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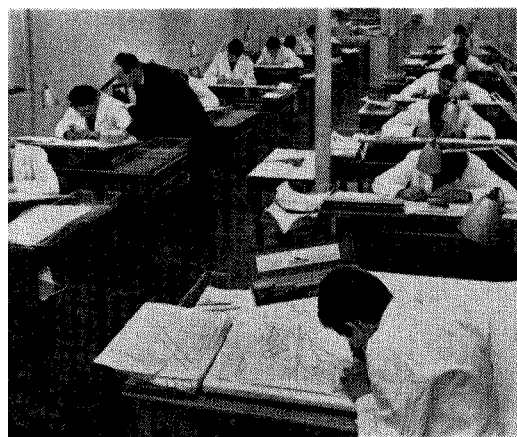
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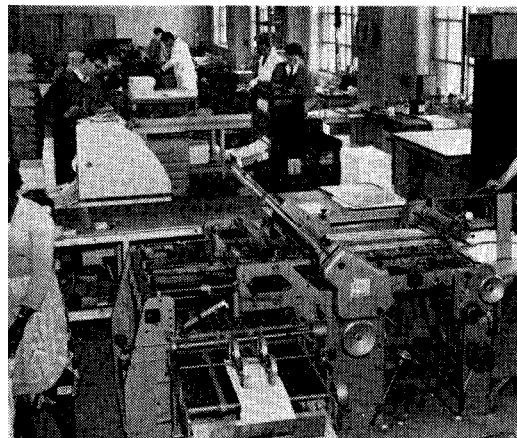
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SOME THEORETICAL AND PRACTICAL PROBLEMS IN THE USE OF ORGANIC REAGENTS IN CHEMICAL ANALYSIS—I

EFFECT OF DONOR π BONDS ON THE STABILITY OF CHELATE COMPLEXES CONTAINING SULPHUR

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Summary—The effect of the donor π bonds on the stability of chelate complexes has been investigated. It has been shown that the stability of chelates which contain sulphur as a donor atom shows a marked dependence on the effect of the donor π bond. On the basis of theory it is possible to explain the optimum pH range for the analytical use of dithizone.

IN the formation of complexes one must consider, in addition to the conventional co-ordinate bonds, the possibility of the formation of donor π bonds by certain metals. In such cases d electrons are delivered by the metal to a free d or p orbital of the ligand. The delivery of an electron raises the electron affinity (electrophilic nature) of the metal, thus increasing the attacking power of nucleophilic ligands, *i.e.*, the strength of the σ bond between the metal and the ligand.

The role of donor π bonds in complex chemistry was first pointed out by Pauling,[1] Philips,[2] Chatt[3] and Dewar.[4] Recently, a number of authors[5–9] have emphasised that the formation of a donor π bond leads to an increase in the stability of the complex. So far, in the field of chelate complexes, no investigations of this type are known, although it would be possible to interpret several anomalies on the basis of this phenomenon.

The object of the present study was to investigate the occurrence and the effect of the donor π bond in the complexes of chelate-forming agents which contain sulphur as one of the donor atoms, and to examine the field of application of molecules of this type (in the present paper dithizone) as organic reagents.

The prerequisites for the formation of a donor π bond are as follows:

(1) The presence of free d electrons among the valence electrons of the central metal atom is essential. With increase in the number of d electrons, the probability of formation of π bonds becomes higher.

(2) A free d or p orbital capable of accepting an electron from the central atom must be present in the external electron shell of the donor atom of the ligand.

(3) A stable σ bond must exist between the central atom and the ligand.

According to existing information, the following cations are capable of forming donor π bonds: Cu^+, Ag^+, Au^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, Cr^{2+}, Mn^{2+}, Mn^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Co^{3+}, Ni^{2+}, Cu^{2+}, Pd^{2+}, Pt^{2+} and Pt^{4+}*. Of the ligands acting as chelate-forming agents, molecules which contain sulphur, selenium, phosphorus or arsenic

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* The formation of donor π bonds can also be presumed in the case of other metals to a lesser extent.

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as donor atoms are capable of forming bonds of this type, in contrast to those which contain nitrogen* or oxygen as donor atoms.

The anomalies connected with the stability and the chemical behaviour of chelate complexes containing sulphur as a donor atom can be interpreted in the following way.

I. The stability exponents of the metal complexes of the following three compounds prepared by Schwarzenbach[11] are presented in Table I.

TABLE I

Metal ion	1 pK_S	2 pK_N	3 pK_O
Mn^{2+}	9·32	7·71	5·55
Fe^{2+}	11·72	9·81	6·78
Co^{2+}	14·67	11·78	7·90
Ni^{2+}	13·75	13·73	9·28
Cu^{2+}	—	15·90	11·86
Zn^{2+}	15·92	11·93	8·93
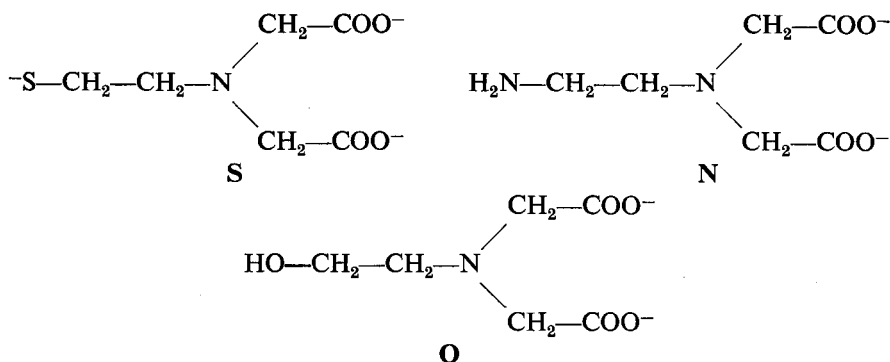
The possibility of the formation of a donor π bond is only present in the molecule S.

The data of Table I prove that the rule derived by Irving and Williams[10] does not hold in the case of complexes containing a donor π bond. In column 1, the zinc complex shows the greatest stability in the series Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}.

On the basis of the crystal field theory the validity of this rule depends on the spin-paired or spin-free state (more exactly low spin-number or high spin-number) of the central atom of the complex. In the case of paired spin arising from the change in electron configuration, the Irving-Williams rule does not hold. As was pointed out in the introduction, if a strong donor π bond exists, the σ bond is also stronger, so that the crystal field energy of the ligands is great, favouring the formation of spin-paired complexes. In the complexes with a strong donor π bond the anomaly in the Irving-Williams rule can be interpreted. The existence of the donor π bond

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* Owing to their capacity for forming donor π bonds, the oximes occupy a particular place among the chelate-forming agents which contain nitrogen as a donor atom. This problem will be discussed in a subsequent paper.

TABLE II

Metal ion	1 pK_O-pK_N	2 pK_S-pK_O	3 pK_{S-N}	4 pK_{S-O}
Mn^{2+}	1·51	3·77	1·6	2·1
Fe^{2+}	1·91	4·94	1·9	3·1
Co^{2+}	2·89	6·77	2·9	4·8
Ni^{2+}	—	4·47	—	2·4
Cu^{2+}	—	—	—	—
Zn^{2+}	3·99	7·59	4·1	5·8

does not mean in all cases a stability of an order which deviates from the Irving-Williams rule. There is no doubt, however, that the stronger the donor π bond that can be formed, the greater is the probability of the Irving-Williams rule being invalid.

The stability exponent values published by Schwarzenbach enable us to calculate the increase of stability caused by the donor π bond for the complexes shown in Table I.

Taking into account the analogous nature of the three molecules, and the identical structure of the complexes formed, the differences, $pK_S - pK_N$ and $pK_S - pK_O$, in the stability exponents denote the increase in stability caused by the replacement of the donor atoms, nitrogen and oxygen, respectively, by sulphur (Table II, columns 1 and 2). Since the substitution of a sulphur atom changes the acidic dissociation constant of the molecules (particularly in the case of oxygen), this fact must also be considered when establishing the stability increase caused by the donor π bond. In the case of the analogues of

$$R-N\begin{cases} CH_2-COO^- \\ CH_2-COO^- \end{cases}$$
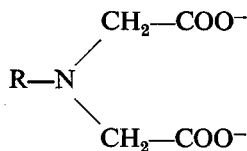
(where the group R did not contain any donor atoms and only altered the acidic dissociation constant of the compound), the stability constants of the complexes were plotted by Schwarzenbach[11] against their acidic dissociation constants. Stability increases caused by the co-ordination of the fourth donor atom, (sulphur in the case of compound S, where $R = {}^-S-CH_2-CH_2$; nitrogen in the case of compound N, where $R = H_2N-CH_2-CH_2$; and oxygen in the case of compound O, where $R = HO-CH_2-CH_2$), were characterised by the distance of the experimentally determined stability constants from the curve in Schwarzenbach's diagram, measured on the ordinate (in terms of pK). From these data, the stability increase resulting from the formation of the donor π bond was calculated (Table II, columns 3 and 4). The values in columns 1 and 3 are approximately identical. This may be ascribed to the fact that the acidic dissociation constants of the compounds S and N are almost the same ($pK_H = 10·79$ for S, $pK_H = 11·05$ for N, but $pK_H = 8·73$ for O). Thus, the stability increase is almost exclusively caused by the donor π bond.

On considering the identical structure of all three complexes (identical ring number, *etc.*), the stability increase (rise of free energy of formation) may be ascribed to the change of enthalpy. The entropy factor remained unchanged. The change of

enthalpy resulting from the formation of the donor π bond can be calculated from the formula

$$-RT \ln \Delta K = \Delta H°.$$

II. The marked differences between the stabilities of the chelate complexes of metals containing 18 electrons in the external electron shell and of those of metals with 18 + 2 electrons when they contain sulphur as the donor atom can be explained by the formation of a donor π bond. In the latter case, the d electrons of the metal are incapable of occupying the free d orbital of sulphur. In this way, it is possible to interpret the differences in the stabilities of the ketodithizonate complexes of Hg^{2+} and Pb^{2+}, and in those of Cd^{2+} and Sn^{2+} (Table III).

TABLE III

Metal ion	Electron orbitals	Stability exponent of ketodithizonate	Ref.
Hg^{2+}	$5s^2,5p^6,5d^{10}$	44·15	12
Pb^{2+}	$5s^2,5p^6,5d^{10}:6s^2$	18·66	13
Cd^{2+}	$4s^2,4p^6,4d^{10}$	19·54	13
Sn^{2+}	$4s^2,4p^6,4d^{10}:5s^2$	15·34	12

III. In the case of metals with an identical external electron shell structure, the strength of the donor π bond depends on the mobility of the d electrons. The mobility of the electrons participating in the formation of a π bond can be characterised by the energy required for the further ionisation of the metal ion in question (in the case of bivalent metals by the third ionisation potential). The lower this value, the more stable is the donor π bond. To prove this statement, the stability exponents of the complexes of the compounds of Schwarzenbach[11] denoted as S, N and O, formed with Zn^{2+}, Cd^{2+} and Hg^{2+} ions, are presented in Table IV, together with the stability exponents of the ketodithizonates of Cd^{2+} and Hg^{2+}. Although it would also be possible to interpret the differences of stability (particularly in the case of the complexes of Cd^{2+} and Hg^{2+}) by the Fajans theory of polarisation, the change of the order of stability values in the case of the compound S supports the postulated effect of the donor π bond.[21]

TABLE IV

Metal ion	Ionisation potential $(Me^{2+} - e \rightarrow Me^{3+})$	Chelating agent (Donor atom, S)	Stability exponent	Chelating agent (Donor atom, N)	Stability exponent	Chelating agent (Donor atom, O)	Stability exponent
Cd^{2+}	37·766	dithizone	19·54	—	—	—	—
Hg^{2+}	34·210	dithizone	44·15	—	—	—	—
Zn^{2+}	39·701	S	15·92	N	11·93	O	8·33
Cd^{2+}	37·766	S	16·72	N	10·58	O	7·52
Hg^{2+}	34·210	S	16·16	N	9·75	O	5·48

IV. On the formation of the donor π bond, the positive charge of the central atom increases slightly, because of a partial release of electrons. In the case of ions of identical electron shell, the probability of formation of π bonds decreases with the increase of the positive charge on the ion. A higher charge on the cation obviously reduces the mobility of the external d electrons. Thus, ligands capable of forming donor π bonds tend to stabilise the lower valence state of metals.*

* It was pointed out by Fischer[15] that Au^I is present in gold dithizonate.

On the basis of the theory of donor π bonds presented above, it is possible to explain the optimum pH range for the analytical use of organic reagents containing sulphur (particularly of dithizone). The greater the capacity of a metal cation, for forming donor π bonds the more stable will be its complex, and the lower will be

TABLE V. OPTIMAL pH RANGE FOR THE EXTRACTION OF METAL DITHIZONATES[19]

Metal ion	Metal:Dithizone	Electron orbitals	Ionisation potential $(Me^{n+} - e \rightarrow Me^{(n+1)+})$	pH range
Ag^+	1:1	$4s^2, 4p^6, 4d^{10}$	21·481	−1·2–7
Hg^{2+}	1:2	$5s^2, 5p^6, 5d^{10}$	34·210	−1·4–4
Pd^{2+}	1:2	$4s^2, 4p^6, 4d^8$	32·921	−1·2–4
Pt^{2+}	1:2	$5s^2, 5p^6, 5d^8$	28·55	−1·2–4
Cu^{2+}	1:2	$3s^2, 3p^6, 3d^9$	37·079	+1·9–5
Bi^{3+}	1:3	$6s^2$		2·0–10
In^{3+}	1:3	$4s^2, 4p^6, 4d^{10}$	57·8	4·0–6·5
Sn^{2+}	1:2	$5s^2$		4·9–9·0?
Zn^{2+}	1:2	$3s^2, 3p^6, 3d^{10}$	39·701	6·0–9·4
Cd^{2+}	1:2	$4s^2, 4p^6, 4d^{10}$	37·766	6·0–14·3
Co^{2+}	1:2	$3s^2, 3p^6, 3d^7$	33·491	6·0–8·0
Ni^{2+}	1:2	$3s^2, 3p^6, 3d^8$	35·165	6·0–8·5
Pb^{2+}	1:2	$6s^2$		7·0–10
Fe^{2+}	1:2	$3s^2, 3p^6, 3d^6$	30·643	7·3–9·5
Mn^{2+}	1:2	$3s^2, 3p^6, 3d^5$	33·690	9·5–10·5
Tl^+	1:1	$6s^2$		

the pH range where its ketodithizonate is suited for use (Table V).* Accordingly, the entirely empirical Wichmann rule[16] loses its validity.†

The effect of the donor π bond on the stability of ketodithizonates proves, in accordance with the experiments of Irving[17] and Geiger,[18,19] and in contrast with the opinion of Fischer,[20] that the sulphur atom of dithizone participates in the formation of complexes as a donor.

Zusammenfassung—Der Effekt der Donor-π-Bindung auf die Stabilität von Chelatkomplexen wird studiert. Es wird gezeigt, dass die Stabilität von Chelaten, die Schwefel als Donoratom enthalten, durch diesen effekt erhöht wird. Auf der Basis der Theorie ist es möglich den optimalen pH-Bereich für die analytische Anwendung von Dithizon zu interpretieren.

Résumé—L'auteur a étudié l'influence de la liaison π d'un donneur sur la stabilité des complexes chelatés. Il a montré que la stabilité des chélates, qui contiennent du soufre comme atome donneur, dépend de l'action de la liaison π du donneur. En se basant sur la théorie de cette liaison, il est possible d'interpréter le domaine de pH le meilleur pour l'utilisation analytique de la dithizone.

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* The number of rings (ratio of metal to dithizone), the configuration of the external electron shell, and the corresponding ionisation potentials are presented in Table V as factors determining the stability.
† The nobler the metal component of the dithizonate the lower is the pH value of extractability (Wichmann).

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ISOTOPIC DILUTION ANALYSIS BY ION–EXCHANGE—I.

DETERMINATION OF TRACES OF IRON

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Summary—Isotopic dilution analysis with the use of ion-exchangers serves for the determination of trace amounts of metals. A theoretical evaluation of this method is given, from which the conditions for the determination of a number of metals can be predicted. The selectivity of the method may be further increased by the use of masking and precipitating agents.

The proposed method has been verified by the determination of iron using EDTA and Dowex 50 cation-exchanger. The average precision of mean values for amounts of 10^{-7} g of Fe/5 ml was 1.2%, for amounts of 10^{-8} g of Fe/5 ml, 4.0% and for amounts of 10^{-9} g of Fe/5 ml, 4.1%. Even a large excess of many metals does not interfere in the analysis. The method has been applied to the analysis of NaI(Tl) crystals. The procedure which has been developed is very simple, and is far more sensitive than colorimetry, activation analysis or other methods used up to now for determining traces of iron.

INTRODUCTION

In previous papers,[1,2,3] it has been shown that isotopic dilution analysis can be used for the determination of trace amounts of an element, if the following conditions are fulfilled: (1) a radio-isotope having a suitable half-life period and high specific activity (or a carrier-free isotope) is available, (2) it is possible to isolate very small, equal amounts of the analysed element from solutions containing it in different amounts. The second condition can be fulfilled by adding equal amounts of a complexing agent to the analysed solutions. The amount of the reagent added must, however, be less than the amount which corresponds stoichiometrically to the element present. The complex which is formed is separated from the excess of the element analysed by solvent extraction (see previous papers[1,2,3]), ion-exchange (this paper), partition chromatography, electrophoresis, electrolysis, *etc.*

In the present paper, general relations have been derived, on the basis of which it is possible to calculate the conditions for the determination of a number of elements by this method. Using suitable masking or precipitating agents it is possible to obtain increased selectivity for the proposed method. The method has been tested by the determination of trace amounts of iron (from 10^{-7} to 10^{-9} g/5 ml) in the presence of an excess of many elements, using EDTA and the cation-exchanger Dowex 50.

THEORETICAL

For the isolation of very small, equal amounts of the ion to be determined from solutions containing various amounts of this ion, it is necessary that the following conditions should be fulfilled: (1) the amount of complexing agent added must be less than corresponds stoichiometrically to the amount of ion present, (2) the complexing agent must react quantitatively with the ion, (3) the complex formed must be easily separable from the excess of the analysed metal. In order that more than

99·9% of the complexing agent H_nY should react to form the complex MY,* the following relation must be valid:

$$[MY] \geqslant 0·999 \, c_{H_nY} \tag{1}$$

where c_{H_nY} is the initial concentration of the complexing agent. The equilibrium concentration of the metal M is given by:

$$[M] = c_M - [MY] = c_M - c_{H_nY} \tag{2}$$

where c_M is the initial concentration of the metal. The equilibrium concentration of the anion Y is calculated from the relation:

$$\sum_{n=0} [H_nY] = [Y] \sum_{n=0} \frac{[H]^n}{k_0 \ldots k_n} \leqslant 0·001 \, c_{H_nY} \tag{3}$$

where

$$k_n = \frac{[H] \cdot [H_{n-1}Y]}{[H_nY]} \text{ and } k_0 = 1. \tag{4}$$

By inserting the relations (1), (2) and (3) into the expression for the stability constant of the metal complex, K_{MY}, we obtain:

$$K_{MY} = \frac{[MY]}{[M][Y]} \geqslant \frac{c_{H_nY}}{c_M - c_{H_nY}} \cdot \frac{\displaystyle\sum_{n=0} \frac{[H]^n}{k_0 \ldots k_n}}{0·001 \, c_{H_nY}} . \tag{5}$$

From relation (5) it may be seen that the term $\dfrac{c_{H_nY}}{c_M - c_{H_nY}}$ has no great influence on the required value of K. At $c_M \geqslant 2 \, c_{H_nY}$, this term will be $\leqslant 1$. Also the term $\displaystyle\sum_{n=0} \frac{[H]}{k_0 \ldots k_n}$ will be equal to 1 at sufficiently high pH-values (*i.e.*, at a pH-value at which the complexing agent will be completely dissociated). For the determination of trace amounts of metals ($c_{H_nY} \leqslant 10^{-5}M$) it will therefore be possible to use only those complexes for which $K_{MY} \geqslant 10^8$. This condition is fulfilled by the complexes of practically all metals with ethylenediaminetetra-acetic acid, 1,2-diaminocyclo-hexanetetra-acetic acid, *etc.*[4,5] For instance the value of $K_{FeY} = 10^{25·1}$. It follows from relation (5) that iron[III] can be determined by this method at pH 2 to 3, when hydrolysis is not yet measurably evident, even when using very low EDTA concentrations ($\sim 10^{-8}M$). The use of complexones has the advantage that the complexes formed are either neutral or negatively charged, so that they can be very easily separated from the excess of positively charged ions of the element being determined by the use of ion-exchange, paper chromatography, electrophoresis, *etc.*

From the stability constants of the various complexes it is also possible to determine the influence of interfering ions:

$$\frac{[M'Y]}{[M''Y]} = \frac{K_{M'Y}[M']}{K_{M''Y}[M'']} . \tag{6}$$

When $[M'']$ is equal to $[M']$, it is possible to determine $[M']$ in the form of the complex M'Y, when $\dfrac{K_{M'Y}}{K_{M''Y}} \geqslant 10^3$, for $[M''] = 100[M']$ the value of $\dfrac{K_{M'Y}}{K_{M''Y}}$ must be $\geqslant 10^5$, *etc.*

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* For the sake of simplicity the magnitude of the charges has been omitted.

For instance, in the determination of iron[III] in the form of a complex with ethylene-diaminetetra-acetic acid, no interference will be observed from most uni- or bi-valent metals, because for these the relation $\dfrac{K_{\mathrm{FeY}}}{K_{\mathrm{M''Y}}} > 10^5$ holds.[4] The metal which forms the strongest complex with a certain reagent can therefore be determined even in the presence of most other metals. By the use of masking agents which form complexes MB_n with the interfering metals (the masking agent may also be the hydroxyl ion—forming hydroxy-complexes—ammonia, etc.), it is even possible to determine selectively a number of other metals. In the presence of a masking agent the total concentration of the metals is:

$$c_{\mathrm{M}} = [\mathrm{M}] + [\mathrm{MY}] + [\mathrm{MB_n}] = [\mathrm{M}]\,[1 + K_{\mathrm{MY}}[\mathrm{Y}] + K_{\mathrm{MB_n}}[\mathrm{B}]^n] \qquad (7)$$

where

$$K_{\mathrm{MB_n}} = \frac{[\mathrm{MB_n}]}{[\mathrm{M}]\,[\mathrm{B}]^n}. \qquad (8)$$

In this case:

$$\frac{[\mathrm{M'Y}]}{[\mathrm{M''Y}]} = \frac{K_{\mathrm{M'Y}}[\mathrm{M'}](1 + K_{\mathrm{M''Y}}[\mathrm{Y}] + K_{\mathrm{M''B_n}}\cdot[\mathrm{B}]^n)}{K_{\mathrm{M'Y}}\cdot c_{\mathrm{M''}}} \qquad (9)$$

It may be seen from relation (9), that at high values of the term $K_{\mathrm{M''B_n}}\cdot[\mathrm{B}]^n$ it is possible to carry out the determination of the metal M' even in the presence of an excess of the metal M'', which would otherwise interfere in the determination (the value $\dfrac{K_{\mathrm{M'Y}}}{K_{\mathrm{M''Y}}} < 1$). For instance, in the presence of chloride ions strong complexes are formed with Hg^{II} and Tl^{III}, and therefore even an excess of these elements does not interfere in the determination of iron[III] in the form of a complex with ethylene-diaminetetra-acetic acid, although the $K_{\mathrm{M''Y}}$ values for these elements are close to the value of K_{FeY}.[4] To increase selectivity, precipitating agents may be used in a way similar to the masking agents. In this case:

$$\frac{[\mathrm{M'Y}]}{[\mathrm{M''Y}]} = \frac{K_{\mathrm{M'Y}}\cdot S_{\mathrm{M'}}}{K_{\mathrm{M''Y}}\cdot S_{\mathrm{M''}}} \qquad (10)$$

where S_{M} is the solubility product. For instance, it would be possible to use diethanol-dithiocarbaminate to mask metals of the first to third analytical groups when determining Ca and Sr in an ammoniacal medium, since $S_{\mathrm{Ca(Sr)}} \gg S_{\mathrm{M''}}$.

The use of dilution analysis also brings another advantage. This is the fact that after adding the radio-isotope to the solution being analysed, losses of the element being determined, occuring in further operations (when it is impossible to determine the element selectively in a single operation) do not influence the result of the analysis.

EXPERIMENTAL

Instruments

Scintillation counter with well-type NaI(Tl) crystal.
Set of 12 ion-exchanger columns, diameter 0·7 cm, height 10 cm.

Reagents

Twice distilled water: Further purified by passage through a column of ion-exchanger; used for dissolving all reagents, and for all other operations.

HCl: Prepared by dissolving twice distilled gaseous HCl in water. The gaseous HCl was prepared from a mixture of HCl, AnalaR and H_2SO_4, AnalaR.

Disodium salt of EDTA: AnalaR

Ferric chloride: 120·85 mg of ferrum reductum, AnalaR, was dissolved in HCl, boiled with a few ml of H_2O_2, AnalaR, Merck, and made up to a volume of 1 litre. The solution thus prepared was diluted to the appropriate concentration by 0·01N HCl.

Ferric chloride: Tagged by [59]Fe. A solution of 500 mc/g was diluted to a suitable concentration using 0·01N HCl.

Cation-exchanger: Dowex 50 Wx in Na-form, 50/100 mesh, total capacity 5·2 ± 0·3 meq per dry g.

Preparation of the columns

The columns were filled with cation-exchanger Dowex 50 Wx and washed first 3 to 5 times with a solution of EDTA-disodium salt, then 3 to 5 times with water. This purification was repeated after each experiment.

