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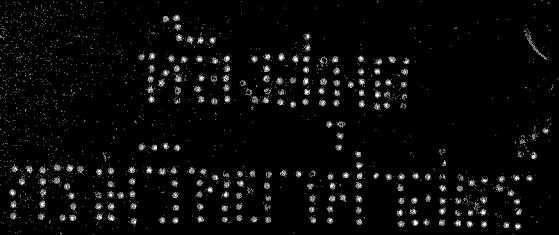

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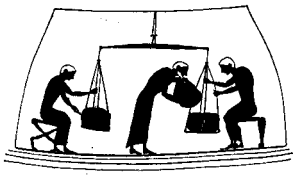

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[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals*. A.E.R.E., M/R 6329, 1962.

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

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TALANTA

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SOME CONSIDERATIONS ON MASKING EFFECTIVENESS

ADAM HULANICKI
Department of Inorganic Chemistry, The University, Warsaw, Poland

(*Received* 23 *November* 1961. *Accepted* 20 *February* 1962)

Summary—A new term, the masking coefficient, has been derived and introduced in analytical considerations involving masking of precipitation reactions. The masking coefficient is expressed by an equation:

$$pM' = \frac{1}{j+i}[pS - i\log(j/i)] - \frac{j}{j+i}\log\alpha_M - \frac{i}{j+i}\log\alpha_A$$

where the first term is related only to the properties of the precipitate, the second to masking of the cation, and the last to masking of the anion. If suitable diagrams have been prepared for calculating the "side reaction coefficients"—log α_M and log α_A—all calculations can be easily performed. The utility of the masking coefficient criterion to predict whether masking or precipitation occurs has been confirmed experimentally. Some examples of calculation of the masking coefficient for well known analytical reactions are given.

THE immense development of analytical chemistry has demanded the introduction of many new selective reagents and so-called masking agents, which may greatly improve the selectivity and specificity of analytical reactions.[1,4] Recently Cheng[2] has presented an extensive study on the use of some masking agents, especially ethylenediaminetetra-acetic acid (EDTA) combined with many inorganic and organic precipitants.

The correct choice of a suitable masking agent for a given principal reaction (as called by Cheng[2]), is very often solved experimentally by trying a sufficiently large set of available reagents. This procedure is rapid, but does not provide any instant indication of how effective the process of masking is, especially when compared with other masking reactions. Evaluation of detailed conditions for the equilibrium position or its shift is obviously possible on the basis of a knowledge of corresponding equilibrium constants. This will give accurate results, but the exact mathematical treatment is, in most cases, rather long and complicated.

The use of conditional constants[3,5] offers some advantages if they are used in calculation instead of the thermodynamic constants. Nevertheless it would be worthwhile to have a general expression for simple evaluation of the equilibrium position in systems containing metal ion, precipitating and masking agents.

Recently Cheng[2] has attempted to do this by introducing the term "Selectivity Ratio" (S.R.), which he has defined as:

$$\text{S.R.} = (pM_p)^2/pM_m$$

where pM_p and pM_m denote the negative logarithm of the metal ion concentrations dissociated from the metal principal agent complex (or precipitate) and metal masking agent, respectively.

Calculation of Cheng's Selectivity Ratio should give for any system an indication whether the principal or the masking reaction will proceed. The limiting value, according to Cheng, is approximately equal to 7·0. If S.R. is greater than 7·0 the

precipitate will be obtained, but if it is smaller then masking is more effective. Nevertheless, a more careful inspection of S.R. indicated some disadvantages of this procedure. Firstly, S.R. is not directly related to any physical magnitude and represents a rather artificially formed term. Thus it is not possible to give in any general way an intermediate range, where reasonable changes of reagent concentrations may shift an equilibrium in any direction. Furthermore, pM_m values correspond to a very special system, containing a $1M$ concentration of metal complex and stoicheiometrically equal concentrations of metal ion and free ligand. The use of conditional constants, already mentioned, is not readily applicable in S.R. calculation, but if conditional constants have been used the simplicity of S.R. calculations suffers seriously. In spite of the fact that S.R. in some instances gives experimentally verified results, cases can be found where its indications are false. This occurs, for example, in the masking of silver chloride or silver ferricyanide by ammonia, and of silver ferrocyanide by potassium cyanide. Those erroneous indications appear especially in systems for which pM_p and pM_m values do not differ significantly.

Taking into account the mentioned facts it is concluded that the Selectivity Ratio method is not sufficiently accurate in many practical systems to be of analytical value. In the present paper another method of evaluation of masking effectiveness is proposed and examples are given. This treatment will be concerned with principal reactions based on precipitation and their masking by complexation.

THEORETICAL CONSIDERATIONS

Direct comparison of stability constants of complexes and solubility products of precipitates does not give any prompt indication about the position of the equilibrium in the case where reaction products have a different metal ion:complexing (or precipitating) agent ratio. The correct conclusion can be drawn when the concentration of metal ion is calculated from the amount of ions produced from salt dissociation in the absence of any common ions. In the general case of a salt M_jA_i with a solubility product S, the metal concentration is given by:

$$[M] = \sqrt[j+i]{S(j/i)^i} \tag{1}$$

or in a logarithmic form:

$$pM = \frac{1}{j+i}[pS - i\log(j/i)] \tag{2}$$

The presence of a masking agent increases the solubility of this salt when complexing occurs. To calculate the solubility it is necessary to use in this case conditional constants instead of thermodynamic constants. The relationship between the thermodynamic and conditional constants is given by:

$$S'_{M_jA_i} = S \cdot \alpha_M^j \cdot \alpha_A^i \tag{3}$$

where $S'_{M_jA_i}$ represents the conditional solubility product, and α_M and α_A are the side reaction coefficients for the cation and anion of the salt M_jA_i, respectively.

By the term conditional solubility product, S', an expression is understood which in contrast to the thermodynamic solubility product, S—a function of free precipitate forming ions—is a function of total metal and precipitating agent in solution, independent of whether they exist as free ions or in the form of other species (*e.g.* complexed,

protonated, *etc.*), as long as they are in equilibrium with the precipitate. Thus

$$S' = [M']^j[A']^i.$$

On the other hand, the side reaction coefficients, α_M and α_A, represent the ratio of the total concentration of the metal-containing, and anion-containing species (not involved in the principal reaction, in this case precipitation) to concentration of their free ions, respectively. According to these definitions

$$\alpha_M = \frac{[M']}{[M]} \quad \text{and} \quad \alpha_A = \frac{[A']}{[A]}.$$

In special cases, when a given ion undergoes only one type of reaction or when the contribution of the other reaction can be neglected, instead of $[M']$, $[A']$, *etc.* one can use analytical concentrations of these species.

Considering the process of masking, we are interested in the total concentration $[M']$ of a metal ion in equilibrium with the precipitate, but not in the actual concentration of free (hydrated) ions, and thus we can write instead of (2), a "primed" equation:

$$pM' = \frac{1}{j+i}[pS - i \log (j/i)] \tag{4}$$

From (3) and (4) we obtain a relationship between the thermodynamic solubility products and the side reaction coefficients α_M and α_A, which in fact depend on the experimental conditions of masking. Thus the total metal ion concentration equals:

$$pM' = \frac{1}{j+i}[p(S\alpha_M^j \alpha_A^i) - i \log (j/i)] \tag{5}$$

and

$$pM' = \frac{1}{j+i}[pS - i \log (j/i)] - \frac{j}{j+i} \log \alpha_M - \frac{i}{j+i} \log \alpha_A \tag{6}$$

The pM' value, described as the masking coefficient of the salt M_jA_i is equal to the sum of three factors:

$-\frac{1}{j+i}[pS - i \log (j/i)]$ which describes the properties of the salt M_jA_i,

$-\frac{j}{j+i} \log \alpha_M$ which describes the effectiveness of cation masking,

and $-\frac{i}{j+i} \log \alpha_A$ which describes the effectiveness of anion masking.

The values of the first factor for various types of salts are summarised in Table I. On this basis it is possible to calculate it simply and rapidly for different salts; these data are given in Table II.

In the term depending on cation masking, α_M is equal to the ratio of total to free metal ion concentration and may be expressed as a function of stability constants of successive complexes:

$$\alpha_M = 1 + \beta_1[X] + \beta_2[X]^2 + \ldots \beta_n[X]^n \tag{7}$$

TABLE I—VALUES OF $\frac{1}{j+i}[pS - i \log (j/i)]$ FOR DIFFERENT SALT TYPES.

$j:i$	$\frac{1}{j+i}pS - [i \log (j/i)]$
1:4	$\frac{1}{5}pS + 0{\cdot}48$
1:3	$\frac{1}{4}pS + 0{\cdot}39$
2:5	$\frac{1}{7}pS + 0{\cdot}28$
1:2	$\frac{1}{3}pS + 0{\cdot}20$
2:3	$\frac{1}{5}pS + 0{\cdot}11$
3:4	$\frac{1}{7}pS + 0{\cdot}08$
1:1	$\frac{1}{2}pS$
4:3	$\frac{1}{7}pS - 0{\cdot}05$
3:2	$\frac{1}{5}pS - 0{\cdot}05$
2:1	$\frac{1}{3}pS - 0{\cdot}10$
5:2	$\frac{1}{7}pS - 0{\cdot}11$
3:1	$\frac{1}{4}pS - 0{\cdot}12$
4:1	$\frac{1}{5}pS - 0{\cdot}12$

TABLE II—VALUES OF $\frac{1}{j+i}[pS - i \log (j/i)]$ FOR VARIOUS SALTS.

Salt	Solubility product	$\frac{1}{j+i}[pS - \log (j/i)]$	Salt	Solubility product	$\frac{1}{j+1}[pS - \log (j/i)]$
AgOH	2×10^{-8}	3·85	$Cu(OH)_2$	$1{\cdot}6 \times 10^{-19}$	6·33
Ag_2CrO_4	$1{\cdot}3 \times 10^{-12}$	3·87	$Cu_2Fe(CN)_6$	$1{\cdot}3 \times 10^{-16}$	5·20
Ag_3PO_4	$1{\cdot}3 \times 10^{-20}$	4·85	$Cu(DDTC)_2$	$2{\cdot}8 \times 10^{-30}$	10·05
AgCl	$1{\cdot}8 \times 10^{-10}$	4·87	CuS	$8{\cdot}0 \times 10^{-36}$	17·55
$Ag_3Fe(CN)_6$	1×10^{-22}	5·38	$Cu_3(AsO_4)_2$	$7{\cdot}6 \times 10^{-36}$	6·97
AgNCS	1×10^{-12}	6·00	$Ni(OH)_2$	$2{\cdot}8 \times 10^{-16}$	5·38
AgBr	$4{\cdot}3 \times 10^{-13}$	6·13	$Ni(DDTC)_2$	$8{\cdot}5 \times 10^{-24}$	7·89
AgCN	$1{\cdot}2 \times 10^{-16}$	7·96	$Ni(DMG)_2$	2×10^{-22}	7·43
AgI	$8{\cdot}3 \times 10^{-17}$	8·04	NiS(α)	1×10^{-22}	11·0
$Ag_4Fe(CN)_6$	$1{\cdot}6 \times 10^{-41}$	8·04	$Zn(OH)_2$	$1{\cdot}9 \times 10^{-17}$	5·64
AgDDTC	$2{\cdot}6 \times 10^{-20}$	9·80	$Zn(DDTC)_2$	$1{\cdot}2 \times 10^{-17}$	5·84
Ag_2S	$5{\cdot}5 \times 10^{-51}$	16·65	ZnS	$1{\cdot}6 \times 10^{-22}$	11·4

DMG–dimethylglyoximate anion.
DDTC–diethyldithiocarbamate anion.
Values of solubility products at 25° are cited according to data listed in references 6 and 7 (for metal diethyldithiocarbamates).

where β_1, $\beta_2 \ldots \beta_n$ are successive overall stability constants, and $[X]$ is the concentration of the free masking ligand.

Calculation of α_M can easily be performed using a diagram which presents the relationship between the logarithm of α_M and the logarithm of free ligand concentration. Such diagrams have been cited in many papers dealing with conditional constants.[3,5] In Fig. 1 examples are given of ammonia, cyanide, EDTA and NTA (nitrilotriacetic acid) complexes of some metals.

In (7) the free ligand concentration, $[X]$, must be considered. If the analytical concentration of the ligand significantly exceeds the metal concentration, *i.e.* $C_A \gg C_M$, which usually happens in analytical masking reactions, and the ligand is the anion of a strong acid, or of a weak acid but at a given pH completely dissociated, the free ligand concentration is equal to its analytical concentration.

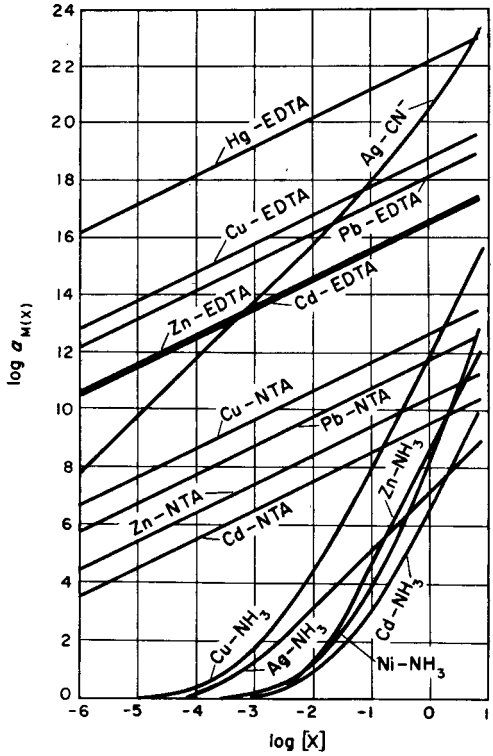

FIG. 1.—Diagrams of log $\alpha_{M(X)}$ *vs.* log [X] for some common metal complexes, plotted for $\mu = 0{\cdot}1$ and t = 25° for NH_3-complexes,[8] NTA-complexes,[9] EDTA-complexes,[10] CN^--complex.[11] When appropriate data were not available approximate estimation was applied using data in slightly different conditions.

Otherwise the free ligand concentration should be calculated from known dissociation constants

$$[X] = \frac{C_X}{\alpha_{X(H)}} = \frac{C_X}{1 + k_1[H^+] + k_1k_2[H^+]^2 + \ldots} \tag{8}$$

or

$$\log [X] = \log C_X - \log \alpha_{X(H)} \tag{9}$$

where C_X represents the analytical concentration of the masking ligand, $\alpha_{X(H)}$ is the coefficient of side reaction for acid-base ligand dissociation and k_1, k_2 . . . are successive dissociation constants of the ligand.

The last term of (6) includes the effect of masking of salt anion. It is usually performed by pH changes, masking with hydrogen ion, but may also be realised by the presence of another metal ion, which forming stable complexes with the anion A decreases its effective concentration. The value of $\alpha_{A(H)}$ is given by:

$$\alpha_{A(H)} = 1 + k_1[H^+] + k_1k_2[H^+]^2 \ldots \tag{10}$$

but can be evaluated by means of appropriate diagrams. These diagrams are given in Fig. 2 for a number of anionic precipitants. The same figure can serve for calculation of $\alpha_{X(H)}$, the side reaction coefficient for acid-base dissociation of some complexing

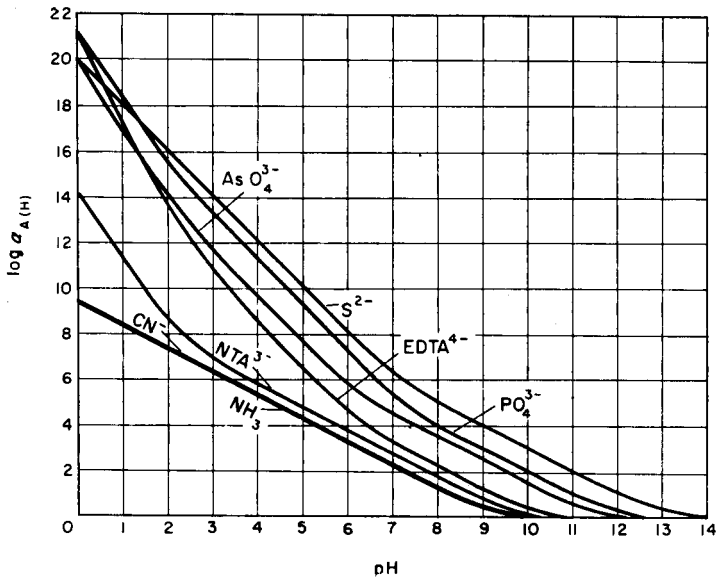

FIG. 2.—Diagrams of log $\alpha_{A(H)}$ or log $\alpha_{(XH)}$ *vs.* pH for some precipitating or complexing anions of weak acids, plotted for $\mu = 0{\cdot}1$ and t = 25°, for NH_3,[8] CN^-,[12] AsO_4^{3-},[13] PO_4^{3-},[14] S^{2-},[15] $EDTA^{4-}$,[16] NTA^{3-}.[9] When appropriate data were not available approximate estimation was applied using data in slightly different conditions.

agents used for masking. Thus obtained, log $\alpha_{X(H)}$, introduced in (9), makes possible evaluation of the logarithm of free ligand concentration.

Equation (6) makes possible the direct calculation of pM', *i.e.* the masking coefficient. The physical meaning of this magnitude is clearly seen from the derivation of (6). The resulting pM' value denotes simply the maximum analytical concentration of metal ion which can be present in given experimental conditions in equilibrium with an equivalent analytical concentration of the precipitate forming anion. Taking into account that in analytical procedures the metal concentration is usually of the order of $10^{-3} - 10^{-5}M$, complete masking can be expected if $pM' < 3$, and complete demasking if $pM' > 5$. Of course, for other conditions these limiting pM' values should be changed, respectively. An obvious significance of the pM' value enables a full understanding of the meaning of any obtained numerical pM' value. If its value is less than 3, or even negative, masking should be effective. The greater the pM' value, the more effective and complete the precipitation reaction and less disturbing the presence of a complexing agent.

EXAMPLES

To visualise more clearly the manner of calculation of pM' values and their practical application some examples are given below.

(a) For the masking of silver chloride ($pS = 9{\cdot}75$) by $0{\cdot}1M$ ammonia solution:

$$pM' = \tfrac{1}{2} \cdot 9{\cdot}8 - \tfrac{1}{2} \cdot 5{\cdot}0 = 2{\cdot}5.$$

The value of 2·5 indicates that no precipitation occurs in $0{\cdot}1M$ ammonia solution, unless the total silver concentration exceeds $10^{-2{\cdot}5}$ ($0{\cdot}003M$). In $1M$ ammonia

solution masking is more effective ($pM' = 1{\cdot}3$), and so in these conditions the silver concentration should not exceed $10^{-1{\cdot}3}$ ($0{\cdot}05M$).

(b) For the masking of silver ferricyanide ($pS = 22{\cdot}0$) by $0{\cdot}1M$ ammonia solution:

$$pM' = \tfrac{1}{4}[22{\cdot}0 - 0{\cdot}1] - \tfrac{3}{4} \,.\, 5{\cdot}2 = 1{\cdot}6.$$

The value of 1·6 indicates that more effective masking occurs than in the previous example. This is in good agreement with experimental facts. In both cited examples the precipitating anion is completely dissociated in an ammoniacal medium and therefore the last term, containing α_A, in (6) can be omitted.

(c) Consider the precipitation of copper diethyldithiocarbamate ($pS = 29{\cdot}6$) in $0{\cdot}1M$ EDTA solution at pH 10. For $0{\cdot}1M$ EDTA solution at pH 10 the logarithm of the actual free ligand concentration, according to (9), is $-1{\cdot}0 - 0{\cdot}45 = -1{\cdot}45$. Therefore, from Fig. 1, for the copper-EDTA complex $\log \alpha_{Cu(EDTA)}$ is 17·4 and

$$pM' = \tfrac{1}{3}[29{\cdot}6 + 0{\cdot}6] - \tfrac{1}{3} \,.\, 17{\cdot}4 = 4{\cdot}3.$$

In this example $\log \alpha_{DDTC}$ equals 0, because of complete dissociation of diethyldithiocarbamate at pH 10. The result indicates that, in spite of the precipitation of copper diethyldithiocarbamate, the masking is so strong that in a very dilute copper solution no precipitate can be formed, or the copper precipitation is not very complete. This is in good agreement with experiment.

(d) Consider the masking of copper arsenate ($pS = 35{\cdot}12$) by $0{\cdot}01M$ EDTA solution at pH 8·0. In this case both cation and anion are masked. The logarithm of actual free ligand ($EDTA^{-4}$) concentration is $-2{\cdot}0 - 4{\cdot}0 = -6{\cdot}0$, and $\log \alpha_{Cu(EDTA)}$ is 12·8, so that

$$pM' = \tfrac{1}{5}[35{\cdot}12 - 0{\cdot}25] - \tfrac{3}{5} \,.\, 12{\cdot}8 - \tfrac{2}{5} \,.\, 3{\cdot}5$$
$$= 7{\cdot}0 - 8{\cdot}1 - 1{\cdot}4 = -2{\cdot}5.$$

The negative value of pM' indicates very effective masking, which indeed takes place. Another conclusion from the calculation is that the decisive factor in this case is the masking of the cation, and masking of the arsenate by hydrogen ions plays a less important role.

(e) Consider the masking of silver phosphate ($pS = 19{\cdot}9$) by a hydrogen ion concentration of 10^{-3}. In this case only anion masking occurs, and therefore:

$$pM' = \tfrac{1}{4}[19{\cdot}9 - 0{\cdot}5] - \tfrac{1}{4} \,.\, 14{\cdot}2 = 1{\cdot}30$$

which can be demonstrated experimentally.

DISCUSSION AND CONCLUSIONS

The introduction of a new term, the masking coefficient, has an important significance in the theoretical prediction of the direction in which a reaction will proceed in a complicated system containing a metal ion, a complexing and precipitating agent. The masking coefficient, pM', is expressed by the negative logarithm of the total metal concentration present in solution in equilibrium with the equivalent amount of a precipitant. The easily demonstrated physical significance of this expression makes possible its application in various analytical conditions. A border-value of pM' for either masking or precipitation of 3–5 is usual.

In a calculation of this type one must be warned not to expect a very high accuracy

of pM'. This follows from the limited accuracy of determination of various constants, *i.e.* solubility products, stability constants and dissociation constants. For these, especially in the determination of solubility products a rather significant error can be involved in most cases, which is connected with difficulties of attaining a true equilibrium between a solid phase and solution. Further, constants have been evaluated in various conditions of ionic strength, temperature and presence of foreign salts, and in most cases one is obliged to compare data not exactly corresponding to each other. All of these parameters influence the calculated masking coefficient and usually the reliability of the results is of the order of one, which corresponds to one order of concentration of the metal in solution.

The pM' value, taken with proper caution in accordance with the above mentioned facts, gives correct indications when the total metal concentration (not precipitated) and total precipitant concentration are equivalent. In practice this condition corresponds to a situation when one is going to dissolve a pure precipitate (not contaminated with any of the precipitate ions) in a masking agent. In some cases the equilibrium in such a system can be additionally shifted by adding an excess of precipitant. Theoretically, a sufficiently large excess can in any case cause precipitation, but practically the analyst is limited by conditions actually encountered. In the view of the present author, the properties of a system are most adequately described in the manner here proposed.

Acknowledgement—The author is greatly indebted to Professor Kemula for helpful and stimulating discussion concerning this work.

Zusammenfassung—Der "Maskierungskoeffizient" wurde als neuer Begriff abgeleitet und auf analytische Probleme im Zusammenhang mit der Maskierung von Fällungsreaktionen angewandt. Der Koeffizient is durch die folgende Gleichung definiert

$$pM' = \frac{1}{j+i}[pS - i\log(j/i)] - \frac{j}{j+i}\log\alpha_M - \frac{i}{j+i}\log\alpha_A$$

Das erste Glied bezieht sich auf Eigenschaften des Niederschlages, das zweite Glied auf die Maskierung des Kations und das dritte auf die Maskierung des Anions. Wenn geeignete Diagramme konstruiert wurden um die Seitenreaktionkoeffizienten $\log\alpha_M$ und $\log\alpha_A$ zu berechnen ist es leicht möglich alle Berechnungen durchzuführen. Die Vorraussagen (aufgrund der Berechnungen) ob Maskierung oder Fällung eintritt wurden experimentell geprüft und bestätigt. Einige Beispiele für Berechnungen analytisch gut bekannter Systeme werden gezeigt.

Résumé—Un nouveau terme, le "coefficient de dissimulation", a été introduit pratiquement dans les études analytiques mettant en jeu la formation de complexes dans les réactions de précipitation. Ce coefficient s'exprime par l'équation:

$$pM' = \frac{\mathrm{I}}{j+i}\left[pS - i\log\left(\frac{j}{i}\right)\right] - \frac{j}{j+i}\log\alpha_M - \frac{i}{j+i}\log\alpha_A$$

dans laquelle le premier terme se rapporte seulement aux propriétés du précipité, le deuxième à la dissimulation du cation, le dernier à la dissimulation de l'anion. Si des diagrammes convenables ont été préparés pour le calcul des "coefficients de réaction secondaire", $\log\alpha_M$ et $\log\alpha_A$, tous les calculs peuvent etre effectués facilement. L'utilité du "coefficient de dissimulation", pour prévoir si la formation de complexes ou la précipitation va se produire, a été confirmée par l'expérience. Des exemples de calcul de ce coefficient, pour des réactions analytiques bien connues, sont donnés.

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DETERMINATION OF ^{90}STRONTIUM IN BONE*

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Summary—A procedure for the assay of ^{90}Sr in bone is presented, which is applicable for the determination of low levels of ^{90}Sr using ordinary counting equipment. The procedure involves extraction of the ^{90}Y daughter into a solution of dibutylphosphoric acid in scintillation fluid from a dilute nitric acid solution containing ^{90}Sr which had been concentrated from bone by the standard fuming nitric acid procedure. The extracted ^{90}Y in scintillation fluid can be counted directly without further preparation.

INTRODUCTION

NUMEROUS reports [1–5] on methods for the assay of ^{90}Sr in biological materials have been published over the past few years. Justification of adding still another to the literature lies in a novel approach to the problem, which simplifies ^{90}Sr assay in bone considerably, allows the use of ordinary counting equipment, and has potential application in the assay of other radioisotopes. The unique aspect of this procedure is extraction of the isotope to be assayed into a scintillation medium which can be counted without further preparation.[6]

In ^{90}Sr application, the procedure involves extraction of the ^{90}Y daughter by dibutylphosphoric acid in scintillation fluid from a dilute nitric acid solution containing ^{90}Sr which had been concentrated from bone by the standard fuming nitric acid procedure.[6] The basis for this procedure is an adaptation of a method for preparation of ^{90}Y by Dyrrsen.[7]

EXPERIMENTAL

Procedure

(1) To 100 g of bone ash powder add 50 ml of strontium carrier solution (10 mg of Sr^{2+}/ml in distilled water) and 30 ml of distilled water, followed by 225 ml of yellow fuming nitric acid (95%). Stir with a mechanical stirrer for 1 hr to ensure complete solution of the bone ash and precipitation of the strontium.

