

THE DETERMINATION OF SOME LESS COMMON ANIONS

R. BELCHER

Department of Chemistry, The University, Birmingham 15, UK

ABSTRACT

Developments in the determination of some less common anions and in the separation of anions of similar species are described. The anions which are considered are the Group Va hexafluorides, vanadates, tungstates, the per-acids, oxyanions of phosphorus and some organic acids. A new method for the determination of chloride, based on GLC, and capable of very high sensitivity is mentioned. This method could probably be applied to the simultaneous determination of chloride, bromide and iodide at very low concentrations.

In general, anions have provided more difficulties in their determination than cations, but in recent times many of the older problems have either disappeared or appear likely to be solved soon, partly because of the development of new techniques and partly because of the discovery of new reagents and reactions¹. Despite these advances, however, some new problems have arisen during the last decade. New anions have been prepared and have become of commercial importance. Moreover, anions having very similar chemical properties, which were once grouped together for convenience, now require to be differentiated because of their industrial importance, e.g. the oxyanions of phosphorus. Several investigators have examined these problems and notable progress has been made; the present account describes some of these advances.

HEXAFLUOPHOSPHATE, -ARSENATE AND -ANTIMONATE

These anions are very similar in chemical behaviour, especially hexafluophosphate and fluoarsenate; fluoantimonate is much more readily hydrolysed. Their applications are wide and have been described in several reviews²⁻⁶. Lange⁷ and his co-workers, who first synthesized hexafluophosphate in 1928, noted that the reactions were very similar to those of perchlorates and the first determinations were made by precipitating and weighing the nitron salt. The less stable difluoride also precipitated, but this interference could be eliminated by first hydrolysing. No other reagents were to be used for more than a quarter of a century.

Dess and Parry⁸ determined hexafluoroarsenate gravimetrically after precipitation with tetraphenylarsonium chloride (TPA); a similar method for hexafluophosphate was described some years later⁹ by Affsprung and Archer. A comparison was made with the nitron method and it was

shown that TPA produced the more insoluble precipitate and was far less susceptible to co-precipitation. Although difluophosphate also precipitated, it was readily removed by prior hydrolysis. Monofluophosphate, phosphate and fluoride did not interfere.

The same authors also described an amperometric method using TPA as titrant¹⁰ and a spectrophotometric-extraction method¹¹; the latter is based on formation of the ferriin salt which is extracted into *n*-butyronitrile. This is an extension of an earlier method developed for the determination of perchlorate¹². The same procedure was shown to work equally well for the determination of hexafluoroarsenate¹³.

Up to this period, no direct method for the determination of hexafluoroantimonate was available; hence Archer and Twelves¹⁴ examined the possibilities of applying the methods which had proved successful for the other two Group Va hexafluoride anions. Two gravimetric methods, based on precipitation with nitron and TPA, and a ferriin extraction method were developed. All methods were satisfactory and the tendency of this anion to hydrolyse was readily overcome by dissolving in dimethylformamide and adding suitable amounts of this stock solution to the various reagents. In all these methods, anions which precipitated or extracted with the various reagents interfered. However, it was considered that hydrolysis products had negligible interference and this was checked experimentally.

An interesting method has been described recently by Behrends¹⁴. Either hexafluorophosphate or hexafluoroarsenate is titrated with TPA in the presence of 1,2-dichloroethane and a trace of potassium permanganate as indicator. At the end-point, TPA permanganate is formed and passes into the organic layer. The end-point is detected either visually or, preferably, photometrically.

It will have been observed that TPA has proved to be a valuable reagent for the determination of the Group Va hexafluorides. This reagent was first proposed by Willard and Smith¹⁶; it can be used for the precipitation of perchlorate, permanganate, perrhenate, periodate and certain other ions. Tetraphenylphosphonium (TPP) and tetraphenylstibonium (TPS) chlorides were later recommended by Willard and Perkins¹⁷. In general, the reactions are similar to those of TPA, but in one or two instances there are some advantages. A detailed examination of the arsonium reagents has been made by Loach¹⁸⁻²⁰.