Procedure

To 5 ml of a solution containing, in addition to iron[III], an excess of other metals, a precisely known amount, y, of radio-iron is added (see Table I) and 1 ml of a solution of EDTA-disodium salt of such concentration (Table I) that there is insufficient to correspond stoichiometrically to the iron present. The pH of the solution is brought to 2–3 by adding HCl. After allowing the solution to stand for 20–30 min at elevated temperature (30 to 40°) to permit the reaction of iron and EDTA to go to completion, the solution is passed through the cation-exchanger column at a rate of 0·3 ml/min. After washing the column with water the eluate is made up to 10 ml, and the activity of 3 ml of the eluate (A_2) is measured by a scintillation counter. A solution containing only radio-iron is treated in exactly the same way. The amount of radio-iron present in this solution need not be known precisely, but must, however, be more than stoichiometrically equivalent to the EDTA-disodium salt added. The amount of EDTA-disodium salt must be precisely the same as in the first case. After measuring the activity of 3 ml of the eluate (A_1), the amount of iron present, x, is calculated from the relation

$$x = y \left[\frac{A_1}{A_2} - 1 \right]. \tag{10}$$

The results of the determination of iron in amounts of 10^{-7} to 10^{-9} g in 5-ml volumes are given in Table I.

The determination of traces of iron in sodium iodide

Traces of iron present in NaI crystals influence unfavourably their luminescent properties, which are made use of in scintillation techniques. For the determination of amounts of iron of the order of 10^{-3}–10^{-5} % by a colorimetric method, 10–20 g of the sample must be used.[6] A further increase in the sensitivity of the colorimetric methods is not possible. If, however, iron is separated by extraction with acetylacetone (to free it from excess NaI, and possibly some of the interfering metals) it is possible to determine as little as 10^{-7} % of iron in a 1-g sample.

Procedure

An amount of NaI between 0·1 and 1·0 g is dissolved in 5 ml of purified water, 1–5 ml of hydrogen peroxide are added and the solution is brought to the boiling point and evaporated till dry. To the residue 5 ml of water are added, the solution is boiled, and to the hot solution a known amount of radio-iron, y, is added. The pH of the solution is brought to 4–7 by adding a few drops of (twice distilled) ammonia, and the solution is extracted by 0·01M-acetylacetone in benzene. The organic phase is separated (a quantitative extraction of iron need not be carried out) and evaporated to dryness, to remove excess acetylacetone. To the residue 5 ml of 0·01–0·001N HCl are added and the required amount of EDTA-disodium salt, and the analysis is completed in the way already described.

TABLE 1—DETERMINATION OF TRACES OF IRON
(1·2 × 10⁻⁷–2·4 × 10⁻⁹ g of Fe/5 ml)

Iron taken, μg (X)	Active iron added, μg (y)	Activity of extracts[a]		Iron found, μg (x)	Deviation from mean, μg Δ	Other metals present, μg	Deviation[b]
		A_1	A_2				
0·12085	0·04275	44350	11860	0·1171	−0·0052	10 Al³⁺	
		44350	11534	0·1216	−0·0007	0	$\sigma = 0\cdot1223$
		44350	11110	0·1279	+0·0056	10 Cd²⁺	$\delta = \pm0\cdot0014 = \pm1\cdot2\%$
		44350	11207	0·1264	+0·0041	10 Zn²⁺	$\sigma - X = \pm0\cdot0014 = \pm1\cdot2\%$
		44350	11265	0·1256	+0·0032	10 Hg²⁺	
		44350	11512	0·1219	−0·0004	10 Tl⁺	
		40295	10650	0·1190	−0·0033	10 Ag⁺	
		40295	10670	0·1187	−0·0036	10 Co²⁺	
0·012085	0·021380	3693	2405	0·01145	−0·00108	1 Mn²⁺	
		3693	2420	0·01125	−0·00128	1 Cd²⁺	$\sigma = 0\cdot01253$
		3693	2192	0·01464	+0·00211	1 Co²⁺	$\delta = \pm0\cdot00050 = \pm4\cdot0\%$
		3693	2415	0·01131	−0·00122	1 Cr³⁺	$\sigma - X = \pm0\cdot00044 = \pm3\cdot6\%$
		3693	2210	0·01434	+0·00181	1 Pb²⁺	
		3693	2383	0·01175	−0·00078	1 Ni²⁺	
		5561	3561	0·01201	−0·00052	0	
		5561	3410	0·01348	+0·00095	1 Al²⁺	
0·002417	0·010690	4034	3189	0·002831	+0·000010		e
		4034	3070	0·003356	+0·000535		$\sigma = 0\cdot002821$
		4034	3200	0·002786	−0·000035		$\delta = \pm0\cdot000114 = \pm4\cdot1\%$
		4034	3255	0·002558	−0·000263		$\sigma - X = \pm0\cdot000404 = \pm14\%$
		4034	3200	0·002786	−0·000035		
		4034	3166	0·002930	+0·000109		
		4034	3150	0·002999	+0·000178		
		4034	3332	0·002251	−0·000570		

[a] In the range 1·2 × 10⁻⁷ g of Fe/5 ml, C_{HnY} = 1·0 × 10⁻⁶M; A_1, A_2, expressed in cp 5 min.
In the range 1·2 × 10⁻⁸ g of Fe/5 ml, C_{HnY} = 1·0 × 10⁻⁷M; A_1, A_2, expressed in cp 5 min.
In the range 2·4 × 10⁻⁹ g of Fe/5 ml, C_{HnY} = 1·0 × 10⁻⁷M; A_1, A_2, expressed in cp 10 min.

[b] $\sigma = \dfrac{\sum\limits_{x=1}^{x=n} x}{n}$; $\delta = \pm \sqrt{\dfrac{\Sigma\Delta^2}{n(n-1)}}$

Together with the analysis of the sample a blank is run in precisely the same way. The amount of iron present in $1·00$ g of NaI was found to be $3·6 \times 10^{-7}$ g (mean of 3 measurements), *i.e.*, $3·6 \times 10^{-5}$ %. The amount of iron in the blank was $0·6 \times 10^{-7}$ g, (mean of 3 measurements) *i.e.*, $0·6 \times 10^{-5}$ %.

DISCUSSION

From the results given in Table I, it follows that iron can be determined in amounts of $1·2 \times 10^{-7}$ g/5 ml with an average precision of the mean value of $1·2$ %, in amounts of $1·2 \times 10^{-8}$ g/5 ml with an average precision of $4·0$ % and in amounts of $2·4 \times 10^{-9}$ g/5 ml with an average precision of $4·1$ %.

From stability constant values (see Theoretical) it may be expected that even a one hundred-fold excess of the following metals will not interfere in the determination of iron^{III} in the form of an EDTA complex: Tl^+, Ag^+, Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, or Al^{3+}. The stability of the Cr^{3+}-EDTA complex is approximately the same[7] as for the Fe^{3+} complex; but since the Cr^{3+} complex is only formed in boiling solutions, even a one hundred-fold excess of chromium does not interfere in the determination of iron. Other metals which form very strong complexes with EDTA (*e.g.*, In^{3+}, Ga^{3+}, Bi^{3+}, Th^{4+}) interfere in the determination of iron. Contrary to what might be expected from the theory, a ten-fold excess of copper interferes in the determination of iron, even though the stability constant of the copper-EDTA complex is six orders of magnitude lower than that of the iron-EDTA complex. This effect may perhaps be interpreted as indicating that in passing through the column the original equilibrium of Fe-EDTA-Cu is shifted to the disadvantage of iron. The interfering effect of copper is eliminated only when the concentration of copper is lower than that of iron.

In conclusion, it must be mentioned that in the solution being analysed there should not be present a large excess of indifferent ions ($\gg 0·1M$), which would lead to displacement of the adsorbed iron. Also there should not be present in the solution any complexing agents which would form negatively charged complexes with iron^{III}.

From a comparison of our results with literature data[8] it follows that the determination of iron by this method is more sensitive (maximum sensitivities of the various methods are given in brackets) than the determination by flame photometry (2×10^{-6} g/ml), by the graphite DC arc (2×10^{-7} g/ml), by the copper spark (5×10^{-7} g/ml), colorimetrically (5×10^{-8} g/ml) or by activation analysis (neutron flux 10^{13} neutrons. cm^{-2} sec^{-1}: $4·5 \times 10^{-7}$ g/ml).

CONCLUSION

In the present paper a selective determination of traces of iron is described, in amounts of 10^{-7}–10^{-9} g/5 ml, carried out by the method of isotopic dilution analysis using ion-exchange. The proposed method may be used to determine trace amounts of a number of metals, and its sensitivity may be further increased by the use of carrier-free radio-isotopes.

Zusammenfassung—Isotopenverdünnungsanalyse in Verbindung mit Ionenaustauschern dient zur Bestimmung von Spurenmengen von Metallen. Theoretische Betrachtungen werden mitgeteilt und anhand der ableitungen lassen sich die optimalen Bedingung für die Bestimmung verschiedener Metalle voraussagen. Die Selektivität der Methode kann durch Anwendung von Maskierungs- und Fällungsmittel weiter gesteigert werden. Die vorgeschlagene Methode wurde anhand der Eisenbestimmung unter Verwendung von EDTA und Dowex 50 (Kationenaustauscher) getestet. Die mittlere Genauigkeit des Mittelwertes für Eisenmengen von 10^{-7} g Fe per 5 ml war $1·2$ %. Für 10^{-8} g

Fe per 5 ml 4·0% und für 10^{-9} g Fe per 5 ml 4·1%. Die Methode wurde zur Analyse von NaI(Tl) Kristallen herangezogen. Die entwickelte Methode ist recht einfach und wesentlich empfindlicher als Kolorimetrie, Aktivierungsanalyse oder irgendeineder anderen bisher entwickelten Methoden.

Résumé—L'analyse par dilution isotopique avec utilisation des échangeurs d'ions permet le dosage de traces de métaux. Les auteurs donnent la théorie de la méthode, d'après laquelle les conditions de dosage d'un certain nombre de métaux peuvent être prévues. La sélectivité peut être augmentée ultérieurement par l'utilisation d'agents complexants et de précipitation. La méthode proposée a été choisie pour le dosage du fer utilisant l'EDTA et la résine échangeur de cations Dowex 50. La précision moyenne des valeurs moyennes était: 1,2% pour des quantités de fer 10^{-7} g. pour 5 ml, 4,0% pour 10^{-8} g. de fer pour 5 ml et 4,1% pour 10^{-9} g. de fer pour 5 ml. Même un grand excès de nombreux métaux ne gêne pas l'analyse. La méthode a été appliquée à l'analyse de cristaux de NaI(Tl). La technique mise au point est très simple et beaucoup plus sensible que la colorimétrie, l'analyse par activation, ou toute autre méthode, utilisée jusqu'à maintenant, pour doser des traces de fer.

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CHELATOMETRIC DETERMINATION OF CYANIDE, THIOCYANATE AND CHLORIDE IN PRESENCE OF ONE ANOTHER

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Summary—A chelatometric method for the determination of cyanide, thiocyanate and chloride in the presence of one another is described. In one portion of the sample all three ions are precipitated by adding silver nitrate in excess. The silver precipitates are boiled with concentrated nitric acid. Silver chloride is not affected by this treatment while silver cyanide and thiocyanate are decomposed. The latter is oxidised to sulphate, the cyanide being expelled. The silver chloride precipitate is dissolved in a solution of potassium tetracyanonickelate and the liberated nickel is titrated with EDTA, the chloride content thus being determined indirectly. The sulphate solution after oxidation of thiocyanate is treated with a known volume of barium chloride solution and the excess of barium is titrated with EDTA solution of the same molarity. The difference between the volumes of barium chloride and EDTA solutions multiplied by a factor gives the thiocyanate content of the sample.

In a second portion of the sample, cyanide is determined by adding a known volume, in excess, of nickel sulphate solution and titrating the excess of nickel that has not combined with the cyanide. The difference between the volumes of the nickel and EDTA solutions multiplied by a factor gives the cyanide contents.

The method is rapid and accurate. A very small quantity of one of the components in the presence of large amounts of the others can be determined.

INTRODUCTION

THE classical titrimetric methods are too tedious for the separation and determination of cyanide, thiocyanate and chloride in the presence of one another. The chelatometric procedure described is rapid because use is made of the same operation for determining chloride and thiocyanate.

The principle of the chelatometric method is that silver chloride is not dissolved by hot nitric acid, while silver cyanide and thiocyanate are decomposed and dissolve, the latter being oxidised to sulphate. The silver chloride is filtered, washed, then dissolved in a solution of potassium tetracyanonickelate and the liberated nickel is titrated with EDTA,[1,2] thus determining the chloride content indirectly:

$$2AgCl + [Ni(CN)_4]^{2-} \rightarrow 2[Ag(CN)_2]^- + Ni^{2+} + 2Cl^-.$$

The sulphate contained in the filtrate is precipitated by adding a known volume, in excess, of barium chloride solution and the barium that has not precipitated is titrated, without filtering, with EDTA.[3,4] The difference in volumes of the barium and EDTA solutions (both solutions having the same molarity) multiplied by a factor gives the thiocyanate content.

Cyanide is determined in a separate portion of the sample by adding a known volume, in excess, of nickel sulphate[5] and the nickel that has not reacted in the formation of nickel tetracyanide is titrated with EDTA solution (both solutions having the same molarity). The difference between the volumes utilised, multiplied by a factor gives the cyanide content.

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EXPERIMENTAL

Reagents

Silver nitrate solution: 5% and 0·1%.

Nitric acid: Conc. and 1%.

0·1M EDTA solution: 37·21 g of disodium ethylenediaminetetra-acetic acid in 1 litre of water.

Saturated aqueous solution of murexide.

0·1M Potassium tetracyanonickelate solution: Prepared by titrating exactly 0·1 mole of nickel sulphate (in solution) after being made ammonial, with 1M potassium cyanide solution. The end-point is indicated when the solution changes from yellow to purple.

0·1M Barium chloride solution: The molarity of this solution should be adjusted exactly with that of the EDTA solution.

0·1% Aqueous solution of metal phthalein This should contain a few drops of ammonia solution.

Ammonia solution: Conc.

Sodium hydroxide solution: About 1M.

0·1M Nickel sulphate solution: The molarity of this solution should be adjusted exactly with that of the EDTA solution.

Procedure

One g of the sample (or its equivalent of solution) is introduced into a beaker and 200 ml of water are added. An excess of 5% silver nitrate solution is poured slowly into the neutral solution and all three ions are precipitated. The suspension is warmed slightly, then allowed to stand. A little more 5% silver nitrate solution is added to the supernatant liquid to ensure that precipitation is complete. The precipitate is filtered on glass wool or asbestos, washed twice with 0·1% silver nitrate solution, then twice with 1% nitric acid.

The precipitate is transferred to a beaker and sufficient conc. nitric acid is added to cover the precipitate. The beaker is covered with a watch glass and the contents are boiled gently for 1 hr. More acid is added in case of rapid evaporation. The contents of the beaker are cooled, then water is added and the solution is filtered on a Gooch. Care must be taken not to use strong suction to avoid clogging of the filter. The silver chloride is washed twice with 0·1% silver nitrate solution, then twice with 1% nitric acid. The filter with the precipitate is transferred to a beaker containing sufficient potassium tetracyanonickelate solution for complete immersion of the precipitate. The contents of the beaker are stirred and warmed gently to aid solution.[6] As soon as the precipitate is dissolved, dilute the solution, add 1 ml of murexide solution and titrate slowly with EDTA to a yellow-to-purple end-point: 1 ml of 0·1M EDTA solution ≡ 7·091 mg of Cl⁻.

The filtrate and the washings are collected in a beaker and brought to the boil. A known volume of 0·1M barium chloride solution, in excess, is added and the solution boiled for another 5 min so as to obtain a crystalline precipitate. The suspension is neutralised with approx. 0·1M sodium hydroxide solution, mixed with ethanol in the ratio of about 1:1, 5 ml of conc. ammonia solution added for every 100 ml of the mixture, followed by some drops of the indicator (metal phthalein) and the excess of barium titrated with 0·1M EDTA solution without delay: Each 1 ml difference in volume of 0·1M BaCl₂ and 0·1M EDTA solutions ≡ 5·808 mg of SCN⁻.

To determine cyanide in the sample, 1 g is dissolved in water (or its equivalent of solution is taken), then a known volume of 0·1M nickel sulphate solution is added and some drops of murexide solution. The excess of nickel that has not combined with the cyanide is titrated with 0·1M EDTA solution: Each 1 ml difference in volume of 0·1M Ni(SO₄)₂ and 0·1M EDTA solutions ≡ 10·407 mg of CN⁻.

RESULTS

The described method is rapid and makes use of very stable solutions. Some typical results obtained with artificially prepared samples are reproduced in Table I. The samples were prepared by mixing together accurately measured volumes of solutions of sodium chloride (1 ml ≡ 1 mg or 10 mg of Cl⁻), sodium cyanide (1 ml ≡ 1 mg or 10 mg of CN⁻), and sodium thiocyanate (1 ml ≡ 1 mg or 10 mg of SCN⁻). The method is very satisfactory and works well even when a very small quantity of one of the components is in the presence of large amounts of the others.

TABLE I—SOME TYPICAL RESULTS OBTAINED WITH THE DESCRIBED METHOD

Taken, mg			Found, mg		
Cl⁻	CN⁻	SCN⁻	Cl⁻	CN⁻	SCN⁻
10	200	200	10·3	201·2	197·3
50	250	100	49·4	249·4	101·5
100	50	250	100·8	50·6	248·6
200	50	500	201·5	50·3	497·2
500	100	50	498·7	97·7	50·1
50	500	50	49·8	497·5	50·3
100	100	100	100·7	99·6	99·7
200	50	200	198·4	49·7	201·2
50	100	200	50·3	98·6	199·5
100	200	50	101·0	200·5	49·7
100	200	400	99·3	197·8	401·6
100	50	200	101·6	50·4	198·3

Zusammenfassung—Eine chelatometrische Methode zur Bestimmung von Cyanid, Rhodanid und Chlorid wird beschrieben. In einem Teil der Probe werden alle drei Ionen durch Zugabe von Silbernitrat gefällt. Der Niederschlag wird mit conc. Salpetersäure behandelt. Rhodanid wird hierbei zu Sulfat oxydiert, während Cyanid entweicht. Der Silberchloridniederschlag wird mit gelöstem Nickeltetracyanid umgesetzt und das in Freiheit gesetzte Nickel mit ÄTDE titriert. Zum Filtrat vom Chloridniederschlag wird eine gemessene Menge Bariumchlorid zugesetzt und der Überschuss an Barium mit ÄDTE bestimmt. In einem zweiten Teil der Probe wird Cyanid bestimmt durch Zugabe einer gemessenen Menge Nickelsulfats und Rücktitration des überschüssigen Nickels mit ÄDTE. Die Methode is rasch und genau. Sehr kleine Mengen einer Komponente können in Gegenwart grosser Mengen der beiden anderen Ionen bestimmt werden.

Résumé—L'auteur décrit une méthode complexométrique de dosage de cyanure, thiocyanate et de chlorure en présence l'un de l'autre. Sur une portion d'échantillon, les trois ions sont précipités par addition de nitrate d'argent en excès. Les précipités sont portés à ébullition avec de l'acide nitrique concentré. Le chlorure d'argent n'est pas altéré par ce traitement, cependant que le cyanure et le thiocyanate d'argent sont décomposés. Ce dernier est oxydé en sulfate, le cyanure étant chassé. Le précipité de chlorure d'argent est dissous dans une solution de tétracyanonickelate de potassium et le nickel libéré est titré par l'EDTA; les teneurs en chlorure sont déterminées indirectement. La solution de sulfate, après oxydation du thiocyanate, est traitée par un volume connu d'une solution de chlorure de baryum et l'excès de baryum est titré par une solution d'EDTA de même molarité. La différence entre les volumes de solution de chlorure de baryum et d'EDTA multipliée par un facteur donne les teneurs en thiocyanate de l'échantillon.

Le cyanure est dosé sur une deuxième partie d'échantillon en ajoutant un volume connu, en excès, d'une solution de sulfate de nickel et en titrant l'excès de nickel non combiné au cyanure. La différence entre les volumes des solutions de nickel et d'EDTA multipliée par un facteur donne les teneurs en cyanure.

La méthode est rapide et précise. Elle permet de doser de très faibles quantités de l'un des anions en présence de grandes quantités des autres.

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5-AMINO-2-BENZIMIDAZOLETHIOL AS AN ANALYTICAL REAGENT—II*

SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM AND THE SIMULTANEOUS DETERMINATION OF RHODIUM AND PALLADIUM

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Summary—5-Amino-2-benzimidazolethiol has been found to be a highly sensitive reagent for the colorimetric determination of rhodium^{III}. The orange-yellow complex of rhodium^{III} with the reagent, developed by heating in the pH range 2–5, shows maximum absorption at 370 mμ; it is practicable to use wavelength 390 mμ, where the reagent absorption is negligible. The colour system obeys Beer's law from 0·5 to 4·0 ppm of rhodium^{III}, the optimum concentration range being 1·0–3·5 ppm where the percentage relative error per 1 % absolute photometric error is 2·88. Sandell's spectrophotometric sensitivity of the reaction is 0·004 μg/cm^2. Most of the common ions and rare metal ions, including uranium^{VI}, are without effect on the complex. Palladium^{II} interferes, producing a colour, but a simultaneous colorimetric method for determining rhodium^{III} and palladium^{II} in a mixture has been developed by determining rhodium and palladium together in hot solution and then subtracting the palladium determined in the cold. Interferences from ruthenium^{III} and larger amounts of iridium^{IV} are avoided by using EDTA (disodium salt) as a masking agent. The continuous variation and the molar ratio methods, applied at pH 3·42, indicate that rhodium^{III} forms with the reagent both 1:2 and 1:3 complexes, their dissociation constants being 2·7 $\times$ 10^{-12} and 6 $\times$ 10^{-17}, respectively.

INTRODUCTION

IN a previous communication,[1] the author introduced 5-amino-2-benzimidazolethiol as a very sensitive reagent for the colorimetric determination of micro amounts of palladium^{II}. It was shown that palladium can be determined at 390 mμ after developing the colour in the cold at pH 3·42 for 35 min. Rhodium^{III} gives no colour with the reagent in the cold, but when heated on a steam bath it develops an intense orange-yellow colour suitable for its spectrophotometric determination.

Until recently only the stannous chloride method for the colorimetric determination of rhodium has been widely studied by various workers but this method suffers from the drawback that almost all other platinum metals, present even in traces, will seriously interfere, hence their removal is absolutely necessary.[2] Recently thiomalic acid was introduced as a colorimetric reagent for rhodium,[3] but its sensitivity is lower than that of the stannous chloride method[4] or that of the present method developed by the author. Moreover, the tolerance limits of various ions, including the platinum metals, towards thiomalic acid seem to be very low.[3,5] There is therefore a need to search for new colorimetric reagents for rhodium which will not only be very sensitive but will also be relatively free from the interference of diverse ions including the platinum metals.

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The author after a critical study of the colour reaction of 5-amino-2-benzimidazolethiol with rhodium[III], finds that the reagent is ideally suited for the colorimetric determination of micro amounts of the metal.

EXPERIMENTAL

Apparatus

A Beckman DK1 automatic recording spectrophotometer was used for determining the wavelength-transmittance curves, and the absorbances of other solutions were obtained with a Beckman DU Spectrophotometer. In all cases, 1·00-cm silica cells were used.

A Beckman model G pH meter was employed for the pH determinations.
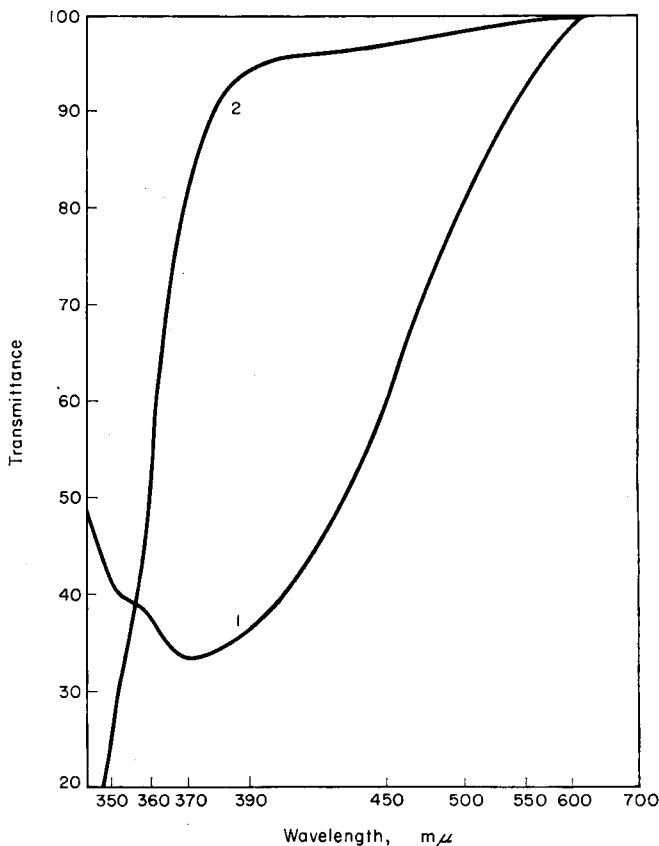
FIG. 1.—Wavelength-transmittance curves of 5-amino-2-benzimidazolethiol and its rhodium[III] complex at pH 3·42.
Curve 1: 1·9 ppm of rhodium[III] + 10 ml of 0·5% reagent.
Curve 2: 10 ml of 0·5% reagent diluted to 25 ml with buffer of pH 3·42.

Reagents

Standard rhodium solution: A rhodium[III] stock solution was prepared from sodium rhodium chloride (Na_2RhCl_5) by dissolving it in dilute hydrochloric acid containing 10 ml of conc. HCl/litre. This solution was standardised by the 2-thiobarbituric acid method of Beamish *et al.*[6]

Other reagents: Solutions of reagent, buffer and other platinum metals and common ions were prepared in the manner described previously.[1,7]

Recommended procedure

Ten ml of 0·5% reagent solution were added to 1 ml of rhodium^{III} solution (12·5 to 100 μg of Rh) taken in a 25-ml beaker, and the mixture was heated on a steam bath for 25 min for complete colour development, and then cooled to room temperature. The orange-yellow coloured solution was transferred to a 25-ml volumetric flask, and the volume was made up with sodium acetate-acetic acid buffer of pH 3·42. The absorbance was then measured against a reagent blank prepared identically without rhodium.

