The Analyst

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Summaries of Papers in this Issue

Analysis of Silicates—Ceramic and Geochemical
A Review

Summary of Contents

Introduction
Chemical Methods
   Schemes for "complete" analysis
     Sample preparation
   Individual determinations
     Decomposition
     Silicon
     Aluminium
     Iron
     Titanium
     Calcium
     Magnesium
     Alkali metals
Instrumental analysis
   Emission spectroscopy
   Atomic-absorption spectrophotometry
   X-ray fluorescence spectroscopy
Possible future trends

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Stability of Iron(III) - Thiocyanate Complexes and the Dependence of Absorbance on the Nature of the Anion

The dependence of the colour intensity of the iron(III) - thiocyanate complex formed at two different ratios of thiocyanate to iron on the nature and concentration of the acid anion was studied. Four different acids were tested over the concentration range 0.05–1.0 N: perchloric acid, nitric acid, hydrochloric acid and sulphuric acid. Fading of the iron(III) - thiocyanate colour was ascribed to a specific effect of the anion caused by progressive masking of iron(III) ions of the highly dissociated iron(III) - thiocyanate by the more strongly complexing anion ligand. The results were interpreted in the light of the calculated values of side-reaction coefficients between iron(III) and the added ligand, as well as on the magnitude of conditional stability constants of iron(III) - thiocyanate in the various media. That the order of effectiveness of the added anions towards complexing iron(III) ions is $SO_4^{2-} > Cl^- > NO_3^- \geqslant ClO_4^-$ was further substantiated.

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Determination of Selenium in Blood and Plant Material by Hydride Generation and Atomic-absorption Spectroscopy

A method is described for the routine determination of selenium in blood and plant samples at concentrations in the range 0.01–0.50 μg g^{-1}. Samples of mass 1 g are digested with nitric and perchloric acids and then selenium hydride is generated from diluted digests by the controlled introduction of a solution of sodium borohydride. The selenium is subsequently atomised in a nitrogen - hydrogen - entrained air flame. Digests can be analysed at a rate of four per minute. For a pasture sample, which contained a 0.038 μg g^{-1} concentration of selenium, and a blood sample, which contained 0.029 μg g^{-1} of selenium, relative standard deviations of 7.9 and 4.3%, respectively, were obtained. The mean recovery of added selenium was 100.5%, with a relative standard deviation of 4.7%. The efficiency of hydride generation was 95%.

Keywords: *Selenium determination*; *blood*; *plant materials*; *atomic-absorption spectrophotometry*; *hydride generation*

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Loss of Trace Elements During Dehydration of Marine Zoological Material

Possible losses of trace elements during dehydration of marine zoological material with a high water content were studied by means of radioactive tracers, using the oyster *Crassostrea gigas* as an example. It is probable that no losses occurred with chromium, iron, manganese, cobalt and zinc, but serious losses of selenium, cadmium and lead were observed, both during freeze drying and oven drying at low temperatures. The analytical applicability of dehydration techniques in general thus requires re-assessment.

Keywords: *Trace element loss*; *dehydration*; *marine zoological material*; *radiotracers*

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Detection of the Presence of BHA by a Rapid Spectrofluorimetric Screening Procedure

A rapid screening procedure for detecting BHA in miscellaneous materials such as foodstuffs is presented. It is based on the sensitive fluorimetric detection of BHA following its isolation from complex sample matrices by steam distillation. Because of the sensitivity achieved, only small samples are required and time-consuming extractions of the antioxidant are eliminated. The rationale for the procedure, and some of its limitations, are discussed.

Keywords: *Butylated hydroxyanisole detection*; *foodstuffs*; *steam distillation*; *spectrofluorimetry*

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Keywords: *Review*; *silicate analysis*; *ceramics*; *geochemistry*

Introduction

This is a particularly appropriate time at which to review the analysis of silicates because, after a period of intense change and development since the end of the Second World War, at present there appears to be a period of relative stability. Chemical methods, both accurate standard and "rapid" procedures, are not only fully developed, but are tending to fall into disuse. Most analytical needs, in both geochemistry and the ceramic and allied industries, are being met by instrumental methods, X-ray fluorescence spectroscopy where throughput is sufficiently high and atomic-absorption spectroscopy in smaller units. This situation has removed the urgency of the need for improved "wet" chemical procedures and although papers are still appearing regularly on this topic, they are commonly peripheral. Both X-ray fluorescence and atomic-absorption spectroscopy have progressed through their periods of infancy and growth and now appear as techniques fully capable of answering the demands made upon them. The acceptance of the fused, cast bead technique in X-ray fluorescence spectroscopy has enabled analyses to be carried out that can be bettered only by chemical work of the highest accuracy. As a result, most analysts who have these instruments available must be anticipating a fairly lengthy period of stability.

It is, therefore, the intention within this review to survey the whole of this formative period, from the mid-1940s to the present day, as an entity with a beginning, a development and an end. It is realised that the end is not a full stop, probably merely a colon, but as the pause has occurred it is logical to take advantage of it. The review also tries to take in two parallel streams of action, that being pursued by the geochemist and that by the ceramic analyst, in particular the refractories' analyst. The reviewer falls into the second category, and the review almost certainly reflects this field of interest. The apparently obvious fact that the ceramic industries' raw materials are a significant part of the range of interest

of the geochemist seems consistently to be overlooked. Papers to be found in the geochemical journals are rarely seen by the ceramic analyst and, similarly, papers in glass or ceramic journals remain unnoticed by the geochemist. Only when publication is made in the analytical journals does the cross-fertilisation take place. It is true that the information sought differs, so that the emphasis differs and the types of method developed have also tended to differ. Whereas the geochemist will concern himself with H_2O, $H_2O + CO_2$, etc., the ceramic analyst will determine simply "loss-on-ignition" on a sample dried at 110 °C, as the final product will, in fact, contain the ignited raw material. The differences are, however, of far less consequence than the similarities.

At the end of the Second World War, virtually the only method of analysis available to the silicate analyst was the "classical" method, involving successive separations by precipitation (and usually re-precipitation) of silica, R_2O_3, calcium oxalate and magnesium phosphate. Alkali metal oxides were determined by the Lawrence-Smith method, again with successive separative precipitations. For rough analysis, suitable for routine work only, an analysis could be completed in four days, while accurate work, including all the necessary steps, increased this time to seven or eight working days. Only highly competent and well organised analysts could run more than two or three analyses successively together. Thus, for work of average quality, two and a half to three analyses in duplicate per week was an optimum performance. Clearly, this performance was not in line with the increasing demands for either geochemical or ceramic analysis. The increase in geochemical research demanded vast numbers of analyses, while a similar increase in industry possibly applied less numerical pressure, but results were needed much more quickly. Thus the demand arose for rapidly performed methods that would give rise to higher productivity per analyst and earlier results.

The geochemist concentrated very early on colorimetric methods, whereas the ceramic analyst, who was more concerned with the absolute accuracy, particularly of major contents, tended to seek direct methods with gravimetric finishes, e.g., alumina by the quinolin-8-ol and silica by the quinoline molybdosilicate method. The ceramic analyst, having passed through a phase of using colorimetric methods, tended then to concentrate more on improving referee methods, looking for accuracy by newer techniques and hopefully gaining speed also. This aim was accomplished primarily by eliminating the sequential nature of the classical method.

More recently, of course, both disciplines have tended to rejoin in their common use of both atomic-absorption and X-ray fluorescence methods, so that once again both groups are using methods similar in type. The current full range of standard referee methods, being both accurate and fast, seem likely to remain substantially unchanged, not because they have achieved perfection, but rather because they are at least adequate for current needs and are likely to be used less and less in the future. The need for accurately analysed standard samples will provide a continuing use for these methods as, even if instrumental methods can be based on synthetic standards, they still remain less fundamental than chemical procedures. The samples, if chemically analysed, are then available as primary or secondary calibration standards for instrumental methods.

In order to fit this review into a reasonable compass, it clearly had to be restricted. It is concerned almost exclusively with the acquisition of elemental analytical data, and is further restricted in that the only elements dealt with at length are those normally sought in the conventional "complete" analysis of an aluminosilicate ceramic, viz., silicon, titanium, aluminium, iron, calcium, magnesium and alkali metals.

On ceramic aspects it seems only proper that in reviewing the work of the past 30 years tribute should be paid to the efforts of two committees who carried out detailed and careful research in this field for almost the whole of the period. These are the committees sponsored by the British Ceramic Research Association (B.Ceram.R.A.) and the Society of Glass Technology. Although not necessarily responsible for the original research work, these committees investigated and developed possible analytical methods to the point at which it was possible to record their efforts in the form of British Standard methods. These methods are now serving the needs of industry for speedy and accurate referee methods. As their names do not appear individually in the references concerned with the work, it is appropriate here to name some of the distinguished inorganic analysts who have taken part. They include Mr. B. Bagshawe, Dr. R. C. Chirnside, Dr. H. J. Cluley, Mr. F. Hartley, Dr. C. W. Herd, Mr. G. Padget, Mr. G. Speight, Prof. L. S. Theobold, Mr. H. V. Thompson and Mr. N. T. Wilkinson.

The review is divided into two main sections, the first dealing with "wet" chemical methods and the second with instrumental techniques. The chemical section is divided further into schemes for "complete" analysis, individual determinations and methods of decomposition. In the instrumental section, the main emphasis is laid on those techniques, such as atomic-absorption and X-ray fluorescence spectroscopy, which are especially relevant today.

Chemical Methods

Schemes for "Complete" Analysis

The analysis of silicate materials up to the 1940s was carried out exclusively by the "classical" method, which in essence was a quantitative exploitation of the "group" methods of qualitative analysis taught to all students of chemistry until a few years ago. Names such as Bergman,[1] Berzelius,[2] Wöhler,[3] Rose,[4] Fresenius,[5] Washington,[6] Hillebrand and Lundell[7] and Mellor[8] are notable among the many who laid the foundations of the method. The most significant fact concerning the "classical" method was its essentially sequential nature, which, combined with the fact that "group" separations were based on precipitation, usually at least double precipitations, made the method very slow. A complete and carefully performed analysis might take as long as 10 d. Even when "short cuts" were used, reducing the accuracy for routine purposes, the final result would not be available in less than 4 d.

With the development of analytical chemistry during and after the Second World War, great interest was being shown in faster methods of analysis so as to permit realistic through-puts in geochemistry. These rapid methods were of two types; those which were simply modifications of the original methods, and those which utilised new reagents and techniques. The former generally gained their extra speed by sacrificing accuracy by "short cutting" the full procedure. Virtually all of these procedures have been superseded by newer tech-niques, showing that this line of development was merely an expedient, events proving it to be the wrong approach to the problem. The latter could be subdivided into procedures designed to utilise recent developments in order to achieve accuracy as good as or better than that previously attainable, preferably with a gain in speed, and into procedures designed for speed even at the expense of accuracy.

In the first of these types, speed was generally achieved because the method was "direct," *i.e.*, the determination could be completed without a series of prior separations. A typical example is the use of quinolin-8-ol in the determination of alumina in feldspars,[9] involving a decomposition with hydrofluoric acid. Koenig[10] modified the method, introducing a fusion with sodium hydroxide in a nickel crucible, and, with filtration, achieved the separation of iron, titanium and nickel hydroxides from aluminium. He also introduced the use of 1,10-phenanthroline as a complexing agent in order to prevent trace amounts of iron from escaping this separation. The Analysis Committee of the B.Ceram.R.A. carried out a detailed investigation of this procedure[11] and improved the accuracy, enabling it to be published as a British Standard method.[12]

The development of the flame photometer as a commercial instrument[13] also occurred at about this time, and almost immediately released the analyst from the rigours of the Lawrence-Smith technique. The determination of sodium and potassium could be carried out in 1 d compared with about 3 d, with a corresponding saving in actual analyst's time of about 1 d; the accuracy of the result was better and, in the hands of other than highly skilled analysts, was much better.

The other form of development, the rapid method, in practice usually sacrificed some accuracy, although this aspect was not always recognised. Most of these methods were based on colorimetry for the major constituents, as well as for iron and titanium. Among these, the first was probably by Hedin of the Swedish Cement and Concrete Institute.[14] Other schemes were proposed by Shapiro and Brannock,[15] Corey and Jackson[16] and Bennett *et al.*[17] A rapid method, using gravimetric finishes for the major contents, was also described by Bennett *et al.*[18]; this method used a quinoline molybdosilicate precipitation for silica and an aluminium oxinate precipitation for aluminium, and had an accuracy rather better than that of the spectrophotometric methods. The results obtained by these types of methods are rarely better than $\pm 0.5\%$ absolute for silica and alumina, although the gravimetric methods approach an accuracy of 0 to -0.5%. Restriction of the range of application arises from the use of a decomposition step with hydrofluoric acid or sodium hydroxide as a flux.