Although none of these methods differentiates between the Group Va hexafluorides, it is unlikely that they would be present together. If they were, the only problem would be to differentiate between hexafluorophosphate and hexafluoroarsenate, for the hexafluoroantimonate could be readily eliminated by hydrolysis. The methods are quite selective in differentiating a particular Group Va hexafluoride from associated anions, which is the most important requirement.

VANADATE AND TUNGSTATE

TPP has proved useful for differentiating certain anions from closely allied species. For example, TPP precipitates only the decavanadate from solutions containing other vanadium(v) anions²¹. The precipitate has the composition $[(C_6H_5)_4P]_3H_3V_{10}O_{28}$; it is soluble in ethylene chloride.

The anion is determined by extracting the TPP compound into ethylene chloride and measuring the absorbance.

In textbooks of qualitative analysis, pyro- and metavanadates are distinguished by their reactions with copper(II) sulphate. The metavanadate is said to give a green precipitate and the pyrovanadate a yellow precipitate. Carter²² has recently shown that these statements are incorrect and it is the converse which is true. Both precipitates are basic copper vanadates, but have different $\text{CuO}:\text{V}_2\text{O}_5$ ratios. The yellow metavanadate precipitate has the composition, $8\text{CuO}\cdot 3\text{V}_2\text{O}_5\cdot 8\text{H}_2\text{O}$ and the green pyrovanadate precipitate, $5\text{CuO}\cdot \text{V}_2\text{O}_5\cdot 6\text{H}_2\text{O}$. It is noted that the mineral turanite has the latter composition and is green.

In the iso- and heteropolytungstate series, only the anions of the form $\text{XW}_{12}\text{O}_{40}^{(8-n)-}$ (where n is the oxidation number of X) are precipitated by TPP²³. The dodecatungstate is precipitated quantitatively. By the use of this reagent it was possible to study potentiometrically the formation of dodecatungstate under various conditions of pH, time, temperature and dilution.

It is of interest to note that Dupuis²⁴ while studying the precipitation of tungstates with chloropentammine cobalt(III) chloride observed that at pH 2.0–3.1 the metatungstate was precipitated, and at pH 5.1–6.8, the paratungstate; these precipitates are quite pure. At pH 3.9–4.5 and pH 9.0 the tritungstate and normal tungstate are formed respectively, but the composition is not constant.

THE PER-ACIDS

The most important and interesting member of this group of anions is undoubtedly perchlorate. It can hardly now be considered as a less common anion, in view of the extensive use of perchloric acid and perchlorates in many analytical processes. Nevertheless, the determination of perchlorate has always presented certain problems and for this reason, some recent developments are included in this section. Other anions of this group are perbromate, periodate, perrhenate and pertechnetate. Permanganate, which is also a member of the group, will not be considered further; because of its higher oxidation potential, its analytical chemistry poses no problems. Its precipitation reactions are only of academic interest.

Perchlorate

The perchlorate ion is comparatively inert and only powerful reductants react with it; accordingly there are few titrimetric methods available, based on redox reactions. At one time hardly any insoluble perchlorates were known, apart from those of the heavier alkali metals, but several precipitants are now available. In 1928, Lange and Mueller²⁵ pointed out that the reactions of perchlorate are very similar to those of hexafluorophosphate (and hence, by inference, to the other Group Va hexafluorides). This observation has served as a useful guide in the development of methods of analysis for the latter compounds, and led to the introduction of reagents such as nitron, TPA and TPP.

Possibly the best methods for the rapid determination of perchlorate are those which use powerful reductants such as titanium(III), but these

involve problems of storage and blank determinations. It has been shown that vanadium(III) sulphate is an efficient reductant²⁶. The chloride formed is titrated potentiometrically with silver nitrate or alternatively the vanadium(IV) produced is determined spectrophotometrically; the excess of reagent does not have to be removed for the silver nitrate titration.