(2) Filter through a medium-grade sintered-glass suction filter, and discard the filtrate. Wash the precipitate with 80% nitric acid.

(3) Dissolve the precipitate by passing hot distilled water through the filter.

(4) Bring the solution of dissolved precipitate to a volume of approximately 50 ml and adjust to pH 1.

(5) Store the solution for 14 days for establishment of ^{90}Sr/^{90}Y equilibrium.

(6) Transfer the sample to a separatory funnel, and shake for 5 min with 40 ml of a mixture of 2·5% dibutylphosphoric acid, 0·05% POPOP,‡ and 0·5% *p*-terphenyl in toluene. Note the time of extraction. The dibutylphosphoric acid is purified by the method of Stewart and Crandall.[8]

(7) Separate the aqueous phase. This can be saved for repeated milking, if checks are necessary. Dry the organic portion with silica gel for approximately 15 min.

(8) Draw off 30 ml of organic phase into a 10-dram counting vial and count in a standard liquid scintillation counting set-up.[9] Note the counting time.

(9) Correct for decay of the ^{90}Y between time of extraction and time of counting.

(10) Recount the yttrium fraction at least twice more over a period of 1 week to determine the decay time of activity as a check on identity of the ^{90}Y.

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‡ 2,2′-*p*-Phenylenebis(5-phenyloxazole).

RESULTS AND DISCUSSION

The following studies and measurements were carried out to evaluate the procedure and to judge its merits.

Counting and extraction efficiency

Known amounts of ^{90}Sr were added to 0·1*N* nitric acid solution and extracted and counted by the method described above. This procedure was performed each day a "run" was done on a series of unknowns, to check reagents and counter. Results of 18 different determinations showed an average recovery of 90·58 ± 1·73%. When the nitric acid solution was re-extracted shortly after the first extraction, less than 1% of ^{90}Y was obtained, which indicated an essentially complete extraction in the first pass. The 10% or so diminution from the expected values undoubtedly was due to counting inefficiency.

*Recovery**

Each set of determinations included a blank consisting of tricalcium phosphate "spiked" with ^{90}Sr. This was run through as a check for over-all recovery in the procedure. The largest and most variable loss was found in the step involving separation of strontium and calcium by precipitation with fuming nitric acid. Final values were corrected by this recovery factor (see Table I).

TABLE I.—RECOVERY OF ^{90}STRONTIUM

^{90}Sr added, *d/min*	^{90}Sr recovered, *d/min*	Efficiency, %
35,774	32,898	91·96
39,384	35,032	88·95
76,799	67,506	87·90
41,025	33,673	82·08
13,128	9,900	75·41
16,410	11,983	73·02
147,149	119,529	80·90
97,147	79,048	81·37
	Average	82·70
	Standard deviation σ ±	6·70

Reproducibility

Table II shows the results for bone samples assayed in triplicate.

Sensitivity

To a large extent, interest in ^{90}Sr determinations lies in low-level samples. In our study, sample sizes of 100 g were used to gain sensitivity. However, smaller samples could have easily been used for good counting statistics without recourse to complicated counting with good equipment and prolonged counting times. Table III

* John Harley of the New York Operations Health and Safety Laboratory points out in a personal communication that a much more desirable recovery procedure can be accomplished by adding ^{85}Sr to each sample and then counting the strontium-separated solution in a scintillation γ-counter. In this way, each sample can be checked for recovery rather than each batch of samples, as was done in the procedure above.

shows the counting times necessary to obtain a given accuracy for samples at different levels of activity. Calculations are based on the following considerations:

(1) Fifty-g bone samples.
(2) Background equal to 70 c/min.
(3) Percentage standard deviation equals

$$\frac{100\sqrt{\frac{R_{(S+B)}}{t_{(S+B)}}+\frac{R_B}{t_B}}}{R_S} \quad \text{and} \quad \frac{t_{(S+B)}}{t_B}=\sqrt{\frac{R_{(S+B)}}{R_B}}$$

where $R_{(S+B)}$ = counting rate of sample plus background
R_B = counting rate of background
R_S = counting rate of sample
$t_{(S+B)}$ = time for counting sample plus background
t_B = time for counting background

TABLE II.—REPRODUCIBILITY OF RESULTS

Type of sample	Year	Place	^{90}Sr, *d/min/g*
Reindeer antler	1958	Alaska, USA	85·32; 86·38; 93·28
Elk antler	1956	Missouri, USA	23·25; 23·24; 22·17; 23·37; 23·46
Deer antler	1958	New Mexico, USA	12·61; 12·36; 12·06
Deer antler	1955	New Mexico, USA	5·35; 6·37; 6·80
Deer long bone	1957	New Mexico, USA	8·31; 9·80; 9·40; 10·08
Elk antler	1957	Colorado, USA	12·84; 12·13; 13·47
Elk skull	1957	Colorado, USA	17·07; 17·88; 18·13
Elk antler	1956	New Mexico, USA	8·47; 8·16; 8·45
Moose antler	1953	Yukon, Canada	2·21; 2·17; 2·30
Caribou antler	1953	Yukon, Canada	4·11; 5·35; 4·99

TABLE III.—COUNTING TIMES REQUIRED TO OBTAIN GIVEN ACCURACY

^{90}Sr content, *d/min/g*	Standard deviation, %	Counting time, *min*
5	10	< 1
	5	1·5
	1	35
1	10	6·4
	5	26
	2	160
0·5	10	24
	5	100
	2	608

As can be seen from the table, use of 50-g samples gives good counting statistics with reasonable counting times at the 1-d/min/g level of ^{90}Sr. At levels below this, it is advisable to use larger samples; at levels above this, smaller samples can be used advantageously.

Interfering isotopes

No specific attempt has been made to eliminate interfering radioisotopes in the procedure described above, since it was unnecessary in the studies judged by purity of ^{90}Y extracted. However, under certain conditions (*i.e.*, work with fresh fission product mixtures), it might be necessary to take steps to remove interfering activity. Both the strontium nitrate separation and the organic solvent extraction remove most interfering metals. However, lanthanum, lead, thorium, and radium daughters can appear in the final counting solution unless suitable measures are taken (*i.e.*, unless they are eliminated). ^{140}Lanthanum can be eliminated by removing ^{140}Ba through use of the chromate separation procedure described in the Harwell ^{90}Sr assay method. Lead and thorium are readily removed by a preliminary separation of the strontium solution with dibutylphosphoric acid/scintillator solution before the growth period of the yttrium. Radium daughters can be eliminated as interfering activity by boiling the strontium solution for 1 hr just before the final extraction of ^{90}Y.

Zusammenfassung—Eine Methode zur Bestimmung von geringen Mengen ^{90}Sr in Knochen unter Verwendung gewöhnlicher Zähleinrichtungen wird beschrieben. Das Tochterelement ^{90}Y wird in eine Lösung von Dibutylphosphorsäure in Scintillationflüssigkeit extrahiert und zwar aus der Lösung die das Strontium in verdünnter Salpetersäure enthält, wie es nach der üblichen Sappertsäureveraschung vorliegt. Das Yttrium wird ohne weitere Behandlung direkt gezählt.

Résumé—Les auteurs présentent une méthode de dosage de ^{90}Sr dans les os; cette méthode s'applique à détermination de faibles teneurs en ^{90}Sr permettant d'utiliser un équipement de comptage ordinaire. Le procédé met en jeu l'extraction de ^{90}Y formé par une solution d'acide dibutylphosphorique dans un fluide à scintillation à partir d'une solution d'acide nitrique diluée contenant ^{90}Sr; ce dernier a été concentré par la méthode courante de l'acide nitrique fumant. ^{90}Y extrait dans le fluide à scintillation peut être compté directement sans préparation ultérieure.

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ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF SCANDIUM WITH TIRON

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Summary—A method is described for the spectrophotometric determination of 3–250 μg of scandium with tiron. The molar extinction coefficient of scandium in an acetate buffer (pH 6·0) is 8×10^3 at 310 mμ. Small amounts of aluminium, titanium, iron, cerium, molybdenum, thorium and zirconium seriously interfere. Organic anions such as oxalate, citrate, tartrate and malate form complexes with scandium. Both 1:1 and 1:3 complexes of scandium with tiron are suggested.

WELL established colour reagents are lacking for the spectrophotometric determination of scandium. Alizarin red S appears to be the reagent that has been utilised most successfully. A detailed separation procedure has been achieved for this reagent.[1] Scandium also gives a sensitive fluorescence reaction with morin[2] in neutral or weakly acidic solution. Recently, an oxine method[3] has been described, although it is highly unselective. A new photometric method for scandium using tiron is suggested in this paper.

Tiron (disodium 1,2-dihydroxybenzene-3,5-disulphonate) was first proposed by Yoe[4,5] as an analytical organic reagent for the determination of titanium and iron. The composition of their complexes has been determined by Harvey and Manning.[6,7] Schwarzenbach and Willi[8] have evaluated the stability constants of tiron-iron complexes by potentiometric and photometric methods. Photometric methods using tiron have also been described for the determination of traces of cerium,[9] niobium,[10] molybdenum[11,12] and uranium.[13]

Tiron reacts with scandium to give a colourless complex absorbing strongly at 310 mμ. The reaction is not selective, like other reagents for scandium, but it is very sensitive.

EXPERIMENTAL

Apparatus

A Hitachi Model EPU–2A spectrophotometer was used for making precise absorbance measurements at a given wavelength. Matched silica cells of 1·00-cm optical path were used. Measurements of pH were carried out with a Toa Dempa Model HM-5 pH-meter with glass and calomel electrodes. In the potentiometric titration of tiron in the absence of and in the presence of metal ions, measurements were made at 30° $\pm$ 0·05°.

Reagents

Standard scandium solution: 153·38 mg of scandium oxide (Yokosawa Chemical Co., Ltd.) were dissolved in 20 ml of concentrated hydrochloric acid and the solution was diluted to 100 ml with water. The strength of the stock solution was further checked by titration against ethylenedinitrilotetraacetate (EDTA) previously standardised against analytical reagent primary standard zinc metal, using Xylenol Orange[11,12] as indicator. This standard stock solution (1000 ppm of scandium) was diluted further as required.

0·10% *Tiron solution:* Prepared by dissolving 0·100 g of tiron (disodium 1,2-dihydroxybenzene-3,5-disulphonate) in 100 ml of water. The reagent stock solution was stable for at least 3 months.

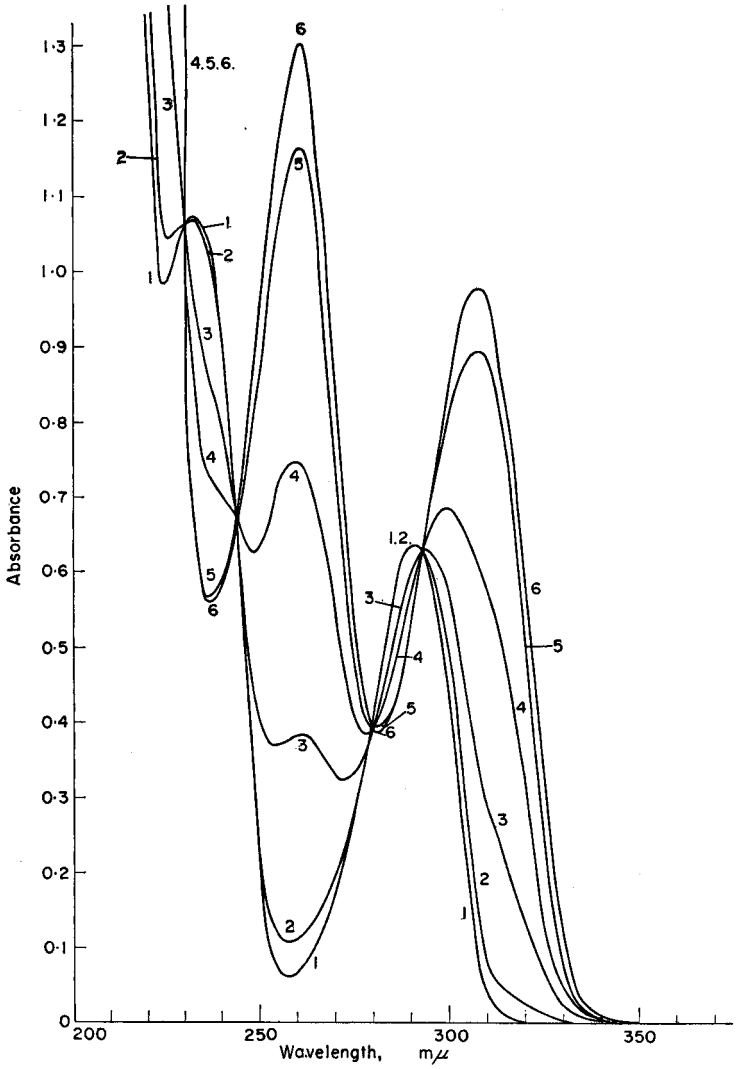


FIG. 1.—Absorption spectra for tiron at various pH values (concentration of tiron: $1{\cdot}86 \times 10^{-7}$ mole/litre):
(1) pH 5·90, (2) pH 6·80, (3) pH 7·77,
(4) pH 8·30, (5) pH 9·30 and (6) pH 10·80.

Solutions of diverse ions: The solutions of salts used in studying the effect of various ions were prepared to contain 1 mg/ml of the desired ion. All inorganic chemicals used were of reagent grade quality.

Acetate buffer solution (*pH* 6·0): Prepared by mixing 16 parts of 0·1*N* sodium acetate with 1 part of 0·1*N* acetic acid.

Ammonia-ammonium chloride buffer (*pH* 10·5): Prepared by mixing 32 parts of 0·1*N* ammonia solution with 1 part of 0·1*N* ammonium chloride.

Procedure:

Transfer the sample solution (dilute perchloric or hydrochloric acid solution) containing 3–250 μg of scandium to a 50-ml volumetric flask. Add 3 ml of 0·1% tiron solution and 20 ml of acetate buffer solution to adjust the pH to 6·0. If the acidity of the sample solution is too high, neutralise excess of acid with sodium hydroxide solution. After diluting to the mark with water and mixing, measure the absorbance of the solution in a 1-cm silica cell at 310 mμ against a reference solution containing the same amounts of tiron and the other reagents.

RESULTS AND DISCUSSION

Absorption spectra

To investigate the relation between pH and the absorption spectra, two series of solutions that contain tiron only and tiron plus scandium were prepared and scanned

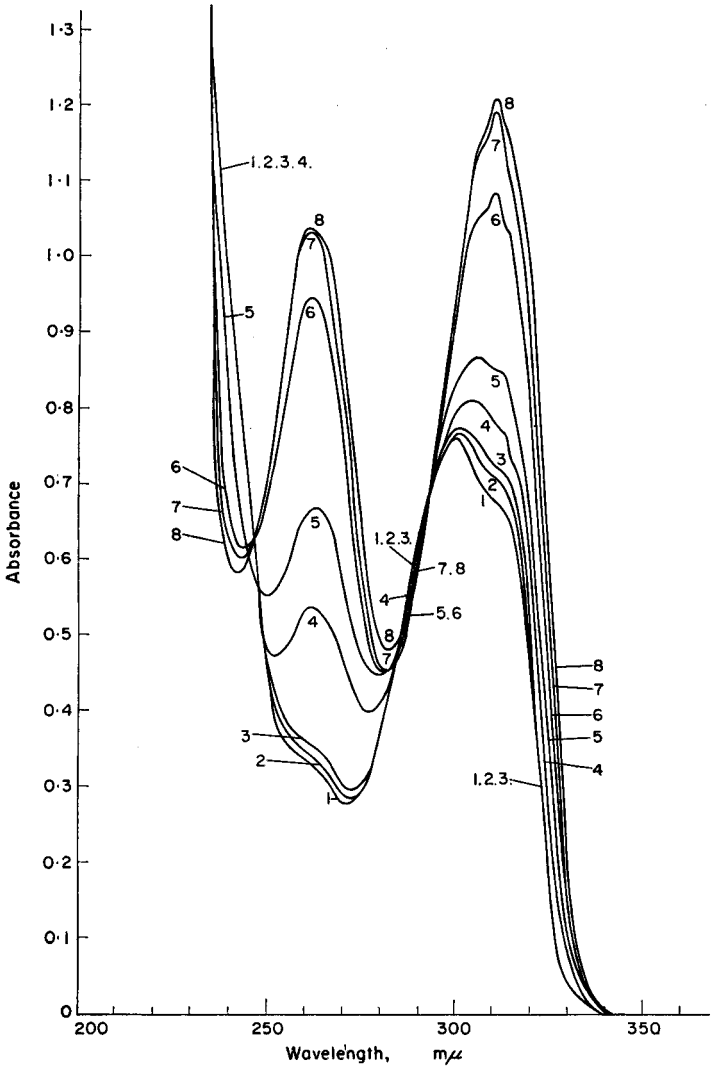


FIG. 2.—Absorption spectra for the scandium-tiron complex at various pH values (concentration of scandium: $7{\cdot}44 \times 10^{-8}$ mole/litre; concentration of tiron: $1{\cdot}86 \times 10^{-7}$ mole/litre):
(1) pH 3·61, (2) pH 5·92, (3) pH 6·46, (4) pH 7·58,
(5) pH 7·82, (6) pH 8·63, (7) pH 9·59 and (8) pH 11·30.

over the wavelength range from 220 to 350 mμ. The absorption spectrum of each solution was measured against water as a reference. The results are illustrated in Figs. 1 and 2. As shown in Fig. 1, the spectra of tiron exhibit pronounced absorption over the ultraviolet region with two peaks at 230 mμ and 290 mμ in the acidic media (<pH 6·80) and with two peaks at 260 mμ and 308 mμ in the alkaline ones. The complex

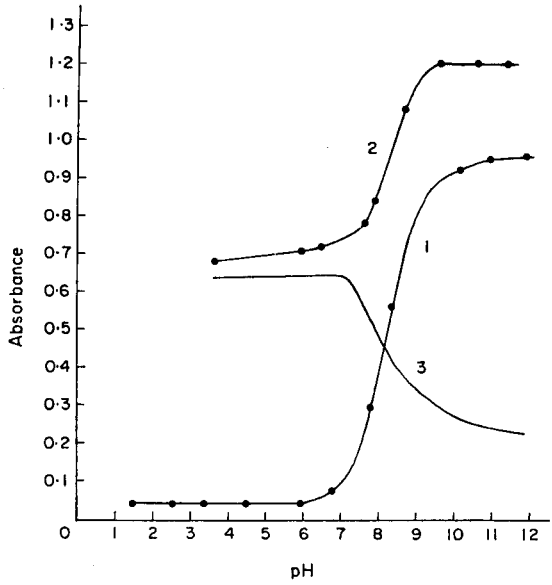


FIG. 3.—Effect of acidity on absorbance at 310 mμ.
(1) Tiron ($1{\cdot}86 \times 10^{-7}$ mole/litre) against water.
(2) Tiron ($1{\cdot}86 \times 10^{-7}$ mole/litre) plus scandium ($7{\cdot}44 \times 10^{-8}$ mole/litre) against water.
(3) Reagent blank.

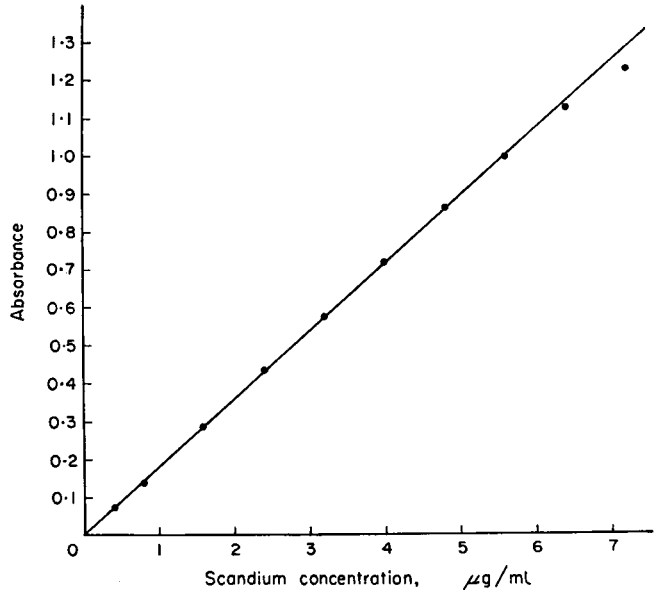


FIG. 4.—Scandium calibration curve.

also exhibits strong absorption in the ultraviolet region with a peak at 310 mμ over a wide range of pH values.

Effect of pH

pH has a considerable effect on the absorption of the complex at 310 mμ, as illustrated in Fig. 3. Curve 1 indicates the effect of pH on the absorbance of tiron measured

against water at 310 mμ and curve 2 the effect on that of the complex. Subtracting curve 2 from 1, curve 3 results, which is the net absorbance of the complex. At pH values ranging from 7 to 3·5, the absorbance of the complex is almost constant.

Effect of tiron concentration

A study of the variation in the net absorbance (310 mμ) of the complex at pH 6·0 as a function of the amount of tiron added indicated that reaction is complete when at least 3 times as much tiron as the amount of scandium is present.

Time of standing

The scandium-tiron complex forms almost instantly at pH 6·0 and an essentially constant absorbance reading is obtained over a period of at least 2 hr.

Conformity to Beer's law

The linearity between the absorbance of the scandium-tiron complex and the scandium concentration was tested by varying the scandium concentration in a number of test solutions and measuring the absorbances at a wavelength of 310 mμ and pH 6·0. As shown in Fig. 4, the absorbance is proportional to the scandium concentration in the range of 0·05 to at least 5 ppm of scandium (3–250 μg per 50 ml). At 310 mμ the molar extinction coefficient is 8×10^3. The spectrophotometric sensitivity is estimated to be 0·05 μg of scandium/cm^3, corresponding to $\log I_0/I = 0{\cdot}001$.

Composition of the scandium-tiron complexes

The composition of the scandium-tiron complexes was determined by Job's method of continuous variation. The experiments were carried out at room temperatures ranging from 25 to 29°. Two series of eleven solutions were prepared, each containing scandium and tiron in different proportions, but in each solution the combined concentration of scandium and tiron was always $9{\cdot}03 \times 10^{-6}$ mole per 50 ml. These two series of solutions were adjusted to pH 6·0 and 10·5 by adding the acetate and ammonia buffer solutions, respectively. Ten ml of 0·1*N* sodium acetate solution were added to each solution (pH 8·5, 10·5, 12·7) to prevent hydrolysis of scandium.

The results confirm the presence of two types of complex according to the pH range. Throughout the survey by Job's method over the possible pH range it is indicated that 1:1 and 3:1 complexes in ligand: metal ratio can exist below pH 6·5 and above 8·5, respectively. Typical Job's continuous variation plots at pH 6·0 and 10·5 are illustrated in Figs. 5 and 6, respectively.

Potentiometric titration curves of solutions containing 1 and 3 moles of ligand per mole of scandium offer additional information about the nature of the chelating process.

The curves for the system are shown in Fig. 7, in which the abscissa denotes the number of moles of standard base added per mole of scandium ion (n). It is found from curve 1 that the reaction of scandium^{III} ions with tiron results in the liberation of 1 mole of hydrogen ion per mole of scandium ion before the first pronounced inflection occurs at $n = 1$. The first reaction step corresponds to the formation of the 1:1 metal chelate in accordance with the reaction:

$$(HO)_2L^{2-} + Sc(H_2O)_6^{3+} + OH^- \rightarrow ScO(OH)L{\cdot}(H_2O)_5 + 2H_2O$$

where $(HO)_2L^{2-}$ denotes tiron in solution. Further reaction with a second mole of hydroxyl ion is indicated by the fact that the titration curve has an additional buffer region and a second inflection at 2 moles of base per mole of scandium ion.

This reaction cannot be explained as being associated with the formation of a higher

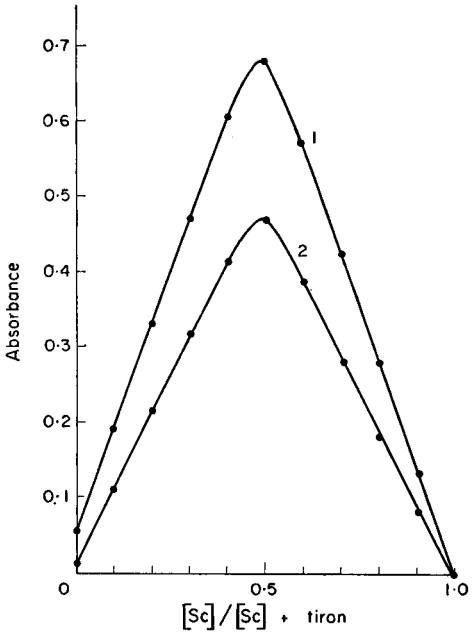


FIG. 5.—Continuous variation plot for the scandium-tiron complex at pH 6·00: (1) 310 mμ, and (2) 320 mμ.

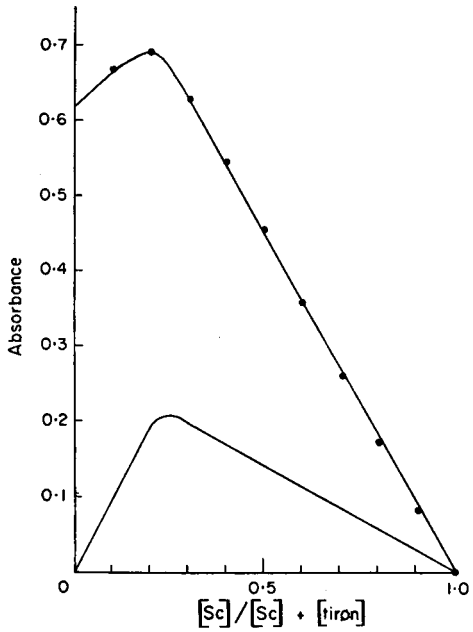
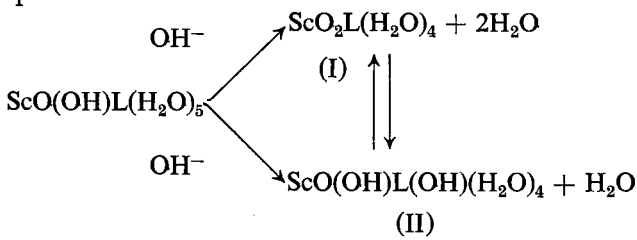


FIG. 6.—Continuous variation plot for the scandium-tiron complex at pH 10·48.

chelate. If the formation of a higher chelate results, the following disproportionation reaction should be postulated:

$$ScO(OH)L + OH^- \rightarrow \tfrac{1}{3}Sc_2[O(OH)L]_3 + \tfrac{1}{3}Sc(OH)_3.$$

No precipitation occurs throughout the titration range. Therefore, the possibility of the formation of a 2:3 chelate can be eliminated. As a result possible reaction at $n = 2$ appears to be such that the second reaction step involves the neutralisation of a hydrogen ion from either the co-ordinated water molecule or the co-ordinated phenolic hydroxy group:



Structure I involves the species resulting from neutralisation of a hydrogen from the co-ordinated phenolic hydroxy group and structure II corresponds to a hydroxo complex species resulting from neutralisation of a hydrogen from the co-ordinated

water molecule. Structures I and II are tautomeric and the metal chelate in solution may actually be an equilibrium mixture of the two forms.