DISCUSSION

Spectral curves

It is evident from the wavelength-transmittance curve of the complex (Fig. 1) that the maximum absorption (*i.e.* minimum transmittance) takes place at 370 mμ. But as the reagent absorption is also high in this region (*cf.* Fig. 1), a practical wavelength of 390 mμ was chosen for all subsequent measurements, the reagent absorption at this wavelength being negligible.

Effects of pH, reagent concentration and time

The complex is free from change of absorbance in the pH range 2–5. At higher pH values, however, there is a slight increase in the absorbance.

For 2–4 ppm of rhodium^{III}, 10 ml of 0.5% reagent are necessary for full colour development.

The colour does not develop at room temperature, but if heated on the steam bath for 20 min the full colour develops, and the absorbance value does not alter even after a longer heating period. Once formed, the complex maintains a constant absorbance for 24 hr.

Beer's law, optimum range and accuracy

The complex obeys Beer's law in the range 0·5–4·0 ppm of rhodium^{III} (*cf.* Fig. 2). The optimum concentration range, as obtained from Ringbom's[8] curve (Fig. 3), is between 1 and 3·5 ppm, where the percentage relative error per 1% absolute photometric error, evaluated by Ayres method,[9] is 2·88.

Sensitivity and molecular absorptivity

Sandell's spectrophotometric sensitivity,[4] as calculated from Beer's law data, is 0·004 μg/cm^2. The molecular absorptivity for the 1:3 complex is 1·5 × 10^5.

Reproducibility

Ten samples of rhodium^{III} solution were taken for an examination of the reproducibility of the colour. The first five sets contained 2 ppm of rhodium^{III} in each case and absorbance values for these were found to be 0·475, 0·475, 0·470, 0·475 and 0·473. The second five sets contained 4 ppm of rhodium^{III} in each case and absorbance values were 0·93, 0·93, 0·93, 0·92 and 0·93. These results confirm the reproducibility of the method.

Effect of diverse ions

The effect of various ions on the colour system was investigated by adding different
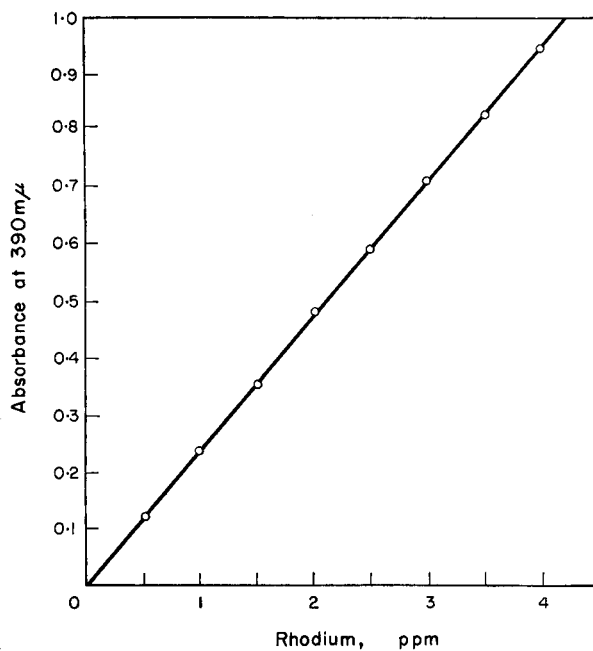
FIG. 2.—Beer's law plot for the rhodium^{III} complex at pH 3·42.
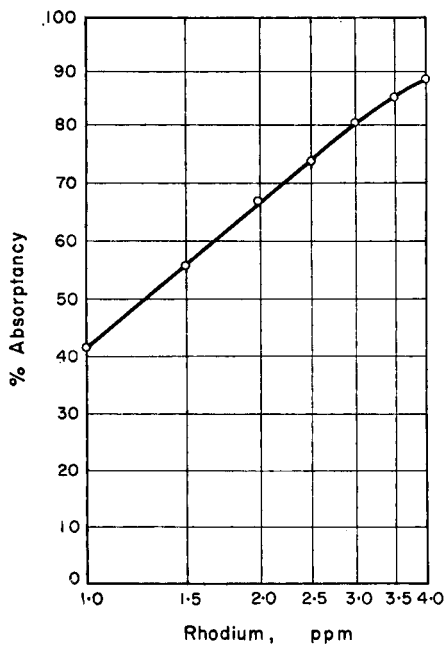
FIG. 3.—Calibration curve for the rhodium^{III} complex at 390 mμ; pH 3·42.

amounts of the ionic species to the rhodium^{III} solution and then developing the colour as outlined under recommended procedure. An increase or decrease of 0·005 unit in the absorbance value was taken to be an interference. It was observed that disodium

salt of ethylenediaminetetra-acetic acid (EDTA) could appreciably increase the tolerance limits for various ions. The results are given in Table I.

TABLE I.–DETERMINATION OF RHODIUM[III] IN PRESENCE OF DIVERSE IONS
Rhodium taken, 4 ppm in each case

Ions	EDTA (disodium salt) added, *ppm*	Maximum amount of ion tolerated, *ppm*	Ions	EDTA (disodium salt) added, *ppm*	Maximum amount of ion tolerated, *ppm*
Ru^{3+}	32	4	Cd^{2+}	—	40
Ir^{4+}	—	4	As^{3+}	—	40
Ir^{4+}	32	8	Pb^{2+}	—	40
Au^{3+}	—	8	Mn^{2+}	—	20
Cu^{2+}	32	8	UO_2^{2+}	—	>70
Ni^{2+}	32	16	MoO_4^{2-}	—	40
Co^{2+}	—	32	WO_4^{2-}	—	40
Zn^{2+}	—	16	Cl^-	—	>300
Zn^{2+}	32	32	NO_3^-	—	>300
			SO_4^{2-}	—	>300

Platinum[IV] should be absent, and osmium should be separated by distillation[4] of the volatile osmic acid (OsO_4).

Simultaneous determination of rhodium and palladium

Simultaneous determination of rhodium[III] and palladium[II] from a mixture is possible by taking advantage of the fact that palladium[II], when treated with the reagent at room temperature, develops its full colour intensity which does not change even after heating at 100°, whereas rhodium[III] gives a colour with the reagent only after heating. Experiments also showed that the absorbance values of rhodium and palladium complexes at 390 mμ are quantitatively additive in character.

Procedure

An aliquot of the synthetic mixture of rhodium[III] and palladium[II] solutions was treated as described earlier for the determination of rhodium. The absorbance was measured at 390 mμ against a reagent blank to obtain the total amount of rhodium and palladium. To another aliquot of the same mixture of rhodium[III] and palladium[II] taken in a 25-ml volumetric flask, 10 ml of 0·5% reagent solution were added and the volume was made up with the buffer solution of pH 3·42. After allowing to stand for 35 min at room temperature, the absorbance was measured against a reagent blank at 390 mμ to ascertain the amount of palladium present. The absorbance value for palladium was then deducted from the total absorbance value for rhodium and palladium and the amount of rhodium was determined from this with reference to a standard curve.

The results as given in Table II show that rhodium and palladium can be determined from a mixture when they are present in a 1:1 or a 1:2 ratio. The latter figure represents the limit of applicability of the determination.

Composition of the complex in solution

The composition of the complex in solution was studied by the continuous variation[10] and molar ratio[11] methods.

For these studies, equimolecular solutions of rhodium[III] and the reagent were mixed in the correct proportions in 25-ml beakers, and after heating on a steam bath for 25 min and subsequent cooling to

TABLE II.—Simultaneous determination of rhodium and palladium

Rhodium[III] taken, ppm	Palladium[II] taken, ppm	Rhodium[III] found, ppm	Palladium[II] found, ppm
4·0	4·0	4·0	4·0
4·0	4·0	3·9	4·1
4·0	4·0	3·95	4·05
2·0	4·0	2·0	4·0
2·0	4·0	1·98	4·02
2·0	4·0	2·0	4·0

FIG. 4.—Determination of the ratio of rhodium[III] to reagent by the continuous variation method.
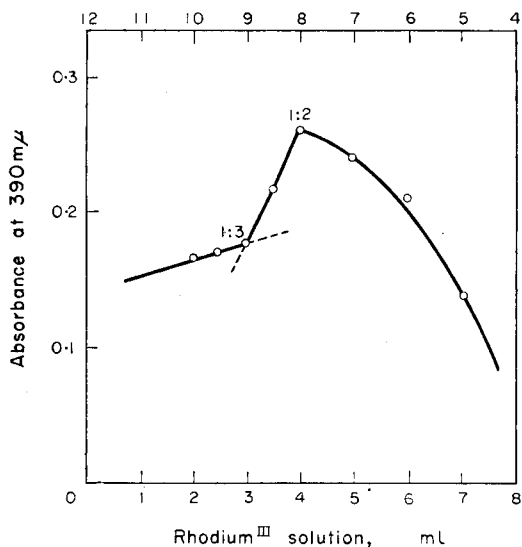Concn. of rhodium[III] = concn. of reagent = $5·69 \times 10^{-4}M$.
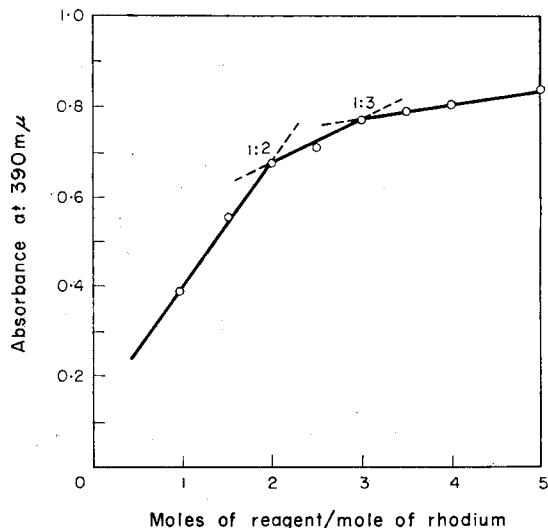Total volume in each case = 12 ml; pH 3·42.

FIG. 5.—Determination of the ratio of rhodium[III] to reagent by the molar ratio method.
Rhodium[III] concn. = $9·1 \times 10^{-5}M$ (constant); reagent concn. varied.

room temperature, the volume was made up to 25 ml in volumetric flasks by the buffer of pH 3·42. The absorbances were measured at 390 mμ against a water blank.

The results, as represented in Figs. 4 and 5, indicate that under the conditions employed rhodium[III] forms both 1:2 and 1:3 complexes with the reagent. It appears from Fig. 5 that first the 1:2 complex is formed, and this quickly changes to the 1:3 complex when excess of the reagent is present.

Dissociation constants

By employing the absorption values of Fig. 5, the dissociation constants of both the 1:2 and 1:3 complexes were calculated from the equations $K = (\alpha C)(n\alpha C)^n/C(1 - \alpha)$ and $\alpha = (E_m - E_s)/E_m$ of Harvey and Manning.[12] The values were found to be $2·7 \times 10^{-12}$ for the former complex and 6×10^{-17} for the latter.

Zusammenfassung—5-Amino-2-benzimidazolthiol wurde als hochselektives Reagens für die kolorimetrische Bestimmung von Rhodium(III) gefunden. Ein orangegelber Komplex entwickelt sich beim Erhitzen im pH-Bereich 2–5; das Absorptionsmaximum liegt bei 370 mμ; man kann auch bei 350 mμ arbeiten, wo die Absorptions des Reagenses vernachlässigbar ist. Beer's Gesetz wird zwischen 0.5 und 4.0 p.p.m. Rh erfüllt. Der optimale Konzentrationsbereich ist 1·0–3·5 ppm, wo der perzentuelle Fehler pro 1 % absolutem photometrischem Fehler 2·88 beträgt. Sandell's spectrophotometrische Empfindlichkeit der Reaction ist 0·004 μg/cm². Die meisten gewöhnlichen Ionen, sowie seltenen Metallionen, einschliesslich U (VI) sind ohne Einfluss. Pd(II) stört durch Färbung; es ist aber möglich Pd + Rh in heisser Lösung und Rh in kalter Lösung zu bestimmen und so beide Metall zu ermitteln. Störungen durch Ru(III) und grossen Mengen Ir(IV) werden durch Maskieren mit ADTE ausgeschaltet. Bei pH 3·42 enstehen 1:2 und 1:3 Komplexe deren Dissoziationskonstanten zu $2·7 \times 10^{-12}$ und 6×10^{-17} bestimmt wurden.

Résumé—L'auteur a trouvé que le 5-amino-2-benzimidazolethiol était un réactif très sensible pour le dosage colorimétrique du rhodium(III). Le complexe jaune orangé rhodium(III)-réactif, formé en chauffant dans le domaine de pH 2–5, présente un maximum d'absorption à 370 mμ; il est pratique d'utiliser une longueur d'onde de 390 mμ, pour laquelle l'absorption du réactif est négligeable. Le système coloré suit la loi de Beer de 0,5 à 4,0 p.p.m. de rhodium(III), le domaine de concentration le meilleur étant 1,0 à 3,5 p.p.m. dans ce domaine le pourcentage d'erreur relative, pour une erreur photométrique absolue de 1 %, est 2,88. La sensibilité spectrophotométrique de Sandell de la réaction est 0,004 μg/cm². La plupart des ions communs et des ions métalliques rares, l'uranium(VI) y compris, n'ont aucune influence sur le complexe. Le palladium(III) gêne en donnant une couleur, mais l'auteur a mis au point une méthode colorimétrique de dosage simultané de rhodium(III) et palladium(II) dans un mélange: le rhodium et le palladium sont déterminés ensemble dans la solution chaude, puis le palladium déterminé à froid est soustrait. Les interférences du ruthénium(III) et de grandes quantités d'iridium(IV) sont évitées en complexant ces métaux par l'E.D.T.A. (sel disodique). Les méthodes de variation continue et du rapport molaire, appliquées à pH 3,42, indiquent que le rhodium(III) forme avec le réactif les complexes 1/2 et 1/3; leurs constantes de dissociation sont respectivement $2,7 . 10^{-12}$ et $6 . 10^{-17}$.

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THE DETERMINATION OF TRACES OF GOLD IN SAMPLES OF PLATINUM BY NEUTRON-ACTIVATION ANALYSIS

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Summary—A neutron-activation method has been developed to determine very small concentrations of gold in samples of platinum. The Harwell nuclear reactor DIDO has been used as the source of neutrons. Following irradiation, gold has been separated radiochemically from samples and standards. ^{198}Au activity has been assayed by a discriminated γ-counting method in which ^{199}Au activity produced from activation of platinum is not recorded. Results are quoted for the gold contents of some pure platinum samples.

OWING to limitations of conventional methods of analysis, radioactivation procedures have been developed to determine very small quantities of impurities in samples of platinum.[1-3] In this paper the determination of traces of gold in platinum by neutron-activation is reported. The nuclear reactor DIDO at Harwell has been used as the source of neutrons and a comparative method of analysis has been employed. To avoid neutron self-screening differences between samples and standards,[4] standards have been prepared by the admixture of small known quantities of gold with analytical samples.

Gold has only one stable isotope, ^{197}Au. On irradiation with neutrons of thermal energies this yields the radionuclide ^{198}Au by a nuclear reaction of the (n,γ) type. The ^{198}Au may undergo a further (n,γ) reaction giving ^{199}Au. Activation cross-sections,[5] σ, for the reactions are

$$^{197}\text{Au}(n,\gamma)^{198}\text{Au} \qquad \sigma = 96 \text{ barns}$$

$$^{198}\text{Au}(n,\gamma)^{199}\text{Au} \qquad \sigma = 26{,}000 \text{ barns}$$
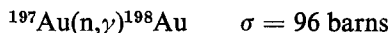
and nuclear data[6] for the radionuclides ^{198}Au and ^{199}Au are given in Table I.

TABLE I. PROPERTIES OF THE RADIONUCLIDES GOLD-198 AND GOLD-199

Nuclide	Half-life, days	Decay modes, radiations and energies (MeV)	Decay product
^{198}Au	2·697	β^- 0·960 ($\sim$100%), (others) γ 0·411 (96·4%), 0·675, 1·087,	^{198}Hg (stable)
^{199}Au	3·14	β^- 0·460 (6·4%), 0·302 (69·3%), 0·251 (24·3%) γ 0·0497, 0·1583, 0·2080	^{199}Hg (stable)

The neutron-activation analysis of traces of gold in platinum is made difficult by the fact that ^{199}Au is produced in considerable yield from platinum by the sequence

$$^{198}\text{Pt}(n,\gamma)^{199}\text{Pt} \xrightarrow[t_{1/2}\,=\,31\text{ min}]{\beta^-} {}^{199}\text{Au}.$$
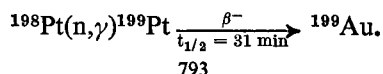
The problem arises, therefore, of assaying small amounts of ^{198}Au in the presence of a preponderance of ^{199}Au. Because ^{198}Au and ^{199}Au have such similar half-lives it is impossible to resolve the activities satisfactorily from decay measurements. However, the differences in the energies of the γ-rays emitted by the two radionuclides do enable the ^{198}Au to be measured.

^{198}Au may be produced from platinum by the sequence

$$^{196}Pt(n,\gamma)^{197}Pt \xrightarrow[t_{1/2} = 18\ hr]{\beta^-} {}^{197}Au(n,\gamma)^{198}Au$$
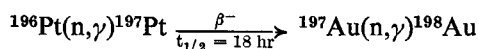
but calculation[7] shows that under the conditions employed in the present work this would give rise to a spurious gold content of platinum samples corresponding to only *ca.* 10^{-4} ppm.

EXPERIMENTAL

Irradiation

The samples of platinum for analysis were in the form of powdered metal sponge. Weighed quantities of 0·1 g were sealed in silica tubes of internal diameter 4 mm. Standards were prepared by adding weighed portions (*ca.* 0·02–0·04 g) of a standard solution of gold (100 mg of Au/litre) to 0·1-g samples of platinum in silica tubes. The liquid was allowed to soak into the metal powder, then was carefully evaporated to dryness, after which the tubes were sealed.

Standards containing the added gold and samples to which no gold had been added were packed together with silica wool in standard aluminium cans, 3 in. long and 1 in. diameter, and were sent to Harwell for neutron activation. Irradiation was for 2·5 hr in the Pile DIDO with a thermal neutron flux of 8 × 10^{11} n/cm^2/sec.

Following delivery from Harwell after irradiation, the samples and standards were analysed radiochemically for ^{198}Au.

Radiochemical separation

The chemical procedure for the separation of gold involved the use of carrier chemistry, solvent extraction and precipitation.

After dissolution of the samples and standards in *aqua regia*, together with gold carrier, the gold was separated from most other elements by extraction into ether.[8] Further purification was achieved by precipitation of gold metal by means of reduction with hydroquinone. The last traces of contaminating elements were removed by extraction of gold^{III} from hydrochloric acid solution into ethyl acetate. The gold^{III} was finally converted by hydroquinone reduction to the metallic state in which form it was counted.

Rather similar separation procedures have been employed by other workers in radioactivation analyses of gold in geological,[9,10] cosmological,[4] and biological[11,12] materials and in refined silver and nickel cathodes.[13]

Details of the radiochemical separation used in the present work are as follows:

Step 1. Open the silica irradiation tubes and transfer the activated samples and standards to clean 50-ml glass centrifuge tubes. To each add 1 ml of Au carrier (10 mg of Au/ml as Au^{III} in 0·1M HCl) and 2 ml of 12M HCl. Wash out the irradiation tubes thoroughly with hot 6M HCl and transfer the washings to the centrifuge tubes. Add 1 ml of 16M HNO$_3$ and slowly dissolve each sample of platinum by heating on a water bath. Boil for *ca.* 10 min and during this period add two 1-ml portions of 12M HCl.

Step 2. Adjust the strength of the solution to *ca.* 1M in HCl and cool. Agitate the solution with three successive 10-ml portions of diethyl ether. Separate and combine the organic layers. Wash the combined extract twice with 10-ml portions of 2M HCl saturated with ether and reject the washings. Separate the organic phase into a clean 50-ml centrifuge tube and warm on a water bath until the ether has completely evaporated.

Step 3. Dilute the residue with 20 ml of hot H$_2$O and heat to boiling. Add 2 ml of a freshly prepared 5% aqueous solution of hydroquinone and digest for several min. Centrifuge and discard the supernate.

Step 4. Dissolve the precipitate of gold in 1 ml of *aqua* regia, add 1 ml of 12*M* HCl, and dilute to 20 ml with H_2O. Extract with two successive 10-ml portions of ethyl acetate. Combine the organic layers in a clean 50-ml centrifuge tube, wash twice with 10 ml of 2*M* HCl and reject the washings. Evaporate off the ethyl acetate and to the residue add 25 ml of hot 1*M* HCl.

Step 5. Heat on a water bath and add 2 ml of 5% hydroquinone solution. Digest for 10 min, centrifuge and discard the supernate. Wash the precipitate of gold twice with 10 ml of hot H_2O and once with ethanol. Transfer the metal powder as a slurry in ethanol with a pipette onto a weighed aluminium counting tray (A.E.R.E. Cat. No. 4–3/1068). Dry under a heater-lamp and weigh to establish the chemical yield (usually *ca.* 75%).

Counting of the final gold precipitates

The final precipitates of gold from samples and standards were counted through an Al–Pb sandwich absorber (852 mg/cm² Al, 1·80 g/cm² Pb, 98 mg/cm² Al) with a 1·5-in. diam. × 1 in. NaI(Tl) crystal scintillation counter. A discriminator bias voltage was applied to the output of the counter to cut out the γ-rays of [199]Au. The observed counting rates were corrected for background and chemical yield and for any decay of significance between counting samples and standards.
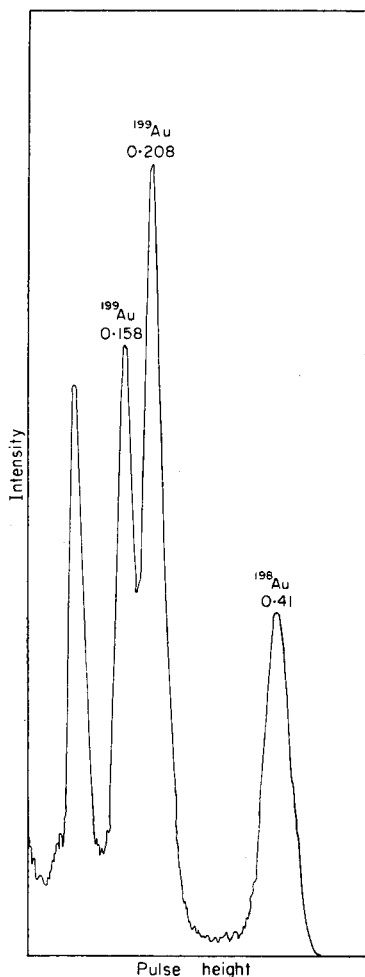
FIG. 1.—γ-Ray spectrum of gold radiochemically separated from neutron-irradiated platinum. (Energies in MeV).

The spectrum obtained from a final gold precipitate measured through an Al-Pb sandwich absorber with a NaI(Tl) crystal γ-ray spectrometer is shown in Fig. 1. It can be seen from this that by application of sufficient bias voltage γ-rays of ^{198}Au may be counted with no interference from ^{199}Au.

An additional check that only ^{198}Au activity from the final precipitates was being counted was obtained from decay measurements. Decay curves were straight lines corresponding well with published values[6] for the half-life of ^{198}Au (Fig. 2).
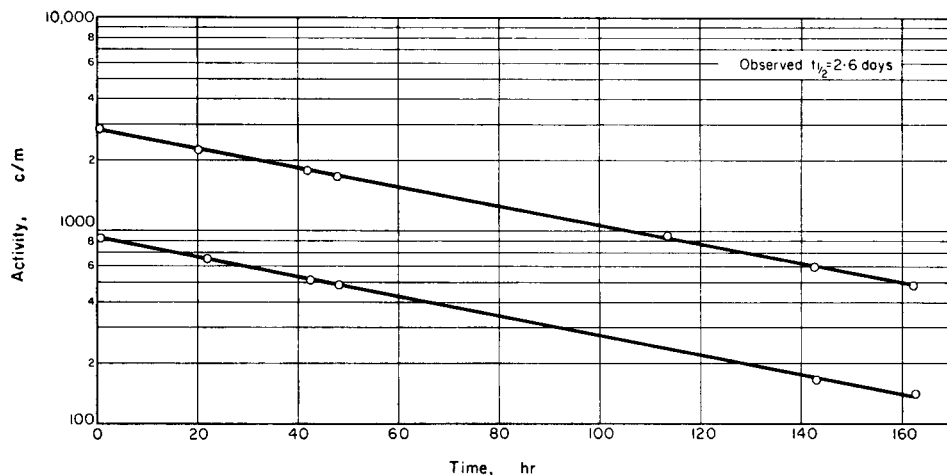
FIG. 2.—Decay curves of final gold precipitates measured by discriminated γ-scintillation counting.

RESULTS AND DISCUSSION

In Table II are shown results of neutron-activation analyses of pure samples of platinum.

TABLE II. GOLD CONTENTS OF SAMPLES OF PLATINUM
DETERMINED BY NEUTRON-ACTIVATION ANALYSIS

Sample	Gold content, *ppm*
Pt 1	0·61, 0·69, 0·69
Pt 2	3·4, 3·6
Pt 3	0·70, 0·78, 0·83, 0·74
Pt 4	0·86, 0·81
Pt 5	2·5, 2·7
Pt 6	1·0, 1·0
Pt 7	1·1, 1·1, 1·1

Neutron-activation normally provides an exceptional sensitivity for the analysis of gold, *e.g.* Gibbons[12] has reported that as little as 10^{-10} g of the element can be determined in biological materials. In the special case of platinum samples, nuclear considerations prevent full realisation of the potential sensitivity; nevertheless, 0·1 ppm of gold* may be determined by the method described in the present work, and this level appears to cover industrial requirements.

