procedure for the estimation of gallium is unlikely to find such application since this element is easily determined by direct DC arc excitation procedures in almost all silicates except those that are poor in aluminium, such as dunite. However, gallium, in contrast to aluminium, is concentrated in the heavy alkali metal fraction during the 3 *N* HCl elution from a 38 × 1.7 cm column of Dowex 50 (p. 569) and can thus be estimated together with these elements with little extra effort; in this way a check analysis is provided.

Procedure. Pipette a 50-ml aliquot of the 3 *N* HCl effluent containing the heavy alkali metals and gallium, and 2 ml of 0.001% In internal standard solution into an 80-ml evaporating dish and carefully evaporate to dryness. Load the residue into a graphite anode (2.4 mm I.D. × 5 mm deep). As a considerable amount of material may be lost from the electrode during the initial arcing period if moisture is present, the sample must be thoroughly dry before loading. Samples are arced at 3 A to alkali metal completion. In 4101.77 Å is used as the internal standard line, and Ga 4172.06 Å as the analysis line.

Molybdenum. The concentration of molybdenum in common rock types and soils often borders on its spectrochemical detection limit. Molybdenum may be determined in both granites and basic rocks as follows.

Procedure. Adsorb a 2 *N* HCl aliquot equivalent to 1 g of original rock on Dowex 50 as described on p. 565. (Previously wash the column with 2–3 column volumes of 2–5 *N* HCl.) Elute with 2.5 *N* HCl at a flow-rate of 15 ml/h. Collect the fraction 60-95 ml from the commencement of elution, transfer to an 80-ml silica basin and evaporate to near dryness. Add 20 mg of carbon powder containing 0.2% $(NH_3)_4Pd(NO_3)_2$ and evaporate to dryness. Load the residue into a graphite anode (2.4 mm I.D. × 5 mm deep) and arc as described on p. 561.

(2) *The heavy alkali metals (K, Rb and Cs)*

Potassium, rubidium and caesium. Potassium is the only abundant heavy alkali metal and may be detected and estimated by direct DC arc excitation procedures in almost all silicate rocks (granite, basic rocks and ultramafic rocks), meteorites and minerals[20,47]. For many purposes — particularly at low concentration levels — the accuracy so obtained is satisfactory (the relative deviation is usually 4–8%) but if greater accuracy is required other techniques (*e.g.* flame photometry) should be used. By means of direct DC arc excitation procedures, rubidium may be estimated in granites, basic rocks, chondrites (under certain conditions) but not in ultramafics, either without an internal standard or using Na or K as variable internal standards[20,47]. Caesium may be estimated similarly in most granites, very rarely in basic rocks and not in chondrites or ultramafic rocks. Techniques are described here which allow estimation of K, Rb and Cs in granite, basic rocks, chondrites and some ultramafic rocks. The column procedures are varied according to whether granite, basic rock, chondrite, or ultramafic rock is to be analysed.

(*a*) *Granites and basic rocks.* Two procedures are possible. In the first, the 380–470 ml 2 *N* HCl fraction is collected for granites and for basic rocks the 240–340 ml 2 *N* HCl fraction (Figs. 4 and 5). These fractions are then processed as described below. However, a procedure described by AHRENS *et al.*[4] is generally preferable. Soak the

2 N HCl solution containing 1 g of silicate material into Dowex 50 as described on p. 565. (Previously equilibrate the column with 2–3 column volumes of 3 N HCl.) As soon as the liquid level reaches the resin surface, start elution with 260 ml of 3 N HCl at a flow-rate of 20 ml/h. After 160 ml has passed through the column, collect the next 100 ml in a 250-ml beaker; this (the 'K fraction') contains all the K, Rb, Cs and some Ca.

For the estimation of caesium in granites (the concentration usually lies between 1 and 20 p.p.m.) and related rocks, dilute the 'K fraction' to the mark with 3 N HCl in a 200-ml standard flask; use a 50-ml aliquot of this solution; evaporate to dryness in a silica basin and analyse the resultant residue spectrochemically as described below. For basic rocks (the caesium concentration usually lies between 0.3 and 2 p.p.m.) most of the calcium must be removed in a second column: evaporate the whole 'K fraction' to near dryness and soak into a 22 × 1.9 cm column of Dowex 50 (8X, 200–400 mesh) resin at a flow-rate of 0.25 ml/min. (Previously equilibrate the column with 2–3 column volumes of 3 N HCl.) Elute with 180 ml of concentrated HCl (s.g. 1.18) at a flow-rate of 25 ml/h. Collect the whole effluent, evaporate to dryness in a silica basin and analyse the resultant residue spectrochemically.

Load the K–Rb–Cs concentrates into graphite anodes (2.4 mm I.D. × 5 mm deep) and arc at 5 A. Stop the exposure shortly before the whole of the sample is consumed, otherwise CN red emission interferes excessively with Cs 8521 Å; the other analysis lines are K 6911 Å and Rb 7947 Å.

(*b*) *Special procedure for the estimation of caesium at very low concentrations (as in chondrites and certain ultramafic rocks).* As the concentration level of caesium (*ca.* 0.1 p.p.m.) in chondrites is low, considerable enrichment must be achieved before a quantitative spectrochemical estimate can be attempted. Calculation shows that the principal constituents of chondrites (Si, Mg, Fe, Al, Ca and Na) have to be almost completely removed; the spectrochemical determination is carried out on a potassium-rich fraction containing the two heavy alkali metals, Rb and Cs. For this purpose, the following scheme has been evolved[4].

Procedure. Moisten two separate 5-g samples of chondrite powder (*ca.* 100 mesh) with water in platinum basins and treat with 15 ml of perchloric acid (70%) and 20 ml of hydrofluoric acid (40%). After slow evaporation, add 30 ml of concentrated HCl (s.g. 1.18) and warm for 5 min while stirring. Decant the HCl into a 100-ml polythene bottle. Combine the residues and treat with 15 ml of perchloric acid and 10 ml of hydrofluoric acid and slowly evaporate to dryness. When cool, add 20 ml of concentrated HCl. Warm the contents, stir for 4 min and decant into the polythene bottle containing the first HCl decantation solution; add 5 ml of perchloric acid to the small residue in the platinum dish. Continue evaporation until evolution of copious fumes ceases. When the resultant residue is warmed with 10 ml of concentrated HCl, only a very small dark residue should remain; spectrochemical analysis has shown this to contain only Fe and Cr and it may accordingly be discarded. Add the HCl-soluble fraction, together with a 2–3 ml of concentrated HCl rinse of the basin, to the contents of the polythene bottle.

To remove iron by means of anion exchange, soak the concentrated HCl solution containing iron as an anionic chloro-complex into a 15 × 3 cm column of Amberlite IRA 400 (8X, 100–200 mesh, chloride-form) at a flow-rate not exceeding 0.5 ml/min. (Previously equilibrate the column with 500 ml of concentrated HCl at a flow-rate of 1–2 ml/min.) Elute with 600 ml of HCl (s.g. 1.18) at a flow-rate of 0.5 ml/min. Fe, Ga, Zr, Co and Ti remain on the column, while Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Al and a few other rare elements appear in the effluent, which is collected in a 600-ml beaker.

Before further use, remove adsorbed Fe, Ga, Zr, Co and Ti from the column by elution first with 200 ml of 0.5 *N* HCl and then with 100 ml of deionized water, both at a flow-rate of 1 ml/min.

To remove aluminium (and some Mg and Ca), evaporate the HCl effluent to 40–50 ml and transfer to an 80-ml silica basin; wash the beaker twice with 10-ml portions of deionized water. Add 10 ml of perchloric acid (70%) and evaporate to dryness. Heat the dried perchlorate residue for 20 min at 550° in an electric muffle, cool and transfer to an agate mortar; grind and return to the silica basin to which add 50 ml of deionized water and heat almost to boiling; when cool, transfer the aqueous extract to a 75-ml centrifuge tube and centrifuge. Pour the supernatant liquid into a 500-ml beaker and return the residue to the silica basin; the operation should be carried out about seven times.

Spectrochemical analysis of the dried combined aqueous extracts showed the presence of Li, Na, K and Rb (Cs not detectable) plus Mg, Ca, Sr and Ba. The leached residue (oxides) from the thermal decomposition of the perchlorates contained Al (presumably all of it), Mg, Ca, V, Ni, Cr and a very small trace of Na (highly sensitive D-lines barely detectable); otherwise the alkali metals were not detectable.

To remove sodium, dissolve the aqueous extract residue in 5 ml of 1 *N* HCl. Wash the beaker with 5 ml of 1 *N* HCl and combine with the first solution. Adsorb onto a 22 × 1.9 cm column of Dowex 50 (8X, 200–400 mesh, H-form) at a flow-rate not exceeding 0.25 ml/min. (Previously equilibrate the column with 150 ml of 1 *N* HCl at a flow-rate of 1–2 ml/min.) Pass 270 ml of 1 *N* HCl through the column at a flow-rate of 0.5 ml/min. The effluent contains Li and Na but no detectable K, Rb or Cs and is discarded. The effluent from elution with 325 ml of 2 *N* HCl (0.5 ml/min) contains K, Rb, Cs with varying amounts of Mg and a little Ca. As caesium is usually detected only in those effluents which contain a minimum of magnesium, this element must be removed in a final step. The column may be regenerated by passing 500 ml of 6 *N* HCl at a flow-rate of 30–35 ml/h followed by 200 ml of 1 *N* HCl at the same rate.

To remove the residual magnesium, evaporate the 2 *N* HCl effluent to 20–30 ml and transfer together with two 5-ml washings with deionized water, to an 80-ml silica basin and take to dryness. Add 10 ml of 3 *N* perchloric acid, warm and soak into Dowex 50 as described on p. 565. (Previously wash the column with 5 column volumes of 3 *N* $HClO_4$.) Wash the basin with warm 3 *N* perchloric acid and transfer the washings to the column. When the liquid level in the chromatography tube has reached the resin surface, elute with 165 ml of 3 *N* $HClO_4$ at a flow-rate of 25 ml/h. Collect the effluent containing the heavy alkali metals in a 250-ml beaker, take to dryness and load into a graphite anode (2.4 mm I.D. × 5 mm deep). After elution with another 500 ml of 3 *N* $HClO_4$ at the rate employed above, the column is again ready for use.