Two reviews dealing with silicate analysis during this period were published by Chirnside[19] and by Chalmers.[20] The former is more of an essay on the state of the art, with the forthright expression of view that one would expect from the author and covering the formative period of the newer procedures. The second is a more comprehensive review, and it is of interest to note the progress made in the intervening 5 years. In the late 1950s, the "classical" method was still the arbiter but, by the early 1960s, there was a growing acceptance that a change in accurate methods of analysis was not only acceptable but desirable. A third review, by Hey,[21] is concerned primarily with historical development and analysts, and is essential reading for those interested in this subject.

This need for accurate standard procedures was reinforced by the development of direct-reading spectrometers and X-ray fluorescence equipment and their application to silicate analysis. These instruments produced a need for standard samples of known analyses, and the demand coincided with a realisation that chemical parameters could be included in ceramic specifications because of the recently developed interest in analysis. These requirements, in turn, revealed the shortcomings of the then current methods in terms of output per analyst. The demand also revealed that the classical method made high demands on skill, and that relatively few of the increasing number of ceramic analysts could achieve the high standard necessary.

This is an area of work which was mostly left to those organisations connected with the ceramic industries and Standards organisations in various countries. Individual manufacturer and user laboratories were often content with results of control accuracy, using rapid or direct procedures. Geochemical laboratories who required analysis in the mass rather than ultimate accuracy of major contents tended to use the methods of Shapiro and Brannock,[15] until such time as instrumental analysis, particularly X-ray fluorescence spectroscopy, replaced "wet" methods almost entirely. Thus, at about this time (about 1960), the two streams of development drifted apart, the emphasis in geochemistry appearing to be on speed, whereas that of the ceramic analyst was on accuracy and reliability.

The first steps were taken by the Chemical Analysis Committee of the Society of Glass Technology,[22] who utilised a low-flux ratio decomposition as proposed by Finn and Klekotka.[23] The sample analysed was a sillimanite with an alumina content of 54%, so that the advantages conferred by using only a small amount of flux in reducing contamination and washing of precipitates was significant. Other features of the procedure were the use of furnaces at 1 200 °C for fusion and ignitions and a 75-ml platinum basin for decomposition, dissolution of the melt and dehydration of the silica, and the recommendation of a direct alumina determination with quinolin-8-ol as an alternative to the difference method. The increase in ignition temperature could have been responsible for reducing the apparent alumina content by as much as 0.5%, thereby permitting the achievement of an acceptable analytical total. The presence of a small amount of sulphuric acid during dehydration reduced the impurities in the precipitated silica and increased the efficiency of dehydration.

This work was followed by the B.Ceram.R.A. Analysis Committee's development of a modified method for the determination of silica in high-silica and aluminosilicate materials. A low ratio of flux to sample (2 g of sodium carbonate to 1 g of sample) was used without the addition of borax. Borax is required to ensure complete decomposition of aluminosilicate material not derived solely from clay. This method was circulated privately in 1956,[24] and published as an amendment to BS 1902 : 1952 in 1961.[25]

In 1960, Jeffery and Wilson[26] published a method for the determination of silica in which the need for a second dehydration was eliminated by carrying out a colorimetric determination of the silica remaining in solution after a single evaporation. The authors seemed to be concerned only with the determination of silica, and made no reference to further determinations on the filtrate from the silica. Bennett *et al.*,[27] thinking along the same lines, utilised the low-flux procedures but carried out a single dehydration and determined the silica remaining in solution as the yellow molybdosilicate. Aliquots of the filtrate from the silica determinations were also used for the colorimetric determination of iron and titanium, quinolin-8-ol gravimetric determination of aluminium after a cupferron - chloroform separation of iron and titanium and EDTA titrations for calcium and magnesium. This method eliminated the sequential nature of the "classical" method and allowed an analyst to complete a typical analysis in 2 d; individual determinations, *e.g.*, calcium or magnesium, could be carried out without a prolonged series of separations. This method formed the basis for

a revised British Standard method,[28] the main change introduced as a result of co-operative work by the B.Ceram.R.A. Analysis Committee being the introduction of a molybdenum-blue finish for the determination of residual silica in order to obviate interference by phosphate, together with an actual determination of phosphorus as P_2O_5. The molybdenum-blue method was based on that of Greenfield.[29] Early in the following year (1965), an amendment was published[30] recommending a titrimetric EDTA finish for the determination of alumina, based on the method of Vänninen and Ringbom.[31] This method was extended to cover materials with alumina contents greater than 42% by adding a small amount of borate to the flux.[32] A further innovation was the addition of sorbitol to the solution of the melt before dehydration in order to eliminate interference by boron. Methanol had previously been used for this purpose, but this method needs great care in order to avoid spurting, and a considerable length of time.

The single dehydration was the slowest individual stage in the process, and the need for this step was avoided by Bennett and Reed,[33] who coagulated the gravimetric portion of the silica with poly(ethylene oxide) resin a few minutes after dissolution of the melt and determined the residual silica in solution colorimetrically. The resin was shown not to interfere with any of the subsequent determinations made on the filtrate. The method has a further convenience, in that, having demonstrated freedom from interference by boron[34] even in the presence of high silica contents, a single flux can be adopted for all materials in the silica - alumina range. This flux was selected so as to achieve effective and rapid dissolution of the melt or sinter, but retaining as far as possible a low flux to sample ratio. This method was subjected to co-operative study and was published as a British Standard method.[35]

The use of 1,2-diaminocyclohexanetetraacetic acid (DCTA) in place of EDTA in the titrimetric determination of aluminium offered a further saving in time, as the former reacts with aluminium in the cold,[36] thereby avoiding boiling and cooling. The reagent had been applied to the determination of aluminium in silicate materials,[37-39] and was adapted as a replacement for EDTA in the standard method,[40] but is not likely to be incorporated until BS 1902: 1964 is due for complete revision.

It is possibly interesting to compare the results of the work on sillimanite carried out by the Society of Glass Technology and that by the B.Ceram.R.A. Analysis Committee about 15 years apart. Although much of the work on the later method was carried out by less experienced analysts, nevertheless, where major changes in method are concerned, *i.e.*, for silicon, aluminium, calcium and magnesium, it is still interesting to compare quoted precisions (Table I).

TABLE I

COMPARISON OF ANALYTICAL RESULTS ON SILLIMANITE OBTAINED IN
1953 AND 1968

| Organisation | Parameter | Constituent | | | |
		SiO_2	Al_2O_3	CaO	MgO
Society of Glass Technology (1953)	Standard deviation, %	0.20	0.29	0.17	0.06
	Number of results	19	33	14	14
British Ceramic Research Association (1968).. ..	Standard deviation, %	0.13	0.24	0.06	0.03
	Number of results	28	22	26	26

It is not possible to compare the results for alkali determinations, as the later work did not include them. It would not be proper to draw detailed conclusions from these figures, and it is probably sufficient to say that, taking into account improvements in reagents and equipment, the newer methods are at least as accurate as the "classical" method under the best conditions, and are probably better. The increase in speed of analysis from the "classical" method to the latest standard methods must involve a factor of 3 or 4. These methods are now penetrating into Europe, where they are being published as national standards and also as an ISO standard.

Before leaving this section on complete schemes of analysis, it may be worth casting the net a little wider. Similar types of method have been investigated and developed for other refractory materials. The same general principles have been applied to the analysis of mag-

nesites and dolomites[41] and to chrome ores and refractories,[42] both of which have been published as BS methods,[43,44] the co-operative work in both instances being carried out by the B.Ceram.R.A. Analysis Committee. In the latter method, great difficulty was experienced in the determination of silica, and the Committee ultimately reverted to a quinoline molybdosilicate gravimetric finish. Chromium was separated from the remaining constituents by using a liquid ion-exchange resin - solvent extraction technique.[45]

The capabilities of instrumental methods, particularly X-ray fluorescence spectroscopy, are now such that most silicate analysis is carried out instrumentally. Most laboratories with sufficient throughput have purchased X-ray fluorescence instruments, and many smaller laboratories are committed to atomic-absorption spectroscopy for routine purposes. The remainder of the smaller laboratories tend to use either the BS methods or varieties of the Shapiro and Brannock colorimetric method,[15] depending on whether their interests are ceramic or geochemical. The demand for "accurate" methods of analysis now lies with the very infrequent referee analysis and with the smaller ceramic laboratory, where their attraction is speed combined with reliability. This lack of demand seems to suggest that, barring discovery of new reagents or "wet" techniques that offer very significant improvements, the present range of "accurate" methods as represented by BS methods will remain unchanged and of progressively decreasing importance. It may possibly be justly claimed that they represent the true inheritors of the "classical" method.

It is possibly fair to select three English-language texts as adequately covering the modern scene in the "wet" chemical analysis of rocks and ceramics. The first two, by Maxwell[46] and by Jeffery,[47] are monographs on rock and mineral analysis and include determinations of a number of trace elements. The third, by Bennett and Reed,[48] is directed more towards the conventional "complete" analysis of ceramic materials, and gives a full and detailed scheme of analysis for each type.

Sample preparation

The problems of sample preparation tend to be scantily reported in the literature. Each analyst faces a particular problem and solves it to his own satisfaction, usually treating it as only incidental to the analysis. Materials covered by this review are classable as "hard" and a considerable number as "very hard." It is important to remember that there can be no grinding without contamination, so that it is very desirable that decomposition methods should be able to cope with relatively coarse samples. Many samples can be ground to 100 or 120 BS mesh (150 or 125 μm) with acceptable contamination, but grinding to 200 BS mesh (75 μm) may be inadmissible. This is particularly true in the field of ceramics, where modern products are increasingly designed for denseness, and thereby hardness; abrasion resistance is a desirable property.

It is impossible to generalise concerning grinding, and each case has to be treated on its own merits. Relatively recent developments in materials and machinery have lightened the lot of the analyst and offered him a wider choice of options. Until relatively recently, the chemical analyst tended to be confined, in his choice of mortars for "hard" materials, to agate and alumina, neither of which is ideal. The more recent development of boron carbide mortars offers an almost universal panacea. Boron carbide is extremely hard and abrasion resistant,[48a] and the contaminating elements generally do not offer any problems in the subsequent analysis. It is, however, expensive and relatively brittle, so that it has not yet been used in mechanical devices. Tungsten carbide, now generally in use, has many of the advantages of boron carbide; it is less expensive and much tougher, but it is likely to add significant amounts of tungsten and cobalt, which are difficult to handle in "wet" chemical procedures. For X-ray fluorescence purposes, the contaminating material dissolves during the fusion and offers no interference; the degree of contamination can easily be monitored and allowed for.

Full treatment of the problems of sample preparation will be found in most standard text-books.[46–48]

Individual Determinations

Decomposition

The first step in the actual analytical process, after sample preparation, is to prepare a solution of the sample or, at least, to bring into solution those elements which are to be

determined. With most silicate materials, decomposition depends either on the formation of volatile silicon tetrafluoride with hydrofluoric acid or fluorides, or on the formation of alkali metal silicates and aluminates by reaction with molten alkali metal salts. Other rocks, *e.g.*, carbonates, can be adequately decomposed by acids, such as hydrochloric, sulphuric and perchloric acid; the last acid and orthophosphoric acid have been used with materials that are more difficult to decompose, such as chrome ore.

The choice of a decomposition procedure may depend on the elements to be determined, particularly with respect to trace elements. Fusion methods may be inadmissible because of the volatility of the elements sought at high temperatures; equally, a number of fluorides are volatile. In some instances, trace amounts of fluorine remaining after a fluoride decomposition may cause serious interferences, especially in the determination of aluminium contents greater than a few per cent. and often with calcium.

Hydrofluoric acid. The decomposition of silicates with hydrofluoric acid is an established procedure, but a number of silicates fail to respond readily, *e.g.*, beryl, tourmaline and zircon.

Most aluminous materials [with aluminium(III) oxide contents greater than 42%] are not brought into solution, although all of the alkali metals appear to be extracted. The normal method of open evaporation in the presence of a second acid such as nitric, perchloric or sulphuric acid, of course, eliminates the silica, but more recent techniques using a sealed PTFE container permit analyses for silicon.[49,50] This development has found use mainly in determinations carried out by atomic-absorption spectrophotometry, but when used in this way it has the disadvantage of discharging hydrofluoric or fluoroboric acid to the atmosphere unless special provision is made for their disposal.

Alkaline fusion. In the "classical" method, the sample was decomposed with 4–20 times its mass of sodium carbonate, a flux which becomes progressively less effective as the alumina content of the sample rises. Referee-type methods of analysis have retained the use of alkali metal carbonates, but often with the addition of boric acid or an alkali metal borate. The large amounts of flux created problems during the washing of precipitates, and Finn and Klekotka[23] showed that efficient decomposition was possible by sintering with about an equal mass of sodium carbonate.