Titration curve 2 of the solution containing a 1:3 mole ratio of scandium and tiron also has an inflection point at n = 1, in accordance with the formation of a 1:1

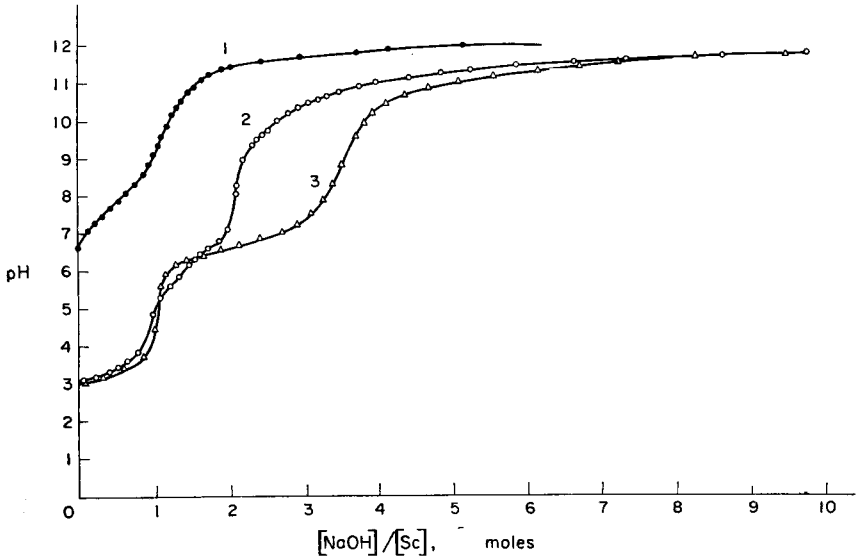


FIG. 7.—Titration curves of tiron and tiron-scandium complexes in 0·1*N* potassium chloride solution:
(1) Tiron = 10^{-3} mole/litre.
(2) Tiron: Scandium = $3{\cdot}71 \times 10^{-4}$ mole/litre.
(3) Tiron = $1{\cdot}11 \times 10^{-3}$ mole/litre and scandium = $3{\cdot}71 \times 10^{-4}$ mole/litre.

chelate in solution. A rather obscure second inflection point is observed at n = 3. The second reaction step of the 1:3 titration may be represented by:

$$ScO(OH)L(H_2O)_5 + 2(HO)_2L + 2OH^- \rightarrow Sc[O(OH)L]_3(H_2O)_3 + 4H_2O.$$

The formation of a monohydroxo complex can occur, however, above pH 7, as indicated in the titration of the solution containing a 1:1 metal:ligand ratio. The possibility could not be overlooked of the formation of higher hydroxo complexes including two or three hydroxyl groups in the pH range above 9. Competitive formation of these complexes against that of $Sc[O(OH)L]_3(H_2O)_3$ may be thought of as a possible cause for the rather obscure occurrence of the second inflection points in the titration of the 1:3 mixture.

Effect of diverse ions

The effect of many ions on the determination of scandium was studied under the conditions used in the proposed procedure. The results are summarised in Table I.

Table I suggests that the common cations known to react with tiron seriously interfere. The anions in Table I also diminish the absorbancy of solutions. Chloride, perchlorate, and nitrate do not interfere.

To overcome difficulties from interfering ions the following procedure for separating scandium by a cation exchanger seems to be valuable.

TABLE I.—EFFECT OF DIVERSE IONS

Interfering ions	Ions added, $\mu g/ml$	Sc found,[a] $\mu g/ml$	Ions added, $\mu g/ml$	Sc found,[b] $\mu g/ml$
Al^{3+} (as nitrate)	3	6·50	30	∞
Sn^{4+} (as sulfate)	3	3·82	30	0·00[c]
Fe^{3+} (as chloride)	3	6·72	30	∞
Fe^{2+} (as chloride, ascorbic acid added)	3	6·42	30	5·79
Ce^{4+} (as nitrate)	3	4·34	30	6·95
La^{3+} (as oxide)	3	4·15	30	2·04
Mo^{6+} (as ammonium molybdate)	3	4·11	30	6·51
Th^{4+} (as nitrate)	3	4·73	30	7·00
Zr^{4+} (as oxychloride)	3	4·63	30	∞
Oxalate	3	3·48	30	0·20
Citrate	3	3·12	30	0·00
Tartrate	3	3·08	30	0·74
Malate	3	2·84	30	0·42
NH_4SCN	3	3·88	30	1·22

[a] 4·05 μg/ml of Sc taken.
[b] 1·35 μg/ml of Sc taken.
[c] Because the 1:6 titanium-tiron complex is suggested by Yoe, free reagents in the test solution may not exist.

Prepare a column, 20 cm in length and 1·1 cm in diameter and packed at the bottom with glass wool. Slurry 10 g of the cation-exchange resin (Diaion SK 1, styrene-base strong acid type, equivalent to Dowex 50–x8, 100–200 mesh, hydrogen form) into the column. The height of resin bed usually amounts to approximately 16 cm. Before use the column is conditioned by running a solution, 2*M* in ammonium thiocyanate and 1*M* in hydrochloric acid, then converted to the hydrogen form with 3*M* hydrochloric acid and washed with water. Load the sample solution containing 1–2 mg of scandium onto the column. Rinse the column with small amounts of water. For separating scandium from rare earths and thorium elute with a solution 1*M* in ammonium thiocyanate and 0·5*M* in hydrochloric acid, collecting the effluent containing scandium. Rare earths and thorium remain on the column. If necessary, they are detached from the column by elution with a solution 2*M* in ammonium thiocyanate and 0·5*M* in hydrochloric acid. Iron and aluminium can be readily eluted by the same elutriant as for scandium prior to leakage of scandium. Iron may effectively be eluted even with more dilute elutriant, say 0·5*M* in ammonium thiocyanate and 0·5*M* in hydrochloric acid. Scandium is then detached with 3*M* hydrochloric acid or, more easily, with the solution 2*M* in ammonium thiocyanate and 0·5*M* in hydrochloric acid. The separation of titanium and zirconium is also possible. Titanium is completely separated from scandium by eluting it with the elutriant 0·5*M* in ammonium thiocyanate and 0·5*M* in hydrochloric acid, leaving scandium remaining on the column. To separate zirconium the use of an

TABLE II.—SEPARATION OF SCANDIUM FROM INTERFERING IONS

Interfering ion	Ion added, *mg*	Sc added, *mg*	Sc found, *mg*
Al^{3+}	5·60	2·37	2·43
Ti^{4+}	1·50	2·27	2·29
Fe^{3+}	14·14	2·40	2·24
La^{3+}	15·12	2·27	2·42
Sm^{3+}	4·73	2·27	2·27
Th^{4+}	4·76	2·37	2·37
La^{3+} + Th^{4+}	15·12 + 8·52	2·27	2·27
Zr^{4+}	2·70	2·27	2·21

elutriant 1*M* in ammonium thiocyanate and 1*M* in hydrochloric acid is recommended. Zirconium is eluted prior to scandium. To assure complete separation of zirconium, however, a somewhat longer column than that suggested above is desirable.

After destroying the ammonium thiocyanate with nitric acid and fuming with perchloric acid, scandium can be successfully determined photometrically with tiron. Scandium is also conveniently determined by an EDTA titration method in the presence of thiocyanate using Xylenol Orange as indicator at pH 3·5. Table II lists some results on the separation of scandium from interfering ions given in Table I. Scandium was determined by the EDTA titration method in the presence of ammonium thiocyanate. A detailed account of the ion-exchange separation of scandium will be published later.

Zusammenfassung—Eine Methode zur Bestimmung von 3–250 μg Scandium mit Tiron wird beschrieben. Der molare Absorptionskoeffizient des Scandiumkomplexes in Acetatpuffer von pH 6 beträgt 8000 bei 310 mμ. Bereits kleine Mengen von Al, Ti, Fe, Ce, Mo, Th und Zr stören beträchtlich. Oxalat-, Citrat-, Tartrat- und Malation stören durch Komplexierung des Scandiums. Evidenz für 1:1 und 1:3 Komplexe zwischen Scandium und Tiron wird nachgewiesen.

Résumé—Les auteurs décrivent une méthode de dosage spectrophotométrique de 3 à 250 μg de scandium par le tiron. Le coefficient d'extinction molaire du scandium en tampon acétate (pH 6,0) est de $8 . 10^3$ à 310 mμ. De faibles quantités d'aluminium, de titane, de fer, de cérium, de molybdène, de thorium et de zirconium gênent sérieusement. Les anions organiques comme les acides oxalique, citrique, tartrique et malique forment des complexes avec le scandium. Les auteurs suggèrent la formation des complexes scandium-tiron 1/1 et 1/3.

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SALTING-OUT CHROMATOGRAPHY—VIII§

ANALYSIS OF MIXTURES OF MONOALKYL ESTERS OF ALKANE-PHOSPHONIC ACIDS AND DIALKYL ESTERS OF PHOSPHORIC ACID

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Summary—A method is described for the determination of each compound in a mixture of 19 acids of phosphorus.

THIS investigation was concerned with the analysis of mixtures of the phosphorus-containing decomposition products of certain insecticides and related compounds. The compounds studied were orthophosphoric acid, methanephosphonic acid, the dialkyl esters of orthophosphoric acid and the monoalkyl esters of the alkanephosphonic acids, The alkyl groups found in these compounds were methyl, ethyl, isopropyl and n-butyl, hereinafter designated as Me, Et, Pr, and Bu, respectively.

The marked similarity of chemical and physical properties of these compounds made it unlikely that quantitative separation of them could be achieved by paper chromatography. Attempts to use gas chromatography[1] were unsuccessful because the compounds were insufficiently volatile. Anion-exchange chromatography also failed to yield quantitative separations[1] because of the very small differences in the ionisation constants of the acids and in the selectivity coefficients of their conjugate bases.[1–3] As reported previously[4] for the analysis of a simpler mixture of organophosphorus acids, salting-out chromatography with low-capacity Dowex cation-exchange resins was found to be more successful than anion-exchange chromatography.

DEVELOPMENT OF THE METHOD

Preliminary elutions through the previously described low-capacity cation exchangers[4] indicated that the elution graphs were essentially Gaussian if the column was maintained at 50° and the flow rate at about 0·15 cm per min. These conditions were used throughout the work.

Evaluation of C *and* P

Each phosphorus compound was eluted individually several times, each time with a different concentration of LiCl and/or HCl. From the resulting elution graphs, the values of C and P were calculated for each compound with each eluent. C denotes the distribution ratio, and P the number of plates per cm of column. The equations for calculating these parameters from an elution graph are given elsewhere.[5,6] The values of P depended on the compound being eluted and on the eluent. The average P was 20. The values of C are given in Table I.

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§ Part VII—see reference 4.

Major elution

From these values, the minimum length of column required for a quantitative separation of all 19 compounds in one elution was calculated.[5,6] The calculations revealed that the quantitative separation of compounds 5 and 6 (Table I) with 4*M* LiCl + 1*M* HCl (P = 20) requires a column 5,100 cm long. This figure demonstrates

TABLE I.—VALUES OF LOG C OF THE PHOSPHORUS ACIDS

No.	Compound	Group	No LiCl 1*M* HCl	2 *M* LiCl 1 *M* HCl	4 *M* LiCl 1 *M* HCl	6 *M* LiCl 1 *M* HCl	8 *M* LiCl 1 *M* HCl
1	H_3PO_4				−0·018		+0·056
2	$MePO(OH)_2$				+0·216	0·301	0·417
3	MePO(OH)OMe	1		0·425	0·479	0·583	0·700
4	$HOPO(OMe)_2$	1		0·400	0·476	0·648	0·927
5	MePO(OH)OEt	2		0·550	0·715	0·811	0·997
6	EtPO(OH)OMe	2		0·553	0·694	0·823	1·045
7	MePO(OH)OPr	3		0·673	0·870	1·033	1·299
8	EtPO(OH)OEt	3		0·725	0·892	1·093	1·387
9	$HOPO(OEt)_2$	3	0·505	0·741	0·934	1·196	
10	EtPO(OH)OPr	4	0·690	0·865	1·045	1·314	
11	PrPO(OH)OEt	4	0·740	0·899	1·107	1·346	
12	MePO(OH)OBu	5	0·789	1·029	1·250	1·525	
13	$HOPO(OPr)_2$	5	0·763	1·045	1·309	1·643	
14	BuPO(OH)OMe	5	0·832	1·049	1·281	1·551	
15	BuPO(OH)OEt	6	0·991	1·236	1·509	1·823	
16	EtPO(OH)OBu	6	1·000	1·250	1·516	1·841	
17	PrPO(OH)OBu		1·186	1·477			
18	$HOPO(OBu)_2$		1·405	1·812			
19	BuPO(OH)OBu		1·467	1·820			

the impracticability of separating all 19 compounds in a single elution. Further calculations revealed that a column 50 cm in length should isolate compounds 1, 2, 17, 18 and 19 from all the others and also separate the others into six groups of "inseparable compounds" as indicated in Table I. It was therefore decided to use a 50-cm column for the "major elution" and to devise other methods for the determination of the individual compounds in each of the six groups.

It was very desirable to change the concentration of LiCl in the eluent during the major elution. If dilute LiCl were used exclusively, the more hydrophilic compounds of phosphorus would be eluted very rapidly and appear very incompletely separated in the first few hundred ml of eluate. On the other hand, if concentrated LiCl were used exclusively, very large volumes of eluent, and hence long periods of time, would be required to elute the more hydrophobic compounds. For example, with 4*M* LiCl + 1*M* HCl as eluent and with a column of the dimensions finally selected, 50·5 cm × 2·51 cm^2, the peak of compound 16 would appear at 2,220 ml. Although the C values of compounds 17, 18 and 19 were not determined with this eluent it is certain that more than 3 litres would be required to complete the elution.

Several preliminary experiments indicated that the sequence of eluents given in Fig. 1 was most satisfactory. Perhaps a gradient change in eluent concentration would be more efficient but the stepwise changes were preferred because it would have been much more difficult to devise a satisfactory gradient.

Fig. 1 shows the results of two elutions. The continuous line represents the elution of a mixture of compounds 1, 2, 3, 5, 9, 10, 13, 15, 17, 18 and 19. The dotted line

represents the elution of a mixture of compounds 4, 6, 7, 8, 11, 12, 15 and 16. Compound 14 was inadvertently omitted from the second mixture, but other experiments demonstrated that it is quantitatively contained in the eluate fraction from 575 to 700 ml. Fig. 1 confirms the calculations, mentioned above, that a 50-cm column should separate the mixture of all 19 phosphorus compounds into five compounds and six groups.

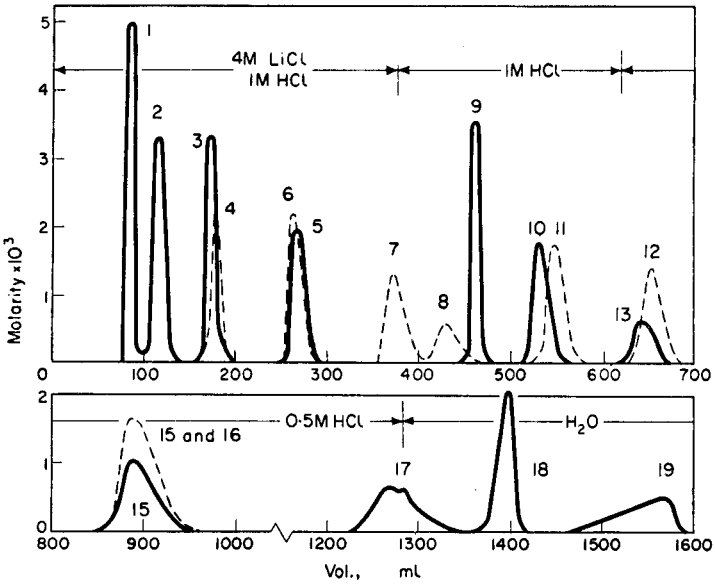

FIG. 1.—Chromatogram of the "major elution"
Column 50·5 cm × 2·51 cm², Temp. 50° ± 1°, Flow rate 0·05 to 0·15 cm/min.
Sequence of eluents: 4*M* LiCl + 1*M* HCl-0 to 374 ml, 1*M* HCl-374 to 614 ml, 0·5*M* HCl-614 to 1264 ml, H_2O-1264 to 1600 ml.

Hydrolysis of the esters

It remained to devise methods of determining each compound in the "inseparable groups."

Inspection of Table I revealed that the chief factor governing the C values with any given eluent is the number of carbon atoms per molecule and that structural considerations are relatively unimportant. Further inspection of Table I revealed that the hydrolytic removal of the alkoxyl groups from the compounds in any group will yield phosphorus compounds differing from each other in their carbon content. For example, hydrolysis of Group 2 should yield $MePO(OH)_2$ and $EtPO(OH)_2$. These compounds should be readily separable by a secondary elution. Preliminary experiments[3] proved that the alkoxyl groups are quantitatively removed from all of the compounds by refluxing for 2·5 hr with 6*M* HCl.

Separation of the phosphorus compounds from HCl *and/or* LiCl

Still another preliminary step was necessary before the secondary elutions could be successful. Groups 4, 5 and 6 were found in the eluate along with large amounts of HCl. Groups 1, 2 and 3 were found in the eluate accompanied by large quantities of both HCl and LiCl. Each group of phosphorus compounds had to be separated from

almost all of these electrolytes in order that it could be dissolved in a small volume and applied to the column for the secondary elution.

The removal of HCl from Groups 4, 5 and 6 presented no difficulty. It was accomplished simply by evaporation in a vacuum to a small volume.

For the analysis of Group 1, a non-chromatographic method was devised that did not require the removal of LiCl or HCl.

For the analysis of Groups 2 and 3, however, the removal of these electrolytes was essential and presented considerable difficulty. Among the inefficient or unsuccessful methods investigated were liquid-liquid extraction with chloroform, solid-liquid extraction after evaporation to dryness, precipitation of the organophosphorus anion, gathering by aluminium hydroxide and ion exclusion. Finally, at the suggestion of Dr. Yurow,[7] selective adsorption of the phosphorus compounds by cellulose impregnated with zirconia was tried. This method proved to be successful. By passage of an acid solution of the mixture through a column of the impregnated cellulose, the phosphorus compounds were retained on the column while the LiCl passed through. The phosphorus compounds were then recovered by passing dilute ammonia through the column.

DETAILS OF THE PROCEDURE

Reagents

Most of the phosphorus compounds were supplied by the Army Chemical Center. The low-capacity cation-exchange resin has been described previously.[4] It was used in columns provided with water jackets through which water at 50° ± 1° was pumped. A Rinco Rotating Vacuum-type Evaporator, Model VE-1000-A, was used to evaporate solutions without application of heat.

The cellulose impregnated with zirconia was prepared as follows: Ten g of cellulose powder were mixed with a hot solution of 10 g of zirconyl nitrate in 100 ml of 1*M* sulphuric acid. After filtration with suction, the cellulose was dried on a glass plate at room temperature for 48 hr. It was then passed through a 40-mesh sieve and slowly added with stirring to 100 ml of 3*M* ammonia. It was filtered again and washed with three 100-ml portions of water. It was stored in 0·01*M* hydrochloric acid. A column of 0·76 cm^2 cross-sectional area was filled to a depth of 12·5 cm with this material.

Samples of the mixture of phosphorus compounds were prepared for analysis by pipetting a known volume of a standard solution of each compound into a beaker and evaporating the solution to dryness in a vacuum oven at room temperature. A known volume of the first eluent, 4*M* LiCl + 1*M* HCl, was added to dissolve the residue.

Major elution

An aliquot of 2·00 ml of the foregoing solution was pipetted carefully into the chromatographic tube. The solution was drained to the top of the resin bed. Three portions of 2 ml of the first eluent were added; each portion was applied so as to rinse the inside walls of the tube and was drained to the level of the resin before the next was added. The collection of 5·5-ml fractions of eluate was started with the addition of the sample. In changing eluents, each eluent was drained to the level of the resin before the next was added. Care was taken not to permit air to enter the column. The fractions of eluate containing any one isolated compound of phosphorus or any one inseparable group were combined, as indicated by Fig. 1.

With each change of eluent, the resin expanded. The first effect of this swelling was a decrease in the interstitial volume, and hence a decrease in flow rate to about 0·05 cm per min with the same hydrostatic head. However, the column length gradually expanded, thus increasing the flow rate to about the original value of 0·15 cm per min. The final length of column was 88 cm.

Analysis of eluate fractions

A suitable aliquot of the eluate fraction containing compound 1, 2, 17, 18 or 19 was analysed by converting the organophosphorus compound to orthophosphate by treatment with alkaline persulphate and subsequent spectrophotometric determination of the orthophosphate. Details of this procedure have been published elsewhere.[4,8]

Group 1 contains MePO(OH)OMe and $HOPO(OMe)_2$ mixed with LiCl and HCl. An aliquot containing not more than 40 meq of LiCl was mixed with an equal volume of 12*M* HCl and refluxed for 2·5 hr to convert the phosphorus compounds to $MePO(OH)_2$ and H_3PO_4, respectively. The solution was evaporated to dryness to get rid of the acid. The residue was dissolved in water and diluted to

100 ml in a volumetric flask. An aliquot of this solution was treated with alkaline persulphate to convert the methanephosphonate to orthophosphate. Details of this step have been published elsewhere.[4,8] Then the total phosphorus in this solution was determined by the spectrophotometric method of Barton.[9]

Another aliquot of the solution was treated by the method of Barton without the application of persulphate. Thus only orthophosphate was determined because $MePO(OH)_2$ does not give a colour reaction with vanadomolybdate reagent. From the results of these two determinations, the quantity of each organophosphorus compound in the group was calculated.

Group 2 contains MePO(OH)OEt and EtPO(OH)OMe mixed with LiCl and HCl. The pH was adjusted to 2·0 with NaOH and HCl. The solution was then passed through the column of cellulose impregnated with zirconia at 2·7 ml per min. Then 100 ml of 0·01*M* HCl was passed through the column. Thus all the lithium was found in the effluent and all the organophosphorus compounds in the column. Elution with 100 ml of 0·1*M* ammonia served to elute the latter completely. This solution was evaporated to about 10 ml, mixed with an equal volume of 12*M* HCl and refluxed for 2·5 hr to convert the phosphorus compounds to $MePO(OH)_2$ and $EtPO(OH)_2$, respectively. This solution was evaporated to dryness under vacuum to remove the HCl. The residue was dissolved in a measured volume of 8*M* LiCl + 1*M* HCl. An aliquot of this solution was transferred to a column, 12·5 cm × 3·82 cm², of the low-capacity cation exchanger and eluted at 50° with 8*M* LiCl + 1*M* HCl. The elution

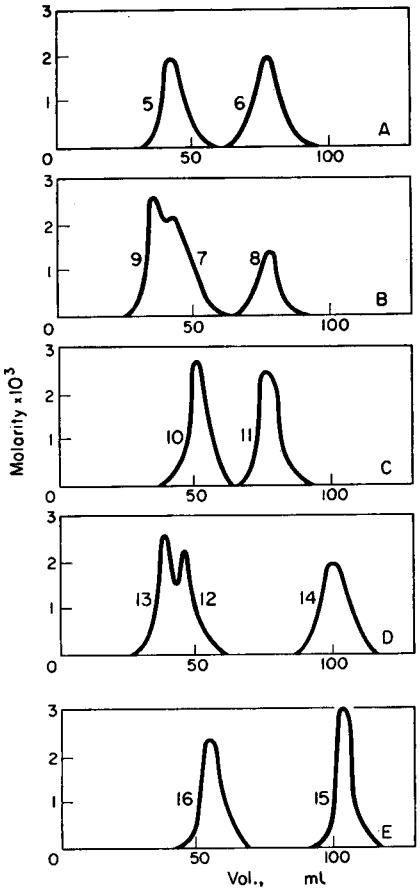

FIG. 2.—Chromatogram of the "secondary elutions"

Temp. 50° ± 1° Flow rate approx. 0·15 cm/min.
A and B: Column 19 cm × 3·8 cm²; eluent 8*M* LiCl + 1*M* HCl.
C: Column 14 cm × 3·8 cm²; eluent 4*M* LiCl + 1*M* HCl.
D and E: Column 12·5 cm × 3·8 cm²; eluent 1*M* HCl.
Numbers refer to hydrolysis products of the compounds listed in Table II.

graph is given in Fig. 2A. The eluate fractions containing the $MePO(OH)_2$ and the $EtPO(OH)_2$ were treated separately with alkaline persulphate and vanadomolybdate to determine the MePO(OH)OMe and EtPO(OH)OEt, respectively, in the sample.

Group 3 contains MePO(OH)OPr, EtPO(OH)OEt and $HOPO(OEt)_2$. Upon hydrolysis, it yields $MePO(OH)_2$, $EtPO(OH)_2$ and H_3PO_4, respectively. It was treated exactly like Group 2 through the elution. Fig. 2B reveals that the elution separated $EtPO(OH)_2$ from the other phosphorus compounds but did not separate $MePO(OH)_2$ from H_3PO_4. The fraction containing $EtPO(OH)_2$ was treated with alkaline persulphate and vanadomolybdate to determine the original EtPO(OH)OEt. Aliquots of the fraction containing $MePO(OH)_2$ and H_3PO_4 were treated as in the analysis of Group 1. Thus each compound of this group was determined.

Group 4 contains EtPO(OH)OPr, PrPO(OH)OEt and HCl but no LiCl. The HCl was removed by vacuum evaporation. The residue was dissolved in 20 ml of 6*M* HCl and refluxed for 2·5 hr to convert the phosphorus compounds to $EtPO(OH)_2$ and $PrPO(OH)_2$. The hydrochloric acid was removed by vacuum evaporation. The residue was dissolved in 4*M* LiCl + 1*M* HCl. An aliquot was chromatographed at 50° through a column, 14 cm × 3·8 cm^2, of the low-capacity resin. Fig. 2C reveals that the two phosphonic acids were quantitatively separated. Each was determined by treatment with alkaline persulphate and vanadomolybdate as described above.

