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TITRIMETRIC ANALYSIS WITH CHLORAMINE-T—I

THE STATUS OF CHLORAMINE-T AS A TITRIMETRIC REAGENT

E. BISHOP and V. J. JENNINGS*
Washington Singer Laboratories, The University, Exeter, Devon, England

(*Received* 3 *March* 1958)

Summary—The behaviour of Chloramine-T as a titrimetric reagent is fully discussed. Methods of standardising solutions of the reagent have been critically examined.

MANY papers have appeared on the applications of chloramine-T in titrimetry since Noll[1] first advocated its use, but this literature is marred by vagueness, discordance and uncertainty, which are reflected in the standard textbooks, even in the latest reference text.[2] Aside from the lack of good visual indicators, only one of which has been checked potentiometrically,[3] and the inadequate investigation of conditions with those which have been proposed, dissatisfaction with published accounts of the reagent arises in several ways:

(*a*) the purity of the reagent is usually either unspecified or assumed to be 100%;
(*b*) ambiguity arises because of sparse and often vague experimental detail, and the range of conditions investigated is often narrow, giving rise to apparent contradiction between accounts;
(*c*) the absolute accuracy of the determination of many substances is uncertain, because methods of standardisation or purification are not given, and the specification of the reagents and their treatment in solution preparation is omitted;
(*d*) the hydrolysis of chloramine-T is often incompletely described, so that chloramine-T and hypochlorite solutions are regarded as completely similar in properties.

These matters will be illustrated where appropriate, but point (*d*) may be further discussed. The tacit assumption follows from this that chloramine-T may be substituted directly for hypochlorite; or for bromate in the presence of bromide, iodate in the presence of iodine monochloride, or iodine in the presence of iodide. Though these substitutions are often possible, and the indicators used with the original reagent may be applicable to chloramine-T, this is by no means invariably the case. For example, chloramine-T cannot be substituted for bromate in the determination of hydrazine, hydroxylamine, antimony^{III} or thallium^{I}.

It is commonly stated[2] that chloramine-T hydrolyses in water to *p*-toluene sulphonamide and sodium hypochlorite (1) (the *p*-toluenesulphonyl—part of the molecule $CH_3C_6H_4SO_2$—is designated by the symbol R—),

$$RNClNa + H_2O \rightleftharpoons RNH_2 + NaOCl \qquad (1)$$

Obviously the latter will then ionise and, except in alkaline solution, the hypochlorite

* Present address: S.E.R.L., Baldock, Herts

ion will hydrolyse to hypochlorous acid, which is then taken to be the reacting species, giving rise to the assumptions noted above.

The present work, and that of Soper,[4] Dietzel and Taufel[5] and Morris *et al.*[6] indicate that quite different equilibria are set up in the hydrolysis. Chloramine-T is the sodium salt of the acid *p*-toluenesulphon-N-chloramide, which is a fairly strong acid, since the salt is very little hydrolysed in solution; the pH of a 0·05*M* solution is 7·7, giving an apparent value for the ionisation constant of $2{\cdot}38 \times 10^{-3}$. Though the acid has not been isolated, there is ample evidence[4,6,7] for its existence in solution. The salt is a strong electrolyte which first dissociates:

$$RNClNa \rightleftharpoons RNCl^- + Na^+ \tag{2}$$

The anion then takes up hydrogen ion to form the free acid:

$$RNCl^- + H^+ \rightleftharpoons RNHCl \tag{3}$$

which disproportions to give *p*-toluenesulphonamide and sparingly soluble dichloramine-T:

$$2RNHCl \rightleftharpoons RNCl_2 + RNH_2 \tag{4}$$

The equilibrium constant[6] for the disproportioning is $6{\cdot}1 \times 10^{-2}$. The dichloramine-T and the free acid hydrolyse:

$$RNCl_2 + H_2O \rightleftharpoons RNHCl + HOCl \tag{5}$$

$$RNHCl + H_2O \rightleftharpoons RNH_2 + HOCl \tag{6}$$

The hydrolysis constants for these two reactions[4,6] are 8×10^{-7} and $4{\cdot}88 \times 10^{-8}$; hydrolysis is therefore slight. Finally the hypochlorous acid ionises, K_a being $3{\cdot}3 \times 10^{-8}$.

The disproportioning (4) is not itself hydrogen ion-dependent, but formation of the dichloramine-T (the white precipitate formed on acidifying chloramine-T solution) depends on the prior formation of the free acid (3) which is hydrogen ion-dependent, and significant amounts of the dichloramine-T are formed in moderately or strongly acid solution. First-approximation calculations based upon a decinormal (0·05*M*) solution of chloramine-T indicate the order of the concentrations of the various species present at various pH values (Table I), and show that in strong acid medium the free acid and dichloramine predominate, but as the pH rises the anion of the acid assumes importance, reaching predominance in weak acid or neutral solution. Even in weakly alkaline medium the acid anion predominates over hypochlorite; hypochlorous acid maintains a constant concentration throughout the range.

Though hypochlorous acid, or even hypochlorite ion, may be the reactive species in chloramine-T oxidations, it is reasonable to suppose that the species present in greater concentration should react directly, and that such reactions should differ in certain circumstances from those of hypochlorous acid or hypochlorites. Certain dissimilarities have been recorded in the past,[5-10] and others will be reported in due course. Thus chloramine-T even in strong acid medium has feeble oxidising powers in the absence of added halides, and fails to react in the presence of chloride at pH values greater than 1, but will react in the presence of bromides up to pH 5 and in

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TABLE I. CONCENTRATIONS OF VARIOUS SPECIES PRESENT IN A 0·05*M* CHLORAMINE-T SOLUTION OVER A RANGE OF pH VALUES

pH	[$RNCl^-$]	[RNHCl]	[$RNCl_2$] = [RNH_2]	[HOCl]	[OCl^-]
0	$9{\cdot}6 \times 10^{-5}$	$4{\cdot}01 \times 10^{-2}$	$9{\cdot}9 \times 10^{-3}$	$3{\cdot}95 \times 10^{-7}$	$1{\cdot}3 \times 10^{-14}$
1	$9{\cdot}6 \times 10^{-4}$	$4{\cdot}01 \times 10^{-2}$	$9{\cdot}9 \times 10^{-3}$	$3{\cdot}95 \times 10^{-7}$	$1{\cdot}3 \times 10^{-13}$
2	$7{\cdot}8 \times 10^{-3}$	$3{\cdot}24 \times 10^{-2}$	$7{\cdot}98 \times 10^{-3}$	$3{\cdot}95 \times 10^{-7}$	$1{\cdot}3 \times 10^{-12}$
3	$2{\cdot}83 \times 10^{-2}$	$1{\cdot}18 \times 10^{-2}$	$2{\cdot}92 \times 10^{-3}$	$3{\cdot}95 \times 10^{-7}$	$1{\cdot}3 \times 10^{-11}$
4	$3{\cdot}84 \times 10^{-2}$	$1{\cdot}60 \times 10^{-3}$	$3{\cdot}95 \times 10^{-4}$	$3{\cdot}95 \times 10^{-7}$	$1{\cdot}3 \times 10^{-10}$
5	4×10^{-2}	$1{\cdot}67 \times 10^{-4}$	$4{\cdot}1 \times 10^{-5}$	$3{\cdot}95 \times 10^{-7}$	$1{\cdot}3 \times 10^{-9}$
6	4×10^{-2}	$1{\cdot}67 \times 10^{-5}$	$4{\cdot}1 \times 10^{-6}$	$3{\cdot}95 \times 10^{-7}$	$1{\cdot}3 \times 10^{-8}$
7	4×10^{-2}	$1{\cdot}67 \times 10^{-6}$	$4{\cdot}1 \times 10^{-7}$	$3{\cdot}95 \times 10^{-7}$	$1{\cdot}3 \times 10^{-7}$
8	4×10^{-2}	$1{\cdot}67 \times 10^{-7}$	$4{\cdot}1 \times 10^{-8}$	$3{\cdot}95 \times 10^{-7}$	$1{\cdot}3 \times 10^{-6}$

the presence of iodides up to pH 9. It would thus appear to be virtually restricted to oxidation of halides, except perhaps in strong acid solution.

No matter how the reduction of chloramine-T is formulated, two electrons and two hydrogen ions are consumed per initial molecule of reagent, so that its equivalent is always the same, and the final products after completion of the reaction (other than the decompositive oxidation of the reagent molecule by itself to form acidic compounds[5]) are *p*-toluenesulphonamide and chloride ion. Nevertheless, formulation through the more probable reacting species safeguards against misconstruction. In strong acid solution the free acid and dichloramine predominate and may react directly:

$$RNHCl + H^+ + 2e^- = RNH_2 + Cl^- \quad (7)$$

$$RNCl_2 + 2H^+ + 4e^- = RNH_2 + 2Cl^- \quad (8)$$

It is notable that chloramine-T in the presence of chloride fails as an oxidant when the free anion $RNCl^-$ begins to predominate; the reactions of this ion may be limited to oxidation of bromide or iodide to free halogen:

$$RNCl^- + 2H^+ + 2e^- = RNH_2 + Cl^- \quad (9)$$

The occasional behaviour of chloramine-T at variance with the reactions of hypochlorites, and the general uncertainty as to conditions and quantitativeness of its reactions led to a detailed examination of the reagent with a view to resolving the uncertainties and ambiguities, searching for new indicators, developing its applications, and establishing with certainty its status as a standard titrimetric oxidant.

At first sight, chloramine-T offers many attractive features. It is cheaply and readily available in reasonable purity as a by-product of saccharine manufacture. It may be purified by simple crystallisation, and is neither hygroscopic nor efflorescent, so being susceptible of direct weighing in the preparation of solutions. It has a high equivalent weight. Hypochlorites, hypochlorous acid and monochloramine (NH_2Cl) effect many useful oxidations, but are difficult to prepare and purify, and cannot be obtained as pure solids. Chloramine-T (or its homologue chloramine-B) appear to offer a very convenient substitute in a solid weighable form for these reagents, and

for the more expensive iodine, iodate and bromate. Against this, the presence of three molecules of water of hydration in the solid render it suspect as a primary standard. To establish its status firmly it is necessary to ascertain whether it can be prepared in a purity closely approaching 100%, or, if not, whether a reproducible purity can be attained in a simple fashion; and, in the latter case, whether solutions can readily be standardised with a high degree of accuracy. The stability on storage

TABLE II.—PURIFICATION OF COMMERCIAL CHLORAMINE-T BY RECRYSTALLISATION FROM WATER

	% Purity of solid chloramine-T trihydrate. Assay precision ±0·03%
Original sample	98·50
Original sample stored 10 weeks in open dish	98·48
After first recrystallisation	99·14
After second recrystallisation	99·55
After third recrystallisation	99·54
After fourth recrystallisation	99·55

of the solid and solution must also conform to the requirements of a standard reagent. Once these points are settled, attention can be turned to the applications.

PURIFICATION OF CHLORAMINE-T

Recrystallisation from water is generally adopted,[1,4,6,11–16] and the crystals are dried either in air or in a vacuum desiccator. Many authors assume the commercial pure grade to be 100% pure; of those quoted, some assume that the product of crystallisation is pure, others[12,16] claim it to be, but others make no such claim. Determination of total chloride, as by Morris,[6] may give a figure in agreement with theory, but since the principal impurities are sodium chloride and *p*-toluenesulphonamide, this can be misleading.

Large scale successive crystallisations from conductivity water increased the purity to 99·5%, but further recrystallisations gave no further improvement (Table II). Repetition of the recrystallisation of the sample of 99·5% purity from (*a*) 0·01*M* sodium hydroxide, (*b*) 0·01*M* sodium hypochlorite, freshly prepared at 0° and free from chlorate, (*c*) a combination of (*a*) and (*b*), (*d*) 0·1*M* sodium chloride, and (*e*) a combination of (*c*) and (*d*), gave no significant improvement.

An anhydrous compound is more acceptable as a standard, so attempts were made to dehydrate the trihydrate. Heating in an air oven above 40°, or on a water or steam bath, produced a sintered yellow substance, believed to be dichloramine-T, which decomposed on further heating. At higher temperatures this decomposition is violent, becoming explosive at 120°. Dehydration over sulphuric acid indicated some stability of a dihydrate, but further dehydration led to the gradual formation of the yellow substance. Complete removal of water could not be effected over sulphuric acid. Rehydration in a hygrostat of the fine powder produced by dehydration was unprofitable, as the material continued to absorb water in excess of $3H_2O$.

Samples of a high and reproducible purity can therefore be prepared by recrystallisation, but the maximum attainable purity is inadequate for a primary standard. Though the 0·5% deficiency may perhaps be largely moisture, there is no simple method of removing this without decomposing the trihydrate. The hopes, based on earlier optimistic reports of the purity of the reagent, that chloramine-T might be a useful addition to the range of primary standards are not fulfilled.

TABLE III. STABILITY OF SOLID CHLORAMINE-T
STORED IN BROWN GLASS SCREW CAP BOTTLE EXPOSED TO DAYLIGHT

Time of exposure, months	% Purity of sample (precision ±0·03%)
0	99·18
10	99·06
19	98·86

STABILITY OF CHLORAMINE-T

Chloramine-T in all its forms has been shown to be unstable to heat, and unstable on storage in any but the trihydrate form, which is neither effloresecent nor hygroscopic. There are conflicting reports[5,8,17,18,19] on the stability of chloramine-T in the solid state. The most significant work is that of Dietzel and Taufel,[5] who report a decline in assay of 1·4% in 12 months on storage in brown glass, and 5% in clear glass.

Storage in a brown glass screw cap bottle on an open shelf in these laboratories caused a decline in strength of only 0·02% per month, as indicated in Table III. Stored in clear glass, the contents close to the glass wall on the sides facing the windows darkened to a pale creamy yellow colour, and samples from this region showed a decline in strength of 5–7% in 12 months, though samples from the interior of the bottle were little affected. Protected from sunlight by storage in brown glass, therefore, chloramine-T in the solid state is of admirable stability.

Stability in solution has been examined,[1,3,5,11,14,18–24] and, while there is some agreement that solutions exposed to sunlight are unstable,[3,11,25] and that solutions protected from daylight hold their titre well enough for four weeks, there is considerable disagreement over longer term stability.[1,3,5,11,20,21,22,24] For example, Komarowski *et al.*[21] report a loss of titre of 1·3% in 4½ months, while Poethke and Wolf[20] claim a loss of less than 0·1% in the same period.

To settle this point, five two-litre batches of 0·05*M* chloramine-T solution were prepared, standardised, and stored in winchester bottles fitted with polythene screw caps. Four of the bottles were of brown glass, and one of clear glass. Three of the brown glass bottles (solutions I, II and III) were stored in a cupboard and the contents analysed at intervals. Solution IV in brown glass and solution V in clear glass were stored side by side on an open laboratory shelf, and similarly analysed at intervals. The results given in Table IV show that storage in darkness or daylight makes no difference so long as the solution is stored in brown glass. Only after 5 months is any change perceptible, in agreement with Poethke and Wolf, while the loss in one year is only 0·5%. Exposure to daylight, however, causes an immediate and continuous drop in titre; 0·4% in the first week, and nearly 20% in one year. Solutions stored in brown glass remained perfectly clear, and there was no detectable change

TABLE IV.–THE STABILITY OF CHLORAMINE-T IN AQUEOUS SOLUTION

(*a*) SOLUTIONS STORED IN BROWN GLASS WINCHESTERS IN THE DARK

Length of storage, months	Factor of 0·05*M* Chloramine-T solution		
	Solution I	Solution II	Solution III
0	0·989	1·007	1·011
9	0·986	1·004	1·005

(*b*) SOLUTION IV STORED IN BROWN GLASS, SOLUTION V IN CLEAR GLASS, EXPOSED TO DAYLIGHT ON LABORATORY SHELF

Length of storage	Factor of 0·05*M* Chloramine-T solution	
	Solution IV	Solution V
0 weeks	1·005	1·005
1 week	1·005	1·001
2 weeks	1·005	0·997
3 weeks	1·005	0·992
4 weeks	1·005	0·989
6 weeks	1·005	0·985
3 months	1·005	0·970
5 months	1·004	0·947
7 months	1·002	0·904
9 months	1·001	0·859
12 months	1·000	0·811

in pH from the initial value of 7·7. In clear glass, the solution soon became cloudy. This precipitate was not the same as the dichloramine-T thrown down in acid solution, and the pH fell to 5·6 over 12 months, giving support to the contention of Dietzel and Taufel[5] that the photochemical, self-oxidation decomposition products are acidic in nature.

Though chloramine-T is unstable in direct daylight, brown glass vessels afford sufficient protection to permit of storage of the reagent both in the solid state and in solution, and the stability over periods of three months or more is sufficient to meet the requirements of a standard reagent.

STANDARDISATION OF CHLORAMINE-T SOLUTION

The principal methods advocated for the standardisation are:

(a) titration against standard arsenic^{III} solution in bicarbonate buffer in the presence of a small amount of iodide, with starch as indicator,[1,3,12,13,21,25–29] and

(b) titration with thiosulphate of the iodine liberated on addition of potassium iodide to an acidified chloramine-T solution, again with starch as indicator.[1,13,17,21,23,27,28,30,31]

Descriptions of these methods are somewhat vague,[2] conditions are ill-defined, and details of the influence of the nature or concentration of the buffer or acid, or the amount of iodide used are lacking. No simple method is available for standardisation against arsenic^{III} in acid solution.

1. *Standardisation through arsenic*^{III}

A very thorough investigation of the chloramine-T-arsenic^{III} reaction, from which optimum conditions for the present methods were selected, has been made and will be reported later; only the special investigation relevent to standardisation will briefly be recounted here. Direct standardisation is possible if arsenious oxide of a suitable grade is available, or, since the highest precision and accuracy are attainable with the bromate-arsenic^{III} reaction,[32] and the iodate–arsenic^{III} reaction is accepted as being of a similar calibre,[33] chloramine-T may be standardised against bromate or iodate through arsenious oxide.

(a) *In acid solution.* Though arsenic^{III} has been titrated in acid media of uncertain concentration at unspecified temperatures,[3,20,25] no recommendations for a standardisation appear to have been made, probably because of the dearth of suitable indicators. Since rosaniline hydrochloride, a sensitive specific reagent for free bromine,[34] has proved eminently satisfactory in bromate titrimetry,[32,34] having an excellent and very sharp, though irreversible, colour change from pale yellow to bright purple and a negligible indicator error, it was thought that this reagent would prove useful in chloramine-T titrations in acid solution in the presence of bromide. Such is the case,[7,35] and a precise standardisation procedure on this basis is proposed. Replicate titrations on 50-ml aliquots of 0·05*M* arsenic^{III} solution by this method gave factors for a 0·05*M* chloramine-T solution of 1·053, 1·053, 1·053.

The effect of acid concentration. This was examined by holding the bromide concentration constant at 0·1*M* and varying the end-point hydrochloric acid concentration from 0·1 to 3·0*M* in small steps. The results replicated perfectly in complete agreement with the standardisation up to 2·5*M* and the end-points between 0·5*M* and 2·5*M* were sharp and pleasing. At 3·0*M* the colour change became sluggish and 0·15% late, while in 0·1*M* the acid concentration is insufficient to convert the magenta colour of the free rosaniline base into the yellow ionic form of the hydrochloride, though the end-point is still easily seen.

Effect of bromide concentration. The bromide concentration controls the bromine/bromide potential, and hence the effective oxidation potential of the system. In 2*M* hydrochloric acid, increasing the potential by reduction of the bromide concentration to 0·01*M* does not affect the sharpness or accuracy of the titration. Potentiometrically, the position of the end-point is unaltered by the same change, but the magnitude of the potential jump is increased from 200 to 260 mV in agreement with theory.

End-point concentrations of 0·01 to 0·1*M* bromide and 0·5 to 2·5*M* hydrochloric acid yield equally precise and accurate results using rosaniline hydrochloride as indicator. The preference for 2*M* hydrochloric acid and 0·1*M* bromide is based upon general felicity of titration and quality and character of end-point.

(b) *In "neutral" solution.* As will be shown in a later paper, the reaction between chloramine-T and arsenic^{III} is dependent on the generation of free halogen as an intermediate oxidant. In solutions of pH greater than 4, this intermediate is specifically iodine, and the reaction is essentially that between iodine and arsenic^{III}. Iodine

oxidises arsenic^{III} quantitatively in neutral solution, but the potential of the As^{V}/As^{III} system increases with increasing hydrogen ion concentration, while iodine/iodide is unaffected, and there comes a point, about pH 4 when the reaction is no longer quantitative. Care must therefore be taken to ensure that the pH of the solution remains high enough to ensure quantitative reaction. The chloramine-T reaction producing the iodine consumes hydrogen ion; nevertheless, starting in neutral unbuffered solution, as is often suggested,[2] it will produce sufficient arsenic acid to run the pH below the quantitative limit, even discounting the net increase in hydrogen ions of reaction which may occur. A buffer medium is therefore essential. The permissible variation of pH does not seem to have been investigated.

The amount of iodide to be used is variously described as a little, a crystal, a small crystal, a pinch, etc., of potassium iodide, or a few drops of unspecified strength of solution. Only very seldom is any actual amount specified.[2] Preliminary irritating experience of these directions showed that if too little were used the appearance of the blue starch colour was subject to an induction period of anything from a few seconds to 24 hours, or did not occur at all; and too much iodide gave sluggish or premature end-points. It appeared that sufficient should be used to cause a blue colour to be formed momentarily during titration, when presumably an imperceptible amount of the starch complex remained to catalyse the reaction and remove the induction period.

A method is therefore proposed in which conditions are fully specified. Replicate titrations of 50-ml aliquots of a 0·05*M* arsenic^{III} solution by this method gave factors for a 0·05*M* chloramine-T solution of 1·053, 1·053, 1·053, in complete agreement with the method in acid solution using rosaniline as indicator.

Influence of conditions. Titrations at lower pH values than that of the bicarbonate buffer (or in higher iodide concentrations than those recommended) are disturbed by the slowness, or even incompleteness with which iodine, formed by local excess of titrant and complexed with starch, reacts with the arsenic^{III}, so tending to give low titration figures. The iodine/iodide potential is controllable by the iodide concentration, and by reducing the latter the iodine must be generated at a higher potential and should therefore react more quickly with the arsenic^{III}. By the same token, reducing the iodide concentration should extend to a lower pH the range over which the reaction is quantitative. At the upper end of the pH range, hypoiodite may be formed which will not react with starch or arsenic^{III}, giving rise to high titration figures, but by increasing the iodide concentration, this hydrolysis should be inhibited, thus extending the quantitative range to higher pH values. Investigation revealed evidence for the truth of these arguments.

Variation of iodide and buffer concentration in bicarbonate buffer. Titrations in iodide concentrations of 0·0005*M* to 0·05*M*, and in buffer concentrations of 0·2 to 0·4*M* gave uniformly accurate results (Table V), but in 0·0005*M* the colour change was very sluggish.

Variation of iodide concentration in various buffers. Results in Table VI of titrations in various buffers of pH 2·4 to 9·9 show that, as predicted, appropriate control of iodide concentration allows extension of the range over which quantitative reaction occurs, but there is no advantage to be gained in using buffers other than bicarbonate, particularly when the iodide concentration range is most convenient in this medium.

Quantitativeness of the reaction. Although the results by the two very different

methods are in entire agreement, there is still a possibility that both reactions are incomplete to the same small extent. This lingers from the claims in the literature about the purity of chloramine-T, in contrast to the maximum assay of 99·5% by the rosaniline method. The reaction may become quantitative only with excess reductant, and, since this is the condition under which many analytical determinations finish, it is important to have a decision on this point. Since the bromate–arsenic^{III} reaction

TABLE V.—VARIATION OF IODIDE AND BUFFER CONCENTRATIONS: TITRATIONS OF 25 ML OF 0·05*M* ARSENIC SOLUTION (FACTOR 1·001) IN BICARBONATE BUFFER CONTAINING POTASSIUM IODIDE WITH 0·05*M* CHLORAMINE-T SOLUTION USING STARCH AS INDICATOR

Concentration of bicarbonate, *M*	Concentration of iodide, *M*	End-point,* *ml*	Factor of chloramine-T solution
0·4	0·05	24·93	1·004
0·4	0·005	24·93	1·004
0·4	0·0005	24·93	1·004
0·2	0·05	24·93	1·004
0·2	0·005	24·93	1·004
0·2	0·0005	24·93	1·004

* Titration in acid solution with rosaniline as indicator gave a factor of 1·004, and hence a calculated end-point of 24·93 ml.

in acid solution is known to be quantitative,[32] addition of an aliquot of chloramine-T to an excess of arsenic^{III}, followed by titration of the excess by bromate should show whether consumption of arsenic^{III} by chloramine-T is greater than in the direct titration. Such titrations gave exactly the same value for the factor of the chloramine-T solution as methods (*a*) and (*b*) above (Table VII). A fourth confirmation was given by potentiometric titration in the same media as in the recommended methods, and further by yet a different method, titration in 2*M* hydrochloric acid free from other halides. The curves gave no indication of any side reactions or other interference, and showed that the reactions proceed smoothly with intermediate halogen production. The perfect agreement between a diversity of methods under very different conditions supports the conclusions that the reaction is quantitative, and that the indicator errors, compared with potentiometric results, are negligible. This contention will be further examined in a later paper.

2. *Standardisation through thiosulphate*

Though not itself a primary standard, thiosulphate can be accurately referred to the primary standard potassium iodate,[2] and offers an alternative path for relating chloramine-T to this standard, provided the chloramine-T–iodide reaction can be shown to be quantitative. This is a less advantageous method than those above, but is of particular value in standardising chloramine-T solutions which are to be used for liberating iodine in excess for a reaction where the excess is to be backtitrated with thiosulphate.

The iodine–thiosulphate reaction is not hydrogen ion-dependent, but the pH

TABLE VI.—VARIATION OF IODIDE CONCENTRATION IN VARIOUS BUFFER MEDIA

Conditions	Iodide concentration, *M*	End-point, *ml*	Factor of chloramine-T solution
(*a*)	0·00033	25·08	1·0235
	0·00016	25·11	1·025
	0·000033	25·12	1·0255
(*b*)	0·005	25·11	1·025
	0·0005	25·11	1·025
	0·00005	25·11	1·025
(*c*)	0·0225	25·11	1·025
	0·0045	25·12	1·0255
	0·000225	25·13	1·026
(*d*)	0·1	25·12	1·0255
	0·05	25·13	1·026
	0·005	no starch-iodine blue colour produced	—

(*a*) 50 ml of 0·2*M* potassium hydrogen phthalate and 10 ml of 0·5*M* hydrochloric acid added as buffer. Volume of titrated solution at the end-point 150 ml. Measured pH at the end-point 2·4.
(*b*) 25 ml of 0·6*M* sodium acetate, 1·4*M* acetic acid added as buffer. Volume of titrated solution at the end-point 100 ml. Measured pH at the end-point 4·1.
(*c*) 50 ml of saturated aqueous solution of borax added as buffer. Volume of titrated solution at the end-point 110 ml. Measured pH at the end-point 8·5.
(*d*) 1·59 g of anhydrous sodium carbonate added as buffer. Volume of titrated solution at the end-point 110 ml. Measured pH at the end-point 9·9.

must be kept low to keep the reaction fast and to prevent the formation of hypoiodite. If the pH is allowed to rise, hypoiodite, and indeed iodine itself, will oxidise thiosulphate to sulphate, and, since this consumes eight equivalents of oxidant instead of one, the volume of thiosulphate used will be low. The oxidation of iodide by chloramine-T consumes 2 moles of hydrogen ion per mole of oxidant, and if only just sufficient acid is present for this reaction, the pH may run undesirably high and cause low results. The amount of acid used is therefore of importance.

Furthermore, hypochlorites (and chlorine or bromine) oxidise thiosulphate to sulphate. Tests showed that chloramine-T does the same, but the reaction is not quantitative and other reactions also occur, so that oxidation to sulphate is not analytically useful. Nevertheless, if less iodide than the amount equivalent to the chloramine-T is initially added, and the solution titrated with thiosulphate, some of the latter may be oxidised to sulphate, and, as before, the end-point will be early. The iodide concentration is therefore also important.

Neither of these points, nor the effect of the nature of the acid used appear to have been systematically investigated before, and apparently conflicting recommendations have been made.

TABLE VII.—QUANTITATIVENESS OF THE CHLORAMINE-T–ARSENIC^{III} REACTION

(*a*) 20 ML OF 0·05*M* CHLORAMINE-T ADDED TO 50 ML 0·05*M* ARSENIC^{III} (FACTOR 1·005) IN 2*M* HYDROCHLORIC ACID AND 0·1*M* POTASSIUM BROMIDE, AND EXCESS ARSENIC^{III} TITRATED WITH 0·01667*M* POTASSIUM BROMATE (FACTOR 1·014) USING ROSANILINE HYDROCHLORIDE AS INDICATOR

Volume of bromate required, *ml*	Factor of chloramine-T solution*
28·76	1·053
28·77	1·0525
28·76	1·053

(*b*) POTENTIOMETRIC TITRATION OF 50 ML OF 0·05*M* ARSENIC^{III} SOLUTION (FACTOR 1·005) WITH 0·05*M* CHLORAMINE-T

Medium	End-point, *ml*	Factor of chloramine-T solution*
2*M* hydrochloric acid	47·70	1·0535
2*M* hydrochloric acid, 0·1*M* potassium bromide	47·72	1·053
0·5*M* sodium bicarbonate, 0·005*M* potassium iodide	47·72	1·053

* Arsenic^{III} and chloramine-T solutions as in Table V.