The K–Rb–Cs concentrates are acred at 5 A. Exposures are superimposed where necessary and recorded on Kodak 1-L plates. Care should be taken to stop the exposure shortly before the whole sample is consumed because CN emission otherwise interferes excessively with Cs 8521 Å, the analysis line. Background may nevertheless be quite intense in several spectra and a special effort might therefore have to be made to estimate and correct for the presence of background[4].

The standard diabase W-1[21,22] may serve as a standard for caesium and potassium.

(*3*) *Ca; the abundant rare earths* (*Y, La, Ce and Nd*) *and Sc; Sr and Ba*

Calcium. From granites and related rocks, the 640–940 ml 2 *N* HCl fraction is collected and from basic rocks the 240–740 ml 2 *N* HCl fraction (Figs. 4 and 5). Various procedures may be employed to estimate calcium[5] (precipitation as oxalate, titration with EDTA or flame photometry). According to VINCENT[5], "few silicate analysts have achieved success" with flame photometric estimation of calcium.

If estimated, calcium may serve as a variable internal standard for the spectrochemical estimation of certain other elements, notably strontium and barium, in the direct DC arc excitation of the rock powder[20].

The abundant rare earths (yttrium, lanthanum, cerium and neodymium) and scandium. Whether or not these elements can be estimated by means of direct DC arc excitation of rock powders depends primarily on the rock type. Scandium is easily detectable in basic and ultramafic rocks, but may be difficult to estimate in granites and acid rocks because its concentration in these rocks is much lower than in basic rocks. The reverse concentration relationship generally holds for the rare earth elements, lanthanum, cerium, and neodymium. Lanthanum, neodymium and yttrium can usually be estimated in most granites. Cerium is often not detectable in these rocks because of poor spectrochemical sensitivity. Aside from providing possible check determinations, the principal application of the procedure to be described here is for the estimation of scandium in granites and related rocks and cerium in both granites and basic rocks.

Procedure. Either route (*1*) or (*2*) may be used. (*1*) After 900 ml of 2 *N* HCl (granites, Fig. 4) or 800 ml of 2 *N* HCl (basic rocks, Fig. 5) have passed through the column, pass 800 ml of 6 *N* HCl through the column and collect the whole of this volume. (2) The following column procedure employing 3 *N*–6 *N* HCl is recommended for concentrating Y, La, Ce and Nd in common silicate rocks (EDGE AND AHRENS[10]). Soak the 2 *N* HCl solution containing 1 g silicate material into Dowex 50 as described on p. 565. (Previously wash the column with 2–3 column volumes of 3 *N* HCl.) Begin elution with 330 ml of 3 *N* HCl at a flow-rate of 15 ml/h. Then elute with 700 ml of 6 *N* HCl at a flow-rate of 20 ml/h. Fig. 6 illustrates the elution of Y, Nd, and La under these experimental conditions. Collect the 0–60 ml 6 *N* fraction separately and discard it.

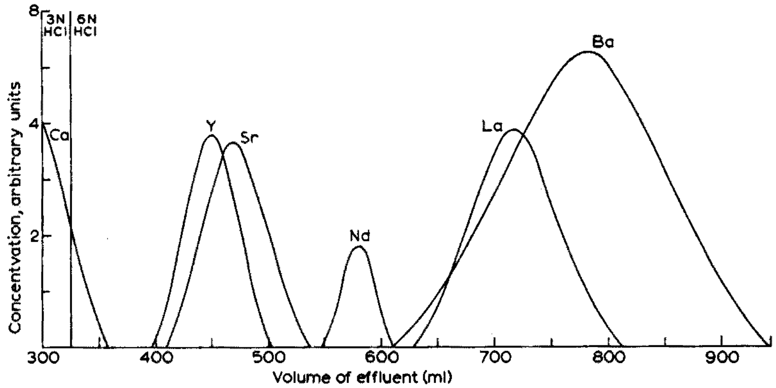

Fig. 6. Location of Y, Nd and La (1 mg each of Y_2O_3, Nd_2O_3 and La_2O_3) in the effluent from the 3–6 *N* HCl elution of 1 g Cape Granite.

The main 6 *N* HCl fractions from (*1*) or (*2*) are prepared in the following way for spectrochemical analysis. Evaporate the 6 *N* HCl effluent to 40–50 ml in a beaker. Transfer to an 80-ml porcelain evaporating basin containing 5 mg 5% ZrO_2 (internal standard)–carbon powder mixture. Since the quantity of residue is comparatively small (*ca.* 5–10 mg) the ZrO_2–C mixture aids in collecting the residue and serves as a matrix for subsequent spectrochemical analysis. Load the material into a graphite anode cavity (2.4 mm I.D. × 3 mm deep). As a considerable amount of material may be lost from the electrode during the initial arcing period because of some moisture, the sample must be thoroughly dry before loading it into the electrode. Arc to completion at 7 A. Zr 3914 Å may be used as the internal standard line with the following analysis lines: Sc 4246.83 Å, Y 4398.02 Å, La 4333.73 Å, Ce 4296.68 Å, and Nd 4303.57 Å.

Emission from Ca 4302.52 Å is intense in rare earth concentrates from some basic rocks and can interfere with Nd 4303.57 Å; if so, Nd 4451.55 Å may be used. Prepare working curves from standard rocks G-1[21,22] and W-1[21,22] which can be carried through the same column and spectrochemical procedure as the rock samples.

Strontium and barium. These elements are easily determined by direct DC arc excitation in most minerals, rocks, soils and meteorites, but as they are concentrated in the rare earth fraction during the 6 *N* HCl elution (see Fig. 6 and p. 571), they could probably be estimated together with the rare earths with little extra effort. Lanthanum could serve as a variable internal standard for Sr and Ba[20].

Loveridge *et al.*[61] have used cation-exchange chromatography with 2.5 *N* HCl elution for separating strontium from silicates for isotope dilution analysis.

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SUMMARY

An attempt is made to integrate into an analytical "scheme" a series of investigations on the complete analysis of the naturally occurring silicates. Emphasis is placed on simplicity, high sensitivity (if necessary), wide element coverage, speed and satisfactory accuracy. The analytical operations involve ion exchange, solvent extraction and spectrochemical techniques. Observations are made on the following elements: Ag, Al, Au, Ba, Bi, Ca, Cd, Ce, Cs, Cu, Fe, Ga, In, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, Pb, Pd plus other elements of the platinum group, Rb, Sc, Si, Sn, Sr, Ti, Tl, V, Y, Zn and Zr.

RÉSUMÉ

Un essai a été fait pour intégrer en un schéma une série de recherches sur l'analyse complète de silicates naturels. On a tenu compte de la simplicité, de la sensibilité (si nécessaire), de la rapidité et de la précision. Les différentes opérations analytiques comprennent: échange d'ions, extraction par solvant et techniques spectrochimiques.

ZUSAMMENFASSUNG

Beschreibung eines vollständigen Analysenganges für Silikate, der auf neueren Trenn- und Bestimmungsverfahren wie Ionenaustausch, Lösungsmittel-extraktion und spektrochemischen Methoden beruht. Hierbei wurde besonders Wert gelegt auf Einfachheit, Empfindlichkeit, Zeitersparnis und genügende Genauigkeit.

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Short Communications

The oxygen flask in qualitative organic analysis: detection of nitrogen

Combustion in an oxygen-filled flask is now a very well known technique in quantitative organic analysis. In a recent review STEPHEN[1] suggested the use of the oxygen flask as a simple method for the destruction of organic material in the first stage of qualitative organic analysis, and HASLAM *et al.*[2] have successfully applied the method to the detection of "additional elements" in polymers and other plastic materials on a 20-mg scale. It is obvious that with suitable refinement it should provide an excellent method for qualitative organic analysis on a 0.5–1 mg scale.

Although widely used, the classical Lassaigne fusion procedure[3,4] for the detection of nitrogen, halogens, and sulphur is not entirely reliable. The technique is not without hazard, particularly with completely unknown materials, and certain compounds may even escape reaction[1,5]. Modifications such as those of CASTELLANA[6] and MIDDLETON[7], although simple in appearance, are reported by TUCKER[4] to require a fair amount of skill and are still not completely safe.

The present investigation was undertaken in order to test the possibility of replacing the conventional Lassaigne fusion procedure by one using an appropriately sized oxygen flask in a general scheme for the detection of the elements in organic compounds on a 0.5–1 mg scale. In order that the method could be readily used in teaching and research laboratories, all apparatus has been kept as simple as possible.

Detection of nitrogen by the oxygen flask

Little is known of the fate of nitrogen from an organic compound following combustion in an oxygen-filled flask. INGRAM's study[8] of the products of decomposition of nitrogen-containing compounds in a conventional carbon and hydrogen combustion train would suggest that some oxides of nitrogen are always formed even from compounds such as azobenzene which might be expected to split out nitrogen. HASLAM *et al.*[2] investigated the detection of nitrogen by the oxygen flask but with particular reference to plastic materials where the percentage of nitrogen present is normally relatively low. Using 20-mg samples on relatively large pieces of filter paper, they found that a substantial nitrite blank was always obtained when the very sensitive Griess test was used. For this reason they favoured the less sensitive nitrite test of Peach involving the nitrosation of resorcinol followed by reaction of the product with iron(II); positive tests for a wide range of nitrogen-containing compounds were then obtained. Their suggestion that this method could also be used for the semi-quantitative estimation of nitrogen requires clarification. INGRAM in his study of the conversion of nitrogen in organic compounds to oxides of nitrogen showed variations in successive experiments on one compound and enormous variations with changes in the nitrogen function.

Extensive testing of the method described below has shown that oxides of nitrogen produced during the combustion of nitrogen-containing samples may be detected by the sensitive Griess reagent[9] following absorption in dilute alkali. Provided that the piece of filter paper used to hold the sample is small, the nitrite blank is also small and is easily distinguished from a positive nitrogen test. Compounds were selected to give a range of different chemical types and also to give as wide a variation of combinations of the elements as possible. Where necessary combinations were obtained by mixing samples containing the desired elements. All the nitrogen-containing compounds tested, except those containing bromine as well as nitrogen which do not appear to have been investigated by HASLAM *et al.*, gave a very definite reaction with the Griess reagent. Halogen-containing compounds were investigated further. It was found that fluorine, chlorine, and iodine did not interfere in the Griess test, the test for nitrite in the absorbent solution being positive in all cases where nitrogen was present in the sample. With bromine-containing samples the presence of nitrate in the test solution could be shown by carrying out the Griess test after reduction with zinc dust in dilute acetic acid, but the colour produced was not very intense.