Mellor[8] reported the use of both boric acid and borax during the nineteenth century as fluxes for materials such as zircon and corundum and for fluorine-bearing minerals. The Society of Glass Technology Analysis Committee used the low-flux ratio principle of Finn and Klekotka[23] together with the addition of a small amount of borax in its method for the analysis of sillimanite.[22] In the use of borate-containing fluxes, there appears to have been some suspicion that the boron would create interferences. Boron may well be expected to contaminate the precipitate of silica during dehydration; methods involving methyl borate evaporation, although common, offer practical problems because of the difficulty of avoiding spurting. Low-flux ratios with the presence of only small amounts of boron(III) oxide minimise these problems and the adoption of single dehydration or coagulation techniques, where the only gravimetric determination is that of silica, has also reduced the possibility of interference. BS 1902 : Part 2B : 1967,[32] describing the chemical analysis of aluminous materials, recommends the addition of sorbitol prior to the evaporation so as to form a more readily soluble sorbitoboric acid. The method proposed by Bennett and Reed,[33] using poly-(ethylene oxide) as a coagulant, results in contamination by boron(III) oxide at a level not greater than 0.2 mg, *i.e.*, 0.02%. The use of non-sequential methods has also enabled a 1-g sample to be used, permitting greater accuracy, as there is now no need to attempt to precipitate and wash R_2O_3 precipitates with ignited masses greater than 0.5 g. When using these low-flux methods, however, it is important that furnace temperatures are at 1 200 °C, as otherwise the complete decomposition of samples with higher alumina contents may not be achieved.

Sodium peroxide sinters at temperatures between 450 and 500 °C were in vogue for a number of years after their development by Rafter and Seelye[51,52] and Milner and Woodhead,[53] but the increasing use of borate-containing fluxes has probably had the effect of reducing their significance. Strict control of the temperature of the furnace is needed, as otherwise the platinum crucible can be severely damaged and problems can arise from the variable purity of the material. Sodium peroxide used in nickel or iron crucibles offers the possibility of a rapid fusion procedure and can be of great value when a limited range of elements are being sought and an oxidising flux is required. This flux was chosen by Bryant and Hardwick[54] for the

determination of chromium in chrome ore, although Theobald[55] preferred to mix sodium hydroxide with the peroxide. The latter mixed flux was chosen by the B.Ceram.R.A. Analysis Committee for the first British Standard method, but within 5 years the current standard replaced the peroxide-bearing flux with a borate-rich carbonate flux.[44] This change was made because the peroxide flux failed with some types of sample, whereas the later flux appeared to be universally applicable.

Lithium fluxes. Lithium fluxes, particularly the meta- and tetraborates, have found increasing use during the past few years, chiefly in instrumental analysis and atomic-absorption and X-ray fluorescence spectroscopy. Much of this increase in popularity may have arisen from their availability at higher levels of purity; sodium and potassium contents are now extremely low in the grades used for analysis. There is obviously an advantage in using a flux that will permit the determination of alkali metal oxides with the same decomposition as in the remainder of the analysis. Lithium metaborate is generally used when dissolution of the sample is necessary after decomposition. This technique has been widely advocated by Ingamells,[56] who used it for spectrometric[57] and colorimetric analysis.[58] The technique has been widely adapted to atomic-absorption spectrophotometry.[59,60] Dissolution of the melt is not so rapid as with sodium fluxes, and several of the co-operating analysts on the B.Ceram.R.A. Analysis Committee reported some deposition of silica. This phenomenon is in keeping with the general observation that rapid dissolution of any melt is imperative if silica is to be brought fully into solution. This limitation could be a fundamental weakness in the use of lithium fluxes. Lithium tetraborate is even more difficult to dissolve and, although it is a more effective flux for some materials, *e.g.*, samples with high alumina contents, it is rarely employed except when the solid melt is used, as in X-ray spectrometry. This use is dealt with later under X-ray Fluorescence Spectroscopy.

Alkali metal hydroxides. Sodium hydroxide is the most commonly used, but all alkali metal hydroxides suffer from the important disadvantage that they cannot be used in platinum vessels because the latter are severely attacked. Recourse has to be made to nickel, silver, gold, iron or zirconium crucibles, and most of these materials are attacked sufficiently for the presence of the appropriate element to be a significant contaminant in the subsequent analysis. These hydroxides are also very hygroscopic and tend to froth and spurt when heated. This property is often overcome by first melting the flux in the fusion vessel, transferring the sample to the surface of the cooled melt and adding a few drops of ethanol to "damp down" the sample, drying off the ethanol at a low temperature before fusing the sample. The range of samples that can be decomposed successfully is limited, and the nature of the fusion is such that it yields slightly lower precisions than with carbonate - borax. Iron may also be lost to the nickel crucible,[61] so that it may be necessary to carry out a different method of decomposition for this element. Its advantage of speed of fusion and dissolution makes this technique very suitable for "rapid" methods, and its use has been recommended by many workers for this purpose.[15,18,62] The speed of dissolution and transfer from alkaline extraction to acidic solution retains virtually all of the silica in the unpolymerised form and permits methods based on molybdosilicate to be used.

Other methods. Potassium pyrosulphate has been proposed on a number of occasions as a flux, but it has very few advantages compared with the modern carbonate - borate fluxes. Its main use has been for re-dissolving the R_2O_3 precipitate in the "classical" method after ignition and weighing. It is surprising to find, in the early literature, its use for decomposing chrome-bearing materials; its use in this way often appears to result in the production of virtually insoluble basic chromium sulphates.

Alkali metal fluorides have often been recommended as fluxes when the determination of silica is not required. The technique achieves the decomposition of the sample and elimination of the silica in one process. It is useful for some of the less common silicates of niobium, tantalum, beryllium and zirconium.[46] Biskupsky[63] used a mixture of lithium fluoride and boric acid to decompose a range of materials, claiming that the fluoride eliminated the silica, the lithium tetraborate formed was a powerful flux and that subsequent heating with sulphuric acid eliminated the excess of boron and fluorine. Mixtures of zinc oxide and sodium carbonate have been used for the determination of fluorine,[64,65] and most analysts are familiar with the Lawrence-Smith method involving the use of calcium carbonate - ammonium chloride sinter for the determination of alkalis.

The decomposition of silicates by attack with hydrochloric acid by heating in sealed tubes[66]

has the advantage that no alkali metal salts are required, and the technique has found use in the decomposition of alumina.[67]

The use of these more unusual fluxes is designed generally for specific materials or determinations. Most silicate analyses are now carried out using carbonate - borate or lithium borate decomposition, together with treatment with hydrofluoric acid for the determination of alkalis, usually by flame photometry or atomic-absorption spectrophotometry.

Silicon

Four basic methods have been used, over the years, for the determination of silicon: gravimetric determination as silica; precipitation as an organic molybdosilicate; precipitation as potassium fluorosilicate; and colorimetry as molybdosilicate or molybdenum blue. These methods have been subject to little change in the past few years and, in fact, most of the significant evaluation was completed by 1960.

Precipitation by dehydration. The significant developments in this technique have already been dealt with in the section on schemes for complete analysis of silica - alumina materials. In early work, most dehydrations were carried out in porcelain vessels, but with the advent of low-flux methods[23] there has been an increasing tendency for fusion and dehydration to be conducted in the same platinum basin,[22] and this procedure tends to increase the measured results very marginally. The elimination of the second dehydration and combination of a gravimetric determination of the main silica with a colorimetric determination of the residual silica[26] again increased the measured results slightly. Finally, the improved decomposition arising from the incorporation of a small amount of borate in the flux when the silica is coagulated with poly(ethylene oxide),[33] together with the elimination of hydrolysis of salts during evaporation, resulted in lower residues. As part of these residues is converted into sulphate during the removal of the silica with hydrofluoric acid - sulphuric acid, and not all of this sulphate is decomposed during ignition of the residue, the mass of residue is greater than that of the corresponding oxides. This effect, in turn, means that the apparent mass of silica removed is in error to the extent of the mass of residual sulphur trioxide. The lower residues (1–2 mg) obtained with the coagulation method thus result in slightly higher results for silica. The effect of all of these changes is probably of the order of 0.2–0.3% for a sample containing 30–40% of alumina and 50–60% of silica.

Dehydration methods are subject to interferences, particularly by fluorine. With materials that contain significant amounts of fluorine, it is often more accurate to use one of the variants involving molybdosilicate or potassium fluorosilicate. It is not very clear which stage of the process, fusion, dissolution or dehydration, engenders loss of silica, nor is the extent of the loss clear. Some results have been reported on quartz[68] using the method of Jeffery and Wilson,[26] showing a loss of about 0.5% of silica arising as a result of the addition of 3% of fluorine (as sodium fluoride). The addition of borate to the flux is claimed to reduce this interference, which is generally thought to occur during dehydration. It is, therefore, very likely that, if the silica is coagulated rather than dehydrated, the effect of fluorine would be reduced very considerably. In the absence of fluorine, there is no doubt that a gravimetric determination by single dehydration or coagulation, followed by a colorimetric determination of the silica remaining in solution, provides the best method when accuracy is of prime importance. It may also be added that even when speed is important, a method using coagulation can be competitive.

Precipitation as an organic molybdosilicate. Brabson *et al.*[69] proposed a gravimetric determination as quinolin-8-ol molybdosilicate using a sodium hydroxide decomposition, where Wilson[70] preferred a titrimetric finish using quinoline as precipitant. Armand and Berthoux[71] studied the factors governing the formation of yellow molybdosilicate, confirming the findings of Strickland[72] with regard to the formation of α- and β-complexes and developed a method involving quinoline that permitted either titrimetric or gravimetric finishes. The paper by Armand and Berthoux[71] demonstrated the importance of controlling the acidity and ammonium molybdate concentration. This method was exploited by Bennett *et al.*[18] for the analysis of clays and other pottery materials; several small details were shown to affect the accuracy of the results. The total mass of silica in the aliquot of solution to be precipitated was restricted to 40 mg, and it was shown that allowing the precipitate to be sucked dry on the sintered-glass mat resulted in positive errors. The method proved popular in the

ceramic industries, so much so that in about 3 years over 100 analysts were trained in 1-week courses to carry out this determination and others were trained in the complete scheme. Surprisingly, the method is still in use in several laboratories, its main attractions being simplicity and cheapness in terms of capital equipment. Errors, provided adequate care was taken, were 0–0.5% in the range 50–100% of silica, a level of accuracy that is typical of most rapid, direct methods of this type. All of these methods were restricted in their range of use by the use of sodium hydroxide as the flux.

Miller and Chalmers[73] used sodium carbonate as a flux with a micro-sample (2–3 mg); they preferred 2,4-dimethylquinoline as precipitant, and destroyed the precipitate by heating it to 500 °C, with subsequent weighing as molybdosilicic anhydride.

Methods based on precipitation with organic bases of molybdosilicic acid are subject to interferences by phosphate, vanadate, etc., but for many materials the high content of silica and low levels of phosphate, etc., permit the use of the technique provided that results of the highest accuracy are not required. Great care, however, needs to be taken at all stages so as to ensure that the quality of the results is maintained.

Precipitation as potassium fluorosilicate. The use of potassium fluorosilicate in the determination of silica in glass was recommended in 1947 by Hollander and Rieman,[74] the finish being an alkalimetric titration and the method being derived from that of Travers.[75] Maxwell and Budd[76] proposed a similar method for glass, sand and refractories. Sajo[62] also used the procedure as part of his analysis scheme for rocks, ores, slags, refractories, etc. Several other workers have recommended this method during the last 20 years; as recently as 1972, Kalocsai and Hockley[77] used the finish but introduced a separation by means of volatilisation. The insolubilities of calcium and aluminium fluorides have caused problems, the latter causing serious interference. Experience with the method in the earlier days suggested that its value was doubtful for samples that contain more than 1–2% of aluminium. It is, nevertheless, a useful method in the presence of fluorine.

Colorimetry as molybdosilicate or molybdenum blue. When ammonium molybdate is added to an acidic solution containing silicon, a yellow colour is produced owing to the formation of molybdosilicic acid. This compound occurs in two forms, α- and β-, and by selecting appropriate conditions of acidity, ammonium molybdate concentration, etc., one form or the other can be produced. These facts provide the basis for the determination of silica as molybdosilicate, but the procedure is subject to interference by phosphate, vanadate, etc. In order to increase the sensitivity and, on occasion, eliminate interference from phosphate, many proposals have been made for reducing the complex with a variety of reducing agents to produce molybdenum blue. The amount of work carried out on these determinations is immense, although the basic work appeared to have produced a range of reliable methods before 1960. In view of the reported accuracies of better than 0.5% of the amount present, the volume of subsequent work seems surprising.

Strickland[72] investigated the formation of molybdosilicate in some detail, and most of his findings were confirmed by Armand and Berthoux.[71] Anderson[78] claimed that the change from the unstable β-form to the stable α-form is not complete in the normal methods and recommended heating on a steam-bath for 3 h or even longer for high concentrations of silica. Ringbom *et al.*[79] dissolved the melt in EDTA and controlled the pH at a higher level (3.0–3.7) than in many procedures. Bennett *et al.*[17] used the molybdosilicate method in a widely used procedure for routine control analysis of pottery materials. Interference from phosphorus is normally corrected for rather than removed in the above procedures.