Influence of the nature and amount of the acid used

With the iodide maintained constant at 3 equivalents, various amounts of several acids were used with the results shown in Table VIII. As expected, if barely, or less than, the right quantity of acid required for the chloramine-T reaction is present, there is a marked increase in the pH of the solution and the end-points are early. In solutions containing more than 5 ml of 10*N* hydrochloric or sulphuric acid (20 equivalents) the end-points are not so sharp, though 10 ml of 10*N* acetic acid (40 equivalents) did not affect the quality of the end-point. Otherwise, with two or more equivalents of acid present, the reaction is quantitative.

Variation of iodide concentration was studied while maintaining the amount of acid initially added at 4 equivalents (10 ml of 1*N*). The results in Table IX show that with hydrochloric or sulphuric acid, the reaction is quantitative when one or more equivalents of iodide are used, but if less than one equivalent is added, the expected early end-points result. In the case of acetic acid, however, three equivalents of iodide are necessary for satisfactory titration. With two equivalents the reaction became slow, and with one equivalent there was no permanent end-point.

TABLE VIII.—EFFECT OF VARIATION OF ACID CONCENTRATION IN STANDARDISATION OF CHLORAMINE-T AGAINST POTASSIUM IODATE THROUGH SODIUM THIOSULPHATE: TITRATION OF 25 ML OF 0·05*M* CHLORAMINE-T SOLUTION (FACTOR 1·004)* IN ACID SOLUTION CONTAINING 3 EQUIVALENTS OF IODIDE (15 ML OF 0·5*M* POTASSIUM IODIDE) WITH 0·1*M* SODIUM THIOSULPHATE (FACTOR 1·008)† USING STARCH AS INDICATOR

Volume added		Acid					
		Hydrochloric		Sulphuric		Acetic	
ml	*N*	End-point, *ml*	pH at end-point	End-point, *ml*	pH at end-point	End-point, *ml*	pH at end-point
10	0·1	21·7	10·4				
25	0·1	24·70	6·70	24·66	6·70	24·77	6·74
5	1	24·90	1·66	24·90	1·82	24·90	4·33
10	1	24·90	1·14	24·90	1·30	24·90	4·05
25	1	24·90		24·90		24·90	3·63
5	10	24·90		24·90		24·90	3·34
10	10	24·91		24·91		24·90	3·02
20	10	25·90					

* Obtained by standardisation against arsenic^{III} in 2*M* hydrochloric acid and 0·1*M* bromide using rosaniline as indicator, giving a calculated equivalence point of 24·91 in above titrations.

† Obtained by standardisation against potassium iodate, see text.

TABLE IX.—EFFECT OF VARIATION OF ACID CONCENTRATION. TITRATION OF 25 ML OF 0·05*M* CHLORAMINE-T SOLUTION (FACTOR 1·004)* IN ACID MEDIA (10 ML OF 1*N* ACID) CONTAINING POTASSIUM IODIDE WITH 0·1*M* THIOSULPHATE (FACTOR 1·008)† USING STARCH AS INDICATOR

Volume 0·5*M* potassium iodide added, *ml*	Ratio of number of equivalents of iodide to chloramine-T used	End-points, *ml*		
		Hydrochloric acid	Sulphuric acid	Acetic acid
30	6	24·90	24·90	24·90
15	3	24·90	24·90	24·90
10	2	24·90	24·90	24·90
5	1	24·90	24·90	(24·82)
4	0·8	22·50	23·47	(24·58)
3	0·6	19·29	19·96	
2	0·4	15·38	17·19	
1	0·2	11·56	13·89	

* Obtained by standardisation against arsenic^{III} in 2*M* hydrochloric acid and 0·1*M* bromide using rosaniline as indicator, giving a calculated equivalence point of 24·91 in above titrations.

† Obtained by standardisation against potassium iodate, see text.

Chloramine-T and thiosulphate solutions as in Table VIII.

Potentiometric titrations with thiosulphate of the iodine liberated by chloramine-T on treatment with 4·6 equivalents of iodide and 4 equivalents of hydrochloric, sulphuric or acetic acid fully confirmed the quantitativeness of the overall reaction, and failed to reveal any side reactions or interference. Replication was perfect and in complete agreement with the arsenic figures.

The reactions involved in this method of standardisation are of a quality a little less than the highest required in the most refined work, and this method is not therefore recommended unless it ties in with the application in view. Nevertheless, with appropriate care, the results are no less accurate than those of the arsenic methods, and subject to the minimal requirements of acid and iodide, this method is suitable for the standardisation of chloramine-T solutions.

EXPERIMENTAL

Apparatus

Specially adjusted analytical balances of sensitivities 0·05 and 0·01 mg were used where appropriate, together with standard weights. Volumetric glassware was calibrated and used at 20°. All corrections were made. For potentiometric titrations, an open 400-ml beaker served as titration vessel, the solution was magnetically stirred, indicator electrodes of either 1 inch of 22-swg. bright platinum wire, or 1 cm^2 of 26-swg. bright platinum foil backed with glass, sealed into glass probes, were employed, in conjunction with a saturated calomel cell connected to the titration solution by means of a flushable saturated potassium chloride bridge plugged with filter paper; the potential across the cell was measured on either a mains-driven Marconi TF717A pH meter or a battery-driven Doran-type M4981 pH meter.

Reagents

Chloramine-T: usually May and Baker reagent grade; occasionally a recrystallised material. 0·05*M* aqueous solutions prepared in 2- or 10-litre batches.

Arsenious oxide: AnalaR dried at 120°, or, for exact work, sublimed in pure oxygen under reduced pressure. 0·05*M* solutions prepared by direct weighing, dissolving in pure sodium hydroxide solution and acidfying with pure hydrochloric acid to pH 1·2.

Potassium bromate and iodate: AnalaR grade recrystallised 5 times from conductivity water and dried to constant weight at 160°. 0·01667*M* solutions prepared by direct weighing.

Sodium thiosulphate: 0·1*M* solutions prepared from AnalaR pentahydrate in 0·01% sodium carbonate solution; standardised against potassium iodate immediately before use.

Potassium iodide: free from other halides and sulphate, but contained 0·35% potassium carbonate after drying.

Starch indicator: fresh 1% solution prepared daily.

Rosaniline hydrochloride: 0·1 g rosaniline base dissolved in water containing 1·0 ml of 2*M* hydrochloric acid, boiled, decanted and diluted to 100 ml.

Other reagents: of analaR grade. All reagents tested for active and inactive impurities by the appropriate methods.[2,36] Dust- and grease-free conductivity water was used throughout.

Purification of chloramine-T

750 g of chloramine-T were added to 1 litre of boiling conductivity water, filtered through a sintered-glass funnel fitted with a hot sleeve, and allowed to crystallise; the product was collected on sintered-glass, and washed with conductivity water. Filtration and washing were difficult because the crystals are soft, and felt together. A sample of the product was reserved and the remainder was recrystallised. This was repeated several times. The moist samples would not drain well at the pump, and drying was difficult. Microscopic examination of the crystals failed to reveal any vacuole inclusions of mother liquor. Desiccation over calcium chloride or sulphuric acid removes water of crystallisation, and heating, even at low temperature leads to formation and decomposition of dichloramine-T. Finally the samples were air-dried for 10 weeks in large basins protected from light and dust. Since chloramine-T has been reported to be efflorescent, a sample of the original product

was stored alongside the drying samples. This did fall to a fine powder, but analysis showed that there was no loss of water (Table II).

Assay of the dried samples and of other solid samples in this work was carried out by accurate preparation of 2 litres of 0·05*M* solution and titration against standard arsenic^{III} solution by the rosaniline hydrochloride method described below.

TABLE X.—STANDARDISATION OF CHLORAMINE-T SOLUTIONS: A COMPARISON OF METHODS

Method	Factor of 0·05*M* chloramine-T solution			
Against oxygen-sublimed As_2O_3 in 2*M* HCl, 0·1*M* KBr, rosaniline	1·0022	1·0021	1·0021	1·0021
ditto, potentiometric	1·0021	1·0020	1·0021	1·0021
in 0·5*M* $NaHCO_3$, 0·005*M* KI, starch	1·0021	1·0022	1·0021	1·0022
ditto, potentiometric	1·0022	1·0021	1·0021	1·0021
in 2*M* HCl, potentiometric	1·0022	1·0020	1·0021	1·0021
excess As^{III}, back titrated with bromate as in Table VII	1·0021	1·0022	1·0021	1·0021
Against ultimate standard $KBrO_3$ through pure As_2O_3 2*M* HCl, 0·1*M* KBr, rosaniline	1·0021	1·0023	1·0021	1·0021
0·5*M* $NaHCO_3$, 0·005*M* KI, starch	1·0021	1·0021	1·0020	1·0021
Against ultimate standard KIO_3 through $Na_2S_2O_3$, using 4 equivalents of acid and 3 equivalents of iodide				
H_2SO_4, starch	1·0021	1·0023	1·0021	1·0020
HCl, starch	1·0021	1·0019	1·0021	1·0022
HOAc, starch	1·0021	1·0022	1·0018	1·0021

Standardisation of chloramine-T

In the recommended methods below, the quantities actually used (Table X) are given in parentheses.

Method 1(*a*). *Against arsenic^{III} in acid solution using rosaniline hydrochloride as indicator.* Pipette an aliquot (50 ml) of standard 0·05*M* arsenic^{III} solution into a titration bottle (250–300 ml bottle with a well-ground glass stopper), add sufficient hydrochloric acid (40 ml of 10*M*) and potassium bromide (20 ml of 1·0*M*) to give concentrations of 2*M* and 0·1*M* respectively in the expected end-point volume (200 ml) and dilute appropriately (90 ml — volume of washings). Titrate with 0·05*M* chloranime-T to within 0·1 ml of the end-point. Add 2 drops (0·1 ml) of 0·1% aqueous rosaniline hydrochloride per 100 ml of solution, and complete the titration split-dropwise till the very pale yellow colour changes to bright purple. The purple colour develops over a period of 5–10 secs. On each addition of titrant, rinse down, stopper the bottle, immediately shake vigorously and allow to stand for 15 secs. Rinse down stopper and repeat. Any delay in shaking, or too large an increment of titrant, will allow premature bromination of the indicator, and reddening of the solution. Warning of the end-point is given by a purple tint in the foam.

For a clean, brilliant end-point, it is necessary to delay addition of the indicator till within 0·05 to 0·1 ml before the end-point. To locate this point, a preliminary titration may be done to the first

faintly perceptible smell of free bromine, or with a reversible indicator such as quinoline yellow or *o*-dianisidine (*cf.* Part II) and 0·1 ml deducted from the result. However, premature bromination of the rosaniline does not prevent observation of the end-point, and this indicator will serve in the rough titration if its addition is delayed as long as possible, and the titration solution mixed vigorously, as quickly as possible, after each increment of titrant. As the red colour develops, further indicator is added, 4 drops at a time. At the end-point, the red colour will suddenly deepen to a much more intense purplish-red. To check the end-point, a further addition of indicator is made. If the tint does not change, or becomes more intense, the end-point has been reached, but if the colour reverts to orange-red, the titration is incomplete.

Method 1(*b*). *Against arsenic*^{III} *in neutral buffer, using starch as indicator.* Pipette an aliquot (50 ml) of standard 0·05*M* arsenic^{III} solution into a conical flask, add sufficient sodium bicarbonate (100 ml of 1·0*M* solution) and potassium iodide (10 ml of 0·1*M* solution) to give concentrations of about 0·5 and 0·005*M* respectively in the expected end-point volume (200 ml), and titrate with 0·05*M* chloramine-T solution, adding 1 ml of freshly prepared 1% starch solution about 0·5 ml before the end-point. Finish slowly to a permanent clear very pale blue colour.

Method 2. *Against potassium iodate through thiosulphate.* Pipette an aliquot (25 ml) of 0·05*M* chloramine-T into a titration bottle, add three equivalents (15 ml of 0·5*M*) potassium iodide, and four equivalents (10 ml of 1·0*M*) hydrochloric acid, and titrate with 0·1*M* thiosulphate, adding 2 ml of freshly prepared 1% starch solution as indicator 0·5 ml before the end-point.

Standardise the thiosulphate by substituting an aliquot of standard 0·01667*M* iodate for the chloramine-T in the above process.

A direct comparison of the various methods on a 5-litre batch of chloramine-T solution is given in Table X, and illustrates the excellence of the standardisation, particularly against, or through, arsenic^{III}.

Zusammenfassung—Das Verhalten von Chloramin-T als titrimetrisches Reagens wird eingehend erörtet. Die Methoden zür Einstellung der Reagenslösung werden kritisch untersucht.

Résumé—Discussion détaillée du comportement de la chloramine-T comme réactif titrimétrique. On examine de façon critique des méthodes pour standardiser des solutions de ce réactif.

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USE OF BRUCINE AS AN OXIDATION-REDUCTION INDICATOR IN CERIMETRY

G. GOPALA RAO and T. P. SASTRY
Andhra University, Waltair, S. India

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Summary—The use of brucine as an internal indicator in the cerimetric determination of iron^{II} and ferrocyanide has been investigated. A 0·1% solution of brucine in 3*N* sulphuric acid is quite stable. Ten drops of this solution give a good end-point; with a slight excess of ceric salt solution a pink colour appears. The brucine indicator has slight advantages over the diphenylamine class of indicators.

SEIKICHI MIYAGI[1] appears to have been the first to employ brucine as internal indicator in the determination of ferrous iron with potassium dichromate. He employed 20 drops of a 1% solution of brucine in concentrated sulphuric acid for each titration. At the end-point, with a slight excess of dichromate, the indicator is reported to change to a vivid scarlet. Miyagi has also employed brucine as an internal indicator in the titration of stannous salts with dichromate. Narayana Murty and Seshadri[2] have also recommended the use of brucine in the titration of iron^{II} with potassium dichromate. Alexejewa and Andronikowa[3] have preferred the use of brucine as an indicator in the titration of Fe^{II} with potassium dichromate in the presence of hydrochloric acid, stating that when diphenylamine is used as an internal indicator the end-point is indefinite. We have now investigated the use of brucine as an internal indicator in cerimetric titrations.

EXPERIMENTAL

Indicator solution: A study of the stability of the indicator in sulphuric acid has led the authors to conclude that the stability depends upon two factors: (1) the concentration of the sulphuric acid; (2) the concentration of brucine. It is observed that the stability of the indicator solution decreases as the concentration of sulphuric acid is increased above 3·0*N*. The indicator solution also deteriorates with increasing rapidity as the concentration of brucine increases beyond 0·1%. Storage in an amber-coloured bottle did not improve the stability of the indicator solution.

A 0·1% solution of brucine in 3·0*N* sulphuric acid is most suitable as a stock indicator solution. Ten drops of this solution are enough to give a good indication of the end-point in most redox titrations, although one can go up to thirty drops without any significant indicator correction being necessary. Such a solution assumes a pale orange colour, when kept for a period of two months and a red colour after six months. Even after this apparent deterioration, the solution can still be used as an indicator without any correction. A 0·1% solution of brucine in 2·0 to 3·0*N* acetic acid can also be used as a good indicator.

Indicator correction: The correction to be applied when brucine is used as an indicator in titrations with ceric sulphate has been determined. For this purpose an aliquot volume of an iron^{II} solution was titrated with a 0·01*N* ceric sulphate solution in the presence of excess of ferric sulphate employing a known volume of the stock brucine solution as internal indicator. The average deviation between such a titre value and the average value obtained in a potentiometric titration was taken as the indicator correction. This is negligible when 0·5 ml to 1·5 ml of a freshly prepared 0·1% solution of brucine is employed. When higher amounts are used, significant deviations are obtained from the potentiometric titre values, showing the need for a high indicator correction.

Titration of iron^{II} with ceric sulphate using brucine as indicator in sulphuric acid medium

Brucine works as a good indicator in the titration of iron^{II} with ceric sulphate in sulphuric acid medium. For the purpose 0·5 ml of 0·1% brucine solution has been employed. The end-point is indicated sharply by the appearance of a pink colour which is stable for about a minute. The titration of iron^{II} can be successfully carried out in solutions of varying concentration of sulphuric acid, 0·5*N* to 8·0*N*. The concentration of ceric sulphate can also be varied from 0·01*N* to 0·1*N*. The brucine indicator has an advantage that it can be used even in the absence of phosphoric acid, unlike the diphenylamine class of indicators. Tungstic acid does not interfere in the titration, as it does in the case of diphenylamine and diphenylbenzidine. Nickel salts do not interfere in the titration up to 1 g in 100 ml of the solution; cobalt salts interfere above 0·1 gm per 100 ml, since the colour of the cobalt ion is somewhat similar to that of the oxidised indicator. Typical results obtained by the authors on the determination of iron, under varying conditions, are given in Table I.

TABLE I

0·1*N* ceric sulphate (Indicator correction negligible)			0·01*N* ceric sulphate (indicator correction—0·02 ml)		
Iron^{II} taken (Potentiometric) *m-moles*	Iron^{II} found, *m-moles* Overall acid concentration		Iron^{II} taken, *m-moles*	Iron^{II} found, *m-moles* Overall acid concentration	
	0·05*N* H_2SO_4 without H_3PO_4	1·0*N* HCl without H_3PO_4		0·5*N* H_2SO_4 without H_3PO_4	1·0*N* HCl without H_3PO_4
0·2212	0·2218	0·2220	0·01894	0·01890	0·01896
0·4424	0·4422	0·4422	0·03788	0·03780	0·03792
0·5531	0·5533	0·5540	0·05682	0·05670	0·05708
0·6636	0·6633	0·6646	0·06630	0·06632	0·06632
0·7235	0·7239	0·7245	0·07576	0·07561	0·07568

Titration of iron^{II} in hydrochloric acid medium

In titrations of Fe^{II} in the presence of hydrochloric acid, the authors have found that the colour change at the end-point is from yellow to orange. This is presumably due to the toning down of the red colour of the oxidised brucine by the yellow colour of the ferric iron in hydrochloric acid medium. However, it has been found that the addition of phosphoric acid helps the attainment of an almost pink colour at the end-point. Moreover, the end-point colour is less stable in hydrochloric acid medium than in sulphuric acid. In titrations of Fe^{II} in 1·0*N* to 2·0*N* overall hydrochloric acid, the orange colour appears sharply enough at the stoichiometric end-point but fades in about twenty seconds. If the hydrochloric acid concentration exceeds 2*N*, the end-points are extremely fleeting. This difficulty increases with increasing hydrochloric acid concentration. Above a concentration of 4*N* hydrochloric acid, it is not possible to perceive any colour change at any stage of the titration. Even the addition of phosphoric acid (5 ml of syrupy phosphoric acid in 100 ml) does not improve matters. It is thus obvious that the titration of Fe^{II} in hydrochloric acid medium can be carried out only so long as the acidity does not exceed an overall concentration of 2*N*.

Determination of ferrocyanide with ceric sulphate using brucine as indicator

During the titration of ferrocyanide with 0·01*N* ceric sulphate (using 0·5 ml of 0·1% brucine solution as indicator), the pink colour of the oxidised brucine is masked by the deep colour of the ferricyanide that is formed. The difficulty can, however, be overcome by diluting the titration mixture before carrying out the titration. After dilution to 200 ml, 5 to 10 ml of 0·05*N* solution of ferrocyanide can be titrated with a 0·05*N* solution of ceric sulphate using 1 ml of a 0·1% solution of the indicator. In these titrations, the sulphuric acid concentration should not exceed 4*N*, because at higher acidities the ferricyanide that is formed can itself oxidise the brucine indicator, giving

premature end-points. The titration of ferrocyanide should be carried out in 0·5*N* to 1*N* sulphuric acid. Some typical results are presented in Table II.

TABLE II

No.	Ferrocyanide taken, *m-mols*	Ferrocyanide found, *m-mols*
1	0·0216	0·0217
2	0·0433	0·0434
3	0·0865	0·0862
4	0·1619	0·1624
5	0·2428	0·2421
6	0·3238	0·3247

Results 1, 2, and 3 are taken from the titrations with 0·01*N* ceric sulphate, after deducting 0·02 ml from the titre value. Results 4, 5, and 6 represent titrations with 0·1*N* ceric sulphate employing 1 ml of 0·1 % brucine solution as the indicator; no indicator correction has been applied in this case.

Acknowledgement—One of us (T. P. Sastri) desires to thank the Government of India for the award of a Research Scholarship, which enabled him to participate in this investigation.

Zusammenfassung—Der Gebrauch von Brucin als innerer Indikator in der cerimetrischen Bestimmung von Eisen-II und Eisen-II-cyanid untersucht.

Eine 0,1 % Lösung von Brucin in 3*N* Schwefelsäure ist sehr stabil. Zehn Tropfen dieser Lösung geben einen guten Endpunkt; bei geringem Überschuss von Ceri-Salzlösung entsteht eine rosa Farbe. Der Brucin-Indikator hat kleine Vorteile gegenüber den Indikatoren der Diphenylaminklasse.

Résumé—On a utilisé la brucine comme indicateur interne pour le dosage cérimétrique du fer^{II} et du ferrocyanure. Une solution de brucine à 0·1 % dans l'acide sulfurique 3*N* est stable. Dix gouttes de cette solution donnent une fin de réaction très nette. Une coloration rose apparaît si l'on ajoute de la solution cérique en léger excès. La brucine comme indicateur a de légers avantages sur les dérivés de la diphénylamine.

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แผนกห้องสมุด กรมวิทยาศาสตร์
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URONIC ACID DETERMINATION

S. A. BARKER, A. B. FOSTER, I. R. SIDDIQUI and M. STACEY
Chemistry Department, The University, Birmingham, 15, England

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Summary—Modifications of the McCready, Swensen and Maclay apparatus for uronic acid determination are described which enable determinations to be made on 20-mg samples.

DURING structural studies of two complex acidic polysaccharides elaborated by *Aerobacter aerogenes* (N.C.T.C. strains 418 and 8172) the small amounts of material available rendered difficult the determination of their uronic acid content by existing

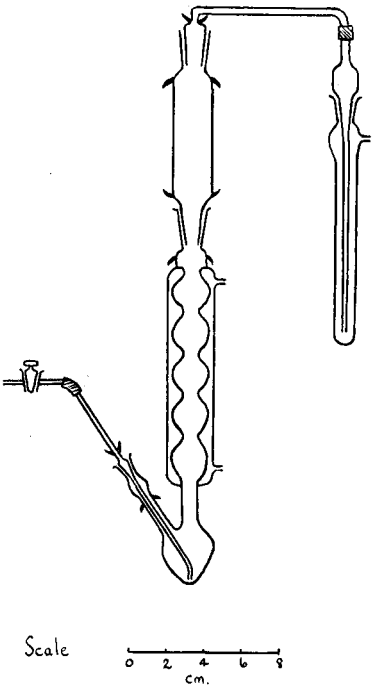

FIG. 1

methods. Colorimetric methods based, for example, on carbazole[1] and anthrone[2] have been used for the determination of the uronic acid content of micro amounts of polysaccharides. The possibility that response to these colorimetric tests may be influenced by the nature of the uronic acid and by its molecular environment[2] suggests that alternative methods would be of value in those cases where the nature of the uronic acid is not known, or where more than one type of uronic acid is present in the polysaccharide. Analysis for uronic acid based on decarboxylation appears to be independent of the nature of the uronic acid. Modifications were therefore introduced to the apparatus described by McCready, Swensen and Maclay[3] which enabled the uronic acid content of 20-mg samples to be determined instead of the 250 mg recommended by these workers. No alterations, except those involved in scaling down, were introduced to their experimental procedure which involved decarboxylation with 19% hydrochloric acid, absorbing the carbon dioxide in

standard 0·25*N* sodium hydroxide, and back titration with standard 0·1*N* hydrochloric acid. Nitrogen was used as the carrier gas in place of air. Control determinations on samples of crystalline glucurone gave reproducible results.

APPARATUS

The apparatus (Fig. 1) consisted of a pear-shaped flask with a sealed condenser and a Quickfit B7 neck carrying a narrow Quickfit tube reaching to the bottom of the flask. On top of the condenser, a trap was fitted containing closely packed granulated zinc held in position by silicon wool plugs. The top of the apparatus was connected by a tube to the absorption apparatus which consisted of an ordinary air-leak (B14/joint) fitted in a Quickfit tube with a side-arm. The entire apparatus was kept free of atmospheric carbon dioxide by ordinary calcium chloride tubes containing Ascarite retained by silicon wool plugs. The rate of flow of nitrogen was carefully controlled by a screw-clip and tap (see Fig. 1). All the Quickfit joints were lubricated with Silicone grease and held together by springs.

METHOD

The apparatus was cleaned with a warm chromic-sulphuric acid mixture, rinsed and dried before use.

The sample was weighed in a narrow tube (length 1 cm), placed in the dry reaction flask and 3 ml of 19% hydrochloric acid (51·3 ml of B.D.H. micro-analytical hydrochloric acid made to 100 ml with water) introduced by means of a pipette. A stream of carbon dioxide-free nitrogen was passed into the reaction flask to remove traces of carbon dioxide before connecting the absorption apparatus. The absorption apparatus was swept free of carbon dioxide and standard *ca.* 0·25*N* sodium hydroxide (5 ml) added to the absorption tube. The absorption apparatus was connected, the flow rate of nitrogen adjusted to *ca.* 1 bubble every 2–3 sec and the oil bath, previously heated to 145°, placed in position; the level of the oil was 0·25 cm below that of the liquid level in the reaction flask. Heating at 145° was continued for 2 hr. The bath was then removed and the flow rate of nitrogen increased to 2–3 bubbles per sec for about 10 min. The absorption apparatus was then disconnected and the contents carefully transferred and washed (5 × 5 ml) in a conical flask by fixing a rubber teat to the air leak.

A 10% solution of barium chloride dihydrate (2 ml) and two drops of phenolphthalein indicator were added to the titration flask and the excess alkali was titrated against standard *ca.* 0·1*N* hydrochloric acid. Control standardisations without the sample were also performed. The method was checked on samples of glucurone. All titrations were performed in an atmosphere of CO_2-free nitrogen.

RESULTS

TABLE I.—URONIC ACID DETERMINATIONS

Sample	Sample weight, *mg*	Volume of 0·106*N* HCl added	Titration difference, *ml*	% of uronic acid
Blank	—	12·5	0·0	—
Glucurone	22·90	10·05	2·45	99·6
,,	19·72	10·4	2·10	99·2
,,	20·74	10·25	2·25	100·8
,,	20·74	10·25	2·25	100·8
Polysaccharide	22·86	12·1	0·4	16·4
N.C.T.C. 418[a]	19·86	12·15	0·35	16·6
Blank	—	12·25[c]	0·0	—
N.C.T.C. 8172[b]	21·46	11·55[c]	0·70	28·7

[a] Contains[4] glucuronic acid and mannuronic acid.
[b] Contains[5] glucuronic acid.
[c] 0·10*N* Hydrochloric acid used in these titrations.

Zusammenfassung—Modifikationen des Apparates von McCready, Swensen und Maclay für die Bestimmung von Uronsäure werden beschrieben, die diese Bestimmungen auf 20 mg Proben ermöglichen.

Résumé—On décrit certaines modifications de l'appareil de M'Cready, Swensen et Maclay pour le dosage de l'acide uronique qui permettent d'effectuer des déterminations sur des échantillons de 20 mg.

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SUBSTITUTIVE HALOGENATION OF AROMATIC COMPOUNDS IN AQUEOUS SOLUTION BY INTERHALOIDS—II

PREPARATION AND INVESTIGATION OF A STANDARD SOLUTION OF BROMINE MONOCHLORIDE

E. SCHULEK and K. BURGER
Institute of Inorganic and Analytical Chemistry, L. Eötvös University,
Budapest, VIII. Muzeum-körút 4(b), Hungary

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Summary—A new method has been evolved for the preparation of a bromine chloride solution containing hydrochloric acid. In a hydrochloric acid solution bromate reacts quantitatively with bromide forming bromine chloride, provided that they are present in equivalent amounts. A 0·1*N* solution of bromine chloride containing hydrochloric acid showed less than 3–5% change of titre on storage for 3 months.

A new method has been evolved for the determination of the bromate content of the bromine chloride solution. The interaction of bromine chloride and cyanide yields chloride ions and cyanogen bromide, the latter after basic hydrolysis to bromide and cyanate ions, when acidified, hydrolysing to ammonium ions and carbon dioxide. Subsequently bromate can be measured by iodometry. A method has also been evolved for the determination of the content of elementary chlorine in bromine chloride solutions.

For purposes of bromination by excess bromine chloride, the use of a 0·1*N* solution of bromate which contains potassium bromide in an amount equivalent to bromate is suggested.

IN aqueous solution bromine monochloride shows an unequivocal action, behaving solely as a bromination agent.[1] The stability of an aqueous solution of iodine monochloride containing hydrochloric acid, and the fact that it acts exclusively as an iodinating agent, have been utilised for analytical purposes. Whilst an aqueous solution of iodine monochloride containing hydrochloric acid was first applied by Heisig[2] and Kubina[3] as an oxidizing agent, it was later used as an analytical standard solution by Gengrinovich, Fialkov and co-workers,[4] and by Cihalik and Vavrejnova.[5–7] The titre of the 0·1*N* solution of iodine chloride, about 0·4*N* with respect to hydrochloric acid, remained unchanged for 3–4 months. It was prepared by allowing appropriate quantities of potassium iodate and potassium iodide to react in a hydrochloric acid medium.

In addition to iodine monochloride (although very rarely) iodine monobromide dissolved in an organic solvent has been applied as a standard oxidising solution.[8] To the best of our knowledge, a standard solution of bromine monochloride of stoichiometric composition has not been used up to the present.

Schulek recently pointed out that bromine monochloride developed in a hydrochloric acid medium plays in certain bromometric measurements both a catalytic and a controlling role.

EXPERIMENTAL

Preparation of bromine monochloride solution

Having confirmed[1] that in aqueous solution, bromine monochloride reacts unequivocally with organic compounds, we set out to prepare a stable aqueous solution of bromine monochloride.