INGRAM[8] has shown that the presence of platinum in a conventional carbon and hydrogen combustion train has a catalytic effect on the production of oxides of nitrogen. But combustion of a bromine-containing compound on a platinum gauze gives free bromine and this oxidises nitrite to nitrate. Thus although oxides of nitrogen may be produced in the initial combustion, nitrite is not detected in the absorbent solution because it is so readily oxidised to nitrate by the bromine simultaneously produced.

If the simple Griess nitrite test[9] is to be retained as a method for the detection of nitrogen, bromine must be removed before it reacts with the nitrite ions. This may be satisfactorily accomplished by burning the sample in the normal manner but with a copper gauze in place of the platinum gauze; the bromine then reacts with the copper and no difficulty is experienced in obtaining a positive Griess nitrite test on the absorbent solution from nitrogen-containing samples. Between analyses the copper gauze should be thoroughly washed in hot water and carefully ignited (without melting) in a Bunsen flame. A silver gauze was also found to be satisfactory in the detection of nitrogen in the presence of bromine.

Experimental

Combustion technique. Combustion of the sample is carried out in an oxygen-filled 100-ml conical flask (B14 S.T. ground neck). Samples (*ca.* 0.5 mg) are folded into a piece of filter paper (Whatman No. 44) about 15 mm square with a "tail" or "fuse" about 3 mm × 15 mm as in quantitative analysis. This is clamped in a folded oblong of platinum gauze (8 mm × 16 mm) attached to a piece of platinum wire sealed into a B14 stopper or air-leak tube. A similar gauze is made from copper and attached to a copper wire sealed into a B14 stopper.

Sodium hydroxide (2 ml of 0.1 *M* solution) is added to the flask and the air is displaced by a rapid stream of oxygen. The fuse is ignited and the stopper inserted and held in the flask which is inverted until combustion is complete. After 5–10 min of occasional shaking, the flask is opened and a drop of the test solution is transferred to a spot tile by means of a capillary pipette.

Detection of nitrogen

Reagent. (*1*) 1% Solution of sulphanilic acid in 30% acetic acid. (*2*) 0.1% Solution of 1-naphthylamine in 30% acetic acid. Equal volumes of (*1*) and (*2*) are mixed just before use to give the Griess reagent.

Method. Add one drop of the Griess reagent to a drop of the test solution in the depression of a spot tile. Nitrogen in the sample yields nitrite in the test solution which causes an immediate red coloration or red precipitate. A blank test should be carried out on the filter paper; it may give a light pink coloration but a positive test for nitrogen is easily distinguished.

If bromine is present in the sample, the combustion must be repeated under similar conditions but with a copper gauze.

Detection of other elements by the oxygen flask

The solution obtained from combustion on a platinum gauze as above is suitable for the detection of halogens, sulphur, phosphorus and certain other elements. The method described yields sufficient solution to permit tests being carried out for other elements as well. Where it is desired to check the presence of only one or two elements on a small scale the size of the flask may be conveniently reduced to 50 ml and the volume of absorbent solution to 0.5 ml — sufficient to wet the inside of the flask. Many metals may be detected by carrying out conventional spot test reactions on the absorbent solution following combustion of the sample in a flask containing 2 *M* hydrochloric acid. A detailed scheme for the qualitative analysis of organic compounds will be published elsewhere.

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Calculation of equilibrium concentrations of complex ions from stability constant data

Stability constants of many complex ions have been determined. It is often necessary to be able to calculate from the stability constants the concentrations of the various ionic species at equilibrium, as for example, in the calculation of the heat changes associated with the various steps occurring in complex salt formation. The graphical solution of this problem is rather tedious and the following procedure has been developed for use with a desk machine, or better, with a digital computer.

As an illustration, the method is applied to the silver–pyridine system, *a* and *b* being the initial concentrations of silver and pyridine respectively.

$$\underset{(a-x)}{\mathrm{Ag}^+} + \underset{(b-x-y)}{\mathrm{py}} \rightleftharpoons \underset{(x-y)}{[\mathrm{Agpy}]^+} \qquad k_1 = \frac{(x-y)}{(a-x)(b-x-y)} \tag{1}$$

$$\underset{(x-y)}{[\mathrm{Agpy}]^+} + \underset{(b-x-y)}{\mathrm{py}} \rightleftharpoons \underset{y}{[\mathrm{Agpy}_2]^+} \qquad k_2 = \frac{y}{(x-y)(b-x-y)} \tag{2}$$

x and *y* may be found graphically but the method is tedious and of limited accuracy.

A solution of this problem may be found by solving the equations

$$\begin{aligned} k_1(a-x)(b-x-y) - (x-y) &= 0 \\ k_2(x-y)(b-x-y) - \quad y \quad &= 0 \end{aligned} \tag{3}$$

$$\begin{gathered} 0 < x < a \\ 0 < x + y < b \end{gathered} \tag{4}$$

Disregarding (4) for the moment, solution of set (3) yields a cubic equation and for practical values of the known parameters *a*, *b*, k_1, k_2, this cubic may have three real roots; the computations involved in deriving the necessary coefficients for cubic solution are rather more than the few complete iterations in the method proposed here.

It is easy to show that the physically meaningful root of (3) and (4) lies on the curve

$$y = \frac{b + \frac{1}{k_2}}{1} - \sqrt{\left(\frac{b + \frac{1}{k_2}}{2}\right)^2 - x(b-x)} \tag{5}$$

Consequently, if no other approximation is available, $x = 0$ will do as a starting value. The iterative scheme becomes

"If *x* is an approximation to the root, then $x + h$ is a better one where

$$h = -\frac{(\alpha - 2y)(x^2 + xy - \beta x - \gamma y + ab)}{(2x + y - \beta)(\alpha - 2y) + (b - 2x)(x - y)} \tag{6}$$

where

$$\alpha = b + \frac{1}{k_2}, \quad \beta = a + b + \frac{1}{k_1}, \quad \gamma = a - \frac{1}{k_1}$$

and y given by (5)".

For example, in the silver–pyridine system it may be necessary to determine the concentrations of all the ionic species in solution. Commencing with an initial concentration a of silverion and b of pyridine, the concentrations of all the ionic species can be found by the evaluation of x and y.

For this system the stability constants k_1 and k_2 are 100 and 140 respectively. In a particular experiment the initial concentrations a and b were 0.0448 and 0.0482 mol/l respectively. It is required to find x and y. As a first attempt to solve (5) put $x_0 = 0$ and calculate y_0. In this case, $y_0 = 0$. Putting $x_0 = 0$, $y_0 = 0$ in equation (6), h_0 is found to be 0.016198.

Now let $x_1 = x_0 + h_0$, that is, 0.016198, place this value for x in (5) and calculate y_1. In this case $y_1 = 0.011945$.

Putting $x_1 = 0.016198$, $y_1 = 0.011945$ in equation (6), h_1 is found to be 0.007810.

After five such iterations h_0 is found to be $-2 \cdot 10^{-9}$ and so the solution of (5) for x and y is correct to six places.

The calculations are tabulated and for the initial a and b as indicated above, the results for x and y are 0.026999 and 0.013768 respectively, correct to six decimal places.

The concentrations of all the ionic species can now be found:

Ag^+	$= (a - x)$	$= 0.0448 - 0.0270$	$= 0.0178$ mol/l
py	$= (b - x - y)$	$= 0.0482 - 0.0270 - 0.0138$	$= 0.0074$ mol/l
$[Agpy]^+$	$= (x - y)$	$= 0.0270 - 0.0138$	$= 0.0132$ mol/l
$[Agpy_2]^+$	$= y$	$= 0.0138$	$= 0.0138$ mol/l.

EXAMPLE OF CALCULATION (6 DECIMAL PLACES ONLY)

Data: $k_1 = 100$, $k_2 = 140$, $a = 0.0448$, $b = 0.0482$.

Starting value		$x_0 = 0.000000$	and x_0 in (3) gives $y_0 = 0.000000$
x_0 and y_0 in (4) give		$h_0 = 0.016198$	
First iteration	$x_0 + h_0 =$	$x_1 = 0.016198$	and x_1 in (3) gives $y_1 = 0.011945$
x_1 and y_1 in (4) give		$h_1 = 0.007810$	
Second iteration	$x_1 + h_1 =$	$x_2 = 0.024008$	and x_2 in (3) gives $y_2 = 0.014073$
x_2 and y_2 in (4) give		$h_2 = 0.002709$	
Third iteration	$x_2 + h_2 =$	$x_3 = 0.026717$	and x_3 in (3) gives $y_3 = 0.013824$
y_3 and y_3 in (4) give		$h_3 = 0.000280$	
Fourth iteration	$x_3 + h_3 =$	$x_4 = 0.026997$	and x_4 in (3) gives $y_4 = 0.013769$
x_4 and y_4 in (4) give		$h_4 = 0.000002$	
Fifth iteration	$x_4 + h_4 =$	$x_4 = 0.026999$	and x_4 in (3) gives $y_4 = 0.013768$
x_4 and y_4 in (4) give		$h_4 = -2 \cdot 10^{-9}$,	so that the iteration has converged to 6 places.

In machine operation on this problem it was found that an average of 5 to 6 iterations yielded x and y correct to five significant figures. The method seems ideally suited to computer work where a large number of quartets a, b, k_1, k_2 are available and the corresponding values of x and y are needed for interpretation of the experiments.

For the particular machine used (I.B.M. 1620, using FORTRAN language) the very simple programme for the above yielded the relevant five-figure solutions (x, y) for a number of different quartets (a, b, k_1, k_2) at much less than half a minute per quartet.