Reduction to molybdenum blue is usually used when attempts are being made to eliminate interference by phosphate. Organic acids such as oxalic, tartaric and citric acid have been variously recommended for this purpose,[80] as also have a variety of reducing agents. This procedure was adopted by Shapiro and Brannock[15] in their widely and successfully used method for the analysis of rocks. Greenfield,[29] on the other hand, eliminated the interference of phosphate by control of the acid concentration before reduction.

In view of the wide-ranging recommendations in terms of acidity, reagent concentration, choice of interference suppression and reducing agent, one might assume that, provided the conditions chosen provide stability, most procedures will give reliable results with adequate care and control. The basic failing of the technique must, however, remain; a colorimetric method is being strained when the content being measured is greater than 10%, and precisions of better than 0.5% of the amount present are extremely difficult to achieve.

Aluminium

In the classical method, aluminium is precipitated with ammonia, together with iron and titanium. In addition, any silica still in solution, phosphate, zirconia and many other constituents are also precipitated. Normally, in the course of a routine analysis, only iron and titanium would be determined, phosphorus and the remaining silicon when more accurate results were required, but other elements only rarely. Thus, the figure for alumina, being obtained by difference, would include these additional elements, and was almost inevitably high. The determination of aluminium was probably the least satisfactory of all, and it was for this reason that attempts were made in early work to achieve a direct determination.

The exploitation of quinolin-8-ol has already been described,[9–12] with the use of a separation with sodium hydroxide to remove the iron and titanium. The replacement of this separation by a cupferron - chloroform solvent extraction[81] virtually eliminated any escape of iron, and the need to complex it with 1,10-phenanthroline. Miller and Chalmers[82] used a similar method on a micro-scale as part of their analysis scheme for silicate rocks. Benzoic acid was also used as a precipitant for aluminium prior to a quinolin-8-ol determination,[83] for the determination of aluminium in chrome-bearing materials. If a titrimetric finish is preferred, it is possible to dissolve the precipitate and carry out a titration. Milner and Woodhead[53] combined both of these separations, *i.e.*, cupferron solvent extraction and benzoate precipitation, before a titrimetric finish with EDTA.

Gravimetric finishes are relatively time consuming and, although the conversion factor of the precipitate to alumina was favourable, the method lost ground as EDTA became available. Vänninen and Ringbom[31] described a technique involving a back-titration with zinc solution using diphenylthiocarbazone (dithizone) as indicator, and this procedure was combined with a cupferron - chloroform separation,[84] forming the method for the determination in British Standard methods for silicate[28] and aluminous materials,[32] magnesites and dolomites.[43] Weibel[85] described a similar method, but used hydrofluoric and perchloric acids for decomposition, then complexed excess of fluorine with beryllium sulphate prior to the determination. With the advent of the Health and Safety at Work Act, many analysts might well seek other procedures rather than risk the toxicity of beryllium. A number of methods have been based on successive titrations with EDTA, before and after the addition of fluoride.[86,87] The amount of EDTA released by the complexing action of the fluoride on aluminium permits the determination of the latter. The results are marginally less accurate with high level contents of aluminium, but this effect can be anticipated because of the need for a double titration. The Chemical Analysis Committee of the Society of Glass Technology compared the fluorine method with a direct titration procedure after the removal of interfering ions[38]; the content of alumina was low and that of iron(III) oxide very low, and both methods were shown to be reliable. It is also interesting to note that the Committee found that the "classical" figure for alumina was about 0.1% high at the 1.5% level. This result was attributed to contamination of the R_2O_3 precipitate by silica. At this level of aluminium, fluorine was found not to interfere.

More recently, DCTA has replaced EDTA as the titrant in these determinations, the attraction being that DCTA complexes with aluminium in the cold, thereby avoiding boiling and cooling,[36] saving time and avoiding interference by chromium. Pritchard[37] used the reagent by adding it during the separation of iron and titanium with sodium hydroxide, but according to Mercy and Saunders[38] this method fails to overcome the difficulties that arise from the presence of large amounts of magnesium. Bennett and Reed[40] recommended its use, but reported that if the reagent was used after a cupferron - chloroform separation, addition of hydroxylammonium chloride was necessary in order to prevent destruction of the indicator. In the same paper,[40] it was noted that addition of sulphate prior to the titration with either EDTA or DCTA prevented interference by calcium.

Colorimetric methods. A range of reagents have been recommended for the colorimetric determination of aluminium, but this element is less amenable than many others to the simple formation of stable coloured compounds. There is also the disadvantage that the aluminium content of many minerals is higher than the natural range of colorimetric methods. At levels of alumina up to about 2%, it is probable that colorimetric methods are more accurate, between 2 and 5% there is little to choose, but over 5% suitable titrimetric or gravimetric methods are more accurate. Colorimetric methods, however, offer great speed and are therefore often used in situations where speed is more important than ultimate

accuracy, but they are now tending to be replaced by atomic-absorption methods, which have much the same attributes.

Quinolin-8-ol has been used by many workers and still finds current use; the reagent lacks specificity, and separations or the use of complexing agents are called for. Gentry and Sherrington[89] proposed the use of the reagent, measuring the absorption after solvent extraction into chloroform. Riley[90] used the procedure on silicate rocks, using 2,2'-bipyridyl and beryllium sulphate as complexing agents; copper, cobalt and zirconium, if present, were removed with 2-methyl-8-hydroxyquinoline (8-hydroxyquinaldine)[91] prior to the determination, and procedures were given for a range of separations. Chalmers and Basit[92] determined alumina after ligand exchange with aluminium acetylacetonate, interfering elements being removed by extraction into *o*-dichlorobenzene from 1 M hydrochloric acid.

Aluminium forms lakes with a number of dyestuffs, and Alizarin Red S was selected by Shapiro and Brannock[15] in their scheme. Interference by iron is eliminated with potassium hexacyanoferrate(II) and thioglycolic acid. Eriochrome cyanine was used by Glemser *et al.*[93] for the determination of aluminium in clays and refractory materials, thioglycolic acid being used to complex the iron. Hill,[94] in using the reagent with iron ores, measured the aluminium lake colour (with the iron complexed by thioglycolic acid) against a blank in which the aluminium itself was complexed with EDTA. This method was applied to clays, etc., by Bennett *et al.*[17] in a scheme for routine control analysis.

Triammonium aurinetricarboxylate (aluminon) has also been used; Poole and Segrove[95] recommended it in the analysis of glass sands, and André[96] concluded that a colorimetric method using aluminon gives a better accuracy than the "classical" method for the determination of alumina in silica bricks.

Both Alizarin Red S and aluminon require high blank corrections owing to the colour of the reagent; this is one of the reasons why Wilson and Sergeant[97] proposed the use of pyrocatechol violet, reducing interference from iron by the formation of the iron(II) - 1,10-phenanthroline complex.

Most colorimetric reagents used for the determination of aluminium are extremely sensitive, aliquots of up to 80 μg of alumina yielding full-scale deflection. When micro-analysis is necessary, this sensitivity is a great advantage, but when work can be conducted on a macroscale, the conversion of absorbances into major content values often leads to a lack of precision. In addition, any fluoride coming into contact with the final solution can have a disastrous effect and, in laboratories where hydrofluoric acid is a commonly used reagent, this is by no means unlikely.

Iron

Although geochemists are vitally interested in iron(II) to iron(III) ratios in materials, ceramic analysts are rarely concerned with anything other than total iron expressed as iron(III) oxide. This state is again determined by the way in which the material is used, for after heating under oxidising conditions to form a ceramic, most of the iron will be in the iron(III) state. Methods for the determination of iron(II) have been reviewed in 1966 by Schafer,[98] and changes since then have been mainly in technique.

In the classical method of analysis, iron was usually determined in the R_2O_3 precipitate after dissolution in potassium pyrosulphate and sulphuric acid. Determination was effected either by a titrimetric method using a tin(II) chloride reduction, or colorimetrically with thiocyanate. Titrimetric or colorimetric methods remain the most commonly used methods. One of the main risks in the determination of iron lies in its reduction by a gas flame and subsequent alloying with the metal of the crucible.[61,99] Except when concerned with very low iron contents, *e.g.*, in glass sands, this effect can be overcome almost completely by carrying out ignitions and fusions, firstly with care over a gas burner, and subsequently in an electric furnace under oxidising conditions.

Usually, iron determinations are carried out on an aliquot of a solution of the sample, possibly from a filtrate after the removal of silica, or a re-dissolved R_2O_3 precipitate. However, when iron contents are very low, it is probable that a separate portion of sample would be used, *e.g.*, by hydrofluoric acid decomposition. Titrimetric methods usully depend on a reduction to iron(II) with hydrogen sulphide,[100] sulphur dioxide, tin(II) chloride,[101] titanium-(III) chloride, Jones reductor or silver reductor. Each of these procedures has its adherents

and its own advantages and disadvantages. Hydrogen sulphide can be used jointly to remove the platinum and to reduce the iron, but it is often difficult with both hydrogen sulphide and sulphur dioxide to remove trace amounts of sulphur. The usual problem with tin(II) chloride is to avoid adding too great an excess, with possible high results. Hume and Kolthoff[102] added cacotheline to indicate the presence of excess of tin(II) chloride, which was then titrated with cerium(IV) sulphate before the titration of iron. The Jones reductor method, using amalgamated zinc, is less suitable than the silver reductor method, as titanium, chromium and vanadium interfere in the former method, while only vanadium of the above interferes in the latter. Mercy and Saunders[38] studied both tin(II) chloride and the silver reductor as part of their work, in which they concluded that titrimetric were preferable to colorimetric methods. Miller and Chalmers[103] consider the silver reductor method to be the only suitable method for covering the whole range of iron contents. More recently, Blanchet and Malaprade[104] have recommended the use of titanium(III) chloride as titrant. Final titration of the reduced iron is normally carried out with either dichromate or permanganate, although cerium(IV) salts have also been used.

Colorimetric methods have been used for the determination of total iron for many years, thiocyanate being the normal reagent. Iron(III) thiocyanate colours tend to vary, depending on the nature of the other salts present, and visual comparison of the blood-red colour of the standard solution with an indeterminate brown - red of the sample solution in a pair of Nessler glasses was an art rather than a science. The development of commercial monochromatic spectrophotometers with a high inherent stability enabled precisions of about 0.5% of the amount present to be achieved. This precision allows determinations of contents of iron(III) oxide up to 20% to be competitive with titrimetric results; a much greater speed and simplicity is generally possible with colorimetry. In addition, most titrimetric methods tend to show small positive errors, due either to interferences from other elements in the sample or to the addition of other reductants during the process.

Countless reagents have been proposed for the colorimetric determination of iron, but only a small number have found extensive use. Among the earlier replacements for thiocyanate was thioglycolic acid,[100] its chief disadvantage being its unpleasant smell. Tiron[105] has found use for this purpose, the same reagent being used for titanium. Two reagents dominate most procedures, namely 1,10-phenanthroline[7,28] and 2,2'-bipyridyl,[7] the former probably being most widely used. Both reagents are used in a similar manner, are relatively free from interference, do not demand precise control of pH and yield stable colours. Batho-phenanthroline[106] finds occasional use when great sensitivity is required. 1,10-Phenanthroline has been used at very low levels of iron, *e.g.*, in colourless glass,[107] and also at high levels, *e.g.*, in chrome-bearing materials,[42] thus showing a wide range of application.

Titanium

The general level of content of titania in rocks and ceramic materials is low, and it is thus most appropriate to carry out the determination by colorimetric methods.

Hydrogen peroxide is the most universally applied reagent, and directions for its use can be found in most of the text-books[7,46–48] or standard methods.[30,32,43,44] For contents of titania greater than 0.1–0.2%, the method has the advantage of speed and simplicity; it is not greatly subject to interferences, except by vanadium and fluorine. There is rarely sufficient vanadium present to affect the results, but care has to be taken to ensure the prior elimination of fluoride. The yellow colour due to iron(III) salts is usually masked with orthophosphoric acid. Lower contents of titanium are rarely significant in ceramic technology, so that hydrogen peroxide is used for the whole range of contents (0–6%), but in geochemistry reagents such as tiron[108,109] and chromotropic acid[110] are often recommended for their greater sensitivity. Jeffery and Gregory[111] have recommended the reaction with 4,4'-diantipyryl-methane; the method is less sensitive than that with tiron, but is less subject to interferences from other cations or variations in acid concentration.

Calcium

Calcium can be present in ceramic materials and rocks as either a minor or a major constituent. In most silica - alumina materials, the content will be less than 1% (often about 0.2–0.3%), while materials such as dolomite, calcite and bone ash can have calcium oxide

contents above 50%. The determination of calcium over the whole range calls for different types of methods, although the use of EDTA can now provide an almost universal coverage, provided that the techniques selected are appropriate to the content.