Group 5 contains MePO(OH)OBu, $HOPO(OPr)_2$ and BuPO(OH)OMe. Upon hydrolysis it yields $MePO(OH)_2$, H_3PO_4 and $BuPO(OH)_2$, respectively. The analysis of this group is like that of Group 4 up to the elution. Then a column, 19 cm × 3·8 cm^2. and 1*M* HCl were used. As in Group 3, the higher phosphonic acid is separated from the other phosphorus compounds (Fig. 2D) and is determined by treatment with alkaline persulphate and vanadomolybdate. The unseparated $MePO(OH)_2$ and H_3PO_4 were determined as in Group 2.

Group 6 contains BuPO(OH)OEt and EtPO(OH)OBu, yielding $BuPO(OH)_2$ and $EtPO(OH)_2$, respectively, on hydrolysis. The analysis was performed like that of Group 5 through the elution. Fig. 2E reveals that the separation of the two phosphonic acids was quantitative. Each was determined by treatment with alkaline persulphate and vanadomolybdate.

RESULTS AND DISCUSSION

One solution containing known concentrations of all 19 phosphorus compounds was analysed in triplicate. A similar solution was analysed in duplicate. These results

TABLE II.—ANALYSIS OF KNOWN MIXTURES

No.	Compound	Solution 1				Solution 2		
		Taken, *mmol*	Recovery, %			Taken, *mmol*	Recovery, %	
			1	2	3		1	2
1	H_3PO_4	0·0392	96	95	95	0·0594	98	97
2	$MePO(OH)_2$	0·0440	99	97	101	0·0630	103	101
3	MePO(OH)OMe	0·0080	105	108	101	0·0235	102	98
4	$HOPO(OMe)_2$	0·0321		104	106	0·0361	99	102
5	MePO(OH)OEt	0·0335	97	90	91	0·0520	88	90
6	EtPO(OH)OMe	0·0408		90	87	0·0635	86	86
7	MePO(OH)OPr	0·0362		89	89	0·0582	86	84
8	EtPO(OH)OEt	0·0192	95	95	92	0·0325	91	88
9	$HOPO(OEt)_2$	0·0395		89	88	0·0604	89	89
10	EtPO(OH)OPr	0·0390	102	87	98	0·0595	92	94
11	PrPO(OH)OEt	0·0406		91	94	0·0615	93	90
12	MePO(OH)OBu	0·0194		98	95	0·0320	95	96
13	$HOPO(OPr)_2$	0·0386	98	84	92	0·0585	97	92
14	BuPO(OH)OMe	0·0390		92	93	0·0612	95	96
15	BuPO(OH)OEt	0·0382	103	90	92	0·0592	93	93
16	EtPO(OH)OBu	0·0378		93	94	0·0587	98	95
17	PrPO(OH)OBu	0·0388	105	95	94	0·0606	99	100
18	BuPO(OH)OBu	0·0396	100	106	98	0·0618	97	96
19	$HOPO(OBu)_2$	0·0395	95	102	99	0·0612	98	96
Mean			100	94	95		95	94
Standard Deviation			4	6	5		5	5

are recorded in Table II. In the first analysis of solution 1, the individual compounds of the inseparable groups were not determined separately.

The table indicates that the accuracy and precision of the results are satisfactory for mixtures as difficult as these. In general, compounds 5, 6, 7, 8 and 9 show slightly lower recoveries than the others. The fact that these are the only compounds which were passed through the column of cellulose impregnated with zirconia indicates that incomplete desorption from the zirconia may account for low results. An application of the t-test revealed that the probability that the low results for these compounds are caused by chance alone is about one in four.

Acknowledgements—The authors express their gratitude to the Army Chemical Center for financial and material assistance and to The Dow Chemical Company for supplying the low-capacity cation-exchange resin.

Zusammenfassung—Eine Methode zur Bestimmung jeder Komponente in einer Mischung von 19 Säuren des Phosphors wird mitgeteilt.

Résumé—Les auteurs décrivent une méthode de dosage de chaque composé dans un mélange de 19 acides de phosphore.

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TITRIMETRIC ANALYSIS WITH CHLORAMINE-T—V*

TITRATIONS IN HYDROCHLORIC ACID MEDIA USING IODINE MONOCHLORIDE AS A REACTION INTERMEDIATE

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Summary—A critical appraisal has been made of the use of chloramine-T in conjunction with iodine monochloride as a reaction intermediate in Andrews-type titrations of arsenic^{III}, antimony^{III}, hydrazine, thiocyanate and thallium^{I}. Location of the end-point by potentiometric means and by several visual indicators has been examined over a very wide range of conditions. Optimum conditions for each determination have been established and have proved to be rather limited in most cases, severely so for antimony^{III}, while for hydrazine accurate results cannot be obtained under any conditions.

PRIOR to the present work, a solitary reference to the use of chloramine-T in Andrews-type reactions could be found. Berry[2] had titrated iodide under vaguely defined conditions to iodine monocyanide, with starch as indicator. He also titrated thallium^{I} in the presence of an excess of iodine monochloride at unspecified acidity with carbon tetrachloride as indicator. His results were reported to a rather low precision. During the course of this work Singh and Sood[3,4] reported a superficial examination of a number of determinations under apparently uniform, but rather ill-defined conditions using chloroform as indicator. Some of the determinations were made at suboptimum conditions. They have similarly reported[5,6] on the use of chloramine-B. A critical examination and delineation of reaction conditions is therefore to be desired.

A number of determinations have accordingly been examined at the highest volumetric precision over a wide range of conditions and by a number of techniques. The selection of determinations has been made (a) with a view to covering a representative cross-section of the possible reactions, (b) so that primary standard purity compounds or compounds of high purity easily and accurately assayed are available, and (c) to include the basic reaction with iodide,[1] the primary standards arsenic^{III} and hydrazine, reversible reactions—iodide and thallium^{I}, partially reversible reactions—arsenic^{III} and antimony^{III}, and irreversible reactions—hydrazine and thiocyanate, and some of the most useful reactions, particularly thiocyanate.

The substitution of chloramine-T for the more expensive potassium iodate in Andrews-type titrimetric reactions involves the addition of iodine monochloride as a reaction intermediate, and requires re-oxidation of reduction products of iodine monochloride by the titrant. The oxidation of iodide and the iodine to monopositive iodine ion in the hydrochloric acid media has been investigated over a wide range of conditions, and found to be perfectly stoicheiometric over only rather narrow limits of hydrochloric acid concentration.[1] However, the deviations from stoicheiometry in the normal working range with comparatively large quantities of iodide become much less

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significant when relatively small quantities of iodine monochloride are used as a reaction intermediate. Thus, though the determination of iodide is accurate only in 3·0–4·0*M* hydrochloric acid, when 2 ml of 0·1*M* iodine monochloride is used as a reaction intermediate the error is 0·01 ml or less in 1·0 to 5·0*M* hydrochloric acid, and for 5 ml the range is 2·0 to 4·0*M* hydrochloric acid for the same error. This does not, of course, include other errors which may arise in particular determinations. In fact for all five substances examined, under all of the conditions from 1·0 to 5·0*M* hydrochloric acid and 1·0 to 25·0 ml of 0·1*M* iodine monochloride, the titration error does not exceed 0·3%, with the single exception of potentiometric determination of thallium[I] in 5·0*M* hydrochloric acid and 5·0 ml of iodine monochloride, where the error is 0·4%. The error can be reduced to one tenth of this value by suitable choice of conditions except in the determination of hydrazine.

EXPERIMENTAL

Apparatus and reagents

Complete details have been given elsewhere;[7] the apparatus and most of the reagents and indicators have already been described.[8,9,10] The remaining reagents were as follows. Titration conditions refer to the end-point concentrations.

Antimony[III]*:* A 0·05*M* solution prepared from AnalaR potassium antimonyl tartrate after drying for 1 hr at 100°. The solution was standardised against ultimate standard 0·01667*M* potassium bromate in a medium 2*M* in hydrochloric acid and 0·1*M* in potassium bromide, both potentiometrically (factor 1·0035) and with rosaniline as visual indictor[8] (factor 1·003, 1·0035, 1·003).

Thallium[I]*:* A 0·05*M* solution prepared from AnalaR thallium sulphate. The solution was standardised by titration in 3·5*M* hydrochloric acid with primary standard 0·025*M* potassium iodate,[11,12] potentiometrically (factor 0·998), visually with carbon tetrachloride (factor 0·997, 0·997) and visually with amaranth (factor 0·9975, 0·9975).

Hydrazine sulphate: A 0·025*M* solution prepared from AnalaR hydrazine sulphate. The solution was check standardised against primary standard 0·025*M* potassium iodate by titration in 4*M* hydrochloric acid,[11,13] potentiometrically (factor 0·9904) and with the visual indicator amaranth (factor 0·991, 0·991, 0·991).

Thiocyanate: A 0·01667*M* solution prepared from AnalaR potassium thiocyanate after drying at 150° for 2 hr. The solution was standardised by titration in 4*M* hydrochloric acid with primary standard 0·025*M* potassium iodate,[11,14] potentiometrically (factor 1·0175), with the visual indicators amaranth (factor 1·0184, 1·0179) and carbon tetrachloride (factor 1·0175, 1·017, 1·017).

Iodine monochloride: A 0·1*M* solution in 5·0*M* hydrochloric acid was prepared by dissolving 7·12 g of AnalaR potassium iodate in warm water, adding 11·16 g of AnalaR potassium iodide to the cooled solution followed by 500 ml of 10*M* hydrochloric acid and dilution to 1 litre. Before use, a portion of this solution was titrated with 0·025*M* potassium iodate (or occasionally 0·1*M* potassium iodide) to the equivalence point using 10 ml of carbon tetrachloride as indicator.

Procedure

Carbon tetrachloride was used as the indicator for the extractive end-point, 5 ml being employed in a final volume of 100 ml, instead of chloroform which is more usual. The higher partition coefficient in the former solvent renders the titration slower, in the end-point region, but with an extended period of vigorous shaking between titrant increments in this region rather sharper and more accurate and precise end-points were achieved and considered desirable in the present appraisal.

Potentiometric and visual indicator titration methods have been described.[1,7–10] The concentrations recorded are those at the equivalence point. All determinations were replicated, but the potentiometric results recorded in Table II are those of the individual titrations illustrated in the figures: only the visual indicator results are means of triplicate determinations.

RESULTS AND DISCUSSION

Iodide

The direct titration of iodide to iodine monochloride has been examined.[1] From this work, the corrections shown in Table I have been calculated for customary additions of reaction intermediate at a range of concentrations of hydrochloric acid for both

potentiometric titration and visual indication using carbon tetrachloride. These corrections have been applied to the results given in Table I.

TABLE I

End-point location	Potentiometric			Carbon tetrachloride		
Volume of 0·1*M* ICl, *ml*	2·0	5·0	25·0	2·0	5·0	25·0
HCl concentration, *M*						
1·0	+0·008	+0·02	+0·10	+0·004	+0·01	+0·05
2·0	+0·006	+0·015	+0·075	+0·003	+0·01	+0·04
3·0	+0·004	+0·01	+0·05	+0·002	+0·005	+0·025
4·0	—	—	−0·01	+	+	+0·01
5·0	−0·014	−0·035	−0·175	+	+	+0·01

Arsenic^{III}

By the use of iodine monochloride as a reaction intermediate, the direct titration of arsenic^{III} by the Andrews procedure becomes possible with chloramine-T, permitting replacement of the more expensive potassium iodate as the titrant. Furthermore, this procedure affords an additional means of standardising chloramine-T solutions not only against the primary standard arsenious oxide, but also indirectly against the ultimate standard potassium iodate as an alternative to the rather more complex route via iodine and thiosulphate.[8] This method is particularly advantageous for chloramine-T which is to be used in Andrews type determinations.

Potentiometric and carbon tetrachloride end-points are highly precise.

Using carbon tetrachloride indication, with 1 ml of 0·1*M* iodine monochloride the end-points were late in acid concentrations below 5*M*; with 2 ml of reaction intermediate the results were high in acid concentrations of 2*M* or less, but highly accurate in 3*M* or higher concentrations, with an amount of reaction intermediate (25 ml of 0·1*M*) equivalent to the total amount of reductant no significant error is introduced in 4*M* acid. A hydrochloric acid concentration of 3–5*M* with 2 ml of 0·1*M* iodine monochloride gives optimum results.

Using amaranth[9] (0·2 ml per 100 ml) or *p*-ethoxychrysoïdine[9] (0·3 ml per 100 ml), added about 0·1–0·2 ml prior to the equivalence point, the colour changes from pink to the pale yellow of iodine monochloride. The end-points are late, particularly with *p*-ethoxychrysoïdine which shows no signs of reversibility in this titration, and neither indicator can be recommended for other than rough work.

Potentiometric titration (Fig. 1) in 1–5*M* hydrochloric acid using 2 ml of 0·1*M* iodine monochloride gives accurate results and affords a rapid, pleasing and convenient method of determination. The potentials are highly reproducible and attain equilibrium, even in the equivalence-point region, very quickly. This is the best method for potentiometric titration of arsenic^{III} with chloramine-T. The titration in 3*M* acid using 1 ml of reaction intermediate confirms that carbon tetrachloride indication does give a late end-point under these conditions, and the results in general show that the errors with visual indicators are properly attributed to the indicators themselves and not to the reaction.

Antimony^{III}

Carbon tetrachloride proved to be unusable as an indicator, no purple colour being

produced in the solvent layer before the equivalence point. The same phenomenon has been observed with potassium iodate as titrant by Smith and Willcox.[11] The interference is ascribed to the tartaric acid liberated on acidification of the tartrate complex. In the absence of tartaric acid, solvent extraction indication is feasible.[15]

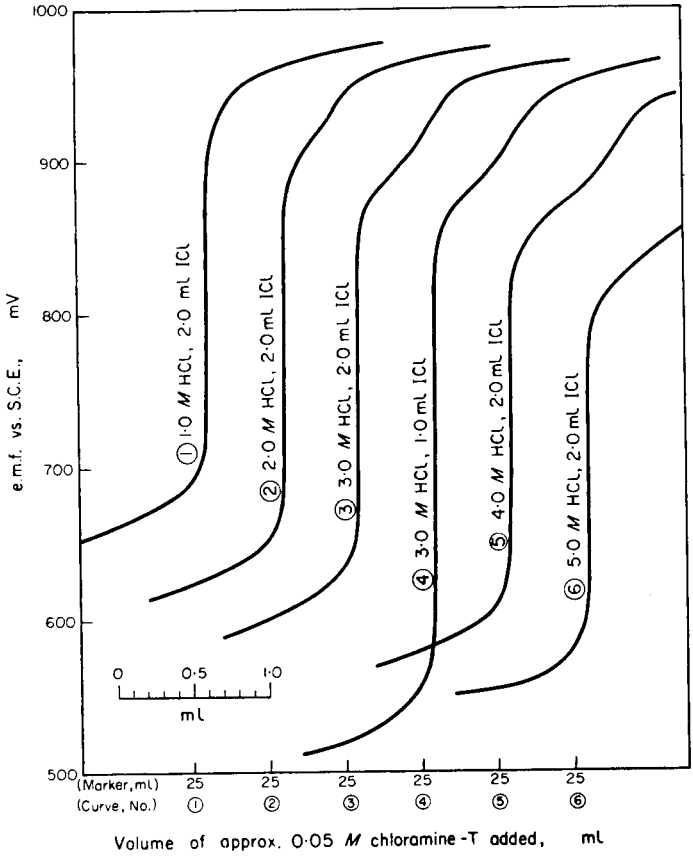

FIG. 1.—Titration of 25-ml aliquots of approx. $5 \times 10^{-2}M$ arsenic^{III} diluted to an equivalence point volume of 200 ml, with approx. $5 \times 10^{-2}M$ chloramine-T.

Amaranth, with a colour change from orange-pink to pale yellow, gives accurate results over the range of conditions recorded in Table II, with 2–5 ml of $0{\cdot}1M$ iodine monochloride and a hydrochloric acid concentration of $3M$ as optimum. In $4M$ acid, the colour faded appreciably prior to the end-point, while in $2M$ acid the end-point was not sharp because either of hydrolysis of the iodine monochloride or of slowness of reaction (*vide infra*).

The results of the potentiometric titrations (Fig. 2) are in substantial agreement with the amaranth figures, and confirm that the optimum acid concentration is $3M$. At $2M$, the reaction is distinctly slow, the potentials requiring 6 min to reach equilibrium in the equivalence point region, and at $4M$, the Sb^{V}/Sb^{III} potential is sufficiently elevated to offset the tail potentials, offering an explanation of the fading end-points with amaranth.

The range of acid concentration within which accuracy is maintained is rather

TABLE II.—TITRATIONS WITH CHLORAMINE-T USING IODINE MONOCHLORIDE AS A REACTION INTERMEDIATE

Equivalence point conditions		End-points,[a] ml of 0·05*M* chloramine-T						
					Visual Indicators			
Concn. of HCl, *M*	Vol. of 0·1*M* ICl, *ml*	Calculated	Potentiometric	Error[b]	CCl_4[c]	Error[b]	Amaranth[d]	Error
Iodide					Iodide			
1·0	nil	39·94	39·85	−0·09	39·90	−0·04		
2·0	nil		39·88	−0·06	39·91	−0·03		
3·0	nil		39·91	−0·03	39·92	−0·02		
4·0	nil		39·95	+0·01	39·93	−0·01		
5·0	nil		40·08	+0·14	39·93	−0·01		
Arsenic^{III}					Arsenic^{III}			
1·0	2·0	25·11	25·10	0	25·16	+0·05		
2·0	2·0		25·11	+0·01	25·12	+0·01		
3·0	1·0		25·10	0	25·17	+0·06		
3·0	2·0		25·10	−0·01	25·11	0	25·15	+0·04
3·0	2·0						25·18[e]	+0·07
4·0	1·0				25·17	+0·06		
4·0	2·0		25·11	0	25·11	0	25·14	+0·03
4·0	2·0						25·17[e]	+0·06
4·0	25·0				25·11	+0·01		
5·0	1·0				25·11	0		
5·0	2·0		25·10	−0·02	25·11	0		
Antimony^{III}					Antimony^{III}			
2·0	2·0	23·81	23·82	+0·02	[f]		23·82	+0·01
3·0	2·0		23·805	0			23·81	0
3·0	5·0		23·82	+0·01			23·81	0
4·0	2·0		23·87	0			23·79	−0·02
Thallium^{I}					Thallium^{I}			
3·0	5·0	24·82	24·80	−0·01	24·81	0		
4·0	5·0		24·80	−0·03	24·81	−0·01		
4·0	25·0		24·75	−0·08	24·81	0		
5·0	5·0		24·82	−0·03	24·81	−0·01		
Hydrazine					Hydrazine			
3·0	2·0	23·52	23·57	+0·05	23·57	+0·05	23·56	+0·04
3·5	5·0		23·55	+0·03				
4·0	2·0		23·55	+0·03	23·55	+0·03	23·56	+0·04
4·0	5·0				23·59	+0·07		
4·0	25·0		23·58	+0·05	23·58	+0·07		
5·0	2·0		23·56	+0·03	23·57	+0·05	23·57	+0·05
Thiocyanate					Thiocyanate			
3·0	2·0	25·31	25·31	0	25·31	0	25·40	+0·09
3·0	5·0		25·31	+0·01	25·31	0		
4·0	2·0		25·31	0	25·31	0	25·40	+0·09
4·0	5·0		25·30	−0·01	25·31	0	25·39	+0·08
4·0	25·0		25·275	−0·04	25·31	+0·01		
5·0	2·0		25·32	0	25·31	0	25·40	+0·09
5·0	5·0		25·29	−0·05	25·31	0		

[a] The potentiometric results are the end-points of the titrations recorded in the figures. Other end-points are means of three replications.

[b] The errors for potentiometric and carbon tetrachloride end-points have been corrected for the iodine monochloride error given in Table I.

[c] 5·0 ml of carbon tetrachloride was used for a final titration solution volume of 100 ml.

[d] 0·2 ml of 0·1% aqueous amaranth for a final titration solution volume of 100 ml.

[e] Results for p-ethoxychrysoïdine. 0·3 ml of 0·1% aqueous solution of indicator for a final titration solution volume of 100 ml.

[f] Carbon tetrachloride cannot be used as an indicator in the presence of tartrate.

sharply delineated. For the visual indicator amaranth, the range is about 2·5 to 3·5*M*, for potentiometric titration it is about 2·5 to 4*M*. These ranges may be compared with those determined for potassium iodate as titrant by Hammock *et al.*[15] as 2·5–3·5*M* and by Mutschin[16] as 1·8–3·6*M*.

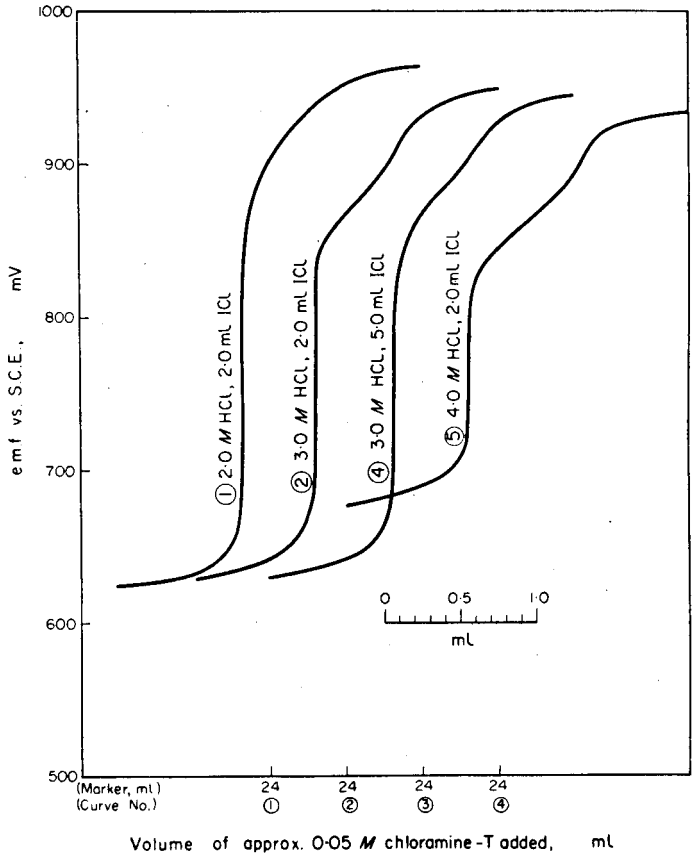

FIG. 2.—Titration of 25-ml aliquots of approx. $5 \times 10^{-2}M$ antimony^{III} diluted to an equivalence point volume of 200 ml, with approx. $5 \times 10^{-2}M$ chloramine-T.

Thallium^{I}

The formation and slow redissolution of a precipitate of thallium^{I} chloride slows the reaction sufficiently to preclude the use of colour indicators, but carbon tetrachloride is a precise and effective indicator, giving satisfactory results in the range 3–5*M* hydrochloric acid and 5 to 25 ml of reaction intermediate. The titration with iodate was found to be more rapid than that with chloramine-T and iodine monochloride.

Potentiometric titrations (Fig. 3) give accurate results in 3–4*M* hydrochloric acid with 5 ml of reaction intermediate, but reveal a negative error if the acid concentration is increased to 5*M* or if the amount of iodine monochloride is increased to 25 ml of 0·1*M*. Equilibration of the potentials was rapid throughout.

Reaction in the presence of iodine monochloride provides the only accurate method for the direct titration of thallium^{I} with chloramine-T, as will be demonstrated in a later paper.

Hydrazine

Hydrazine sulphate being a primary grade standard substance, and being titratable to high accuracy with bromate[17] and iodate[11,13], hopes were entertained of a similar favourable reaction with chloramine-T and iodine monochloride, thus providing another alternative means of standardisation. Although the end-points are sharp and precise, and the results are reproducible and consistent between the various methods

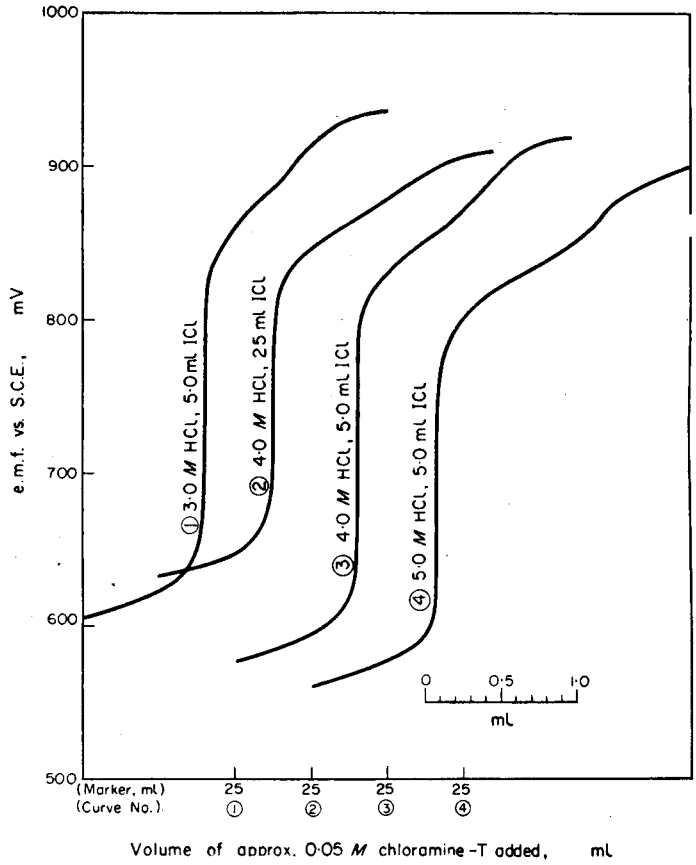

FIG. 3.—Titration of 25-ml aliquots of approx. $5 \times 10^{-2}M$ thallium[I] diluted to an equivalence point volume of 200 ml, with approx. $5 \times 10^{-2}M$ chloramine-T.

of indication, there is a positive error of 0·15 to 0·2%, and so the method must be rejected as a means of standardisation. With the application of the appropriate correction deduced from Table II, the method does give an accuracy of about $\pm$ 0·05% which is adequate for routine applications.

Over the full range of conditions reported in Table II, potentiometric and visual indication with both carbon tetrachloride and amaranth give satisfactory results, with a slight advantage in favour of 2 ml of 0·1*M* iodine monochloride and 3*M* hydrochloric acid. Potentials rapidly attained equilibrium and the potentiometric method is considered to be best of all the methods investigated for this determination. Titration curves are shown in Fig. 4.

Thiocyanate

The facile and highly accurate determination by the Andrews method of thiocyanate and of many important metals such as copper, mercury and zinc, through their compounds or complexes with thiocyanate render this one of the most important applications of iodate titrimetry.