* This content of gold would give *ca.* 50 cpm above the background count.

Zusammenfassung—Neutronenaktivierung wurde zu Bestimmung sehr kleiner Mengen von Gold in Platinmetal angewendet. Der Harwellreaktor DIDO wurde als Strahlenquelle eingesetzt. Nach der Bestrahlung wurde Gold mittels radiochemischer Methoden aus Probe und Standard isoliert und die Aktivität des ^{199}Au selektiv gezählt. Resultate für einige Platinproben werden mitgeteilt.

Résumé—Les auteurs ont mis au point une méthode pour doser de très faibles concentrations d'or dans des échantillons de platine par activation neutronique. Le réacteur nucléaire DIDO de HARWELL a été utilisé comme source de neutrons. Après l'irradiation, l'or a été séparé radiochimiquement des échantillons et des étalons. L'activité de ^{198}Au a été déterminée par une méthode de comptage des rayons gamma dans laquelle l'activité de ^{199}Au produit par l'activation du platine n'est pas enregistrée. Les résultats sont donnés en teneurs en or des échantillons de platine pur.

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SIMULTANEOUS INFRARED DETERMINATION OF SULPHATE, NITRATE AND NITRITE IN WATER SAMPLES

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Summary—Small quantities of nitrate, nitrite and sulphate ions may be determined simultaneously by infrared spectrophotometry, utilising the potassium bromide disk technique. The solid samples are prepared by freeze-drying aqueous solutions of these ions containing potassium bromide. An anion-exchange procedure is readily coupled with the infrared measurement through the freeze-drying step. This permits the concentration of very dilute sample solutions, and eliminates the interferences of phosphate, carbonate, and organic matter. The method has been applied to the determination of nitrate, nitrite and sulphate in water samples, where it is found to compare favourably with other methods.

ALTHOUGH infrared spectrophotometry has become a routine tool for the solution of countless analytical problems, there have been few applications to the determination of inorganic ions. The catalogue of Miller and Wilkins[3] showed that many inorganic ions exhibit potentially useful infrared absorption bands. Studies in this laboratory demonstrated that small quantities of sulphate could be determined by infrared spectrophotometry, and that freeze-drying coupled with the potassium bromide disk technique, permitted the ready adaptation of infrared measurements to samples presented as aqueous solutions.[2,5] Furthermore, these techniques can be combined easily with preliminary chromatographic and ion-exchange separations.

In a detailed study of the infrared measurement of sulphate, nitrate, and nitrite ions in a potassium bromide matrix,[4] it was found that small quantities of these three ions could be readily determined, singly or in admixture with an accuracy adequate for many purposes. The most serious interfering substances likely to be encountered in practical work were found to be phosphate, carbonate, and organic matter. This paper describes a simple ion-exchange separation that eliminates these interferences and permits the simultaneous infrared determination of sulphate, nitrate and nitrite in realistic analytical situations. To demonstrate the utility of the method, its application to the analysis of water samples is described.

EXPERIMENTAL

Apparatus and reagents

Infrared spectra were recorded with a Perkin-Elmer Model 137 "Infracord" spectrophotometer. Disks were prepared with a Hilger H920 die obtained from Jarrell-Ash Co., Newtonville, Mass., using a Loomis 20-ton hydraulic press. Solutions were freeze-dried in lipless test-tubes about 10 cm long, using a 24-port VirTis freeze-dryer.

The anion-exchange column was a conventional one, about 10 × 1 cm, packed with Dowex 1-X8, 100–200 mesh. After ordinary washing with dilute reagent solutions, the resin continued to bleed sufficient organic matter to interfere seriously with the infrared measurements. This difficulty was eliminated by washing the column with 10M nitric acid, after which it was converted to the bromide form for use in the analytical procedure.

A special grade of potassium bromide suitable for infrared work, manufactured by E. Merck, Darmstadt, Germany, was obtained from Terra Chemicals Inc., New York, N.Y. All other chemicals were of the usual reagent grade.

Preliminary experiments

According to Wheaton and Bauman,[6] who studied the selectivity of Dowex 1 in the chloride form for a number of univalent anions, nitrite, nitrate and bisulphate are retained much more strongly on the resin than are bicarbonate and dihydrogenphosphate. Because the column in the present work was in the bromide form and because pH values were not such as to give exclusively univalent ions, it was necessary to establish experimentally column operating conditions that would ensure a clean separation of phosphate and carbonate from nitrate, nitrite and sulphate. In a series of preliminary experiments, the elution behaviour of the five anions was studied with potassium bromide solutions ranging from 0·01 to 1*M*, using spot tests to estimate concentrations in the eluate. In all cases, the order of elution was: phosphate, carbonate, sulphate, nitrite, nitrate. Later quantitative infrared measurements of freeze-dried eluates confirmed this order.

The following procedure was established as a result of these studies: after a mixture of the five anions has been placed on a 10-cm column, phosphate and carbonate are eluted with 0·05*M* potassium bromide solution, then sulphate, nitrite, and nitrate are eluted with 1*M* potassium bromide. About 7 column volumes of the 0·05*M* eluant solution remove phosphate and carbonate completely, whereas the desired anions do not break through until 9 or 10 column volumes have passed. The latter are then eluted very rapidly by increasing the eluant concentration to 1*M*. Fig. 1 shows the elution of the anions under these conditions. Organic matter, in the quantities encountered in typical water samples, is reduced below the interference level during the ion-exchange procedure.
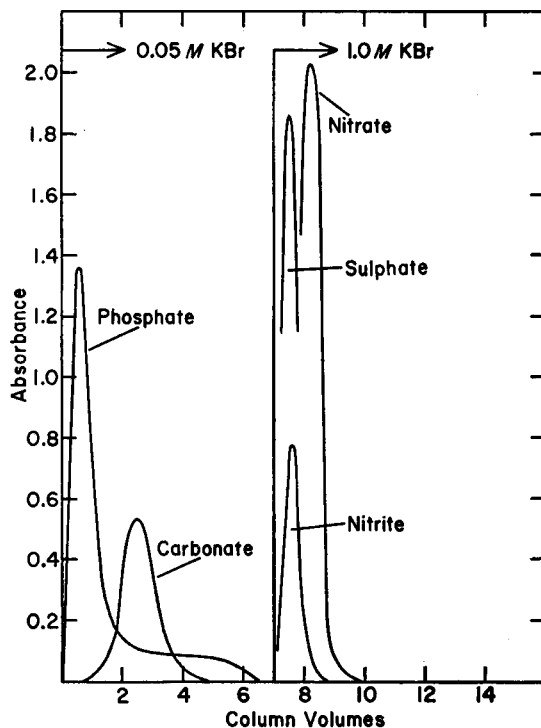
Fig. 1.—Elution curves for phosphate, carbonate, sulphate, nitrite and nitrate from Dowex I column under conditions of procedure given in text.

Fig. 2 shows the infrared spectrum of a typical freeze-dried column eluate containing nitrate, nitrite and sulphate. As is nearly always the case with infrared absorption bands, it is difficult here to decide exactly how to establish the base-lines from which to measure I and I_0 values for absorbance calculations. In the present work, the best reproducibility was obtained using base-lines connecting points at fixed distances on either side of the minimum. For example, with the nitrate band (7·23 μ, 1383 cm^{-1}), the baseline was drawn between transmittances at 7·1 and 7·5 μ. With the nitrite band
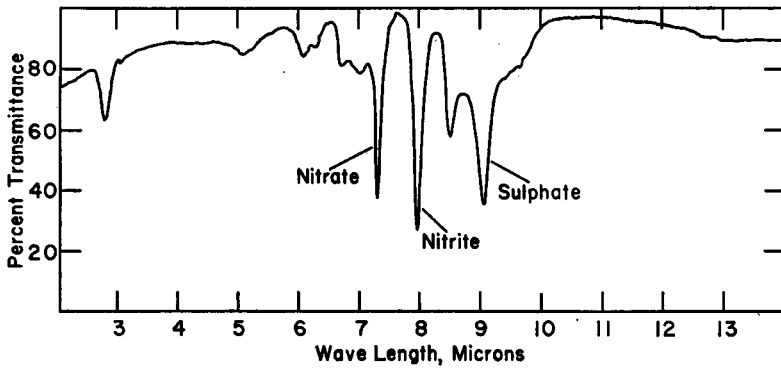
FIG. 2.—Infrared spectrum of freeze-dried column eluate containing nitrate, nitrite and sulphate.

(7·87 μ, 1271 cm^{-1}), distances of 0·2 μ on either side were again used, while with the sulphate band (9·00 μ, 1111 cm^{-1}), the distances were 0·3 μ. It is recognised that other workers may have different preferences regarding base-lines

Fig. 3 shows calibration curves for nitrate, nitrite and sulphate. The curves are seen to be linear over the absorbance range where one would normally work. With standard solutions of these ions, the same curves are obtained whether or not the ion-exchange step is included, showing that quantitative recovery from the column is obtained. The calibration curves are reasonably reproducible but, of course, it is good practice to run standards through the procedure along with the unknown samples.
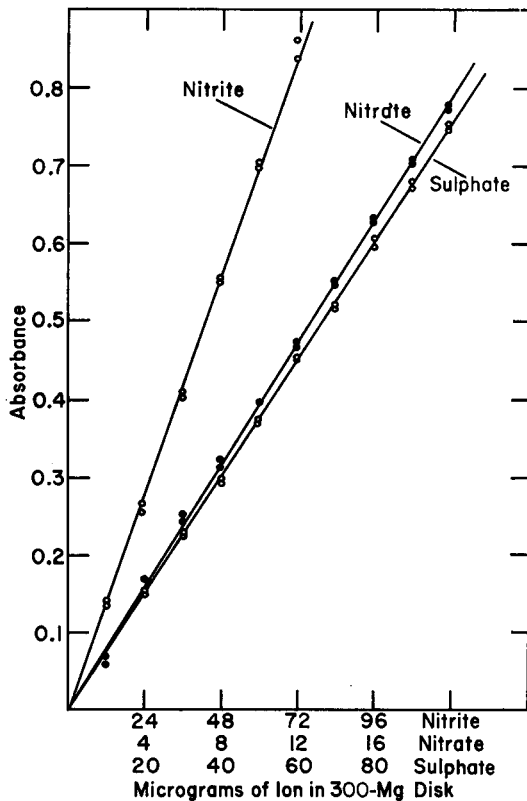
FIG. 3.—Calibration curves for nitrate, nitrite and sulphate.

Procedure

A new anion-exchange column should be washed with several column volumes of strong nitric acid; about 50 ml of 10M acid was used in this work. Then rinse the column with distilled water, convert it into the bromide form by treatment with several column volumes of 4M potassium bromide, and finally wash it with distilled water. The column is now ready to receive the sample. Such a column may, of course, be used repeatedly.

The volume of water sample passed through the column may be varied widely depending upon its composition, the extent to which the eluate is diluted, and the quantity of eluate taken for freeze-drying. One often knows from experience the approximate concentrations in the sample, and can adjust the conditions accordingly. With typical fresh-water samples, a volume of 500 ml was passed through the column in the present work. A flow rate of 5 ml per min. was satisfactory. On the other hand, a 50-ml sample of sea-water was sufficient.

Wash the column with about 30 ml of distilled water. Elute phosphate and carbonate using about 70 ml of 0·05M potassium bromide solution. In the present work, this eluate was discarded. Then elute sulphate, nitrate and nitrite with about 40 ml of 1M potassium bromide solution. It is important to know how much of this potassium bromide solution is used, and to recover practically all of it from the column, because this potassium bromide appears in the disk finally taken for infrared measurement and determines what we may call a dilution of the sample. Thus, it is well to rinse the column with a little distilled water after the 1M potassium bromide has passed, and to add these washings to the eluate solution. Any 0·05M potassium bromide remaining in the column prior to this final elution, on the other hand, contributes negligibly to the total quantity of potassium bromide ultimately obtained.

Dilute the column eluate to some known volume. In the present work, 50 ml was generally convenient for fresh-water samples. Place an aliquot of this solution (1 ml was usually used here) in a freeze-drying tube, and add potassium bromide, either as weighed solid or as a standard solution, to bring the total quantity of potassium bromide in the tube to the weight desired for a disk. The authors prefer 300-mg disks but other weights are permissible. After mixing the solution thoroughly, dip the tube into a freezing mixture of dry ice and acetone with a swirling motion so that the liquid freezes rapidly in a thin layer extending part way up the wall of the tube. Keep the sample in the freezing mixture until it is to be evacuated, then freeze-dry it overnight. Once the freeze-drying begins, the sample remains frozen without further external cooling, and the process requires no attention.

Transfer the freeze-dried material from the tube to the die, form it into an even layer, and press the disk. The authors evacuated the die for about 1 min, then pressed the disk with a total applied force of about 20,000 lb for 5 min. This force corresponds to a pressure of a little over 100,000 lb per sq. in. with the die used in this work. Remove the disk from the die and record its spectrum from about 6 to 11 μ, using a pure potassium bromide disk of the same weight in the reference beam. Draw the baselines on the chart, measure I and I$_0$ values for the nitrate, nitrite and sulphate bands, and calculate their absorbance values. Weigh the disk, and correct the absorbance values for any of the material that may have been lost in transfer from the freeze-drying tube to the die. Compare these corrected absorbances with calibration curves obtained by running known quantities of nitrate, nitrite and sulphate through the procedure to obtain the quantities of these ions in the disk. Then, using appropriate dilution factors, calculate the quantities in the original sample.

Samples may sometimes be encountered in which the concentrations of the three anions are not appropriate for the simultaneous measurement. It may be, for example, that if a workable quantity of sulphate is obtained in the final disk, the nitrate absorbance will be too large for measurement with the desired accuracy. In such cases, it may be best to freeze-dry two aliquots, one larger than the other, in order to place both absorbance measurements in the desired range.

RESULTS

Synthetic solutions

To aliquots of a solution containing 40 ppm of sulphate, 48 ppm of nitrite and 8 ppm of nitrate, were added varying quantities of phosphate and carbonate. These solutions were run through the ion-exchange separation and infrared determination. It was found that the results were not affected by the presence of phosphate until the

level of 800 ppm was reached, after which the column separation broke down and interfering phosphate bands appeared in the infrared spectrum. Presumably a column of sufficient length could achieve the separation of any desired quantity of phosphate, but the 10-cm column described here is certainly adequate for most water samples. Similar quantities of carbonate are likewise adequately separated.

The reproducibility of the method was studied with synthetic solutions containing nitrate, nitrite and sulphate. Within the absorbance range where errors are nearly minimal, say 0·2 to 0·8, the standard deviations for 20 samples were about 2% relative for each of the three ions.

Water samples

The method was tested on three water samples: tap water from the Dekalb County, Georgia, public water supply; a small creek in the Atlanta area; and a sea-water sample taken from the Gulf of Mexico near Sarasota, Florida. For comparison purposes, the same samples were analysed by other methods as follows: sulphate by the barium chloranilate colorimetric method;[1] nitrite by the sulphanilic acid-alpha-naphthol colorimetric method;[7] and nitrate by reduction to nitrite with zinc followed by the above nitrite method.[7] The results are summarised in Table I. It may be seen that the only serious discrepancy occurs with nitrate, higher results being obtained with the infrared method. The colorimetric method, predicated as it is upon quantitative reduction of nitrate to nitrite, is suspect, in the authors' opinion. It is important

TABLE I. RESULTS OF ANALYSIS OF WATER SAMPLES

Sample	Ion	Infrared method, *ppm*	Other methods (see text) *ppm*	Difference between methods, %
Tap water	NO_3^-	0·36	0·32	11·1
	NO_2^-	0·00	0·00	—
	SO_4^{2-}	4·31	4·35	0·9
Creek water	NO_3^-	0·93	0·82	11·8
	NO_2^-	0·020	0·018	7·5
	SO_4^{2-}	4·79	4·69	2·1
Sea water	NO_3^-	0·96	0·91	5·7
	NO_2^-	36·8	35·8	2·7
	SO_4^{2-}	385	379	1·6

to note that the infrared method was much faster than the sum of the others for the three ions, provided we do not count the freeze-drying time. Since freeze-drying requires no attention except at start and finish, and since many samples can be freeze-dried together, it is reasonable to exclude it in determining operator time per sample.

Zusammenfassung—Kleine Mengen von Nitrat, Nitrit und Sulfat können mittels Infrarotspektro-photometrie gleichzeitig bestimmt werden. Die Proben werden durch Gefriertrocknung der Lösungen, die Kaliumbromid enthalten, zubereitet. Einsatz von Anionenaustauschern erlaubt Anreicherung der

Ionen und gleichzeitige Abtrennung von störendem Phosphat, Carbonat und organischem Material. Die Methode wurd zur Bestimmung der Ionen in wasser herangezogen und die Resultate stimmten mit denen nach anderen Methode erhaltenen gut überein.

Résumé—De petites quantités d'ions nitrate, nitrite et sulfate peuvent être dosées simultanément par spectrophotométrie infra-rouge, en utilisant la technique du disque de bromure de potassium. Les échantillons solides sont préparés en désséchant par congélation les solutions aqueuses de ces ions contenant du bromure de potassium. Une méthode d'échange d'anions est facilement associée à la mesure infra-rouge après le stade de séchage par congélation. Cela permet d'utiliser des solutions d'échantillon très diluées et élimine l'interférence des ions phosphaté, carbonate et des matières organiques. La méthode a été appliquée au dosage de nitrate, nitrite et sulfate dans des échantillons d'eau; on peut la comparer favorablement aux autres méthodes.

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VOLUMETRISCHE BESTIMMUNG VON MAGNESIUM IN GEGENWART VON CALCIUM

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Zusammenfassung—Auf Grund der verschiedenen Stabilität der Magnesium-, Calcium-, und Barium-ÄDTE und -ÄGTE Komplexe, wird eine volumetrische Methode vorgeschlagen, die auf folgender Reaktion:

$$Mg^{+2} + Ca^{+2} + Ba\text{-}\ddot{A}GTE + SO_4^{-2} \rightarrow Ca\text{-}\ddot{A}GTE + BaSO_4 + Mg^{+2}$$
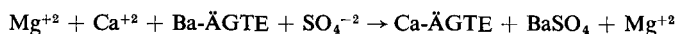
Die Methode erlaubt die Magnesiumbestimmung bei Gegenwart von Calcium bis zum Verhältnis 1:150. Die Ergebnisse werden durch den $BaSO_4$-Niederschlag nicht wesentlich beeinflusst.

Die chelometrische Bestimmung von Calcium und Magnesium hat eine weite Anwendung in der Analyse verschiedener Materialien gefunden.[1] Bei den bisher vorgeschlagenen Methoden erhält man den Magnesiumgehalt entweder aus der Differenz nach Titration der Summe von Calcium und Magnesium (pH 10) mit Eriochromschwarz T als Indikator in einem Aliquot das Calcium nach der Ausfällung des Magnesium als Hydroxyd bei pH 12,5 oder mehr, oder durch Titration des Magnesium nach vorheriger Ausfällung des Calcium in einem zweiten Aliquot.

Vor kurzem haben Reilley und Mitarbeiter[2] und Ringbom mit Mitarbeitern[3] die Calciumbestimmung in Gegenwart von Magnesium durchgeführt, indem sie eine Lösung von ÄGTE (Äthylenglykol-bis-(β-aminoäthyläther)-N,N'-tetraessigsäure) als Masslösung anwandten. Wegen der geringen Stabilität des Mg-ÄGTE-Komplexes (log K = 5,21)[4] hat man jedoch diesem Chelon als Masslösung wenig Aufmerksamkeit geschenkt. Der Unterschied in der Stabilität des Calcium- und Magnesium-ÄGTE-Komplexes-von Reilley[2] und Ringbom[3] zur Calciumbestimmung benutzt- und die Tatsache, dass der Barium-ÄGT-Komplex ebenfalls stärker ist als der Magnesium-Komplexes (log $K_{Ba-\ddot{A}GTE}$ = 8,41)(4), aber schwäeher als der Calcium-Komplex (log $K_{Ca-\ddot{A}GTE}$ = 10,97), macht jedoch die Maskierung des Calcium bei der Titration des Magnesium mit ÄDTE möglich. Dazu verwendet man die folgende Reaktion:

$$Mg^{+2} + Ca^{+2} + Ba\text{-}\ddot{A}GTE + SO_4^{-2} \rightarrow Ca\text{-}\ddot{A}GTE + BaSO_4 + Mg^{+2}$$
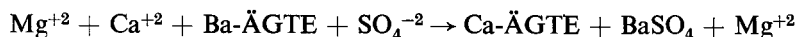
Das Calcium verdrängt quantitativ das Barium aus seinem Komplex und das freigewordene Ba^{+2} fällt mit dem an-wesenden Sulfation aus. Im Gegensatz dazu ist das Magnesium nicht fähig, das Barium aus seinem Komplex zu verdrängen, weshalb man mit ÄDTE und Erichromschwarz T in ammoniakalischem Medium titrieren kann.

Die Methode erlaubt die Magnesiumbestimmung bei Gegenwart beliebiger

Calcium-Mengen, wobei die Trennung vom gefälltem $BaSO_4$ nicht nötig ist, weshalb das Verfahren viel rascher und genauer ist als irgendeines der bisher angewendeten.

EXPERIMENTELLER TEIL

Reagentien und Lösungen

0,05 m ÄDTE (zweisbasiches Salz)

0,05 m Ba-ÄGTE. In ca. 700 ml zweifachdestillierten Wassers werden 19,1000 gr ÄGTE (Chel DE, Geigy) und 9,8500 gr reinstes Bariumcarbonat verteilt. Man schüttelt bis zur völligen Lösung, filtriert und verdünnt auf 1 Liter.

1%ige Lösung von wasserfreiem Natriumsulfat.

0,2%ige Lösung von Methylrot

Eriochromschwarz T und NaCl im Verhältnis 1:200 gemischt.

Puffer pH 10, nach Schwarzenbach.

Verfahren

Zu 50 ml der fast neutralen Lösung fügt man einen leichten Überschuss der Ba-ÄGTE-Lösung hinzu, verdünnt mit Wasser, gibt die Pufferlösung und genügend Na_2SO_4-lösung zu, Sedass alles freiegewordene Barium ausgefällt wird, und 2 Tropfen Methylrotlösung, sowie eine Messerspitze der Eriochromschwarz T-NaCl-Mischung. Anschliessend titriert man das Magnesium mit der 0,05 m ÄDTE-Masslösung bis zum Farbumschlag von Rot auf ein fast farbloses Grau.

ERGEBNISSE

Wir haben eine Reihe von Bestimmung durchgeführt, in welchen eine gleichbleibende Menge von Magnesium (10 ml der 0,05 m Lösung) in Gegenwart wechselnder Calciummengen bestimmt wurde (von 4 ml einer 0,05 m Lösung bis 150 ml einer 0,5 m Lösung) in der Absicht, die Anwendbarkeit des Verfahrens bei im Verhältnis zu Magnesium viel grösseren Calciummengen zu überprüfen. In Tab. 1 (Abb. 1) sind die erhaltene Werte bis zum Verhältnis Mg:Ca 1:50 zusammengefasst.

Die Tabelle 2 (Abb. 2) zeigt die erhaltenen Ergebnisse bei einem Verhältnis Mg:Ca von 1:75 bis 1:150.

TABELLE I. BESTIMMUNG VON MAGNESIUM IN GEGENWART VON CALCIUM BEI EINEM VERHÄLTNIS Mg:Ca BIS ZU 1:50

Num.*	Mg^{+2} gegeben, *mg*	Ca^{+2} zugefügt, *mg*	Verhältnis Mg/Ca	0,05 m ÄDTE verbraucht, *ml*	Mg^{+2} gefunden, *mg*	Unterschied, *mg*
1–1	12,16	8,02	1:0,4	9,96	12,11	−0,05
2–1	12,16	16,03	1:0,8	10,06	12,23	+0,07
3–1	12,16	24,05	1:1,2	9,96	12,11	−0,05
4–1	12,16	32,06	1:1,6	10,08	12,26	+0,10
5–1	12,16	40,08	1:2	10,08	12,26	+0,10
6–1	12,16	48,10	1:2,4	9,88	12,01	−0,15
7–1	12,16	56,11	1:2,8	10,16	12,36	+0,20
8–1	12,16	80,16	1:4	10,21	12,42	+0,26
9–1	12,16	150,30	1:7,5	10,11	12,29	+0,13
10–1	12,16	200,40	1:10	10,08	12,26	+0,10
11–1	12,16	501,00	1:25	10,15	12,34	+0,18
12–1	12,16	1.002,00	1:50	10,12	12,31	+0,15

* Die Werte sind die Mittel von 5 Bestimmungen
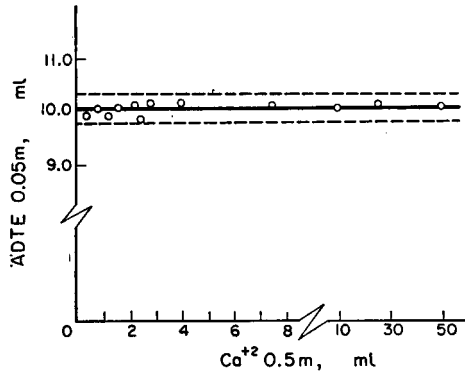
Abb. 1

TABELLE II. Bestimmung von Magnesium in Gegenwart von Calcium bie einem
Verhältnis Mg:Ca von 1:75 bis 1:150

Num.*	Mg^{+2} gegeben mg	Ca^{+2} zugefügt, g	Verhältnis Mg:Ca	0,05 m ÄDTE verbraucht, ml	Mg^{+2} gefunden, mg	Unterschied, mg
1–2	12,16	1,503	1:75	10,14	12,33	+0,17
2–2	12,16	1,804	1:90	10,26	12,48	+0,32
3–2	12,16	2,204	1:110	9,97	12,12	−0,04
4–2	12,16	2,605	1:130	10,34	12,57	+0,41
5–2	12,16	3,006	1:150	10,16	12,36	+0,20

* Die Werte sind die Mittel von 5 Bestimmungen.
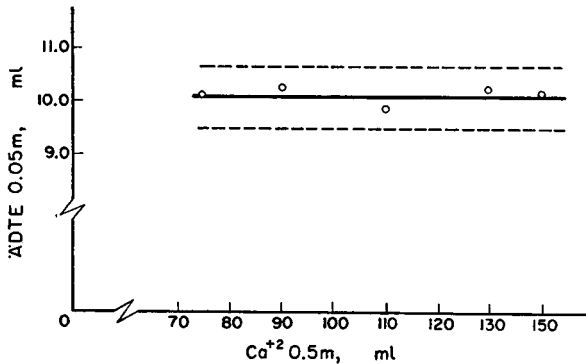
Abb. 2

Um zu überprüfen, ob die Gegenwart des gefallten Bariumsulfates die Magnesium-
bestimmung mit ÄDTE merklich beeinflusst, haben wir einige Magnesiumbestim-
mungen im Filtrat der Bariumsulfat-Trennung durchgeführt. Die Ergebnisse sind
aus Tabelle 3 ersichtlich.