In the classical method of analysis, calcium was precipitated as oxalate after the removal of the R_2O_3 with ammonia. The amount of foreign salts is so great that a second precipitation after dissolution is needed so as to ensure the purity of the precipitate. This is especially true in the presence of a considerable content of magnesium, as post-precipitation of magnesium oxalate readily occurs. Barium and strontium, if present, will be partially or wholly precipitated with the calcium, but Maxwell[46] suggests that less than 0.5 mg of barium will be eliminated during the two precipitations, whereas strontium will be retained. The second precipitate is generally ignited, but the weighing form may be the carbonate[112] or the oxide. The latter is simpler, but the former offers a better weighing factor, although the precipitate needs to be collected on a Gooch crucible as it is not possible to burn off all of the carbon readily at the low ignition temperature (475 ± 25 °C). Although a gravimetric finish is acceptable, a number of analysts prefer to complete the determination by dissolving the second precipitate and titrating the oxalate with potassium permanganate solution, particularly for low calcium contents. This procedure is more rapid and can be more accurate for small amounts, but it has to be remembered that permanganate will react with any oxalate ion, not only from calcium, and again it is advisable to use an alternative to paper as the filter.

Precipitation from homogeneous solution, using the hydrolysis of urea to give the required pH or an ester of oxalic acid to generate oxalate ions, is claimed to produce large-grained, easily filterable precipitates.[113,114] It is questionable whether the advantages of the techniques are worthwhile, as the standard method presents little difficulty.

The precipitation of calcium in the presence of large amounts of magnesium presents particular problems. Post-precipitation of magnesium is a normal occurrence and is of such a magnitude that a third precipitation is usually required. A comprehensive investigation of this problem under the guise of the determination of calcium in magnesite was carried out by the British Ceramic R.A. Analysis Committee.[115] The range of methods was reviewed, and several were chosen for study. The method of Gilbert and Gilpin,[116,117] in which a solution of the sample is treated with a large excess of oxalate at a pH of about 5–6, proved to be the most successful technique involving oxalate precipitation. Even so, the method failed at calcium oxide contents below 1%, yielding low results. The technique of Caley and Elving,[118] who first carried out a separation by precipitation as calcium sulphate in a strongly methanolic medium, had no advantages, and took longer. Separation with naphthylhydroxamic acid[119] was also fully investigated without success.

The development of complexometric methods has caused an almost complete transfer to the determination of calcium by titrimetry. Earlier methods involved removal of iron and titanium by an ammonia separation,[120] but these separations were rarely conducted with sufficient care to ensure that no calcium or magnesium was lost in the precipitate. Few ceramic materials contain sufficient amounts of elements such as manganese, copper and nickel to cause significant interferences; of these elements, manganese is the most common and, together with iron, titanium and aluminium, can conveniently be complexed with triethanolamine.[121] If the content of manganese in a sample exceeds a few milligrams, brown or green colours result from the use of triethanolamine and end-points become very difficult to detect. Another problem with the use of triethanolamine is that in the presence of more than a fraction of 1% of iron(III) oxide, oxidation of Solochrome indicators occurs and the end-point disappears. However, indicators such as murexide, calcein, 2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid,[122] thymolphthalein complexone and methyl thymol blue are satisfactory with triethanolamine; murexide, however, even when screened with Naphthol Green B, yields relatively poor end-points.

When the removal of R_2O_3 is preferred, the use of a precipitation with ammonia can lead to difficulties in buffering, and may cause some magnesia to remain in solution at the high pH normally used for determination of calcium.[123] The precipitation of all of the magnesium as hydroxide at a high pH is fundamental to the determination of calcium. Cluley[124] and Riley[125,126] avoided this precipitation by using an extraction of quinolin-8-olates of iron and titanium into chloroform at pH 5. When the contents of both calcium and magnesium are low, a direct titration with EDTA after removing or complexing the ammonia-precipitable group oxides with a preferred indicator of the many that are available, offers few problems

once familiarity with the end-point has been achieved. It is under these circumstances that the most significant errors from the presence of strontium and barium occur, as these elements are also generally titrated stoicheiometrically. From the ceramic technologist's point of view, the minor error introduced by the presence of these elements is of no concern, but arguments ensue between the "wet" analyst and his colleague using instrumental methods, such as atomic-absorption or X-ray fluorescence spectroscopy. These discrepancies have resulted in the revision of some certificates showing the analysis of British Chemical Standards by the use of instrumental methods.

With higher calcium levels, in situations when either calcium or magnesium predominates, it is often necessary to use specific methods. When the magnesium content is high, the precipitation of its hydroxide in the alkali metal hydroxide solution normally used to increase the pH to 12 often causes some loss of calcium in solution. This effect has been avoided by adding an excess of EDTA before the precipitation, then carrying out a back-titration with a calcium solution.[127] In the original method murexide was used as indicator, but in a B. Ceram. R.A. Analysis Committee investigation of the determination of lime in magnesite,[115] Patton and Reeder's indicator[122] was preferred and, more recently, calcon[128] has been used. The back-titration is carried out in the presence of the precipitate, but in the British Standard method[43] a coagulant is added, the magnesium hydroxide filtered off and the excess of complexone, in this instance ethylene glycol tetraacetate (EGTA), titrated in the clear filtrate. The use of EGTA rather than EDTA reduces the problem of interferences and improves the visibility of the end-point.

Colorimetric methods have been used for the determination of calcium, but it is not readily susceptible to colorimetric reagents. As early as 1950, Ostertag and Rinck[129] used murexide for this purpose, and since then a number of other indicators have been proposed, particularly glyoxal bis(2-hydroxyanil) [di(2-hydroxyphenylimino)ethane][130] and Calcichrome,[131] but none of the procedures appears to have found general favour.

Now that atomic-absorption spectrophotometry offers such relatively simple procedures, it seems likely that the instrumental methods will progressively replace most of the other methods for the determination of calcium at low to medium levels. The analyst then knows that he is determining calcium and not an almost unresolvable mixture of alkaline earth metal oxides.

Magnesium

The development of methods for the determination of magnesium almost exactly parallels that for calcium. Starting with the "classical" method, the discovery of EDTA resulted in a wide range of procedures, the more successful of which are still in use. There were the same sporadic attempts to develop colorimetric methods, few of which found favour outside the originating laboratory, and finally methods for determining lower levels were replaced by methods based on atomic-absorption spectrophotometry.

The "classical" method utilised the precipitation of ammonium magnesium phosphate and its ignition to magnesium pyrophosphate, with a gravimetric finish. Ammonium salts tend to prevent the precipitation, and it is usual to remove the accumulated ammonium salts from the R_2O_3 and calcium separations by evaporation with nitric acid. Double precipitation is necessary in order to remove contamination and to ensure the correct magnesium precipitate. Ignition to the pyrophosphate again requires care, as grey precipitates are common owing to trapping or reaction with carbon in the filter-paper. The precipitate can be almost invariably rendered white by ignition to 1 150 °C.[132] Quinolin-8-ol has also been used as a precipitant for magnesium; its main advantage is a favourable conversion factor, but it lacks specificity.

Magnesium can be readily titrated with EDTA, but purists dislike the normal procedures in which magnesium is determined by a difference between a calcium titration and a calcium plus magnesium titration. There is a very similar range of separation procedures and an equally long list of possible indicators. Methods after separation of R_2O_3 with ammonia and by complexing with triethanolamine parallel those for calcium. Solochrome Black T is often used as an indicator, but problems will arise when triethanolamine is used owing to destruction of the indicator in the presence of iron(III). This problem can be overcome by using o-cresolphthalein complexone or methyl thymol blue. The former was used in

an automatic titration by Pouget,[133] and the latter by Přibil and Veselý,[134] who also used (1,2-cyclohexylenedinitrilo)tetraacetate as titrant. These two indicators, although not giving end-points as sharp as those with Eriochrome Black T at its best, appear to function more reliably overall. Their end-points tend to drag with increasing magnesium contents, so that at higher levels it is often better to use the Eriochrome dye. In order to achieve satisfactory end-points with magnesite, interfering elements are best removed. The B. Ceram. R.A. Analysis Committee[41] remove iron by solvent extraction with sodium diethyldithiocarbamate and aluminium (which yields high results if present at over 1% content) with cupferron. DCTA was used as titrant as the concensus of opinion was that it yielded sharper end-points than EDTA; finally, Eriochrome Blue Black B (Solochrome Black 6B) was preferred as the indicator, the ultimate colour being colder and clearer than that with Eriochrome Black T.

With high contents of magnesium there is a high risk of precipitating some hydroxide, as the solution is made alkaline. This effect can lead to low answers and reverting end-points, but it can be largely overcome by adding the bulk of the titrant prior to increasing the pH, although care has to be taken to avoid complexing other elements at lower pHs, thus forming complexes that are not then decomposed.

Jordan and Monn[135] determined magnesium in the presence of large amounts of phosphate, *e.g.*, phosphate rocks, and various amounts of calcium by titration with DCTA.

Colorimetric methods have been proposed, many of them based on titan yellow, using various dispersants and colour stabilisers.[136,137] Abbey and Maxwell,[138] more recently, have used magon and magon sulphate for the determination of magnesium. It seems unlikely that any of these techniques will long survive the advent of atomic-absorption spectrophotometry as the detection limit of the latter technique is competitive and the procedures are much simpler.

Alkali metals

In the "classical" method, a separate decomposition was used for the determination of alkalis, usually by the method of Lawrence-Smith, with a sinter of the sample with calcium carbonate and ammonium chloride. This method was followed by a series of separations to remove interfering elements and then by volatilisation of ammonium salts. The whole process occupied 3–4 d and was a searching test of the skill of the analyst. For referee analysis and in laboratories particularly concerned with accurate analyses, great care would be taken. Potassium would have been determined by either the perchlorate or the chloroplatinate methods and lithium, if present, determined as sulphate after separating the potassium with a butanol - ethyl acetate mixture and sodium by precipitation as chloride in butanol. In the refractories industry, for the purpose of routine analysis alkali metals other than sodium or potassium were normally ignored and the relative amounts of these two elements were often assessed by the change in mass after conversion from chlorides into sulphates. Potassium was occasionally determined as the hexanitritocobaltate(III), but more frequently sodium was chosen for determination by one of the simpler triple acetate procedures. The other metal was then obtained by difference.

As early as 1950, the commercial flame photometer was revolutionising this determination; the EEL instrument proved capable of achieving results with an accuracy equal to that of the classical procedure except at high levels of the elements.[19] Within a few years, almost all routine determinations of alkali metal oxides, including lithia, were being carried out by using flame photometry after a Berzelius decomposition of the sample with hydrofluoric acid. The lack of precision and occasionally accuracy of the flame photometer manifests itself at high contents of the elements, such as in glass,[139] and the Society of Glass Technology Analysis Committee[140] prefers gravimetric finishes for accurate work, using uranyl zinc acetate for sodium and tetraphenylboron for potassium. With the change from town gas to natural gas, significant interferences between alkali metals were noted when using the EEL instrument, and the use of a radiation buffer (caesium) and an inhibitor for calcium was recommended.[141]

Interferences are generally dependent on the type of instrument used, and it has not proved possible to lay down specific working recommendations as is done for "wet" chemical methods. Interference effects are often eliminated by adding to the standard solutions the amounts of other ions present in the sample solution, and by using two "bracketing" standard solutions where the concentration of the sought element in solution in one instance is marginally below

the anticipated level and in the other is above it. These techniques are clearly valid in routine control analysis, but are more difficult to apply to a wide range of casual samples. In the latter instance, the use of the slightly less accurate technique of adding buffers and inhibitors may be preferable.

Atomic-absorption spectrophotometry has been used for these determinations[142]; it has the advantage of greater degree of specificity and a lower level of interferences. The determination of small amounts of lithium,[143] rubidium[144] and caesium becomes relatively simple.

Instrumental Analysis

The few years of the present decade, for many of the laboratories engaged in ceramic or geochemical analysis, have witnessed a revolution. The installation of X-ray fluorescence and atomic-absorption spectroscopic equipment has proceeded at a great pace, replacing not only "wet" chemical methods but also spectrographic and direct-reading spectrometric methods. Possession of both instruments in most, if not all, instances offers to the analyst an almost immediate solution to the determination of almost all of the metallic elements. The development of methods of analysis for the non-metals, *e.g.*, carbon, sulphur, boron and fluorine, is relatively less advantageous. It is true that pyrolysis followed by an infrared determination permits the rapid determination of carbon and sulphur, and ion-selective electrodes perform the same function for the latter, but even so the level of instrumentation is scarcely the same.

Most of this section is concentrated on X-ray fluorescence and atomic-absorption methods, as these are of prime importance. Atomic-absorption spectrophotometry and flame photometry for the determination of alkali metals have been included in the "wet" chemical section; in one sense, this arrangement may seem illogical, but it is an approach that few silicate analysts would dispute, as these two techniques are so much a part of the ordinary "wet" methods of analysis that any other treatment would be inappropriate. Flame photometry, at the height of its vogue 15–20 years ago, was used for determinations of many elements other than the alkali metals, but few laboratories adopted the procedures and even less have retained them. The advent of atomic-absorption spectrophotometry must, by now, have reduced very considerably the number of workers who are still using flame photometry as a general technique.