At first, the simple apparatus evolved by Schulek and Pungor[9–10] was used for the preparation. Analogous to the preparation of solutions of iodine monochloride, an attempt was made to prepare a solution of bromine monochloride by reacting stoichiometric quantities of potassium bromate and potassium bromide in the presence of hydrochloric acid, according to the equation

$$KBrO_3 + 2KBr + 6HCl \rightarrow 3BrCl + 3H_2O \quad (1)$$

Bromine monochloride containing hydrochloric acid prepared by this reaction was compared with a bromine monochloride solution of identical concentration, containing the same quantity of hydrochloric acid, produced by the Schulek apparatus. On establishing the ultraviolet absorption spectra of both solutions, the curves showed complete coincidence. At the same time, the ultraviolet

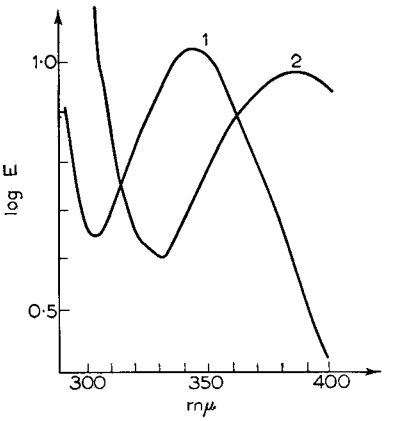

FIG. 1.—Ultraviolet absorption curves of a solution of bromine monochloride containing hydrochloric acid (1), and of a bromine solution containing hydrochloric acid (2), respectively.

absorption spectrum of bromine water of identical concentration and identical content of hydrochloric acid was established as well. It was found that it possesses a shape quite different from those of bromine monochloride solutions (Fig. 1). For establishing the ultraviolet absorption spectra, a Beckmann D.U. quartz spectrophotometer was applied, with 1 cm-quartz cuvettes. A hydrogen lamp served as light source.

In the course of experiments to be described elsewhere it was observed that the rate of the reaction between salicylic acid and bromine ranges much below that between salicylic acid and bromine monochloride. Therefore, bromination tests were carried out with bromine monochloride solutions prepared in the Schulek apparatus from bromate. On applying identical bromination periods, the consumption of bromine proved to be quite identical with both types of solution.

These experiments confirmed that, in a hydrochloric acid medium, potassium bromate and potassium bromide in stoichiometric proportions form bromine monochloride. The reaction proceeds in two steps. At first, elementary bromine is formed, being oxidised later by bromate to bromine monochloride. Although the reaction does not take place instantaneously, it is completed rather quickly in the presence of excess hydrochloric acid. (The preparation of 1000 ml of a 0·1*N* solution of bromine monochloride, which is at least 0·5*N* in hydrochloric acid, requires about 1–2 minutes.) On raising the concentration of hydrochloric acid, the rate of reaction increases (in the case of 1·5–2·0*N* hydrochloric acid only 10–20 seconds are necessary).

Preparation of the standard solution

On dissolving 2·7835 g of potassium bromate, (analytical grade) and 3·9670 g of potassium bromide, (analytical grade), in a 1000-ml measuring flask in 400–500 ml of water, 365 ml of 20% HCl is poured into the liquid, allowed to stand until it turns yellow, then made up to volume with distilled water.

The standard solution should be stored, with exclusion of sunlight, in a glass-stoppered flask completely filled.

Investigation of bromine monochloride solution

Determination of the content of bromate in the solution of bromine monochloride: On applying excess bromate to the preparation of the bromine monochloride solution, this excess reacted with hydrochloric acid to form elementary chlorine. In the course of the examination of bromine monochloride solution, this reaction was also subjected to a study. For this purpose, a method was evolved for the determination of bromate and elementary chlorine in the presence of excess bromine monochloride. No difficulties were encountered when determining the content of bromate in the solution of bromine monochloride. About 0·5 g of potassium cyanide was dissolved in the reaction mixture. On making the solution alkaline by addition of 20 ml of 2*N* sodium hydroxide, bromine monochloride reacted with the cyanide to form cyanogen bromide which hydrolysed in the alkaline medium to bromide and cyanate ions. On acidification, the latter extremely quickly hydrolysed to ammonium ions and carbon dioxide. Thus the oxidising power of bromine monochloride with respect to iodide ion was destroyed.[11] Subsequently on standing for 5 minutes, the bromate content of the solution was measured by iodometry.

This method proved to be suitable for the determination of the bromate content of bromine water, and of alkaline solutions of hypobromite or hypochlorite.[12]

By this method it has been proved that a bromine monochloride solution containing hydrochloric acid, (provided its concentration of hydrochloric acid is sufficiently high), does not contain any bromate some minutes after its preparation, even when a 5–10% excess bromate was originally added.

Determination of the content of elementary chlorine in a bromine monochloride solution: It proved to be more difficult to determine elementary chlorine in the presence of bromine monochloride. The method was based on differences in the behaviour of cyanogen bromide and cyanogen chloride.[13] About 0·2 g of potassium cyanide was added to the bromine monochloride solution containing hydrochloric acid. After some minutes, about 0·5 g of potassium iodide was dissolved in the reaction mixture and on allowing to stand for about 10 minutes, iodine liberated by the cyanogen bromide was measured. It is known that cyanogen chloride converts, when allowed to stand some minutes, into an electromeric form incapable of oxidising iodide.[9] Thus, the chlorine content of the solution of bromine monochloride was determined by subtracting the volume of standard thiosulphate consumed by iodine liberated in the reaction with cyanide from the volume of thiosulphate solution consumed by iodine directly liberated by the solution of bromine monochloride. This procedure afforded correct results in the cases when the solution of bromine monochloride actually contained free chlorine.

However, the method can only be applied under experimental conditions. According to our tests, results lower than actual values are obtained when a stoichiometric solution of bromine monochloride, containing no free chlorine at all, reacts with potassium cyanide. A similar experience is also mentioned by Molnár.[10] Accordingly, bromine monochloride reacts *quantitatively* with cyanide solely when elementary chlorine is present, the reaction affording cyanogen bromide.

This method proved suitable to establish that, on preparing a solution of bromine monochloride with the use of a known excess of bromate, the solution obtained contains a quantity of free chlorine precisely equivalent to the excess of bromate applied.

Reaction of bromine monochloride with bromide ions

The reaction between bromine monochloride and bromide ions was also subjected to an examination. It was found that bromine monochloride and bromide ions react, in an acid medium, to liberate elementary bromine.

Attempts to evolve an analytical method suitable for the determination of minute amounts of bromine in the presence of large quantities of bromine monochloride failed.

It follows that, on preparing bromine monochloride of stoichiometric composition in a hydrochloric acid solution, precisely equivalent quantities of carefully dried potassium bromate and potassium bromide of analytical grade should be weighed.

Determination of the titre of the standard solution of bromine monochloride

The titre of the standard solution of bromine monochloride has been determined in two ways: by iodometry, and by direct measurement of hydrazine sulphate.

(1) *Iodometric determination of the titre:* Ten ml of standard solution was added to 0·5 g of potassium iodide in about 30 ml of water, in a 100-ml Erlenmeyer flask. The liberated iodine was titrated by a standard solution of sodium thiosulphate.

(2) *Determination of the titre by hydrazine sulphate:* About 0·30 g of hydrazine sulphate (analytical grade) accurately weighed, was dissolved in water in a 100-ml measuring flask, made up to volume. Then 10-ml portions of this stock solution were transferred into a titration flask, diluted with distilled water to 30–50 ml, acidified with 2–10 ml of 20% hydrochloric or 10–20 ml of 2*N* sulphuric acid and, in the presence of one drop of a solution of *p*-ethoxychrysoïdine as indicator, titrated with a 0·1*N* standard solution of bromine monochloride.

1 ml of a 0·1*N* standard solution of bromine monochloride is equivalent to 3·253 mg of hydrazine sulphate.

Both methods yielded identical results.

Stability of the bromine monochloride solution

In further tests, the storage properties of bromine monochloride solutions prepared by the above methods, and containing various amounts of hydrochloric acid were examined. It was found that, during a storage for 3 months in a dark place, in a completely filled flask, the titre of a 0·1*N* solution of bromine monochloride (1·5–2·0*N* referred to hydrochloric acid) showed changes not exceeding 3–5% (Table I).

TABLE I

No.	Date of analysis	Concentration of HCl, *N*	Measured, *ml*	Consumed 0·1*N* $Na_2S_2O_3$ *ml*	Titre	Change in titre, %
1	Feb. 29, 1956	1·5	4·850	4·85	1·000	
	April 6, 1956		4·850	4·77	1·017	
	June 7, 1956		4·850	4·65	1·049	+4·9%
2	July 2, 1956	2·0	10·03	9·78	1·025	
	Sep. 25, 1956		10·03	9·53	1·052	+2·5

According to our investigations, bromine monochloride is present in the form of a complex, in aqueous solution containing chlorides, and this fact is responsible for the relatively high stability of the solution. The physical chemistry of the chloride complex of bromine monochloride will be discussed elsewhere in detail.

In bromination processes with excess bromine monochloride, a 0·1*N* standard solution of potassium bromate containing potassium bromide in a quantity equivalent to the bromate according to equation (1), proved to be practical, due to its stable titre.

Preparation

2·7835 g of potassium bromate and 3·967 g of potassium bromide, (analytical grade) were dissolved in distilled water and diluted to 1000 ml.

The solution thus obtained showed, when stored properly, a stable titre. On acidification by hydrochloric acid it converted into a bromine monochloride solution (the solution should be 1·5–2·0*N* with respect to hydrochloric acid, after acidification).

The solution lends itself to analytical methods based upon bromination by excess bromine, particularly when bromine monochloride is to be used as a bromination agent.

Determinations with this solution are conducted analogously to the Koppeschaar method of bromination except, that the reaction mixture does not contain excess bromide.

The conditions of application of bromine monochloride as a bromination and standard oxidimetric solution will be discussed elsewhere in detail.[14–15]

In order to be able to prepare quickly a bromine monochloride solution containing hydrochloric acid, suitable for direct titration, it is practical to store a bromate solution containing bromide as follows.

2·7835 g of potassium bromate and 3·967 g of potassium bromide (analytical grade) are dissolved in water and diluted to 250 ml. The required 0·1*N* standard solution of bromine monochloride may be prepared at any time quickly by acidifying 25·00 ml portions of this stock solution with 36·5 ml of 20% hydrochloric acid and diluting with water to 100 ml.

The titre of the standard solution can be determined either by iodometry or against hydrazine sulphate.

Zusammenfassung—Es wird eine neue Methode für die Herstellung einer salzsäurehaltigen Bromchlorid-Lösung entwickelt.

In genügend stark salzsaurer Lösung reagiert das Bromat mit dem Bromid quantitativ unter Bildung von Brommonochlorid, vorausgesetzt, dass beide Bromat und Bromid in dem Molverhältnis 1 : 2 vorhanden sind.

Eine auf dieser Weise hergestellte 0,1*N* Bromchlorid-Lösung erwies sich nach 3 monatiger Aufbewahrung auf 3–5% als titerbeständig. Es wurden Methoden zur Bestimmung des eventuellen Bromatgehaltes, sowie des eventuellen Gehaltes an freiem Chlor der Bromchlorid-Lösungen ausgearbeitet. Die Reaktion zwischen Bromchlorid und Bromid-Ionen wurde eingehend untersucht.

Zur Bromierung durch überschüssige Bromchlorid-Lösung wird eine vollkommen titer-beständige neutrale 0,1*N* Bromat-Bromid-Lösung in Vorschlag gebracht deren Molverhältnis Bromat-Bromid genau 1 : 2 bemessen ist.

Résumé—Une nouvelle méthode a été élaborée pour préparer une solution de chlorure de brome contenant de l'acide chlorhydrique. En solution chlorhydrique, à condition qu'ils soient présents en quantités équivalentes, le bromate réagit quantitivement avec le bromure avec formation de chlorure de brome. La solution titrée 0·1*N* contenant de l'acide chlorhydrique s'est conservée pendant trois mois sans révéler des changements de titre excédant 3 à 5 pour cent.

On a mis au point une nouvelle méthode permettant de déterminer la teneur en bromate de cette solution. Le chlorure de brome a été traité au cyanure en milieu alcalin. La réaction du chlorure de brome et du cyanure donne le bromure de cyanogène lequelle s'hydrolyse en solution alcalin en ions bromure et cyanate. (Ceux-ci, acidifiés, s'hydrolysent trés rapidement en ions d'ammonium et CO_2, ce qui les rend inefficaces du point de vue iodométrique.) On peut par la suite mesurer le bromate par iodométrie. Une méthode pour déterminer la teneur de chlore élémentaire dans des solutions de chlorure de brome a été élaborée.

Pour opérer la bromuration au moyen du chlorure de brome en excès on propose l'utilisation d'une solution 0·1*N* de bromate, contenant en quantités équivalentes le bromure de potassium et le bromate.

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SUBSTITUTIVE HALOGENATION OF AROMATIC COMPOUNDS IN AQUEOUS SOLUTION BY INTERHALOIDS—III

DETERMINATION OF AROMATIC COMPOUNDS BY BROMINATION WITH BROMINE MONOCHLORIDE

E. SCHULEK and K. BURGER
Institute of Inorganic and Analytical Chemistry, L. Eötvös University,
Budapest, VIII, Muzeum-körút (4b), Hungary

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Summary—Bromination of certain phenols by bromine chloride was investigated, and the method was applied to quantitative measurements.

Bromine chloride was prepared in the bromination flask in a hydrochloric acid medium from equivalent amounts of bromate and bromide (1*M* : 2*M*).

It was found that whilst the application of bromine chloride does not increase the number of compounds capable of being brominated, it raises the rate of bromination appreciably.

THE quantitative bromometric determination of phenols, aromatic amines and their derivatives is based on substitution reactions with bromine, *i.e.*, on bromination, the *o*- and *p*-hydrogen atoms of the phenol ring are readily exchanged by bromine atoms. Bromination is carried out, according to the method of Koppeschaar,[1] in the presence of excess bromide, in a hydrochloric acid medium, by use of a standard bromate solution. Excess bromine is measured iodometrically.

Investigation of the reactions of bromine monochloride[2] proved that bromine chloride reacts unequivocally with organic aromatic compounds, acting solely as a brominating agent.

It was observed in the course of preparing bromine monochloride[3] that the interaction of bromate and bromide ions in a hydrochloric acid medium yields bromine monochloride, provided the bromate and bromide are applied in equivalent amounts, according to the reaction scheme

$$KBrO_3 + 2KBr + 6HCl \rightarrow 3BrCl + 3KCl + 3H_2O \qquad (1)$$

In the light of both of these facts, we were able to deal with the bromination of phenols by bromine monochloride and to apply this reaction in certain cases to the quantitative determination of phenols.

The present determinations were conducted in a way similar to the Koppeschaar method, except that the standard solution of bromate contained an equivalent amount of bromide, according to equation (1). Thus, on acidification with hydrochloric acid, instead of elementary bromine, bromine monochloride and its chloride complex were formed, and subsequently reacted with the substance to be determined.

EXPERIMENTAL

Preparation of the standard solution

2·7835 g of potassium bromate and 3·967 g of potassium bromide, analytical grade, were weighed accurately, dissolved in distilled water and diluted to 1000 ml.

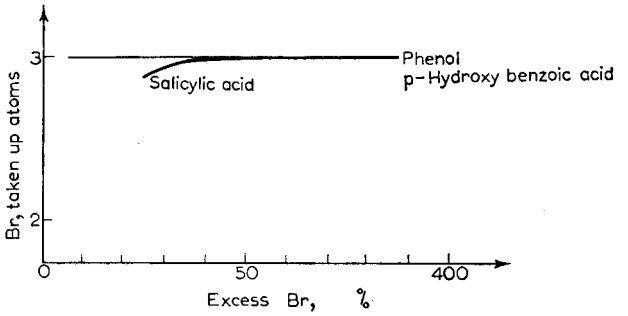

FIG. 1.—Bromination by bromine monochloride. Br taken up, atoms: Excess Br, %

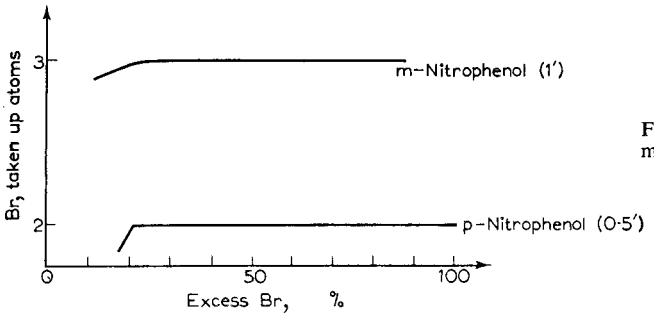

FIG. 2.—Bromination by bromine monochloride. Br taken up, atoms: Excess Br, %

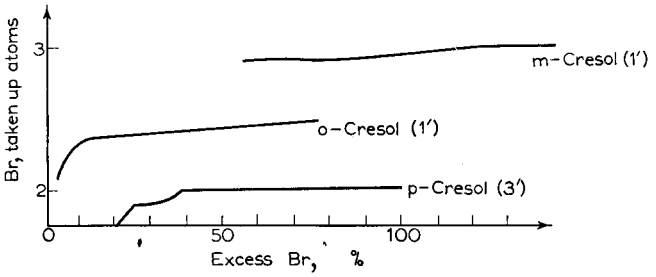

FIG. 3.—Bromination by bromine monochloride. Br taken up, atoms: Excess Br, %

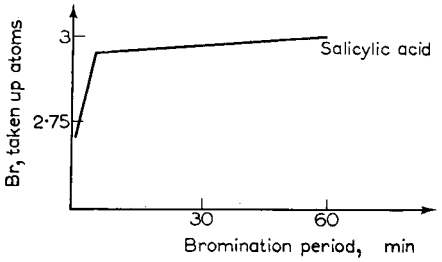

FIG. 4.—Bromination according to Koppeschaar. Br taken up, atoms: Bromination period, minutes

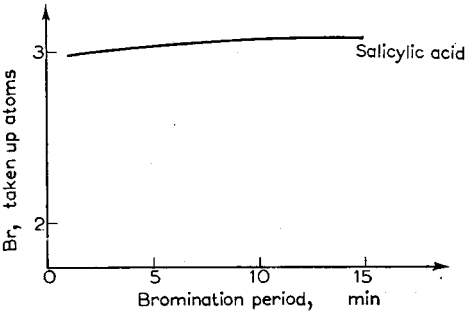

FIG. 5.—Bromination by bromine monochloride. Br taken up, atoms: Bromination period, minutes

Measurements were carried out as follows.

A 0·1*N* aqueous solution (referred to the component to be determined) was prepared from the test substance. When required, some sodium hydroxide was used in the preparation of this solution. 5–10-ml portions of the stock solution were quantitatively transferred to 300 ml Buchböck bromination flasks and diluted with distilled water to about 80–100 ml. Subsequently, an amount of standard solution corresponding to the planned excess of bromine was added and about 10 ml of 20% hydrochloric acid as an agent of acidification, were placed in the wide part of the neck of the bromination flask. On loosening the stopper, the acid flowed into the flask. After completing the bromination period, potassium iodide was added to the reaction mixture in the same way. On allowing to stand for about 3–5 minutes, the iodine liberated by the excess of bromine monochloride was titrated with 0·1*N* solution of sodium thiosulphate.

The bromination of phenol, *p*-hydroxybenzoic acid, salicylic acid, *o*-, *m*- and *p*-cresol, and *o*-, *m*- and *p*-nitrophenol was investigated by this method (cf. Tables I–IX and Figures 1–3).

The end-product of the reaction was tribromophenol in the case of phenol, *p*-hydroxybenzoic acid and salicylic acid (equivalent weight 1/6th part of the molecular weight); the corresponding dibromo-product in the case of *p*-cresol and *o*- and *p*-nitrophenol (equivalent weight 1/4th part of the molecular weight); and the corresponding tribromo-product in the case of *m*-cresol and *m*-nitrophenol (equivalent weight 1/6th part of the molecular weight).

Accordingly, 1 ml of standard solution is equivalent to 1·567 mg of phenol, 2·301 mg of *p*-hydroxybenzoic acid, 2·301 mg of salicylic acid, 2·702 mg of *p*-cresol, 3·478 mg of *o*-nitrophenol, 3·478 mg of *p*-nitrophenol, 1·801 mg of *m*-cresol or 2·318 mg of *m*-nitrophenol.

DISCUSSION

It was noted during the present tests that the bromination period required is appreciably reduced when bromine monochloride is applied as a bromination agent instead of the conventional reagent (Table X). This appears most strikingly in the determination of salicylic acid which requires by the Koppeschaar method a bromination period of 60 minutes (Fig. 4) whilst a quantitative bromination is attained by the new method in only two minutes (Fig. 5).

According to our investigations, by the present method a bromination period of 1 minute is necessary for the determination of phenol, *p*-hydroxybenzoic acid, *m*-nitrophenol and *m*-cresol, whereas half a minute proved satisfactory with *o*- and *p*-nitrophenol. A bromination period of two minutes was required for salicylic acid, and three minutes for *p*-cresol. *o*-Cresol could not be determined by bromination with bromine monochloride (as in the Koppeschaar method, an extremely high overconsumption was observed).

It was found at the same time that, whilst the application of bromination periods exceeding the necessary duration did not affect the values obtained in the determination of phenol, *p*-hydroxybenzoic acid and salicylic acid by the Koppeschaar method, high results were obtained in the bromine monochloride procedure.

The correlation of bromination results with the amount of excess bromine monochloride was less close with the new method proposed, provided that properly chosen bromination periods were applied.

Owing to the short bromination periods (1–3 minutes) applied in the bromine monochloride method, the results may also be affected by the volume of solution. With small volumes of solution (20–30 ml), the precipitate formed during bromination may occlude unbrominated molecules which, owing to the relatively short duration of the bromination periods, are not capable of reacting with the reagent. However, in an extremely large volume (200 ml), reaction rates appreciably decrease, due to diminished concentrations, and the otherwise adequate bromination periods prove

TABLE I. BROMINATION OF PHENOL BY BROMINE MONOCHLORIDE

No.	Substance weighed, *mg*	Excess 0·1*N* BrCl added, *ml*	Consumed 0·1*N* $Na_2S_2O_3$ *ml*	Consumed 0·1*N* BrCl, *ml*	Substance found, *mg*	Bromination period, *min*	Percentage of excess BrCl: ratio of columns 4 : 5	Amount of Br taken up by 1 mole, *atoms*	Volume of 20% HCl used for acidification
1	8·53	10·03	4·79	5·24	8·21	0·5	91	28·9	
			4·66	5·37	8·42		87	2·96	
			4·59	5·44	8·53	1	84	3·00	
			4·58	5·45	8·54				
			4·58	5·45	8·54	5		3·00	
			4·59	5·44	8·53				
			4·59	5·44	8·53	10		3·00	
			4·59	5·44	8·53				
2	16·92	20·00	9·18	10·82	16·96	1	85	3·00	
			9·16	10·84	16·99				
			9·11	10·89	17·07	5	83	3·03	
			9·10	10·90	17·09				
			8·95	11·05	17·32	60	81	3·07	
			8·94	11·06	17·34				
3	8·53	10·03	7·00	3·03	4·75	1		1·62	5
			5·56	4·47	7·01			2·47	
			4·59	5·44	8·53	1		3·00	10
			4·59	5·44	8·51			3·00	
			4·59	5·44	8·53	1		3·00	15
			4·59	5·44	8·53				
			4·59	5·44	8·53	1		3·00	20
			4·59	5·44	8·53	1			

TABLE II. BROMINATION OF *p*-HYDROXYBENZOIC ACID BY BROMINE MONOCHLORIDE

No.	Substance weighed *mg*	Excess 0·1*N* BrCl added, *ml*	Consumed 0·1*N* $Na_2S_2O_3$ *ml*	Consumed 0·1*N* BrCl *ml*	Substance found, *mg*	Bromination period, *min*	Percentage of excess BrCl: ratio of columns 4 : 5	Amount of Br taken up by 1 mole, *atoms*
1	7·133	10·03	6·92	3·11	7·156	0·5	221	3·01
			6·93	3·10	7·133			3·00
			6·92	3·11	7·156	1		3·01
			6·94	3·09	7·110			3·00
			6·93	3·10	7·133	2		3·00
			6·92	3·11	7·156			3·01
2	14·14	10·03	3·84	6·19	14·24	1	62	3·02
			3·84	6·19				
		20·00	13·83	6·17	14·20	1	224	3·01
			13·82	6·18	14·22			3·02
3	7·133	3·44	0·34	3·10	7·133	1	11	3·00
		3·75	0·65	3·10	7·133	1	21	3·00
		4·03	0·93	3·10	7·133	1	30	3·00
		4·66	1·55	3·11	7·156	1	50	3·01
		5·27	2·17	3·10	7·133	1	70	3·00
		5·89	2·79	3·10	7·133	1	90	3·00
		6·53	3·42	3·11	7·156		110	3·01

TABLE III. BROMINATION OF SALICYLIC ACID BY BROMINE MONOCHLORIDE

No.	Substance weighed, *mg*	Excess 0·1*N* BrCl added, *ml*	Consumed 0·1*N* $Na_2S_2O_3$ *ml*	Consumed 0·1*N* BrCl *ml*	Substance found *mg*	Bromination period, *min*	Percentage of excess BrCl: ratio of columns 4 : 5	Amount of Br taken up by 1 mole, *atoms*	Total volume, *ml*
1	11·34	10·03	5·10	4·93	11·34	1	103	3·00	
			5·11	4·92	11·32			2·99	
			5·10	4·93	11·34	2		3·00	
			5·10	4·93	11·34			3·00	
			5·06	4·97	11·44	5	102	3·03	
			5·04	4·99	11·48			3·04	
			4·97	5·06	11·64	15	98	3·08	
			4·98	5·05	11·62			3·07	
2	22·48	20·00	10·76	9·24	21·26	1	116	2·84	80–100
			10·90	9·10	20·94			2·79	
			10·23	9·77	22·48	2	105	3·00	
			10·23	9·77	22·48			3·00	
3	11·67	10·03	4·95	5·08	11·69	2	98	3·01	
			4·95	5·08	11·69			3·01	
	23·17	20·00	9·95	10·05	23·13	2	99	2·99	
			9·95	10·05	23·13			2·99	
4	23·17	20·00	10·23	9·77	22·48	2	105	2·91	30–40
			10·39	9·61	22·11			2·86	
			9·95	10·05	23·13	2	99	2·99	80–100
			9·91	10·09	23·22			3·01	

TABLE IV. BROMINATION OF *o*-NITROPHENOL BY BROMINE MONOCHLORIDE

No.	Substance weighed, *mg*	Excess 0·1*N* BrCl added, *ml*	Consumed 0·1*N* $Na_2S_2O_3$ *ml*	Consumed 0·1*N* BrCl *ml*	Substance found, *mg*	Bromination period, *min*	Percentage of excess BrCl: ratio of columns 4 : 5	Amount of Br taken up by 1 mole, *atoms*
1	16·87	10·03	5·10	4·93	17·15	0·5	103	2·03
			5·14	4·89	17·01			2·02
			4·70	5·33	18·54	1	88	2·19
			4·78	5·25	18·26			2·17
			4·52	5·51	19·16	2	82	2·27
			4·48	5·55	19·30			2·28
2	33·45	20·00	10·40	9·60	33·39	0·5	108	2·00
			10·30	9·70	33·73			2·02
						sec		
3	12·63	10·03	6·65	3·38	11·75	15	197	1·86
			6·25	3·78	13·15	30	166	2·08
	16·87	10·03	5·10	4·93	17·15	30	103	2·03
4	25·06	20·00	13·14	6·86	23·26	15	192	1·90
			12·42	7·58	26·36	30	164	2·10
	33·45	20·00	10·30	9·70	33·73	30	106	2·02

TABLE V. BROMINATION OF *m*-NITROPHENOL BY BROMINE MONOCHLORIDE

No.	Substance weighed, *mg*	Excess 0·1*N* BrCl added, *ml*	Consumed 0·1*N* $Na_2S_2O_3$ *ml*	Consumed 0·1*N* BrCl *ml*	Substance found, *mg*	Bromination period, *min*	Percentage of excess BrCl: ratio of columns 4 : 5	Amount of Br taken up by 1 mole, *atoms*
1	17·40	10·03	2·54	7·49	17·37	1	34	2·99
			2·52	7·51	17·41			3·00
			2·51	7·52	17·44	2	33	3·01
			2·52	7·51	17·41			3·00
		20·00	12·50	7·50	17·39	1	167	3·00
			12·50	7·50	17·39			
2	34·70	20·00	5·01	14·99	34·75	1	33	3·00
			5·03	14·97	34·71			3·00
3	12·32	5·86	0·68	5·18	12·00	1	13	2·92
		6·37	1·10	5·27	12·22	1	21	2·98
		6·87	1·56	5·31	12·31	1	29	3·00
		10·00	4·69	5·31	12·31	1	88	3·00
4	12·32	5·86	0·56	5·30	12·29	2	11	2·99
			0·53	5·33	12·36		10	3·01
		10·03	4·67	5·36	12·43	2	87	3·03
			4·67	5·36				
	24·46	20·00	9·30	10·70	24·81	2	87	3·04
			9·34	10·66	24·72			3·03