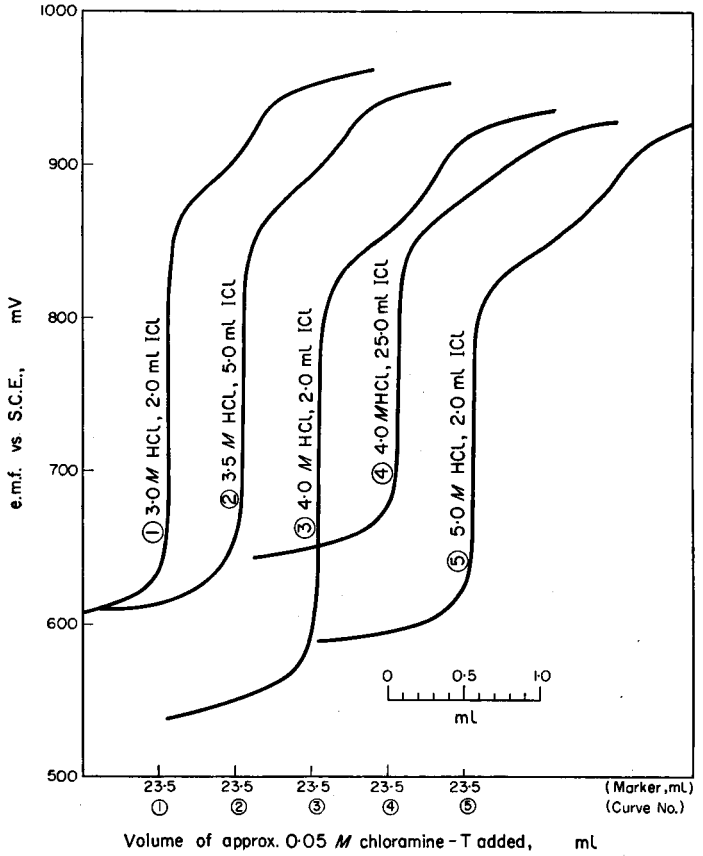

FIG. 4.—Titration of 25-ml aliquots of approx. $2{\cdot}5 \times 10^{-2}M$ hydrazine diluted to an equivalence point volume of 200 ml, with approx. $5 \times 10^{-2}M$ chloramine-T.

With chloramine-T as titrant, carbon tetrachloride yields sharp end-points and highly accurate results in 3–5*M* hydrochloric acid and with 2–25 ml of reaction intermediate, though in 3*M* acid the violet colour of iodine in the solvent globule was very faint until quite close to the end-point.

The poor colour change of amaranth and the high positive indicator error do not commend this indicator.

The potentiometric titrations (Fig. 5) are precise and accurate with moderate amounts of reaction intermediate, but appreciable negative errors arise with large amounts of iodine monochloride. Equilibration of potentials is rather less rapid than in some other determinations, but is quite satisfactorily fast.

Overall, 2–5 ml of 0·1*M* iodine monochloride and an equivalence point concentration of 4*M* hydrochloric acid are recommended. Chloramine-T compares favourably with iodate in this useful determination.

The Second Potentiometric Inflection

Except at very low hydrochloric acid concentrations, all of the potentiometric curves show evidence of a second small inflection at high potentials. The existence of this inflection has previously been noted.[9] No sign of this phenomenon has been detected other than potentiometrically and in high hydrochloric acid concentrations in the absence of other free halides. In the titration of iodide with permanganate, such an inflection has been correctly ascribed[18] to oxidation to iodate, but early tentative

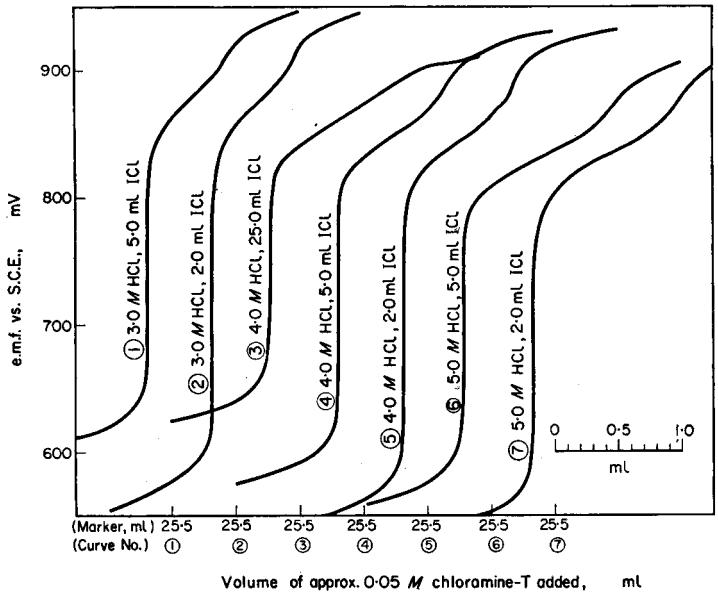

FIG. 5.—Titration of 25-ml aliquots of approx. $1{\cdot}667 \times 10^{-2}M$ thiocyanate diluted to an equivalence point volume of 200 ml, with approx. $5 \times 10^{-2}M$ chloramine-T.

indications[19] that chloramine-T could oxidise iodine to iodate at pH 7–9 proved illusory,[1,7] and the indications were traced to hydrolysis of iodine to hypo-iodite and iodide. In high acid concentrations, the oxidation is even less likely, nor do the potentials or inflections agree with such a hypothesis. Nor can the reaction be oxidation of I^+ to I^{3+} since the inflections occur much too early and, moreover, the inflections have been observed in media free from iodine and iodine monochloride.[9] The inflections are not all regular, as the values in Table III show, but they do appear to be independent of the iodine monochloride concentration, and to increase with increasing hydrochloric acid concentration according to the equation:

$$\Delta = 0{\cdot}24[\mathrm{HCl}] - 0{\cdot}17$$

where Δ is the difference in ml between the main and second inflections. The cause of this is obscure. It may be caused by a change of redox system after the addition of a certain amount of excess oxidant, but no satisfactory change has yet been formulated, and at such concentrations the activation energy of charge transfer at the electrode surface should have no effect and, as has been said, potential changes reach equilibrium very rapidly. The most reasonable explanation seems to be the existence of some impurity in the hydrochloric acid which is oxidisable only at very high potentials,

but no identification has been possible. Whatever it is, there is abundant evidence that it does not affect the analytical accuracy of determinations by chloramine-T titrimetry.

TABLE III.—THE SECOND INFLECTION IN POTENTIOMETRIC CHLORAMINE-T TITRATIONS IN THE PRESENCE OF IODINE MONOCHLORIDE

Concentration of HCl, *M*	Volume of 0·1*M* ICl used, *ml*	Δ, *ml*	Mean Δ, *ml*
1	2	—	—
2	2	0·4	0·4
3	1	0·55	
3	2	0·52	0·54
3	5	0·56	
3·5	5	0·65	0·65
4	2	0·76	
4	5	0·90	0·79
4	25	0·74	
5	2	0·99	1·03
5	5	1·10	

The volume difference Δ in ml between the two inflections is given as the mean of all the determinations employing the specified conditions, and illustrated in the figures.

CONCLUSIONS

Chloramine-T with the assistance of iodine monochloride as a reaction intermediate affords a convenient substitute for potassium iodate. The titrimetric precision and accuracy in the reactions examined are of the same order as with potassium iodate. In view of the experience, particularly with hydrazine and antimony, caution must be exercised in any attempt to generalise, and it is desirable that other reactions should be checked against the iodate method before being accepted, but the reactions chosen have been reasonably representative of the whole. Again with caution, it could be deduced that the use of 2–5 ml of 0·1*M* iodine monochloride and an equivalence point concentration of 3–4*M* hydrochloric acid generally gives the best results.

The rapid equilibration and the reproducibility of the potentials make the potentiometric method attractive, and the results under the correct conditions are accurate. Carbon tetrachloride as an extractive solvent gives very accurate results, though the iodine colour in the solvent layer is often weak, and this indicator cannot be used in the presence of tartaric acid. It is essential that adequate amounts of reaction intermediate and hydrochloric acid be present. Except, fortunately, in the determination of antimony, amaranth and *p*-ethoxychrysoïdine have little advantage. The colour changes are poor and the errors positive and rather high.

The range of conditions giving accurate results is generally rather restricted, more so for the potentiometric method than with extractive indicators, calling for the exercise of some care, particularly in the determination of antimony. This situation is not peculiar to chloramine-T.

Analysis and interpretation of the potentiometric curves will be deferred to a later paper, but it may presently be noted that the curves attest to two-electron transfer, to the anagenic effect of iodine monochloride and the katagenic effect of chloride ion, and to a change in molecular complexity during reaction.

Zusammenfassung—Eine kritische Untersuchung für die Anwendung von Chloramin-T im Zusammenhang mit Jodmonochlorid als Zwischenprodukt in Titrationen nach Andrews von As(III), Sb(III), Hydrazin, Rhodan und Tl(I) wurde durchgeführt. Die Festlegung des Endpunktes erfolgte sowohl potentiometrisch als auch mittels verschiedener visueller Indikatoren und wurde über einen weiten Bereich von Milieuänderungen untersucht. Die optimalen Bedingungen für jede Titration wurden ermittelt; sie liegen alle ziemlich enge, besonders für Sb(III), während Hydrazin unter keinen Bedingungen genau bestimmt werden konnte.

Résumé—Les auteurs ont fait une estimation critique de l'utilisation de la chloramine-T en liaison avec le monochlorure d'iode comme réaction intermédiaire dans les titrages, du type Andrews, de l'arsenic(III), de l'antimoine (III), de l'hydrozine, du thiocyanate et du thallium(I). La détermination du point équivalent par potentiométrie et par différents indicateurs visuels a été étudiée dans un très grand domaine de conditions. Les conditions les meilleures ont été établies pour chaque dosage et se sont révélées assez limitées dans la plupart des cas, assez rigoureusement pour l'antimoine(III), alors que, pour l'hydrazine, des résultats précis ne peuvent être obtenus dans aucune condition.

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TITRIMETRIC ANALYSIS WITH CHLORAMINE-T—VI*

THE CHLORAMINE-T–ANTIMONY^{III} REACTION

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Summary—A critical investigation has been made of the determination with chloramine-T of antimony^{III} under a wide range of conditions in hydrochloric acid, sulphuric acid and buffer media in the presence and absence of varied concentrations of halide ion and complexing agent by the potentiometric method. A wide variety of reversible and irreversible indicators has also been examined for usefulness under these conditions. Accurate determinations are possible by potentiometric titration in 1–4*M* hydrochloric acid and using amaranth as indicator in 1–3*M* hydrochloric acid. Several other indicators are useful in 2*M* hydrochloric acid. Both potentiometric and visual indicator methods give late end-points in the presence of bromide, but sulphuric acid with or without added halide is an unsuitable medium. Titration in adequately buffered media of pH 6·5–7·5 in the presence of 5×10^{-4} to 5×10^{-3}*M* iodide gives excellent results and is probably the best method. In 3*M* hydrochloric acid with the addition of 2–5 ml of 0·1*M* iodine monochloride, satisfactory results are given using either amaranth or potentiometry to locate the end-point but the conditions are critical.

The reactions of chloramine-T with arsenic^{III} have been subjected to detailed and extensive investigation,[2,3] and it has been demonstrated that chloramine-T can be directly substituted for potassium bromate or iodine in the determination of arsenic^{III} under the appropriate conditions. It has further been shown[1] that chloramine-T can be substituted for potassium iodate in the same determination if iodine monochloride is used as reaction intermediate. It was hoped that antimony^{III} would be similarly amenable to determination with this reagent.

Earlier literature has been criticised on several counts,[4] and accounts of the chloramine-T-antimony^{III} reaction are no exception, being characteristically vague. Chloramine-T has been used to titrate antimony^{III} in a bicarbonate solution of unspecified strength containing a "little" iodide and "some" tartaric acid[5] using starch as indicator, in 1*M* hydrochloric acid at an elevated but undefined temperature,[6] at room temperature in hydrochloric acid of unspecified concentration[7] by the potentiometric method, in 1*M* hydrochloric acid at an "elevated" temperature with methyl red as indicator,[8] and in 5% concentrated hydrochloric acid (? $\sim$ 0·6*M*) at room temperature with brilliant carmoisine as indicator.[8] No investigation of conditions has been reported.

The reactions of antimony^{III} may be expected strongly to parallel those of arsenic^{III} with differences arising from the lower electronegativity of the Period V element and the consequent shift of stability towards the lower oxidation state. In particular, three factors will produce differences in behaviour from arsenic: the higher (0·17 V) oxidation potential of the Sb^{III}/Sb^{V} system enhanced by the presence of tartrate, the decreased solubility of hydrolysis products of both states, and the greater ease of

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complex formation. Thus, experience predicted that complexation and sparing solubility in sulphuric acid media would be troublesome. All these expectations were fulfilled during the investigation.

Although the conditions for quantitative reaction with arsenic are wide, they are sharply defined at the extremities,[2,3] so a similarly wide range of conditions has been investigated by the potentiometric method for antimony, in order precisely to delimit them. Arsenic is determinable with bromate under a wide range of conditions, again sharply delimited,[9] but during an extensive investigation of bromate titrimetry,[9] a curious phenomenon was encountered with antimony.[2] Positive errors were encountered in extremes of acidity as with arsenic, both in the presence and absence of bromide, but with antimony a marked deviation in the opposite sense was found in the absence of added bromide within the acidity range of approximately 0·2–1·0*M* acid, the sign of error reversing again at the lower limit. This region of reaction has been submitted to kinetic examination.[10] Stepwise coverage of the acid conditions has, therefore, been included in the present investigation to discover whether a similar phenomenon exists in chloramine-T titrimetry.

The dearth of visual indicators for this determination is evident form the literature survey, and none of those proposed has been checked potentiometrically. A number of reversible and irreversible indicators have been developed for use in chloramine-T titrimetry and have been tested in the arsenic^{III} reaction,[3] and compared with potentiometric titrations[2] in order to define the indicator errors. The application of these indicators to the antimony determination has also been investigated and the results compared with potentiometric titrations.

Finally, the ease of hydrolysis of antimony compounds and the sparing solubility and slow reaction of the hydrolysis products requires in many conditions the addition of a complexing agent, of which the most popular is tartaric acid, in order to make reaction feasible. No investigation of the effects of such additions has been reported. Furthermore, though it is possible to use high purity antimony metal for solution preparation, the solutions emerge with slightly indeterminate acid concentrations, and the presence of unknown amounts of oxide with the metal still necessitates standardisation of the solution. Consequently, the antimonyl tartrate complex was used for preparing solutions and the influence of tartrate concentration was investigated.

Determination in high hydrochloric acid concentrations with the aid of iodine monochloride as a reaction intermediate, by the Andrews process, has already been reported.[1] Accurate results by potentiometric titration or by the use of amaranth as an internal indicator can be obtained, but only within rather narrow limits of hydrochloric acid concentration. Solvent extraction indication cannot be used in the presence of tartrate.

EXPERIMENTAL

Apparatus and reagents

Quantitative balances and glass-ware and the instruments for potentiometry have been described,[4] and the methods of preparation and standardisation of quantitative solutions have been given.[1–4,11] Other reagents, indicators and buffer solutions have been specified.[1–4,11] The tartaric acid used was AnalaR.

Procedures

Full details have been given,[12] and the methods for potentiometric[2] and visual indicator[3,4] titrations have been described. Titrimetric manipulative procedures have been discussed.[12,13] Concentrations quoted refer to the equivalence point volume, 100 ml for visual indicator titrations and 200 ml for potentiometric titrations.

RESULTS AND DISCUSSION

1. *Reaction in hydrochloric acid*

(*a*) *Potentiometric titration.* Curves are shown in Fig. 1 for titrations in 0·25–4·0*M* hydrochloric acid with or without the addition of further quantities of tartaric acid. Pre-end-point potentials were unsteady and became more unsteady with additional

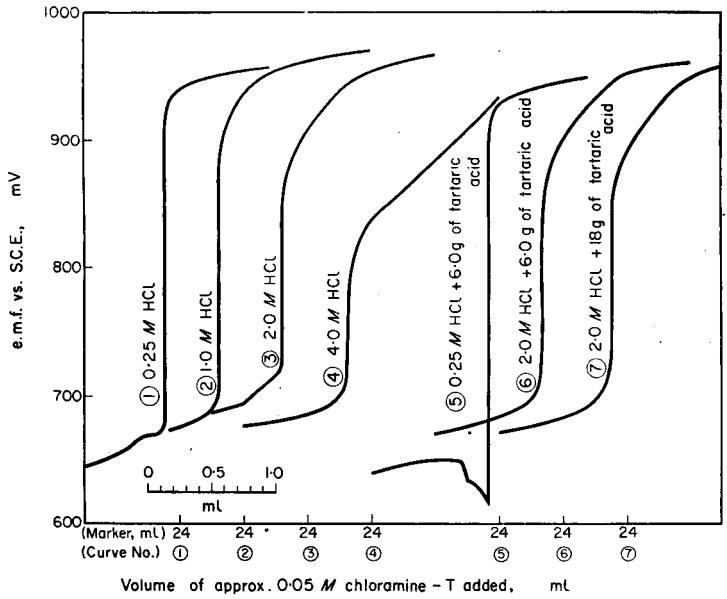

FIG. 1.—Direct titration with approx. $5 \times 10^{-2}M$ chloramine-T of 25-ml aliquots of approx. $5 \times 10^{-2}M$ antimonyl tartrate in hydrochloric acid media at an equivalence point volume of 200 ml.

tartaric acid. The reactions in 0·25*M* hydrochloric acid were very slow. Post-end-point potentials equilibrated rapidly. The results in Table I show that the titrations are accurate in 1–4*M* hydrochloric acid in the absence of additional tartaric acid, but below 1·0*M* positive errors occur which are enhanced by the addition of tartaric acid which also leads to late end-points in higher acid concentration, the effect increasing with increasing tartaric acid concentration.

In 1–4*M* hydrochloric acid, therefore, the chloramine-T-antimony^{III} reaction is stoicheiometric, but the addition of more than 6% of tartaric acid causes small positive errors.

(*b*) *Visual indicators.* Amaranth was examined as a visual indicator over the full range of hydrochloric acid concentration; the results are shown in Table I. The titration is accurate over the range of 1–3*M* hydrochloric acid, but outside this range the end-points are late as shown for 0·5 and 4·0*M* acid. In 0·25*M* acid, there was merely a slow fading of the colour with no definite end-point.

Since 2·0*M* hydrochloric acid proved satisfactory in both potentiometric and amaranth titrations, this condition was selected for examination of other indicators; results are given in Table I. Quinoline yellow and *o*-dianisidine changed colour prematurely and were therefore unsuitable. Methyl orange and tartrazine gave satisfactory colour changes, but the end-points are late by more than 0·1%. *p*-Ethoxychrysoïdine

gave fairly accurate results, but the colour change is not satisfactory. Neither tartrazine nor *p*-ethoxychrysoïdine showed reversibility after the first colour change. Bordeaux alone gave both a satisfactory colour change and accurate results. Methyl red[8] proved unsatisfactory since its normal pink colour changed to yellow early in the titration.

TABLE I.—TITRATION OF ANTIMONY^{III} IN HYDROCHLORIC ACID MEDIA WITH APPROX. 0·05*M* CHLORAMINE-T

HCl concentration, *M*	Potentiometric end-point *ml*	Potentiometric error %	Indicator	Indicator end-point *ml*	Indicator error %
0·25	23·89	+0·34	Amaranth	none	
0·5	—		Amaranth	23·88	+0·29
1·0	23·81	0	Amaranth	23·81	0
2·0	23·81	0	Amaranth	23·81	0
3·0	—		Amaranth	23·82	+0·04
4·0	23·82	+0·04	Amaranth	23·87	+0·21
0·25 + 6g tartaric acid	23·92	+0·46			
2·0 + 6g tartaric acid	23·84	+0·13			
2·0 + 18g tartaric acid	23·88	+0·29			
2·0			Methyl orange	23·84	+0·13
2·0			Methyl red	none	
2·0			Bordeaux	23·81	0
2·0			*p*-Ethoxychrysoïdine	23·82	+0·04
2·0			Quinoline yellow	none	
2·0			*o*-Dianisidine	none	
2·0			Tartrazine	23·85	+0·17

Calculated equivalence point, 23.81 ml.

Amaranth and bordeaux are recommended as indicators for the titration of antimony^{III} in 1·0–3·0*M* hydrochloric acid with chloramine-T. Tartrazine, *p*-ethoxychrysoïdine and methyl orange may also be used.

2. *Reaction in sulphuric acid*

Titrations in 0·125, 1·0 and 2·0*M* sulphuric acid using amaranth as indicator were unsuccessful. Even after 2 hr standing with a 0·2-ml excess of chloramine-T the solutions still retained the pink colour of the indicator. Attempted potentiometric titrations in 1·0 and 2·0*M* sulphuric acid confirmed the conclusion that the reaction is too slow to be of analytical use. Even with an excess of titrant present, the potentials continued to drift for many hr.

3. *Reaction in hydrochloric acid containing bromide*

(*a*) *Potentiometric titration.* Titration curves for 0·1*M* bromide over a range of hydrochloric acid concentrations are shown in Fig. 2. The results in Table II show that the end-points are all late, and that the addition of tartaric acid (Fig. 3, curve 5) does not enhance the error. Curves for 0·01*M* bromide are shown in Fig. 3, together with a set of curves at 2·0*M* hydrochloric acid for 0·01*M* bromide, 0·1*M* bromide and 0·1*M* bromide plus 6 g of tartaric acid so that the effects may be compared. Pre-end-point potentials were unsteady. After the end-point, equilibration was rapid and the colour of liberated bromine appeared within 0·05 ml past the end-point. The results

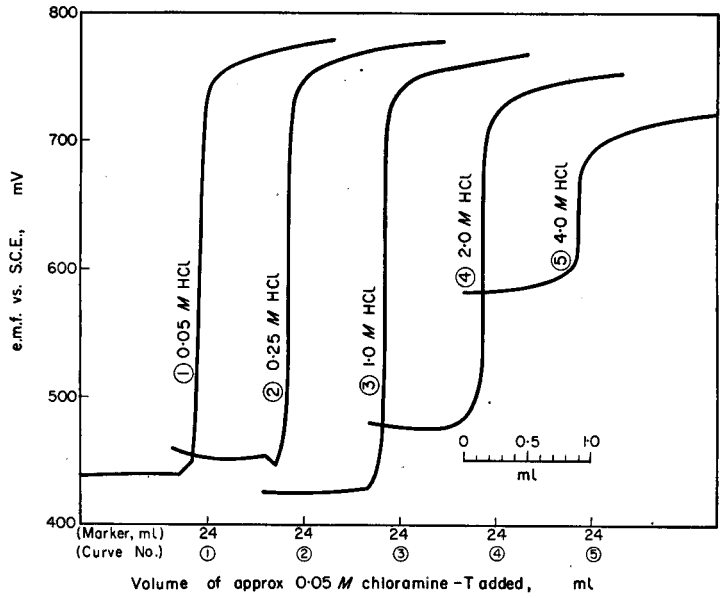

FIG. 2.—Direct titration with approx. $5 \times 10^{-2}M$ chloramine-T of 25-ml aliquots of approx. $5 \times 10^{-2}M$ antimonyl tartrate in hydrochloric acid media $0{\cdot}1M$ in bromide at an equivalent point volume of 200 ml.

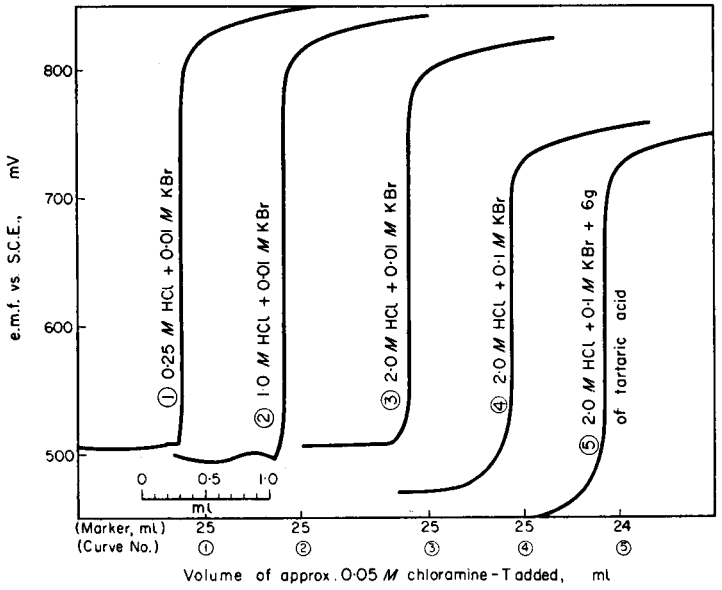

FIG. 3.—Direct titration with approx. $5 \times 10^{-2}M$ chloramine-T of 25-ml aliquots of approx. $5 \times 10^{-2}M$ antimonyl tartrate in hydrochloric acid-bromide media under various conditions at an equivalence point volume of 200 ml.

show that, while still high, the results are improved by the increase of potential caused by the ten-fold reduction in bromide concentration.

Reaction in hydrochloric acid in the presence of bromide is subject to positive

TABLE II.—TITRATION OF ANTIMONY^{III} IN HYDROCHLORIC ACID-BROMIDE MEDIA WITH APPROX. 0·05*M* CHLORAMINE-T

Concentrations, *M*		Equivalence point, *ml*	Potentiometric end-point error		Rosaniline end-point error	
HCl	KBr		*ml*	%	*ml*	%
0·05	0·1	23·81	23·93[a]	+0·50	—	—
0·25	0·1	23·81	23·88[a]	+0·29	none	—
0·25	0·01	24·81	24·82[b]	+0·04	24·82	+0·04
0·5	0·1	24·81	—	—	24·84	+0·12
0·5	0·01	24·81	—	—	24·82	+0·04
1·0	0·1	23·81	23·88[a]	+0·29		
		24·81			24·83	+0·08
1·0	0·01	24·81	24·86[b]	+0·20	24·83	+0.08
2·0	0·1	23·81	23·89[a]	+0·34		
		24·81	24·90[b]	+0·36	24·83	+0·08
2·0	0·1					
+6g tartaric acid		23·81	23·88[b]	+0·29		
2·0	0·01	24·81	24·85[b]	+0·16	24·82	+0·04
4·0	0·1	23·81	23·90[a]	+0·38	—	—

[a] see Fig. 2.
[b] see Fig. 3.

errors and cannot, therefore, be recommended. This is in sharp contrast to the high accuracy of the determination with bromate under similar conditions.[9]

(*b*) *Rosaniline as visual indicator.* Titrations conducted by the method described[4] for arsenic^{III} in 0·01 and 0·1*M* bromide over a range of concentrations of hydrochloric acid, using rosaniline hydrochloride as indicator, gave the results shown in Table II. The accuracy of *ca.* 0·05 to 0·1% is more apparent than real, because the appearance of the purple colour at the end-point was not sharp, though it was sharper in 0·01*M* than in 0·1*M* bromide. No definite end-point could be located in 0·25*M* acid with 0·1*M* bromide. This again is in sharp contrast to the bromate titration.[9]

4. *Reaction in sulphuric acid containing bromide*

(*a*) *Potentiometric titration.* Titration curves for 0·1*M* bromide over a range of sulphuric acid concentrations are shown in Fig. 4. The results in Table III show that the end-points are late and the shapes of the curves indicate that the end-points are not

TABLE III.—POTENTIOMETRIC TITRATION OF ANTIMONY^{III} IN SULPHURIC ACID CONTAINING POTASSIUM BROMIDE WITH APPROX. 0·05*M* CHLORAMINE-T

Conditions, *M*		Calculated end-point, *ml*	Determined end-point, *ml*	Error %
H_2SO_4	KBr			
0·125	0·1	23·81	23·88	+0·29
1·0	0·1	23·81	23·88	+0·29
2·0	0·1	23·81	23·95	+0·36
1·0	0·01	24·81	24·87	+0·24
1·0	0·1	24·81	24·88	+0·28

sharp. Increase of the bromide/bromine potential by lowering the bromide concentration to 0·01*M* gave some improvement, but the end-point remains late. A pair of

curves in 1M sulphuric acid and 0·1 and 0·01M bromide is included in Fig. 4 by way of illustration. The results are similar to those with hydrochloric acid plus bromide.