Polarography is another technique that has never been generally accepted in silicate analysis, probably because the elements generally sought are not readily amenable to the application of this technique. The increase in interest in potentially soluble toxic elements, notably lead, cadmium, arsenic, antimony and zinc, has created some interest in polarography and anodic stripping voltammetry, but even here, atomic-absorption spectrophotometry remains a serious competitor.

Electron-probe microanalysis and the use of a scanning electron microscope with analytical facilities find considerable use in both ceramic and geochemical analysis, but the information provided by them is of a different quality from the "ultimate" analysis with which this review is concerned. Ample information about their capabilities can be found in the many books on physicochemical methods of analysis of minerals and ceramics.[145–147] Mass spectrometry also offers a wide-ranging technique for the determination of trace elements, but is outside the scope of this review. The topic has been discussed at successive Ceramic Chemists conferences[148–150]; there are a number of analysts who have considerable reservations concerning the value of the technique because of problems of calibration and investigation of inter-element effects. Nuclear techniques are valuable in specific instances, but they are not easily available to the general range of laboratories. Smales[151] has described a number of these uses in a generally descriptive paper.

This section is concerned primarily, therefore, with atomic-absorption and X-ray fluorescence techniques, with some recognition of the place of emission spectroscopy, even though it is increasingly becoming of only historical interest.

Emission Spectroscopy

The spectrograph has been used in silicate analysis for many years, but it suffers from two major disadvantages. Firstly, the technique lacks a high level of precision and its

accuracy can leave much to be desired, and secondly, the processing and reading of the film or plate is very lengthy, becoming increasingly so as one attempts to improve the quality of the results. To overcome this disadvantage, it is possible to use a direct-reading spectrometer, but this course, however, is open only to laboratories with a sufficiently large throughput.

Silicate and other ceramic materials or minerals, if presented to the instrument in powder form, will produce results with a precision of the order of 5%, and the accuracy will depend on how closely the samples conform to the standards in terms of particle size, composition and mineral structure. Some form of cup electrode or pressed-disc or cylinder electrode is normally used, often together with a buffer and one or more internal standards. The number of variants is almost endless, and the methods are generally of only quantitative value when the sample is almost a single oxide, *e.g.*, silica, as in glass sands.[152,153] The general principles of optical spectrography have changed little, and the description of appropriate techniques described by Ahrens[154] and Mitchell[155] are still relevant. These same techniques have been applied to direct-reading spectrometers; this application limits the number of elements whose determination can be attempted, but greatly increases the speed of analysis. This has enabled the instrument to be used in mineral surveys where many thousands of analyses on a wide range of elements are required each year.[156] Pre-fusion of the sample improves both precision (3%) and accuracy, but involves an increased sample preparation time.[157]

Good precisions and accuracies have been achieved by using solution techniques and a rotating-disc electrode,[158,159] and the method proved particularly suited to single oxide materials, high silica, alumina and magnesia, better results being achieved than by chemical methods. At the time (mid-1960s), results for chrome ores and refractories were comparable with those obtained by chemical methods, but this comparability arose solely because the "classical" method as applied to these types of materials left much to be desired. Sample decomposition and dissolution were relatively prolonged so that the advent of equally reliable X-ray fluorescence methods has resulted in the progressive abandonment of the direct-reading spectrometer as a fully quantitative analytical tool. The scanning facility on the X-ray fluorescence instrument is replacing the spectrograph even for qualitative or semi-quantitative work.

The use of a plasma torch could overcome many of the problems associated with the rotating-disc technique, but it would still be necessary to prepare solutions. The sensitivity of the plasma is so great that there are many opportunities that can be exploited for the determination of trace elements. Greenfield and co-workers[160,161] attached this torch to a direct reader and automatic sampling device, with considerable success.

Atomic-absorption Spectrophotometry

Atomic-absorption spectrophotometry, when it first made its appearance, was generally thought to be almost entirely devoid of interferences; this, regrettably, is not so. However, the speed of determination, once a solution is available and the necessary procedure known, is so great that the technique has answered a need in many laboratories. Rarely has an instrumental technique found so many applications in so many laboratories as atomic-absorption spectrophotometry. Many determinations can be carried out without prior separations, and with large ranges of application. Sensitivities generally are high, permitting the determination of a wide range of elements at trace levels, and modern instruments have stabilities that are good enough to permit the determination of elements at high contents.

There is no shortage of good books on atomic-absorption spectrophotometry, all of which give good coverage of the various techniques.[162–164] It is sufficient for the purposes of this review to cover the more general aspects and trends.

Decomposition is achieved either with hydrofluoric acid or by fusion, usually in a borate flux. If hydrofluoric acid is used, silica is lost except when the whole is enclosed, although Langmhyr and co-workers showed that with an excess of the acid, and by preventing too strong heating, silica could be retained.[165] They recognised that different types of material required different decomposition procedures with hydrofluoric acid, including the use of the reagent in a sealed PTFE bomb.[166] They published a series of methods for various types of material.[167–173] Bernas[50] has made such a bomb available commercially. The decomposition with hydrofluoric acid has the advantage of not introducing large amounts of salts into the

solution, but retention of the silica also involves retention of large amounts of hydrofluoric acid. Nebulisation of such a solution, followed by vaporisation in the flame, demands extremely efficient fume extraction, even if the excess is converted into fluoroboric acid by the addition of borate. The technique also has the disadvantage that its effectiveness is not certain. Samples have to be finely ground, at the risk of additional contamination, but, even so, some minerals resist attack, necessitating a second attempt; second attempts are very undesirable in a busy laboratory. Fusion methods are often preferred as being more reliable, but they result in the presence of large amounts of extraneous ions. These ions, in turn, can cause problems by blocking burner systems, which again is a great inconvenience. Dilution of the solution helps to overcome this problem, but it increases detection limits in the sample itself. Lithium metaborate is the generally used flux,[59,60] having most of the normal advantages of a borate flux and still permitting determinations of sodium and potassium. It is a very effective flux, enabling most types of materials to be brought into solution, but difficulty can arise in retaining all of the silica in solution.

More interferences occur when using air - acetylene than dinitrogen oxide - acetylene. For example, in the determination of calcium with an air - acetylene flame it is necessary to add lanthanum or strontium to the solution, whereas when a dinitrogen oxide - acetylene flame is used no buffer is needed. Other additives have been used, such as quinolin-8-ol and EDTA, with the idea of forming complexes with the aluminium, etc., so as to prevent the formation of, say, calcium aluminate in the flame, but it is difficult to subscribe fully to the theory. It is true that EDTA affects the calcium absorption, but addition of the same amount of sodium as that in the EDTA has virtually the same effect.

Methods for the determination of most common elements in a wide range of materials are now well established and can generally be found in the books on the subject, so that there is no need to repeat them here. The technique in terms of conventional analysis appears to be equivalent in status to the "rapid" methods, particularly spectrophotometric methods, which it is rapidly replacing in many smaller laboratories. Determinations of silicon and aluminium are never likely to have the accuracy that can be achieved by the use of appropriate "wet" chemical methods. Precision errors of 1–2% must be expected and, therefore, for these types of determinations the technique is suitable only for rapid routine analyses. When the contents of elements are low, however, then precision errors become less significant so that, provided correct calibration and interference suppression procedures have been used, the results should be at least equal to those from chemical methods. The provisos in the previous sentence are important. For example, in the determination of calcium, results from atomic-absorption spectrophotometry are almost inevitably lower than those obtained by chemical methods. Analysts using atomic-absorption spectrophotometry claimed that chemical results were high owing to interference from strontium and barium, and that atomic-absorption spectrophotometric results were correct. More recent work on a number of British Chemical Standard samples, using X-ray fluorescence and direct-reading spectrometry, have confirmed the former claim, but have not always substantiated the latter. Unless great care is taken, atomic-absorption spectrophotometric results for calcium can still be lower than those obtained by X-ray fluorescence and direct-reading spectrometry, suggesting a failure to cure all interference effects. Nevertheless, the speed and simplicity of atomic-absorption spectrophotometric procedures for conventional analysis make the technique very attractive for many purposes, but it is necessary to bear its limitations in mind.

A second field of use for atomic-absorption spectrophotometry, and possibly the more significant, is in the determination of trace elements. Geochemically, there has always been a great interest in the determination of trace elements, whereas with bulk ceramics the interest is of fairly recent origin, but is growing. In the ceramic field the interest can take one of two forms, general or specific, *i.e.*, knowing which trace elements are present with only a rough idea of how much of each, or knowing quantitatively the amounts of each of a few elements present. In the latter instance, the elements are often toxic and may, in certain uses of the material, come into contact with food. Atomic-absorption spectrophotometry is extremely useful in this instance, but for general purposes other instrumental techniques have greater value. The range of elements to be determined often decides the procedure to be used for decomposition; some fluorides are volatile, whereas other constituents may be lost at the temperature needed for fusion. When fusion is used, it is rarely convenient to make up the solution containing 1 g of sample to less than 25 ml, and often 50 ml is the

optimum volume. Thus, only those elements with good sensitivity can be determined by direct aspiration. Solvent extraction, *e.g.*, with ammonium tetramethylenedithiocarbamate,[174] enables 1 g of sample to be transferred into 10 ml of an organic solvent (isobutyl methyl ketone), thus reducing the dilution, and the solvent often enhances the response. This procedure allows the determination of a further range of elements. Hydride-generation techniques,[175] in which aliquots are taken from the fusion solution, enable other elements to be determined, *e.g.*, arsenic, antimony, bismuth, tin and selenium. The sensitivities obtained when using the hydride-generation technique are remarkable; in solution, as little as 0.001 mg l^{-1} of arsenic, antimony, bismuth and tin and 0.02 mg l^{-1} of tellurium can be determined, with possible selenium levels being only marginally higher.

Atomic-absorption spectrophotometry with electrothermal atomisation has, over the past few years, become a useful alternative in the search for improved sensitivities. Although the graphite furnace dates back to 1961[176] and the resistance-heated furnace to 1968,[177] the advances in application are only now coming to the fore. The graphite furnaces, heated rods, etc., generally have the advantage of lower limits of detection, and use only 10–100 μg of solution, thus permitting many more determinations to be made on the same volume of solution. Hence the technique is applicable to numerous situations in which conventional atomic-absorption spectrophotometry would be cumbersome and, in some instances, impossible. The electrothermal atomisation technique is generally less reproducible than the flame technique and, in the common situation where fusion of the sample is required, interference by alkali metal salts is often very difficult to overcome, and even solvent extraction can pose problems because of the properties of the solvent. Price[178] summarised the situation in the recent past, and drew similar conclusions.

L'vov[179] has recently reviewed the state of the art of trace-element determinations using powdered samples. He describes capsule-in-flame and circular-cavity techniques that offer high sensitivities without the problems of sample preparation. He claims precisions of 5–10% for homogeneous samples, with a speed permitting the determination of ten elements in each of ten samples in 5 h.

X-ray Fluorescence Spectroscopy

X-ray fluorescence spectroscopy has developed over a period of about 15 years from an interesting embryo to an adult that can compete on favourable terms over almost the whole range of "conventional" analysis of silicate and related materials. For those laboratories with a high throughput it is, without question, the method of choice. It is rapid and, using the latest technique of sample presentation, it is capable of good precision and accuracy. It also has the very significant advantage, in these accountancy conscious days, of a considerable cost margin over almost any other technique. Provided that the instrument is reasonably fully utilised, the cost of a conventional aluminosilicate analysis by X-ray fluorescence spectroscopy will be only one half to one third of that by "wet" chemical methods. It has to be admitted that the results for major contents of silica and alumina cannot be guaranteed to better than $\pm0.5\%$, although in practice the results rarely deviate by more than $\pm0.3\%$. Minor constituents are generally determined with an accuracy equal to that of even good quality "wet" analysis. Experience at the B. Ceram. R.A. laboratories has shown that when handling a wide range of samples, "unexpected" elements can cause serious errors in "wet" analysis, errors which, if only "wet" analytical techniques were available, would probably remain undetected. This disadvantage, of course, may be less of a problem in a geochemical laboratory, where nature rather than man has been responsible for the composition of the sample. Thus, the specific nature of an X-ray fluorescence determination can often lead to a better all-round performance, even though satisfactory analytical totals may require prolonged searches for the missing elements.