Die Werte der Bestimmungen 1 bis 3 sind die Mittel von 5 Bestimmungen, die von
4 bis 7 von 3 Bestimmungen.

TABELLE III. BESTIMMUNG VON 12,16 mg MAGNESIUM IN GEGENWART WECHSELNDER
CALCIUMMENGEN NACH VORHERGEHENDER FILTRATION VON BaSO$_4$

Ca^{+2} zugefuegt, g	Verhältnis Mg:Ca	0,05 m ÄDTE verbraucht, ml	Mg^{+2} gefunden, mg	Unterschied, mg
0,008	1:0,4	9,93	12,073	−0,087
0,040	1:2	10,02	12,182	+0,022
0,056	1:2,8	10,01	12,172	+0,012
0,150	1:7,5	9,98	12,141	− 0,021
0,200	1:10	10,04	12,203	+0,043
0,501	1:25	10,07	12,242	+0,082
1,002	1:50	10,12	12,301	+0,141

DISKUSSION

Aus der statistischen Berechnung der Ergebnisse jeder der beiden Reihen (Tab. 4 u. 5) kann man folgern, dass die Gegenwart von Ca im untersuchten Intervall keinen bestimmenden Einfluss auf die Ergebnisse der Magnesium-Titration mit ÄDTE hat,

TABELLE IV. ANALYSE DER VARIANZ FÜR DIE WERTE DER TAB. I UND ABB. 1

	Summe der Quadrate	Freiheitsgrade	Mittelwert der Quadrate	Berechnete Faktoren	Tabellisiert Faktor	Bedeutung
Wiederholungen	1,2281	4	0,3070	2,698	3,83	1%*
Behandlungen	0,8685	11	0,0789	0,693	2,70	1%†
Fehler	5,0055	44	0,1138			
Total	7,1021	59				

TABELLE V. ANALYSE DER VARIANZ FÜR DIE WERTE DER TAB. II UND ABB. 2

	Summe der Quadrate	Freiheitsgrade	Mittelwert der Quadrate	Berechnete Faktor	Tabellisiert Faktor	Bedeutung
Wiederholungen	0,5224	4	0,1306	0,360	4,77	1%‡
Behandlungen	0,5837	4	0,1459	0,402	4,77	1%‡
Fehler	5,8042	16	0,3624			
Total	6,9103	24				

* Zwischen 4 und 40
† Zwischen 10 und 50.
‡ Zwischen 4 und 16.

und man erhält als Ergebnis einen sicheren Grenzwert 0,167 der einen und 0,157 der anderen Versuchsreihe.

Wie sich aus den Ergebnissen der Tab. 1 und 2 ergibt, ist das Verfahren auf die Bestimmung von Magnesium in Gegenwart 150 mal grösserer Calciummengen anwendbar. Das bedeutet einen wichtigen Vorteil gegenüber den Verfahren, bei denen

man das Magnesium aus der Differenz erhält, denn wenn die Menge des vorhandenen Magnesium viel kleiner als die des Calcium ist, häufen sich in den Magnesium-Werten die Fehler von zwei Bestimmungen an, womit das Ergebnis wenig sicher wird und in gewissen Fällen, wie z.B. um ungenügende Mengen in Pflanzen festzustellen, ist der Magnesium-Wert viel wichtiger als der Calcium-Wert.

Anderseits hängt bei den Verfahren, in welchen das Calcium durch Fällung ausgeschieden wird, die Magnesiumbestimmung von einer vorhergehenden quantitativen Calcium-Trennung ab. Diese wird schwierig, wenn in der Lösung auch andere Jonen vorhanden sind, die bei dieser Trennung stören können. Man hat die Calcium-Trennung durch Fällung mit Oxalat, Molybdat oder Wolframat vorgeschlagen, doch ist bei all diesen Verfahren eine vorherige Entfernung des ausgefällten unlöslichen Calciumsalzes und ein gründliches Auswaschen der Niederschlages nötig um alles mitgerissene Magnesium zu entfernen.

Im vorgeschlagenen Verfahren wird eine Einwirkung des Calcium durch seine Maskierung in einem löslichen Komplex ausgeschaltet. So-mit wird die Bestimmung von Magnesium in Gegenwart von Calcium auf die Bestimmung von Magnesium in reiner Lösung zuruckgeführt.

Summary—The differences in the stability constants of the calcium, magnesium and barium complexes of EDTA and EGTA are used to develop a new volumetric determination of magnesium in the presence of up to a 150 fold excess of calcium.

$$Mg^{+2} + Ca^{+2} + Ba - EGTA \rightarrow Ca - EGTA + BaSO_4 + Mg^{+2}$$
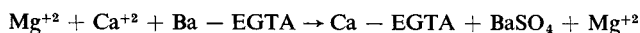
The results of the titration are not significantly influenced by the presence of the barium sulphate precipitate.

Résumé—Les auteurs utilisent les différences des constantes de stabilité des complexes du calcium, du magnésium et du baryum avec l'EDTA et l'EGTA pour mettre au point un nouveau dosage volumétrique du magnésium en présence d'un excès de calcium plus de 150 fois plus important.

La présence de précipité de sulfate de baryum n'a pas d'influence signaficative sur les résultats du titrage.

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QUANTITATIVE PAPER RADIOCHROMATOGRAPHY USING TOLLENS REAGENT—I

THE APPLICATION OF ^{131}I TO RADIOMETRIC ESTIMATION OF MONOSACCHARIDES AND POLYOLS

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Summary—For the estimation of saccharides, a radiochromatographic quantitative method, based on the reaction with ammoniacal silver nitrate, has been developed. Conditions for the quantitative deposition of silver on the filter paper have been established. The silver deposit formed was transformed into Ag^{131}I. The radioactivity of ^{131}I located in the spots is related to the amount of the substance determined. The method has been checked using six substances, representing aldoses, ketoses, hexitols and cyclitols. The relationships between integrated spot activity, maximal spot activity and radiometrically estimated spot length, and the amount of substance have been studied.

LABELLING directly on paper of chromatographically separated substances represents one of the recently developed techniques of quantitative microanalysis. Kaufmann and Budwig,[9] Winteringham et al.[17] and others have described some reactions of this kind carried out with simple radioactive reagents. Jaarma[8] suggested the possibility of using ^{110}Ag for the determination of aldoses and ketoses. Budzyński, Zubrzycki and Campbell in this laboratory have developed a method for the radiochromatographic determination of unsaturated fatty acids. This method is based on an addition of ^{131}I to double bonds.[3,4] The same authors have put forward a more complicated technique called by them "double decomposition radiochromatography". In this procedure, the labelling of chromatograms is carried out in two steps. The first one is a reaction of the substance being determined with a non-radioactive ion; the latter, in the second step, combines with the radioactive tracer.[4,18]

In the present paper a new series of transformations which allow the radiometric determination of chromatographically separated substances will be described.

In a search for systems suitable for the determination of various reducing compounds, attention was drawn to ammoniacal silver nitrate, the so-called Tollens reagent. This reagent, commonly used in qualitative chromatography, is characterised by a high sensitivity, and the ability to react with a wide variety of compounds. As the result of such reactions elementary silver is deposited on the paper. The use of silver, because of its physical and chemical properties, and also because of its ability to form numerous sparingly soluble compounds, proved to be especially advantageous. The chemical affinity of elementary silver for iodine is marked, and the rate of the reaction between the two elements depends mainly on the state of dispersion of the reactants.[1,12,15] Examination of this reaction, using an aqueous solution of ^{131}I, resulted in the working out of the conditions necessary for the quantitative formation of Ag^{131}I from a silver deposit on the paper.

The application of these transformations to the quantitative radiochromatography of monosaccharides and polyhydric alcohols is described below.

EXPERIMENTAL

Reagents

Monosaccharides and polyhydric alcohols: Glucose, xylose, rhamnose, fructose, mannitol and inositol; commercial preparations, analytical grade were used in all experiments.

Ammoniacal silver nitrate: Solutions used in paper chromatography usually contain from 1·7% to 5% of AgNO$_3$.[2,6,7,10,13,16] It was found that this range of concentrations is insufficient for the quantitative oxidation of more stable substances. Therefore solutions containing 9–17% of silver nitrate in concentrated ammonia were used in these experiments. Sodium hydroxide, which accelerates the reaction was found to be an indispensable component of these solutions. Several reagents of different composition were tested. Two of them which ensure the quantitative course of the reaction and give comparatively low background have been chosen. The composition of these solutions is given in Table I.

TABLE I. AMMONIACAL SILVER NITRATE SOLUTIONS. COMPOSITION AND
REACTION TIME FOR SILVER DEPOSITION

Silver nitrate, g	8·5	15·0
Sodium hydroxide, g	0·3	0·1
Ammonia 25%	up to 100 ml	
Heating time for chromatograms at 105°, min	25	15

Chromatography

Whatman No. 1 paper strip chromatograms, 350 mm long and 15 mm wide, were prepared. The substances to be tested, in amounts of $1·5 \times 10^{-2} - 60 \times 10^{-2} \mu M$, were put on the starting point located 60 mm from the lower end of the strip. The chromatograms were developed by the ascending technique for 18 hr at room temperature, using the system n-butanol:acetic acid:water = 6:1:2.[11] Before further operations the chromatograms were air-dried for 24 hr.

Deposition of elementary silver on paper

Chromatograms were placed horizontally on specially designed racks and sprayed. Fifteen mg of the solution applied to 1 cm² of the paper was found to be a sufficient excess for the quantitative course of the reaction. Full details of the spraying technique will be published elsewhere.

Wet chromatograms were transferred on racks to the oven and heated at 105°. The optimal heating time is given in Table I. These reaction conditions cause the formation of dark-brown or black spots on a dark-yellow background. It is recommended that the conditions should not be changed so as to obtain a less intense background since this prevents the quantitative deposition of the silver.

Immediately after deposition of silver, excess of Tollens reagent was removed using 0·02% aqueous ammonia. The strips were washed with this solution for 2 min, then with water three times for 5 min, and finally air-dried.

Transformation of elementary silver into Ag^{131}I

One hundred ml of a solution containing 0·4 g of potassium iodide and 0·02 g of potassium iodate were added to 300 μC of carrier-free K^{131}I. Free iodine was liberated from this solution by 0·4 ml of 10% sulphuric acid just before use. Ten ml of this reagent can transform on paper into iodide an amount of silver equivalent to 50 μg of glucose in 20 min.

The reaction was carried out in vertical paraffin vessels of slit-like cross-section,[4] 4 mm × 16 mm for 60 min. The iodinated strips were washed with water three times for 5 min.

Estimation of activity on strips

The distribution of activity on air-dried radiochromatograms was estimated using an end-window counter, with a mica-window 4 mg/cm². The chromatograms were placed under the 4-mm thick Perspex screen. A 2-mm slit cut in the screen allowed counting of β-particles from a defined area of the chromatogram.

RESULTS

The technique described was applied to the radiochromatographic determination of the following typical representatives of different classes of monosaccharides and polyols: glucose, xylose, rhamnose, fructose, mannitol and inositol.

Typical results for the activity estimation of a radiochromatogram prepared in such a way are presented graphically in Fig. 1.
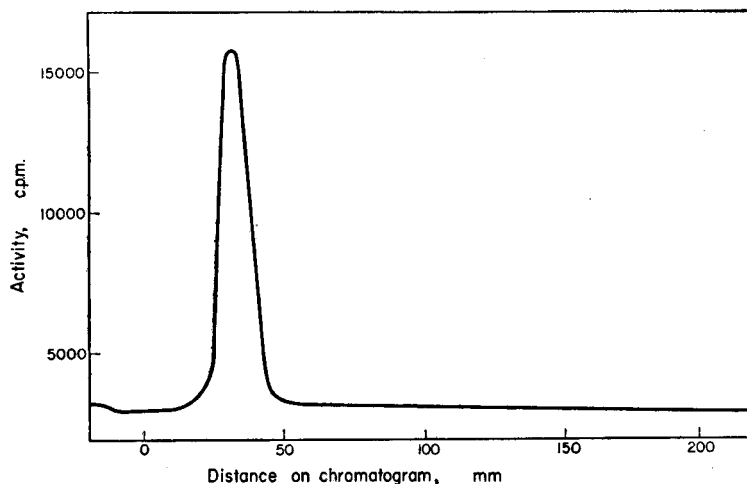

FIG. 1.—Distribution of activity on chromatogram of 100 μg of glucose after $Ag^{131}I$ formation in place of sugar.

The integrated spot activity, *i.e.*, the sum of activities estimated from individual 2-mm sectors of the strip, minus background activity, was calculated as the main parameter. The linear relationship between this parameter and the amount of chromatographed substances is presented in Figs. 2 and 3. The ranges for which this regularity was proved and the average errors of determinations are listed in Table II. Although in every case it was possible to determine as little as $1·5 \times 10^{-2}$ μM, it was found that these determinations were accompanied by considerable errors ranging from $\pm 8\%$ to $\pm 23\%$. The average error for amounts larger than 10×10^{-2} μM was $\pm 3·5\%$ to $\pm 7·6\%$.

TABLE II. REGION OF PROPORTIONALITY BETWEEN INTEGRATED SPOT ACTIVITY AND AMOUNT OF SUBSTANCE, AND AVERAGE ERRORS OF THE METHOD FOR AMOUNTS HIGHER THAN 10×10^{-2} μM

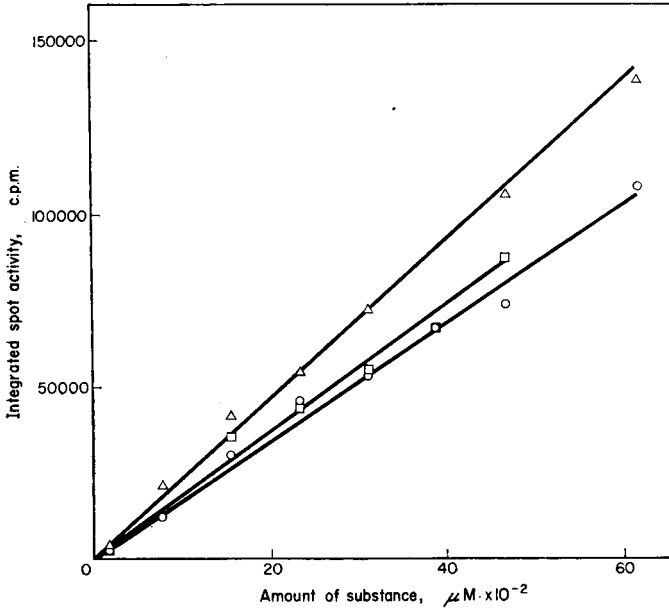| Substance	Region of proportionality, $\mu M \times 10^{-2}$		Average error for amounts higher than 10×10^{-2} μM
	from	to	
Glucose		60	$\pm 6·7$
Xylose		45	$\pm 7·6$
Rhamnose		60	$\pm 5·5$
Fructose	1·5	30	$\pm 3·5$
Mannitol		30	$\pm 5·7$
Inositol		23	$\pm 4·3$

FIG. 2.—Relationship between integrated spot activity and amount of substance:
○ — glucose, □ — xylose, △ — rhamnose.
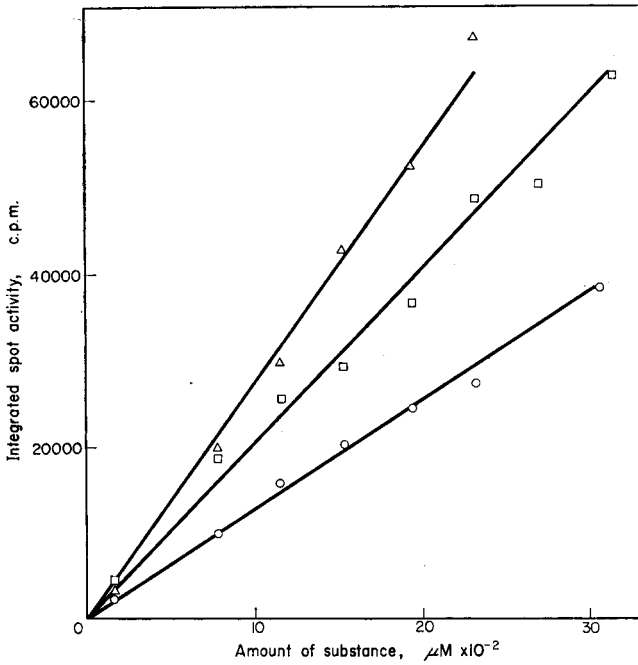

FIG. 3.—Relationship between integrated spot activity and amount of substance:
○ — fructose, □ — mannitol, △ — inositol.

It is necessary, in order to analyse chromatographically separated mixtures, to set up calibration curves based on simultaneously performed determinations of known amounts of the corresponding standard substances. Because of the character of the relationships presented, it is sufficient to estimate only one point on the curve.

For the quantitative determinations of saccharides, other parameters that characterise the spots can be also used. The linear relationship between maximal spot activity and the logarithm of spot content has previously been observed in the case of radiochromatographic determinations of saturated and unsaturated fatty acids and inorganic phosphates.[4,18] This relationship was tested for all the sugars and alcohols examined. Fig. 4 shows the relationship between maximal spot activity (i.e., maximal activity determined on the 2-mm segment of the strip) and the logarithm of spot content.
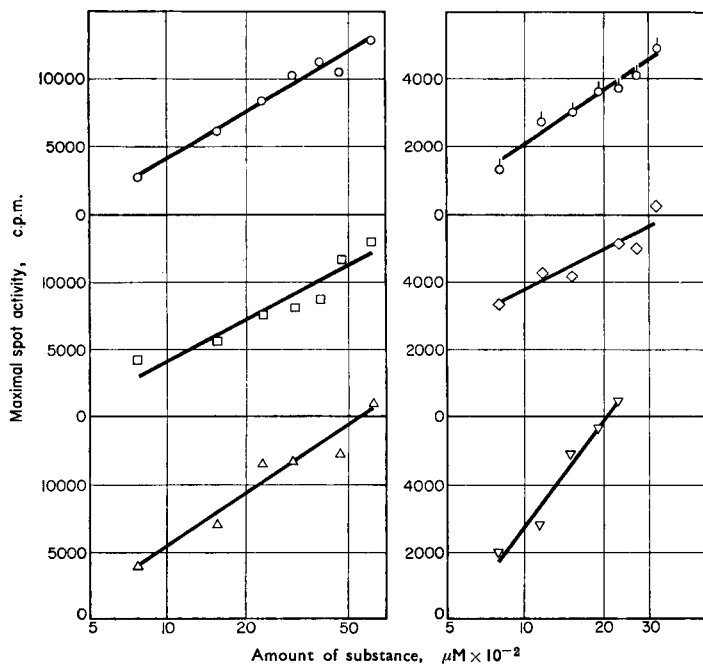
FIG. 4.—Relationship between maximal spot activity and logarithm of amount of substance:
○ — glucose, □ — xylose, △ — rhamnose, ⌀ — fructose, ◇ — mannitol, ▽ — inositol.

The distribution of activity on a labelled chromatogram can serve as a basis for the determination of spot length.[4,18] The parameter calculated in such a way is directly proportional to the quantity of the chromatographed substance. Fig. 5 shows the relationship between the radiometrically determined spot length and the amounts of sugars and alcohols examined.

Maximal spot activity, as well as spot length, can be used as a basis for rapid determinations which do not require activity measurements along the whole spot length. The minimal amount of substance that gave the linear relationships mentioned was $7.5 \times 10^{-2} \mu M$. The average error of determinations based on maximal spot activity measurement usually ranged from $\pm 8\%$ to $\pm 13\%$, and of those based on spot length from $\pm 8\%$ to $\pm 15\%$. Maximal spot activity measurement seems to be particularly useful for the determination of substances overlapping on chromatograms.
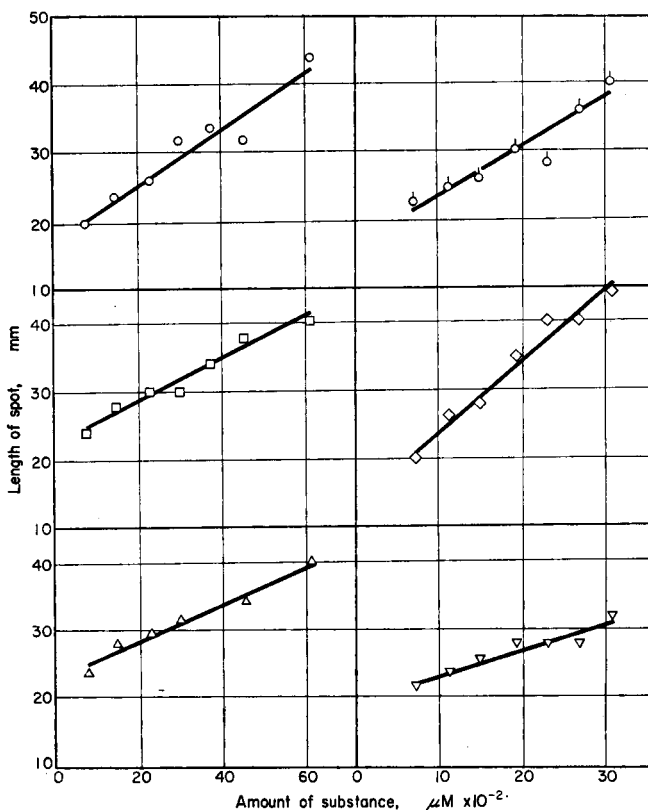
FIG. 5.—Relationship between radiometrically estimated spot length and amount of substance: ◯ — glucose, ☐ — xylose, △ — rhamnose, ⟨⟩ — fructose, ◇ — mannitol, ▽ — inositol.

DISCUSSION

The results described above prove that transformations with simple radioactive reagents, carried out on paper, can be applied to the quantitative chromatography of saccharides and related compounds. The chemical properties of the substances used in these experiments permit one to make the assumption that the technique, if properly elaborated, could have a general application to all monosaccharides, aldoses as well as ketoses, and to all chain and cyclic polyols. Other compounds related to sugars, e.g., uronic acids, amino-sugars, alkylated sugars, lactones, esters, amides and glucosides also give a positive Tollens reaction.[7] The results obtained with compounds which react slowly with ammoniacal silver nitrate, such as mannitol and inositol, indicate that this technique can be applied here also.

Most of the known methods for the determination of sugars and related compounds permit the analysis only of compounds which belong to definite chemical groups. It is well-known that the determination of more stable, so called non-reducing compounds presents one of the more difficult analytical problems. Therefore it would be very convenient to possess a method which would allow the determination of a wider variety of compounds, separated on a single chromatogram. Such a method could be used for estimation of the sugar components of glucosides, glucoproteins, etc., as well

as for examination of polysaccharides. No existing methods allow such complex analyses to be performed directly on paper chromatograms.

The estimation of the silver deposited on paper can be also performed by optical methods. McFarren *et al.*[10] and Wallenfels *et al.*[16] elaborated methods for the determination of aldoses on the basis of such measurements. The determination of more stable compounds, however, encounters serious difficulties connected with more drastic reaction conditions required, which lead to the oxidation of paper cellulose. The dark background that is formed under such conditions prevents densitometric evaluation of the chromatograms. In the application of radiometric techniques, side reactions which take place along the whole chromatogram do not interfere basically. The use of β-emitters whose energy is sufficiently high eliminates the difficulties connected with variations in the thickness of the filter paper, which are the main source of errors in photometry.

The deposition of elementary silver on paper, and its transformation into $Ag^{131}I$, might also be applied to the determination of other groups of chemical compounds. In addition to various kinds of saccharides, the following substances react with Tollens reagent: aldehydes, polyhydroxyphenols, aminophenols, hydroxycarboxylic acids, α-diketones, primary ketols, sulphinic acids, certain aromatic amines, hydrazo compounds, hydrazines, hydroxylamines, *etc.*[5] The technique described may find an application in the radiochromatography of these compounds, provided that the conditions for quantitative deposition of silver are established.

Zusammenfassung—Eine quantitative radiochromatographische Methode zur Bestimmung von Monosacchariden und Polydroxyalkoholen wurde entwickelt. Sie beruht auf der Reaktion von ammoniakalischer Silbernitrat lösung mit den zu bestimmenden Substanzen. Die Bedingungen für quantitative Präzipitation des Silbers wurden bestimmt. Der so erhaltene Niederschalg wurde in $Ag^{131}J$ umgewandelt. Es wurde nachgewiesen daß die Radioaktivität des ^{131}J als Maß des Gehaltes der zu bestimmenden Substanzen dienen kann. Die Methode wurde nachgeprüft für sechs verschiedene Substanzen, die Aldosen, Ketosen, Hexite und Cyclite repräsentieren. Es wurden die Beziehungen zwischen der Menge der Substanz und der Gesammtaktivität der Flecken, ihre maximale Aktivität und die radiometrisch bestimmte Länge des Fleckes untersucht.