TABLE VI. BROMINATION OF *p*-NITROPHENOL BY BROMINE MONOCHLORIDE

No.	Substance weighed, *mg*	Excess 0·1*N* BrCl added, *ml*	Consumed 0·1*N* $Na_2S_2O_3$ *ml*	Consumed 0·1*N* BrCl *ml*	Substance found, *mg*	Bromination period, *min*	Percentage of excess BrCl: ratio of columns 4 : 5	Amount of Br taken up by 1 mole, *atoms*
1	17·58	10·03	4·98	5·05	17·56	0·5	99	2·00
			4·98	5·05	17·56			2·00
			4·96	5·07	17·63	1	98	2·01
			4·95	5·08	17·66			2·01
			4·91	5·12	17·81	2	96	2·03
			4·89	5·14	17·88			2·03
2	17·58	10·03	4·99	5·04	17·53	0·5	99	1·99
			5·00	5·03	17·49			
	34·90	20·00	9·96	10·04	34·92	0·5	99	2·00
			9·95	10·05	34·95			2·00
3	17·42	5·56	0·90	4·66	16·21	0·5	19	1·86
		6·06	1·07	4·99	17·35	0·5	21	1·99
		6·50	1·50	5·00	17·39	0·5	30	2·00
		7·06	2·05	5·01	17·42	0·5	41	2·00
		7·56	2·52	5·04	17·52	0·5	50	2·01
		8·06	3·05	5·01	17·42	0·5	61	2·00
		9·05	4·07	4·98	17·32	0·5	82	1·99
		10·03	5·02	5·01	17·42	0·5	100	2·00
		20·00	14·97	5·03	17·49	0·5	298	2·01

TABLE VII. BROMINATION OF *o*-CRESOL BY BROMINE MONOCHLORIDE

No.	Substance weighed, *mg*	Excess 0·1*N* BrCl added, *ml*	Consumed 0·1*N* $Na_2S_2O_3$ *ml*	Consumed 0·1*N* BrCl *ml*	Substance found, *mg*	Bromination period, *min*	Percentage of excess BrCl: ratio of columns 4 : 5	Amount of Br taken up by 1 mole, *atoms*
1	12·35	10·03	4·62	5·41	14·61	0·5	85	2·37
			4·56	5·47	14·78		83	2·39
			4·36	5·67	15·32	1	77	2·48
			4·38	5·65	15·26			2·47
	13·98	10·03	3·70	6·33	17·10	1	58	2·45
			3·74	6·29	16·99			2·43
			3·48	6·55	17·69	2	53	2·53
			3·47	6·56	17·72			2·53
			2·98	7·05	19·05	5	42	2·72
			2·99	7·04	19·02			2·72
2	12·35	5·00	0·21	4·79	12·94	0·5	4·4	2·09
			0·20	4·80	12·97		4·1	2·10
			0·21	4·79	12·94	1	4·4	2·09
			0·20	4·80	12·97		4·1	2·10
		5·17	0·35	5·22	14·10	1	7	2·28
		6·07	0·72	5·35	14·45	1	13	2·34
		7·06	1·59	5·47	14·78	1	29	2·39
		8·56	2·98	5·58	15·07	1	53	2·44
		10·03	4·36	5·67	15·22	1	77	2·48

TABLE VIII. BROMINATION OF *m*-CRESOL BY BROMINE MONOCHLORIDE

No.	Substance weighed, *mg*	Excess 0·1*N* BrCl added, *ml*	Consumed 0·1*N* $Na_2S_2O_3$ *ml*	Consumed 0·1*N* BrCl *ml*	Substance found, *mg*	Bromination period, *min*	Percentage of excess BrCl: ratio of columns 4 : 5	Amount of Br taken up by 1 mole, *atoms*
1	5·94	10·11	6·79	3·32	5·98	1	200	3·02
			6·80	3·31	5·96			3·01
			6·69	3·42	6·16	2	195	3·11
			6·68	3·43	6·18			3·12
2	12·15	10·11	3·64	6·47	11·65	1	56	2·88
			3·66	6·45	11·62			2·87
		20·00	13·32	6·68	12·03	1	200	2·97
			13·32	6·68				
3	5·94	6·07	2·88	3·19	5·75	1	90	2·91
		7·06	3·80	3·27	5·89		116	2·97
		8·06	4·74	3·32	5·98		143	3·02
		9·06	5·74	3·32	5·98		173	3·02
		10·11	6·80	3·31	5·96		205	3·01

TABLE IX. BROMINATION OF *p*-CRESOL BY BROMINE MONOCHLORIDE

No.	Substance weighed, *mg*	Excess 0·1*N* BrCl added, *ml*	Consumed 0·1*N* $Na_2S_2O_3$ *ml*	Consumed 0·1*N* BrCl *ml*	Substance found, *mg*	Bromination period, *min*	Percentage of excess BrCl: ratio of columns 4 : 5	Amount of Br taken up by 1 mole, *atoms*
1	13·80	10·03	5·37	4·66	12·59	1	115	1·82
			5·37	4·66	12·59			
			4·99	5·04	13·62	2	99	1·97
			4·99	5·04	13·62			
			4·92	5·11	13·80	3	96	2·00
			4·92	5·11	13·80			
			4·46	5·57	15·05	5	80	2·18
			4·46	5·57	15·05			
2	15·78	10·03	4·18	5·85	15·80	3	72	2·00
			4·18	5·85	15·80			2·00
	31·29	20·00	8·40	11·60	31·34	3	72	2·00
			8·43	11·57	31·26			2·00
			8·41	11·59	31·31			2·00
3	27·37	11·07	1·93	9·14	24·69	3	21	1·80
	13·80	6·07	1·25	4·82	13·02	3	26	1·89
	27·37	12·11	2·65	9·56	25·82	3	28	1·89
		13·12	3·36	9·76	26·37	3	34	1·93
	13·80	7·06	1·99	5·07	13·70	3	39	1·99
		8·06	2·99	5·07	13·70	3	58	1·99
		9·06	4·00	5·06	13·67	3	79	1·98
		10·09	5·02	5·06	13·67	3	99	1·99

TABLE X. BROMINATION PERIODS FOR THE BROMINATION OF AROMATIC COMPOUNDS ACCORDING TO KOPPESCHAAR AND BY THE BROMINE MONOCHLORIDE METHOD

No.	Substance	Bromination periods, *min*	
		Koppeschaar method	BrCl method
1	Phenol	5–30	1
2	*p*-Hydroxybenzoic acid	5–30	1
3	Salicylic acid	60	2
4	*o*-Nitrophenol	30	0·5
5	*m*-Nitrophenol	5–30	1
6	*p*-Nitrophenol	5–30	0·5
7	*p*-Cresol	1	3
8	*m*-Cresol	1	1

to be too short. The interfering action caused by extremely large or extremely small volumes of liquid also appears in determinations conducted by the Koppeschaar method. In this case, however, it is of less significance since bromination periods may usually be prolonged; (in general, it is conventional to use, instead of the shortest period necessary, periods 1·5 to 2 times as long): prolonged bromination periods eliminate both errors. In the bromine monochloride method, however, it is not possible to apply prolonged periods of bromination.

To complete our studies, the effect of varying hydrochloric acid concentrations was studied. It was found that correct values were obtained on acidifying with 10–15 ml of 20% hydrochloric acid. Whilst the increase of concentration of hydrochloric acid did not interfere with the results, the application of lower concentrations resulted in values below the actual ones. This may be due to the fact that the decrease of acid concentration reduces the rate of formation of bromine monochloride. In this way, also, elementary bromine liberated in the first stage of preparation of bromine monochloride participates in the substitution reaction. On bromination with elementary bromine, bromide ions form which reduce to bromine some of the bromine monochloride. On bromination with bromine monochloride, chloride ions are formed.

The reaction with bromine monochloride of aromatic compounds which are not brominated by bromine itself was examined. As an example, bromination by bromine monochloride of benzoic and acetylsalicylic acids (the latter without hydrolysis) was attempted and it was found that under the experimental conditions, bromination of these compounds by bromine monochloride was also unsuccessful.

These investigations indicate that on applying bromine monochloride, the range of compounds which can be brominated does not increase, although the rate of bromination increases appreciably.

Increased rates of reaction made possible the application of extremely short bromination periods. This may be of a great practical significance, *e.g.*, in the determination of the components of drug mixtures without previous separation.

The fact that the bromination period of one hour prescribed so far for the determination of salicylic acid could be reduced to only two minutes made possible the precise determination of salicylic acid in the presence of acetylsalicylic acid, thus enabling the investigation of the decomposition of the salts of acetylsalicylic acid. Acetylsalicylic acid cannot be brominated without previous hydrolysis. When, however, a bromination period of one hour, prescribed by Koppeschaar for the determination of salicylic acid, is applied, a partial hydrolysis of acetylsalicylic acid takes place, and salicylic acid formed as a product of this hydrolysis will also be brominated. In contrast, during the bromination period of two minutes required for the bromine monochloride method, practically no decomposition of acetylsalicylic acid occurs, and this source of error is eliminated. Studies carried out in connection with the decomposition of salts of acetylsalicylic acid will be published elsewhere.

Zusammenfassung—Die Bromierung gewisser Phenole durch Bromchlorid wird untersucht, und die Methode wird auf quantitative Messungen angewandt.

Die Anwendung von Bromchlorid vermehrt nicht die Anzahl der Verbindungen, die man bromieren kann, sondern hebt die Geschwindigkeit der Bromierung merklich.

Résumé—On a étudié la bromuration de certains phénols au moyen du chlorure de brome et a utilisé cette méthode comme moyen de dosage.

A partir du bromate et du bromure en quantités équivalentes ($1M : 2M$), le chlorure de brome a été préparé dans la fiole à bromuration en milieu acide chlorhydrique.

On a trouvé que, bien que l'application du chlorure de brome n'augmente pas le nombre de composés susceptibles d'être bromurés, elle accroît sensiblement la vitesse de bromuration.

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THE COMPLEXOMETRIC TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM. A CRITICAL STUDY

R. BELCHER, R. A. CLOSE and T. S. WEST
Department of Chemistry, The University, Birmingham 15, England

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Summary—A critical examination has been made at the 0·01*M* level of the performance of various indicators for the titration of calcium in the presence or absence of magnesium with EDTA. The *bis*-azo dye Acid Alizarin Black SN is recommended for the titration of calcium in pure solution, and for solutions where the magnesium/calcium ratio does not exceed 1:12. For higher ratios, quantitative recovery of calcium and satisfactory end-points are only obtained when Calcon is used as indicator.

The range of application of Acid Alizarin Black SN can be extended if 1:2-diamino-propane-N:N′-tetra-acetic acid is used in place of EDTA as titrant.

IN THE original procedure of Schwarzenbach, Biedermann and Bangerter[1] total hardness is determined in the presence of Solochrome Black T as indicator at pH 10; calcium is determined at pH > 12, in the presence of the precipitated magnesium

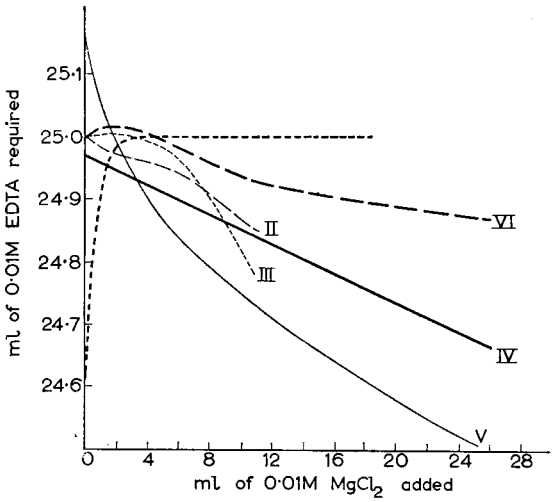

FIG. 1. Recovery of 25·00 ml of 0·01*M* calcium in the presence of magnesium.
I Calcon; II Methyl Thymol Blue; III Acid Alizarin Black SN; IV Murexide; V Calcein; VI Acid Alizarin Black SN with 1:2-Diaminopropane-N:N′-tetra-acetic acid.

hydroxide, with Murexide as indicator. Several other indicators have since been advocated. The present paper describes an examination we have made of several of these indicators. Where possible the indicators have been used under standardised conditions except for some variation in the reagents used for adjustment of the necessary pH conditions.

Fig. 1 shows the recovery of calcium obtained in the presence of varying amounts of magnesium when using the different indicators. These titrations were carried out

at the 0·01*M* level. The various indicators are also considered separately; details of indicator response and tables of results are given showing the variation in recovery of calcium.

Each entry in the tables represents the mean of ten titrations. A measure of the reproducibility of each indicator may be deduced from the standard deviation. More than 350 determinations were carried out.

Murexide

When no magnesium is present, the pink to purple end-point in the EDTA titration of calcium is sharp but the colour contrast is poor, though it may be improved by screening.[2] Our results show a tendency for low recoveries to occur even in the absence of magnesium, but this may be partly due to personal reactions to the colour change of the indicator.

TABLE I.—TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM, MUREXIDE AS INDICATOR

ml of 0·01*M solutions*

Calcium taken	Magnesium added	Calcium found	Standard deviation
25·00	0·00	24·97	0·03
25·00	1·00	24·96	0·03
25·00	2·00	24·95	0·02
25·00	5·00	24·91	0·05
25·00	10·00	24·84	0·05
25·00	25·00	24·68	0·07

The error in the recovery of calcium appears to be proportional to the amount of added magnesium, and the quality of the end-point deteriorates progressively both with regard to sharpness and colour contrast. In these titrations, diethylamine was used as the buffer substance. In our experience this affords a better colour change than the conventional sodium or potassium hydroxide reagents.

Calcein

Calcein[3] screened with thymolphthalein[4] gives a sharp end-point from fluorescent green to dark red in the titration of calcium in pure solution. The recovery of calcium appears to be high when the indicator is titrated to a definite colour change, but this may be due to the presence of impurities in the commercial sample of indicator which we used. When magnesium is present, the end-point is less sharp and the green fluorescence does not entirely disappear, though the dark red colour is very strong in transmitted light. The recovery of calcium falls off markedly as the ratio of magnesium to calcium is increased. The indicator action is also complicated by the occurrence of premature end-points before the equivalence-point. Furthermore, the green fluorescence reappears less than a minute after the end-point.

With this indicator, either sodium or potassium hydroxide was preferred to diethylamine for the adjustment of pH since the last mentioned base tended to cause premature end-points and colour reversion.

TABLE II.—TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM, CALCEIN AS INDICATOR
ml of 0·01M solutions

Calcium taken	Magnesium added	Calcium found	Standard deviation
25·00	0·00	25·16	0·07
25·00	1·00	25·06	0·03
25·00	2·00	24·99	0·04
25·00	5·00	24·87	0·03
25·00	10·00	24·75	0·05
25·00	25·00	24·51	0·04

Methyl thymol blue

This substance, which was recently proposed by Körbl and Přibil,[5] gives a sharp, easily detected blue to colourless end-point in the titration of calcium in pure solution. The recovery of calcium appears to be quantitative. When the magnesium/calcium ratio is greater than 1:5, premature end-points occur, but the colour reverts to blue in *ca.* 10 seconds. This reversion also occurs beyond the equivalence-point.

TABLE III.—TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM, METHYL THYMOL BLUE AS INDICATOR
ml of 0·01M solutions

Calcium taken	Magnesium added	Calcium found	Standard deviation
25·00	0·00	25·00	0·03
25·00	1·00	24·98	0·02
25·00	2·00	24·97	0·02
25·00	5·00	24·96	0·01
25·00	10·00	24·87	0·02
25·00	25·00	—	—

The end-point was judged to be that point in the titration at which the colour reversion no longer occurs quickly—as it does with the first premature end-points. When the magnesium/calcium ratio approached unity, it was not found possible to obtain reproducible results because of the profusion of premature end-points and the repeated reversion of colour even beyond the equivalence-point.

Diethylamine was used as the buffer substance, but caustic soda serves equally well provided that care is taken not to raise the pH much above 12·5. The indicator is permanently blue at higher pH values.

Calcon (B.C.I. No. 202)

Calcon, proposed by Hildebrand and Reilley,[6] does not give a sharp end-point when calcium is titrated with EDTA in the absence of magnesium, or when the magnesium/calcium ratio is less than 1:12. The recovery of calcium is markedly low,

cf. Table IV. The indicator shows a long purple intermediate shade with a diminishing red shade which finally disappears leaving a pure blue solution *before* the equivalence point, *cf.* Fig. 1. The colour change may spread over 6–8 drops of 0·01*M* titrant. However, the quality of the end-point improves markedly with increasing amounts of magnesium, so that for magnesium/calcium ratios between 1:10–1:5 sharp end-points are obtained and the recovery of calcium appears to be quantitative.

TABLE IV.—TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM, CALCON AS INDICATOR
ml of 0·01*M solutions*

Calcium taken	Magnesium added	Calcium found	Standard deviation
25·00	0·00	24·63	0·10
25·00	1·00	24·86	0·10
25·00	2·00	24·99	0·03
25·00	5·00	25·00	0·06
25·00	10·00	24·99	0·07
25·00	25·00	25·01	0·06

In the presence of larger amounts of magnesium, brief premature end-points appear before the equivalence point, but since these revert in 2–3 seconds it is possible to locate the true end-point without much difficulty. Even beyond the equivalence-point, reversion of colour from blue to purple-red occurs after a period of more than 10 seconds. Diethylamine was used as the buffer substance.

Hildebrand and Reilley applied Calcon to the titration of solutions having much higher ratios of magnesium to calcium (10 molar proportions). They comment that the end-point is sluggish when there is a heavy precipitate of magnesium hydroxide.

Acid Alizarin Black SN (B.C.I. No. 337)

In a previous publication, we proposed the use of this *bis*-azo dye for the titration of calcium.[7] In the absence of magnesium, or with magnesium/calcium ratios less

TABLE V.—TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM, ACID ALIZARIN BLACK SN AS INDICATOR
ml of 0·01*M solutions*

Calcium taken	Magnesium added	Calcium found	Standard deviation
25·00	0·00	25·00	0·01
25·00	0·50	24·99	0·03
25·00	1·00	25·00	0·01
25·00	2·00	24·99	0·02
25·00	5·00	24·97	0·05
25·00	10·00	24·81	0·12
25·00	25·00	—	—

than 1:12, a very sharp red to turquoise-blue end-point is obtained and the recovery of calcium appears to be quantitative.

In the presence of larger amounts of magnesium, the end-point response of the indicator becomes less well defined; the colour changes through purple and blue to turquoise-blue. In addition, the recovery of calcium falls below the theoretical value. In the presence of large amounts of magnesium the titration should be carried through to the final shade, but the intermediate colours may spread over 8–10 drops. Brief reversion of colour occurs before the equivalence-point as with the other indicators, but beyond equivalence the end-point is stable for several minutes.

Diethylamine was used as the buffer substance.

Titration of calcium in the presence of magnesium with 1:2-*diaminopropane*-N:N′-*tetra-acetic acid*

As a result of work being carried out in this laboratory on various chelating agents related to EDTA,[8] we have examined the application of 1:2-diaminopropane-N:N′-tetra-acetic acid to this titration. Our examination was confined to the use of Calcon and Acid Alizarin Black SN as indicators, since these appeared to be the most suitable substances in the light of our previous experiments using EDTA. It was found that no better result was obtained when using Calcon—indeed we prefer the use of EDTA in conjunction with the indicator, but the performance of Acid Alizarin Black SN was considerably improved.

TABLE VI.—TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM WITH 1:2-DIAMINOPROPANETETRA-ACETIC ACID, ACID ALIZARIN BLACK SN AS INDICATOR

ml of 0·01*M solutions*

Calcium taken	Magnesium added	Calcium found	Standard deviation
25·00	0·00	25·00	0·00
25·00	1·00	25·00	0·03
25·00	2·00	25·02	0·04
25·00	5·00	25·01	0·05
25·00	10·00	24·93	0·06
25·00	25·00	24·88	0·08

Very sharp end-points and quantitative recoveries of calcium were obtained when the magnesium/calcium ratio did not exceed one fifth. Thereafter, increasingly large amounts of magnesium caused less sharp end-points and low recoveries of calcium. It would appear from Fig. 1 that slightly high results are obtained for low magnesium contents, but it must be stressed that the results shown are the arithmetic mean titres and the divergence from theory is within the limits of measurement of the 50-ml burettes used in these experiments.

EXPERIMENTAL

Reagents

0·01*M EDTA:* Standardised against pure magnesium metal using Solochrome Black 6B at pH 10 as indicator.[9]

0·01*M Calcium chloride:* Prepared from A.R. calcium carbonate by dissolution in a slight excess of hydrochloric acid.

0·01*M Magnesium Chloride:* Prepared from pure magnesium metal.

Buffers: Diethylamine
2*N* Sodium or potassium hydroxide

Indicators: Calcon—0·5% Ethanolic solution
Murexide—1% Dispersion in sodium chloride.
Calcein—1% Calcein, 0·6% thymolphthalein dispersion in potassium chloride
Methyl Thymol Blue—1% Dispersion in potassium nitrate
Acid Alizarin Black SN—2% Dispersion in sodium chloride.

Procedure

25·00 ml of 0·01*M* calcium chloride solution were pipetted into a 250-ml conical flask and the requisite amount of magnesium chloride solution was added from a burette. To every 25 ml of this test solution were added 5 ml of diethylamine or 5 ml of alkali hydroxide. The mixture was shaken and allowed to stand for 5 minutes. A sufficient amount of the appropriate indicator was then added to impart the necessary colour to the solution and the titration was carried out with 0·01*M* EDTA to the end-point. Ten determinations were made for each molar ratio of calcium to magnesium and the mean recovery and standard deviation were recorded in each case.

DISCUSSION

As a result of these studies it appears to us that the conventional Murexide indicator for the titration of calcium in the presence of magnesium is less suitable than some of the newer indicators both on the grounds of low recoveries of calcium and the quality of the end-point. The presence of appreciable amounts of magnesium causes a deterioration in the quality of the end-point of all these indicators except Calcon and favours low recoveries. The behaviour of Calcon is unsatisfactory in the absence of magnesium hydroxide, but is considerably improved in its presence. For calcium in the absence of magnesium all the other indicators examined, except possibly Calcein and Murexide, are satisfactory, but the most precise and clear-cut end-point is obtained with Acid Alizarin Black SN. This indicator is particularly useful in that it functions best in the region of magnesium/calcium ratios where Calcon cannot be applied very successfully, *cf.* Fig. 1. Accordingly we recommend that Acid Alizarin Black SN be used for the titration of calcium in pure solution and for magnesium/calcium ratios less than 1:12 (0·01*M* solutions); for higher ratios of magnesium to calcium, Calcon should be applied.

The occurrence of premature end-points is almost certainly due to the co-precipitation of calcium with the magnesium hydroxide, but the reversion of colour which occurs even after the equivalence-point with those indicators which are capable of responding to magnesium ions with a high degree of sensitivity, *viz* Methyl Thymol Blue, Calcein and Calcon, suggests that the magnesium takes part in the reaction either by direct solution of the hydroxide precipitate or by kinetic exchange with the chelated calcium in the solution.

The indicator of Patton and Reeder[10] was not included in this comparison, because in spite of its excellent colour change in the titration of calcium in the presence of magnesium, in our experience it is somewhat unstable in strongly alkaline solution.

The extension of the range over which Acid Alizarin Black SN gives a sharp end-point with quantitative recoveries of calcium when 1:2-diaminopropane-N:N′-tetra-acetic acid is used as titrant is interesting, but in view of the excellent response of Calcon with EDTA in this extended region, there is little advantage to be gained.

Acknowledgements—We are grateful to the Clayton Aniline Company for the award of a research grant and for the gift of a sample of Acid Alizarin Black SN.

Zusammenfassung—Es wurde eine kritische Untersuchung verschiedener Indikatoren für die Titration von Calzium mit 0·01*M* Lösung von ÄDTA in Anwesenheit oder Abwesenheit von Magnesium gemacht. Der *bis*-azo Farbstoff Acid Alizarin Black SN wird für die Titration von Calzium in reiner Lösung vorgeschlagen sowie für Lösungen in denen das Magnesium/Calzium Verhältnis 1:12 nicht übersteigt. Bei Größeren Verhältnissen wird nur dann Calzium quantitativ erfasst und eine gute Endpunkt erhalten, wenn Calcon als Indikator gebraucht wird.

Man kann den Anwendungsbereich von Acid Alizarin Black SN ausdehnen, wenn 1:2-Diaminopropan-N:N′-Tetraessigsäure and Stelle von ÄDTA als Masslösung gebraucht wird.

Résumé—Un examen critique a été fait à partir des solutions 0·01*M* du fonctionnement de divers indicateurs utilisés pour le titrage du calcium, soit suel, soit en présence de magnésium, au moyen de l'EDTA. Le colorant *bis*azoïque "Acid Alizarin Black SN" est recommendé pour le titrage du calcium en solution pure, et pour des solutions où le rapport magnésium/calcium ne dépasse pas 1:12. Où les rapports sont plus hauts la récupération quantitative du calcium et des fins de réaction satisfaisantes ne sont obtenues qu'en utilisant comme indicateur le calcon.

On peut porter plus loin les limites d'application de l'Acid Alizarin Black SN en remplaçant l'EDTA comme solution titrante par l'acide 1:2-diamine-propane-N:N′-tetracétique.

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AN IMPROVED ALTERNATING CURRENT POLAROGRAPH

TAKEO TAKAHASHI and EIJI NIKI
Institute of Industrial Science, University of Tokyo, Japan

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Summary—Results obtained with the a.c. bridge polarograph devised by the authors are given.

THE polarogram obtained instantaneously by means of the oscillograph could offer a versatile technique in rapid polarographic analysis or in following chemical reactions. But this technique has been faced with troublesome problems arising both from the difficulty of construction of a suitable oscillograph and from theoretical defects based on diffusion phenomenon.

In such oscillographic polarography, sine-wave, saw-tooth-wave, or triangle-wave a.c. current has been applied to the polarographic cell and the mechanism of chemical reaction on the surface of the electrode has been studied.[1–5]

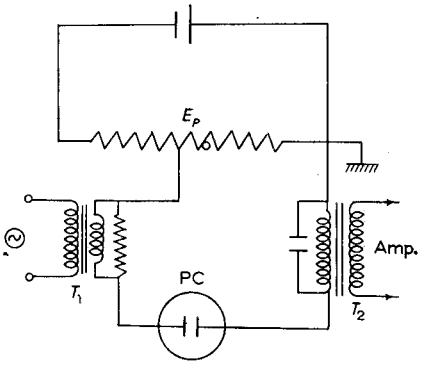

FIG. 1. Principle of a.c. polarograph (MacAleavy).

R. H. Müller[6] measured the a.c. current in the polarographic current by superimposing a.c. voltage on the d.c. voltage. J. Boeke[7] carried out the same measurement by observing the figure shown on a Brown tube (a.c. voltage applied as abscissa and a.c. current as coordinate) and found the value of the half-wave potential from the change of the figure with gradual change of applied d.c. voltage. He also determined the amount of the substance by measuring the resistance at the half-wave potential by means of a Kohlrausch's bridge.

So-called a.c. polarography is different from the oscillopolarography just described. One measures the a.c. current separated from d.c. current flow with an ammeter when a weak a.c. voltage was applied on top of the d.c. voltage to the polarographic cell. Such a.c. polarography has recently been developing in both theory and application, especially in the field of chemical analysis.

An example of the circuit used in a.c. polarography is illustrated in Fig. 1 (MacAleavy's circuit).[17] The a.c. voltage is applied to the polarographic cell through the transformer T_1 and the a.c. component in the electrolytic current is separated through the transformer T_2, amplified and then measured.[9,10]

B. Breyer,[11] J. E. B. Randles[12] and others have developed the theory of this type of polarography and also its practical application. P. Delahay *et al.*[13] instituted the vector method in order to compensate for the differential capacity due to the resistance of the cell solution and the electric double layer.

Graham[14] also derived a fundamental equation of a.c. polarography based on theoretical considerations of the rate of the electrode reaction. Ishibashi and Fuginaga[15] have proposed a differential polarograph which uses a rectangle-wave as a.c. source. Tachi and Senda[16] recorded an a.c. polarogram, by picking up the a.c. component from transformer T_2, rectifying to d.c. current and leading this to a conventional d.c. polarograph.

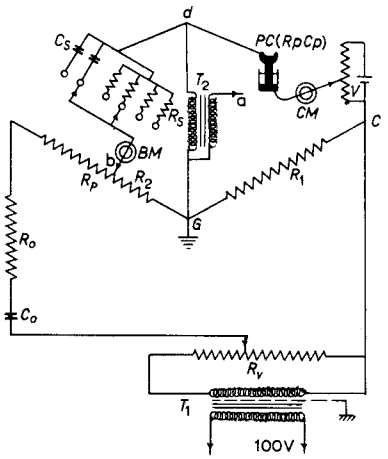

FIG. 2. Principle of a.c. polarography. $R_X = 16{\cdot}7\ \Omega$, $R_1 = 16{\cdot}7\ \Omega$ (and $+33{\cdot}3\ \Omega$), $R_s =$ 100 Ω, 200 Ω, 300 Ω, 500 Ω, 2, 3, 5 KΩ, $C_s = 0{\cdot}1, 0{\cdot}2, 0{\cdot}5, 1, 2, 4\ \mu$F, PC = polarographic cell, E_p 0–2·5 V., T_2 = input trans. (1/10), BM = two-phase balancing motor, CM = synchronous motor.

A.c. polarography is the measurement of the fluctuating phenomenon during the dropping of mercury just as in d.c. polarography. Therefore, it is certain that a recording method is the most straightforward and effective one in a.c. polarography for measuring the fluctuating phenomenon precisely.

In measuring the a.c. current by means of MacAleavy's circuit or a related one, the a.c. voltage superposed on the d.c. voltage should be kept constant. Even though this is done, the a.c. voltage on the surface of the dropping mercury (electric double layer) may change the amplitude and phase of a.c. current in accordance with the gradually changing voltage of d.c., since a change of the Faradaic impedance on the surface of the electrode occurs so that more a.c. current flows, resulting in a depression of the a.c. voltage. Thus it is certain that in a.c. polarography the relationship between the a.c. current and the concentration of the substance to be reduced may deviate from a linear relationship.