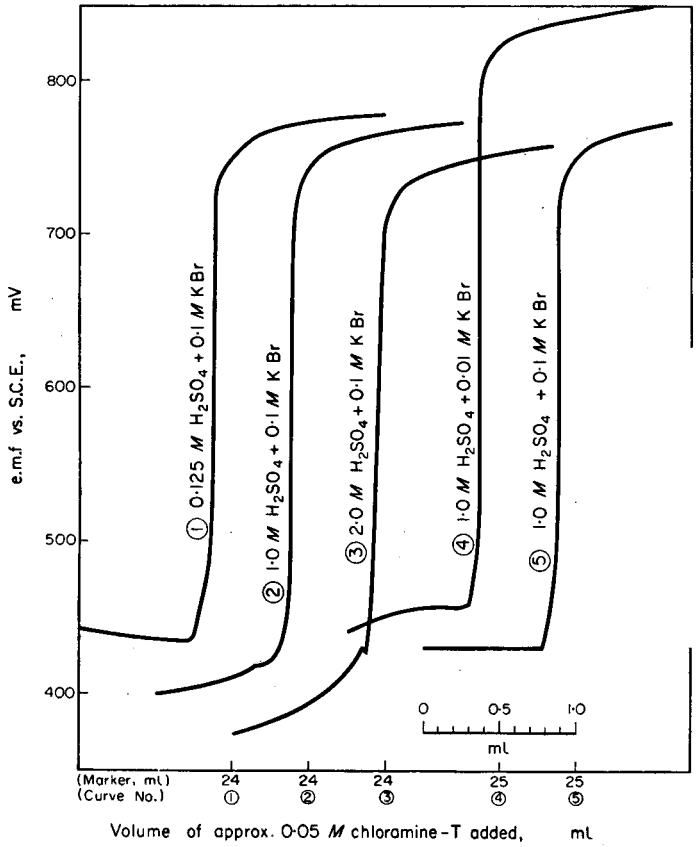

FIG. 4.—Direct titration with approx. 5 × $10^{-2}M$ chloramine-T of 25-ml aliquots of approx. 5 × $10^{-2}M$ antimonyl tartrate in sulphuric acid-bromide media at an equivalence point volume of 200 ml.

Since arsenic^{III} can be accurately titrated in either acid under the same conditions,[2] it is evident that the late end-points are caused by the higher potential of the antimony system, with which chloramine-T reacting through the active species bromine is unable to cope, but with which bromate reacting through bromine monochloride[14] can deal

(*b*) *Rosaniline as visual indicator.* Attempted titrations in 0·125, 0·25, 1·0 and 2·0M sulphuric acid in either 0·01 or 0·1M bromide were unsuccessful since no sharp end-points were found. The purple colour of the brominated rosaniline appeared gradually somewhere near the calculated equivalence point, but it was impossible to decide to within 0·05 ml the exact location of the end-point.

5. *Reaction in bicarbonate buffer containing iodide*

(*a*) *Starch as visual indicator.* Titrations in two strengths of bicarbonate solution over a range of iodide and tartrate concentrations were conducted using 2 ml of fresh 1% starch solution as indicator added 1 ml before the end-point. Titration proved

impracticable with just the amount of tartrate furnished by the standard antimony solution or with the addition of 0·2 g of tartaric acid, since hydrolysis produced precipitates which reacted very slowly with the iodine formed as the reacting species. With an additional 0·5–1 g of tartaric acid, the results (Table IV) were excellent and highly accurate in 0·2–0·4*M* bicarbonate and 5×10^{-3} to 5×10^{-4}*M* iodide.

(*b*). *Potentiometric titration.* Potentiometric titration under the conditions out-

TABLE IV.—TITRATION OF ANTIMONY^{III} IN BICARBONATE BUFFER CONTAINING IODIDE AND TARTRATE WITH APPROX. 0·05*M* CHLORAMINE-T, USING STARCH AS INDICATOR[b]

Volume of 1*M* $NaHCO_3$ added, *ml*	Tartaric acid added, *g*	Iodide concn., *M*	Measured pH at end-point	End-point, *ml*	Error, %
20	0	5×10^{-3}	—	none	—
20	0·15	5×10^{-3}	—	none	—
20	0·2	5×10^{-3}	7·06	23·81	0
20	0·5	5×10^{-4}	7·10	23·81	0
20	1·0	5×10^{-3}	6·40	23·81	0
20	1·0	5×10^{-3}	—	23·82[a]	+0·04
20	1·0	5×10^{-4}	6·33	23·81	0
40	0	5×10^{-3}	—	none	—
40	0·2	5×10^{-3}	—	none	—
40	0·5	5×10^{-3}	7·28	23·81	0
40	0·5	5×10^{-3}	—	23·82[a]	+0·04
40	0·5	5×10^{-4}	7·28	23·81	0
40	1·0	5×10^{-3}	7·06	23·81	0
40	1·0	5×10^{-3}	—	23·82[a]	+0·04
40	1·0	5×10^{-4}	7·06	23·81	0
40	1·0	5×10^{-4}	—	23·81[a]	0

[a] Potentiometric titration, see Fig. 5.
[b] Calculated equivalence point 23·81 ml.

lined in (a) amply confirmed the accuracy of the method. Four sample curves for various conditions are given in illustration in Fig. 5, and the end-points are included in Table IV. The second inflection in curve 1 corresponds to the oxidation of all the iodide present to iodine.

Titration in amply buffered media with adequate additions of iodide and complexing agent affords an accurate determination of antimony.

CONCLUSIONS

1. Chloramine-T can be used for the accurate determination of antimony^{III} in hydrochloric acid solution in the absence of other halides in the range of acid concentration 1–4*M* by the potentiometric method and 1–3*M* using amaranth as a visual indicator. Tartaric acid up to 6% w/v can be tolerated within these ranges without introducing errors, but positive errors arise with greater quantities of tartaric acid.

2. Amaranth and bordeaux are particularly recommended as indicators for the titration in 2*M* hydrochloric acid. Tartrazine, *p*-ethoxychrysoïdine and methyl orange are also useful, but are subject to certain errors and defects.

3. Addition of bromide to the titration solution affords no advantage. Late end-points arise in the presence of bromide and become later as the bromide concentration increases. The indicator rosaniline gives reasonably correct results, best in 0·5–1·0*M* hydrochloric acid and 0·01*M* bromide. Whilst antimony^{III} can be determined in the presence of bromide, the method is not of sufficient merit to warrant recommendation.

4. Sulphuric acid is an unsuitable medium for the reaction. End-points are obtainable in the presence of bromide but are of poor quality and the results are very high. This state of affairs is not peculiar to the titrant chloramine-T, and is caused in part by the formation of sulphate complexes of antimony.

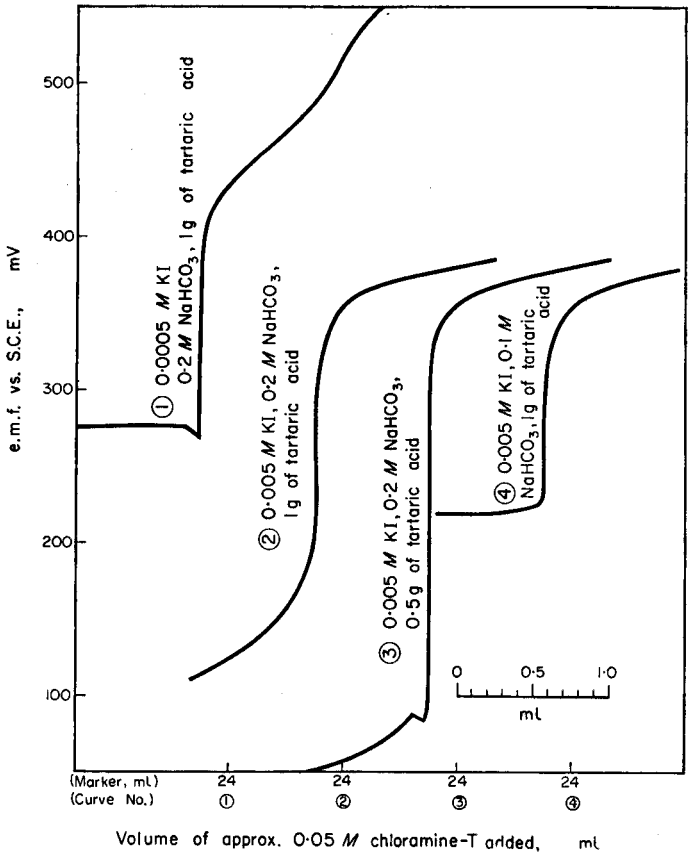

FIG. 5.—Direct titration with approx. $5 \times 10^{-2}M$ chloramine-T of 25-ml aliquots of approx. $5 \times 10^{-2}M$ antimonyl tartrate in bicarbonate buffer containing iodide and tartrate, at an equivalence point volume of 200 ml.

5. Titration with chloramine-T gives highly accurate results in adequately buffered media of pH 6·5–7·5 in the presence of 5×10^{-4} to $5 \times 10^{-3}M$ iodide if sufficient tartrate is added to prevent the formation of a precipitate. At low pH values the reaction is inhibited by the increased oxidation potential of the Sb^{V}/Sb^{III} system, and ceases at higher pH values because of hydrolysis of iodine. Since the primary reaction of chloramine-T with iodide to produce the active oxidising species, iodine, consumes hydrogen ion,[4] care must be taken to provide adequate buffer capacity to prevent the pH running undesirably high.

6. Accurate determination of $antimony^{III}$ with chloramine-T has also been shown[1] to be possible in $3M$ hydrochloric acid with the addition of 2–5 ml of $0{\cdot}1M$ iodine monochloride both potentiometrically and with amaranth as indicator, but the acid concentration is critical.

Zusammenfassung—Ein kritische Untersuchung der Titrationen von Sb(III) mit Chloramin-T wurde durchgeführt. Weite Änderungen in Konzentration von Salz- und Schwefelsäure, sowie der Einfluss von Puffern, in Gegenwart und Abwesenheit von Halidsalzen und Komplexbildnern wurde studiert. Zahlreiche reversible und irreversible Indicatoren wurden ebengalls untersucht. Genaue Resultate werden erhalten in 1–4 m Salzsäure mit potentiometrischer Anzeige und in 1–3 m Salzsäure mit Amaranth als Indicator. Beide Znzeigen erfolgen zu spät in Gegenwart von Bromid und Schwefelsäure, mit oder ohne Halidzusätzen. Einige andere Indicatoren sind in 2 m Salzsäure anwendbar. Titration in ausreichend gepufferter Lösung von pH 6.5–7.5 in Gegenwart von 5×10^{-4}–5×10^{-3} n Jodid geben die besten Resultate. In 3 m Salzsäure werden zufriedenstellende Resultate erhalten, wenn 2–5 ml 0.1 m Jodmonochlorid zugesetzt werden. Potentiometrische Indication und Amaranth arbeiten gut, doch sind die Bedingungen innerhalb eines engen Bereiches einzustellen.

Résumé—Les auteurs ont fait une étude critique du dosage de l'antimoine par la chloramine-T dans un grand domaine de conditions en milieux acide chlorhydrique, acide sulfurique et tamponné, en présence et en l'absence de concentrations variées d'ion halogénure et d'agent complexant, par la méthode potentiométrique. Un grand nombre d'indicateurs réversibles et irréversibles ont aussi été étudiés dans ces conditions. Des dosages précis sont possibles par titrage potentiométrique dans l'acide chlorhydrique 1 à 4*M*, et en utilisant comme indicateur l'amarante dans l'acide chlorhydrique 1 à 3*M*. Divers autres indicateurs sont utilisés dans l'acide chlorhydrique 2 *M*. Les deux méthodes, potentiométrique et avec indicateur visuel, donnent des points équivalents retardés en présence de bromure; et l'acide sulfurique avec et sans addition d'halogénure est un milieu qui ne convient pas. Le titrage dans des milieux convenablement tamponnés de pH 6,5 à 7,5 en présence d'iodure $5 \cdot 10^{-4}$ à $5 \cdot 10^{-3}M$ donne d'excellents résultats et est probablement la meilleure méthode. En milieu acide chlorhydrique 3*M*, avec addition de 2 à 5 ml. de monochlorure d'iode 0,1*M* des résultats satisfaisants sont obtenus en utilisant soit l'amarante, soit la potentiométrie pour déterminer le point équivalent, mais les conditions sont critiques.

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TITRIMETRIC ANALYSIS WITH CHLORAMINE-T–VII*

THE CHLORAMINE-T—HYDRAZINE REACTION

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Summary—The determination with chloramine-T of hydrazine in hydrochloric acid, sulphuric acid and buffer media with and without the addition of halides under a wide variety of conditions has been critically examined both potentiometrically and using a number of visual indicators. Under suitable conditions, analytically useful results are obtainable, but expectations raised by the ease of purification of hydrazine sulphate and the very high accuracy of its determination with other oxidants have not been fulfilled, and chloramine-T cannot be recommended for the accurate determination of hydrazine under any conditions.

THE remarkable promise, at present under investigation, of hydrazine sulphate as a primary standard, and the precision and accuracy of its titrimetric reactions with bromate,[2] iodate,[3,4] and alkalis,[5] suggested that it might afford a valuable alternative to arsenic^{III} in the standardisation of chloramine-T solutions.[6] Arsenious oxide, even after sublimation in oxygen, is slightly hygroscopic, which renders weighing difficult, whereas hydrazine sulphate does not suffer from this disadvantage. Preliminary investigations, however, quickly showed that the reaction in the presence of bromide with chloramine-T could not replace the oxidation of hydrazine by bromate.

Previous work on this reaction is scanty. Hydrazine has been titrated in sodium bicarbonate solution containing "a crystal" of potassium iodide and with starch as indicator;[8] no study of conditions is reported. It has also been titrated potentiometrically in hydrochloric acid solution of unspecified concentration,[9] and in the presence of bromide;[10] no details are given. Titration by the Andrews method has already been critically examined.[11]

Cahn and Powell[12] have studied the mechanism of oxidation of hydrazine in aqueous solution, and report three possible reactions, depending on the nature of the oxidant:

$$N_2H_5^+ = 4\varepsilon + N_2 + 5H^+ \quad (1)$$

$$2N_2H_5^+ = 2\varepsilon + 2NH_4^+ + N_2 + 2H^+ \quad (2)$$

$$2N_2H_5^+ = 4\varepsilon + HN_3 + NH_4^+ + 5H^+ \quad (3)$$

Certain oxidants, notably acidified iodate, give reaction (1) quantitatively, some give reactions (1) and (2) simultaneously, while reaction (3) is rare. In the attempt to oxidise hydrazine with chloramine-T according to reaction (1), should the other reactions occur then less than the amount of chloramine-T calculated for reaction (1) will be consumed. As will be shown, the errors are mostly positive, and in such instances as yield negative errors there is strong evidence that these are caused by slowness of

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reaction. Under favourable conditions, therefore, reaction (1) occurs to the exclusion of the alternatives. At hydrochloric acid concentrations of 1*M* or more, in the absence of other halides, very low and highly erratic results indicate that reaction (2) may be occurring.

EXPERIMENTAL

The preparation and purity of materials, the preparation and standardisation of solutions, and the preparation of reagents, indicators and buffers have been described.[1,6,7,11,13–15]

The methods of conducting visual indicator and potentiometric titrations have also been described.[6,7,13,14] The equivalence point volume of visual indicator titrations was arranged to be 100 ml, that of potentiometric titrations 200 ml, and the concentrations quoted refer to the equivalence point, due allowance for washing being made.

RESULTS AND DISCUSSION

1. *Reaction in chloride media*

Direct titration of hydrazine in hydrochloric acid of concentrations from 2·0 to 0·5*M* using amaranth as indicator gave inaccurate and irreproducible results, as shown in Table I, though it appears that the consumption of oxidant increases with decrease in

TABLE I.—TITRATION OF HYDRAZINE IN HYDROCHLORIC ACID MEDIUM WITH CHLORAMINE-T

Concentration of HCl, *M*	Indication	Titre, *ml*	Error, %
2	Amaranth	20·50	−12·8
2	Amaranth	21·00	−10·7
1	Amaranth	21·50	−8·6
1	Amaranth	21·87	−7·0
0·5	Amaranth	23·89	+1·6
0·5	Amaranth	23·73	+0·9
0·1	Potentiometric	23·83	+1·3

Calculated equivalence point, 23·52 ml.

acid concentration. Titration in hydrochloric acid of concentration greater than 0·5*M* is clearly valueless, while at lower acid concentrations the indicator amaranth merely fades slowly in the absence of bromide and gives no clear end-point. Potentiometric titration (Fig. 1) at an acid concentration of 0·1*M* gave high results, in agreement with amaranth at 0·5*M*. Though the potentials equilibrated rapidly before and after the end-point, the potentials at the end-point required more than 30 min to become steady.

Titration by any means in pure hydrochloric acid medium is totally unsatisfactory, in disagreement with the statement of Singh and Rehmann.[9] It may be noted that bromate gives similarly erratic results in the absence of added bromide.[2]

Reaction at high hydrochloric acid concentrations in the presence of iodine monochloride as a reaction intermediate[11] gives reasonable results, fairly consistent both potentiometrically and with carbon tetrachloride as indicator, but still about 0·1% high, amaranth giving yet higher results. This method has been commended[11] as the most satisfactory with chloramine-T as the titrant.

2. *Reaction in bromide media*

The influence of bromide at an equivalence point concentration of 0·1*M* was investigated both potentiometrically and with visual indicators over a wide range of acid concentrations.

(*a*) *Using rosaniline or amaranth as internal indicators.* With rosaniline, the colour change in 4·0*M* hydrochloric acid was poor and slow, while in 1·0*M* hydrochloric acid the purple colour was faintly visible 0·1 ml before the end-point which was itself early. Acid concentrations of 2 and 3*M* gave sharp end-points, but the reproducibility was

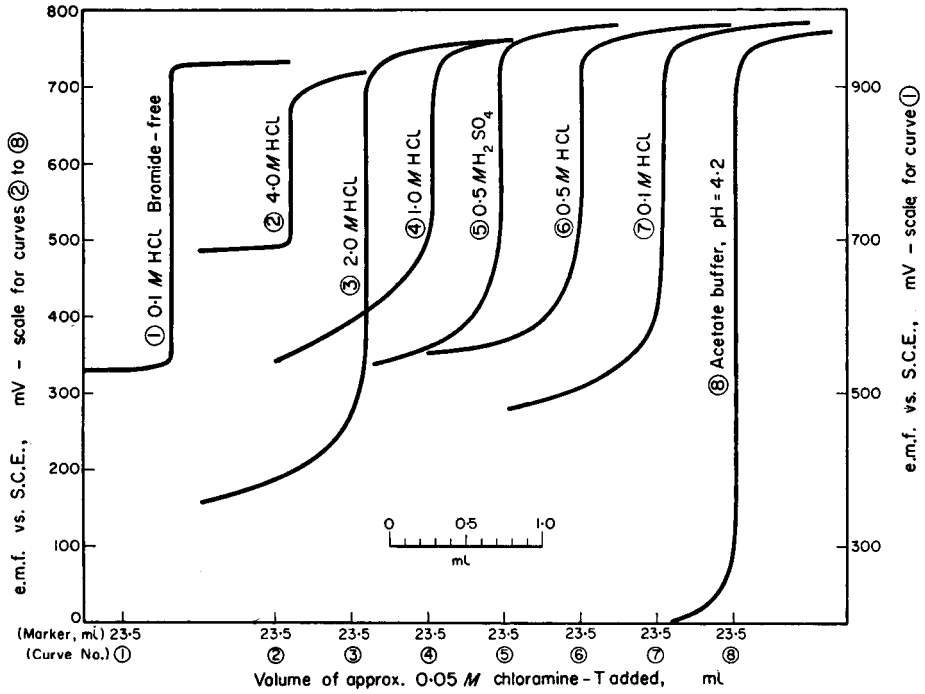

FIG. 1.—Direct titration of 25-ml aliquots of approx. $2·5 \times 10^{-2}M$ hydrazine in media 0·1*M* in bromide (except curve 1) at an equivalence point volume of 200 ml, with approx. $5 \times 10^{-2}M$ chloramine-T.

unsatisfactory. This contrasts sharply with highly accurate results obtainable with bromate under the same conditions. With amaranth, the end-point occurs progressively earlier as the hydrochloric acid concentration falls from 2·0 to 0·5*M*, then becomes later at 0·1*M* and in acetate buffer of pH 4·2. Although the end-points are reasonably sharp, they are not reproducible and vary widely with acid concentration. The results recorded in Table II are individual values given in illustration of the variation observed.

(*b*) *Potentiometric titration.* Titrations conducted under conditions similar to those in (*a*) gave curves shown in Fig. 1. Pre-end-point potentials were unsteady but after the end-point the equilibration was rapid. The shape of the curve follows a form of progression from pH 0 to pH 4·2. Variations in the results (Table II) similar to those with amaranth were observed, but the agreement in values is poor. That the nature of the acid is unimportant is indicated by the resemblance between the curves for 0·5*M* hydrochloric and 0·5*M* sulphuric acids, though the disparity in end-point (0·04 ml) is greater than the experimental error.

TABLE II.—TITRATION[b] OF HYDRAZINE IN MEDIA 0·1*M* IN POTASSIUM BROMIDE WITH CHLORAMINE-T

Conditions at equivalence point	Potentiometric		Amaranth		Rosaniline	
	End-point *ml*	Error %	End-point *ml*	Error %	End-point *ml*	Error %
4·0*M* HCl	23·60	+0·34	—		23·62	+0·43
3·0*M* HCl	—		—		23·58	+0·26
2·0*M* HCl	23·60	+0·34	23·57	+0·21	23·57	+0·21
1·0*M* HCl	23·54	+0·09	23·49	−0·13	23·45	−0·30
0·5*M* HCl	23·51	−0·04	23·42	−0·43	—	
0·5*M* H_2SO_4	23·48	−0·17	—		—	
0·1*M* HCl	23·54	+0·09	23·50	−0·09	—	
Buffer[a] pH 4·2	23·51+	0	23·52	0	—	

[a] Add 25 ml of a solution 0·6*M* in sodium acetate and 1·4*M* in acetic acid for an equivalence point volume of 100 ml.

[b] Calculated equivalence point, 23·52 ml.

The presence of bromide gives a considerable improvement in the results, which are fairly satisfactory at hydrogen ion concentrations of 10^{-4} to 4·0*M* for the potentiometric method, 10^{-4} to 2·0*M* for amaranth, and 2·0–4·0*M* for rosaniline. The results do not in any way compare in precision or accuracy with the bromate method, so chloramine-T cannot be recommended for the accurate determination of hydrazine even in the presence of bromide. The end-points are sharp, and fall within ±0·1 ml of the equivalence point over the range of conditions examined, and occasional results are in quantitative agreement with theory, but the end-points are not reproducible, and there is therefore an uncertainty which enforces the conclusion that the method is not sound.

3. *Reaction in iodide media*

Audrieth and Ogg[16] report that in the titration of hydrazine with iodine solutions, the pH of the titration solution should be maintained between 7 and 7·4. At lower values, the reaction between iodine and hydrazine is quantitative but slow, while at higher values low results occur because of air oxidation of the hydrazine. The present investigation covers a range of pH values and iodide concentrations.

(*a*) *Using starch as an internal indicator.* Addition of 2 ml of 1% starch solution 1 ml before the equivalence point and titration to the first perceptible permanent blue colour gave the results shown in Table III. The results appear to be equally satisfactory or unsatisfactory in all the conditions examined. However, at pH 6·6, the reaction was slow, iodine being liberated prematurely and disappearing gradually. This effect is most marked at the highest iodide concentration. At pH 7·1 the titrations were qualitatively satisfactory and the results were reasonably reproducible though still high, except in $5 \times 10^{-3}M$ iodide when unusually early end-points appeared. At pH 8·3, the end-points became less sharp as the iodide concentration is increased because of the production of a brown colour prior to the iodine blue. The results do not indicate air oxidation of hydrazine.

(*b*) *Potentiometric titration.* An illustrative family of curves is given in Fig. 2 and the results in Table III. In all of the titrations the potentials were unsteady before the

TABLE III.—TITRATION OF HYDRAZINE IN IODIDE MEDIA WITH CHLORAMINE-T

Calculated equivalence point, 23·52 ml.

Buffer	Iodine concn, *M*	Potentiometric End-point *ml*	Potentiometric Error %	Starch End-point *ml*	Starch Error %
20 ml of I	0·005	23·60	+0·34	23·51	−0·04
	0·025	23·60	+0·34	23·57	+0·21
	0·05	23·57	+0·21	23·57	+0·21
15 ml of II	0·005	23·49	−0·13	23·40	−0·51
	0·025	23·57	+0·21	23·57	+0·21
	0·05	—		23·57	+0·21
	0·10	23·58	+0·26	23·57	+0·21
20 ml of III	0·005	23·60	+0·34	23·56	+0·17
	0·025	23·60	+0·34	23·58	+0·26
	0·05	23·60	+0·34	23·61	+0·38

Buffer solutions:

I. Solution 0·1*M* in potassium dihydrogen phosphate and 0·233*M* in disodium hydrogen phosphate; measured pH at equivalence point, 6·6 for starch, 6·7 for potentiometric titration.

II. Solution 0·0167*M* in potassium dihydrogen phosphate and 0·317*M* in disodium hydrogen phosphate; measured pH at equivalence point 7·1 for starch, 7·2 for potentiometric titration.