Résumé—On a élaboré une méthode de la radiochromatographie quantitative pour la détermination des glucides. Cette méthode est basée sur la réaction du nitrate d'argent ammoniacal donnant le précipité d'argent élémentaire. On a établi les conditions de la déposition quantitative d'argent sur le papier. Le précipité ainsi obtenu a été transformé en $Ag^{131}J$. On a démontré, que la radioactivité de ^{131}J déposée sur les radiochromatogrammes peut servir pour détérminer des quantités des substances dosées. La méthode décrite a été verifiée sur des exemplaires des six substances représentatives pour les aldoses, cétoses, hexitols et cyclitols. On a étudié les rélations entre la quantité de la substance dosée, et l'activité totale de la tâche, la maximum d'activité de la tâche, et la longueur de la tâche, determinée radiométriquamment.

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A UNIVERSAL AUTOMATIC RECORDING TITRATOR*

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Summary—A universal automatic macro-micro recording titration unit is described which has the capabilities of a multitude of commercial single-purpose titration instruments without the attendant duplication of hardware. It is based on a modified Precision Dow Recording Titrator and offers the operator a choice of liquid or coulometrically generated titrants and potentiometric, amperometric, thermometric, photometric, or conductometric end-point detection systems.

The potentiometric system gives straightforward curve-presentation; the photometric mode employs a monochromator for maximum sensitivity and is equally adaptable to colorimetric, turbido-metric, and chemiluminescent titrimetry; the conductometric mode employs a novel electrolytic conductivity transducer which produces a d.c. signal proportional to the 60-cycle a.c. current between the electrodes. All components are easily constructed or are commercially available.

INTRODUCTION

IN recent times, the discovery of new and useful techniques of analytical chemistry has been followed, not long after, by the availability of commercial instrumentation designed to utilise the technique and impart to it such well-recognised advantages of instrumentation as improved accuracy, sensitivity, specificity, operating economy, *etc.* For the small analytical control or research laboratory, the availability of such instrumentation is a mixed blessing; while its use enables the laboratory to operate more efficiently and to cope with a broader range of analytical problems, the acquisition of much of this instrumentation results in an astonishing duplication of instrument components with attendant expense and storage problems.

Since automatic titrating instruments form the bulk of available laboratory instrumentation, and since the analytical chemist is becoming increasingly dependent upon end-point phenomena which are detectable only by instrumental means, it seemed probable that considerable progress in the versatilisation of existing commercial laboratory instruments could be made in this area. The authors have, therefore, assembled an automatic macro-micro recording titration unit which has the capabilities of a multitude of commercial single-purpose titration instruments without the attendent duplication of hardware. A Precision Dow Recording Titrator provides titrant delivery, end-point anticipation, and curve recording functions and is utilised, unmodified, for potentiometric end-point detection. Commercially available or easily constructed add-on components are used for coulometric generation of titrant and for detection of conductometric, photometric, amperometric, and thermometric end-points. Fig. 1 shows a titrator equipped for all but photometric end-point detection; the photometric titrator is pictured in Reference 5. Fig. 2 shows the block diagram of all components in relation to the Precision Dow Titrator.

Conductometric titration capability is unique to this titrator and permits the

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chemist to utilise the well-known advantages of conductometric titrimetry over potentiometric titrimetry, while retaining automatic operation. Recently, a single purpose automatic conductometric titrator was described by Colvin and Propst,[1] but the conductance bridge described in the present paper can be adapted for use with any automatic potentiometric recording titrator. Photometric titration capability is broader than that found in most available instruments and includes provisions for
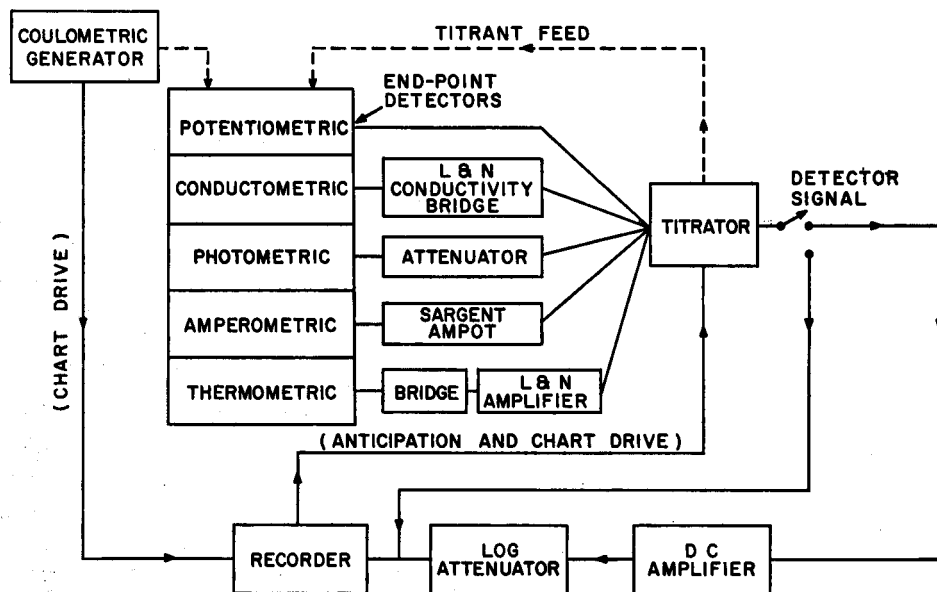

FIG. 2.—Block diagram for universal automatic recording titrator.

end-point detection using visual, near ultraviolet and fluorescent indicator systems; a monochromator is utilised, making the unit particularly adaptable to sensitive and precise mixed indicator end-points.

　　Dead-stop methods of titration terminations are not used; rather the complete titration curve is drawn leaving the analyst free to inspect the titration system for unexpected behaviour, locate end-points on asymetrical curves, etc. Although dead-stop methods could be employed, the full-curve technique has proved its value repeatedly in non-control analytical work.

EXPERIMENTAL

Potentiometric end-point titrator

　　The Precision Dow Recording Titrator, a commercial version of the instrument described by Robinson,[5] is designed for use only with potentiometric titrations. The unit essentially consists of the titrant-delivery system, recorder and potentiometric indicating system.

　　The delivery system normally comprises two separate 1-, 5-, or 50-ml precision-bore glass feed pumps, glass titrant delivery lines with burette tips, three-way stopcocks and syphon tubes. The selection of either the right or left feed system is accomplished by manually shifting the selector knob on the control panel.
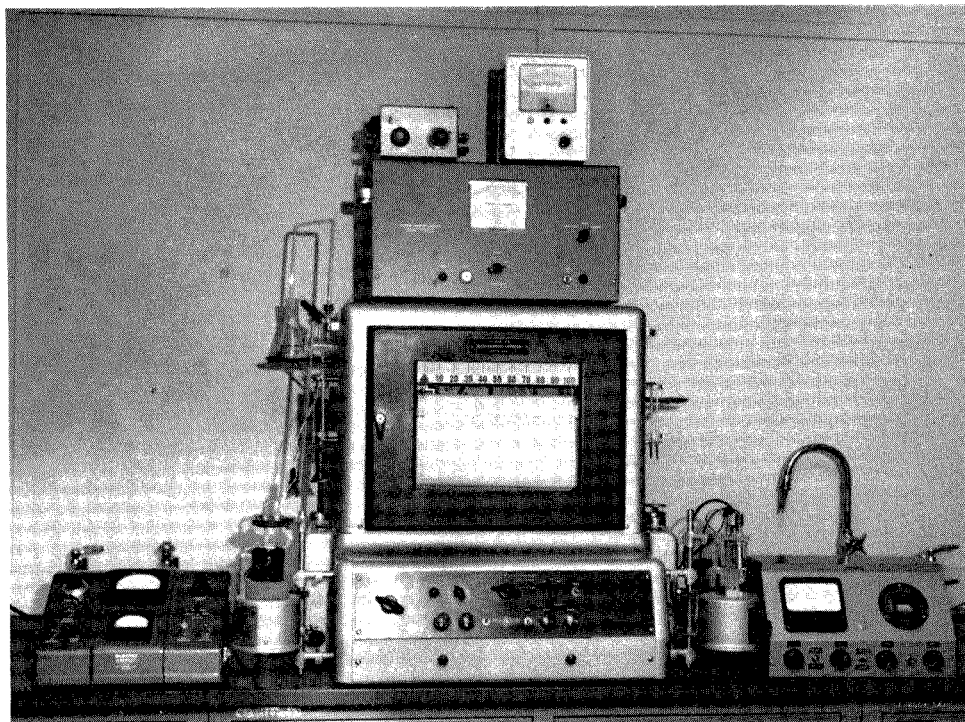
Fig. 1.—Universal automatic recording titrator

Centre: Precision Dow Automatic Recording Titrator;
Right: Coulometric generator;
Left: Sargent Ampot;
Top centre: Leeds and Northrup Microvolt Amplifier;
Top left: bridge circuit for thermometric titrations;
Top right: Leeds and Northrup Conductivity Bridge.
The thermometric titration cell is shown on the left and the coulometric titration cell shown on the right of the Precision Dow Titrator.

The plunger of the feed pump is automatically driven by a relay-operated motor with the feed rate being adjustable to a maximum of 3 ml per min. The upper limit of plunger travel is controlled by a limit switch which protects the feed pump and other glassware from damage. If titrant should run low during a titration, the feed pump may be refilled and the titration resumed without the loss of the sample.

Because the titrant feed and chart advancing systems are mechanically linked, the chart reflects the actual amount of titrant added. One major chart division (approximately 23 mm) equals 1, 0·2, or 0·05 ml of titrant, depending on which feed pump is used.

The 22-sec 1 mV Brown Electronik Potentiometer furnished with the Precision-Dow instrument is an especially modified, 6-range, unit. A balanced-tube vacuum tube voltmeter links the titrator circuit to the potentiometer and allows only equilibrium values of e.m.f. to be plotted. When an e.m.f. change of as little as 5 mV occurs in the input to the titrator, the potentiometer is instantaneously unbalanced, and a feed control relay cuts off the feed motor and the chart drive until both the input e.m.f. and the potentiometer are again in balance. In this manner, fairly constant titrant addition is maintained during the early stages of a titration, when buffer action is strong, while additions become more widely spaced as buffer action is reduced.

The motor driving the feed system is equipped with a friction brake which allows close control of the incremental reagent additions.

Conductance end-point titrator

Automatic recorded conductance titrations can be performed by using a modified Leeds and Northrup Model 4958 conductivity bridge in conjunction with the Precision-Dow Titrator. The conductivity bridge is a small, portable instrument, which provides manual and/or automatic temperature compensation and produces a d.c. signal proportional to the conductivity of the solution in which the electrodes are immersed. A stabilised a.c. voltage of known value (obtained from a constant voltage transformer) is applied to the electrodes, resulting in a current flow that is directly proportional to the conductivity of the solution. The magnitude of the resultant current is measured by connecting a resistance circuit of relatively low impedance in series with the cell to obtain an a.c. signal proportional to the current. The a.c. signal is then coupled to a transistorised demodulator by a coupling and isolating transformer. The rectified output of the demodulator is measured by a d.c. microammeter. A 0–10 mV d.c. signal for operating a recording instrument is obtained from a precision
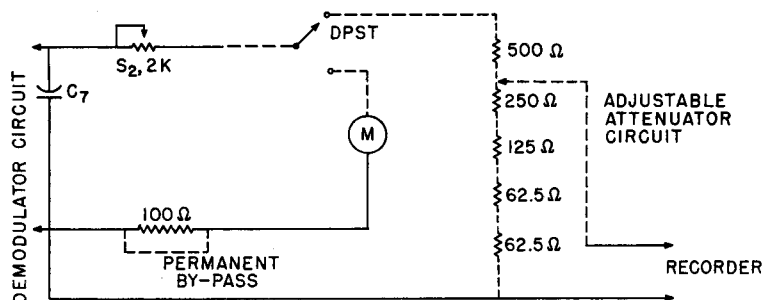
FIG. 3.—Modifications to the Leeds and Northrup Conductivity Monitor, Model 4958.
Modifications shown as broken lines
Other components shown:
  S_2: 2K-potentiometer
  C_7: 50 μF(Std. 2645–53)023213 capacitor
  M: 0–100 microammeter

resistor connected in series with the d.c. microammeter. However, the Brown recorder in the Precision-Dow has a range of 0–50 mV so that the nominal full-scale signal from the bridge would be only 1/5 the full-scale range of the recorder. Therefore, it was necessary to modify the bridge to accommodate the recorder in the Precision-Dow Titrator. This modification is given in Fig. 3. The 0–100 microammeter employed in the conductivity monitor has a 1000 Ω internal resistance, and with the 100-Ω precision resistor connected with it in series, gives a full scale d.c. signal of 0–10 mV. In

the modification, the 100-Ω precision resistor was by-passed, and a double pole single throw (DPST) switch was incorporated to permit operation of the recorder through an attenuator circuit containing resistance totalling 1000 Ω. The recorder leads are tapped across 500 Ω, giving a signal range of 0–50 mV to accommodate the recorder. By switching to the proper additional attenuator resistor, one can effectively change the recorder full scale from 50 to 400 mV without further adjustment. This is an important feature, since many conductance titrations have varied initial conductance readings. For relatively high conductance, one is forced to work in a region of higher voltage output from the monitor, thereby requiring an adjustment in the total resistance to get the signal on the recorder scale.

A second modification was needed to introduce the bridge output directly to the recorder in the titrator. This was accomplished by mounting a double pole double throw (DPDT) switch on the terminal board inside the recorder housing. With the switch in one position, the bridge is wired directly into the recorder input, while the switch in the opposite direction allows for normal operation of the Precision-Dow Titrator. When using the recorder as part of the conductance titrator, the anticipation circuit of the titrator is still available, since the recorder amplifier, and not the titrator detector circuit itself, is the sensitive element in the anticipation circuit.

Prior to operation, the potentiometric indicating electrodes on the Precision-Dow are replaced by a conventional conductivity electrode. The electrode leads are connected to binding posts located in the back of the Leeds and Northrup bridge, and the monitor is connected to the recorder through the DPDT switch previously described. A solution containing the sample and a "Teflon"*-covered magnetic stirring bar is positioned on the magnetic stirrer and the electrodes immersed so that the burette tip and the electrodes are below the surface of the liquid. Stirring should be adequate but not sufficiently vigorous to allow an air cavity to form in the vicinity of the electrodes. The recorder, which is set at the $\pm$1-V range with the position selector knob at zero, is turned on and the pen brought on scale by using the attenuator control mounted in the back of the monitor. This instrument has a linear range up to 800 μmhos. The dilution effect common to conductometric titrations can be minimised by using a micro-titration pump. Temperature control has not been found necessary.
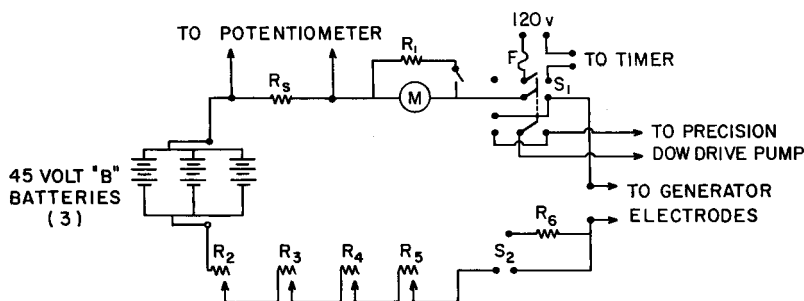

FIG. 4.—Electrical circuit for coulometric analyser

M: milliammeter 0–10 0–100 mA, calibrated
R_1: resistor 0·63 Ω
R_2: 10-Ω 4-W wire wound variable resistor
R_3: 100-Ω 25-W wire wound variable resistor
R_4: 1000-Ω 50-W wire wound round variable resistor
R_5: 5000-Ω 25-W wire wound variable resistor
R_6: 5000-Ω 25-W wire wound fixed resistor
R_s: resistor of a measured value (standard), in this circuit, the resistor measures 9·716 Ω
F: fuse, 2 A 250 V
S_1: TPDT centre off switch
S_2: SPDT switch

Photometric end-point titrator

Titrations requiring photometric end-point detection can be performed by using a Precision-Dow Titrator modified in a manner recently described by the authors.[4] Briefly, the modification comprises a Beckman Model B spectrophotometer with a specially designed compartment for the titration cell and a logarithmic attenuator, which seems to produce a signal from the spectrophotometer which is

* Trademark for du Pont's tetrafluoroethylene resin.

proportional to the solution absorbance. The normal titrant delivery tube and burette tip supplied with the titrator is replaced by one which leads directly from the feed pump to the modified cell compartment of the spectrophotometer. The titrator is suitable for colorimetric, nephelometric, and fluorescent indicator titrimetry. The modified cell compartment is provided with a hydrogen lamp as an ultraviolet source for fluorescent indicator titrimetry.

Coulometric titrator

The Precision-Dow Titrator can be modified to perform coulometric titrations by the addition of a relatively inexpensive battery operated constant current source. The circuitry (Fig. 4) for the constant current source is a modification of the one given by Cooke and Furman.[3] Three 45-V "B" batteries are used as the source of current, and an electric timer is included in the circuit in such a way that when the current is turned on, the timer and the recorder, or the recorder alone, in the titrator is turned on simultaneously. The calibrated milliammeter M can be made to read 10 or 100 mA at full scale by closing or opening the shunt resistor R_1 to the generating current. The generating current is adjusted by simple manipulation of the variable resistors in the circuit. These resistors are of the high wattage type so that they operate with relatively little temperature rise. A calibrated resistor, Rs, is included in the circuit for the purpose of checking out the circuit with a potentiometer. It was found that if three 45-V "B" batteries are connected in parallel, the current decreases less than 0·2% for a 10-min operating period at 10 mA. The chart is actuated when the current is turned on by making a jumper connection to the titrant pump motor relay from the constant generator as illustrated in Fig. 4. In this application, the titrant delivery glassware and the pump on one side of the titrator are completely removed, and a suitable holder containing the indicating and generating electrodes necessary for a particular run are mounted in the normal position over the magnetic stirrer as illustrated in Fig. 1. For example, in titrating acids, the hydroxyl ion was generated from a platinum cathode with the platinum anode isolated in a glass tube containing 10% sodium sulphate in agar gell and sealed at the end exposed to the solution with a sintered glass disc. The supporting electrolyte was 5% sodium sulphate in water and the titration was followed with glass-calomel electrodes. By disengaging the jaw which connects the titrant pump and the pump motor, the feed control can still be used and the forward movement of the chart controlled. The chart is calibrated in mequiv. per chart division by allowing the chart and timer to run simultaneously at a specified current and a fixed chart speed setting. Once the calibration has been made, a titration can be conducted without using the timer.

Amperometric end-point titrator

Coulometric titrations usually employ the dead-stop or amperometric end-point detecting system. The Precision-Dow Titrator can be modified to automatically record amperometric end-points by simply running a jumper connection from the binding posts of the microammeter in a Sargent
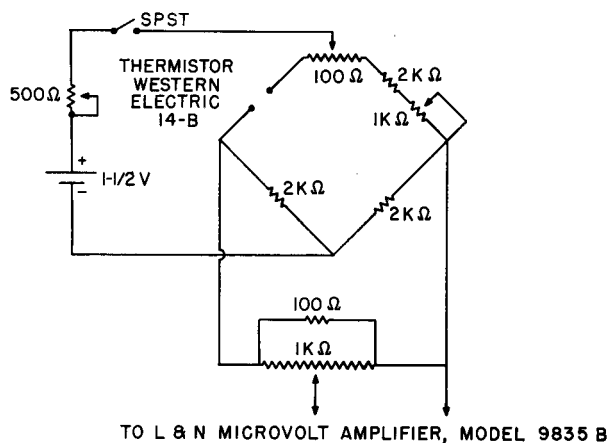

FIG. 5.—Bridge circuit for automatic recording thermometric titrator.

"Ampot" directly into the titrator recorder. This setup can be successfully used, for example, to standardise a solution of sodium thiosulphate by coulometrically generating iodine from potassium iodide. Two micro platinum electrodes can be used to detect the end of the titration.

Thermometric end-point titrator

Thermometric end-points have been achieved with this titrator using a technique similar to that described by Linde, Rogers and Hume.[3] A Western Electric 14B glass enclosed thermistor is ganged into a Wheatstone bridge powered by a 1·5-V battery (Fig. 5). Two variable resistors constituting the coarse and fine zero adjustments are included in the bridge circuit. The output from the bridge, which can be controlled by the variable span resistor, is fed into a Leeds and Northrup Model 9835B Microvolt Amplifier which has an imput range from 50 to 2000 mV and a 10 and 50 mV full-scale output for each input range. The output from the amplifier is fed directly to the input of the 50 mV Brown recorder in the Precision Dow Titrator. Gross changes in thermistor response caused by sudden changes in temperature will activate the attenuator circuit, stopping the flow of titrant until the system has equilibrated. Titrations were carried out in a small Dewar flask as shown to the left in Fig. 1.

DISCUSSION

Performance

The automatic recording coulometric titrator can be adapted for any type of titration that can be performed by constant current coulometric techniques provided the proper generating and indicating electrodes are used. Plot *A* in Fig. 6 illustrates the type of curve obtained when titrating 0·01 mequiv. of phosphoric acid with coulometrically generated hydroxyl ions. It was found that a precision of better than ±1% was achieved when titrating 0·01 mequiv. of hydrochloric acid with coulometrically generated hydroxyl ion at a current density of 5 mA. Actually, titrations can
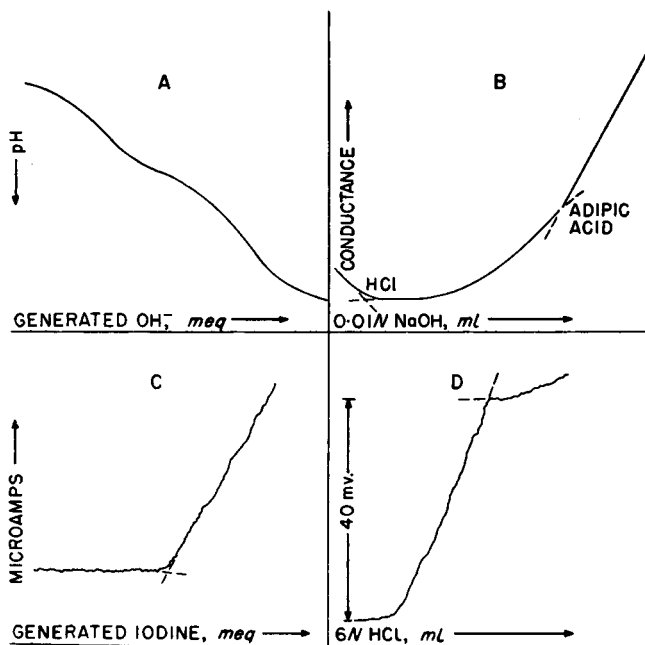

FIG. 6.—Typical titrations.
A: coulometric titration of phosphoric acid
B: conductometric titration of hydrochloric acid and adipic acid
C: coulometric titration of sodium thiosulphate illustrating amperometric end-point
D: thermometric titration of sodium hydroxide

be carried out at a current of 20 mA before noticeable interaction between generating and indicating electrodes are encountered. Plot *B* represents the automatic conducto-metric titration of 0·065 mequiv. of adipic acid in the presence of 0·015 mequiv. of hydrochloric acid. The estimated precision obtained in determining 0·065 mequiv. of adipic acid is about ±2·9%, compared to ±5% for the same concentration by manually plotting the data. Plot *C* represents the titration of 0·01 mequiv. of sodium thiosulphate with coulometrically generated iodine (from potassium iodide) to an amperometric end-point. Plot *D* illustrates the thermometric titration of 0·6 mequiv. of sodium hydroxide with 6·0*N* hydrochloric acid. The slight upward drift in the curve is caused by the stirring action and other background effects.

Zusammenfassung—Eine universelle Makro-Mikro-Titrationseinheit für automatische Titrationen wurde beschrieben. Das Gerät ist eine Modifikation des Dow-Präzisions-Titrationsschreibers und erlaubt Titrationen mit Masslösungen, culometrisch erzeugten Reagenzien und kann zur potentio-metrischen, amperometrischen, thermometrischen photometrischen oder konduktometrischen Endpunktbestimmung herangezogen werden.

Die potentiometrische Titration kann sowohl wie üblich als aüch in zweiter Ableitung durchgeführt werden. Die photometrische Einheit enhält einen Monochromator zur Erhöhung der Empfindlichkeit und kann auch für nephelometrische, turbidimetrische und fluorometrische Titrationen eingesetzt werden. Der konduktometrische Teil enthält einen neuartigen elektrolytischen Leitfähigkeitstrans-ducer, der ein Gleichstromsignal erzeugt, des deru Wechselstrom von einer Frequenz 60 zwischen den Elektroden proportional ist. Alle Teile sind leicht herzustellen oder käuflich erwerbbar.

Résumé—Les auteurs décrivent une unité de titrage universelle automatique pour les dosages, avec enregistrement. Cette unité offre les possibilités d'un grand nombre d'appareils de titrage commerci-aux simples sans l'inconvénient d'en avoir plusieurs.

Elle est basée sur un titrimètre enregistreur modifié "Précision-Dow" et offre à l'opérateur un choix de liquides ou de réactifs titrants préparés par coulométrie, ainsi que différentes méthodes pour décaler le point équivalent: potentiométrie, amérométrie, thermométrie, photométrie ou conducti-métrie.

La méthode potentiométrique offre le choix pour présenter la courbe, soit directement, soit en passant par la dérivée seconde; la méthode photométrique emploie un monochromateur pour avoir une sensibilité maximale, celui-ci est également adaptable aux titrimétries colorimétrique, turbidi-métrique, chimioluminescente; la méthode conductimétrique emploie un nouveau système qui produit un signal continu proportionnel au courant alternatif de 60 périodes entre les électrodes. Tous les constituants de l'appareil sont facilement construits ou sont disponibles.

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NEW REDOX SYSTEMS—IV*

## OXIDATION OF COBALT^{III} WITH IRON^{II} CHLORIDE IN 2,2'–BIPYRIDYL

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Summary—The oxidation of cobalt^{II} with iron^{III} chloride in the presence of 2,2'-bipyridyl has been studied potentiometrically and colorimetrically. The course of this reaction corresponds to a previously studied redox reaction in which 1,10-phenanthroline was used as the complex forming reagent. The formal redox potentials of the studied reaction have been calculated and their dependence on the concentration of 2,2'-bipyridyl and pH values studied. The possibility of utilisation of this redox system for the determination of cobalt is discussed.