The improvement in X-ray fluorescence analysis has been caused by two factors that proceeded more or less independently. The first factor is improvement in instrument design and, therefore, performance, and the second resulted from changes in the presentation of the sample to the instrument. X-ray fluorescence equipment, although available in 1960, was lacking in performance for the determination of light elements. Silicon and aluminium were near the limit of its capabilities, while lighter elements, such as magnesium and sodium, could not be measured. X-ray tubes with greater power, better geometry, thinner windows

and newer crystals have brought silicon and aluminium well into the range, and sodium and magnesium are now elements that can be determined adequately. The introduction of the thallium acid phthalate crystal[180],[181] finally brought sodium[182] into this range of capability. Current thin-window tubes can detect oxygen and fluorine can be measured at least semi-quantitatively. Windowless tubes[183] give an even better capability with light elements; calibration graphs can be constructed for both carbon and boron. Electron-beam excitation[184] was suggested as another equally valid approach to analyses for light elements, but its short-coming in requiring the sample to be electrically conducting has caused a great diminution of interest since the use of fused, cast beads became the main method of presenting the sample to the instrument.

At first, powdered samples were used,[185]–[189] but it was soon realised that in order to achieve any measure of success the range of samples analysed with a single calibration had to be severely restricted and close control of particle size was required.[190]–[196] Fluorescent X-ray intensities measured from powdered samples are dependent on the mineralogical composition of the sample and on particle size.[190]–[199] Thus, except in favourable circumstances, such as monitoring the production of a relatively uniform quarry or clay-pit, adequate accuracies were not attainable. Powdered samples were usually pressed into discs with a binder or with graphite, the latter being used with electron-beam excitation.

Fusion of the sample[188],[190],[198]–[203] was then used in order to overcome the errors due to the mineralogical composition of the sample and, to a lesser extent, particle size. The cooled melt was ultimately crushed, ground to a fine powder and a pressed pellet manufactured.[190],[198] Accuracies and precisions were improved by this procedure and, with careful work, the standard of analysis was increased sufficiently to satisfy the needs of a number of laboratories; these laboratories were mainly in the geochemical field, with a few industrial laboratories whose demands for control of major element content were not too rigorous. Much of industry was still waiting for further improvements and, of those who purchased X-ray fluorescence equipment at this stage, many regarded it as a research topic for development.

The real breakthrough that brought X-ray fluorescence spectroscopy to the standard of a practical analytical tool capable of accuracies good enough for almost all analyses of silicate and similar materials was the presentation to the instrument of fused, cast beads.[188],[200]–[207] A variety of fluxes have been used for this purpose, but as sodium became an analysable element, most activity has been concentrated on lithium borates, the tetraborate being most generally used.[185],[186],[188],[190],[204],[206]–[212] Lithium tetraborate at an appropriate flux to sample ratio will decompose most silicate and similar materials, casting into clear glass beads without undue difficulty. Originators of this method cast into pre-heated graphite moulds and then optically polished the lower surface of the bead before presenting it to the instrument. Accuracies and precisions were noticeably improved over earlier techniques, so much so that many laboratories now became seriously interested in the technique. Even so, this preparation method was still significantly dependent on the quality of the final polished surface.[190],[204] The discovery that an alloy of platinum and gold (5%)[213] was not wetted by lithium fluxes of this type led to its use in both fusion vessels and casting dishes.[204],[212],[213] Provided that the contact surface was maintained in good condition, the lower surface of the bead could be presented to the instrument without further preparation, without any loss of accuracy. The wear and tear of constant use, however, still necessitated considerable attention to the maintenance of adequate surface finishes on the casting dishes. During the last 2–3 years, it has been shown to be feasible to use the convexly curved top surface of the bead.[182],[204] The results obtained are equal in quality to those from either of the other procedures for presenting beads to the instrument, and the cost of maintaining casting dishes is greatly reduced.

An alternative technique that has found favour is that developed by Norrish and Hutton,[214] involving a similar fusion, but the melt is not cast into a bead but pressed into a die to give a thin disc. Similar accuracies are possible, less relatively expensive flux is consumed, but the amount of manipulation is greater and there can, in certain circumstances, be uncertainties concerning critical depth.

Most analysts who use these techniques have chosen lithium tetraborate as the flux, but it is not perfect. It has a relatively high melting-point,[215] the melt is viscous even at 1 200 °C, and it does not decompose high-silica materials rapidly. The more alkaline lithium meta-borate has a lower melting-point and produces a free-running melt even at 1 000 °C.[216] It

is slow to decompose high-alumina materials, but a 4 + 1 metaborate - tetraborate mixture is convenient to handle, fully effective in decomposing a wide range of samples and can be poured from the fusion vessel into the casting dish with negligible retention in the former. The variable transfer of melt into the dish, as can occur with the more viscous tetraborate, causes differing convexities of the upper surface, giving reduced precisions when this surface is presented to the instrument. The choice of an appropriate flux and, to some extent, the flux to sample ratio, is determined by the basicity or acidity of the major oxides in the sample.

Inter-element effects, although predictable, are a potential source of error, and several approaches to reducing or eliminating such errors have been attempted. Calibration graphs constructed so as to cover only a short range of composition avoid the problem by ensuring that the theoretical corrections do not reach significant proportions. Clearly, in a laboratory in which more than a few types of sample are analysed this approach can be very cumbersome. "Multi-dilution" techniques have been applied by Tertian[217] and adopted by a number of laboratories.[210] Here, for major contents at least, two beads are prepared at different flux to sample ratios and, in the calculation of the results from these ratios, inter-element effects can be eliminated. The technique has disadvantages in that twice the work is involved for major contents and two possible sets of errors are introduced in place of one. Co-operative work between several laboratories did not reveal any improvement in results over those normally obtained by reading directly from a medium-range calibration graph.

Ambrose[188,204] amongst others,[214] reduced the inter-element effect by using the "heavy absorber" lanthanum oxide. When it is added to the flux, widely diverging types of materials such as slags, cements, iron and chrome ores and various refractories give results that fall on the same calibration graph. The technique appears to be very sound for major-content elements, but is less satisfactory for minor-content elements. The disadvantage of using a heavy element in the flux is that sensitivities are reduced. Although the reduction in intensity for light elements is less than that for heavy elements, sensitivity is so important, especially with sodium, that even a small decrease is critical. With lanthanum there is the further disadvantage of the overlap of the lanthanum Mα line with the sodium Kα line.

The fourth technique is to prepare the appropriate synthetic standard in order to establish the level of inter-element effects, *i.e.*, α-coefficients.[218–220] Once established, provided that no changes are made in the operating procedures or instrumental parameters, the α-coefficients remain valid. Experience has shown, as a result of handling a very wide range of sample compositions, that the need for correcting for inter-element effects, if accurate results are required, is much more widespread than appears to have been generally realised. For example, when boron is present in the sample, corrections need to be applied for its presence even though the flux contains several grams of boron(III) oxide. The building up of the information needed is time consuming and tedious and in many circumstances one of the other approaches may be preferred but, for general purposes, it gives a satisfactory performance.

The problem of interferences is, of course, one aspect of the more general problem of calibration procedures. When samples were used in the non-fused condition recourse had to be made to chemically analysed standards. When using fusion techniques, however, synthetic standards of any desired composition can be used, with very considerable advantages. A word of caution may not be inapt; while most analysts would recognise the possibility of obtaining incorrect analytical figures even on carefully analysed standard samples, few would anticipate problems with pure oxides. Neglecting the rare occasion when there is an accidental impurity in a "pure" oxide, it does not necessarily follow that a material that has only 0.001% of "impurity" contains 99.999% of the oxide. Oxides such as silica and alumina absorb and retain water even at high temperatures, and other oxides may absorb carbon dioxide or be in a partially incorrect oxidation state. Synthetic standards are extremely valuable, but their preparation and use demand care and intelligent appreciation.

Presentation of a fused, cast bead or pressed-glass disc to the instrument now seems to be the generally accepted technique when accuracy is important. It is simple, involves the minimum of manipulation and, most important, can be calibrated synthetically. Its main disadvantage is that the fusion process causes the loss of some volatile elements (fluorine and chlorine are usually completely lost), sulphur may be retained or lost (partially or completely) and cadmium and possibly other volatile metals can be lost, certainly at higher

temperatures. It also has to be remembered that it is not the sample that is being analysed but the bead, and correct results can be obtained only if the masses of sample and flux in the melt are the same as those in the standard melt. If volatile components have been lost, the total melt will have a lower mass, giving apparently higher concentrations. Hence, it is important to have ignited the sample freshly, or at least to have allowed, in the mass taken, for its loss on ignition, and also to have allowed for current levels of hydration of the flux. Even so, further losses in mass can occur during the fusion, *e.g.*, in the presence of large amounts of sulphate. When this is to be expected, it is possible either to complete the fusion, cool the melt and weigh it, then rapidly melt and cast the bead, or to use appropriate internal standards.

Non-dispersive X-ray fluorescence spectroscopy[221] is a more recent development that has not yet made its mark in this area. It has a number of disadvantages as yet, certainly being lacking in precision for use in quantitative analysis. Instruments that contain a radioactive source[222–224] have been used successfully for the determination of silica and are being introduced into industrial use for this and other determinations.

Possible Future Trends

The present pattern of analysis in the geochemical field and ceramic industry seems likely to remain basically unchanged in the foreseeable future. Current trends away from "wet" analysis towards increased instrumentation will undoubtedly continue, smaller laboratories aiming for an atomic-absorption spectrophotometric capability, and the larger for X-ray fluorescence equipment. Whereas up to about 10 years ago even a medium-sized laboratory could be considered to be competently equipped if it possessed a flame photometer and spectrophotometer, the ever widening demands made on the analyst would now require atomic-absorption and X-ray fluorescence equipment to provide equally adequate coverage. These instruments will surely continue to provide the bulk of analytical information in the future. It is difficult to visualise a new physical technique being developed that would be capable of producing accurate information with less sample preparation, greater speed or significantly less capital cost. Any new instrumental technique will, almost certainly, be based on a physical approach that will almost equally certainly mean that mineralogical and particle-size factors will necessitate fusion or solution. Thus, the only material advantage likely to accrue would be a lower capital cost, which seems to be unlikely in practice.

Non-dispersive X-ray fluorescence spectroscopy is still in its early development, and could conceivably compete with more conventional X-ray fluorescence techniques, but the fact remains that the latter is known to be successful. Unless the present cost-conscious outlook reverts to a more liberated scientific approach, few analysts will care to risk expenditure on the unknown unless the advantages of such a move could be considerable.

The range of instrumentation is limited at present, in that the methods for the determination of non-metals (carbon, sulphur, fluorine, boron, etc.) are inadequate. Pyrolysis and infrared techniques for the determination of carbon and sulphur have speeded up these determinations and the ion-selective electrode has materially assisted with the determination of fluorine, so that even these problems have been reduced. Even so, the current techniques used with these elements are still not comparable with X-ray fluorescence techniques. Boron, at present, escapes almost all the modern approaches; for major contents modified Wherry's methods are used, and for smaller amounts colorimetric methods using concentrated sulphuric acid solutions. There are hopes that molecular emission cavity analysis may prove of value here,[225] and that this technique may be useful not only for the determination of sulphur but also for identification of its state of combination.[226] Even atomic-absorption spectrophotometry fails with boron at present because of its low sensitivity, but it is possible that a special technique may be developed, as has happened already with mercury and with the hydride-generation technique for arsenic, etc.

There is also little doubt that there will be an increasing interest in the determination of trace elements in industry and that efforts will be progressively concentrated on their accurate determination. Powder techniques seem liable to decrease in consequence, more emphasis being placed on fusion and mainly on solution techniques. Powders may well continue to be used in the process of decreasing limits of detection, and when using solutions it is possible to anticipate increasing competition for atomic-absorption spectrophotometry from plasma-

source instruments, particularly because of their ability to permit the simultaneous determination of a number of elements.

Electron-probe microanalysis, scanning electron microscopy with energy-dispersive analysis and similar techniques will be increasingly used as interest in micro-structures increases. It is appreciated that these and other valuable analytical techniques have received scant mention in this review. This omission has been deliberate, in that if they had been included, together with thermal methods, differential thermal analysis, X-ray diffraction, infrared and mass spectrometry, etc., the subject would have become impossible.

The greatly increased speed and relatively reduced cost with which analytical data can now be produced must cause increased demands. Industrial control, in the past, has had a bias towards physical methods as they are faster, cheaper and provide information directly concerned with manufacturing processes and properties. As most physical information can be deduced from analytical data, both compositional and structural, there seems little doubt that the balance of advantage is swinging towards the analyst, and that as additional information is built up about these relationships, this swing will continue.