With a view to removing the above difficulties of a.c. polarography, the present authors have tried to apply an a.c. bridge and after much investigation have succeeded in constructing a very versatile polarograph, which may be called an "a.c. polarograph with a.c. bridge". Fig. 2 illustrates the principle of this polarograph, which is pen-recording with automatic balance.

In this instrument the polarographic cell PC, standard resistance R_S, the variable slide resistance R_2 and the fixed resistance R_1 form an a.c. bridge, and the minute and definite a.c. voltage is superimposed on the gradually changing d.c. voltage applied to the polarographic cell. When the d.c. voltage reaches a certain voltage and at the same time the electrolytic current begins to flow suddenly, the conductivity of the solution in the polarographic cell reaches a maximum value.

The a.c. bridge cannot retain balance when the conductivity changes in this way. Thus generated unbalanced a.c. current, subsequently amplified, passes to the two-phase balancing motor, and moves the variable slide resistance R_2 until the a.c. bridge is again balanced. The movement of the slider indicates the conductivity of the polarographic cell and is written on the chart which is synchronised with gradually increasing voltage of d.c.

When the a.c. voltage E changes differentially, dI/dE (where I is the electrolytic a.c. current) is given as a true conductivity, measured precisely by the bridge, if we correct the minute change of the capacity of the small electrode by means of a condenser in parallel with a standard resistance.

In Fig. 2, the a.c. source, either 50 or 60 c/min, is applied to transformer T_1 and its output is moderated to a selected voltage by adjusting R_V, and to a suitable phase by means of the condenser C_0 and the resistance R_0. The values of C_0 and R_0 are determined in order to intersect the output from the amplifier in a direction rectangular to the a.c. source (100 V). In the a.c. circuit bridge the following relationship is thus established:

$$R_2/R_S = R_1/R_P$$

where R_P is the equivalent internal resistance of the polarographic cell. Changing the form of the above formula,

$$R_2 = R_S \cdot R_1/R_P$$

the indicating resistance R_2 is seen to be proportional to the reciprocal of the internal resistance of the polarographic cell, $1/R_P$, and since $1/R_P$ corresponds to dI/dE, R_2 indicates the value of dI/dE.

In practice the a.c. voltage superimposed in the polarographic cell is less than 50 mV, when the d.c. voltage changes within 0·05–0·2 V. When the changing range of the a.c. voltage is within 1–100 mV, depending upon the change of either the resistance R_1 or a.c. current flowing through R_1 and R_r, a precise polarogram can be drawn.

The synchronous motor of the potentiometer(V) for which applies the d.c. voltage changes continuously and is connected with the motor of the recorder. D.c. current flows from the potentiometer V, through the electrolytic cell PC, the primary side of the transformer T_2, and resistance R_1, and returns to V; the resistance of the primary side of T_2 and resistance R_1 are kept small in order to make the most of d.c. voltage charge on the polarographic cell; the slide resistance of the potentiometer V is assumed to be negligible in comparison with R_P.

The unbalanced a.c. current generated in the secondary side of T_2 is amplified by means of the amplifier shown in Fig. 3, in which the input of a.c. voltage is amplified by the vacuum tubes V_1 and V_2 and is led into one phase of the two-phase balancing motor BM. If the capacity of the bridge is balanced, the imaginary part of the output current is negligible, so that the output intersects the a.c. source rectangularly,

resulting in revolution of the balancing motor. It is necessary to connect the output to the slider (b) in order to rotate the balancing motor and thus to balance the bridge.

The maximum conductivity of a.c. current appears just at the half-wave potential of the d.c. polarogram. Therefore, it may be concluded that the a.c. polarogram approaches the ideal differential curve as the superposed a.c. voltage becomes smaller and smaller. Furthermore, the fluctuating voltage of the a.c. source has little effect on an a.c. polarogram and therefore on the determination of a reducible substance by polarography.

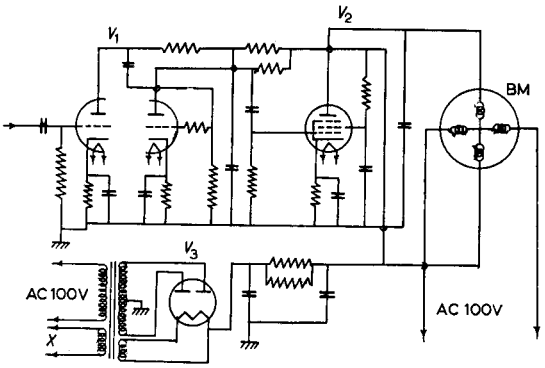

FIG. 3. A.C. amplification circuit.

Results obtained by an a.c. polarograph are more exact than those by d.c. polarography in chemical analysis, because the presence of more easily reducible substances than the substance to be determined has much less influence than in d.c. polarography. Some examples are shown in Figs. 4–8.

The a.c. polarograph, now available in Japan, is constructed as shown in Fig. 9.

Zusammenfassung—Die mit dem von den Verfassern entwickelten Wechselstrombrücke-Polarographen erreichten Resultate werden angegeben.

Résumé—On donne des résultats obtenus à l'aide du polarographe à pont pour courant alternatif, inventé par les auteurs.

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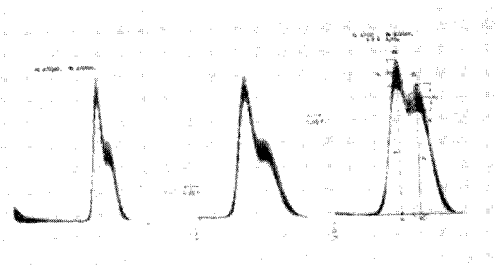

FIG. 4. A mixed solution of Tl and Pb ions in 0·2*M* H_3PO_4
Left: $Pb(NO_3)_2$ *M*/2500 and $TlNO_3$ *M*/2000 (Voltage unit 0·1 V)
Centre: $Pb(NO_3)_2$ *M*/2500 and $TlNO_3$ *M*/2000 (Voltage unit 0·05 V)
Right: $Pb(NO_3)_2$ *M*/2000 and $TlNO_3$ *M*/1000 (Voltage unit 0·05 V)

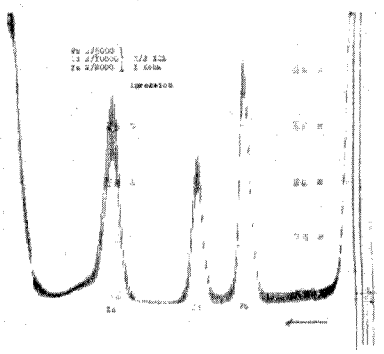

FIG. 5. A mixed solution of Pb, Cd and Zn ions in 0·5*N* KCl
$Pb(NO_3)_2$ *M*/5000, $CdSO_4$ *M*/10000 and $ZnSO_4$ *M*/2000

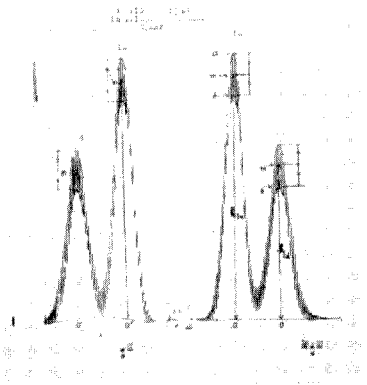

FIG. 6. A mixed solution of Cd and In ions in 1*N* KBr
$CdSO_4$ *M*/1000 and $In(NO_3)_3$ *M*/1000

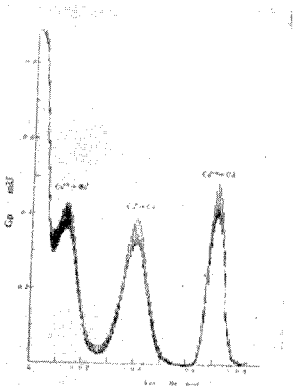

FIG. 7. A mixed solution of Cd and Cu ions in 1*N* NH_4OH and 1*N* NH_4Cl : $CdSO_4$ *M*/2000 and $CuSO_4$ *M*/1000

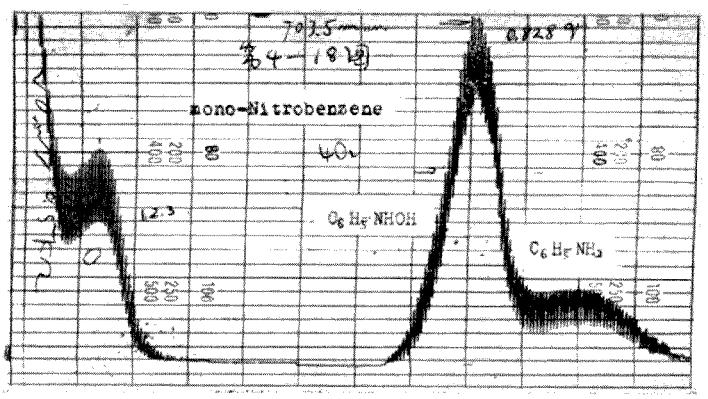

FIG. 8. Mononitrobenzene

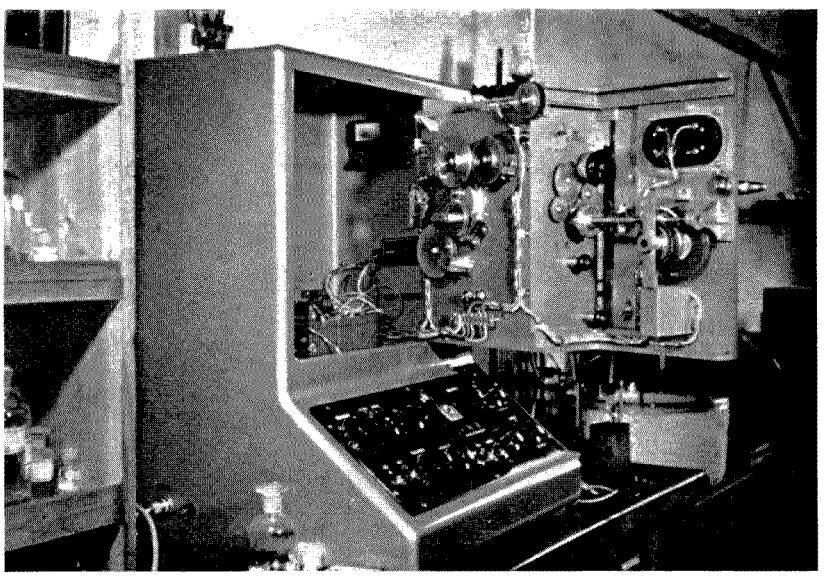

FIG. 9. A view of the self-recording A.C. Bridge Polarograph invented by Authors and sold by Yanagimoto Co., Kyoto, Japan.

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THE ANALYTICAL CHEMISTRY OF THE PYRIDINE THIOCYANATES—I

THE SEPARATION OF COBALT AND NICKEL BY SOLVENT EXTRACTION

J. H. W. FORSYTHE, R. J. MAGEE and C. L. WILSON
Chemistry Department, The Queen's University, Belfast, Northern Ireland

(*Received* 23 *April* 1958)

Summary—A procedure is described for the separation of cobalt and nickel as pyridine thiocyanates using solvent extraction. After separation the metals are determined colorimetrically in the extracts.

REFERENCE to the pyridine thiocyanates of cobalt and nickel in the literature is not new, dating in some cases from the end of the last century.[1,2,3] All of these papers, however, deal with methods for the preparation of the pyridine thiocyanates of the metals and have no analytical significance.

Duval,[4] in his book on thermogravimetric analysis, however, describes the thermogravimetric behaviour of nickel pyridine thiocyanate, showing that it provides a suitable weighing form for the determination of the metal. In recent years, the blue colour formed by cobalt thiocyanate in acetone and other solvents has been used by several workers for the determination of cobalt.[5]

Sharp and Wilkinson,[6] in developing a method for obtaining nickel-free cobalt salts, used ^{57}Ni and ^{60}Co tracers to investigate the separation of the two metals as thiocyanates by solvent extraction. Apart from these investigations, however, it would appear that the analytical value of the pyridine thiocyanates of cobalt and nickel has not been examined to any extent.

This paper describes a procedure for the separation and determination of cobalt and nickel by the formation of the pyridine thiocyanates.

PRELIMINARY INVESTIGATIONS

Under suitable conditions, cobalt and nickel form pyridine thiocyanates readily. The structure for the cobalt complex has been given[1] as $Co\ py_4\ (SCN)_2$ and, for that of nickel[2] as $Ni\ py_4\ (SCN)_2$.

The conditions under which these compounds formed were examined. In the case of cobalt it was found that, if excess thiocyanate is added to a cobalt solution, and the pH is adjusted to 2·5, slow addition of pyridine causes precipitation of cobalt pyridine thiocyanate when the pH has risen to a value of 5·6.

On the other hand, if excess thiocyanate is added to a nickel solution and the same procedure is followed, the nickel pyridine thiocyanate begins to form at pH 4·2 and precipitation is complete at pH 4·6.

Both compounds are very soluble in organic solvents, and it was found possible to effect a separation of the two metals on the basis of these preliminary observations.

As a means of determining the nickel present in the chloroform extract, the absorption spectrum of nickel pyridine thiocyanate in chloroform was determined.

This is shown in Fig. 1. The maxima at 560 mμ and 580 mμ were found to be too small to be of value and measurements were, therefore, carried out at 320 mμ.

For known amounts of nickel a calibration curve was prepared. From this curve the minimum amount of nickel which can be determined with certainty is 100 μg.

On extraction of the cobalt pyridine thiocyanate complex with methyl *iso*butyl ketone (Hexone) the colour of the extract is blue. The absorption spectrum of the solution is shown in Fig. 2. The maximum at 620 mμ is very suitable for measurement and was used throughout. Comparison of the absorption spectrum of this

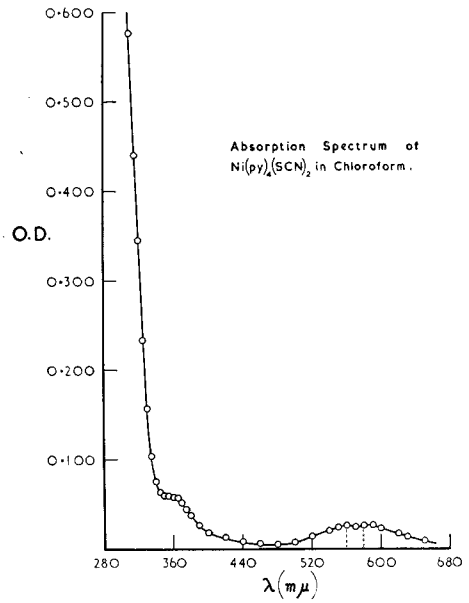

FIG. 1—Absorption spectrum of nickel pyridine thiocyanate in chloroform.

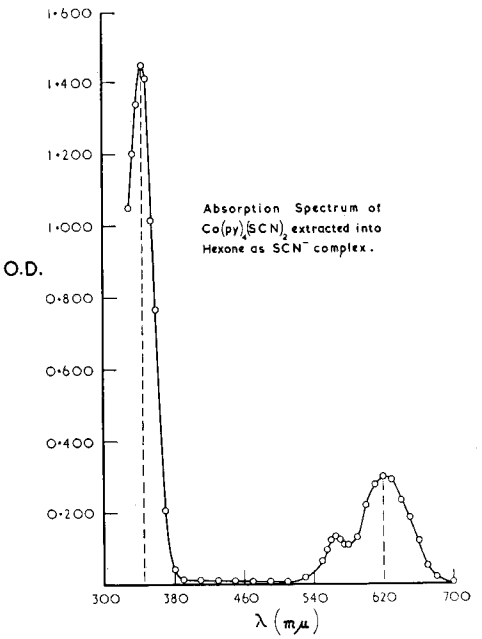

FIG. 2.—Absorption spectrum of cobalt thiocyanate complex in methyl *iso*butyl ketone.

solution with that obtained by extracting cobalt thiocyanate from an aqueous solution between pH 4 and 6 with Hexone showed complete identity. It would appear, therefore, that it is cobalt thiocyanate which is extracted by Hexone.

For known amounts of cobalt a calibration curve was prepared. From this curve the minimum amount of cobalt determinable was 50 μg.

PROCEDURE

Preparation of the nickel complex

1. To about 20 ml of the solution for analysis, which should contain not less than 50 μg cobalt and 100 μg nickel, add 0·5 ml (excess) of a 40% solution of potassium thiocyanate. Make the pH 2·5–3·0 by means of hydrochloric acid.
2. Adjust the pH to 4·6 by the slow addition of pyridine. Nickel pyridine thiocyanate precipitates.
3. Extract the precipitate twice with 10 ml portions of chloroform and make up to 25 ml. This solution contains all the nickel present in the original sample. Under these conditions of precipitation, cobalt, if present, does not form a pyridine thiocyanate and probably exists in solution as cobalt thiocyanate which is not extracted into chloroform.

Determination of nickel

1. Filter the chloroform-extract and pour into the absorption cell of the spectrophotometer. This operation removes small globules of water which are sometimes present.

2. Compare the optical density of this solution against chloroform and calculate the amount of nickel in the solution from the calibration curve.

Preparation of the cobalt complex

1. To the aqueous layer remaining after extraction of nickel (which contains potassium thiocyanate, a trace of pyridine and cobalt, if present) add hydrochloric acid until the pH of the solution is in the region 2·5–3·0.
2. Add pyridine slowly to this solution until the pH is 5·6. Cobalt pyridine thiocyanate precipitates.
3. Extract this precipitate with two 10-ml portions of Hexone and make the volume to 25 ml with Hexone.

Determination of cobalt

1. Filter the Hexone-extract and pour into the absorption cell of the spectrophotometer.
2. Compare the optical density of this solution against Hexone, and from the calibration curve determine the amount of cobalt present.

RESULTS

To test the validity of the proposed method a number of "unknown" mixtures were analysed by one of us (J. H. W. F.). The results are recorded in Table I. Where

TABLE I

No. of sample	Co μg	Ni μg
1	1	100
2	50	trace (50)
3	50	975 (1000)
4	995 (1000)	105 (100)
5	250	—

the experimental results differ from the actual composition, the true are recorded in parentheses.

The results, for cobalt in particular, are very satisfactory. The procedure is rapid and requires no special technique on the part of the operator.

Acknowledgement—One of us (J. H. W. F.) acknowledges gratefully a grant from the Physical Chemistry Group, Imperial Chemical Industries Limited, (Billingham Division) which enabled him to take part in this work.

Zusammenfassung—Es wird ein Extraktionsverfahren zür Trennung von Kobalt und Nickel als Metall–Pyridin–Rhodanid–Komplexe beschrieben. Die Metalle sind in den Extrakten kolorimetrisch bestimmbar.

Résumé—Description d'un procédé pour effectuer la séparation par extraction au moyen d'un solvant du cobalt d'avec le nickel sous forme de thiocyanates pyridiques. Après séparation on dose par colorimétrie les métaux dans les extraits.

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DIFFERENTIATION OF ORGANIC ACIDS IN SPOT TEST ANALYSIS

FRITZ FEIGL and CECILE STARK-MAYER
Laboratorio da Produção Mineral, Ministério da Agricultura,
Rio de Janeiro, Brazil

(*Received* 30 *April* 1958)

Summary—Halogen hydracids are released when aliphatic and aromatic polycarboxylic acids, arylalkyl carboxylic acids or aromatic mono carboxylic acids are heated at 160° along with alkali or ammonium halides. *o*-Nitrophenol shows the same behaviour and can thus be distinguished from its isomers. Aliphatic monocarboxylic, hydroxamic and sulphonic acids are without effect.

The detection of the released halogen hydracid by means of indicator paper (or by the demasking of silver ferrocyanide) makes possible a procedure for revealing the presence of effective organic acids. Microanalytical limits of detection were attained employing spot test techniques.

A SPOT test for succinimide was recently described[1] based on the production of pyrrole through distillation with zinc dust.[2] The product can be identified by means of a colour reaction with *p*-dimethylaminobenzaldehyde.[3] While working on this test it was found that pyrrole is likewise formed when a mixture of succinic acid and ammonium chloride is distilled with zinc dust; and accordingly a test for succinic acid was developed on this basis. It was assumed that when these materials are heated together they undergo metathesis to yield hydrogen chloride and ammonium succinate, which then loses water to yield succinimide. This supposition was confirmed in that acid vapours (change of indicator paper) are evolved when ammonium chloride is heated to 160° along with succinic acid (m.p. = 189°). This finding must be due to the release of hydrogen chloride since at this temperature there is no volatilization of succinic acid nor is ammonium chloride thermally decomposed with production of hydrogen chloride. This release of hydrogen chloride was likewise observed when succinic acid was heated with sodium chloride, potassium chloride, calcium chloride and other alkaline-earth chlorides.

The production of hydrogen chloride from its salts on heating at 160° in the presence of succinic acid is undoubtedly related to the fact that hydrogen chloride is volatile at this temperature in contradistinction to succinic acid and its salts. Since this difference also is true of other halogen hydrides, it could be expected that heating a mixture of an alkali halide and a nonvolatile organic acid (HAc) should give the reaction

$$\mathrm{MeHal} + \mathrm{HAc} \rightarrow \mathrm{MeAc} + \mathrm{HHal}$$

if Me = Na, K, NH_4 and Hal = Cl, Br, I.

The occurrence of this reaction was tested with mixtures of alkali halides and organic acids. The mixtures were heated to 160° and the vapours tested for halogen hydracid with indicator paper (Merck universal indicator paper). The acids tested included aliphatic and aromatic monocarboxylic acids, arylalkyl carboxylic acids, sulphonic acids, hydroxamic acids, and aliphatic and aromatic polycarboxylic acids.

Surprisingly, the release of halogen hydracid proved to be characteristic of aliphatic and aromatic polycarboxylic acids, arylalkyl carboxylic acids, and aromatic monocarboxylic acids. There is no relation between this effect and the melting points of organic acids and their dissociation constants in solution. Therefore it appears that the active acids are far stronger acids in their melts or in the vicinity of their melting points than when dissolved. It seems that this increase in acidity does not occur at all or occurs only to a much less extent in the case of monocarboxylic, sulphonic and hydroxamic acids.

The reactions of molten or solid organic acids resulting in the liberation of halogen hydracid always occur on the surface of the solid alkali halide. Although the limited reaction theatre is a handicap to any extensive reaction, the release of hydrogen chloride from sodium chloride by tiny amounts of monocarboxylic aromatic, di- and tri-carboxylic aliphatic, and arylalkyl carboxylic acids not only occurs to an adequate extent but is so rapid that the effect on indicator paper can serve as a test for the acids of the type just noted.

Procedure. A small quantity of the sample or a drop of its solution is placed in a micro test tube and several cg of sodium chloride added. After complete volatilization of the solvent, if necessary, the test tube, covered with a strip of moist indicator paper (Merck Universal Indicator Paper), is plunged into a glycerol bath previously heated to 160°. The colour of the indicator will change within 2–5 minutes at the outside if active acids are present.

The following acids gave a positive response:

Oxalic acid	HOOC·COOH
Malonic acid	$HOOC \cdot CH_2 \cdot COOH$
Succinic acid	$HOOC \cdot CH_2CH_2 \cdot COOH$
Malic acid	$HOOC \cdot CHOH \cdot CH_2 \cdot COOH$
Maleic acid	HOOC·CH=CH·COOH
Tartaric acid	HOOC·CHOH·CHOH·COOH
Adipic acid	$HOOC(CH_2)_4COOH$
Pimelic acid	$HOOC(CH_2)_5COOH$
Azelaic acid	$HOOC(CH_2)_7COOH$
Citric acid	$HOOC \cdot CH_2C(OH)(COOH)CH_2 \cdot COOH$
Benzoic acid	$C_6H_5 \cdot COOH$
Phenyl acetic acid	$C_6H_5 \cdot CH_2 \cdot COOH$
Cinnamic acid	$C_6H_5 \cdot CH{=}CH \cdot COOH$
Mandelic acid	$C_6H_5 \cdot CHOH \cdot COOH$
Salicylic acid	$C_6H_4 \cdot OH \cdot COOH$ (1: 2)
Phthalic acid	$C_6H_4(COOH)_2$ (1: 2)

An estimate of the sensitivity of the test is provided by the finding that 10 μg of pimelic or mandelic acids, 20 μg of adipic and 100 μg of benzoic acid respond definitely when tested by this procedure.

The following acids did not release hydrogen chloride under the stated conditions: caprylic, capric, lauric, myristic, palmitic, stearic, sulphanilic, 1:5-naphthol sulphonic, anthraquinone-1-sulphonic, anthraquinone-1:5- and -2:6-disulphonic acids.

These findings show that the procedure is suitable for revealing the presence of dicarboxylic acids in mixtures with higher fatty acids, and also for differentiating aliphatic and aromatic monocarboxylic acids. If alkali or alkaline earth salts of organic acids are presented for examination, a little sodium chloride should be added and the mixture then taken to dryness after introducing an excess of dilute hydrochloric acid. The residue is then kept at 120° for 10 minutes to remove the unused hydrochloric acid. If this preliminary treatment is conducted in a micro test tube, the process of heating to 160° and testing the vapour with indicator paper can be accomplished without transfer.

When this procedure is applied, it should be noted that volatile monocarboxylic acids (formic, acetic, propionic, lactic, etc.) will change the indicator paper and thus simulate the release of hydrogen chloride. However, vapours of the latter can also be tested with paper impregnated with silver ferrocyanide and ferric sulphate.[4] The following reaction occurs followed by the formation of prussian blue; the presence of hydrogen chloride is thus established:

$$Ag_4Fe(CN)_6 + 4Cl^- \rightarrow 4AgCl + [Fe(CN)_6]^{4-}$$

Procedure. As before with substitution of silver ferrocyanide-ferric sulphate paper for the acid-base paper.

Reagent paper: Silver ferrocyanide is prepared by adding excess silver nitrate to neutral potassium ferrocyanide solution. The precipitate is washed thoroughly and dissolved in ammonium hydroxide. Quantitative filter paper is bathed in the ammoniacal solution and dried in a current of warm air. The $Ag_4Fe(CN)_6$ remains in the pores of the paper. The paper keeps if stored out of contact with the air.

Trinitrophenol (picric acid), because of its strong acidic nature, releases hydrochloric acid when treated with sodium chloride under the test conditions. 2:4-Dinitrophenol and *m*- and *p*-nitrophenol are inactive, whereas *o*-nitrophenol behaves like the above-mentioned active acids. Thus 5 μg of *o*-nitrophenol may be identified. The behaviour of *o*-nitrophenol permits a sure distinction from its isomers. In a mixture of *o*- and *p*-nitrophenols it was possible to detect 20 μg of *o*-nitrophenol in the presence of 1000 μg of the *p*-isomer.

The behaviour of *o*-nitrophenol and the non-reactivity of its isomers and of 2:4-dinitrophenol show that the action on sodium chloride does not depend on the acidity in solution but on the enhanced acidity when melted, as was assumed before.

Zusammenfassung—Bei Erhitzung von Alkalihaliden mit organischen Säuren auf 160° wurde festgestellt, dass alifatische Monocarbonsäuren, Hydroxamsäuren, aci-Nitroverbindungen und Sulfosäuren ohne Einwirkung sind. Hingegen erfolgt Abspaltung von Halogenwasserstoff durch Polycarbonsäuren, *o*(1)Hydroxycarbonsäuren, sowie Monocarbonsäuren die eine —CH=CH— Gruppe in Nachbarschaft zur COOH— Gruppe enthalten.

Der Nachweis, des aus Natriumchlorid freigelegten Chlorwasserstoffes durch Indikatorpapier (oder Demaskierung von Silberferrocyanid) ermöglicht den Nachweis von wirksamen organischen Säuren. In der Arbeitsweise der Tüpfelanalyse werden mikroanalytische Empfindlichkeiten erreicht.

Résumé—Les hydracides halogènes sont libérés lorsqu'on chauffe avec des halogénures alcalins ou ammoniacaux à 160° les acides polycarboxyliques aliphatiques et aromatiques, les acides carboxyliques arylalkyls ou les acides mono-carboxyliques aromatiques. L'*o*-nitrophénol se comporte de la même façon, ce qui permet de le distinguer de ses isomères. Les acides mono-carboxyliques aliphatiques, hydroxamiques et sulfoniques sont sans effet.

La détection de l'hydracide halogène libéré au moyen de papier indicateur (ou en démasquant

le ferrocyanure d'argent) permet un procédé qui sert à révéler la présence d'acides organiques effectifs. Utilisant des techniques d'analyse à la touche on a pu arriver à des limites de détection microanalytiques.

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THE ORIGINS OF QUANTITATIVE INORGANIC ANALYSIS*

R. E. COULSON
Imperial Smelting Corporation Limited, St. Andrew's Road, Avonmouth, Bristol, England

(*Received* 27 *July* 1958)

Summary—Analytical chemistry owes much to men such as Bergman, Klaproth and Berzelius, who pioneered the analysis of natural materials and developed a systematic approach in spite of incomplete knowledge of the nature of chemical composition.

> "*When you can measure what you are speaking about and express it in numbers, you know something about it, and when you cannot measure it, when you cannot express it in numbers, your knowledge is of a mean and unsatisfactory kind. It may be the beginning of knowledge but you have scarcely in your thought advanced to the state of a science.*"—LORD KELVIN

FROM the earliest days when men extracted metals from their ores, those who practised the art were interested in the "analysis" of different ores to discover which yielded the most metal. It was not analysis as we understand it to-day, the separation of the required metal rarely being complete with the simple dry methods then in use.

Agricola, in his *De re metallica* (1556) describes a considerable number of methods of analysis, many of which, modified to ensure complete extraction, are still in use. He gives full descriptions of the apparatus employed, which included balances enclosed in glass cases and a very wide range of crucibles and furnaces.