IN previous papers of this series[1,2] it was reported that cobalt^{II} can be oxidised with iron^{III} chloride in the presence of 1,10-phenanthroline. This reaction was subsequently used for the direct potentiometric determination of cobalt with iron^{III}.[3] The determination of the concentration of ferroïn, which is formed during this reaction, allows the indirect determination of cobalt. Large quantities of ferroïn (cobalt) can be determined cerimetrically,[4] very small quantities colorimetrically.[5] Recently, this reaction has been used for the amperometric determination of cobalt.[6] For the oxidation of cobalt^{II} with iron^{III} it is possible to replace 1,10-phenanthroline by 2,2'-bipyridyl and the course of the reaction is

$$(Co^{II})_{Bip} + (Fe^{III})_{Bip} \rightleftarrows (Co^{III})_{Bip} + (Fe^{II})_{Bip} \qquad (1)$$
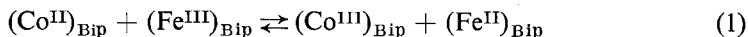
As would be expected, the mechanism and the optimal conditions of this reaction are practically identical with the similar system involving 1,10-phenanthroline. From the potentiometric data the formal redox potentials of the participating redox systems were calculated and their dependence on the concentration of complex forming reagent and pH studied.

EXPERIMENTAL

Reagents

0·01M cobalt^{II} nitrate and 0·01M iron^{III} chloride solutions: Prepared from reagent grade chemicals. 0·001M cobalt^{II} nitrate solution was prepared from the 0·01M solution by suitable dilution. The titre of these solutions was controlled gravimetrically.

0·01M 2,2'-bipyridyl solution: Prepared by dissolving 1·5618 g of analytically pure substance in 1 litre of water, weakly acidified with hydrochloric acid (resulting pH value 3).

Buffer solutions: Prepared by neutralisation of the calculated quantity of chloracetic acid or acetic acid with aqueous ammonia to the necessary pH, while a potentiometric control was maintained with a glass electrode. The resulting molarity of the solutions was 1.

Apparatus

Potentiometric measurements were carried out with a Trüb and Täuber (Switzerland) compensation potentiometer. The indicator electrode was a platinum wire and the reference electrode was a saturated calomel electrode.

* Part III—see reference 4.

Colorimetric measurements were carried out with a colorimeter produced by Laboratorní potřeby, National Corporation, Prague.

POTENTIOMETRIC RESULTS

From a series of potentiometric titrations of cobalt[II] with iron[III] according to reaction (1) the influence of the concentration of bipyridyl and pH on this reaction was found.

To 5 ml of 0·01M cobalt[II] nitrate solution were added 10 ml of a suitable buffer solution and a suitable amount of 0·01–0·1M bipyridyl solution. The solution was then diluted to 100 ml and titrated potentiometrically with 0·01M iron[III] chloride solution.

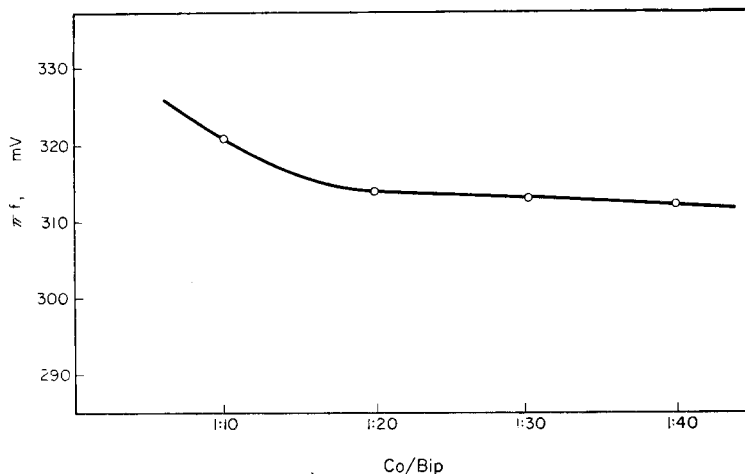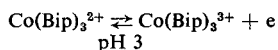The obtained results are in good agreement with the corresponding reaction

FIG. 1.—Influence of concentration of 2,2'-bipyridyl on the formal redox potential of the system:

$$Co(Bip)_3^{2+} \rightleftarrows Co(Bip)_3^{3+} + e$$
$$pH\ 3$$

which proceeds in the presence of 1,10-phenanthroline. The studied reaction was found to be a redox reaction with a one electron transfer and for the quantitative course of this reaction it is necessary to use a six-fold excess of 2,2'-bipyridyl. The optimal pH (from the point of view of the reaction velocity) was found in the range 2–4. The best buffer solution for this case is the mixture of monochloracetic acid and aqueous ammonia.

From the titration curves the formal redox potentials of the following redox systems were calculated:

$$Co(Bip)_3^{2+} \rightleftarrows Co(Bip)_3^{3+} + e \tag{2}$$

$$(Fe^{II})_{Bip} \rightleftarrows (Fe^{III})_{Bip} + e \tag{3}$$
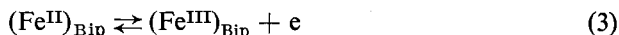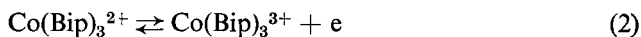
The course of reaction (3) is not given here quite exactly, because the composition of the complex which is formed by reaction of the iron[III] with 2,2'-bipyridyl was not studied. However, it would be expected that a similar hydroxo complex is formed to that in the case of 1,10-phenanthroline, $[Fe_2(OH)_2(Phen)_4]^{4+}$.

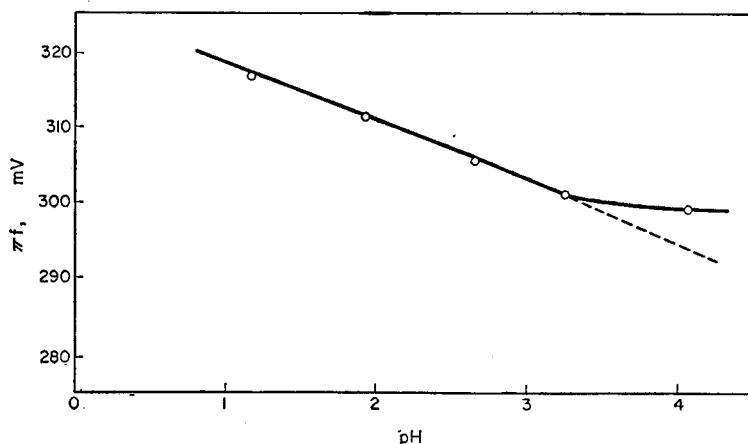Paglia and Sironi[7] have found a formal potential of 0·31 V in chloride media for

FIG. 2.—Influence of pH on the formal redox potential of the system:
$$Co(Bip)_3^{2+} \rightleftharpoons Co(Bip)_3^3 + e$$
ratio Co:Bip = 1:20.

redox system (2). We have found the same value at pH 2 in a buffer solution containing monochloracetic acid and ammonia. Under the same conditions we have found a value of 0·91 V for redox system (3).

The influence of the concentration of 2,2'-bipyridyl and pH (Figs. 1 and 2) on the formal redox potential of system (2) is very slight. This is because both oxidation states of cobalt have the same co-ordination number in the bipyridyl complex.[8]

In the case of system (3) the influence of the concentration of the complex forming reagent and pH on the formal redox potential is very great (Figs. 3 and 4). Here and similarly in the system with 1,10-phenanthroline, the influence of the concentration
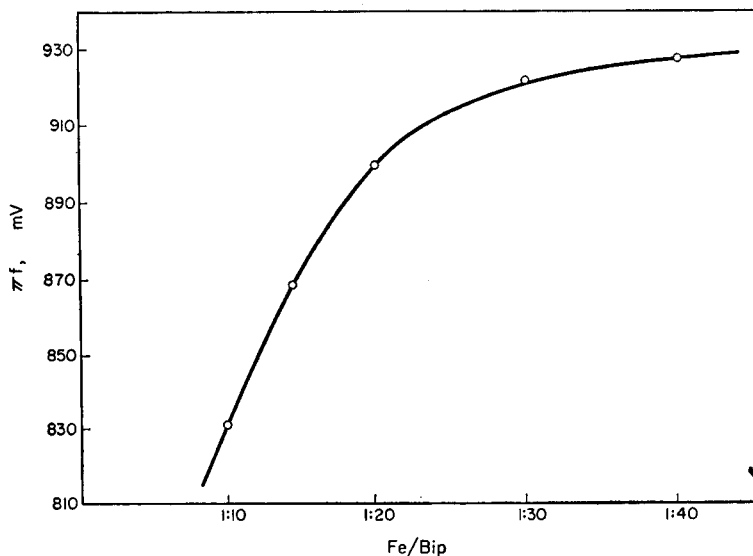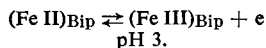
FIG. 3.—Influence of concentration of 2,2'-bipyridyl on the formal redox potential of the system:
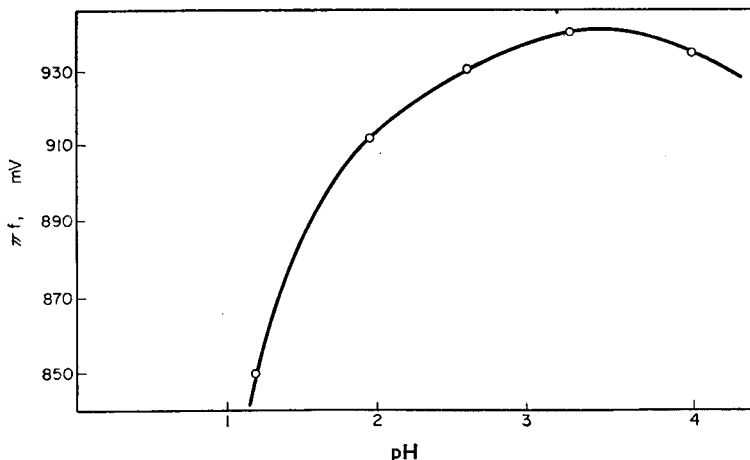$$(Fe\ II)_{Bip} \rightleftharpoons (Fe\ III)_{Bip} + e$$
pH 3.

FIG. 4.—Influence of pH on the formal redox potential of the system:
(Fe II)$_{Bip}$ $\rightleftarrows$ (Fe III)$_{Bip}$ + e
ratio Co:Bip = 1:20.

of the reagent is caused by the different values of the co-ordination number of iron in the complex in the two oxidation states.

COLORIMETRIC RESULTS

For the colorimetric study of reaction (1) the formation of the intensely coloured complex, (Fe^{II})$_{Bip}$ (λ_{max} = 522 mμ, ε_{H_2O} = 8930), which is formed by the reduction of iron^{III} with cobalt^{II} in the presence of 2,2'-bipyridyl has been used.

Under similar experimental conditions to those in the colorimetric study of the oxidation of cobalt^{II} with iron^{III} in the presence of 1,10-phenanthroline[2] identical results were found for the studied redox reaction. From the determination of the ratio of the reacting components it was stated that a one-electron transfer occurs during the reaction (ratio of Co:Bip = 1:1) and that its quantitative course needs a constant excess of 2,2'-bipyridyl [ratio (Co + Fe) : Bip = 1 : 6]. From these results it was confirmed that the composition of the resulting complexes was Fe(Bip)$_3$$^{2+}$ and Co(Bip)$_3$$^{3+}$. During the study of the influence of pH it was found that the quantitative course of this reaction takes 15 min in solutions of pH 1·5–5.

ANALYTICAL APPLICATIONS

The analytical utilisation of reaction (1) for the determination of cobalt is the same as the utilisation of the similar reaction with 1,10-phenanthroline. The difference in the values of the formal redox potentials of redox systems (2) and (3) is 0·60 V, and for the corresponding redox systems with 1,10-phenanthroline this difference is only 0·44 V. The potential change during the titration of cobalt^{II} with iron^{III} is greater in the presence of 2,2'-bipyridyl. The potential jump at the equivalence point is 450 mV per 0·05 ml of 0·01M iron^{III} chloride solution. The velocity of the stabilisation of the potential is practically the same as in the case of using 1,10-phenanthroline.

During the indirect cerimetric titration of cobalt [oxidation of Fe(Bip)$_3$$^{2+}$, which is formed according to reaction (1)] good results were not obtained, probably because Fe(Bip)$_3$$^{3+}$ is not very stable in this medium. Similarly, for the indirect colorimetric determination of very small quantities of cobalt, it is better to use 1,10-phenanthroline
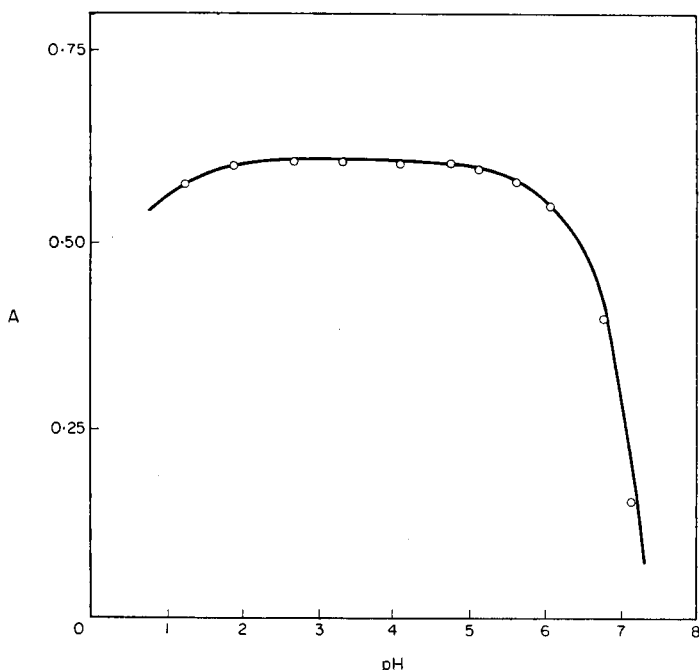
FIG. 5.—Influence of pH on extinction of Fe(Bip)$_3^{2+}$ resulting from the oxidation of cobalt^{II} with iron^{III} chloride solution. 2 ml of 0·001M Co(NO$_3$)$_2$, 5 ml of 0·001M FeCl$_3$, pH adjusted with 0·1N HCl or 0·1N NaOH (glass electrode) and 5 ml of 0·1M 2,2'-bipyridyl of the same pH, total volume of 25 ml. The extinction was measured after 15 min (1 cm cell, 522 mμ).

as the complex forming reagent,[5] because the intensity of the colour of ferroïn is higher ($\varepsilon_{H_2O} = 11\ 100$) than the intensity of the similar complex of iron^{II} with 2,2'-bipyridyl.

Zusammenfassung—Die Oxydation von Cobalt(II) mit Eisen(III) in Gegenwart von 2,2-Dipyridyl wurde potentiometrisch und photometrisch studiert. Die Reaktion ist analog zu der früher mit Phenanthrolin studierten. Die Formalpotentiale der Reaktion wurden berechnet und ihre Anhängigkeit von Reagenzmenge und pH studiert. Die Anwendungsmöglichkeit des Redoxsystems zur Bestimmung von Cobalt wird diskutiert.

Résumé—Les auteurs ont étudié l'oxydation du cobalt(II) par le fer(III) en présence de 2,2-bipyridile par potentiométrie et colorimétrie. La marche de cette réaction correspond à celle dé la réaction d'oxydo-réduction étudiée antérieurement, ou la 1,10 phénanthroline était utilisée comme réactif formant le complexe. Les potentiels normaux apparents de la réaction ont été calculés et leurs variations en fonction de la concentration de 2,2-bipyridile et du pH ont été étudiées. Finalement, les auteurs discutent de la possibilité d'utiliser ce système oxydo-réducteur pour le dosage du cobalt.

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PRELIMINARY COMMUNICATIONS

Evaluation and correlation of partition parameters involved in paper chromatography *†

THE theoretical approach to partition chromatography developed by Martin and his co-workers[1,2] has received wide acceptance and has demonstrated considerable predictive and correlative value.[3-6] However, the inability to evaluate the partition parameters described by Martin and, hence, the failure to correlate them with experimental conditions has meant that the full utility of the theory could not be exploited. The details for evaluating the parameters and several ways in which the knowledge of these functions may be of some aid in selecting experimental conditions are described below.

A graphical procedure to evaluate the partition parameters involved in the mobility of a homologous series of compounds became possible after development of equations presented by Martin,[1] Consden *et al.*[2] and French and Wild[3] into the form:

$$\log_{10} \frac{R_{f_n}}{1 - R_{f_n}} = \log_{10} \frac{A_m}{A_s} - 0.434 \frac{\Delta\mu_y}{RT} \left(\frac{\Delta\mu_x}{\Delta\mu_y} + n - 1 \right). \qquad (1)$$

where R_{f_n} is the R_f of an n-mer, A_m and A_s are the areas of the mobile phase and stationary phase,[2] respectively, $\Delta\mu_x$ and $\Delta\mu_y$ are, respectively, the free energy necessary to transfer a mole of monomer x and the added monomer unit y from the stationary phase to the mobile phase, and n is the chain length. Assuming that $\dfrac{A_m}{A_s}$ and $\dfrac{\Delta\mu_x}{\Delta\mu_y}$ are constants independent of solvent, the parametric equation (1) predicts that if $\log_{10} \dfrac{R_{f_n}}{1 - R_{f_n}}$ is plotted *vs.* $n - 1$ for various values of $\Delta\mu_y$, a family of lines should result, intersecting at the co-ordinate, $\log_{10} \dfrac{A_m}{A_s}$, $-\dfrac{\Delta\mu_x}{\Delta\mu_y}$, with slopes of $\dfrac{-0.434\Delta\mu_y}{RT}$. Furthermore, the intercept at $n - 1 = 0$ will be $\log_{10} \dfrac{A_m}{A_s} - \dfrac{0.434\Delta\mu_x}{RT}$.

To test the veracity of the assumptions and the possibility that equation (1) could lead to a procedure for evaluating the partition parameters for homologues, the mobilities of the maltodextrin saccharides[7] were measured on Whatman No. 2 and Eaton and Dikeman No. 613 paper at 24° ± 1° (after equilibration with the solvent vapours) with various mixtures of water and t-BuOH (miscible in all proportions). Different solvent mixtures were used to produce various values of $\Delta\mu_y$. The results of the experiment are plotted in Fig. 1 on a semilogarithmic graph, and, as predicted, lines intersecting at a common point for a wide range of solvent proportions were found. At very high water concentrations (*cf.* upper curve, Fig. 1), the paper apparently begins to swell[8] excessively and the ratio, $\dfrac{A_m}{A_s}$, increases.

When the maltodextrins were chromatographed with ten different solvents on Eaton and Dikeman paper, it was learned that the ratio, $\dfrac{A_m}{A_s}$, was constant (2.65 ± 0.15) while the ratio, $\dfrac{\Delta\mu_x}{\Delta\mu_y}$, exhibited solvent dependence. The fact that $\dfrac{A_m}{A_s}$ for Eaton and Dikeman paper was significantly different from
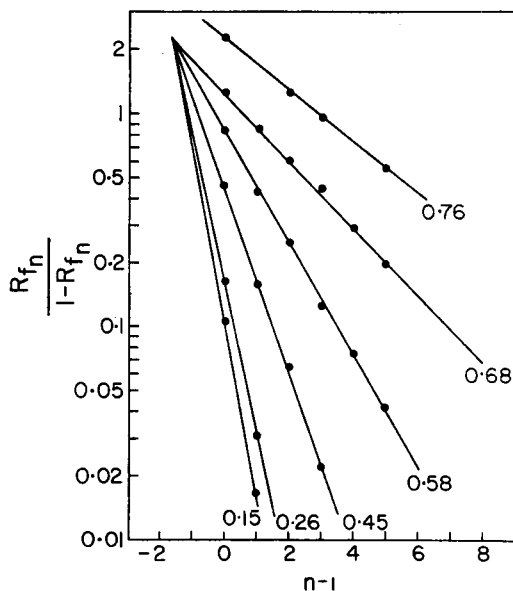
FIG. 1.—Mobility parameters of the maltodextrin saccharides *vs.* chain length minus one. Numbers correspond to mole fraction of water in the mobile phase containing *t*-BuOH as the organic component. Paper is Whatman No. 2.

the ratio of the areas obtained for Whatman No. 2 paper (2.10 $\pm$ 0.05) suggested that this function is primarily a property of the paper. Therefore, by studying the ratio, $\frac{A_m}{A_s}$, as a function of the paper, it should be possible to select the paper most suitable for individual chromatographic needs.

This treatment is not limited to homologous polymers, but can be extended to a general case which allows the parameters of any two similar compounds to be evaluated. Further manipulation of the basic equations leads to the following relationship for two compounds:

$$\log_{10} \frac{R_{t_a}}{1 - R_{t_a}} = \log_{10} \frac{A_m}{A_s} + \left(\log_{10} \frac{R_{t_a}}{1 - R_{t_a}} - \log_{10} \frac{R_{t_b}}{1 - R_{t_b}} \right) \left(\frac{1}{1 - \dfrac{\Delta\mu_b}{\Delta\mu_a}} \right), \qquad (2)$$

where R_{t_a} and R_{t_b} are the R_t of a and b, respectively, and $\Delta\mu_a$ and $\Delta\mu_b$ are respectively, the energies necessary to transport a mole of a and of b from the stationary phase to the mobile phase. Now if compounds a and b are similar in character so that $\frac{\Delta\mu_b}{\Delta\mu_a}$ is reasonably constant when solvent pro-

portions in a given binary system are varied, then a plot of $\log_{10} \frac{R_{t_a}}{1 - R_{t_a}}$ *vs.* $\log_{10} \frac{R_{t_a}}{1 - R_{t_a}}$

$- \log_{10} \frac{R_{t_b}}{1 - R_{t_b}}$ will lead to a straight line with a slope of $\dfrac{1}{1 - \dfrac{\Delta\mu_b}{\Delta\mu_a}}$ and an intercept of $\log_{10} \frac{A_m}{A_s}$.

The validity of equation (2) is verified by Fig. 2 where the appropriate plot is constructed for the two saccharides, glucose and maltose, which were studied in the water-*t*-BuOH system. Again, at high water concentrations the swelling of the paper becomes evident.

From thermodynamic considerations, after making a few simplifying assumptions, it can be shown that $\Delta\mu_a$ and hence $\log_{10} \frac{R_{t_a}}{1 - R_{t_a}}$ (in the mixtures where $\frac{A_m}{A_s}$ is constant) would be linearly
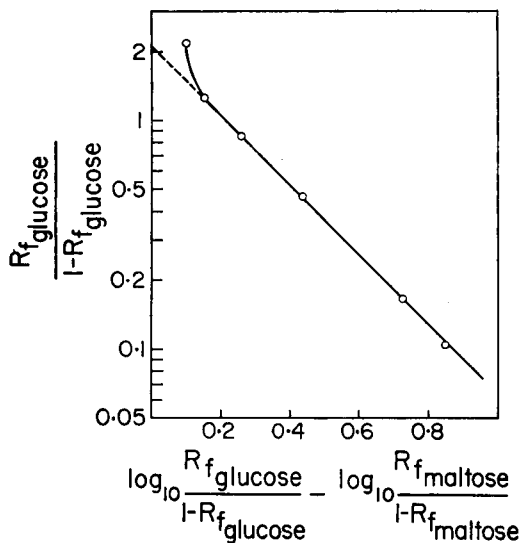
FIG. 2.—Mobility parameters of glucose *vs.* the difference in mobility parameters of glucose and maltose for various solvent proportions of water and *t*-BuOH. Paper is Whatman No. 2.

related to the mole fraction of water, N_{H_2O}, of a binary solvent. From the plot in Fig. 3, it can be seen that a linear relationship between $\log_{10} \dfrac{R_{t_a}}{1 - R_{t_a}}$ (where a represents glucose) and N_{H_2O} does exist over most of the range of solvent proportions tested.

Although the ratio, $\dfrac{\Delta\mu_x}{\Delta\mu_y}$, is a variable function of the solvent composition, it is independent of solvent proportions. Since this free energy ratio is an objective index of the ability of a particular set of components to separate mixtures, it serves as an excellent guide in the selection of solvent components.

The developments presented here suggest a method for selecting the solvent proportions producing

FIG. 3.—Mobility parameter of glucose *vs.* the mole fraction of water in the developing solvent. Paper is Whatman No. 2; organic solvent is *t*-BuOH.

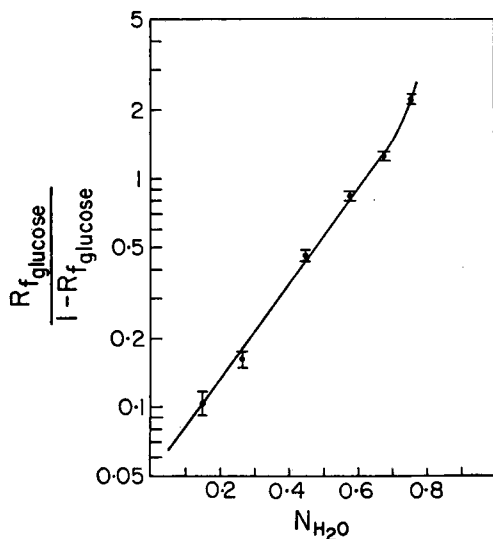maximum separation. From Fig. 2, for example, it is possible by graphical means to determine the R_f of glucose when maximum separation between glucose and maltose is achieved. From Fig. 3, the N_{H_2O} of the solvent producing this R_f for glucose or maximum separation is assessed. Although glucose and maltose are too easily separated to use this technique, it should be useful for the separation of compounds having more similar R_f values.