III. 1*M* sodium bicarbonate; measured pH at equivalence point, 8·3, in both indicator and potentiometric titrations.

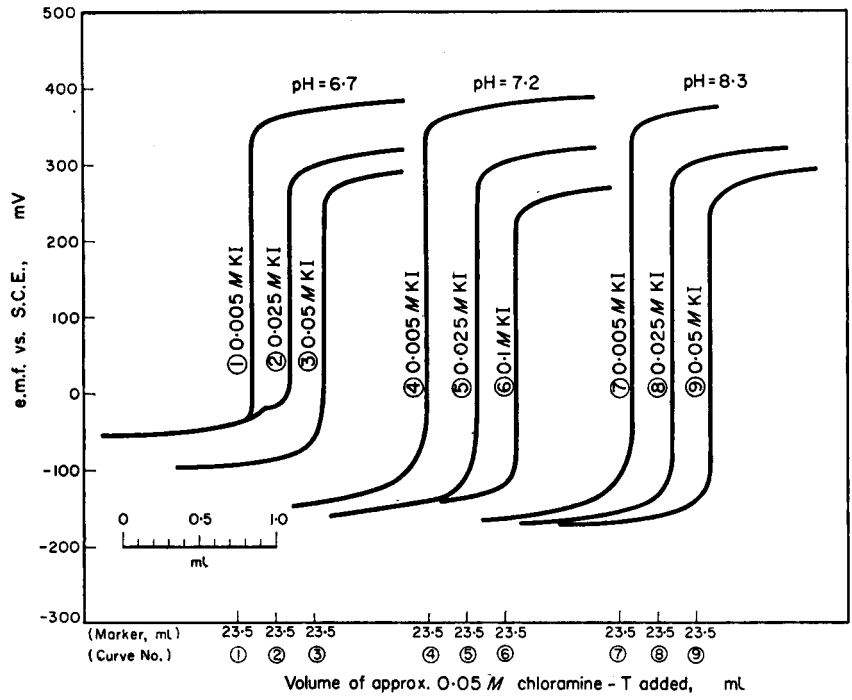

FIG. 2.—Direct titration of 25-ml aliquots of approx. 2·5 × $10^{-2}M$ hydrazine in various buffer media in the presence of iodide, with approx. 5 × $10^{-2}M$ chloramine-T.

end-point, but equilibrated rapidly after the end-point, and the yellow iodine colour became visible 0·02 ml after the recorded end-point. The results agree fairly well with those of the visual indicator titrations, with a tendency to be somewhat later. There is again no evidence for air oxidation at high pH values.

The conditions for titration of hydrazine in an iodide medium are rather critical, the most favourable being a pH of 7·1, in agreement with Audrieth and Ogg,[16] and an iodide concentration of 0·025–0·05*M*. This does not entirely accord with the claims of Komarovsky *et al.*[8] The results are in fair agreement with the preferred method of titration in presence of iodine monochloride at high hydrochloric acid concentrations.[11]

CONCLUSIONS

Expectations of the reaction between chloramine-T and hydrazine have not been fulfilled. Hydrazine can be determined by titration with chloramine-T in media containing bromide, iodide or iodine monochloride under the conditions specified, with an accuracy suitable for routine work, but none of the methods yields results of a calibre suitable for accurate work or for standardising chloramine-T solutions. Chloramine-T cannot, therefore, be substituted for bromate in this determination. The same exclusion applies in the determination of hydroxylamine,[7] for which no satisfactory results are obtainable, and in the determination of antimony,[1,7] and of thallium.[7,17] The reason for this is obscure, because in the presence of bromide both oxidants react through the same active species, bromine.

High results for hydrazine are of frequent occurence under many conditions, and would seem to exclude the reactions (2) and (3) in these conditions. It is possible that reaction (4) occurs to a small extent.

$$N_2H_5^+ + H_2O = N_2O + 7H^+ + 6\varepsilon \qquad (4)$$

No direct indentification of nitrous oxide has been made in this case, but it has been observed in the products of oxidation of hydrazine by vanadate.[18]

Chloramine-T cannot be recommended for the accurate determination of hydrazine under any conditions.

Zusammenfassung—Die Titration von Hydrazin mit Chloramin T in salzsaurem, schwefelsaurem und gepuffertem Medium, mit und ohne Halidzusätzen wurden studiert. Endpunktanzeige war potentiometrisch und visuell mit verschiedenen Indikatoren. Unter geeigneten Bedingungen können verwendbare Resultate erhalten werden. Da jedoch zahlreiche, ausgezeichnete Methode auf anderer Basis existieren wird diese Titration nicht empfohlen.

Résumé—Les auteurs ont étudié d'un point de vue critique le dosage de l'hydrazine par la chloramine T en milieux acide chlorhydrique, acide sulfurique et tamponné, avec et sans addition d'halogénures en faisant varier un grand nombre de conditions; la potentiométrie et un certain nombre d'indicateurs visuels ont été utilisés pour déterminer le point équivalent. Dans des conditions convenables, des résultats utilisables au point de vue analytique ont été obtenus, mais les prévisions attendues à cause de la facilité de purification du sulfate d'hydrazine et de la très grande précision de son dosage par d'autres oxydants n'ont pas été réalisées; la chloramine T ne peut donc pas être recommandée pour le dosage précis de l'hydrazine dans n'importe quelle condition.

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APPLICATIONS OF INFRARED SPECTROSCOPY—VII*

THE BEHAVIOUR OF THIOALKYL COMPOUNDS UNDER ZEISEL REACTION CONDITIONS.

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Summary—Vapour-phase infrared spectroscopy has been used to study the behaviour of a wide range of thioalkyl compounds when refluxed with constant-boiling hydriodic acid. A very wide range of reactivity has been observed. Unusually labile compounds exist which react quantitatively in less than 3 hr; the kinetics of the decomposition of such compounds must be investigated individually, since over-production of methyl iodide can occur. Many thiomethyl compounds, however, do not yield methyl iodide, and others react very slowly, giving variable non-quantitative yields of methyl iodide after reflux for 16-20 hr. It is therefore concluded that the mere extension of Zeisel reaction conditions for prolonged reflux periods does not usefully provide a general method for the functional group analysis of thioalkyl compounds.

THIOALKYL compounds, which are of current interest in sugar chemistry,[1] yeast metabolism,[2] choline-esterase inhibition,[3] and the chemistry of food-stuffs,[4] have received considerable attention in recent years.

A modified Zeisel reaction[5] has long been used in protein studies to determine the thiomethyl group in methionine. Kassel and Brand[6] suggested improvements to Baernstein's method,[5] and the method of Kuhn, Birkofer and Quackenbush[7] was modified[8] so that both alkoxyl and thiomethyl groups could be determined.

Much is known of the chemistry of thioethers.[9,10,11] The analytical methods applicable to mercapto groups, disulphides and sulphides (thioethers) have been reviewed,[12,13,14,15] and special methods continue to be described,[16,17,18] particularly for biological materials. Many thioethers are cleaved at pH 8–10 by silver or mercury salts;[10] fission of the carbon-sulphur bond has been more extensively studied in alkaline solution[19] than in acids.[20] In general, thioethers and thiolesters react much more slowly in aqueous acids than do their oxygen analogues,[20,21] although the ease of cleavage of carbon-sulphur bonds is influenced by the presence of substitution[22] and β-unsaturation[11] in the molecule.

Early investigators[23,24] reported applications of a modified Zeisel reaction to aromatic thiomethyl compounds, in which a longer reaction period (which was not specified) was required (*cf.* ref. 25). It has been observed,[26] however, that some compounds do not give quantitative results; *S*-methylthiamin[27] gives only 33% of the theoretical yield of methyl iodide. It is apparent that early investigators were involved in considerable experimental difficulties,[23,24] particularly when gravimetric methods were used. A wide range of thioethers and thiolesters has therefore been studied by the infrared method[28] in an attempt to clarify some of the reported anomalies.

* Part VI: D. M. W. Anderson, *Talanta*, 1961, **8**, 832

EXPERIMENTAL

Apparatus

The apparatus has been described elsewhere,[28] together with the technique for trapping volatile reaction products and the infrared method for their subsequent identification and estimation.

Compounds

The majority of compounds investigated were reagent-grade commercial samples which conformed, after recrystallisation or distillation where necessary, to literature description. The other compounds investigated were research specimens (kindly provided by Dr. D. Leaver of this department and by Dyestuffs Division, Messrs. I.C.I. Ltd.) for which satisfactory elemental analyses existed or were obtained (Messrs. Weiler and Strauss, Oxford, England).

Procedure

Samples of the compounds listed in Table I were refluxed, for the periods indicated, with hydriodic acid (6 ml of constant-boiling azeotrope, pre-conditioned[28]) using cylinder nitrogen ("N.O.F." grade) as flow-gas (6-8 ml per min). Sample weights giving 1-4 mg of methyl iodide were normally taken: larger samples were used to permit the identification of minor reaction products. The compounds were dissolved with care in molten phenol[28] before addition to the reaction-flask; a recent report[29] has confirmed the effectiveness of this technique. The mixture of volatile products was collected, after passage through Anhydrone, in a trap immersed in liquid nitrogen. The components of each mixture were subsequently identified by vapour-phase infrared spectroscopy by reference to spectra obtained from authentic compounds. None of the mixtures was sufficiently complex for prior separation of the components by G. L. C. to be necessary, and the presence of other components did not interfere with the determination of methyl iodide.

RESULTS

All compounds containing sulphur produce some hydrogen sulphide on reflux with hydriodic acid; only volatile products other than hydrogen sulphide are reported below.

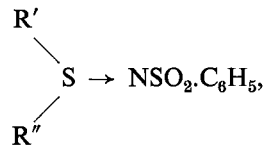
1. *Compounds giving no reaction*

The following thiolesters and thioethers gave no volatile products under Zeisel reaction conditions for reflux periods of 18 hr: methylchlorothiolformate, ethylchlorothiolformate, methyl phenyl sulphide (thioanisole), methyl-α-naphthyl sulphide, 2-thiomethyl-1,4-naphthoquinone, 3-methyl-2-thiomethyl-1,4-naphthoquinone.

The following compounds were partially volatilised, without reaction, from the reaction-flask: methyl and ethyl mercaptan, dimethyl and diethyl sulphide, dimethyl and diethyl disulphide.

2. *Compounds which react but do not yield alkyl iodide*

Dimethyl sulphide was produced from dimethylsulphoxide (fast) and from dimethylsulphone (slow), whilst compounds of the type



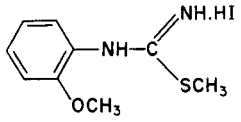
where R′, R″ = *methyl* or *ethyl*, liberated the corresponding dialkyl sulphide. Phenacyl methyl trithiocarbonate gave carbon dioxide, carbon monoxide, and methyl mercaptan.

3. *Compounds which react, yielding alkyl iodide and other volatile products*

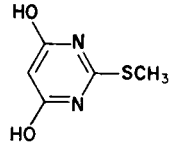
Thiodiglycol and compounds containing the $—S(CH_2.CH_2OH)_2$ grouping gave

ethyl iodide + ethylene in 1-2 hr. Such compounds therefore react similarly to glycols and glycol ethers.[30]

Thiocyanato-methane gave 1 mole of methyl iodide in 2·5 hr, together with some thiocyanogen. The same product was also given by (I) which gives 1 mole of methyl iodide (from the alkoxyl group) in 0·5 hr; the total yield of methyl iodide reached 2 moles after reflux for 20 hr.



(I)



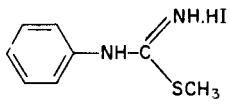
(II)

4. *Compounds which yield only methyl iodide*

Table I lists the kinetic results obtained.

TABLE I.—THE RATE OF PRODUCTION OF METHYL IODIDE FROM SOME THIOMETHYL COMPOUNDS

Compound	Moles of methyl iodide produced per mole of compound
2-(Methylthio)benzo-thiazole	0·44 (0·5 hr); 0·76 (1 hr); 0·87 (2 hr); 0·99 (3 hr); 1·12 (4 hr)
S-Methylthiouronium sulphate	0·35 (2 hr); 0·60 (3 hr); 0·98 (4 hr); 1·05 (4.5 hr)
II	0·30 (1 hr); 0·45 (2 hr); 0·55 (2·5 hr); 0·76 (3-4 hr, const.)
III	0·50 (16 hr); 0·52 (20 hr)
IV	0·49 (20 hr)
V	0·25 (12 hr); 0·30 (18 hr)
Methyl-*p*-tolyl sulphide	0·25 (16 hr)
Methyl-*p*-nitrophenyl sulphide	0·15 (17 hr)
Methionine	0·86 (0·5 hr); 0·96 (1 hr); 0·99 (2 hr); 1·15 (2·5 hr); 1·25 (3 hr)
N-Acetyl-DL-methionine	0·86 (1 hr); 1·00 (1·5 hr); 1·22 (2 hr)
Glycyl-DL-methionine	0·1 (15 hr)
S-Methyl-D(+) cysteine	0·15 (2 hr); 0·36 (4 hr); 0·60 (8 hr); 0·70 (16 hr); 0·76 (22-40 hr, const.)
S-Methylglutathione	0·14 (2 hr); 0·46 (8 hr); 0·57 (12 hr); 0·66 (18 hr); 0·75 (22-40 hr, const.)



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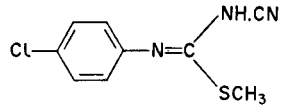
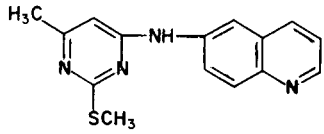


(IV)



(V)

5. *Investigation of amino-acids*

Table I shows the rate of production of methyl iodide from methionine and S-methyl derivatives of amino acids. In connection with the possible over-production

of methyl iodide, it was observed that Baernstein had found[31] all samples of leucine to give small amounts of methyl iodide. Whilst Baernstein considered that this indicated the presence of methionine, the methyl iodide could have arisen from general decomposition of the amino-acid molecules. Whilst one sample of L-leucine (shown by paper chromatography to contain some methionine) did give approximately 0·1 mole of methyl iodide, no methyl iodide was given by two different commercial samples of DL-leucine which gave only one spot when examined by paper chromatography. Similarly no methyl iodide was evolved from the following: cystine, homocystine, djenkolic acid, glutathione (reduced), taurine, glycine, alanine, DL-α-amino-n-butyric acid, DL-α-amino-iso-butyric acid, DL-β-amino-iso-butyric acid, L-valine, DL-valine, DL-nor-valine, DL-nor-leucine, DL-iso-leucine.

DISCUSSION

The results quoted show that, under the conditions of the Zeisel alkoxyl determination, the behaviour of thioalkyl groups is extremely variable. It would be misleading to suggest that the determination of *S*-methyl groups generally follows the procedure for *O*-methyl groups, even if the time of reaction be extended by several hours (*cf.* ref. 25 and 32). Indeed, as might be expected from the known stability of the sulphur-carbon bond,[10,11,20,21] the few labile compounds which do give quantitative yields of methyl iodide can be regarded as exceptions to the general rule; those compounds which react rapidly must be considered as possible sources of anomalous alkoxyl determinations. No generalisations regarding reaction conditions or reflux period required can be made; obviously, the kinetics of decomposition of each thiomethyl compound must be investigated individually (*cf.* ref. 33).

The observed rate of formation of methyl iodide from methionine agrees with that reported by previous workers,[5,6] who observed[6] that small differences in reaction rate can be attributed to variations in the design of apparatus. Baernstein's earliest procedure[5] (1932) recommended a reaction period of 15 hr, but this was later (1934) amended to 3 hr. Our results show the possibility (which does not appear to have been appreciated previously) of over-production of methyl iodide from those thiomethyl compounds which are sufficiently labile to react in short periods.

Theoretical reasons for the failure of aqueous halogen acids to cleave carbon-sulphur bonds as effectively as carbon-oxygen bonds have been discussed (*cf.* refs. 11, p. 36, and 21, p. 677). The very wide range of reactivities observed in thioethers is not unique: a remarkable range of reactivity is also to be found in their oxygen analogues.[34] It is of interest that compound II is not particularly labile, whereas methoxy compounds of this type were found[34] to be unusually reactive in acid solution.

The behaviour of thiomethyl compounds in Herzig and Meyer's pyrolytic procedure[35] for alkimide groups has not been studied. Experiments were made, however, with acid more concentrated (67% HI, sp. gr. 1·94) than the constant-boiling azeotrope (55% HI, sp. gr. 1·70). In agreement with previous reports,[23] the more concentrated acid did not cause appreciably faster liberation of methyl iodide. The addition of large amounts of phenol, propionic anhydride, or mercuric chloride to the reaction mixture[23,24] (*cf.* ref. 11, p. 39) did not influence the kinetic results.

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Zusammenfassung—Infrarotspectroskopie in der Gasphase wurde angewandt um das Verhalten von Thioalkylverbindungen zu studieren, wenn sie unter Rückfluss mit konstant siedender Jodwasserstoffsäure behandelt werden. Ungewöhnlich labile Komponenten existieren, welche weniger als 3 Stunden zur quantitativen reaktion benötigen. Die Kinetik der Zersetzung solcher Komponenten muss individuell studiert werden, da Überproduktion von Methyljodid auftreten kann. Viele Verbindungen jedoch geben kein Methyljodid, ander reagieren sehr langsam, sodass die Ausbeute selbst nach 16–20 Stunden nicht quantitativ ist. Es wird daher geschlossen, dass die blosse zeitliche Ausdehnung der Zeiselmethode keine allgemeine Methode zur Analyse funktioneller Gruppen in Thioalkylverbindungen ergeben kann.

Résumé—Les auteurs ont utilisé la spectroscopie infra-rouge en phase vapeur pour l'étude du comportement d'un grand nombre de composés thioalcoylés chauffés au reflux avec de l'acide iodhydrique bouillant constamment. Ils ont observé un domaine de réactivité très large. Il existe des composés inhabituellement labiles qui réagissent quantitativement en moins de trois heures; la cinétique de la décomposition de tels corps doit être étudiée individuellement, car il peut y avoir surproduction d'iodure de méthyle. Cependant, de nombreux composés thiométhylés ne donnent pas d'iodure de méthyle et d'autres réagissent très lentement en donnant des rendements variables non quantitatifs en iodure de méthyle après reflux pendant 16–20 heures. On peut donc conclure que le simple développement des conditions de la réaction de Zeisel pour des périodes de reflux prolongées n'apporte pas de méthode générale d'analyse du groupement fonctionnel des composés thioalcoylés.

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Talanta, 1962, Vol. 9, pp. 617 to 621. Pergamon Press Ltd. Printed in Northern Ireland

SHORT COMMUNICATIONS

Isotopic-dilution analysis by solvent extraction—IV: *Selective determination of traces of copper with dithizone

(*Received* 6 *February* 1962. *Accepted* 5 *March* 1962)

INTRODUCTION

IN our first communication[1] the theoretical foundation was given for the determination of trace amounts of metals by means of isotopic-dilution analysis by solvent extraction; and in the following papers[2,3] the procedures for highly selective and sensitive determination of zinc and mercury were developed. In the present work, the possibility of using this method for determination of traces of copper has been confirmed. From equilibrium constants of extraction of metal dithizonates[4] it can be seen that in the determination of copper an excess of the following metals will interfere: palladium, mercury, platinum, silver, bismuth and gold. In presence of iodide, which forms very stable complexes with mercury, silver and bismuth,[4] interference from only palladium, platinum and gold may be expected.

EXPERIMENTAL

Apparatus

Scintillation counter with NaI-Tl crystal.

Geiger-Müller end-window counter.

pH-meter: Radiometer TTTl (Copenhagen).

Mechanical shaker.

Glass test-tubes with ground stopper, volume 25 ml.

Reagents

Distilled water: Twice distilled, further purified by passage through a column of ion-exchanger; used for dissolving all reagents.

Carbon tetrachloride: A.R. twice distilled.

Dithizone: A.R.

Buffer solution: Dissolve 15 g of potassium iodide, A.R., 13 g of ammonium acetate, A.R., in 100 ml of water and add glacial acetic acid, A.R., to attain a pH-value of 4·8 ± 0·2. This solution was purified before each experiment by dithizone extraction.

Radio-copper solution (^{64}Cu, $T_{\frac{1}{2}} = 12{\cdot}8$ h): Dissolve copper sulphate (initial specific activity 500 mC/g of copper) in acidified water and dilute to the required concentration.

Non-active copper solution: Dissolve copper sulphate in acidified water and dilute to the required concentration.

Procedure

Add to 10 ml of the test solution of non-active copper (of the order of magnitude of 10^{-7} to 10^{-10} g of copper/ml) which contains a great excess of other metals, a suitable amount of radio-copper, y. The most accurate results are obtained if the amounts of nonactive and active copper are approximately the same. After addition of 1 ml of buffer solution, the pH of the test solution must be 4.8 ± 0.2. If the original solution is too acid, decrease its acidity by addition of a further amount of buffer solution. Extract the solution prepared in this way with about 1 ml of dithizone solution in carbon tetrachloride of suitable concentration (the concentration of dithizone must be always less than the amount which corresponds to the stoicheiometric ratio of copper present). After shaking 10 min, separate the organic phase and measure the activity of 0·6 ml of the solution by a

* Part III: See reference 3.

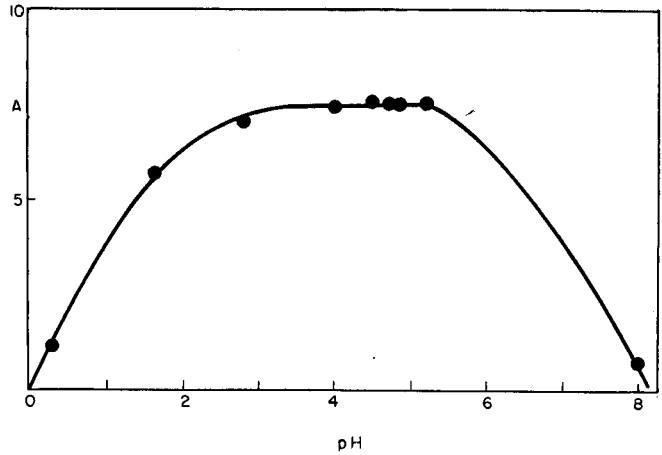

FIG. 1

√.—Influence of pH on activity of extract (10^3 cpm.)

TABLE 1.—EXTRACTION OF COPPER BY DITHIZONE.
($1{\cdot}27 \times 10^{-7} - 2{\cdot}4 \times 10^{-10}$ μg of Cu/ml)[a]

Copper taken, μg (x)	Active copper added, μg (y)	Activity of extracts[b] (A_1)	Activity of extracts[b] (A_2)	Copper found, μg (x)	Deviation, μg	Other metals present, μg
1·271	1·083	15,878	7,608	1·117	−0·094	100 μg Zn, Co, Ni, Cd
		15,878	7,410	1·238	−0·033	100 μg Pb, In, Tl
		15,878	7,502	1·209	−0·062	—
		8,015	3,635	1·305	+0·034	100 μg Hg, Ag, Bi
		8,015	3,675	1·279	+0·008	100 μg Zn, Co, Ni, Cd
		8,015	3,687	1·271	0·000	100 μg Pb, In, Tl
		8,015	3,627	1·310	+0·039	—
0·2542	0·2166	4,054	1,824	0·2647	+0·0105	10 μg Hg, Ag, Bi
		4,054	1,860	0·2400	−0·0142	—
0·2654	0·2780	2,548	1,322	0·2578	−0·0076	10 μg Hg, Ag, Bi
		2,548	1,291	0·2707	+0·0153	10 μg Zn, Co, Ni, Cd
		2,548	1,330	0·2546	−0·0108	10 μg Pb, In, Tl
		2,548	1,290	0·2711	+0·0057	10 μg Mn, Sn, Fe
		2,548	1,303	0·2656	+0·0002	—
0·0237	0·0201	1,060	513	0·0213	−0·0024	1 μg Hg, Ag, Bi
		1,060	458	0·0263	+0·0026	1 μg Zn, Co, Ni, Cd
		1,060	495	0·0228	−0·0009	1 μg Pb, In, Tl
		1,060	450	0·0269	+0·0032	1 μg Mn, Sn, Fe
		1,060	488	0·0235	−0·0002	—
		782	367	0·0228	−0·0009	1 μg Hg, Ag, Bi
		782	376	0·0217	−0·0020	1 μg Zn, Ni, Co, Cd
		782	387	0·0205	−0·0032	1 μg Pb, In, Tl
		782	388	0·0204	−0·0033	1 μg Mn, Sn, Fe
		782	360	0·0237	0·0000	—
0·0024	0·0201	1,060	940	0·0022	−0·0002	—
		782	738	0·0021	−0·0003	—

[a] Volume of solution analysed in all experiments listed in Table I was 10 ml.

[b] In the range $1{\cdot}3 \times 10^{-7}$ g of Cu/ml, concentration of dithizone was $2 \times 10^{-5}M$
$2{\cdot}6 \times 10^{-8}$ g of Cu/ml, concentration of dithizone was $5 \times 10^{-6}M$
$2{\cdot}4 \times 10^{-9}$ g of Cu/ml, and $2{\cdot}4 \times 10^{-10}$ Cu/ml, concentration of dithizone was $5 \times 10^{-7}M$

All activities (cpm) listed in Table I are mean values for 4 or 6 measurements.

scintillation counter (for high activity samples) or by a Geiger-Müller counter (for small activity samples). This activity is A_2. At the same time, treat the solution which contains only radio-copper and 1 ml of buffer solution in exactly the same way. Measure the activity of 0·6 ml of the organic phase in the same way (activity A_1).

The amount of non-active copper (x) is calculated from the equation

$$x = y \cdot \left(\frac{A_1}{A_2} - 1\right).$$

RESULTS AND DISCUSSION

The influence of pH on the extraction of copper by a $2 \times 10^{-5}M$ solution of dithizone in carbon tetrachloride is shown in Fig. 1. The volume of the aqueous phase was ten times larger than the volume of the organic phase. Under these conditions, at pH 4·0 to 5·2 the maximum of copper is extracted, which is in agreement with the predicted value.[1] (For the concentration used, the maximum extraction is in the range pH 3·5–5·0.)

In Table I the results of determinations carried out by the procedure described are given. In this determination even a large excess of metals forming extractable complexes with dithizone (mercury, silver, bismuth, zinc, cobalt, nickel, cadmium, lead, indium, thallium, manganese, tin and iron) does not interfere.

This method has been used for the determination of copper in pure water and in urea.

The method is very simple and rapid. A single extraction of copper from a solution containing an excess of interfering metals is appreciably simplier than the conventional colorimetric determination of copper by dithizone. Comparison of our results with values from the literature[5] indicates that the determination of copper by this method is more sensitive (maximum sensitivities of the methods mentioned are given in brackets) than determination by flame photometry (0·1 μg/ml), by the graphite DC arc (0·2 μg/ml), colorimetrically (0·03 μg/ml) or by activation analysis (0·04 μg/ml—5 . 10^{11} neutron/cm^2 sec; 0·002 μg/ml—10^{13} neutron/cm^2 sec).