The solid reagent is added with OsO_4 catalyst to the solution, which is boiled for five to ten minutes, cooled and titrated. When vanadium(IV) is measured a correction for the absorbance of vanadium(III) must be applied.

TPA, long known as a precipitant for perchlorate, has been used as a titrant for perchlorate²⁷. Ion-selective electrodes were used for potentiometric detection of the end-point. When low temperatures (2°) were used to sharpen the curves, as little as 0.05 m.mol. of perchlorate could be determined. Tetrafluoroborate could be determined similarly. TPS has also been recommended for the amperometric titration of perchlorate²⁸.

Dosch²⁹ has found recently that tetra-*n*-pentyl ammonium bromide is a selective precipitant for perchlorate. Interferences are few and an efficient separation from chlorate is obtained, provided that the latter is present in no more than equivalent amounts. When it is in excess, it is better to reduce the chlorate to chloride. So far only a gravimetric procedure has been developed but it is suggested that titrimetric methods should be possible. The reagent appears to have several advantages over TPA, TPP and TPS.

A novel method for trace amounts of perchlorate has been described and is based on displacement of the erdmannate³⁰. When the liquid ion-exchanger, tetra-*n*-hexylammonium iodide, dissolved in a suitable solvent, is treated with Erdmann's salt, a solution of the quaternary ammonium erdmannate is produced. When this is shaken with an aqueous solution of a salt the coloured erdmannate is displaced to an amount depending on the nature of the anion. Perchlorate is displaced more than all other anions and can be determined in the presence of chlorate, nitrate, sulphate etc. The absorbance of the erdmannate in either layer provides a measure of the perchlorate present. The lowest limit of determination is $25 \mu\text{g}$ of ClO_4^- .

This method might also be of value for the determination of the Group Va hexafluorides.

Perbromate

Until 1968, it was believed that the perbromate ion, BrO_4^- , could not be prepared. Since that time, however, several methods have been discovered^{31, 32}, the most convenient being the oxidation of bromate in alkaline solution by fluorine:



Perbromate behaves similarly to perchlorate apart from its redox properties. Acidification gives a solution of perbromic acid, HBrO_4 , which is a strong acid. A 6*N* solution of the acid is stable almost indefinitely at room temperature, and decomposes only slightly (with release of bromine) after boiling for an hour.

Perbromate is a sluggish oxidant. Although it is more active than the perchlorate ion in aqueous solutions, it is decidedly less effective than the periodate or bromate. Although 1*M* hydrobromic acid rapidly reduces

bromate or periodate, 12M hydrobromic acid is required to reduce perbromate. In dilute solution, perbromic acid oxidizes iodide and bromide only very slowly, whilst chloride is not affected. At 100°, however, 6M perbromic acid rapidly oxidizes manganese(II) to manganese dioxide, chromium(III) to dichromate and cerium(III) nitrate to cerium(IV) nitrate. At this temperature silver ions catalyse the decomposition of perbromic acid. A 3M solution of the acid readily oxidizes stainless steel.

The white potassium perbromate has an aqueous solubility of 0.2M. When heated, potassium perbromate decomposes exothermically at 280° to potassium bromate, and then to potassium bromide at 395°.

The first methods for determining perbromate depended on reduction by 12M HBr to Br_3^- followed by iodimetry or reduction to Br^- , or by conversion to BrCN followed by iodimetry. Although both methods are accurate, they are long and tedious and are probably only suitable for relatively pure solutions. When other bromine species are present, a preliminary step is necessary to remove them.

Brown and Boyd³³ adapted the crystal violet extraction method used originally for the determination of perchlorate³⁴. This enables $1-10 \times 10^{-6}\text{M}$ BrO_4^- to be determined by spectrophotometric measurement in the presence of 1000-fold amounts of bromate or bromide. The method is rapid and accurate.