The problem for finding equilibrium constants for such reactions as

$$\begin{aligned} \mathrm{Ni^{2+}} + \mathrm{en} &\rightleftharpoons [\mathrm{Ni\ en}]^{2+} \\ [\mathrm{Ni\ en}]^{2+} + \mathrm{en} &\rightleftharpoons [\mathrm{Ni\ en_2}]^{2+} \\ [\mathrm{Ni\ en_2}]^{2+} + \mathrm{en} &\rightleftharpoons [\mathrm{Ni\ en_3}]^{2+} \end{aligned}$$

has been handled similarly with a similar simple program of about the same length, using the same iterative technique on the three mass law equations.

It is felt that attention should be paid to other similar chemical problems where an iterative method of solution can replace the usual graphical methods.

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Appendix: FORTRAN Programme

```
 1   FORMAT (F8.4, F8.4, F10.0, F10.0)
 2   FORMAT (4H DATA, 2HA =, F6.4, 2HB =, F6.4, 2HC =, F8.0, 2HD =, F8.0)
 4   FORMAT (3HX =, F9.7, 6H Y =, F9.7)
 5   FORMAT (6H CHECK, 16H CALCULATED C =, F12.2, 3H D =, F12.2)
 8   ACCEPT TAPE 1, A, B, C, D
     X = 0.0
     Y = 0.0
 9   PRINT 2, A, B, C, D
     E = B + 1./D
     F = A + B + 1./C
     G = A - 1./C
10   HNUM = (Y + Y - E)* (X* X + X* Y - F* X - G* Y + A* B)
     HDEN = (X + X + Y - F)* (E - Y - Y) + (B - X - X)* (X - G)
     H = HNUM/HDEN
     X = X + H
     Y = E/2. - SQRT ((E/2.)* (E/2.) - X* (B - X))
     IF ((H* H) - 1.0E - 12) 15, 10, 10
15   PRINT 4, X, Y
     IF (SENSE SWITCH 2) 16, 8
16   AC = (X - Y)/((B - X - Y)* (A - X))
     AD = Y/((B - X - Y)* (X - Y))
     PRINT 5, AC, AD
     GØTØ 8
     END
```

Notes: (1) The correspondence between programme and the illustration is:

A B C D X Y	AC and AD
a b k_1 k_2 x y	check-calculated k_1 and k_2

(2) If sense switch 2 is "ON", the computer will check the values of x and y obtained by calculating k_1 and k_2 for comparison with input data.

(3) The programme is for an I.B.M. 1620 with tape input.

3-Oximinomethylsalicylic acid as a reagent for the gravimetric determination of thorium

Salicylic acid and ammonium salicylate[1] have long been known as reagents for the determination of thorium and its separation from cerium, as well as for the determination of zirconium. Many similar reagents have also been proposed. In order to check if substitution in the benzene nucleus of salicylic acid would lead to an improved reagent, 3-oximinomethylsalicylic acid was prepared and examined for the determination of thorium and for its separation from rare earths and other ions. It was found that the new reagent gave considerably better separations, but it is still necessary to ignite the precipitate to thorium oxide for gravimetric determination.

Reagents and chemicals

3-Oximinomethylsalicylic acid was prepared as follows. A mixture of 3-aldehydosalicylic acid[2] (1 mol), hydroxylamine hydrochloride (1 mol) and sodium hydroxide (1.5 mol) in water (100 ml) was warmed at 40° for 24 h. The clear solution was then cooled and acidified with cold dilute sulphuric acid (1:4 by volume), when 3-oximinomethylsalicylic acid separated in the form of fine crystals. These were washed with cold water and recrystallised from warm water containing some iron-free charcoal. The product was dried in air (m.p. 193°). A 2% solution of the reagent in aqueous alcohol was used.

Stock solutions of thorium nitrate, cerium nitrate and lanthanum nitrate (E. Merck's reagents) were prepared and standardized by the oxalate procedure. Solutions of other metals, such as magnesium, barium, iron, zinc, etc., were prepared by dissolving the nitrates or sulphates (E. Merck) in water and were standardized by the usual methods.

Procedure

A solution of thorium nitrate (containing 0.01–0.09 g of ThO_2) was treated with an excess of the reagent. A solution of ammonium acetate (0.2 g for every 0.02 g of thorium present) was added and the mixture made just neutral to Congo red by cautious addition of dilute alkali. The solution was then heated to boiling and kept on the water bath for about 5 min. The pale yellow flocculant precipitate of the thorium compound was filtered through No. 42 Whatman filter paper. The precipitate was repeatedly washed with boiling water containing a little of the reagent, partially dried and then ignited to thorium oxide to a constant weight in a platinum crucible. The results are recorded in Table I.

RESULTS AND DISCUSSION

The optimum pH range for the precipitation of thorium was found to be 4–5, hence Congo red indicator was used for adjusting the pH.

For the separation of thorium from cerite earths, thorium was precipitated by the procedure described above. The results are given in Table II.

TABLE I

RESULTS FOR THORIUM ALONE

ThO_2 taken (mg)	*ThO_2 found (mg)*	*Error (mg)*
88.98	89.00	+0.02
62.29	62.23	−0.06
53.39	53.35	−0.04
44.49	44.59	+0.10
35.59	35.50	−0.09
26.69	26.60	−0.09
17.79	18.10	−0.31

TABLE II

SEPARATION OF THORIUM FROM CERITE EARTHS

(ThO_2 taken = 44.49 mg; total volume of solution = 75 ml)

CeO_2 present (mg)	*La_2O_3 present (mg)*	*ThO_2 found (mg) by*		*Error (mg)*
		Single pptn.	*Double pptn.*	
53.46		44.60		+0.11
80.20		44.70		+0.21
133.70		44.60		+0.11
200.50		44.75		+0.26
133.70			44.45	−0.04
53.50	38.02	44.60		+0.11
53.50	76.03	44.75		+0.26
200.50	88.71		44.50	+0.01
101.00	253.40		44.75	+0.26

It can be seen that the rare earths do not interfere in the thorium precipitation when present up to a thorium–earth oxide ratio of 1:6.5, beyond which ratio reprecipitation is necessary. The best pH range for this separation was found to be 4–5, as in the case of thorium alone.

TABLE III

SEPARATION OF THORIUM FROM URANIUM

ThO_2 taken (mg)	*U_3O_8 present (mg)*	*Approx. ratio of ThO_2 : U_3O_8*	*ThO_2 found (mg) by*		*Error (mg)*
			Single pptn.	*Double pptn.*	
35.59	37.74	1:1	35.50		−0.04
35.59	15.09	2:1	35.70		+0.11
53.39	37.74	1.4:1	53.50		+0.11
17.79	113.22	1:8	21.80	17.74	+4.00 −0.05
17.79	226.44	1:13		17.80	+0.01
17.79	113.22	1:8		17.75	−0.04
17.79	75.48	1:4		17.80	+0.01
17.79	301.90	1:17		17.95	+0.16
17.79	452.88	1:25		18.00	+0.20

Results for the determination of thorium in presence of uranium are given in Table III; above certain amounts of uranium, reprecipitation is necessary.

3-Oximinomethylsalicylic acid can separate thorium from many other metal ions in the pH range 4–5. Cobalt, nickel and manganese require reprecipitation, even if present in relatively small amounts. Metals such as copper, titanium and zirconium interfere, being precipitated by the reagent under the same conditions as thorium. Some results are collected in Table IV.

TABLE IV

INTERFERENCE OF FOREIGN IONS

(ThO_2 present = 44.49 mg)

Metals as oxide	*Amount added (mg)*	*ThO_2 found (mg)*	*Error (mg)*
CaO	155.50	44.15	−0.34
CaO	311.00	44.10	−0.39
BaO	160.75	44.35	−0.14
BaO	321.50	44.20	−0.29
SrO	101.50	44.20	−0.29
ZnO	152.00	44.50	+0.01
ZnO	504.00	44.90	+0.41
MgO	203.50	44.80	+0.31
NiO[a]	211.40	44.90	+0.41
CoO[a]	102.50	44.80	+0.31
Cr_2O_3	321.00	44.85	+0.36
Al_2O_3	310.50	45.00	+0.51
Al_2O_3	105.30	44.70	+0.21
FeO	31.37	44.70	+0.21
FeO	31.37	44.50	+0.01
Fe_2O_3[a]	69.71	44.55	+0.06
FeO_3[a]	139.50	44.60	+0.11
Fe_2O_3	139.50	44.55	+0.06

[a] Indicates double precipitation. Iron(III) was masked with ascorbic acid.

For the determination of thorium in Indian monazite sand, sulphuric acid extracts of the samples were prepared after phosphoric acid and zirconium had been removed by the method of Rao *et al.*[3]. Thorium and rare earths present were converted to their nitrates. The solution was adjusted to pH 4–5 and thorium was determined as described above. The results compared with those obtained by using *m*-nitrobenzoic acid[4], are given in Table V.

Composition of the precipitate

The thorium salt was precipitated as described above, filtered on a sintered glass crucible, washed several times with boiling water and then with absolute alcohol, and finally dried in air to a constant weight. Ignition of the precipitate gave a ThO_2 content of 39.79%, while drying at 110° indicated a water content of 10.01%; $Th(C_8H_5O_4N)_2 \cdot 4H_2O$ requires ThO_2, 39.89% and H_2O, 10.89%. The composition of the precipitate was, however, found to vary slightly; hence, ignition to ThO_2 is recommended.

TABLE V

ANALYSIS OF MONAZITE SAND[a]

Sample of monazite (g)	*ThO_2 found by* m-*nitrobenzoic acid method (mg)*	*% ThO_2*	*ThO_2 found by proposed method (mg)*	*% ThO_2*
1.1340	82.90	7.31	82.90	7.31
1.2320	90.30	7.32	90.10	7.31
1.2760	93.50	7.32	93.30	7.31

[a] Supplied by the Govt. of India, Ministry of Natural Resources and Scientific Research.

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Bromination of some 8-quinolinols

The determination of metal ions through 5,7-dibromination of the 8-quinolinol (oxine) released by dissolution in acid of the precipitated metal chelate is well established. Usually the dibromination is done by conventional titrimetry, but sensitive coulometric methods involving electrogenerated bromine have also been used. The bromometric determination of metal ions through substituted oxines has been given much less study.