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Summary—Copper is determined by a single extraction in the form of a complex with dithizone in amounts of 10^{-7} to 10^{-10} g/ml. Even a large excess of metals which form extractable complexes with dithizone do not interfere in the analysis. The method is very simple and rapid, consisting of a single extraction of the solution to be analysed, and measurement of the activity of the extract. The procedure is more sensitive than other methods of determining copper.

Zusammenfassung—Kupfer kann nach einer einzigen Ausschüttellung mit Dithizon in Mengen von 10^{-7}–10^{-10} g/ml bestimmt werden. Die Analyse wird selbst von grossen Mengen anderer Ionen, die mit Dithizon extrahierbar sind, nicht gestört. Die Activität des Extractes wird gemessen. Die Methode ist weit empfindlicher als andere Methoden zur Bestimmung von Kupfer.

Résumé—Le cuivre a été dosé par simple extraction sous forme d'un complexe avec la dithizone pour des quantités de 10^{-7} à 10^{-10} g/ml. Dans l'analyse, même un grand excès de metaux, qui forment avec la dithizone des complexes extractibles, ne gêne pas. La méthode est très simple et rapide, car elle consiste en une extraction de la solution à analyser et en la mesure de l'activité du composé extrait. La méthode mise au point est beaucoup plus sensible que les autres méthodes de dosage du cuivre.

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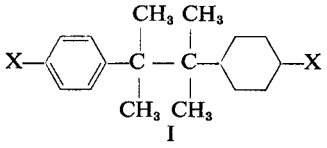
Applications of infrared spectroscopy—VIII*: Investigation of a reported anomalous Zeisel alkoxyl reaction

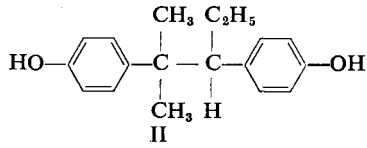
(*Received* 23 *February* 1962. *Accepted* 28 *February* 1962)

SEVERAL examples of molecules which react anomalously in the Zeisel alkoxyl reaction have been reported,[1,2,3] and solvent retention is known[4,5,6] to be a potential source of error in alkoxyl determinations.

Huang and Morsingh[7] reported that 2,3-dimethyl-2,3-diphenylbutane (I, X = H) and certain of



I



II

its derivatives (I, X = OH, NO_2) reacted anomalously in the Zeisel reaction, giving an apparent methoxyl content of 3·3%. Such a result appeared surprising; when it was observed that the experimental results quoted[7] were somewhat variable, and that the specimen used[7] had been prepared by a method[8] involving crystallisation from ethanol, it appeared that the reported anomaly might be, in effect, a further example of solvent retention. If so, application of the infrared alkoxyl method[9] would reveal that ethyl iodide, and not methyl iodide, was the reaction product.

2,3-Dimethyl-2,3-diphenylbutane, prepared by Farmer and Moore's method,[8] was re-crystallised from ethanol. After drying in the normal way, the product had m.p. 118° (lit., 118–119°). Analysis (Weiler and Strauss, Oxford,) England gave %C = 90·51 %H =, 9·34; required, %C = 90·75, %H = 9·25. When treated with constant-boiling hydriodic acid, under the conditions described by Anderson and Duncan,[9] this compound gave no volatile reaction products, even after prolonged reflux overnight. Indeed, so stable is this hydrocarbon that it was recovered unchanged (identity of infrared spectrum) from the hydriodic acid reaction medium. This compound therefore neither retains solvent of crystallisation nor reacts anomalously under *normal* Zeisel conditions.

It is perhaps significant that Huang and Morsingh reported[7] that neither the dimethoxy derivative (I, X = OCH_3) nor compound II reacted anomalously, and that drastic conditions, normally reserved for the analysis of *N*-methyl groups, were used[10] in their analyses. Thus the sample was dissolved in phenol and acetic anhydride and refluxed with hydriodic acid; after evaporation to dryness, the residue was heated above 300°. It is quite unreasonable for results obtained by such a procedure to be described[10] as anomalous Zeisel methoxyl determinations.

Acknowledgement—Financial support from the Sudanese Government (for M. A. H.) and from the P.C.S.I.R., Pakistan (for S. S. H. Z.) is gratefully acknowledged.

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Summary—2:3-dimethyl-2:3-diphenylbutane is stable to reflux with constant-boiling hydriodic acid under standard Zeisel alkoxyl reaction conditions. A previous report that this compound reacts anomalously is therefore incorrect.

Zusammenfassung—2,3-Dimethyl-2,3-diphenylbutan ist stabil, wenn es unter Rückfluss mit konstantsiedender Salzsäure gemäss den Bedingungen einer Alkoxylbestimmuhg nach Zeisel gekocht wird. Eine frühere Mitteilung, dass die Verbindung abnormales Verhalten zeigt, ist daher unrichtig.

Résumé—Le 2-3-diméthyl-2-3-diphénylbutane est stable quand il est chauffé au reflux avëc de l'acide iodhydrique bouillant constamment dans les conditions de la réaction standard de Zeisel pour les alcoyles. Un rapport antérieur prévoyant que ce composé réagit de facon anormale est donc incorrect.

* Part VII: *Talanta*, 1961, **9**, 611.

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Talanta, 1962, Vol. 9, pp. 623 to 624. Pergamon Press Ltd. Printed in Northern Ireland

LETTER TO THE EDITOR

Separation of mercury by extraction with tri-n-butyl phosphate

SIR,

TRI-n-BUTYL phosphate (TBP) has become well-known as an agent for extracting inorganic species from aqueous solutions. The results of Ishimori *et al.*[1] indicate that mercury^{II} differs from many other elements in that it is extracted into TBP from very dilute hydrochloric acid. It seems, therefore, that TBP might prove useful for the separation of traces of mercury. We have measured the distribution coefficient

$$D = \frac{\text{Total } [Hg^{II}] \text{ in the equilibrium TBP phase}}{\text{Total } [Hg^{II}] \text{ in the equilibrium aqueous phase}}$$

for extraction from solutions of hydrochloric acid of different concentrations at 20°. ^{203}Hg (half-life 46·9 d) was utilised as a tracer in the partition measurements and was assayed by γ-scintillation counting. When a_0 and a were the count rates (corrected for background) of identical volumes of equilibrium organic and aqueous phases, respectively, then $D = a_0/a$. In Table I are shown results obtained with

TABLE I. EXTRACTION OF Hg^{II} BY TRIBUTYL PHOSPHATE FROM HCl + H_2O

Initial concentration of Hg^{II} in aqueous phase $2{\cdot}3 \times 10^{-3}M$			Initial concentration of Hg^{II} in aqueous phase $4{\cdot}64 \times 10^{-2}M$		
Initial concn. of HCl in aqueous phase, M	D	E	Initial concn. of HCl in aqueous phase, M	D	E
0·01	61·2	98·6	0·01	52·9	98·4
0·142	77·1	98·9	0·66	63·8	98·6
0·33	117·8	99·3	1·32	71·2	98·6
0·61	122·4	99·3	1·98	123·4	99·3
0·66	131·1	99·3	2·64	107·8	99·2
0·99	108·6	99·2	3·31	168·1	99·5
1·65	152·6	99·4	3·64	156·8	99·5
1·85	171·1	99·5	3·95	159·4	99·5
2·37	189·8	99·5	3·97	144·5	99·4
2·38	195·6	99·5	4·30	175·1	99·6
2·62	208·5	99·6	4·63	147·1	99·5
2·64	224·0	99·6	4·97	143·3	99·5
2·91	217·6	99·6	5·28	107·3	99·3
3·57	173·3	99·5	5·95	104·7	99·3
3·83	220·2	99·6	6·60	66·5	99·0
3·96	194·8	99·6	7·94	49·1	98·7
4·10	134·7	99·4	9·26	26·4	97·8
4·54	139·1	99·4			
4·62	129·6	99·4			
5·15	136·2	99·5			
5·21	126·0	99·4			
5·85	130·1	99·5			
6·26	118·4	99·4			
7·12	91·0	99·3			
7·14	80·5	99·2			
7·26	61·5	98·9			
7·94	51·4	98·8			
9·23	30·4	98·0			
9·24	29·9	98·0			
10·59	16·1	96·5			
11·90	8·86	94·3			

Values of D are average from duplicate measurements.

initial aqueous solutions $2{\cdot}3 \times 10^{-3}$ and $4{\cdot}64 \times 10^{-2}M$ in Hg^{II}. If equal volumes of initial aqueous and organic phase are employed then the percentage extraction $E = 100\,DR/(1 + DR)$, where R is the ratio of the volume of the organic phase to the volume of the aqueous phase after equilibration.

The efficiency of separation of mercury from a number of other elements by the following procedure was tested using radiotracers. A solution of Hg^{II} in $0{\cdot}05M$ hydrochloric acid was equilibrated for several min with an equal volume of TBP. After centrifuging, the aqueous phase was withdrawn using a transfer pipette, and was equilibrated with a further portion of TBP. The organic layers were separated, combined, and washed for 5 min by agitating with a small amount of $3M$ hydrochloric acid. The TBP phase was then separated, and the mercury was removed from it as metal by stirring for several min with 5 ml of 50% hypophosphorous acid and centrifuging at high speed. The procedure gave yields of mercury greater than 99%. The percentage removal from the mercury of different elements present in tracer amounts was Co^{II} 100%, Mn^{II} 99·0%, Tl^{I} 100%, Cs 99·8%, Zn 99·6%. Moreover, in an experiment in which a solution of mixed fission products was added, 99·4% of the initial γ-ray activity was removed by the procedure.

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16 *March* 1962

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Talanta, 1962, Vol. 9, pp. 625 to 626. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEWS

Quantitative Organic Microanalysis. AL STEYERMARK. Second Edition. Academic Press Inc., New York, 1961. Pp. xviii + 665. 118s.

THIS revised and enlarged edition of Steyermark's well-known book might be expected to have the same impact on microchemistry as the first edition had ten years ago. During this time many notable advances in organic analysis have been made and it is not unreasonable to expect that considerable attention would have been given to them in this new edition. Although it would be unfair to say that no mention is made of many of these developments, nevertheless the treatment given to them is generally quite inadequate and completely ridiculous for a book which sets out to be a standard work of reference.

The apparatus of organic microanalysis has provided a happy hunting ground for the many microanalysts who seek to establish uniformity of equipment and techniques. Several committees exist for the sole purpose of standardising the numerous pieces of apparatus; it is well-known, however, that such committees are invariably working against time—that new techniques and apparatus are always being devised to supplant, and often to render obsolete, the equipment and methods undergoing the laborious process of standardisation. While it is foolish to argue against the necessity for a certain amount of standardisation, to accept it as wholeheartedly as the author has apparently done is to introduce an attitude of complacency which is incompatible with the rapidly developing nature of the subject.

In the present text, the conservative approach of the many standardising committees with which the author is actively engaged is painfully evident. Few European laboratories employ the classical Pregl method for carbon and hydrogen and fewer would even contemplate the Carius methods for sulphur and halogens. Yet such methods are the author's choice, while modern procedures are virtually ignored.

The original edition appearing at an opportune time in the immediate post-war period was welcomed by those people who were caught up in the increased demand for routine organic microanalytical laboratories. Few contemporary texts provided the specifications for apparatus so necessary for those embarking on such projects for the first time. Today, this over-elaboration of detail concerning apparatus is of more value to the manufacturer of scientific apparatus than to the practising microanalyst to whom this book is largely addressed.

In conclusion, this book has missed the opportunity of retaining its original status. There is still much useful information to be found in it, but it is doubtful whether this will still appeal to the individualistic temperaments of many microanalysts.

WILLIAM I. STEPHEN

Qualitative Elemental Analysis. E. H. SWIFT and P. SCHAEFER. W. H. Freeman and Co., San Francisco, 1962. Pp. xiv + 469. $6.75

As one would expect of a book written by Dr. Swift, this is an excellent book from the standpoint of the objectives which the authors had in mind when writing it. They point out that a system of qualitative analysis is an effective means for systemisation and correlation of a large body of factual inorganic chemistry; that it provides a student with opportunities to apply chemical principles to laboratory problems; that it provides a useful means of showing the periodicity of chemical properties of the elements; and it teaches a great deal of laboratory technique.

The approach to qualitative analysis in this text is quite different from that of many contemporary texts in that it is a system for identification of *elements* rather than ions. For example, one identifies tin rather than stannous or stannic ion, and nitrogen rather than ammonium, nitrite or nitrate ion. While this approach is ably defended by the authors because it is useful, there are many instructors who will think that identification of ions is more important. The major portion of the system is devoted to metallic and amphoteric elements.

The authors explain that this system is the outgrowth of a more complete system worked out for the Chemical Warfare Service in the early part of World War II. They believe that students will have greater interest in a system that was devised to solve actual problems in contrast to one that is only a system for teaching purposes. The emphasis is practical throughout the text rather than theoretical.

The book is divided into three sections:

Section I—Principles of Analytical Chemistry, 115 pages.

This section deals with the general theories involved in the system. It discusses schemes of qualitative analysis, definition of terms and units, reactions in homogeneous systems, redox reactions, reactions in heterogeneous systems, and periodic properties of the elements. Many instructors will no doubt think the treatment of topics is too brief and too limited. Such topics as activity of ions, ionic equilibria, chemical bonding, complex ions, and competing equilibria are given the briefest possible treatment—often only a paragraph. The discussion of acids and bases is almost entirely the Arrhenius concept, which is hardly in keeping with the more recent ideas of acid-base systems. However, it must be mentioned that additional theory is inserted in the laboratory portion when it is pertinent and timely.

Section II—Techniques of Analytical Chemistry, 57 pages.

This is an excellent description of the laboratory equipment and techniques employed in the system. The drawings are large, clear and descriptive. Correct and incorrect ways of doing things are shown very clearly.

Section III—The System of Analysis, 262 pages.

This section is obviously the largest and is devoted to the laboratory schemes of analysis. The laboratory directions are written very clearly and the many flow sheet and tabular outlines give a clear picture of each group separation, subgroup separation, and identification of each element.

The system is based on the suggestion that unknowns furnished to the students should be natural minerals or metallic alloys, although it provides for unknown solutions. Mineral samples are fused in nickel crucibles with a mixture of NaOH, $NaNO_3$ and Na_2CO_3. The melt is treated with water to separate it into a soluble and insoluble portion. The undissolved residue is called the *Basic Element Group* and contains compounds of Fe, Mn, Ti, the alkaline earths, Ag, Cu and Ni with traces of Pb and Sn. The solution contains the *Amphoteric Element Group* consisting of Pb, Cu, As, Sn, Al, Zn, Cr and V as well as the *Acidic Element Group* of I, Br, Cl, P, As, S and F. The solution is divided into two halves and each is treated differently. Separate samples are analysed for sodium and potassium, and for nitrogen and carbon.

Samples of alloys are dissolved in nitric acid if possible, or a mixture of nitric and hydrochloric acids. Directions are than given for separating the solution into three groups as outlined above for mineral samples.

If the sample is a solution it is evaporated to dryness and fused, as for minerals.

This system includes titanium and vanadium which are often omitted from many schemes of analysis but it omits antimony, bismuth, cadmium, and mercury which are usually included in other schemes of analysis.

Undoubtedly a student will learn a lot of chemistry and many useful laboratory methods from this system but its adoption will certainly mean a radical change for those who have been using conventional texts based upon the identification of ions. The very slight attention given to anions may be objectionable to some instructors.

A separate Teachers Manual is available to teachers. This manual gives much useful information on the use of the text, the time required for laboratory work, the preparation of solutions and sources of unknowns. There is also a very complete section on working problems and answering questions.

T. H. WHITEHEAD

Talanta, 1962, Vol. 9, pp. 627 to 629. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

(Material for this section should be sent directly to the Associate Editor)

BELGIUM

Friday–Saturday 14–15 *September* 1962: **Second Symposium on Chromatography:** *Belgian Society of Pharmaceutical Sciences.* Brussels.

Both theoretical aspects and practical applications of chromatography will be considered. A scientific exhibition will also be held. The official languages will be French, Dutch, English and German.

The Secretary's office of the Belgian Society of Pharmaceutical Sciences, 11 rue Archimède, Brussels 4, Belgium, will forward registration forms upon request, and registrations will be received until 1 August.

CZECHOSLOVAKIA

August 1962: **Spectroanalytical Methods for Extra Pure Substances:** *Association for Spectral Analysis:* Košice.

POLAND

Saturday 20 *October* 1962: **Symposium on Chromatography in Analysis and Preparation of Alkaloids:** *Chromatographic Subcommittee of the Analytical Chemistry Commission, Polish Academy of Sciences.* Poznań.

The address of the Organising Committee is Zaktad Chemii Ogólnej, University, Grunwaldzka 6, Poznań, Poland.

SWITZERLAND

Monday–Saturday 15–20 *October* 1962: **Second International Exhibition and Congress of Laboratory, Measurement and Automation Techniques in Chemistry.** Swiss Industries Fair, Basle (see *Talanta*, 1962, **9**, 401).

In connection with the Exhibition a **Technical Congress** will also be held, this being the 45th Meeting of European Federation of Chemical Engineering. The Congress will consist of a *Programme of Lectures on Automation in Chemistry*, which will constitute the 13th Meeting of the Swiss Federation of Automatic Control, and a *Programme of Lectures on Laboratory and Measurement Techniques*, organised by the Association of Swiss Chemists.

Full details of the *Programme of Lectures on Laboratory and Measurement Techniques* are as follows:

Thursday 18 *October—Separation Methods*

E. STAHL	*Entwicklung und Anwendung der Dünnschicht-Chromatographie.*
M. BRENNER	*Dünnschicht-Chromatographie: R_f-Wert und chemische Struktur.*
H. R. BOLLIGER	*Die Dünnschicht-Chromatographie der Vitamine.*
E. BAYER	*Präparative Gas-Chromatographie.*
R. S. EVANS	*Quantitative Aspects of Gas-Chromatography.*
H. SCHILDKNECHT	*Zonenschmelzen und Kolonnen-Kristallisieren, neue Trenn- und Reinigungsverfahren für kristallisierende Substanzen.*

Friday 19 *October—Determination of Particle Size*

A. PETERLIN	*Rheologische Methoden zur Bestimmung der Größe und Gestalt von Makromolekülen in Lösung.*
J. SADRON	*Optische Methoden zur Bestimmung der Größe und Gestalt von Makromolekülen in Lösung.*

Friday 19 *October—Methods for Determining Constitution and Structure*

J. D. DUNITZ	*Determination of Molecular Structure by X-Ray Methods.*
J. C. KENDREW	*X-Ray Methods in Protein Chemistry.*
J. D. WALDRON	*Appilcation of High Resolution Mass Spectrometry in Organic Chemistry.*
R. F. ZÜRCHER	*Neuere Anwendungen der magnetischen Kernresonanz-Spektroskopie.*

Saturday 20 *October*

A. HORSFIELD	*Recent Applications of Electron Spin Resonance in Chemistry.*
H. G. LEEMANN	*Konstitutionsermittlung mit Hilfe der Rotationsdispersion.*
B. BOEHLEN und A. GUYER	*Methoden der Mikrostrukturbestimmung poröser Stoffe.*

Recent Analytical Procedures

J. JORDAN	*Thermochemical Titrations.*
CH. WAKKER	*Analyse par fluorescence X, applications et limites.*
K. H. WAECHTER	*Das Beta-Gamma-Photometer als einfaches Hilfsmittel zur Elementaranalyse von organischen Substanzen und Lösungen.*

For further information apply to the Secretary's Office of ILMAC, Basle 21, Switzerland.

WEST GERMANY

Sunday–Friday 26–31 *August* 1962: **Thirteenth Session of the International Commission for Uniform Methods of Sugar Analysis.** Hamburg (see *Talanta*, 1962, **9**, 470).

UNGARN

Der Fachausschuss für Emissionsspektralanalyse der Materialprüfungsabteilung des Wissenschaftlichen Vereins für Maschinebau und seine Gruppe in Miskolc geben sich die Ehre, Sie davon zu unterrichten, dass die

V. Ungarische Tagung für Emissionsspektralanalyse

mit Kooperation der Gruppe des Wissenschaftlichen Vereins für Bergbau und Hüttenwesen in Diósgyör sowie mit Teilnahme der Technichen Universität für Schwerindustrie in Miskolc in der Zeit vom 9. bis 10. August in Miskolc stattfindet (*Talanta*, 1962, **9**, 402).

UNITED KINGDOM

British Standards Institution announces the following *New British Standard:*

B.S. 3483: 1962: *Methods for testing pigments for paints.* This describes, amongst other things, determination of matter volatile at 100°, determination of matter soluble in water, determination of acidity and alkalinity of aqueous extract, determination at 25° of pH of aqueous extract, determination of residue on sieve and determination of specific gravity. Price 8s.6d.)

The following *Amendment Slip* is also announced:

Addendum 1: 1960: *to B.S.* 2690: 1956: *Methods of testing water used in industry. Amendment No.* 2: *PD* 4548.

UNITED STATES OF AMERICA

Monday–Tuesday 6–7 *August* 1962: **Fifth Annual Rocky Mountain Spectroscopy Conference:** *Society for Applied Spectroscopy, Rocky Mountain Section.* Olin Hotel, Denver, Colo. (see *Talanta*, 1962, **9**, 546).

Wednesday–Friday 8–10 *August* 1962: **Eleventh Annual Conference on Applications of X-Ray Analysis:** *Denver Research Institute.* Albany Hotel, Denver, Colo.

Monday–Friday 13–17 *August* 1962: **Gordon Research Conference on Analytical Chemistry.** New Hampton School, New Hampton, New Hampshire (see *Talanta*, 1962, **9**, 405).

Tuesday–Friday 21–24 *August* 1962: **International Symposium on Far Infrared Spectroscopy.** Sheraton-Gibson Hotel, Cincinnati, Ohio.

Monday–Friday 27–31 *August* 1962: **Gordon Research Conference on Infrared Spectroscopy.** Kimball Union Academy, Meriden, New Hampshire (see *Talanta*, 1962, **9**, 405).

Wednesday 29 *August–Wednesday* 5 *September* 1962: **Fifth International Congress for Electron Microscopy:** *Electron Microscope Society of America.* Philadelphia.

Thursday–Saturday 1–3 *November* 1962: **Annual Southeastern Regional Meeting of American Chemical Society:** *American Chemical Society, East Tennessee Section* and *Oak Ridge National Laboratory.* Gatlinburg, Tennessee.

GLENN T. SEABORG, Chairman of U.S. Atomic Energy Commission, will present the opening address. In addition to general sessions in various fields of chemistry, symposia will cover Organic Reaction Mechanisms; Coordination Compounds; Radiochemical Techniques in Analytical Chemistry; DNA, RNA and Protein; and Application of High Speed Computors to Chemical Problems.

Further information may be obtained from Dr. F. A. GRIFFITTS, Maryville College, Maryville, Tennessee, U.S.A.

Monday–Friday 4–8 *March* 1963: **Fourteenth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy:** *American Chemical Society, Pittsburgh Section, Analytical Chemistry Group* and *Spectroscopy Society of Pittsburgh.* Penn-Sheraton Hotel, Pittsburgh, Pennsylvania.

Approximately 190 papers on all phases of analytical chemistry and spectroscopy will be presented. A symposium entitled *Solution Techniques in X-Ray and Emission Spectroscopy* will be cosponsored with the Society for Applied Spectroscopy. The Coblentz Society is coarranging a symposium on *Techniques related to Infrared Spectroscopy.* Additional symposia with the titles *Nuclear Magnetic Resonance—Nuclei other than Hydrogen, Gas Chromatographic Analysis of Metallo-Organics and Related Compounds, Uses of Reaction Rates in Analytical Chemistry* and *The Analysis of Refractory Metals* will also be held.

Original papers on all phases of analytical chemistry and spectroscopy are invited. A brief abstract (150 words) of each paper will be printed with the programme. Three copies of this abstract, with a letter listing the names of the authors, the laboratory in which the work was done, and the current addresses of the authors, should be addressed to: Dr. WILLIAM A. STRAUB, Programme Chairman, Fourteenth Pittsburgh Conference, Applied Research Laboratory, United States Steel Corporation, Monroeville, Pennsylvania, U.S.A. The final date for receipt of abstracts is 15 October 1962. One copy of the complete paper must be submitted by 1 January 1963.

In addition to the programme of technical papers there will be an exhibition of the newest analytical instrumentation, and a complete programme of activities for wives and lady attendees at the Conference is planned.

The **Fourth Omnibus Conference on Experimental Aspects of Nuclear Magnetic Resonance Spectroscopy** will be held at Mellon Institute, Pittsburgh, from Thursday 28 February to Saturday 2 March 1963, the week preceding the Pittsburgh Conference. The first day will be devoted primarily to broad-line work, the second to experimental developments of general interest and the third to high resolution techniques. For the convenience of those wishing to attend both meetings the Nuclear Magnetic Resonance sessions of the Pittsburgh Conference will be scheduled for Monday 4 March.

National Bureau of Standards has developed sets of colour standards to check the performance of spectrophotometer-tristimulus integrator combinations, the automatic recording and computing devices used in routine colour measurement. Each set consists of five 2-inch square filters made of selenium orange-red, signal yellow, sextant green, cobalt blue, and selective neutral glass. A detailed report issued with the standards contains instructions for their use as well as colorimetric data which aid in detecting errors inherent in the equipment and in making adjustments to correct for such errors.

ERRATA—VOLUME 9

Page 295: the journal in reference 2 should read *Ind. Eng. Chem.*

Page 355, title, Summary, first paragraph and under Reagents: for *5-(3-nitrophenylazo)salicylate* read *5-(4-nitrophenylazo)salicylate.*

Page 359, Fig. 5: for *5-(3-nitrophenylazo)salicylate* read *5-(4-nitrophenylazo)salicylate;* also, the nitrophenylazo group should be shown in the 5-position and not in the 4-position.

Page 363, Zusammenfassung: for *5-(3-nitrophenylazo)salizylsäure* read *5-(4-nitrophenylazo)salizylsäure.*

Page 364, Résumé: for *5-(3-nitrophénylazo)salicylique* read *5-(4-nitrophénylazo)salicylique.*

Page 452, second paragraph of Introduction: the reagent should read *N-(1-naphthyl)ethylenediamine dihydrochloride.*

Page 457, caption to Fig. 1: the final sentence should read *Reagent solutions contain* 2.5×10^{-5} *mole of* $Cu(NO_3)_2$ [*or* $CuCl_2$] *and* 8.5×10^{-5} *mole of di-octen in hexone medium.*

Talanta, 1962, Vol. 9, p. 630. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Spectrophotometric study of the thorium complex of B-SNADNS-6: SACHINDRA KUMAR DATTA and SACHINDRA NATH SAHA. (3 *May* 1962).

"Complexan Buffer": A new concept useful in theoretical consideration of equilibria involving complexans: MOTOHARU TANAKA. (4 *May* 1962).

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