Periodate

Periodate is comparatively easy to determine, owing to its reactive redox properties. The only problems likely to be encountered are when other oxidizing ions are present. Even so, it is a fairly simple matter to differentiate such anions, e.g. periodate and iodate, by determining the sum of the two anions, followed by selective reduction on another aliquot. Recently, a new method has been described which enables the two anions to be determined successively in the same sample³⁵.

The reaction method depends on the masking action of molybdate ions on periodate, to form the heteropoly acid, $\text{H}_5[\text{I}(\text{MoO}_4)_6]$. Iodide is added and only reacts with iodate. After titration of the released iodine, oxalic acid is added to demask the periodate (by formation of molybdeno-oxalic acid) which then liberates an equivalent amount of iodine from the remaining iodide. The titration is then completed.

This masking reaction has been applied in several analytical processes³⁶.

Perrhenate and pertechnetate

Titrimetric methods for the determination of these two anions generally depend on reduction followed by oxidimetric titration. These methods, for various reasons, do not seem to be popular, and gravimetric methods are more generally preferred. Various inorganic precipitants have been tried, e.g. thallium(I) or silver, but are not satisfactory owing to the appreciable solubilities of the precipitates³⁷. TPA has been used for the determination of perrhenate, both gravimetrically and titrimetrically, but nitron is the most widely used reagent. Even so, it gives poor results with less than 5 mg. The pertechnetates of both these bases are even more soluble than the corresponding perrhenates.

Morton and Stephen³⁸ examined *N*-(*p*-chlorobenzyl)-1-naphthylmethylamine and di-(1-naphthylmethylamine) as reagents for both anions. The latter reagent was found preferable because of the greater permissible variation of conditions. In the determination of perchlorate it is equivalent to nitron in sensitivity and selectivity, but is more easily prepared.

The precipitate with perchlorate has about the same solubility as that of nitron perchlorate, but these investigators did not have sufficient sample to examine the quantitative aspects.

Undoubtedly, there is great room for improvement in the analytical chemistry of these two anions.

Oxyanions of phosphorus

The separation of the complex phosphates has been one of the major problems of analytical chemistry. Chromatographic³⁹ and ion-exchange^{40,41} methods have been studied widely and it is only by such methods that a complete analysis of these complex mixtures can be made.

It is of great interest to note that the reagent recommended by McCune and Arquette in 1955⁴² for the determination of triphosphate, tris-ethylenediamine cobalt(III) chloride, has not been improved on. A large number of coordination compounds has been examined as precipitants for condensed phosphates, but were inferior to tris-ethylenediamine cobalt(III) chloride⁴². Hexa-urea chromium(III) chloride is said to precipitate pyrophosphate quantitatively, but details of the procedure have not been obtained⁴³.

Burns *et al.*⁴⁴ have developed a valuable scheme for the identification of various oxyanions of phosphorus using chemical methods. By simple precipitation and colour reactions they were able rapidly to detect in various mixtures, trimetaphosphate, tetrametaphosphate, orthophosphate, pyrophosphate, tripolyphosphate, hypophosphite, phosphite and hypophosphate. It was not found possible to distinguish between the various high molecular weight compounds examined and these had to be grouped collectively as high molecular weight phosphate. For separation and identification of the latter, probably chromatographic methods are suitable. Nevertheless, this method was much faster than chromatographic methods with the compounds examined, taking 20 minutes as against one hour. As an example of the selectivity of the tests, trimetaphosphate and tetrametaphosphate are distinguished because only the latter gives a precipitate with hexamino cobalt(III) chloride; pyrophosphate and tripolyphosphate can be distinguished by their reactions with tris-ethylenediamine cobalt(III).