This Note is concerned with the rate of dibromination of 2-phenyloxine and of 2-, 4-, and 6-methyloxine, and with the precipitate that can form in a conventional bromometric titration of oxine and these substituted oxines.

Reagents

2-Methyloxine was obtained as described elsewhere[1].

4-Methyloxine was synthesized by a procedure[2] modified by the use of *o*-nitrophenol as an oxidant. The product was recrystallized from aqueous ethanol (m.p. 141–142°; ref.[2]: 141°).

6-Methyloxine was prepared by a Skraup reaction involving 2-amino-5-methylphenol, using a procedure[3] recommended for 5-methyloxine. The product was recrystallized twice from aqueous ethanol (m.p. 94–95°; ref.[4]: 95–96°). The 2-amino-5-methylphenol was synthesized by preparing and reducing 2-nitro-5-methylphenol[5].

2-Phenyloxine was prepared using a procedure[2] recommended for 2-aryloxines. The product was converted to the hydrochloride, which was recrystallized from 3.0 *M* hydrochloric acid and from 80% methanol–20% hydrochloric acid (m.p. 190–194°; ref.[6]: 190–191°).

Bromination procedure

The procedure was that described elsewhere[1] except that the time between the addition of the standard bromate solution and of the iodide was varied. The liberated iodine was titrated with standard thiosulfate.

TABLE I

RATE OF DIBROMINATION OF 4-METHYLOXINE

	Time (min)								
	*0**	*1*	*3*	*5*	*10*	*15*	*20*	*25*	*30*
Dibromination (%)	75.2	94.5	97.8	98.0	99.3	99.7	99.9**	99.9	100.0
Range of values (%)	±1.6	±1.4	±0.2	±0.9	±0.6	±0.5	±0.2	±0.3	±0.1

* "Zero time" represents the point at which all the bromate was added.

** Average of 13 results; other values are the average of at least 2 results, usually more.

The data for 4-methyloxine are given in Table I. The results for the other substituted oxines are discussed below.

DISCUSSION

The dibromination of oxine, of 2-phenyloxine and of 2- and 6-methyloxine is at least 99.6% complete at "zero time", and strictly quantitative (100.0 ± 0.1%) within 1 min. In contrast, as Table I shows, the dibromination of 4-methyloxine is relatively slow. This may be attributed to steric hindrance, occasioned by the methyl group in the 4-position. (A Stuart and Briegleb molecular model shows that rotation of a methyl group so situated is restricted when a bromine atom is in the 5-position. A methyl group in the 6-position, however, rotates freely between bromine atoms in the 5- and 7-positions.) Because of the slow dibromination of 4-methyloxine and the consequent danger of loss of bromine from solution, the bromometric determination of 4-methyloxine requires considerable care.

Other workers[7] have reported that the dibromination of 2-phenyloxine is not quantitative, and suggested that this might be due to electron-withdrawing effects of the phenyl group. We found, however, that the dibromination is quantitative*. The earlier results may have been caused by impurities in the reagent.

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* Precipitation of the dibromo derivative interferes somewhat with the end-point.

We and others[8,9] have observed that in the bromometric determination of oxine and 2-methyloxine a brown precipitate can form when iodide ion is added. This precipitate, thought to be an "adsorption complex" of the dibromo compound and iodine[8], can prevent precise and accurate determinations.

Our work indicates that this substance consists of iodine and 5,7-dibromo-oxine (DBO), in the molar ratio I_2:DBO = 1:1. The iodine is probably bonded to DBO through the nitrogen atom, as in the 1:1 iodine–pyridine complex[10]. This is supported by the facts that brominated oxine, but not brominated α-naphthol, can yield a brown precipitate; and that a solution of iodine in pyridine, but not of iodine in benzene, gives on the addition of water a precipitate similar in both appearance and chemical behaviour to that obtained in the bromometric determination of oxine. Both the I_2–pyridine and the I_2–DBO precipitates dissolve on the addition of excess iodide ion (probably by formation of I_3^-); or of concentrated hydrochloric acid (probably by formation of the hydrochloride); or of thiosulfate (by reduction of the I_2); or of solvents for iodine ($C_6H_5NO_2$, CS_2, $CHCl_3$, CCl_4).

The brown precipitates that can be obtained from 2-phenyloxine and from 2- and 4-methyloxine show a similar behaviour, and presumably have a similar nature. The formation of these precipitates can be prevented, and so interference with the end-point avoided, by control of the excess of bromate[1].

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o-Hydroxyacetophenoneoxime as an analytical reagent
Part III. Determination and separation of palladium*

Comparatively few organic reagents have been used for the gravimetric determination of palladium; dimethylglyoxime[1], α-furildioxime[2], benzoylmethylglyoxime[3], salicylaldoxime[4] and β-furfuraloxime[5] are among the more satisfactory of these. During a systematic investigation of the reactions of *o*-hydroxyacetophenoneoxime with metallic ions[6], it was observed that palladium was precipitated quantitatively at moderately low pH values. Further studies have shown that precipitation is complete between pH 0.8 and 4.5, and, after drying at 105–110°, the precipitate has the composition, $Pd(C_8H_8O_2N)_2$.

Interferences of commoner metallic ions are minimized at the low pH possible; thus palladium can be separated from nickel, cobalt, zinc, cadmium, lead, mercury, manganese, platinum and copper. Iron(III), antimony, bismuth, vanadium, titanium and gold require very slight modifications.

Standard solution

A solution of palladous chloride in dilute hydrochloric acid was prepared and standardized by weighing as palladium dimethylglyoximate; 5 ml of the standard solution contained 17.98 mg of palladium.

All the chemicals used were of A.R. or G.R. quality. The pH values of the solutions were measured with a Cambridge pH meter or B.D.H. indicator papers.

Procedure

Dilute the palladium solution (equivalent to 1–10 ml of the above solution) to 200 ml with distilled water. Adjust the pH to 0.8–4.5 and heat on a water bath. Add 20 ml of a 1% solution of *o*-hydroxyacetophenoneoxime in ethanol to the hot solution with stirring, and leave the mixture on the water bath for about 45 min. Filter the yellow precipitate through a No. 3 sintered crucible, wash thoroughly with hot water and finally dry to constant weight at 105–110°.

RESULTS AND DISCUSSION

Over the range 3.6–36.0 mg of palladium, the error amounted only to ± 0.01 mg. It was found that if the pH values of the solutions were below 0.8 or above 4.5, the metal was not completely precipitated.

The excess of reagent used had no effect on the quantitative precipitation of palladium; the stoichiometric amount of reagent was sufficient to precipitate the metal completely for practical purposes.

In a study of the interferences, the test solution containing palladium and the metal salt being studied was diluted to about 250 ml and the pH was adjusted to 0.8–1.4 (indicator paper); 25 ml of the reagent solution was used for the precipitation as

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* Part II. *Z. Anal. Chem.*, 155 (1957) 327.

described above. When iron(III), antimony, bismuth and vanadium were present, 1 g of tartaric acid was added to the mixture before precipitation; for titanium, oxalic acid was added; in the presence of gold the precipitation was carried out at room

TABLE I

DETERMINATION OF PALLADIUM IN PRESENCE OF OTHER METALS

Metals present (mg)	*Pd found (mg)*	*Error (mg)*	*Metals present (mg)*	*Pd found (mg)*	*Error (mg)*
Pd 17.98	18.01	+0.03	Pd 17.98	18.02	+0.04
Cu 5.27			Hg^{2+} 80.20		
Pd 17.98	18.00	+0.02	Pd 21.60	21.60	0.00
Cu 15.81			Mn 8.05		
Pd 17.98	18.01	+0.03	Pd 21.60	21.59	−0.01
Cu 52.70			Mn 24.16		
Pd 14.40	14.40	0.00	Pd 21.60	21.61	+0.01
Ni 6.06			Mn 80.52		
Pd 14.40	14.40	0.00	Pd 17.98	18.01	+0.03
Ni 12.12			Tartaric acid 1 g		
Pd 14.40	14.36	−0.04	Pd 17.98	17.98	0.00
Ni 60.62			Oxalic acid 1 g		
Pd 14.40	14.37	−0.02	Pd 17.98	18.00	+0.02
Co 6.52			Fe 15.52		
Pd 14.40	14.40	0.00	Pd 17.98	18.03	+0.05
Co 13.04			Fe 46.56		
Pd 14.40	14.38	−0.02	Pd 21.60	21.59	−0.01
Co 65.22			Sb 8.24		
Pd 25.20	25.19	−0.01	Pd 21.60	21.60	0.00
Zn 12.21			Sb 41.20		
Pd 25.20	25.20	0.00	Pd 14.40	14.40	0.00
Zn 24.42			Bi 6.90		
Pd 25.20	25.20	0.00	Pd 14.40	14.38	−0.02
Zn 122.10			Bi 35.20		
Pd 21.60	21.59	−0.01	Pd 21.60	21.60	0.00
Cd 7.01			V 2.17		
Pd 21.60	21.60	0.00	Pd 21.60	21.61	+0.01
Cd 21.03			V 21.65		
Pd 21.60	21.59	−0.01	Pd 28.80	28.77	−0.03
Cd 70.10			Ti 5.00		
Pd 7.20	7.21	+0.01	Pd 28.80	28.80	0.00
Pb 4.12			Ti 50.00		
Pd 7.20	7.21	+0.01	Pd 35.96	36.01	+0.05
Pb 8.23			Pt 2.00		
Pd 7.20	7.20	0.00	Pd 35.96	35.99	+0.03
Pb 41.15			Pt 10.00		
Pd 17.98	18.01	+0.03	Pd 17.98	18.01	+0.03
Hg^{2+} 8.02			Au 1.00		
Pd 17.98	18.00	+0.02	Pd 17.98	17.98	0.00
Hg^{2+} 16.04			Au 10.00		

temperature in order to avoid reduction of gold(III) to the metallic state. Results in the presence of various metals are recorded in Table I.