Alloys containing gold, silver and copper were analysed mainly by comparing the marks which they made on a "touchstone" (a dense flint) with those produced by standard alloys. Other than the parting of gold and silver with nitric acid, wet methods were rarely used, although several qualitative colorimetric methods were known such as the detection of iron in verdigris with extract of nutgalls. Although very highly developed, metallurgy was essentially an empirical art, and there was little effort at seeking an explanation of the ways in which metals could be extracted, or of the differences between ores of the same metal.

The search for an explanation of the composition of matter included the early theory of the four elements of earth, air, fire and water, followed by the "philosophic principles" of sulphur, salt and mercury. In their search for the elixir of life and the philosophers' stone, the alchemists, bemused by their own philosophy, were more interested in the outward appearance of their materials than in their chemical composition. The allegorical way in which their work was recorded makes the study of it very difficult, but the knowledge that was built up was enormous, although of little value until an understanding of chemical composition began to emerge at the beginning of the sixteenth century. Stillman, speaking of alchemists at that time,

* Paper presented at a symposium on the History of Analytical Chemistry, organised by the Midlands Section and the Western Section of the Society for Analytical Chemistry, and held at Shrewsbury on 16–17 May 1958.

says "not only were methods of quantitative analysis lacking but there existed no hypothesis in their philosophy which could have suggested the possibility of such methods."

When chemists became interested in the application of their compounds in medicine, a certain amount of analysis became essential. Antimony was one of the earliest metals so used and the early uncertainty of the antimony content of various preparations caused a certain amount of ill-feeling.

The analysis of minerals and naturally occurring waters was attempted as a means of classification. The systematic use of the balance spread rapidly. Facts were built into theories which in turn suggested further directions for investigation. Chemistry had emerged as a fully qualified science in the terms of Lord Kelvin's definition.

Boyle, often referred to as "The Father of Chemistry", displayed the inability of the alchemists to produce a coherent theory to explain the facts they knew, but could not offer a new theory, only a way in which it must be sought, through the discovery of natural laws. Joseph Friend, a professor of chemistry at Oxford, said in 1712, "Chemistry has made a laudable progress in experiments but we may justly complain that little advances have been made towards the explication of them.... Nobody has brought more light to the art than Mr. Boyle, who, nevertheless, has not so much laid a new foundation of chemistry as he has thrown down the old".

The fundamental concept, upon which the whole structure of chemistry is based, is that of conservation of matter. Many chemists had tacitly assumed this but it was not until 1756 that it was formally expressed by Lomonossof.

In view of the long history of metallurgy it is not surprising that the first great theory dealt with the oxidation of metals and the reduction of the oxides. That some metals gained in weight when heated in air was known at least as early as the eighth century A.D. As soon as the balance came into regular use a number of metals were studied and the Phlogiston theory was put forward by Becher (1635–1682) and later developed by Stahl (1660–1734). Although the basis of the theory was incorrect it did correlate a wide number of phenomena. That Lavoisier later showed that this theory did not offer a correct explanation of the reactions in no way diminishes the important part it played as the first attempt to explain a number of related reactions.

The study of minerals and natural waters exercised the minds of most of the early analysts of whom three made outstanding contributions. Torbern Olaf Bergman (1735–84), a professor at Uppsala, made many analyses but his methods of separation were often very poor. Martin Heinrich Klaproth (1743–1817), the first professor of chemistry at Berlin introduced many improvements and tried to produce general rules for the analysis of these materials. Jons Jacob Berzelius (1779–1848), professor of chemistry at Stockholm, carried out a considerable amount of analysis, often with high accuracy. The main importance of his work, in relation to the general theory of chemistry, was to apply current ideas of structure to the analytical results obtained, both by himself and others.

The work of these three must be viewed against the background of general knowledge existing at the time. During the lives of Bergman and Klaproth the role of metals in minerals was fairly clear but the different valencies of some metals were not understood and many confusions existed with closely related elements. The role of non-metallic elements was not at all clear, particularly in the case of chlorides where the acid was believed to contain oxygen.

Proust's law of constant composition was published in 1800, followed rapidly by the work of Dalton on multiple proportions and on his *New System of Chemical Philosophy* or Atomic Theory. From these ideas Berzelius tried to deduce the composition of minerals.

The main aim of these early workers was to establish a system of classification of minerals from their chemical composition. The identification of constituents by heating with a blowpipe on charcoal arose from the work of Pott (1692–1777) who was asked by the King of Prussia to discover the ingredients from which Saxon porcelain was made and tried fusing various mixtures of likely constituents. This work, in the words of Thomas Thomson "gradually led to the methods of examining materials by the blowpipe. These methods were brought to the present state of perfection by Assessor Gahn of Fahlun, the result of whose labours has been published by Berzelius in his treatise on the blowpipe".

Cronstedt (1727–1765) divided minerals into earths, bitumens, salts and metals, but carried out little chemical analysis. Bergman was the first man to attempt to lay down systematic rules for the chemical analysis of minerals and natural waters. He analysed a number of local waters paying close attention to the colours given with a variety of natural dyes. He distinguished between carbonates and bicarbonates and usually boiled his samples to see what was deposited. Methods of separation were very simple, alcohol was often used for extraction of salts such as calcium chloride, while iron was often separated from metals such as calcium and magnesium by igniting the nitrates to oxides and extracting with dilute nitric acid.

Few reagents were in use for separating metals other than the common acids and alkalies; potassium ferrocyanide was sometimes used to precipitate iron, and oxalic acid to precipitate calcium. The reaction of oxalic acid (produced by the action of nitric acid on sugar) with all the known metals was described by Bergman. That it was not more regularly used to separate calcium may be due to lack of knowledge of how to separate other metals, or prevent their interference. It was not known then that magnesium may be retained in solution with a sufficient concentration of ammonium salts.

Having analysed a water, Bergman usually synthesised it to see if the mixture had the same properties of specific gravity, taste, etc.

In the analysis of minerals, the majority of which would not dissolve in acids, Bergman showed that fine crushing and fusion with sodium carbonate in iron crucibles, followed by leaching with hydrochloric acid, would bring most minerals into solution. The introduction of iron from the crucible was a serious drawback.

The separation of silica by evaporation with hydrochloric acid was usually followed by treatment with ammonia to precipitate iron, aluminium, etc. The solution was then treated with alkali carbonate. Metals such as copper were precipitated as metals, while antimony was separated by evaporation with nitric acid. Chloroplatinic acid was known as a reagent for separating sodium and potassium.

The role of acid radicles in minerals was little understood. In a footnote, Cullen, who made an English translation of Bergman's *Physical and Chemical Essays*, states "Mr. Kirwan considers the acids as pure, and totally free from water; whereas Professor Bergman considers them in a state of considerable concentration indeed, but as containing a very large proportion of water".

It was Klaproth who, in the words of Thomas Thomson, "first systematised

chemical analysis and brought the art to such a state that the processes followed could be imitated by others with nearly the same results."

Klaproth always described the source, physical appearance and gravity of his specimens since he considered that many discrepancies occurred between results obtained by different analysts due to varying degrees of contamination. In an account of his work published in 1801 he gives first an account of the behaviour of more than a hundred minerals when heated in charcoal and in clay crucibles, covered respectively with lids of the same material. He was one of the first to use charcoal crucibles. He gives detailed descriptions of changes in appearance, or chemical reactions such as the separation of iron, and whether any change in weight takes place.

One of the difficulties encountered by Klaproth was the contamination of samples from the flint mortar that he used. To allow for this he analysed the flint, then weighed the mortar before and after use, and deducted the appropriate values from his results.

For samples insoluble in acid, fusion with alkali carbonate or hydroxide was employed, usually in a silver crucible. When employing a hydroxide the sample was often mixed with a strong aqueous solution of the alkali, the mixture gradually dried, and then fused. The methods of separation employed were largely those used by Bergman but several new methods were introduced including the use of succinic acid for the separation of iron from manganese. Hydrogen sulphide was sometimes used, mostly in qualitative tests, but occasionally in quantitative work as in the separation of iron from the rare earths.

One change which Klaproth introduced was to report results as he found them instead of the previous practice of applying a factor to bring the sum of the results to 100%.

The following examples are typical of analyses carried out by Klaproth:

Analysis of red silver ore

1. Treat with nitric acid. Filter.
2. Treat filtrate with hydrochloric acid. Filter. Weigh silver chloride. Treat the filtrate with barium chloride and weigh barium sulphate.
3. Treat the residue from 1 with *aqua regia*, dilute a little and filter. Residue contains sulphur and silver chloride.
4. Dilute filtrate and digest to separate antimony as oxide. Filter. Weigh oxide and reduce with carbon.
5. Treat filtrate with barium chloride and weigh barium sulphate. Result from 500 grains (32.2 g.)

Silver	300
Antimony	101·5
Sulphur	58·5
Concrete sulphuric acid	40
	500

Analysis of Bohemian garnet

1. Fuse with caustic potash, leach with water and filter.
2. Allow filtrate to stand. Hydrated oxide of manganese separates out. Filter.
3. Treat solution with hydrochloric acid to separate silica, then precipitate aluminium with ammonia.
4. Treat residue from 1 with hydrochloric acid to separate silica.

5. Treat filtrate with ammonia to precipitate iron and aluminium.
6. Treat filtrate with sulphuric acid. Separate calcium and magnesium sulphates.
7. Treat residue from 5 with hydrochloric acid. Precipitate iron as ferrocyanide then aluminium as hydroxide.

Result from 200 grains (13 g)	
Silica	80
Alumina	57
Oxide of iron	33
Magnesia	20
Lime	7
Oxide of manganese	0·5
	197·5

Of the acid radicles, carbonate was usually estimated from the loss in weight on treatment with acids, but for one sample of soda from Egypt the amount of nitric acid required for neutralization was weighed and the acid standardised in a similar way against pure sodium carbonate.

Methods of calculating acid radicles were closely linked with existing ideas of the composition of compounds. Sulphur in the form of sulphate could be estimated very accurately but there was little knowledge of how the sulphur existed in the compound, so that sulphidic minerals were often reported to contain sulphate, since that was found due to some of the sulphide being oxidised completely during analysis. Even then there were difficulties. In early work sulphuric acid was calculated in terms of free acid. Later reports are calculated in terms of "concrete sulphuric acid", *i.e.* acid free from water (sulphur trioxide).

This method of calculation led Klaproth into difficulties when dealing with chlorides. He reasoned as follows:—"100 parts of metallic silver yield 133 parts of muriated silver. But as this metal, to be rendered soluble in acids, takes up 12½ parts of oxygen, these must be subtracted so that of this increase by 33 parts, there remain 20½ for the muriatic acid".

Berzelius classified the components of minerals as electronegative and electropositive bodies and sought to show that the components were present in simple proportions. He knew that some oxides could behave as acids or bases according to the substances with which they were combined. He paid great attention to the state of oxidation of metals such as iron and manganese to arrive at the correct amount of oxygen which should be allocated to them.

The desire to find a formula to fit each substance led Berzelius into errors such as the following: "The small proportion of iron in this substance (graphite) long induced me to suppose it to be pure carbon mechanically blended with a little of the carburet of iron. But as the proportion of carbon in the artificial black lead, which crystallises during the fusion of cast iron, exceeds 90%, this body must therefore be a chemical combination, because we cannot suppose that an elementary body can separate itself from all combination with another from the mere disposition to crystallisation. Besides, it is known that the crystallising hydrargyret (amalgam) of potassium does not contain full three per cent of potassium, though it is beyond all doubt a chemical combination. This demonstrates that the maximum of particles (atoms, volumes) of a body which can be combined with a single particle of another must be very great. For if, according to the analysis of Saussure, the pure native

graphite of Cornwall contains 96 parts carbon for 4 parts iron, and if the artificial, according to Berthollet, contains 91 parts carbon for 9 parts iron, one particle of iron in the first instance is combined with 208, and in the second with 98 particles of carbon, or, allowing for a trifling error in the analysis, the former may be Fe + 200C and the latter Fe + 100C".

When seeking a formula for a mineral whose components were oxides, the only facts needed were the proportion of oxygen in the oxides. This was not always easy, except where the metals had been isolated. By the comparison of the combining proportions of bases with various acids, particularly sulphuric acid where the ratio of sulphur to oxygen was known, Berzelius correctly deduced the composition of most oxides from which he calculated atomic weights, tables of which he published in 1814, 1818 and 1826. In the two earlier tables there are many oxides with twice the correct number of oxygen atoms, *e.g.* FeO_2 and FeO_3 because Berzelius considered that the simplest binary compounds must contain one atom of one element combined with 1, 2, 3. . . atoms of the other. Following the work of Dulong and Petit on atomic heats (published in 1819) Berzelius corrected most of these errors but still retained his orginal formulae of the alkaline oxides, *e.g.* KO, NaO although these gave atomic weights double those deduced from the specific heats. The accuracy of some of the values used by Berzelius for the oxygen content of oxides may be judged from the examples in Table I.

TABLE I. OXYGEN CONTENT OF OXIDES

Oxide	According to Berzelius	Modern Value
Silica	49·6	53·3
Alumina	46·7	47·1
Magnesia	38·0	39·7
Lime	28·0	28·5
Baryta	10·5	10·4
Soda	25·7	25·8
Potash	17·0	17·0

Berzelius took the results of many analyses of minerals, some of his own, but others from all sources, and calculated the amount of oxygen contributed by each basic or acidic oxide. Taking the lowest value as unity and reducing higher values accordingly he obtained an empirical formula, calculated what the composition would be, and compared it with the results found.

The following example shows the method:

Composition of Byssolite

Calculated by Berzelius from an analysis by Vauquelin

					Calculated composition	
Silica	47·0		23·6		8	48·00
Magnesia	7·3		2·8		1	7·86
Lime	11·3	contains	3·2	≡	1	10·70
Oxide of iron	20·0	oxygen	6·1		2	19·36
Oxide of manganese	10·0		3·0		1	9·68

Similar methods were employed for compounds of other types, *e.g.* sulphides.

The work of Bergman, Klaproth and Berzelius shows that many analyses could be carried out with a high degree of accuracy, but methods of separation were often inadequate. Beginning with Berzelius, attempts were made to relate the results obtained from the analysis of natural materials to the rapidly developing ideas on the structure of chemical compounds. Chemical analysis was given a sound basis for the great progress which was made in following years.

Zusammenfassung—Die analytische Chemie verdankt viel solchen Männern wie Bergman, Klaproth und Berzelius, die zu der Analyse von natürlichen Stoffen den Weg bahnten und eine systematische Annäherung entwickelten, trotz einer unvollkommenen Kenntnis von der Natur der chemischen Komposition.

Résumé—La chimie analytique doit beaucoup aux hommes tels que Bergman, Kloproth et Berzélius qui pionnèrent l'analyse de matières naturelles et developèrent un rapprochement systématique, malgré une connaissance imparfaite de la nature de la composition chimique.

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THE EXTRACTION OF ZIRCONIUM WITH TRI-*n*-OCTYLPHOSPHINE OXIDE AND ITS DIRECT DETERMINATION IN THE ORGANIC PHASE WITH PYROCATECHOL VIOLET

J. P. YOUNG and J. C. WHITE
Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.

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Summary—A sensitive colorimetric method for the determination of zirconium has been developed for use in organic extracts which contain tri-*n*-octylphosphine oxide (TOPO) in *cyclo*hexane. The method is based on the absorbance of the zirconium-pyrocatechol violet complex in a TOPO-*cyclo*hexane-ethyl alcohol medium at a wavelength of 655 mμ. The molar absorbance index for this complex at 655 mμ is about 40,000. The complex conforms to Beer's law up to a concentration of 1.0 μg of zirconium per ml. When zirconium is extracted from a chloride medium, this method is useful for the determination of zirconium in the presence of large amounts of aluminium, uranium, vanadium, iron, and chromium; moderate amounts of thorium do not interfere. Molybdenum, titanium, and hafnium interfere with the method. The procedure is applicable in the presence of milligram amounts of phosphate and sulphate ion. When zirconium is extracted from a nitrate medium, the method is useful for the determination of zirconium in the presence of aluminium, titanium, molybdenum, vanadium, iron and chromium; however, uranium, thorium, and hafnium interfere. Microgram amounts of phosphate and sulphate ion can be tolerated. This method has the common advantage of most extraction methods in that zirconium which is present in an aqueous sample can be extracted into a smaller organic volume. The coefficient of variation for the determination of zirconium by this method is less than 3%.

INTRODUCTION

TRI-*n*-OCTYLPHOSPHINE oxide (TOPO) in non-polar solvents has been shown by White and Ross[6] to be an effective reagent for the extraction of zirconium from either hydrochloric or nitric acid solutions. The extraction of zirconium can be extended to other acidic media by the addition of sufficient nitric or hydrochloric acid prior to extraction with TOPO. For example, zirconium can be readily extracted with 0.01*M* TOPO in *cyclo*hexane from 1*M* H_2SO_4 which is made 7*M* with respect to hydrochloric acid. It has further been shown, in the colorimetric determination of chromium with diphenylcarbazide[4] and the colorimetric determination of uranium with dibenzoylmethane,[2] that the metal ion in the organic-TOPO phase will undergo reactions such that a colorimetric determination of the metal ion can be made directly in the organic extract. Through combination of extraction with TOPO and the use of a chromogenic reagent, such as pyrocatechol violet, which is one of the most sensitive reagents for the colorimetric determination of zirconium[1,8] in aqueous solutions, a selective and sensitive colorimetric method has been developed for the determination of zirconium in the organic extract.

EXPERIMENTAL

Absorbance spectra

The partial absorbance spectra of the zirconium-pyrocatechol violet complex in a TOPO-*cyclo*hexane-absolute ethanol medium is shown in Figure 1. The maximum

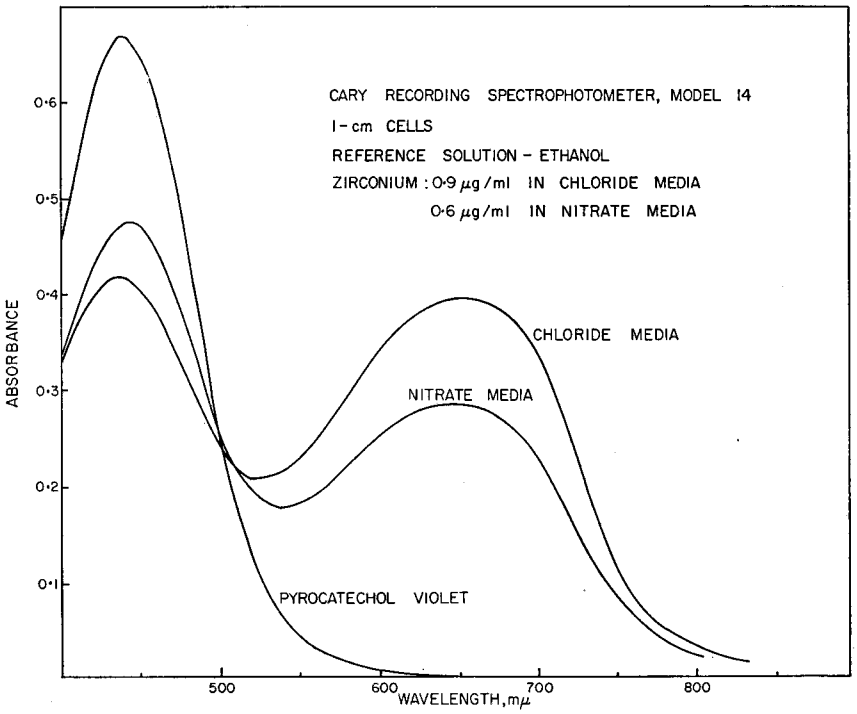

FIG. 1. Absorption spectra of zirconium-pyrocatechol violet complex in TOPO-*cyclo*hexane-ethanol.

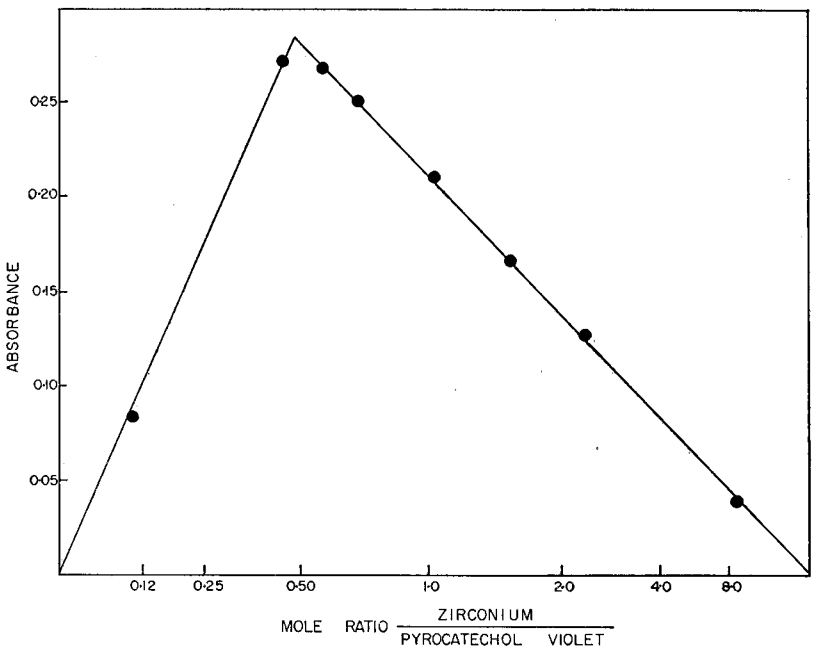

FIG. 2. Molar combining ratio of zirconium and pyrocatechol violet in ethanol.

absorbance of the complex occurs at a wavelength of 655 mμ. The absorbance of a solution which contains all reagents except zirconium is essentially zero, less than 0.005 absorbance units, at this wavelength.

The absorbance of the zirconium-pyrocatechol violet complex in the TOPO-*cyclo*hexane-ethyl alcohol medium conforms to Beer's law up to a concentration of one μg of zirconium per ml. The reciprocal of the slope of the calibration curve is 2.27 μg zirconium per ml per unit absorbance in the hydrochloric medium. The molar absorbance index of the complex at a wavelength of 655 mμ is about 40,000.

Metal-ligand ratio

Stoichiometry of the zirconium-pyrocatechol violet complex in ethanol. The method of continuous variation[3] was applied to the zirconium-pyrocatechol violet complex in ethanol in order to determine its composition. As shown in Figure 2, the complex contains two moles of pyrocatechol violet to one mole of zirconium.

Order of addition of reagents

In order to obtain maximum colour development, no change should be made in the order of addition of reagents as described in the procedure. Low absorbances were observed when the pyrocatechol violet was added directly to the *cyclo*hexane, and also when the test portion was added to either the pyrocatechol violet or the pyridine, or to a mixture of the two. The addition of absolute ethanol to the test portion of the extract is necessary to maintain complete miscibility of pyrocatechol violet and pyridine with the *cyclo*hexane in the test portion.

Effect of water on formation of complex

Absolute ethanol is preferred as the diluent since the absorbance of the test solution is decreased by approximately 20% if 95% ethanol is used. A similar order of decrease in absorbance of the final test solution resulted from the use of a solvent which contained absolute ethanol and known amounts of water. For example, for 1% water in the ethanol the resultant absorbance of the zirconium-pyrocatechol violet complex was lower by 5% than in absolute ethanol diluent. Although no elaborate precautions are necessary to minimize the absorption of water by the absolute ethanol, the solvent should not be exposed to air for unduly long periods of time.

The interference of water in this method is apparently due to some reaction of water which prevents full colour development of the complex since the effect of water on the absorbance of the zirconium-pyrocatechol violet complex is negligible if the water is added after the complex has been formed.

Reagent stability

Solutions of pyrocatechol violet in absolute ethanol should be prepared fresh daily. The use of a solution of the chromogenic reagent which is one day old will cause a decrease in the absorbance of the resultant complex of approximately 10%. This effect is apparently due to the slow decomposition of pyrocatechol violet when dissolved in ethanol. The absorption spectra, from 350 to 750 mμ, of such a solution when measured with respect to time shows no unique changes in general form, but rather there is a gradual, uniform decrease in the absorbance at all wavelengths.

The pyridine concentration of the final test solution can vary from 12 to 28 v/v%.

Lower or higher concentrations result in incomplete development of the complex. The absorbance of a reference solution which contains no zirconium is likewise completely independent of pyridine concentration over the range from 8 to 40 v/v% of this organic base in the final test solution.

Stability

The colour of the zirconium-pyrocatechol violet complex develops immediately and is stable for a period of two hours. As the concentration of zirconium and TOPO in the test solution is increased, the stability of the resultant colour is decreased somewhat. After a period of two hours the test solutions will gradually change in their absorbance, and the zirconium-pyrocatechol violet complex will precipitate from solution. These results are shown in Table I.

TABLE I.—STABILITY OF THE ZIRCONIUM-PYROCATECHOL VIOLET COMPLEX IN A TOPO-*cyclo*HEXANE-ETHYL ALCOHOL MEDIUM
Final volume, 25 ml

Zirconium *μg/ml*	TOPO *mmoles/25 ml*	Absorbance		
		0.0 *hr*	1.0 *hr*	2.0 *hr*
0.16	0.01	0.074	0.077	0.086
0.32	0.01	0.132	0.131	0.138
0.32	0.01	0.140	0.140	0.144
0.63	0.01	0.278	0.280	0.296
0.63	0.02	0.278	0.283	—[a]
1.26	0.02	0.565	0.557	—[a]

[a] Precipitate present in two hours.

Diluents

The maximum amount of zirconium in the test aliquot should be 125 μg. In case of larger amounts dilution should preferably be made with 0.01*M* TOPO. These dilutions are stable at least 24 hours. *cyclo*Hexane can also be used for this dilution if the final concentration of TOPO in the test solution is maintained within the range of 0.003 to 0.03 mmoles/25 ml.

The best diluent for use in the development of the colour of the zirconium-pyrocatechol violet complex is absolute ethanol. Of other diluents tested, such as benzene, *cyclo*hexane, dioxane, 95% ethanol, acetone, amyl alcohol, butyl acetate, and methyl *iso*butyl ketone, all resulted in a decreased sensitivity of the method, and many resulted in rapid precipitation of the complex.

Composition of non-aqueous solution

The concentration of *cyclo*hexane in the final 25-ml volume must be less than 20 v/v %; in higher percentages, the complex precipitates. In order to maintain a miscible solution the volume ratio of *cyclo*hexane to ethanol should never exceed one.

The amount of TOPO in the final volume should be in the range of 0.003 to 0.04 mmoles. If a larger amount of TOPO is present, the absorbance of the complex is decreased by about 5%.

Extraction from acidic chloride solutions

In addition to zirconium, such metals as uranium, titanium, iron, thorium, and chromium are extracted, under certain conditions, by TOPO.[5] Since ions of these metals also react with pyrocatechol violet, steps were necessary either to prevent their extraction or to minimise their interference in the organic solution.

The addition of ammonium thiocyanate to the acidic aqueous solution before extraction was found to be beneficial. The extraction of zirconium from 7*M* hydrochloric acid, and the resultant colour formation of zirconium in the extract with pyrocatechol violet is unaffected by a concentration of ammonium thiocyanate in the aqueous phase from 10 to 200 mg/ml. These results are shown in Table II.

TABLE II.—EFFECT OF AMMONIUM THIOCYANATE ON THE EXTRACTION OF ZIRCONIUM AND ITS DETERMINATION WITH PYROCATECHOL VIOLET

Aqueous Phase, 7*M* HCl		Zirconium, *μg/ml*	
Volume, *ml*	NH_4CNS, *mg/ml*	Present in Aqueous Phase	Found
5	10	7.9	8.0
5	20	7.9	7.9
5	40	7.9	8.0
5	80	7.9	7.8
5	140	7.9	8.0
5	200	7.9	8.0
5	320	7.9	7.2
10	70	3.9	4.0
10	140	3.9	3.8
25	140	1.6	1.6

Up to 200 mg/ml of NH_4CNS can be tolerated; the results were low when 320 mg were present in the aqueous phase. In the highly acidic aqueous phase, ammonium thiocyanate decomposes to form, among other things, polymerised thiocyanic acids and hydrogen cyanide.[7] The decomposition products of this salt will eventually, within one to two hours, depending on temperature and other factors, make the removal of a test portion of the extract impractical. The extraction container will always contain hydrogen cyanide gas in varying concentrations, and precautions should be exercised in the handling of these containers.

The extraction of uranyl ions is essentially eliminated by the presence of thiocyanate ion.[6] Uranium normally extracts quite readily from 7*M* hydrochloric acid into solutions of TOPO.[8] However, only 0.8 % of uranyl ion, at a 200 *μg*/ml concentration level, is extracted from 7*M* hydrochloric acid if the concentration of ammonium thiocyanate is 80 mg/ml. A four-fold increase in the uranium thiocyanate concentration level will reduce the extraction of uranium to 0.02 %. At the concentration level of ammonium thiocyanate that is recommended in the procedure, 140 *μg*/ml, uranyl ion extracts to the extent of 0.2%.

No evidence of ferric ions was found in the organic phase when the extraction was conducted from aqueous solution which contained thiocyanate. The extraction of either vanadyl or vanadate ion is apparently grossly hindered by thiocyanate ion in

TABLE III.—EFFECT OF CATIONS ON THE DETERMINATION OF ZIRCONIUM WITH PYROCATECHOL VIOLET IN A TOPO-*cyclo*HEXANE-ETHYL ALCOHOL MEDIUM

Equilibration time—10 minutes
Aqueous phase—5 ml 7*M* HCl
140 mg NH_4CNS/ml

Cation		Aqueous phase Zirconium, *μg/ml*	
	μg/ml	Present	Found
Al^{3+}	130	11.8	12.2
	260	11.8	12.3
UO_2^{2+}	50	7.9	8.0
	100	7.9	8.0
Fe^{3+}	20	7.9	7.9
	100	7.9	8.0
Cr^{6+}	25	11.8	11.6
	50	11.8	11.6
	100	11.8	11.9
V^{4+}	100	11.8	11.8
	200	11.8	11.7
	600	7.9	7.7
	6000	7.9	7.8
	6000	15.8	16.1
V^{5+}	600	7.9	8.0
	600	15.8	16.6
	1200	7.9	8.0
	1200	11.8	12.1
Th^{4+}	10	11.8	11.9
	20	11.8	12.1
	25	11.8	12.3
	50	11.8	12.7
	100	11.8	13.3
Mo^{6+}	20	11.8	13.0
	30	11.8	14.4
	40	11.8	15.0
Ti^{4+}	3.7	7.9	12.0
	7.4	7.9	16.2
	14.8	11.8	27.7
Hf^{4+}	12.4	0.0	6.2 (Hf = 12.2)
	35.8	0.0	19.2 (Hf = 37.7)

the aqueous phase. Titanium, however, extracts as an intensely yellow thiocyanate complex into TOPO from aqueous solutions which contain thiocyanate ion.