Polarographic methods have achieved some success for the determination of polyphosphate ions. As early as 1942, Cohn and Kolthoff⁴⁵ determined pyrophosphate by precipitating $\text{Cd}_2\text{P}_2\text{O}_7$. They dissolved the precipitate in dilute hydrochloric acid and measured the cadmium polarographically; 9–44 mg of pyrophosphate ions could be determined. When the precipitate was formed at pH 3.6 (acetate buffer) orthophosphate was without effect. Tripolyphosphate was precipitated with tris-ethylenediamine cobalt(II) chloride⁴⁶ at pH 3.6, and the excess of cobalt complex could be determined polarographically without filtration. Recently⁴⁷, we have found that tripolyphosphate forms a soluble complex with cadmium, which has no polarographic wave. It is a simple matter in this instance to determine the

tripolyphosphate by adding a known excess of cadmium ions and measuring the difference. When a trimetaphosphate buffer, pH 7, is used tri- and tetrametaphosphate do not interfere, and up to 5 mole % of pyrophosphate can be tolerated.

ORGANIC ACIDS

The ferroin extraction process mentioned earlier provides a selective method for the determination of trichloroacetate⁴⁸. The absorbance is measured after extraction with nitrobenzene. Phosphate and sulphate, even in large amounts, do not interfere, nor do moderate amounts of chloride, acetic acid and monochloroacetic acid. Dichloroacetic acid in equivalent amounts gives a slight positive error.

The cuproin or neocuproin copper(I) complexes are used to determine phthalic acid; the ion-pair is extracted into methyl isobutyl ketone. The determination is completed either spectrophotometrically⁴⁹ or by spraying the extract directly into a flame and measuring the copper by atomic absorption⁵⁰. Equivalent amounts of isophthalic and terephthalic acids do not interfere.

Pentachlorophenol may also be determined by a similar method using atomic absorption spectroscopy. In this method ferroin is used to form the ion-pair which is extracted into nitrobenzene⁵¹.

The application of copper(II) as a precipitation titrant for organic acids with polarovoltic indication of the end-point, was examined by Ashworth and Fehringer⁵². Although such methods have been described with visual detection of the end-point, instrumental indication has been hardly used. The lower fatty acids formed salts which were too soluble to provide an end-point; lauric acid was the first to give a detectable end-point. Myristic, palmitic and stearic were also titrated. Various other compounds were titrated satisfactorily, e.g. 8-hydroxyquinoline, sodium lauryl sulphate and some other phenols.

The method has a fair degree of selectivity in that higher fatty acids can be titrated in the presence of lower members of the series; and picric acid in the presence of some other substituted phenols. The whole procedure also has the merit of simplicity.

The advantages of enzymatic methods for the determination of organic acids have been described by Guilbault and his co-workers⁵³. They have developed methods for the analysis of mixtures containing a selection of 21 organic acids. Six enzyme systems are used, each system being selective for a particular group of acids.

The methods are based on the conversion of resazurin to the highly fluorescent resorufin. In the concentration range 0.1–500 μg an accuracy and precision of the order of two per cent was obtained.

The methods appear to be of great promise, especially for the analysis of complex mixtures.

To complete this section on organic acids reference is made to the application of an unusual and interesting reagent, xenon trioxide, to the determination of certain organic acids⁵⁴.

This reagent is a powerful oxidant, the redox potential in acidic solution

being 1.8V and in alkaline solution, 0.9 V. It oxidizes diols, alcohols and organic acids to carbon dioxide and water.

Organic acids were determined by treating with a solution of the xenon trioxide and determining the excess of reagent iodimetrically. Dicarboxylic, trihydroxy and amino acids were determined. Amounts as low as 100 µg can be determined but trace impurities of other easily oxidizable substances such as amines, primary and secondary alcohols would interfere. It is possible that monocarboxylic acids could be determined if the solution were buffered at pH 6-8.

As the reactions of xenon trioxide with organic acids proceed at different rates, differential kinetic methods might be used for the analysis of mixtures. This is an interesting possibility, but it would be necessary first to know much more about the basic reactions of xenon trioxide with organic acids.