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Polarographic behaviour of erythritol tetranitrate and mannitol hexanitrate

Erythritol tetranitrate (ETN) and mannitol hexanitrate (MHN) are organic nitrate esters of similar chemical structure. Besides their occasional application in the explosives industry, both nitrates have been used medically as hypertensive drugs. Investigation of their polarographic behaviour is thus of interest, particularly in view of the lack of information in the literature. In the present work, methods were developed for the polarographic determination of both compounds

It was found that the subtractive polarographic method[1] has great advantages for the determination of ETN and MHN at low concentrations The reduction potentials of both nitrates coincide with that of oxygen dissolved in the base electrolyte. At concentrations above 200 μg/ml, both compounds can be determined by single-cell polarography after dissolved oxygen has been removed by bubbling nitrogen for 3–5 min. However, in determining the limit of detection, working at a sensitivity 1/6 of the maximum, it was observed that complete removal of oxygen is achieved only after bubbling oxygen-free nitrogen for 15–20 min. With the subtractive method, the deoxygenation time is reduced to 3 min.

Apparatus

The Differential Polaroscope (Type DP 2, Nash and Thompson, Ltd.) was used with mercury pool anodes.

Reagents

Erythritol tetranitrate (British Drug Houses, Ltd.) — the commercial product is a mixture of equal weights of ETN and lactose ETN — was purified by extraction with diethyl ether and recrystallisation from ethanol.

Mannitol hexanitrate was prepared as described by DAVIS[2].

Base electrolyte. 35 ml of 2 M ammonium nitrate, 10 ml of M potassium nitrate, 30 ml of tetrahydrofurfuryl alcohol (British Drug Houses, Ltd.) and 25 ml of water were mixed. The pH of the base electrolyte was 3.7.

Procedure

Base electrolyte (5 ml) was introduced into each of the twin cells and deoxygenated for 3 min. At the sensitivity 1/6 of the maximum, a slight adjustment of the potential balance knob resulted in a straight line in the potential range 0 to —1.0 V, indicating that the residual oxygen concentration was equal in both cells. At this stage, with single-cell performance, the oxygen wave was present in both cells with its peak at —0.40 V and a height of 35 divisions (full scale: 100 divisions). Further deoxygenation for 10 min only decreased the height to 20 divisions and in the potential range —0.5 to —1.0 V it was impossible to obtain a satisfactory base line to observe the reduction waves of ETN.

After oxygen and impurities in both cells had been balanced as described above, a standard solution of ETN or MHN in methanol (0.5 mg/ml) was added to one cell by means of a micrometer syringe and the same volume of methanol to the other; both were deoxygenated for 3 min. No waves were observed until the concentration of MHN or ETN reached a level of 5 μg/ml of base electrolyte A linear relationship between the wave height and the concentration of the compound was then obtained up to 300 μg/ml of base solution.

The reduction of ETN results in the formation of a single wave with the peak potential —0.55 V.

A typical wave for ETN (peak potential —0.55 V) is shown in Fig. 1 (line A), the derivative presentation being given by line B (start potential —0.25 V). The peak potential was not affected by pH changes in the range 1–6. A typical wave for MHN (peak potential —0.45 V) is shown in Fig. 2 (line A), the derivative presentation being given by line B (start potential —0.2 V).

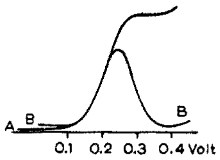

Fig. 1

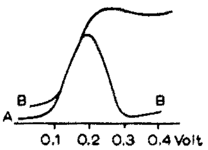

Fig. 2

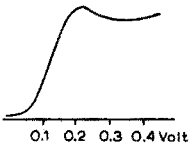

Fig. 3

Fig. 1. A, typical wave for ETN; B, the derivative presentation.
Fig. 2. A, typical wave for MHN; B, the derivative presentation.
Fig. 3. Result of addition of 20% ethanol.

Effect of ethanol or methanol

When ETN was used, replacing tetrahydrofurfuryl alcohol in the base electrolyte by ethanol or methanol caused the formation of two waves with peak potentials of *ca.* —0.6 V and —0.7 V. This could be clearly seen only on derivative presentation.

However, increase in the alcohol content up to 45% separated the waves by 0.2 V with peaks at —0.5 V and —0.7 V. The second wave was about 20 times smaller than the first.

When MHN was used with 30% alcohol, three waves which were very close to each other, could be seen on derivative presentation, but on direct presentation only one wave was visible with a peak potential at —0.55 V. On increasing the alcohol content to 45%, only one broad wave (peak potential —0.4 V) could be seen even on derivative presentation.

Behaviour in acidic media

In *N* sulphuric acid containing 30% of methanol the reduction of ETN produced one badly formed wave; on derivative presentation two peaks became visible at —0.3 V and —0.45 V. The addition of 20% of ethanol made no difference.

In *N* sulphuric acid containing 30% methanol, MHN formed three waves which could be detected on derivative presentation in the range —0.35 to —0.55 V. Increase in the methanol content up to 50% made no difference but the addition of 20% ethanol resulted in the formation of a single wave with a peak potential at —0.45 V (Fig. 3). Derivative presentation also showed a single peak. Consequently, a base electrolyte composed of *N* sulphuric acid, 30% methanol and 20% ethanol may be regarded as the best for MHN, as can be seen by comparison of Figs. 2 and 3. The detection limit was found to be 2 μg/ml of base electrolyte and the relationship between peak height and MHN concentration was linear over a wide range. The addition of pyridine to the samples did not improve the waves, as in the case of nitroglycerine[3].

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A method for radiochemical separation of molybdenum

Molybdenum occurs on one of the peaks of the mass-yield distribution curve for fission of ^{235}U. For understanding the mechanism of fission, radiochemists have been greatly interested in obtaining good separations from a large number of other fission products, and many methods for the radiochemical separation of molybdenum have been described[1]. In these procedures use has been made of almost all the characteristic properties such as precipitation, chelation, solvent extraction, chromatographic and electrochemical behaviour, etc. During a study of some of the short-lived activities formed by bombarding molybdenum with high-energy protons, we were interested in devising a modified method which would be rapid and almost as specific as other methods. As the energy of the bombarding protons was only 230 MeV, fission and fragmentation[2] processes were negligible. Spallation was the dominating process and so a separation from only about ten neighbouring elements, *i.e.* from technetium down through the Periodic Table to about selenium, was required.

Molybdenum in the form of molybdate forms complexes with heteropoly acids of elements such as phosphorus and silicon, and these complexes can also be used to characterize molybdenum, but non-quantitative complexing in the presence of ions such as fluoride and oxalate, which are commonly used to mask niobium and zirconium in fission chemistry, is a serious disadvantage. However, these ions were eliminated in the present work, so that molybdenum could be recovered by complexing with phosphates.

In this method, elements such as technetium, krypton, bromine and selenium, which are gases or whose compounds are volatile, are removed by heating with a mixture of hydrochloric and fuming nitric acid. Strontium and niobium are precipitated as nitrate and oxide respectively. On neutralization with ammonium hydroxide and scavenging with ferric hydroxide, other activities are precipitated. Molybdenum is finally complexed with phosphate at a pH of 2–2.5, buffered with glycine–citrate and precipitated with nitron reagent[3] at room temperature.

PROCEDURE

Heat 10 mg of MoO_3, irradiated with protons, at 200° to remove gaseous products. Transfer this heated powder to a 50-ml flask containing about 5 ml of fuming nitric acid and 1 ml of concentrated hydrochloric acid. Heating without reflux removes the remaining volatile compounds. Add about 10 mg each of Nb, Zr, Y, Sr, Rb and Fe^{3+} in appropriate solution forms as carriers. Boil the whole mixture and centrifuge. Discard the precipitates. Neutralize the supernate with ammonia, adjust the pH to about 9, centrifuge and discard the precipitate. Then add about 10 mg of iron(III), centrifuge and again discard the precipitate. Repeat this process of scavenging twice. Neutralize the supernate with hydrochloric acid and adjust the pH to 2–2.5. Add 0.5 ml of a 2% solution of sodium phosphate and buffer the mixture with glycine–citrate. Add 2 ml of a 2% solution of nitron in ethanol and centrifuge the mixture. Discard the supernate. Collect the precipitate, and wash with 1 *M* hydrochloric acid, water and ethanol. Finally mount, dry at 100° and count the precipitate.

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The radiochemical purity attained by this method was studied by observing the half-lives and β- and γ-ray energies of known[4] and a few new isotopes[5] of molybdenum. Decontamination from zirconium and niobium was further verified by using ^{99}Mo, ^{95}Zr and ^{95}Nb tracers (from Radiochemical Centre, Amersham, Bucks., G.B.). The separated molybdenum activity when counted in a Geiger counter through aluminium absorbers thick enough to stop conversion electrons from ^{99m}Tc, which grows all the time from ^{99}Mo, followed a half-life of 66 ± 1.5 h down to almost the background. By using 3 moles of nitron for each mole of molybdophosphoric acid complex, about 80% of the added molybdenum activity was recovered. The purity factor obtained was about 10^4 and the time required for separation was about 15–20 min.

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Book Reviews

The Application of Organic Bases in Analytical Chemistry, by E. A. OSTROUMOV, Pergamon Press, London, 1962, xxv + 159 pp., 50s.

Let it be said at once that this is a useful compilation of material scattered fairly widely in the literature, and should therefore be available on the library shelf. But let it also be pointed out that the insertion of the word "some" before "organic bases" in the title would give a more accurate description of the contents, since only three bases are considered; pyridine, α-picoline, and hexamine. As the author seems to be concerned with mineral and geochemical analysis, it is surprising that no mention is made of the use of organic bases as precipitants for heteropoly acids. Of the 99 references only 14 are dated later than 1940, and of these only two are more recent than 1950. The book seems to be printed by the photo-litho process from typescript, and the price appears unduly high in view of the lower cost of this method.

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Gmelins Handbuch der anorganischen Chemie, 8. Auflage, Verlag Chemie G.m.b.H., Weinheim/Bergstrasse.
Chrom (System Nr. 52), Teil A, Lieferung 1, 1962, XX + 418 S., 38 Figuren, Gln DM 316.—.