The addition of thiocyanate to the aqueous phase prior to the extraction of zirconium, therefore, leads to quantitative separation from uranium and iron.

Effect of diverse ions

The effect of various cations on the determination of zirconium was studied. An aqueous solution which contained both zirconium and the cation to be studied,

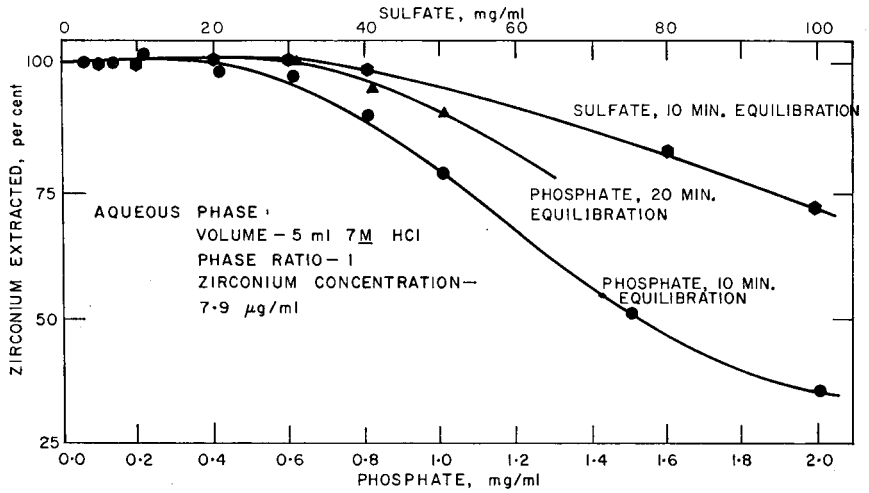

FIG. 3. Effect of phosphate and sulphate ion on the extraction of zirconium and its determination with pyrocatechol violet.

in 7*M* hydrochloric acid, was treated according to the procedure that was described previously. The results of this investigation are presented in Table III.

This method is particularly suited for the determination of zirconium in the presence of large concentrations of aluminium, dichromate, ferric, uranyl, vanadyl, and vanadate ions. At the level of concentration shown in Table III these ions cause no significant error in the determination of zirconium. The tolerance to the other ions which were mentioned is probably much better than shown; however, higher concentrations of these ions were not studied. The alkali metals, alkaline earths, rare earths, lead, nickel, cobalt, arsenic, ferrous iron, and indium do not extract into solutions of TOPO from aqueous solutions which are 7*M* in HCl; therefore, these elements will not interfere with the determination of zirconium by this method.

Small quantities of thorium, molybdenum, titanium, and hafnium interfere. An error of 5% will result if the thorium/zirconium weight ratio is as high as four. At a weight ratio of one, molybdenum will cause a 5% error.

Titanium causes serious interference in this determination, since it is extracted along with zirconium and forms a blue complex with pyrocatechol violet. The presence of even submicrogram amounts of titanium, however, in the aqueous phase can readily be detected by visual observation of the resultant organic extract. Titanium is extracted as a yellow thiocyanate complex; less than 0.5 μg of titanium in 5 ml of the organic phase can be detected by the coloration it imparts to the extract.

This behaviour of titanium is being investigated as a basis for a determination of this element.

The method is apparently equally sensitive to zirconium or hafnium on a molar basis.

This method has quite a high tolerance to phosphate ion as shown in Fig. 3. Under the conditions of the procedure, up to 600 μg of phosphate per ml can be tolerated in the aqueous phase with less than a 5% error in the resultant determination of 7.9 μg of zirconium per ml. If the equilibration time is increased from 10 to 20 minutes 800 μg of phosphate per ml can be tolerated at the same error.

Up to 1.5 mmoles of sulphate ion can be tolerated in 5 ml of 7*M* hydrochloric acid with an error of less than 5%.

The combination of sulphate and thiocyanate ions in the aqueous phase depresses the extraction of zirconium with TOPO.

The effect of other anions on this method was not specifically studied; however, no trouble has been encountered with small concentrations of nitrate or perchlorate ions when these were present in some aqueous samples. Large amounts of nitrate in this strongly acid aqueous phase will result in serious decomposition of the thiocyanate ion.

In comparing the effect of diverse ions on this non-aqueous method and on the aqueous method of Young, French, and White,[9] large amounts of aluminium, iron, and vanadium do not interfere with the non-aqueous method. Iron can be tolerated only to a limited degree in the aqueous method; aluminium and vanadium interfere quite seriously. This non-aqueous method exhibits a tolerance to phosphate ion; phosphate interferes with the aqueous method. However, the aqueous method can tolerate larger amounts of thorium and is more independent of sulphate ion concentration than is the non-aqueous method. Titanium causes serious interference in both methods.

Applications

This method has been applied to the routine determination of microgram quantities of zirconium in solutions which contain small amounts of phosphate and extremely large amounts of vanadyl or vanadate ions. The quadrivalent vanadium solutions were 1*M* with respect to sulphuric acid; the solutions of quinquevalent vanadium were up to 3*M* with respect to perchloric acid. Typical results that were obtained on synthetic samples are presented in Table IV.

Zirconium can be determined in this type of sample with a coefficient of variation of 2%. The slight positive bias shown for the data in Table IV does not appear to have any significance.

No further applications of this method have been made as yet; however, it should be quite useful for the determination of zirconium in aluminium, uranium, iron, rare earths, and certain phosphates, to mention only a few possibilities.

Extraction from acidic nitrate solutions

Fewer elements are extracted by TOPO from acidic nitrate solutions. Essentially only zirconium, uranium, thorium, and tin are extracted. Hence, the method should be less subject to interferences due to mutual extraction from nitric acid solution than from hydrochloric acid solutions. Ross and White[6] reported, however, that based

TABLE IV.—TYPICAL RESULTS FOR THE DETERMINATION OF ZIRCONIUM WITH PYROCATECHOL VIOLET IN THE PRESENCE OF VANADIUM, PHOSPHATE AND OTHER IONS

Aqueous phase: Volume—5 ml 7*M* HCl
140 mg NH_4CNS/ml

Vanadium		Millimoles		Phosphate μg	Zirconium Found, μg
Valence State	*mg*	SO_4^{2-}	ClO_4^-		
		0.00 μg of zirconium present			
4	30	0.2	—	—	0.9
5	6	—	5.5	—	1.2
		39.4 μg of zirconium present			
4	3	0.02	—	—	38.2
4	30	0.2	—	—	38.8
5	3	—	—	—	39.7
5	6	—	2.8	—	40.8
5	6	—	5.5	—	40.0
5	6	—	5.5	310	40.0
				Average	39.6 ± 2%
		59.1 μg of zirconium present			
5	6	—	2.8	—	59.7
5	6	—	5.5	—	61.0
				Average	60.3
		78.8 μg of zirconium present			
4	30	0.2	—	—	79.4
5	3	—	—	—	82.0
				Average	80.7

TABLE V.—EFFECT OF CATIONS ON THE DETERMINATION OF ZIRCONIUM WITH PYROCATECHOL VIOLET IN A TOPO-*cyclo*HEXANE-ETHYL ALCOHOL MEDIUM

Equilibration time—10 minutes

Aqueous phase—5 ml 7*M* HNO_3

Aqueous phase

Cation		Zirconium, $\mu g/ml$	
	$\mu g/ml$	Present	Found
Cu^{2+}	100	11.8	11.7
Fe^{3+}	50	11.8	12.1
	100	11.8	12.2
	200	11.8	12.1
Mo^{6+}	100	11.8	12.1
	200	11.8	12.1
V^{4+}	600	7.9	7.8
	1800	7.9	7.9
	3000	7.9	8.3
V^{5+}	400	7.9	7.9
	800	7.9	8.2
	1200	7.9	8.0
Ti^{4+}	45	11.8	11.8
	90	11.8	12.2
	180	11.8	13.1
Th^{4+}	6	7.9	7.8
	12	7.9	8.3
	18	7.9	8.9

on a TOPO/zirconium molar combining ratio of 2, complete extraction of 100 μg of zirconium from nitric acid requires a molar ratio of excess TOPO of at least 25 in sharp contrast to a figure of 2 for similar extraction from hydrochloric acid. Their results were confirmed in this study.

The extraction of about 100 μg of zirconium is quantitative only when 1 mmole of TOPO is used.

Effect of diverse ions

The effect of various cations on the determination of zirconium was studied. An aqueous solution which contained both zirconium and the cation to be studied in 7*M* nitric acid was treated according to the procedure that was described in this report. The results of this investigation are presented in Table V.

The determination of zirconium in nitric acid medium is unaffected by large amounts of copper, ferric ion, sexivalent molybdenum and vanadium. The alkali metals, alkaline earths, aluminium, rare earths, lead, nickel, cobalt, arsenic, and indium do not extract into solutions of TOPO from aqueous solutions which are

7*M* in NHO_3; therefore, these elements will not interfere with the determination. Thorium interferes with the determination of zirconium. Weight ratios of thorium to zirconium of more than 1.5 cause an error in the subsequent determination of zirconium of at least 5%.

As shown in Table V, titanium in a weight ratio of titanium to zirconium of as high as 10 causes only slight interference with the determination of zirconium. Larger concentrations of titanium do interfere even though the extraction coefficient

TABLE VI.—EFFECT OF VARIOUS ANIONS ON THE EXTRACTION OF ZIRCONIUM IN A NITRATE MEDIUM AND ITS SUBSEQUENT DETERMINATION WITH PYROCATECHOL VIOLET

Equilibration time—10 minutes

Aqueous phase—5 ml 7*M* HNO_3

Aqueous phase

Anion			Zirconium, *μg/ml*	
	M	*μg/ml*	Present	Found
Cl^-	0.2		7.9	7.9
	0.4		7.9	7.7
	0.6		7.9	7.8
	0.8		7.9	7.6
SO_4^{2-}	0.3		7.9	4.4
	0.6		7.9	2.5
	1.2		7.9	1.2
PO_4^{3-}		50	7.9	7.7
		100	7.9	7.0
		200	7.9	6.0

for titanium is low in a nitrate medium. If the original organic phase is backwashed with 7*M* nitric acid, however, weight ratios of titanium to zirconium of 100 and more are tolerated by the method.

The effect of various anions on this determination of zirconium is summarized in Table VI. Chloride ion, as hydrochloric acid, caused no effect on the extraction or determination of zirconium. Sulphate ion, as sulphuric acid, caused serious interference with this method for the determination of zirconium; it is probable that this interference is due to incomplete extraction of zirconium in the presence of sulphate ion. Phosphate ion in concentrations up to approximately 50 μg/ml do not interfere with this method. Larger concentrations of phosphate ion, however, are not tolerable; again this effect is probably due to incomplete extraction of zirconium from the aqueous phase.

Comparison of the effect of diverse ions on the non-aqueous determination of zirconium in chloride or nitrate medium

A re-examination of the effect of various diverse ions on extraction of zirconium with TOPO and its subsequent determination with pyrocatechol violet point up the

utility of this general method. Of the possible interferences that have been mentioned, alkali metals, alkaline earths, rare earths, aluminium, iron, chromium, vanadium, lead, nickel, cobalt, arsenic, and indium do not affect the determination of zirconium regardless of the possible acid which may be present in aqueous phase. The choice of making the initial aqueous sample 7*M* with respect to nitric or hydrochloric acid should be based on the presence in the aqueous sample of thorium, uranium, molybdenum, titanium, sulphate and phosphate ions. In extracting from a chloride-thiocyanate medium, the interference of uranyl ions is eliminated; relatively large concentrations of phosphate and sulphate ions can be present; and thorium can be tolerated up to a weight ratio of thorium to zirconium of four. Titanium and molybdenum interfere seriously with the application of this method to a chloride medium. In extracting from a nitrate medium, the interference of molybdenum and titanium can be completely eliminated. The tolerance of the method, in a nitrate medium, to thorium, phosphate, and sulphate ion is much reduced; uranyl ions will likewise extract and interfere with the subsequent determination of zirconium.

PROCEDURE

Extraction from hydrochloric acid solution

The solution to be extracted is first made approximately 7*M* with respect to hydrochloric acid; at this point the volume of the aqueous phase should be no greater than 25 ml and should preferably contain less than 125 μg of zirconium. About 700 mg of ammonium thiocyanate (as measured by a Coors micro crucible, size 5/0, filled to the top) is added to the acidic solution and the resulting solution extracted for 10 minutes with 5 ml of 0.01*M* TOPO in *cyclo*hexane.

A one- to three-ml aliquot of the organic phase is then transferred to a 25-ml volumetric flask, and in succession are added 10 ml of absolute ethanol, one ml of 0.05% pyrocatechol violet, and 5 ml of pyridine. The resulting solution is diluted to the mark with absolute ethanol and the absorbance measured immediately against ethanol in Corex 1-cm cells at 655 mμ with a Beckman spectrophotometer, Model DU or B.

Extraction from nitric acid solution

The solution to be extracted is first made approximately 7*M* with respect to nitric acid; at this point the volume of the aqueous phase should be no greater than 25 ml and should preferably contain less than 125 μg. of zirconium. The resulting solution is extracted for 10 minutes with 5 ml of 0.02*M* TOPO in *cyclo*hexane. A one- or two-ml aliquot of the organic phase is then transferred to a 25-ml volumetric flask and the colour is developed as described for the hydrochloric acid solution. The absorbance is then measured against ethanol in Corex 1-cm cells at 655 mμ with a Beckman spectrophotometer, Model DU or B.

Work carried out under contract No. W-7405-eng-26 at Oak Ridge National Laboratory, operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.

Zusammenfassung—Eine empfindliche colorimetrische Methode zür Bestimmung von Zirkon in organischen Extrakten, welche Tri-*n*-octylphosphinoxyd (TOPO.) in Cyclohexan enthalten, wurde entwickelt. Die Methode beruht auf der Absorption des violetten Komplexes von Zirkon-Pyrokatechin in TOPO.-Cyclohexan-Äthyl Alkohol bei 655 mμ. Die molare Absorption dieses Komplexes beträgt bei 655 mμ ungefähr 40,000. Der Komplex folgt dem Beer'schen Gesetz bis zu einer Konzentration von 1,0 μg Zirkon pro ml.

Wenn Zirkon aus einem Chloridmedium extrahiert wird, so ist diese Methode zür Bestimmung von Zirkon in Anwesenheit grosse Mengen von Al, U, V, Fe und Cr nützlich. Mässige Mengen von Th stören nicht, Mo, Ti und Hf hingegen stören.

Das Verfahren ist anwendbar bei Anwesenheit von Milligramm-Mengen Phosphat- und Sulfat-Ionen. Wenn Zirkon aus einem Nitratmedium extrahiert wird, so ist die Methode zür Bestimmung von Zirkon bei Gegenwart von Al, Ti, Mo, V, Fe und Cr gut verwendbar. Mikrogramm-Mengen von Phosphat- und Sulfat-Ionen stören nicht.

Diese Methode besitzt den allgemeinen Vorteil, dass Zirkon aus wässerigem Proben in ein kleines Volumen des organischen Lösungsmittels extrahiert werden kann. Die Varianz für die Bestimmung von Zirkon nach dieser Methode liegt unter 3%.

Résumé—Les auteurs ont mis au point une méthode sensible pour le dosage colorimétrique du zirconium qu'on peut utiliser dans des extraits organiques contenant l'oxide tri-*n*-octylphosphine (TOPO) dans le cyclohexane. Cette méthode est basée sur l'absorption du complexe violet zirconium-pyrocatéchine en milieu TOPO—cyclohexane—alcool éthylique à une longueur d'onde de 655 mμ. L'absorption molaire pour ce complexe à 655 mμ est d'environ 40,000. Le complexe suit la loi de Beer jusqu'à une concentration de 1,0 μg de zirconium par ml. Lorsqu'on extrait le zirconium d'un milieu chlorhydrique, cette méthode permet le dosage du zirconium en présence de grandes quantités d'aluminium, d'uranium, de vanadium, de fer et de chrome; des quantités moyennes de thorium ne gênent pas. Le molybdène, le titane et le hafnium gênent avec cette méthode. Le procédé est applicable en présence de quantités de PO_4^{3-} ou de SO_4^{2-} de l'ordre du milligramme. Lorsqu'on extrait le zirconium d'un milieu nitrique, la méthode permet le dosage du zirconium en présence d'aluminium, de titane, de molybdène, de vanadium, de fer et de chrome; cependant l'uranium, le thorium et le hafnium gênent. On peut tolérer des quantités de PO_4^{3-} ou de SO_4^{2-} de l'ordre du microgramme. Cette méthode a l'avantage commun à la plupart des méthodes d'extraction: c'est-à-dire que le zirconium qui est présent dans un échantillon aqueux peut être extrait dans un volume organique plus petit. Le coefficient de variation pour le dosage du zirconium par cette méthode est inférieur à 3 pour cent.

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AMPEROMETRIC DETERMINATION OF MICROGRAM QUANTITIES OF SULPHIDE SULPHUR*

L. LEVIN and W. B. SWANN
Research and Development Laboratory, Socony Mobil Oil Company, Inc.,
Paulsboro, New Jersey, U.S.A.

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Summary—The limiting sensitivity of the starch end-point in the iodimetric titration of microgram quantities of sulphide sulphur has been improved by an amperometric technique. The titration can be performed with a standard amperometric assembly fitted with a twin platinum electrode. As little as 10 to 30 micrograms of sulphur can be determined with a standard deviation of 1.4 microgram. The method has been applied to the determination of sulphides in solids and of hydrogen sulphide in air.

THE analysis of sulphide sulphur in solid materials usually involves acid treatment of the sample, whereby hydrogen sulphide is evolved and absorbed in a cadmium or zinc salt solution. Hydrogen sulphide in air is collected by passing a metered volume through the absorbing solution. The sulphide precipitate that is formed is then estimated by iodimetric titration with starch indicator.[4,6]

One source of error in the analysis of minute amounts of sulphur by this method is the variation of the starch end-point. The amount of iodine necessary to produce a permanent blue colour, under favourable conditions, is of the order of 0.001 to 0.002 milliequivalent. The precision of the blank becomes critical when the amount of sulphur being titrated is equal to or less than this amount. This difficulty precludes the use of the starch end-point for determining microgram amounts of sulphur.

Foulk and Bawden[2] first suggested an amperometric technique, which they termed a "dead-stop" end-point, for applications in iodimetry. Subsequent workers, notably Delahay[1] and Stone and Sholten,[8] investigated the reaction at the electrodes and postulated mechanisms.

Despite the encouraging theoretical investigations, few analytical applications of this amperometric method have been reported. Therefore, the authors investigated the conditions for iodimetric analysis of sulphide sulphur employing an amperometric technique to determine accurately microgram quantities of sulphide sulphur in solids and of hydrogen sulphide in air. In the method presented, the sulphide precipitate reacts in a closed system with excess iodine (added as iodate–iodide solution), and the unreacted iodine is back-titrated amperometrically. By graphing the titration, the end-point is more sharply defined than with the dead-stop technique.

APPARATUS AND REAGENTS

Amperometric assembly: Titrations were performed with a Fisher Elecdropode fitted with a twin platinum electrode and a magnetic stirrer.

Distillation apparatus: The apparatus used to evolve and collect hydrogen sulphide from solid samples consists of a 250-ml Erlenmeyer flask fitted with a ground-glass inlet for introducing purge gas, an exit tube leading into the absorbing solution, and a side-arm for introducing acid.

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Standard potassium iodate solution, 0.001N: Dissolve 0.0713 gram of recrystallised potassium iodate in water. Add 2 grams of sodium hydroxide and 140 grams of potassium iodide, and dissolve in a total volume of 2 litres.

Alkaline cadmium hydroxide suspension: Dissolve 3.85 grams of cadmium chloride dihydrate in water. Add 0.3 gram of sodium hydroxide dissolved in water and make up to 1 litre.

Standard sodium thiosulphate solution: Prepare an approximately 0.002*N* solution with freshly boiled and cooled distilled water. Add about 0.2 ml of chloroform per litre and let stand for several days. Standardise against the standard potassium iodate solution, using the amperometric titration described below. Standardise daily until successive values agree within ±1%. Weekly standardisation thereafter is sufficient.

EXPERIMENTAL

Applied potential

The results of current-voltage measurements of an iodine solution with the twin platinum electrodes are shown in Figure 1 (Curve A). The current-voltage plot shows a plateau between 90 and 130 millivolts. Similar measurements for sodium thiosulphate solution (Curve B) show low and essentially constant current in this range, with a corresponding sharp rise at an applied potential of about 200 millivolts because of dissolved oxygen. An applied potential of 110 millivolts was selected for the titration.

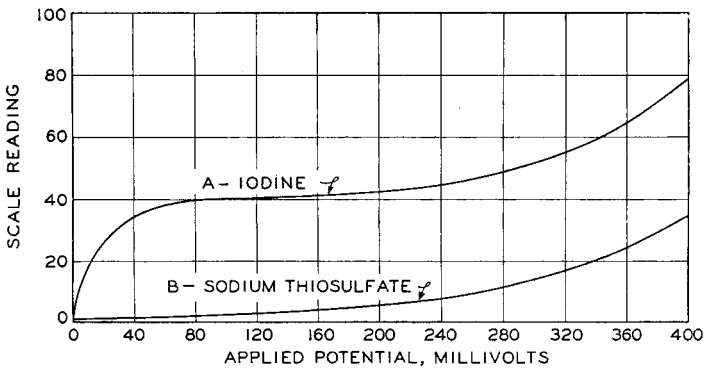

FIG. 1.

Potassium iodide–iodate ratio

The volatility of iodine is sharply reduced by the formation of tri-iodide ion with excess potassium iodide. Usually a ten- or twenty-fold weight ratio of potassium iodide to potassium iodate is added. Therefore, in a 0.001*N* potassium iodate solution, the absolute amount of potassium iodide normally present is small. At these low concentrations, considerable galvanometer drifting was noticed when the potassium iodide–iodate weight ratio was approximately twenty. However, when the weight ratio was increased to approximately two thousand, this instrument drift was effectively eliminated. In the sample analysed in the work on which this report is based, the amount of potassium iodate required per sample was low, and approximately one gram of potassium iodide gave the required iodide–iodate ratio.

Acidification

The collected sulphide precipitate is acidified in the presence of a known excess of potassium iodate solution. The reaction is carried out in a closed system so that hydrogen sulphide and iodine are simultaneously evolved without loss of gaseous hydrogen sulphide, as is possible in direct titration procedures.

High acidity favours air-oxidation of iodide. By adding only a slight excess of acid beyond that required to complete the reaction, this difficulty is avoided. As much as 60 milliequivalents of excess hydrochloric acid may be tolerated in a volume of about 125 ml.

Absorbing solutions

An ammoniacal solution of a zinc or cadmium salt is usually employed to precipitate sulphide. However, the amperometric titration of an ammoniacal blank solution containing a known amount of standard iodate solution gave a value less than the equivalent iodate. The difference varied with the ammonia concentration. Because the ammonia content of sample and blank could not be equated —due to variable purging volumes—other absorbing solutions with constant blank values were sought. Low and essentially constant blanks were obtained with 2% aqueous solutions of cadmium chloride, or cadmium acetate and an alkaline cadmium hydroxide suspension. The cadmium acetate solution was selected for the determination of hydrogen sulphide in air. For sulphide in solids, alkaline cadmium hydroxide suspension was used so as to neutralise any acid that might distil over with the hydrogen sulphide.

TABLE I.—DETERMINATION OF SULPHUR IN NBS INGOT IRON (55 b)

Sample weight *mg*	S present, *micrograms**	S found *micrograms*	S found %
53.8	10.0	10.4	0.0194
102.2	18.9	19.3	0.0189
117.8	21.8	21.7	0.0184
132.0	24.4	21.9	0.0166
154.0	28.4	26.7	0.0173

* Based on 0.0185% sulphur.

Average 0.0181
Standard deviation −0.0010%

Cadmium sulphide stability

Direct sunlight decomposes cadmium sulphide.[3] Even diffused sunlight can cause appreciable error over an extended period of time. For example, a 1-mg sample of reagent grade cadmium sulphide in 30 ml cadmium acetate solution was allowed to stand several hours exposed to diffused natural light. Amperometric analysis of the exposed sample gave a titre 11% lower than that given by an identical sample that was titrated immediately.

In the authors' work, sulphide was absorbed in flasks protected from light by a rubber cover.

SULPHIDE SULPHUR IN SOLIDS

The determination of sulphur in solids by evolution is based on the assumption that the sulphur is present in a form convertible to hydrogen sulphide. In metal alloys, incomplete dissolution and high carbon content contribute to low recovery.[7] National Bureau of Standards Ingot Iron (55 b) was chosen for evaluation of the method since the carbon content is very low and the metal is readily dissolved by dilute mineral acids.

Samples containing between 10 and 30 micrograms of sulphur were analysed by the amperometric method. The results are shown in Table I.

Procedure

Transfer a sample estimated to contain at least 10 micrograms of sulphur to the distillation flask. Connect a small piece of glass tubing to the exit tube and extend it into a 50-ml mixing cylinder containing 30 ml of alkaline cadmium hydroxide. Shake the cadmium suspension well before adding. Introduce about 30 ml of dilute hydrochloric acid (1 : 1) into the flask and heat the mixture moderately. Purge the system with nitrogen until the sulphide evolution is complete.

Disconnect and leave the delivery tube in the mixing cylinder, and add a known excess of standard potassium iodate. Introduce about 5 ml of concentrated hydrochloric acid, stopper quickly, and mix well. Cool the cylinder to approximately room temperature and transfer the solution to the titration beaker.

Apply a potential of 110 millivolts across the platinum–platinum electrodes. Add the thiosulphate

titrant until the iodine colour is pale yellow and adjust the sensitivity dial to bring the galvanometer indicator on scale. Add small increments of titrant and plot the respective scale reading against the total volume. Because the resultant curve is essentially a straight line with a negative slope, it is convenient to plot just four or five well-distributed points. As the end-point is approached, the curve becomes assymptotic with the limiting current value. This limiting current value or baseline is defined as the value at which no appreciable change in current results when excess titrant is added. The intersection of the straight line and the baseline is the end-point. A typical graph is shown in Fig. 2.

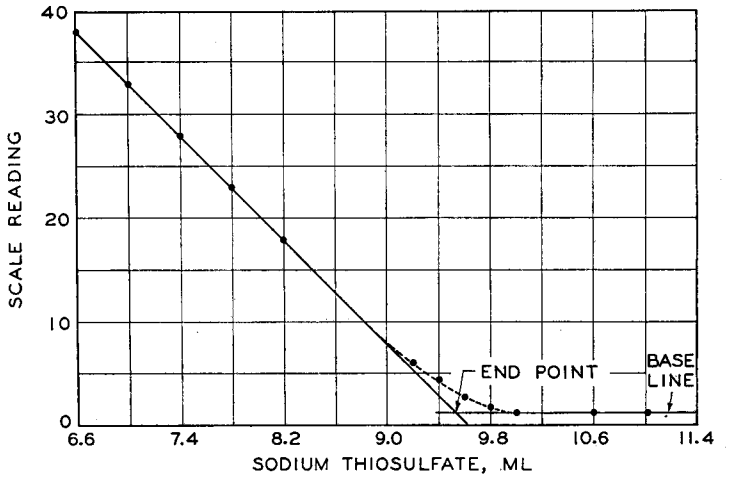

FIG. 2.

A blank titration on the absorbing solution and the same amount of iodate solution is also run. With experience the titration and graphing can be performed in 15 minutes.

HYDROGEN SULPHIDE IN AIR

In blending mixtures of hydrogen sulphide and air, considerable difficulty was encountered with plugging of the capillary flow-meter by mercuric sulphide. Therefore, a metered amount of sulphur dioxide was quantitatively reduced to hydrogen sulphide by passing the gas through a strong stannous chloride solution.[5]

TABLE II.—DETERMINATION OF HYDROGEN SULPHIDE IN AIR

Volume sampled, *litres*	Hydrogen sulphide present, *ppm*	Hydrogen sulphide found, *ppm*
10.13	10.4	10.3
10.06	15.9	15.7
7.11	67.6	68.6
5.02	202	197
1.05	611	640
0.53	1200	1230

The test mixtures were sampled with a covered midget impinger-flask containing 15 ml of 2% cadmium acetate solution. A wet-test meter was used to measure the sample volume. The results of analyses of hydrogen sulphide–air mixtures are presented in Table II.

Procedure

Pass a metered volume of air through a covered absorbing flask containing 2% cadmium acetate solution. Add a known excess of standard potassium iodate, acidify with a few millilitres of

hydrochloric acid, stopper the outlets, and mix well. Transfer the solution to a titration beaker and titrate as previously described.

DISCUSSION

The blank correction with the starch end-point involves a variation equivalent to 16 to 32 micrograms of sulphur; thus, the determination of microgram quantities of sulphur is subject to considerable error. With the amperometric method, samples containing 10 to 30 micrograms of sulphur can be analysed with a standard deviation of only 1.4 microgram (Table I). This is particularly valuable for the analysis of micro-samples. For example, at the authors' laboratory, the method is used for the determination of sulphide sulphur in de-oiled engine deposits, where in many cases only milligram amounts of sample are available.