In conclusion, I should like to mention a new method which has been developed in our Department, for the determination of trace chloride. Although this is by no means a less common anion, an entirely new approach has been used and remarkable sensitivity has been achieved.

Chloride in aqueous solution is treated with phenyl mercuric nitrate and extracted with benzene. Phenyl mercuric chloride is formed quantitatively and passes into the organic solvent. An aliquot is injected into a GLC apparatus where the phenyl mercuric chloride gives a characteristic peak. A sensitivity of 0.001 p.p.m. may be obtained: if more sensitive detectors are used, this sensitivity may be improved. It should also be possible to determine chloride, bromide and iodide simultaneously and further investigations to achieve this end are in progress.

REFERENCES

- ¹ R. Belcher, Lecture at BP Symposium, Brighton, 5 May 1971.
- ² J. H. Simons, *Fluorine Chemistry*, Academic Press: New York, Vol. I (1950), Vol. II (1954), Vol. V (1964).
- ³ I. G. Ryss, *The Chemistry of Fluorine and Its Inorganic Compounds*, State Publishing House for Scientific, Technical, and Chemical Literature, Moscow (1956), English Transl. AEC-tr-3927, Office of Technical Services, US Dept of Commerce, Washington, D.C.
- ⁴ *The Chemistry and Chemical Technology of Fluorine*, Vol. IX, pages 550-551 and 635-649, Interscience: New York (1966).
- ⁵ R. Schmutzler, *Fluorides of Phosphorus*, 'Advances in Fluorine Chemistry', Vol. V, p. 31, (1965).
- ⁶ G. I. Drozd, *Russian Chem. Reviews*, **31**,(1), 1 (1970).
- ⁷ W. Lange and K. Askitopoulos, *Z. Anorg. Allgem. Chem.* **223**, 369 (1935).
- ⁸ H. Dess and R. W. Parry, *J. Am. Chem. Soc.* **79**, 1589 (1957). [H. M. Dess, *Ph.D. Thesis*, University of Michigan (1955)].
- ⁹ H. E. Afsprung and V. S. Archer, *Analyt. Chem.* **35**, 1912 (1963).
- ¹⁰ H. E. Afsprung and V. S. Archer, *Analyt. Chem.* **35**, 976 (1963).
- ¹¹ V. S. Archer and F. G. Doolittle, *Analyt. Chem.* **39**, 371 (1967).
- ¹² J. S. Fritz, J. E. Abbink and P. A. Campbell, **36**, 2123 (1964).
- ¹³ V. S. Archer and F. G. Doolittle, *Talanta*, **14**, 921 (1967).
- ¹⁴ V. S. Archer and R. B. Twelves, **15**, 47 (1968).
- ¹⁵ K. Behrends, *Z. Anal. Chem.* **250**, 246 (1970).
- ¹⁶ H. H. Willard and T. M. Smith, *Industr. Engng. Chem (Analyt.)*, **11**, 186 and 269 (1939).
- ¹⁷ H. H. Willard and L. R. Perkins, *Analyt. Chem.* **25**, 1934 (1953).
- ¹⁸ K. W. Loach, *Anal. Chim. Acta*, **47**, 315 (1969).
- ¹⁹ K. W. Loach, *Anal. Chim. Acta*, **44**, 323 (1969).
- ²⁰ K. W. Loach, *Anal. Chim. Acta*, **45**, 93 (1969).