Die Lieferung 1 zum Teil A beginnt mit einem Kapitel über die Geschichte des Chroms und seiner Entdeckung. Im anschliessenden Kapitel wird auf *ca.* 180 Seiten über das Vorkommen des Chroms berichtet, wobei neben dem ausserirdischen Auftreten (Kosmos, Meteoriten) die verschiedenen irdischen Vorkommen in Gesteinen, Böden, Wasser und Lebewesen aufgeführt werden. Der grössere Teil dieses Kapitels wird von einer topographischen Uebersicht der Fundstätten eingenommen und schliesst mit der Beschreibung wichtiger Chrommineralien. Das nächste Kapitel (83 Seiten) befasst sich mit der Technologie des Chroms und der wichtigsten anorganischen Chromverbindungen. Nach einer Beschreibung der verschiedenen Aufschlussverfahren für Chromeisenstein wird die Herstellung von Chrommetall, Wiedergewinnung aus Abfällen (galvanische Bäder, Gerbereilaugen, etc.) und Reinigung sowie die Herstellung verschiedener Formen (Pulver, Spiegel, etc.) behandelt. Anschliessend wird die Herstellung wichtiger anorganischer Chromverbindungen wie Oxyde, Chloride, Sulfate, Chromalaune, Chromate und Bichromate angeführt. Ein besonderes Unterkapitel ist der Herstellung der anorganischen Chromfarben gewidmet. Den Abschluss des Kapitels bildet die Beschreibung der physiologischen Eigenschaften der Chromverbindungen unter Hinweis auf Vergiftungsgefahren in den einzelnen chromverbrauchenden Industriezweigen. Es folgt als nächstes und letztes Kapitel die Beschreibung des Elementes Chrom, die etwa 130 Seiten einnimmt. Im ersten Unterkapitel wird die Darstellung, vor allem durch Reduktion von Chromverbindungen, behandelt und die Herstellung besonderer Formen, wie Pulver und Sole beschrieben. Hierbei wird auch die Trennung und Anreicherung von Isotopen erwähnt. Es folgt dann eine Beschreibung der physikalischen Eigenschaften mit der Unterteilung in kristallographische, mechanische, thermische, optische, magnetische und elektrische Eigenschaften.

Die Literatur ist bis Ende 1949 berücksichtigt, in einigen besonderen Fällen auch bis 1960. Das Inhaltsverzeichnis in deutscher und englischer Sprache ist sehr übersichtlich.

Kupfer (System Nr. 60), Teil B, Lieferung 2: *Verbindungen Kupfer–Bor bis Kupfer–Wismut*, 1961, IV, XLI + 352 S., 38 Figuren, Gln DM 231.—.

Die Lieferung 2 zum Teil B behandelt die Verbindungen des Kupfers mit den Elementen Bor, Kohlenstoff, Silicium, Phosphor, Arsen, Antimon und Wismut. Der Band beginnt mit einer Beschreibung der Kupfer–Bor Verbindungen (6 Seiten). Das anschliessende Kapitel über die Kupfer–Kohlenstoff Verbindungen umfasst etwa 250 Seiten. Als erstes werden die Acetylenide und die verschiedenen Karbonate beschrieben. Dann folgt als Hauptteil dieses Kapitels eine Besprechung der Kupfersalze organischer Säuren und zwar nach folgender Einteilung: Aliphatische Monocarbonsäuren (bis C_{20} und einzelne höhere Säuren), aromatische Monocarbonsäuren, aliphatische Di- und Polycarbonsäuren, aromatische Dicarbonsäuren, ungesättigte Carbonsäuren, aliphatische und aromatische Oxycarbonsäuren, Nitrocarbonsäuren, Pikrinsäure, Halogen- und Cyanessigsäuren sowie aliphatische und aromatische Sulfonsäuren. Nicht berücksichtigt sind in dieser Lieferung die innerkomplexen Kupferverbindungen, die in einer späteren Lieferung zum Teil B ihren Platz finden werden. Dagegen sind in dieser Lieferung bereits die Acidocuprat Ionen beschrieben, da sie in gewisser Beziehung stehen zu den Kupfertartraten und der Fehling'schen Lösung. Der Schluss des Kapitels befasst sich dann noch mit den Cyaniden, Cyanaten und Rhodaniden des Kupfers. In den restlichen Kapiteln werden die Verbindungen des Kupfers mit Silicium, Phosphor, Arsen, Antimon und Wismut beschrieben und zwar jeweils zuerst die Legierungen und dann die sauerstoffhaltigen Verbindungen wie Silikate, Phosphate, Arsenite und Arsenate, Antimonate sowie wichtige Thioverbindungen. Das Inhaltsverzeichnis in deutscher und englischer Sprache ist zwar sehr übersichtlich, jedoch sollten die Hauptkapitel gegenüber den Unterkapiteln besser hervorgehoben sein.

Calcium (System Nr. 28), Teil B, Lieferung 3: (*Schluss der Verbindungen*), 1961, IV, LXII + 912 S., 133 Figuren, Gln DM 568.—.

Die vorliegende Lieferung 3 des Teiles B bildet den Schlussband des Systems Calcium. Er beginnt mit der Behandlung des Systems Ca–S–O, wobei neben dem Calciumsulfit, Calciumthiosulfat und einigen weniger häufigen Schwefel–Sauerstoffverbindungen des Calciums vor allem das Sulfat in seiner wasserfreien und seinen wasserhaltigen Formen sehr ausführlich behandelt wird. Es folgt dann eine Besprechung der Borate (16 Seiten) und als nächstes grösseres Kapitel die Verbindungen mit Kohlenstoff (*ca.* 200 Seiten). Hier wird zunächst das Calciumcarbid, seine Darstellung, physikalischen und chemischen Eigenschaften besprochen (*ca.* 30 Seiten). Die nächsten 100 Seiten sind dem Calciumcarbonat und seinen verschiedenen Formen gewidmet. Als weitere kohlenstoffhaltige Verbindungen werden dann das Cyanid, Cyanamid und Rhodanid sowie die Calciumsalze einer Anzahl organischer Säuren wie Ameisen-, Essig-, Oxal-, Weinsäure usw. behandelt. Das nächste Kapitel beschäftigt sich auf 86 Seiten mit den Systemen Ca–Si, $CaO–SiO_2$, $CaO–SiO_2–H_2O$ sowie den fluor-, bor- und carbonathaltigen Silikaten. Den Anschluss an die Siliciumverbindungen bilden die phosphorhaltigen Verbindungen (*ca.* 100 Seiten), unter denen die Systeme $CaO–P_2O_5$ und $CaO–P_2O_5–H_2O$ sowie die verschiedenen Calciumphosphatmineralien inkl. der zusammengesetzten Phosphate besonders ausführlich behandelt sind. Unter den nun folgenden Systemen Ca–As, Ca–Sb, Ca–Bi, Ca–Alkalimetalle und Ca–Erdalkalimetalle werden besonders die Silikatsysteme $Ca–Na_2O–SiO_2$, $CaO–K_2O–SiO_2$ und die Carbonatsysteme $CaO–MgO–CO_2$ ausführlich besprochen. Den Schluss des Bandes bildet die Beschreibung des chemischen Verhaltens des Calciums sowie eine ausführliche Behandlung der Nachweisreaktionen und Bestimmungsmethoden von Calcium, Strontium und Barium inkl. Trennungsverfahren. Das Inhaltsverzeichnis in deutscher und englischer Sprache ist sehr übersichtlich angeordnet, wenn es auch manchmal etwas schwierig ist, Haupt- und Unterkapitel zu unterscheiden.

Kobalt (System Nr. 58), Teil A, Ergänzungsband, 1961, IV, LXXII + 886 S., 188 Figuren, Gln DM 556.—.

Dieser Ergänzungsband zum Teil A befasst sich mit den Forschungsergebnissen der Jahre 1932–1949, wobei wichtige Publikationen bis 1960 berücksichtigt wurden. Die ersten 32 Seiten des Bandes behandeln die Geschichte des Kobalts und beschreiben frühe Anwendungen als Färbemittel. Sehr ausführlich wird dann über das Vorkommen des Kobalts berichtet mit Angabe der Fundstätten. Als Schluss dieses Kapitels wird eine Zusammenstellung der Kobaltmineralien gegeben. Anschliessend folgt ein Kapitel von etwa 30 Seiten über die Technologie des Kobalts und seiner Verbindungen, worin neben der Aufbereitung der Erze auch Herstellungsverfahren und Verwendungen von Kobaltoxyden und -fluoriden beschrieben werden. Die nächsten 170 Seiten behandeln das Element Kobalt. Zunächst wird die Darstellung besonderer Formen wie Pulver, Spiegel, Einkristalle und Sole sowie Co-Isotope beschrieben. Es folgen dann die physikalischen Eigenschaften mit der üblichen Unterteilung in mechanische, thermische, optische (vor allem spektrales Verhalten), magnetische und elektrische Eigenschaften. Ausführlicher wird dann das elektrochemische Verhalten, besonders an der Quecksilbertropfelektrode, beschrieben, wobei die elektrolytische Abscheidung des Kobalts auf etwa 20 Seiten behandelt wird. Das chemische Verhalten gegen anorganische und organische Verbindungen sowie Nachweis und Bestimmung bilden den Schluss dieses Kapitels. Das nächste Kapitel befasst sich auf 95 Seiten mit den Legierungen, vor allem mit Sb, Zn, Ti, Sn, Cr, Mo, W und Ni, worunter die Legierungen mit Wolfram besonders ausführlich behandelt sind. Der restliche Teil des Bandes von mehr als 400 Seiten ist den Verbindungen des Kobalts gewidmet. Hervorzuheben sind die Angaben über die Oxyde und Fluoride, letztere vor allem wegen ihrer Bedeutung als Fluorierungsmittel. Ausführliche Kapitel befassen sich mit den Kobaltcarbonylen, deren Anlagerungsverbindungen mit organischen Substanzen und den Systemen Kobalt–Lithium bis Kobalt–Nickel unter besonderer Berücksichtigung der Doppeloxyde und der Systeme von Kobaltsalzen mit anderen Salzen. Nicht unerwähnt soll auch die Beschreibung der zahlreichen Komplexverbindungen bleiben. Ein sehr übersichtlich angeordnetes Inhaltsverzeichnis in deutscher und englischer Sprache erleichtert die Benützung des Bandes.

Lithium (System Nr. 20), Ergänzungsband, 1960, XXXVIII + 525 S., 73 Abbildungen, kart. DM 325.—, Gln DM 330.—.