The evaluation of the influence of environmental factors such as solvent, paper, temperature, salts, *etc.* on the ratios of $\dfrac{A_m}{A_s}$ and $\dfrac{\Delta\mu_x}{\Delta\mu_y}$ should enhance our ability to predict and find better conditions for chromatography.

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Summary—A graphical method has been developed on theoretical grounds for evaluating the partition parameters involved in the mobility of a homologous series of compounds undergoing partition chromatography. The method has been tested by applying it to maltodextrin saccharides. The method permits an assessment of the solvent proportions which would favour maximum separation.

Zusammenfassung—Ein graphische Methode wurde auf Grund theoretischer Erwägungen entwickelt um die Verteilungsparameter homologer Reihen von Verbindungen für gaschromatographische Zwecke zu berechnen. Das Verfahren wurde durch Anwendung auf Saccharide von Maltodextrin getestet. Die Methode gestattet eine Bewertung der Solventeigenschaften um die höchstmögliche Trennung zu erzielen.

Résumé—L'auteur a mis au point d'après des bases théoriques une méthode graphique pour évaluer les coefficients de partage mis en jeu pour une série homologue de composés dans la chromatographie de partage. La méthode a été expérimentée sur les saccharides maltodextrines. Elle permet une estimation des proportions de solvant favorisant une séparation maximale.

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Applications of infra-red spectroscopy—VI*

Recent developments in techniques of increased sensitivity for the analysis of GLC fractions and other small scale samples—a brief review

THE relative cost of acquiring the appropriate apparatus has probably contributed significantly to the unfortunate fact that, of absorption spectroscopic methods, colorimetry and ultraviolet have been more frequently applied to analytical problems than infrared. Recently, however, the availability of

* Part V: D. M. W. Anderson and N. J. King, *Talanta*, 1961, **8**, 497.

less expensive equipment has fostered greatly increased interest in the analytical uses of infrared spectroscopy. The emphasis, however, has been on qualitative applications; the tremendous potential which infrared offers to quantitative analysis does not appear to have been adequately appreciated. Infrared not only identifies unequivocally, but simultaneously gives a basis for accurate quantitative analysis if the appropriate calibration curves on standards are constructed. Moreover, the sample is not destroyed, and the nature of any contaminants is revealed. Generally, contaminants rarely interfere with quantitative determination of the desired compound if the operating conditions are carefully chosen, but if interference does occur, adequate warning is given by the appearance of the spectrum. The literature continues to describe analytical procedures which could be carried out more rapidly and accurately, with decreased interference from other components, by infrared methods.

General interest in the analysis of smaller and smaller amounts of material continues, and has naturally stimulated efforts to increase the sensitivity of all spectroscopic techniques. For infrared this can be approached by the use of auxiliary instrumentation such as scale-expansion,[1] multipathlength cells,[2] or beam condensers—all of which are relatively expensive—or by improving the design of single-pass cells. Techniques are now clearly established[3] for the quantitative analysis of 20–100 μg of material in solution or in the liquid, solid, or gas phase; various techniques and accessories permitting the examination of <1 μl of some samples have also been described[4] or commercially advertised.

The greatest stimulus to the development of increased sensitivity has doubtless come from the challenge for spectroscopists to approach the sensitivity attainable in chromatographic separations. This challenge has been invaluable, since the resulting spectroscopic developments are equally applicable to samples which are not of chromatographic origin. Throughout the development of both techniques, samples obtained as GLC fractions have always tested the minimum limits detectable by infrared; it now appears that spectroscopic techniques may never match the chromatographic sensitivity attained recently through the development of capillary columns.

Indeed, some authorities[5] consider that the identification of GLC fractions may have to be based solely on the use of retention-volume characteristics. Although this is doubtless satisfactory for routine applications, its serious deficiencies when applied to entirely unknown mixtures from research investigations, or to systems which have not been completely characterised, have already received comment.[6] A triangulation method using three stationary phases of differing polarities has been proposed[7] for the positive identification of GLC components, but many investigators are agreed[4,6,8-10] that identification based solely on retention characteristics is inadequate. Compounds can have closely similar retention volumes, even on different column materials; components may only be separable[9] as "shoulders"; and mixtures of similar hydrocarbons[10] or of members of different homologous series[8] may be found under a single chromatographic peak. The collection of fractions and subsequent examination by infrared[4,6,11] or mass spectroscopy[9,10] is therefore desirable; continuous infrared detection of functional groups has also been proposed.[12] If spectroscopic equipment is not available, then functional group analysis[8,13] of the eluted fractions is desirable, and can be operated at the 20-μg level.

Considering now only infrared techniques, it is clear that the dominant difficulty lies in matching the sensitivity of GLC. When co-operation between the two techniques is essential, a possible solution is to operate below maximum GLC sensitivity; this, however, could only be taken a certain length before leading to column overloading or to decreased chromatographic resolution. All too frequently, the particular component to be studied is present in trace amount in a mixture: even although an adequate supply of the mixture is available, insufficient amounts of the required fraction for infrared examination may be given by each chromatographic fractionation. It appears, therefore, that there will always be a demand for the technique of trapping the appropriate peak from a number of consecutive GLC runs, so that eventually a quantity sufficient for spectroscopic identification is collected.[6] Techniques involving collection in liquid nitrogen traps are now frequently used.[4,14] Other methods, such as mixing the eluted fraction with a vapour solvent introduced via a side-arm to the trap,[15] or depositing the desired component at room temperature on finely ground potassium bromide, which is subsequently pressed to form a disc,[16] have also been described.

Although it has clear limitations[6] (cf. ref. 4), the vapour-phase technique remains invaluable for certain types of sample, and any increase in its sensitivity[11] would be advantageous. Although metal cells of uniform rectangular cross-section[4] can increase the sensitivity given by circular glass-cells,[11] they do not, however, give the maximum sensitivity attainable with single-pass cells. Metal cells having

tapered bores of rectangular cross-section, such that all essential rays of the energy beam are exactly enclosed, became available commercially for certain spectrometers during 1960: tapered cells made here for use with the Hilger H800 instrument were shown to visitors to this department during the 3rd International Gas Chromatography Symposium. It is of interest that the asymmetrically placed focus of the H800 spectrometer gives some advantage in designing such a tapered cell for insertion in the energy beam between the point of focus and the spectrometer entrance slit, rather than (a) between the energy source and the point of focus or (b) symmetrically about the focus.

That such rectangular tapered cells are more conveniently constructed of metal rather than of glass introduces no disadvantages; the examination of corrosive or reactive compounds merely requires the surfaces of the cell to be thinly covered with an epoxy or other coating suitably inert to the compound being examined. Indeed there now appears to be a distinct advantage in also constructing the trap and stop-cocks of metal; when trap dimensions are reduced, the increasing fragility of glass is off-set. A trapping device employing hypodermic needle tubing has been described.[17]

Suitably small vacuum-tight metal stop-cocks are now available commercially; these facilitate all-metal construction, although there is no difficulty in incorporating glass stop-cocks[4] in an otherwise metal assembly. It has long been known, however, that the presence of stop-cock grease is undesirable.[18] The importance of using minimal amounts of lubricants was stressed earlier,[6] but in working with ever decreasing amounts of material, there are now distinct indications that all traces of lubricants must be eliminated. High-vac greaseless taps are now offered commercially, and greaseless laboratory devices have been described.[18,19]

The future development of minimum volume, all-metal, greaseless trap-cells may also simultaneously assist the incorporation of heating devices so that the applicability of the vapour-phase technique may be extended above its present limit of about 125° (cf. refs. 4 and 11). Development of heated cells[6] suitable for accurate quantitative work has proved troublesome; difficulty has also been reported by other investigators.[4] Nevertheless a vapour cell operating at $\pm 1°$ up to 180° has been developed.[20] The results of continued efforts in this laboratory will be published in due course.

Finally, the development of new infrared transmitting glass such as "Irtran-2" (Eastman-Kodak Ltd.) which gives $>70\%$ transmission from 2-10 μ, decreasing to 40% at 14 μ, and which has good thermal shock properties, may facilitate the development of a single unit trap-cell which could be cooled directly to trapping temperature, then heated to volatilise the sample. Such cells may also be suitable for aqueous systems. The technique of trapping directly in evacuated gas-cells has recently been used.[14]

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Summary—The advantages of quantitative infrared spectroscopy recommend the technique for wider application to analytical procedures than at present. Micro-scale samples can already be dealt with, and recent developments leading to increased sensitivity are briefly reviewed, with particular reference to the examination of samples in the vapour phase.

Zusammenfassung—Die sehr Vorteilhafte quantitativer IR-Spectroskopie wird zur ausgedehnteren Anwendung empfohlen. Es ist bereits möglich mit Mikroproben zu arbeiten; jüngste Entwicklungen führten zu erhöhter Empfindlichkeit, was im Hinblick auf die Untersuchung von Proben in der Dampfphase behandelt wird.

Résumé—L'auteur recommande les avantages de la spectroscopie infrarouge quantitative pour une application plus importante aux méthodes analytiques. Des échantillons miscroscopiques peuvent déjà être traités; les développements récents conduisant à une sensibilité accrue sont brièvement passés en revue, avec une référence particulière pour l'étude des échantillons en phase vapeur.

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BOOK REVIEW

Gas Sampling and Chemical Analysis in Combustion Processes. G. TINÉ. AGARDograph 47, `
Pergamon Press, 1961. pp. 94. Price 42s.

THE extent of current interest in the chemistry of combustion is reflected in the large number of papers on this subject appearing in the literature. The scope of this interest extends from the purely practical aspects, such as estimations of fuel efficiency and engine performance, to the theoretical interpretation of reaction mechanisms. One problem is common to all of these studies and that is the analysis of reactant and burned gases. Without reliable methods of estimating the composition of gas mixtures no progress would be possible in the field of combustion, and it is, therefore, surprising that up till now no compilation of suitable analytical techniques has appeared. In writing *Gas Sampling and Chemical Analysis in Combustion Processes*, the author has attempted to fill this gap and, to a limited extent, he has succeeded.

The book is essentially a brief review of current methods used in the sampling and analysis of combustion gases. The information contained in it has been collected by the author, during a tour of industrial and university laboratories in countries associated with AGARD and, on the whole, the emphasis is more on the industrial approach than on the academic.

There are two main sections, the first dealing with sampling procedures and the second with gas analysis. The first section contains a brief theoretical discussion of the hydrodynamic problems associated with probe sampling. This is followed by theoretical and practical considerations of probe design and the techniques involved in sample handling and storage. In any analytical method which uses probe sampling, there are two important factors which must always be considered; they are the quenching effect, and possible catalytic effects arising from the probe. Both of these subjects are discussed, the first in considerable detail. It is to be regretted, however, that the second is given relatively little attention.

The second section begins with a review of basic analytical procedures in gas analysis and then deals with the recognised methods of analysis for the main components of a combustion mixture. All of the common components, likely to be encountered in practice, are reviewed, *e.g.*, H_2, O_2, H_2O, CO, CO_2, oxides of sulphur, alcohols, ethers, aldehydes and organic peroxides. A similar section follows this, on the analysis of exhaust gases. Emphasis is laid on modern instrumental techniques, such as gas chromatography, infrared spectral analysis and mass spectrometry. Each section is followed by a brief summary and recommendations.

The book is attractively presented and makes good use of diagrams in all cases where they are necessary. Constructive criticism of the various sampling and analytical procedures is provided throughout, together with references to original papers. It is, however, by no means a comprehensive text on the subject. The compilation of references could profitably be larger and a more detailed description of some of the techniques would have been valuable. Nevertheless, workers in the field of combustion will find this book useful introductory reading and a good guide to recent developments in gas analysis.

W. D. McGRATH

NOTICES

UNITED KINGDOM

Friday 1 *December* 1961: **The Design and Construction of Laboratories:** Mr. R. R. YOUNG, F.R.I.B.A. and Mr. P. J. HARRINGTON: *Society for Analytical Chemistry, North of England Section* and *Royal Institute of Chemistry, Manchester Section.* Manchester Literary and Philosophical Society, 36 George Street, Manchester, 1. 2.00 p.m.

This meeting will be preceded by a visit to I.C.I., Pharmaceuticals Division, Alderley Park, Cheshire. The party will leave central Manchester at 9.00 a.m.

Thursday 7 *December* 1961: **The Ramsay Dinner:** *Society for Analytical Chemistry, Scottish Section.* Central Hotel, Glasgow. 7.00 p.m.

Friday 8 *December*, 1961: **The Structure of Natural Products by Direct X-ray Analysis:** Professor J. MONTEATH ROBERTSON, D.Sc., F.R.S.: *Society for Analytical Chemistry, Scottish Section; Chemical Society; Society for Chemical Industry, Glasgow Section* and *Royal Institute of Chemistry, West of Scotland Section.* Royal College of Science and Technology, George Street, Glasgow. 7.15 p.m.

Friday 8 *December* 1961: **Analytical Research:** Dr. J. HASLAM, D.Sc., F.R.I.C.: *Society for Analytical Chemistry, Western Section* and *Royal Institute of Chemistry, Cardiff and District Section.* University College, Cardiff.

Wednesday 13 *December* 1961: **Fluorescent Indicators for Metals:** Dr. W. I. STEPHEN: *Society for Analytical Chemistry, Midlands Section.* University, Edgbaston, Birmingham, 15. 7.00 p.m.

Wednesday 13 *December* 1961: **Discussion Meeting:** *Society for Analytical Chemistry, Micro-chemistry Group.* The Feathers, Tudor Street, London, E.C.4. 6.30 p.m.

Thursday 14 *December* 1961: **Annual General Meeting** followed by discussion on **Assessment of Antiatherosclerotics:** *Society for Analytical Chemistry, Biological Methods Group.* The Feathers, Tudor Street, London, E.C.4. 6.30 p.m.

Friday 15 *December* 1961: **Applications of Infrared Spectroscopy to Quantitative Analysis:** *Society for Analytical Chemistry* and *Infrared Discussion Group.* King's College, Strand, London, W.C.2. 11.15 a.m.

First Session

Introductory Paper on Principles of Quantitative Infrared Spectroscopy: Dr. W. R. WARD
Quantitative Infrared Analysis of Agricultural Chemicals: Mr. P. G. MARSHALL

Second Session

Quantitative Analysis of Milk and other Emulsions by Infrared Absorption: Dr. J. D. S. GOULDEN
Quantitative Infrared Analysis of Phosphonitrilic Chloride Polymers: Dr. A. C. CHAPMAN
Some Uses of Infrared Spectroscopy in the Pharmaceutical Industry: Dr. H. D. C. RAPSON

The following Amendment Slips are announced by *B.S.I. News:*

B.S. 1016: *Methods for the analysis and testing of coal and coke: Part* 16: 1961: *Reporting of results. Amendment No. 1: P.D* 4254.

B.S. 1121: *Methods for the analysis of iron and steel: Part* 34: 1955: *Determination of molybdenum in iron and steel (absorptiometric method). Amendment No. 1: P.D* 4149.

B.S. 2690: 1956: *Methods of testing water used in industry. Amendment No. 1: P.D* 4220.

B.S. 2782: *Methods of testing plastics: Part* 4: 1958: *Analytical methods and viscosity in solution. Amendment No.* 6: *P.D* 4291.

B.S. 3338: *Methods for the sampling and analysis of tin and tin alloys: Part* 3: 1961: *Antimony in ingot (photometric method). Amendment No. 1: P.D* 4286.

UNITED STATES OF AMERICA

Thursday-Saturday 7–9 December 1961: **Combined Southwest-Southeast Regional American Chemical Society Meeting.** New Orleans, Louisiana.

The tentative programme schedule lists 36 half-day sessions (23 general sessions and 13 symposia). All except the Biochemistry sessions will be held in the Jung Hotel. The final convention programme, containing abstracts of all papers to be presented, will be available at the time of registration.

The tentative programme for the Analytical Chemistry sessions is as follows:

Thursday Morning, 7 December
  Paper Chromatography of Urethian Derivatives of Alcohols: JOHN A. ATTAWAY.
  Spectrophotometric Determination of Zinc in Oilfield Brines: A. GENE COLLINS and TOM G. EBREY.
  Kinetics of Extraction of Zinc Dithizonate: CARL B. HONAKER and HENRY FREISER.
  Radiochemical Determination of Yttrium and Promethium—A Precipitation Technique: M. E. PRUITT, R. R. RICKARD and E. I. WYATT.
  Simultaneous Differential Thermal Analysis and Gas Evolution Analysis—A New Technique: WESLEY W. WENDLANDT.
  O-Dialkyl Phosphorodithionates as Extractants for Metals: THOMAS H. HANDLEY and JOHN A. DEAN.
  Simultaneous Spectrophotometric Determination of Platinum and Palladium with Dibenzyldithio-oxamide: WILLIAM D. JACOBS.
  Gravimetric Determination of Indium by Benzenephosphonic Acid: ANIL K. MUKHERJI.

Thursday Afternoon, 7 December: **Symposium on Electroanalytical Chemistry**
  Faradaic Rectification: PAUL DELAHAY.
  Mechanisms of Electroreductions of Organic Compounds and Methods for their Elucidation: W. H. REINMUTH.
  Electrochemistry of Adsorbed Reactants: F. C. ANSON.

Friday Morning, 8 December: **Symposium on Electroanalytical Chemistry.**
  The Application of Controlled Potential Coulometry to the Study of Electrode Mechanisms: A. J. BARD.
  Reactions at the Hanging Drop Mercury Electrode: IRVING SHAIN.

Friday Afternoon, 8 December
  The Anodic Oxidation of Methyl and Ethyl Alcohols at Platinum Electrodes using Triangular Impulse Polarography: THOMAS C. FRANKLIN and CHARLES LIANG.
  Current-Scan Polarography using a System which Ordinarily Exhibits a Polarographic Maximum: HARRY B. MARK, JR. and CHARLES N. REILLEY.
  Current Programming in Chromopotentiometry: ROYCE W. MURRY.
  A New Potentiometric Reaction Method for the Micro Determination of Carbonyl Compounds: H. V. MALMSTADT and E. C. TOREM, JR.
  Amperometric Titrations with Ethylenedinitrilotetra-acetic Acid using Iron^{II} as the Indication Ion: G. GOLDSTEIN, D. L. MANNING and H. E. ZITTEL.
  Exchange of Copper^{II} between EDTA and Eriochrome Blue Black R: D. W. RODGERS, D. A. AIKENS and C. N. REILLEY.

Saturday Morning, 9 December
  Precipitation of Cobalt 8-Hydroxyquinolate from Homogeneous Solution: ROBERT W. SHERRILL.
  Flame Spectrophotometric Determination of Trace Quantities of Strontium in Macro Quantities of Calcium: T. C. RAINS, H. E. ZITTEL and MARIAN FERGUSON.
  Extraction of Sulphides from Petroleum Fractions by Way of Sulphonium Salts: R. L. HOPKINS, H. J. COLEMAN, C. J. THOMPSON and H. T. RALL.
  Spectrographic Analysis of the Parts of a High-Lithium Rabbit: CHARLES H. SMITH.
  The Extraction of Rhenium with Tributylphosphate: G. W. LEDDICOTE and A. P. GRIMANIS.
  The Determination of Stable Trace Elements in Radioactive Materials by Neutron Radioactivation Analysis: W. T. MULLINS, F. F. DYER, J. F. EMERY, L. C. BATE and G. W. LEDDICOTE.
  The Estimation of Beryllium with Eriochrome Cyanine R using the Ring Oven Technique: PHILLIP W. WEST and PATRICIA R. MOHILNER.

Further details may be obtained from the Publicity Chairman: P. D. ACCARDO, California Chemical Co., Oronite Division, Belle Chasse, Louisiana, U.S.A.

PAPERS RECEIVED

Photometric titrations-VI: The determination of submicrogram quantities of calcium and magnesium: H. FLASCHKA and P. SAWYER. (10 *August* 1961).
Chelometric titrations with amperometric end-point detection: R. T. CAMPBELL and CHARLES N. REILLEY. (11 *September* 1961).
Precipitation of copper salicylaldoximate from homogeneous solution: RICHARD F. PIETRZAK and LOUIS GORDON. (22 *September* 1961).
Infrared spectra of some organophosphorus extractants: L. C. THOMAS and ROSEMARY A. CHITTENDEN. (29 *September* 1961).
The coulometry and polarography of iridium[IV]: JOHN A. PAGE. (2 *October* 1961).

PUBLICATIONS RECEIVED

The Radiochemistry of Vanadium: J. L. BROWNLEE, JR. NAS-NS-3022. National Academy of Sciences, National Research Council. December, 1960. Pp. v + 76. $0.75.
The Radiochemistry of Ruthenium: E. I. WYATT and R. R. RICKARD. NAS-NS-3029. National Academy of Sciences, National Research Council. February, 1961. Pp. vii + 78. $1.00.
The Radiochemistry of Selenium: G. W. LEDDICOTTE. NAS-NS-3030. National Academy of Sciences, National Research Council. April, 1961. Pp. v + 38. $0.50.
The Radiochemistry of the Transcurium Elements: G. H. HIGGINS. NAS-NS-3031. National Academy of Sciences, National Research Council. Pp. v + 34. $0.50.
The Radiochemistry of Aluminum and Gallium: JOHN E. LEWIS. NAS-NS-3032. National Academy of Sciences, National Research Council. April, 1961. Pp. v + 48. $0.50.
The Radiochemistry of Antimony: WILLIAM J. MAECK. NAS-NS-3033. National Academy of Sciences, National Research Council. February, 1961. Pp. vi + 54. $0.50.
The Radiochemistry of Titanium: CHONG KUK KIM. NAS-NS-3034. National Academy of Sciences, National Research Council. March, 1961. Pp. v + 23. $0.50.
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Radioactive Contamination of Materials Used in Scientific Research: JAMES R. DEVOE. Publication 895. National Academy of Sciences, National Research Council. 1961. Pp. vii + 142.
Chromatography with particular consideration of Paper Chromatography: E. MERCK A.G. Verlag Chemie, Weinheim, 1961. Pp. 185. 2nd Edition. DM.18-.
Vitamins—Merck: E. MERCK A.G. Verlag Chemie, Weinheim, 1961. Pp. 203. DM.26.
Reagent Chemicals: American Chemical Society Specifications 1960: Applied Publications, A.C.S., Washington D.C., 1961. Pp. xv + 564.
Acta Chimica Academiae Scientarum Hungarica: Editor Z. CSUROS. Hungarian Academy of Sciences, Budapest, 1961. Vol. 26, pp 518; Vol. 27, pp. 480; Vol. 28, pp. 309.
Gas Sampling and Chemical Analysis in Combustion Processes: G. TINE. Pergamon Press Limited, Oxford, 1961. Pp. 94. 42s.
The Radiochemistry of Gold: J. F. EMERY and G. W. LEDDICOTTE. NAS-NS-3036. National Academy of Sciences, National Research Council. May, 1961. Pp. v + 34. $0.50.
Liquid-Liquid Extraction with High-molecular-weight Amines: FLETCHER L. MOORE. National Academy of Sciences, National Research Council. 15 December, 1960. Pp. v + 83. $1.00.
Principles and Applications of Paper Electrophoresis: CH. WUNDERLY. Elsevier. 1961. Pp. xii + 253. 26s.
Advances in Fluorine Chemistry—II: Editors: M. STACEY, J. C. TATLOW and A. G. SHARPE. Butterworths. 1961. Pp. 220. 45s.

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      £80 per set.

The Encyclopedia of Microscopy: Edited by GEORGE L. CLARKE. Chapman and Hall. 1961. Pp.
      xiii + 693. 200s.

The Encyclopedia of Spectroscopy: Edited by GEORGE L. CLARKE. Chapman and Hall. 1961.
      pp. xvi + 787. 200s.

Systematic Qualitative Analysis: G. A. MORRISON. Butterworths. 1961. pp. ix + 198. 25s.

Rules and Methods for Calculating the Physico-Chemical Properties of Paraffinic Hydrocarbons:
      V. M. TATEVSKII, V. A. BENDERSKII and S. S. YAROVOI. Pergamon Press Limited, Oxford, 1961.
      pp. xi + 128. 30s.

Radiochemistry: Pergamon Press Limited, Oxford, 1961. Vol. I, No. I, pp. 183. £15 p.a.

Separations by Solvent Extraction with Tri-n-octylphosphine Oxide: J. C. WHITE and W. J. ROSS.
      NAS-NS-3102. National Academy of Sciences, National Research Council. 8th February, 1961.
      pp. v + 56. $0.75.

Low-level Radiochemical Separations: T. T. SUGIHARA. NAS-NS-3103. National Academy of
      Sciences, National Research Council. April, 1961. pp. v + 34. $0.50.

A Cross-referenced Index of Radiochemical Teaching Experiments Applicable to Chemistry: GREGORY
      R. CHOPPIN. Publication 905. National Academy of Sciences, National Research Council.
      1961. pp. 50. $1.00.

Quantitative Organic Microanalysis: AL STEYERMARK. 2nd Edition. Academic Press, 1961.
      pp. xvii + 665. 118s.

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      Vol. III. pp. 978.

The Radiochemistry of Tellurium: G. W. LEDDICOTTE. NAS-NS-3038. National Academy of
      Sciences, National Research Council. July, 1961. pp. v + 42. $0.50.

Methods for the Analysis of Non-Soapy Detergent (NSD) Products: G. F. LONGMAN and J. HILTON.
      Society for Analytical Chemistry, 1961. pp. 30. 15s.

A Guidebook to Mechanism in Organic Chemistry: P. SYKES. Longmans, Green and Co. Ltd.,
      1961. pp. xiii + 247. 21s.

Separation of Heavy Metals: ANIL K. DE. Pergamon Press Limited, Oxford, 1961. pp. 308. 60s.

NOTES FOR CONTRIBUTORS

1. General

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

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

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

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

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

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

2. Script Requirements

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

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

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

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

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

$$ \blacktriangle \quad \triangle \quad \boxdot \quad \square \quad \bullet \quad \bigcirc \quad \triangle \quad \odot \quad \oplus \quad \ominus \quad \phi \quad \otimes $$

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

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

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

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[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals*. A.E.R.E., M/R 6329, 1962.

[4] W. Jones, *Brit. Pat.* 654321, 1959.

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