THE DETERMINATION OF SOME LESS COMMON ANIONS

- ²¹ C. Liteanu, I. Luckacs and C. Strusievici, *Anal. Chim. Acta*, **29**, 574 (1963).
- ²² A. H. Carter, *Mikrochim. Acta*, 1097 (1969).
- ²³ R. Ripan and C. Calu, *Talanta*, **14**, 887 (1967).
- ²⁴ T. Dupuis, *Mikrochim. Acta*, 851 (1955).
- ²⁵ W. Lange and E. Mueller, *Ber. Dtsch. Chem. Ges.* **63**, 1058 (1930).
- ²⁶ D. A. Zatko and B. Kratochvil, *Analyt. Chem.* **37**, 1560 (1965).
- ²⁷ M. J. Smith and S. E. Manahan, *Anal. Chim. Acta*, **40**, 315 (1968).
- ²⁸ M. Morris, *Analyt. Chem.* **37**, 977 (1965).
- ²⁹ R. G. Dosch, *Analyt. Chem.* **40**, 829 (1968).
- ³⁰ W. W. Clifford and H. Irving, *Anal. Chim. Acta*, **31**, 1 (1964).
- ³¹ E. H. Appelmam, *J. Am. Chem. Soc.* **90**, 1900 (1968).
- ³² E. H. Appelmam, *Inorg. Chem.* **8**, 223 (1969).
- ³³ L. C. Brown and G. E. Boyd, *Analyt. Chem.* **42**, 291 (1970).
- ³⁴ S. Uchikawa, *Bull. Chem. Soc. Japan*, **40**, 1798 (1967).
- ³⁵ R. Belcher and A. Townshend, *Anal. Chim. Acta*, **41**, 395 (1968).
- ³⁶ G. Nisli and A. Townshend, *Talanta*, **15**, 411, 1377 and 1480 (1968).
- R. Belcher, J. W. Hamya and A. Townshend, *Anal. Chim. Acta*, **49**, 570 (1970).
- R. Belcher, J. W. Hamya and A. Townshend, *Chimie Analitica*, **1**, 23 (1971).
- ³⁷ M. H. B. Morton, *M.Sc. Thesis*, University of Birmingham (1967).
- ³⁸ M. H. B. Morton and W. I. Stephen, *Anal. Chim. Acta*, **44**, 147 (1969).
- ³⁹ F. M. Pollard, G. Nickless, K. Burton and J. Hubbard, *Microchem. J.* **10**, 133 (1966).
- ⁴⁰ H. L. Rothbart, H. W. Weymouth and W. Rieman III, *Talanta*, **11**, 33 (1964).
- ⁴¹ H. L. Rothbart and W. Rieman III, *Talanta*, **11**, 43 (1964).
- ⁴² H. W. McCune and G. J. Arquette, *Analyt. Chem.* **27**, 401 (1955).
- ⁴³ J. N. Brazier, *Ph.D. Thesis*, University of Birmingham (1967).
- ⁴⁴ D. T. Burns, J. D. Lee and L. G. Harris, *Mikrochim. Acta* in press (1972).
- ⁴⁵ G. Cohn and I. M. Kolthoff, *Industr. Engng. Chem. (Analyt.)*, **14**, 886 (1942).
- ⁴⁶ E. M. Golubchik, *Zavod. Lab.* **35**, 926 (1969).
- ⁴⁷ F. A. Sulimany and A. Townshend, *Analyst*, in press.
- ⁴⁸ Y. Yamamoto, T. Kumamaru and Y. Vemura, *Anal. Chim. Acta*, **39**, 51 (1967).
- ⁴⁹ Y. Yamamoto, N. Okamoto and E. Tao, *Anal. Chim. Acta*, **47**, 127 (1969).
- ⁵⁰ T. Kumamaru, Y. Hayashi, N. Okamoto, E. Tao and Y. Yamamoto, *Anal. Chim. Acta*, **35**, 524 (1966).
- ⁵¹ Y. Yamamoto, T. Kumamaru and Y. Hayashi, *Talanta*, **14**, 611 (1967).
- ⁵² M. R. F. Ashworth and R. Fehringer, *Anal. Chim. Acta*, **35**, 111 (1966).
- ⁵³ G. G. Guilbault, S. H. Sadar and R. McQueen, *Anal. Chim. Acta*, **45**, 1 (1969).
- ⁵⁴ B. Jaselskis and R. H. Krueger, *Talanta*, **13**, 945 (1966).