Seit dem Erscheinen des Hauptbandes (1927) hat die technische Bedeutung des Lithiums beträchtlich zugenommen, was in dem doppelt so starken Umfang des Ergänzungsbandes zum Ausdruck kommt.

Der üblichen Einteilung folgend wird zunächst das Vorkommen des Lithiums behandelt und eine topographische Uebersicht gegeben (126 Seiten). Es folgt dann auf 16 Seiten eine Beschreibung der technischen Darstellungsmethoden des Metalles und seiner wichtigsten Verbindungen sowie seine technische Verwendung in der Metallurgie, keramischen Industrie, etc. Anschliessend werden die physikalischen Eigenschaften des Atoms, der Li_2-Molekül und des Lithium-ions beschrieben (*ca.* 20 Seiten). Die folgenden Unterkapitel behandeln die kristallographischen, mechanischen, thermischen, optischen, magnetischen und elektrischen Eigenschaften sowie das elektrochemische Verhalten (*ca.* 45 Seiten). Anschliessend werden das chemische

Verhalten gegen Elemente, anorganische und organische Verbindungen, physiologische Eigenschaften und analytische Methoden beschrieben. Das letzte Unterkapitel behandelt die Legierungen mit Antimon und Wismut.

Etwa die Hälfte des Bandes (280 Seiten) befasst sich mit den Verbindungen des Lithiums, wobei besonders das Hydrid, das Hydroxyd, das Nitrat, das Sulfat, das Carbonat und die Halogenide sehr ausführlich behandelt sind.

Die Literatur ist bis 1950 berücksichtigt. Der Band ist mit Marginalien in englischer Sprache und einem deutsch-englischen Inhaltsverzeichnis versehen.

Quecksilber (System Nr. 3), Lieferung 1: *Geschichtliches, Vorkommen, Darstellung und physikalische Eigenschaften*, 1960, XVII + 466 S., 53 Abbildungen, kart. DM 283.—.

Die erste Lieferung des Bandes Quecksilber beschreibt zunächst auf *ca.* 80 Seiten die Geschichte des Elementes, frühe Darstellungsmethoden und Anwendungen sowohl des Metalles wie auch von Legierungen und Verbindungen zu technischen und medizinischen Zwecken. Die nächsten 100 Seiten behandeln das Vorkommen (*ca.* 80 Seiten), seine Verwendung als Metall und Amalgam sowie die physiologischen Eigenschaften des Metalls und einiger Verbindungen. Es folgt dann auf *ca.* 70 Seiten eine Beschreibung des elementaren Quecksilbers, wobei zunächst die laboratoriumsmässige Darstellung und Wiedergewinnung aus Abfällen behandelt wird. Der letzte Teil dieses Kapitels befasst sich mit der technischen Darstellung des Metalls, seiner Reinigung, Handhabung und Aufbewahrung sowie der Herstellung kolloidaler Formen. Der restliche Teil des Bandes (*ca.* 210 Seiten) beschreibt sehr ausführlich die physikalischen Eigenschaften und ist unterteilt in kristallographische, mechanische, thermische, optische, magnetische und elektrische Eigenschaften des Metalles.

Die Literatur ist bis 1950 berücksichtigt. Der Band ist mit Marginalien in englischer Sprache versehen und enthält ein deutsch-englisches Sachregister.

Schwefel (System Nr. 9), Teil B, Lieferung 2: *Schwefelsauerstoffsauren*, 1960, XXXVIII + 758 S., 146 Abbildungen, kart. DM 66.—, Gln DM 471.—.

Dieser Band befasst sich ausschliesslich mit den Sauerstoffsäuren des Schwefels, wobei etwa die Hälfte des Bandes (*ca.* 400 Seiten) die schweflige Säure und Schwefelsäure sowie die Systeme SO_2-H_2O und SO_3-H_2O behandelt. Der Rest des Bandes verteilt sich auf die Besprechung der übrigen Schwefelsauerstoffsäuren, worunter die Peroxodischwefelsäure $H_2S_2O_8$ auf 44 Seiten, die Thioschwefelsäure auf 104 Seiten und die Polythionsäuren auf 77 Seiten beschrieben werden. Der Text ist ergänzt durch zahlreiche Phasendiagramme. Wie üblich werden jeweils zuerst die physikalischen und dann die chemische Eigenschaften besprochen, wie das Verhalten gegen Metalle, anorganische und organische Verbindungen. Für fast alle Säuren sind die Darstellungsmethoden angegeben. Dem Kapitel über Polythionsäuren ist eine Besprechung der analytischen Methoden angeschlossen.

Die Literatur ist bis 1950 berücksichtigt. Es dürfte kaum eine Publikation auf dem Gebiet der Schwefelsauerstoffsäuren geben, die nicht im Gmelin erwähnt wurde. Das Inhaltsverzeichnis in deutsch-englischer Sprache ist weitgehend aufgegliedert, was das Aufsuchen z.B. der Eigenschaften der einzelnen Säuren sehr erleichtert.

K. EDER (Genf)

Practical Pharmaceutical Chemistry — Quantitative Analysis, A. H. BECKETT AND J. B. STENLAKE, Athlone Press, London, 1962, viii + 378 pp., price 63 s.
This is a valuable addition to the number of books concerned wholly with pharmaceutical analysis.

The book is essentially practical, as of the seventeen chapters only two are entirely theoretical. One of these concerns the theoretical bases of quantitative analysis and deals with the Law of Mass Action and its application to weak electrolytes, hydrolysis of salts, buffers and indicators, precipitation and complex formulation and oxidation reduction potentials. The other is concerned with the theory of absorption spectra and the sources, methods of dispersion and measurement of the different spectral regions. Of the remaining chapters the first gives an account of the general limit tests of the British Pharmacopoeia and includes two useful tables of specific tests for possible contaminants in alkaloids and synthetic organic medicinals, while the second is a welcome "manual in miniature" of important practical points which must be observed if an analysis is to be reliable. A description of the suction type of safety pipettes now available could have appeared with advantage in this chapter. The rest of the book deals with the evaluation and assay procedures for a wide range of medicinal substances. Techniques described include titrations in aqueous and non-aqueous media, complexometric analysis, gravimetry, electrometric methods, solvent extraction and a variety of miscellaneous determinations which are used for the evaluation of drugs and medicinal products. Chapters on emission and absorption spectroscopy and polarography end the book. The value to the student lies in the clear exposition of the reasons underlying the test procedures, which are described in fair detail, and the inclusion of cognate determinations as further illustrations of the technique. Equations and methods of calculation are given in detail.

The proof-reading has been thorough and the index is good. It would have been good to see mention of some of the newer methods which are finding their way — overdue as this may be — into national pharmacopoeias and associated books of standards. Flask combustion is now a common procedure for the "opening-up" of many complex pharmaceuticals; chromatography, on paper and column, is used to detect impurities in steroids and alkaloids; gas–liquid chromatography is making rapid progress in the field of drug analysis; and advanced students might well have been given at least a glimpse of these fields to whet their analytical appetites. Despite the criticism, Beckett and Stenlake is a very useful book and it will undoubtedly be of great value not only to students of pharmacy but also to many analysts in industry and consulting practice who are concerned with pharmaceutical analysis. At 63/— it may stretch the student pocket.

W. H. STEPHENSON (Nottingham)

A. I. BUSEV, *The Analytical Chemistry of Indium*, Translated from the Russian by J. T. GREAVES, Pergamon Press, Oxford, 1962, xi + 288 pp., price 84 s.

Any book that brings together detailed analytical information on a relative newcomer to the majority of analysts is welcome, particularly if the publication is available at a reasonable price. This latest Monograph is a worthy addition to the International Series of Monographs and amply fulfils both of these requirements.

Indium is of importance in certain alloys, for example in dental compositions, and has applications in the optical and atomic energy industries. It is not surprising, therefore, that the analyst is frequently called upon to determine this less familiar element at all levels in a variety of materials. Whether the analyst is a specialist in polarography, emission or X-ray fluorescence spectroscopy, flame-photometry or radio-activation, or is restricted to the more conventional methods of chemical analysis, this book will provide sufficient reliable information to instil confidences It is divided into 10 chapters under headings, apart from those already indicated, such as Precipitation by Inorganic Anions, Formation of Complex Ions with Halides, and the Analytical Characteristics of Compounds of Indium with Organo-Sulphydryl Groups. Methods for the separation, detection and determination of indium in natural and industrial products are discussed, and detailed descriptions of recommended procedures are given.

The analytical information is judiciously condensed and supported not only by the author's personal experiences, but by nearly 500 references. These references contain relevant information up to about the time of publication of the book in Moscow in 1958, although one reference is dated 1959. The presentation, indexing and general production of the book are up to the usual high standard of workmanship of this series, and its technical information is highly commended to anyone involved in the analytical chemistry of indium.

W. T. ELWELL (Birmingham)

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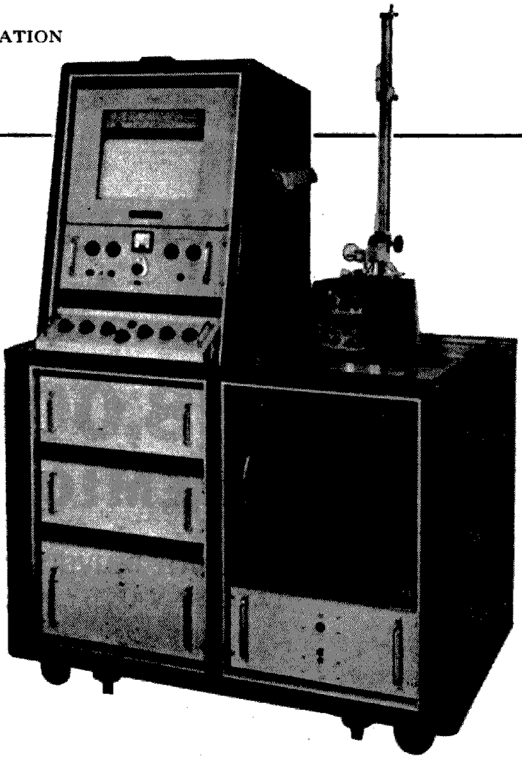

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— while realising that the number of journals in the field of chemistry is considerable,

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