The method has also been used for hydrogen sulphide in air. A maximum error of 5% is indicated for the range of 10 to 1200 parts per million (Table II).

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Zusammenfassung—Die Nachweisgrenze des Stärke-Endpunktes in der jodometrischen Titration bei Mikrogramm–Mengen von Sulphid–Schwefel wird durch eine amperometrische Methode verbessert. Man kann die Titration mit einem gewöhnlichen amperometrischen Apparat mit doppel Platin–Elektroden versehen, ausführen. Es wird so eine kleine Menge wie 10 bis 30 Mikrogramm Schwefel mit einer Standard–Abweichung von 1,4 Mikrogramm bestimmt. Die Methode wird zur Bestimmung von Sulphiden in festen Körpern und Schwefelwasserstoff in Luft verwendet.

Résumé—On a pu par une technique amperometrique abaisser d'avantage la limite de sensibilité du point équivalent mis en évidence par l'amidon dans le titrage iodometrique de quantities de sulfure a l'echelle du microgramme. Pour effectuer le titrage on utilisé un montage amperometrique classique pourvu d'une double electrode du platine. On peut doser jusqu'à 10 a 30 microgrammes de sulfure, l'écart-type étant de 1,4 microgramme. On a appliqué cette méthode au dosage des sulfures dans des solides et de H_2S dans l'air.

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SHORT COMMUNICATION

The use of fluorescein complexone

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FOR the complexometric titrations of calcium, strontium, and barium with the indicator fluorescein complexone [Calcein, Fluorexone] Diehl and Ellingboe[1] and others[2,3] use sodium hydroxide solutions of the samples. The alkalinity of such solutions should be about 0·1*N* NaOH. No systematic study of the most suitable medium for these titrations has been published so far. We have studied the fluorescence and colour properties of fluorescein complexone[4,5] and also the reactions with cations of metals other than those mentioned above.[6] Continuing our research we have now found that fluorescein complexone also gives fluorescence reactions with cations of some alkali metals, the reaction with sodium being particularly pronounced. This may be seen from Fig. 1, where the

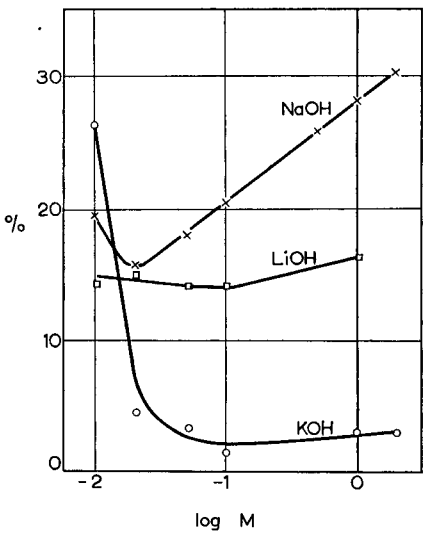

FIG. 1. Dependence of the fluorescence intensities of a 1·2 × $10^{-5}M$ fluorescein complexone on alkali hydroxide concentrations. [Standard: 0·6 × $10^{-5}M$ fluorescein complexone in 0·1*N* KOH with excess of Ca^{2+}.]

fluorescence intensities of the alkaline solutions of the fluorescein complexone (in % as compared with a standard) are plotted against NaOH, LiOH and KOH concentrations respectively. The lowest tendency to form a fluorescent complex with fluorescein complexone is shown by the potassium ion.* On adding sodium chloride to the potassium hydroxide solution of fluorescein complexone the fluorescence increases. This is not the case with an equivalent amount of potassium chloride instead of sodium chloride.

Although in respect of sensitivity the fluorescence reaction of the sodium ion with fluorescein complexone cannot be compared with the analogous reactions of the alkaline earths cations, it is not negligible in the complexometric titrations of these latter metals. There is a great difference in the end-point quality when using sodium or potassium hydroxide for adjusting the samples to be titrated to the required alkalinity. Only potassium hydroxide is satisfactory for this purpose. This applies particularly to barium determination and to indirect sulphate determination.[7]

On the basis of our experiments the avoidance not only of sodium hydroxide but also of other sodium salts in procedures with fluorescein complexone is strongly recommended.

Research Institute for Pharmacy and Biochemistry and J. KÖRBL
Analytical Laboratory of the Czechoslovak F. VYDRA
Academy of Science, R. PŘIBIL
Prague

* Rubidium and caesium ions were not tried.

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Talanta, 1958, Vol. 1, pp. 283-284. Pergamon Press Ltd., London.

PRELIMINARY COMMUNICATION

Elimination of errors in uronic acid determinations

(*Received* 29 *August* 1958)

DURING the past two years a systematic study of the Lefèvre and Tollens[1] decarboxylation method has been made. The form of apparatus described by McCready, Swenson and Maclay[2] has been extensively modified for use on the semi-micro scale. All unnecessary traps and joints have been eliminated; there is no apparatus or reagent "blank", and reproducible results are obtained using 10–15 mg samples of a pure uronic acid, or 20–30 mg of heterogeneous carbohydrate fractions containing 10–50% uronic acid. The CO_2 liberated in the decarboxylation reaction is determined titrimetrically in an absorption trap of special design. The entire apparatus was designed for ease of use in routine analyses, and has been widely used for analysis of carbohydrate fractions isolated by several workers in this department.[3] The apparatus, together with some of the results obtained, will be described fully in a forthcoming issue of this journal.

Using 19% (w/v) aqueous HCl, kinetic studies have shown that, under the experimental contions used, quantitative decarboxylation is not complete in less than 2½ hours. Deviation from the kinetic values of Huber[4] have been found, and decarboxylation using metal ions[5] was not successful. It has been found, however, that traces of metals[6] do have a catalytic effect on decomposition of the non-acidic carbohydrates generally present in a complex uronic acid containing polysaccharide.

It has been reported[7] that amino-sugars and proteins interfere in uronic acid estimations, and also that, in acidic hydrolysis of protein/carbohydrate materials, by-product 5-hydroxymethylfurfural reacts with the protein present.[8] This may be important in analysis of mucopolysaccharides. To date, no interference in uronic acid estimations caused by presence of protein or amino-sugars has been found.

The nature of (*a*) volatile decomposition products from the reaction and (*b*) the solid polymeric materials which form in the reaction flask have been investigated by infra-red spectroscopy and gas chromatography. Contrary to the findings of Bowman and McKinnis,[9] small quantities of carbon monoxide have been found, and the decarboxylation reaction shown to be oxygen-sensitive; further work on this aspect is in progress.

Under the analytical conditions used, the volatile decomposition products from *non-methylated* acidic and non-acidic carbohydrates, either simple sugars or polymers, have been shown to be furan (*not* furfural) and CO_2; the molar ratio of CO_2 to furan produced is dependent on internal configuration. The quantities of CO_2 reported in earlier investigations[10] to be evolved from simple sugars have been generally confirmed. It has been found possible, however, to decrease in some instances the amount of CO_2 evolved by non-acidic substances, by the addition of complex-forming reagents. It is hoped that further work will lead to the general suppression of evolution of CO_2 from undesirable side-reactions to some extent, so making the analytical reaction more specific.

The volatile decomposition products from methyl sugars and from acidic and non-acidic methylated polysaccharides have been shown to include CO_2, methyl chloride, methyl formate, 2-methylfuran and dimethylformal. In analysis of pectins, etc., precautions are therefore necessary to ensure that such substances capable of acidic reaction are not determined together with CO_2. It is hoped that further investigations into these volatile decomposition products will provide some evidence regarding the decarboxylation mechanism.

Full details of the investigations outlined here will be published elsewhere in due course.

The author thanks Professor E. L. Hirst, C.B.E., F.R.S., for his encouragement and interest in this work.

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Department of Chemistry,
The University,
Edinburgh, 9.

D. M. W. ANDERSON

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BOOK REVIEWS

Qualitative Inorganic Analysis. G. CHARLOT, translated by R. C. MURRAY. Methuen, London, 1954. Pp. xi + 354. 42s.

Quantitative Inorganic Analysis. G. CHARLOT and D. BÉZIER, translated by R. C. MURRAY. Methuen, London, 1957. Pp. xi + 691. 84s.

PROFESSOR Charlot has had an excellent idea in bringing together the principles of inorganic and physical chemistry and showing their application to the understanding and development of qualitative analysis. Most practising analysts and teachers of analytical chemistry are aware of these principles, but it is convenient to have them assembled into a text-book. Part I of the text of his qualitative book deals with the theory of the subject, and unfortunately shows signs of careless writing. For example, on p. 5 hydrogen sulphide is said to be a stronger acid than water because sulphur is more electronegative than oxygen (!) whereas on p. 128 the reason given is that the sulphide ion is bigger than the oxide ion. The S^{2-} ion is called the hydrosulphide ion. The definition on p. 45 of condensed ions as "compounds with the ions of water, $Cr_2O_7^{2-}$ for example" is meaningless, and the section on valency theory seems rather inadequate in a modern text. There is a fair amount of repetition in Part I, and quite often ideas are applied in a manner at variance with their initial description. On p. 46, for instance, it is assumed that an increase in ionic strength necessarily implies an increase in activity coefficients. On p. 48 there is confusion between pH and hydrogen ion activities (*e.g.* "Right up to a pH of 9·1, the concentration of Hg ions is independent of pH . . . . Even at pH of 1, approximately 90% of the $Hg(CN)_2$ remains undissociated."). There are a number of typographical errors in this section, some of which may be confusing to the student. On p. 22 V(II+) is said to be reduced to V(IV), and on p. 57 log H^+ is equated with log pH.

Part II deals with the detailed chemistry of most of the elements and has a most useful compilation of equilibrium constants and oxidation potentials. The diagrams showing how solubilities and potentials change with pH are particularly useful. A few minor points should be mentioned however. It is implied on p. 150 that the oxinates of calcium, strontium, and barium do not precipitate in alkaline solution (they come down at pH 9, but dissolve in hot ammoniacal ammonium chloride solution). The statement on p. 137 about the stability of the argentocyanide ion in acid solution seems at variance with that given on p. 88. Perchromates should not be represented by the CrO^{4+} ion (p. 169) and it is at least debatable whether AlO_2^- ions and ZnO_2^{2-} ions exist in solution. The potential of −1·6 volts for the PrO_2/Pr^{3+} couple, and the description of sodium peroxide as a complex of the O_2^- ion are probably printer's errors. Part III gives a brief account of the practical application of the first two parts.

On the whole, this is a useful book which should prove helpful to students of analytical chemistry. The translation seems remarkably free from infelicities, although a few sentences are somewhat vague, notably that on p. 22 referring to equal proportions of oxidant and reductant.

The companion volume on quantitative analysis falls into two parts—one on general principles and methods of analysis, and the other on a systematic description of the determination of the principal elements. Much of the first part of the book on qualitative analysis is repeated in Part I, and in addition there are chapters on sampling, statistics, physical methods, etc. In general, the treatment of the various topics is rather uneven, and sometimes barely adequate. Thus sampling is dealt with in just over a page, emission spectroscopy in five, and radioactivation methods in five and a half, whereas twenty-eight pages are devoted to a very detailed account of electrolysis and another thirty-one to its application.

Part II is a rather uncritical compilation of methods of determination. Many are indicated by a reference and a brief mention of the principle involved; in others an outline of the method is given, but often too sketchily to be of great use. In general the descriptions given are so condensed as to

preclude mention of what may be small but important details of technique (such as the importance of stirring in the determination of aluminium as the oxinate). It is rather surprising to find ferrous ammonium sulphate and ferric alum quoted as primary standards (of guaranteed purity). The error in calcium titrations with EDTA can be reduced from 1–2% (p. 369) to about 0·2% by spectrophotometric detection of the end-point. There are relatively few typographical errors, though +0·1% for +1% on p. 51, and "$n = 1$ measurement" on p. 7 may be confusing.

The translation is, if anything, even more felicitous than that of the companion volume. One feels that at the price the book is more likely to be found in the library than as a personal possession, but in the library it should undoubtedly be.

R. A. CHALMERS

Das Dithizon und seine Anwendung in der Mikro– und Spurenanalyse. GEORG IWANTSCHEFF. Verlag Chemie, Weinheim, 1958. Pp. 272. DM 29.80.

IT is possible that the initial reaction by some to the suggestion of a book on dithizone may be doubt if the reagent has sufficiently wide applicability and interest to merit the writing of a book about its capabilities. It is probably true that such a person will recall that the reagent is excellent for the determination of traces of lead but may be hard pressed to recall many other applications. For such, this book has been written; because it is not a collection of procedures culled from the literature. Indeed, if the claim is correct that all the procedures recommended have been tested and proved in the author's laboratory, the book must be nearly unique among current analytical text-books.

The author is an analytical chemist in the research laboratory of the Siemens-Schuckertwerke AG., Erlangen and has managed to indicate in this publication his obviously very wide knowledge of the subject.

The book consists of five main parts. The first is introductory and deals with dithizone and its inner-complex salts. In the following part, general analytical techniques are considered. Here the basis of methods of determination and separation are discussed, including direct and indirect extractive titrations, single-colour and mixed-colour colorimetric methods and the various techniques which can be used to assist separations.

The "bread and butter" of the book, so to speak, is, however, the section which follows, dealing with the use of dithizone in quantitative analysis. Procedures for eighteen metals are presented, including less familiar metals such as polonium, indium, palladium, platinium, and thallium. So much information is given under each metal that it appears impossible that anything has been missed, and yet the presentation is such that one does not get the feeling of being overwhelmed.

After dealing with the quantitative applications of the reagent, the author illustrates its use in qualitative analysis; and in the final part of the book special applications are discussed, including those in emission spectrographic and polarographic analysis, in adsorption chromatography, and as an indicator in titrimetric analysis.

An appendix contains details of the preparation of dithizone. The bibliography contains hundreds of references, some as recent as 1956. One may feel however after reading this book, if he has an interest in dithizone, that they are superfluous.

This book is recommended to the attention of analytical chemists.

R. J. MAGEE

Gas Chromatography. A. I. M. KEULEMANS. Edited by C. G. VERVER. Reinhold Publishing Corporation, New York: Chapman and Hall, Ltd., London, 1957. Pp. xix + 217. 60s.

THE potentialities of chromatographic separations based on the partition of the components of a volatile mixture between a stationary liquid phase and a moving gas phase were first indicated by Martin and Synge in 1941. It was not, however, until ten years later, when Martin and James demonstrated the feasibility of such separations, that general interest in this technique was aroused.

The subsequent phenomenal rate of growth of that interest has led to a rapidly expanding body of knowledge relating to the technique. Any author attempting to cover a developing field is of necessity at a disadvantage and, in the present instance, the very high rate of development makes the disadvantage a serious one. The author and editor state in their preface to this book that use is made of work published only up to 1st January. 1956. Even work presented at the Dallas and the London Symposia in 1956 had in the main to be omitted, being covered in the more important cases merely by footnotes; and, of course, much has appeared since then. However, the main features of the technique had been delineated by 1956 and it is on these that the author concentrates.

The various types of chromatography are briefly described with a view to systematising nomenclature and defining terms. The main subject matter of the book, namely gas-liquid chromatography, is embarked upon with a brief survey of some typical separations and the effect of the operating conditions thereon. This is followed by a very useful chapter on apparatus. The treatment then becomes theoretical in emphasis and for three chapters (75 pp.) this aspect is explored in relation to the factors which influence resolution; in a further chapter, this treatment is related to the evaluation of thermodynamic parameters. A short chapter on gas-solid chromatography concludes the book. All this is very well done. The style is easy and lucid, and the discussion often revealing. The presentation, including the clarity and helpfulness of the many diagrams, is pleasing. And yet one feels that perhaps this book does not achieve all that one had hoped it might. Having in mind the book's interim nature and the purpose for which it will most often be read, it must be said that the balance of subject matter leaves something to be desired.

In spite of its powers in other directions, gas chromatography has been developed first and foremost as an analytical tool and a book on this subject will be most used by people wanting to solve an analytical problem. Such people would like to find systematised information relating to (*a*) separations already achieved; (*b*) the characteristics of the various stationary liquids, supports and adsorbents available; (*c*) details of apparatus; and (*d*) theoretical treatments to use as a guide in the choice of operating conditions. This book makes no attempt at (*a*); there is not even an alphabetical subject index. Appendix I deals in some measure with (*b*) and will prove very useful. Chapter 3 and Appendix II cover (*c*), but could well have been extended at the expense of some of the following chapters. Great weight has been given to the katharometer for detection, and the author has placed the experience gained in his own laboratory at the disposal of his readers, but a more detailed and critical account of the other methods of detection would have been welcome. As already indicated, a great deal of the book has been devoted to (*d*) and very instructive this section is. Unfortunately, a quantitative theory of gas chromatography is not available. All we have are some semi-quantitative, but mostly qualitative notions of the factors of importance to this technique. These could have been more simply and more forcefully stated in a shorter treatment than given in this book and the analytical chemist will wish that the author had restrained his enthusiasm for and insight into this aspect of his subject. None the less, anybody interested in the difficulties to be surmounted before theoretical treatments become of practical value will find much of interest in this survey.

The book is creditably free from errors, except for some of a trivial character. For example equation (7a), p. 80, should be $\Delta t = -\epsilon(t_u - t_e)$ and the equations derived therefrom adjusted accordingly; equation (10), p. 81, has an "I" too many; p° is the vapour pressure of the solute and not of the solvent as stated on p. 161. It is a pity that the abbreviation "R.V." is used for retention volume after a carefully chosen symbolism has been defined.

To summarize, this is a stylish book which anybody using or thinking of using gas chromatography would do well to read (or even buy, if he can afford it!); it has limitations arising from the distribution of emphasis, but it will do much to enhance the already considerable reputation of gas chromatography as an analytical method.

DESMOND BRENNAN

Papierchromatographie. FRIEDRICH CRAMER. 4., stark erweiterte Auflage; Verlag Chemie, Weinheim/Bergstr., Deutschland, 1958. 215 Seiten, 91 Abb., 8 Farbtafeln. DM 21.

DIE Notwendigkeit einer 4. Auflage in fünf Jahren spricht für die Qualität eines Buches. Die vierte Auflage von Cramers Papierchromatographie ist gegenüber der letzten Auflage hinsichtlich des

Umfanges der Zahl der Tabellen, Abbildungen, Literaturzitate und Farbtafeln fast auf das Doppelte erweitert. Der Charakter des Buches als eine praktische Anweisung für das Laboratorium ist dadurch nicht verlorengegangen. Als neue Abschnitte sind u.a. die Papierchromatographie mit radioaktiven Isotopen, die Trennung von Coenzymen, von Naturfarbstoffen, von Estern und Fetten und für die anorganische Papierchromatographie die Trennung der Phosphorsäuren hinzugekommen. Die neu aufgenommenen Tabellen von Farbreaktionen anorganischer Anionen und Kationen erleichtert für die anorganische Analyse dem Anfänger das umständliche Suchen nach geeigneten Reagentien. Stark erweitert sind die Verfahren zur Trennung von Naturstoffen wie z.B. von Fermenten, Alkaloiden und Vitaminen, ferner die präparativen Vorbereitungen der Ausgangslösungen und der Papiere. Die ausführliche Behandlung der Papierelektrophorese und ihre Aufteilung in die Nieder- und Hochspannungselektrophorese ist bei dieser heute bereits für Serienanalysen angewendeten Methode besonders für den Praktiker zu begrüßen. Die schon bei den ersten Auflagen allgemein anerkannte klare Darstellung und übersichtliche Gliederung des Stoffes wird in der vorliegenden Auflage durch die konsequente Aufteilung in treffend überschriebene Abschnitte noch verbessert. Die Literatur ist bis 1957 erfaßt und gegenüber der letzten Auflage um 200 Zitate erweitert. Bei der großen Fülle der erscheinenden Arbeiten auf dem Gebiet der Papierchromatographie hat der Verfasser eine glückliche Auswahl getroffen, sofern ein Nacharbeiten nach dem Original erforderlich ist. Auch die Beschränkung auf ganz allgemeine Gesichtspunkte für den Reaktionsmechanismus mindert nicht den Wert eines Buches für die Laboratoriumspraxis, da die Theorie des Transportmechanismus noch kein abschließendes Urteil erlaubt und den Rahmen des Buches sprengen würde. Für jeden Chemiker, aber auch für Naturwissenschaftler, die die Papierchromatographie nur als wertvolles Hilfsmittel bei anfallenden chemischen Problemen benutzen, ist das Buch von Cramer wegen seiner ausgezeichneten, leicht verständlichen Darstellung und der klaren Übersicht sehr zu empfehlen. Einband, Druck und Reproduktionen sind hervorragend.

HERMANN SPECKER

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pH Measurements. VICTOR GOLD. Methuen and Co., Ltd., London, 1956. Pp. x + 320. 9s. 6d.
The Book of pH. R. B. WEBBER. George Newnes, Ltd., London, 1957. Pp. 111. 30s.

CHEMISTS are indeed few who have not at some time required to make use of pH measurements. Surprisingly, many scientists still remain vague as to the true chemical concept of pH and its measurement. A thorough discussion of pH, its meaning, physicochemical measurement and application, is attempted in the first of these volumes, which is one of Methuen's Monographs on Chemical Topics. The treatment is, as intended, rigorous.

The book contains nine chapters. The first, introductory in nature, defines pH; and suitable appendices are listed at the conclusion of the book.

Chapter II related the theory of proton transfer with reference to activity coefficient, ionic strength, acidic and basic dissociation constants, and the ionic product of water. This is followed in Chapter III by a study of the principles of galvanic cells using a thermodynamic approach.

Chapters IV and V deal respectively with the interpretation of the pH scale and the techniques used in pH measurement, mainly by e.m.f. methods. The former chapter discusses well the problem of standardising the pH scale, explaining how the practical scale results from a compromise between theory and measurement procedure. The latter chapter describes the practical methods involved in determining pH, tracing the development of various circuits and electrode systems. Three measuring electrodes discussed are the hydrogen electrode, the glass electrode and the quinhydrone electrode.

The role played by proton transfer is next considered in detail (Chapter VI), the emphasis being on the mechanism and kinetics of transfer equilibria. The approach is good, and diagrammatic illustration of the pH changes involved in an acid–alkali titration is given. The kinetics of reaction velocities in relation to pH are then discussed (Chapter VII).

Chapter VIII explains the optical methods of determining pH. Spectrophotometry, absorptiometry, colour-matching and the approximate test-paper method are dealt with in turn. A short treatment of solvents other than water ends a thorough and complete interpretation of pH.

Primarily the book is intended for the non-specialist; yet the thermodynamic approach will make it stiff reading for the general chemist. Also many symbols, particularly in the early stages,

could have been more fully defined and explained. To obtain the maximum benefit from this valuable work, a sound basic knowledge of chemistry is undoubtedly required.

The second of these volumes is meant for the beginner or non-chemist, and its treatment of the subject is accordingly simple and straightforward. The author literally starts from nothing and produces a composite picture.

There are seven sections, of which the first two are introductory, the former promoting a basic idea of pH scale, the latter an interesting preamble, though a trifle long, on the importance of pH in industry. Quite a wide sphere of application is covered, *e.g.*, from bacteriology and allied fields to printing, leather and textiles.

The third section deals with the theory of pH. A chemical picture of matter, elements and compounds, etc., is drawn before the main discussion, which is approached naturally through ionisation, solutions and electrolytes. Acidity, basicity, strength of solutions and chemical titrations are all carefully explained before tackling the main issue of pH value. A discussion on how ionisation, neutralisation and hydrolysis affect pH, along with an account of buffer action conclude this section.

The methods of pH measurement, colorimetric and electrical, constitute the next two sections. Nearly all possible colorimetric methods from the spectrophotometric to use of the B.D.H. Lovibond Nessleriser, are described in one of the sections. In the other the "pH meter" is dealt with; there is a discussion of electrode potentials, the quinhydrone, antimony and glass electrodes, and a description of the potentiometer and electrometer, the main instruments used for measuring potential differences.

The concluding chapters indicate briefly the intricacies involved in a complete study of pH, referring to the activity coefficient of hydrogen, the British Standard pH scale and non-aqueous solutions. Six appendices and a glossary of terms close the book.

The author has presented an excellent elementary approach to the understanding of pH. It should be very useful to technicians and other laboratory personnel, providing a clear picture for the person without chemical training.

JOSEPH DAWSON

Talanta, 1958, Vol. 1, p. 290. Pergamon Press Ltd., London.

NOTICES

The Society for Analytical Chemistry

A Report on *The Use of Radiochemical Methods to Investigate the Recovery of Trace Elements from Organic Materials* will be given by T. T. GORSUCH, B.Sc., A.R.I.C. in the Lecture Theatre of The Royal Institution, 21, Albemarle Street, London, W.1. at 6.30 p.m. on Wednesday 1 October 1958. There will be an introduction by R. SPENCE, C.B., Ph.D., D.Sc. on *Radiochemical Methods.*

Visitors will be welcome. No tickets will be needed.

An Ordinary Meeting of the North of England Section of the Society will be held at 2.15 p.m. on Saturday, 4 October 1958, at the City Laboratories, Mount Pleasant, Liverpool, 3. This will take the form of a discussion on *Laboratory Balances*, to be opened by J. G. LUNT, B.Sc., F.R.I.C. and G. F. HODSMAN, B.Sc., Ph.D. Visitors will be welcome.

An Ordinary Meeting of the Midlands Section of the Society will be held on Wednesday, 8 October 1958, at the Technical College, The Butts, Coventry. A discussion on *The Determination of Trace Impurities in Metals* will be opened by B. BAGSHAWE, A. Met. (*Ferrous Metals*) and W. T. ELWELL, F.R.I.C. (*Non-ferrous Metals*). Visitors will be welcome.

A Discussion Meeting of the Biological Methods Group of the Society will be held at 6.30 p.m. on Thursday, 9 October 1958, in "The Feathers", Tudor Street, (off Bouverie Street, Fleet Street,) London, E.C.4. The subject for discussion will be *Strategy in the Assessment of Disinfectants*, and it will be introduced by G. SYKES, M.Sc., F.R.I.C. Visitors will be welcome.

An Ordinary Meeting of the Midlands Section of the Society will be held at 7.00 p.m. on Tuesday, 14 October 1958, in the Gas Showrooms, Nottingham. A discussion on *The Identification of the New Permitted Food Colours* will be opened by P. S. HALL, F.R.I.C. Visitors will be welcome.

A Joint Meeting of the Physical Methods Group and the North of England Section of the Society with the Modern Methods Analysis Group of the Sheffield Metallurgical Association will be held at 7.00 p.m. on Tuesday, 21 October 1958, in the Conference Room of the British Iron and Steel Research Association, Hoyle Street, Sheffield, 3. Two papers will be presented and discussed: *The Determination of Gases in Metals by the Microvacuum Fusion Method*, by E. BOOTH, B.Sc., and *The Determination of Oxygen and Hydrogen in Steel*, by C. E. A. SHANAHAN, B.Sc., F.R.I.C., F.I.M. Visitors will be welcome.

Talanta, 1958, Vol. 1, pp. 291–292. Pergamon Press Ltd., London.

BOOKS RECEIVED

Methods of Analysis for Petrochemicals. E. R. LITTMANN. Chemical Publishing Co., Inc., New York, 1958. pp. 384. $12.00.

Modern Manufacturing Formulary. EMIL J. BELANGER. Chemical Publishing Co., Inc., New York, 1958. pp. 399. $10.00.

Trace Analysis. JOHN H. YOE and HENRY J. KOCH, Jr. John Wiley and Sons, Inc., New York, 1957. pp. xiii + 672. $12.00.

Qualitative Testing and Inorganic Chemistry. JOSEPH NORDMANN. John Wiley and Sons, Inc., New York, 1957. pp. xii + 488. $6.25.

PAPERS RECEIVED

Chelatometric Determination of Cobalt and Iron using a Fluorescent End-Point. Donald H. Wilkins. (1 *July* 1958.)

Gravimetric Determination of Osmium with 1:2:3-Benzotriazole. Ray F. Wilson and Lawrence J. Baye. (3 *July* 1958.)

Quantitative Determination of Fission and Nuclear Reaction Products. C. E. Crouthamel, Robert Heinrich and Christopher Gatrousis. (4 *July* 1958.)

Determination of Vanadium in High-Alloy Steels by Isotope-Dilution. G. Leliaert, J. Hoste and J. Eeckhaut. (7 *July* 1958.)

Apparatus for Titrations using Ultraviolet Light. Donald H. Wilkins. (18 *July* 1958.)

Studies on Organic Reagents for Inorganic Analysis, V. *m*-Nitrophenylfluorone for the Spectrophotometric Determination of Zirconium. Hirotoshi Sano. (18 *July* 1958.)

A Spectrophotometric Method of Determining Sulphuric Acid Content. Elaine Zimmerman and Warren G. Brandt. (28 *July* 1958.)

Determination of Small Amounts of Cobalt in Titanium, Zirconium and Their Alloys. R. E. Wood and R. T. Clark. (6 *August* 1958.)

Polarographic Determination of Dibutyl Phthalate in Propellant Compositions Containing Nitroglycerine. A. F. Williams and D. Kenyon. (6 *August* 1958.)

The Historical Development of the Public Analyst and his Work in Great Britain. G. V. James. (9 *August* 1958.)

Untersuchung zur extraktiven Trennung von Gallium und Indium mit verschiedenen Lösungsmitteln. H. Specker. (19 *August* 1958.)

Analytical Applications of Xylenol Orange—I: Determination of Traces of Zirconium. K. L. Cheng. (19 *August* 1958.)

The Use of Molecular Filter Membrane in Mounting and Assaying of Radioactive Precipitates. R. E. Jervis. (26 *August* 1958.)

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

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