References

1. Bergman, T., "Opuscula Physica et Chemica (De Minerarum Docimasiā Humida)," Holmiae, Upsalae Aboae, 1780, pp. 349 and 399.
2. Berzelius, J. J., "De l'Analyses des Corps Inorganiques," Paris, 1827.
3. Wöhler, . ., "Praktische Übungen in der Chemische Analyse," Göttingen, 1853.
4. Rose, H., "Handbuch der Analytischen Chemie," Berlin, 1929.
5. Fresenius, C. R., "Quantitative Chemical Analysis," Sixth Edition, Churchill, London, 1873.
6. Washington, H. S., "The Chemical Analysis of Rocks," Fourth Edition, John Wiley, New York, 1930.
7. Hillebrand, W. F., and Lundell, G. E. F., "Applied Inorganic Analysis," John Wiley, New York, 1929.
8. Mellor, J. W., "A Treatise on Quantitative Inorganic Analysis," Volume 1, Griffin, London, 1913.
9. Knowles, H. B., and Redmond, J. C., *J. Am. Ceram. Soc.*, 1935, **18**, 106.
10. Koenig, E. W., *Ind. Engng Chem. Analyt. Edn*, 1939, **11**, 532.
11. British Ceramic Research Association Chemical Analysis Sub-Committee, *Trans. Br. Ceram. Soc.*, 1952, **51**, 438.
12. BS 1902:1952, Amendment No. 1, 1957.
13. Collins, G. C., and Polkinhorne, H., *Analyst*, 1952, **77**, 430.
14. Hedin, R., "Colorimetric Methods for Rapid Analysis of Silicate Materials," Proceedings of the Swedish Cement and Concrete Research Institute, No. 8, Stockholm, 1947.
15. Shapiro, L., and Brannock, W. W., "The Rapid Analysis of Silicate Rocks," U.S. Geological Survey Circular, 1952, No. 165; 1956, No. 1036C.
16. Corey, R. B., and Jackson, M. L., *Analyt. Chem.*, 1953, **25**, 624.
17. Bennett, H., Eardley, R. P., Hawley, W. G., and Thwaites, I., *Trans. Br. Ceram. Soc.*, 1962, **61**, 636.
18. Bennett, H., Eardley, R. P., and Hawley, W. G., *Trans. Br. Ceram. Soc.*, 1956, **57**, 1.
19. Chirnside, R. C., *J. Soc. Glass Technol.*, 1959, **43**, 5T.
20. Chalmers, R. A., *in* Taylor, H. F. W., *Editor*, "Chemistry of Cements," Academic Press, New York, 1964, p. 171.
21. Hey, M. H., *Mineralog. Mag.*, 1973, **39**, 4.
22. Society of Glass Technology Analysis Sub-Committee, *J. Soc. Glass Technol.*, 1953, **37**, 97T.
23. Finn, A. N., and Klekotka, J. F., *J. Res. Natn. Bur. Stand.*, 1930, **4**, 809.
24. British Ceramic Research Association Analysis Sub-Committee, *Br. Ceram. Res. Ass. Spec. Publ.*, 1956, No. 12.
25. BS 1902:1952, Amendment No. 2, 1961.
26. Jeffery, P. G., and Wilson, A. D., *Analyst*, 1960, **85**, 478.
27. Bennett, H., Eardley, R. P., Hawley, W. G., and Thwaites, I., *Trans. Br. Ceram. Soc.*, 1962, **61**, 433.
28. BS 1902:Part 2A:1964, "Chemical Analysis of High-silica and Aluminosilicate Materials."
29. Greenfield, S., *Analyst*, 1959, **84**, 380.
30. BS 1902:Part 2A:1965, Amendment No. 1.
31. Vänninen, E., and Ringbom, A., *Analytica Chim. Acta*, 1955, **12**, 308.
32. BS 1902:Part 2B:1967, "Chemical Analysis of Aluminous Materials."
33. Bennett, H., and Reed, R. A., *Analyst*, 1967, **92**, 466.
34. Bennett, H., "Proceedings of the Fifth Ceramic Chemists Conference," British Ceramic Research Association, Stoke-on-Trent, 1974.
35. BS 1902:Part 2D:1969, "Determination of Silica in High-silica, Aluminosilicate and Aluminous Materials by Coagulation."
36. Přibil, R., and Veselý, V., *Talanta*, 1962, **9**, 23.
37. Pritchard, D. J., *Analytica Chim. Acta*, 1965, **32**, 184.
38. Mercy, E. L. P., and Saunders, M. J., *Earth Planet. Sci. Lett.*, 1966, **1**, 169.
39. Kiss, E., *Analytica Chim. Acta*, 1967, **39**, 233.
40. Bennett, H., and Reed, R. A., *Analyst*, 1970, **95**, 541.
41. Bennett, H., and Reed, R. A., *Analyst*, 1971, **96**, 640.

42. Bennett, H., and Reed, R. A., *Analyst*, 1972, **97**, 794.
43. BS 1902: Part 2E: 1970, "Chemical Analysis of Magnesites and Dolomites."
44. BS 1902: Part 2C: 1974, "Chemical Analysis of Chrome-bearing Materials."
45. Bennett, H., and Marshall, K., *Analyst*, 1963, **88**, 877.
46. Maxwell, J. A., "Rock and Mineral Analysis," Interscience, New York, 1968.
47. Jeffery, P. G., "Chemical Methods of Rock Analysis," Second Edition, Pergamon Press, Oxford, 1975.
48. Bennett, H., and Reed, R. A., "Chemical Methods of Silicate Analysis," Academic Press, New York, 1971.
48a. Boulton, J. F., and Eardley, R. P., *Analyst*, 1967, **92**, 271.
49. Langmhyr, F. J., and Graff, P. R., *Norg. Geol. Unders.*, 1965, 230.
50. Bernas, B., *Analyt. Chem.*, 1968, **40**, 1682.
51. Rafter, T. A., and Seelye, F. T., *Nature, Lond.*, 1950, **165**, 317.
52. Rafter, T. A., *Analyst*, 1950, **75**, 485.
53. Milner, G. W. C., and Woodhead, J. L., *Analytica Chim. Acta*, 1955, **12**, 127.
54. Bryant, F. J., and Hardwick, P. J., *Analyst*, 1950, **75**, 12.
55. Theobald, L. S., *Analyst*, 1942, **67**, 287.
56. Ingamells, C. O., *Talanta*, 1964, **11**, 665.
57. Suhr, N. H., and Ingamells, C. O., *Analyt. Chem.*, 1966, **38**, 730.
58. Ingamells, C. O., *Analyt. Chem.*, 1966, **38**, 1228.
59. Boar, P. L., and Ingram, L. K., *Analyst*, 1970, **95**, 124.
60. Van Loon, J. C., and Parissis, C. M., *Analyst*, 1969, **94**, 1057.
61. Bennett, H., Eardley, R. P., and Thwaites, I., *Analyst*, 1961, **86**, 135.
62. Sajo, I., *Acta Chim. Acad. Sci. Hung.*, 1955, **6**, 243.
63. Biskupsky, V. S., *Analytica Chim. Acta*, 1965, **33**, 333.
64. Grimaldi, F. S., Ingram, B., and Cuttitta, F., *Analyt. Chem.*, 1955, **27**, 919.
65. Shell, H. R., and Craig, R. L., *Analyt. Chem.*, 1954, **26**, 996.
66. Wichers, E., Schlecht, W. G., and Gordon, C. L., *J. Res. Natn. Bur. Stand.*, 1944, **33**, 363.
67. BS 4140: 1967, Addendum No. 2, 1974.
68. Harmer, W. C. E. *Mineralog. Mag.*, 1973, **39**, 112.
69. Brabson, J. A., Mattraw, H. C., Maxwell, G. E., Darrow, A., and Needham, H. F., *Analyt. Chem.*, 1948, **20**, 504.
70. Wilson, H. N., *Analyst*, 1951, **76**, 65.
71. Armand, M., and Berthoux, J., *Analytica Chim. Acta*, 1953, **8**, 510.
72. Strickland, J. D. H., *J. Am. Chem. Soc.*, 1952, **74**, 862.
73. Miller, C. C., and Chalmers, R. A., *Analyst*, 1953, **78**, 24.
74. Hollander, M., and Rieman, W., III, *Ceram. Age*, 1947, **50**, 168.
75. Travers, A., *C. R. Hebd. Séanc. Acad. Sci., Paris*, 1927, **185**, 893.
76. Maxwell, J. M. R., and Budd, S. M., *J. Soc. Glass Technol.*, 1956, **40**, 509T.
77. Kalocsai, G. I. Z., and Hockley, J. J., *Mineralog. Mag.*, 1972, **38**, 618.
78. Anderson, L. J., *Acta Chem. Scand.*, 1958, **12**, 495.
79. Ringbom, A., Ahlers, P. E., and Siitonen, S., *Analytica Chim. Acta*, 1959, **20**, 78.
80. Schwartz, M. C., *Ind. Engng Chem. Analyt. Edn*, 1942, **14**, 893.
81. Meunier, P., *C. R. Hebd. Séanc. Acad. Sci., Paris*, 1934, **199**, 1250.
82. Miller, C. C., and Chalmers, R. A., *Analyst*, 1953, **78**, 686.
83. Bosch, H., and Gonsior, T., *Tonind.-Ztg Keram. Rdsch.*, 1966, **90**, 261.
84. Bennett, H., Hawley, W. G., and Eardley, R. P., *Trans. Br. Ceram. Soc.*, 1962, **61**, 201.
85. Weibel, M., *Z. Analyt. Chem.*, 1961, **184**, 322.
86. Cluley, H. J., *Glass Technol.*, 1961, **2**, 71.
87. Sajo, I., *Acta Chim. Acad. Sci. Hung.*, 1955, **6**, 251.
88. Society of Glass Technology Analysis Committee, *Glass Technol.*, 1969, **10**, 2.
89. Gentry, C. H. R., and Sherrington, L. G., *Analyst*, 1946, **71**, 432.
90. Riley, J. P., *Analytica Chim. Acta*, 1958, **19**, 413.
91. Riley, J. P., and Williams, H. P., *Microchim. Acta*, 1959, **6**, 804 and 825.
92. Chalmers, R. A., and Basit, M. A., *Analyst*, 1968, **93**, 629.
93. Glemser, O., Raulf, E., and Giesen, K., *Z. Analyt. Chem.*, 1954, **141**, 86.
94. Hill, U. T., *Analyt. Chem.*, 1956, **28**, 1419.
95. Poole, P., and Segrove, H. D., *J. Soc. Glass Technol.*, 1955, **39**, 1955.
96. André, J., *Bull. Soc. Fr. Céram.*, 1957, **37**, 59.
97. Wilson, A. D., and Sergeant, G. A., *Analyst*, 1963, **88**, 109.
98. Schafer, H. N. S., *Analyst*, 1966, **91**, 755.
99. Shell, H. R., *Analyt. Chem.*, 1954, **26**, 591.
100. BS 1902: 1952.
101. Methods of Analysis Committee, *J. Iron Steel Inst.*, 1952, **171**, 392.
102. Hume, D. S., and Kolthoff, I. M., *Analytica Chim. Acta*, 1957, **16**, 415.
103. Miller, C. C., and Chalmers, R. A., *Analyst*, 1952, **77**, 2.
104. Blanchet, M. L., and Malaprade, L., *Chim. Analyt.*, 1967, **49**, 11.
105. Yoe, J. H., and Jones, A. L., *Ind. Engng Chem. Analyt. Edn.*, 1944, **16**, 111.
106. Cluley, H. J., and Newman, E. J., *Analyst*, 1963, **88**, 3.
107. Society of Glass Technology Chemical Analysis Committee, *Glass Technol.*, 1973, **14**, 5.
108. Yoe, J. H., and Armstrong, A. R., *Analyt. Chem.*, 1947, **19**, 100.
109. Shapiro, L., and Brannock, W. W., *Bull. U.S. Geol. Surv.*, 1962, No. 1144A, A29.

110. Voinovitch, I. A., Debras-Guedon, J., and Louvrier, J., "L'Analyse des Silicates," Herman, Paris, 1962, p. 489.
111. Jeffery, P. G., and Gregory, G.R.E.C., *Analyst*, 1965, **90**, 177.
112. Holth, T., *Analyt. Chem.*, 1949, **21**, 1221.
113. Bashar, A., and Townshend, A., *Talanta*, 1966, **13**, 1123.
114. Grzeskowiak, R., and Turner, T. A., *Talanta*, 1973, **20**, 351.
115. Thompson, H. V., *Trans. Br. Ceram. Soc.*, 1959, **58**, 353.
116. Gilbert, F. C., and Gilpin, W. C., *Analyst*, 1946, **71**, 235.
117. Gilbert, F. C., *Analyst*, 1947, **72**, 482.
118. Caley, E. R., and Elving, P. J., *Ind. Engng Chem. Analyt. Edn.*, 1938, **10**, 264.
119. Flaschka, H., and Huditz, F., *Radex Rdsch.*, 1952, No. 4, 181.
120. Banks, J., *Analyst*, 1952, **77**, 484.
121. Přibl, R., *Chemické Listy*, 1953, **47**, 1333.
122. Patton, J., and Reeder, W., *Analyt. Chem.*, 1956, **28**, 1026.
123. Kuhn, V., *Chim. Analyt.*, 1958, **40**, 340.
124. Cluley, H. J., *Analyst*, 1954, **79**, 567.
125. Riley, J. P., *Analytica Chim. Acta*, 1958, **19**, 413.
126. Riley, J. P., *Analytica Chim. Acta*, 1959, **21**, 317.
127. Flaschka, H., and Jacobljevich, H., *Radex Rdsch.*, 1954, No. 3, 83.
128. Hildebrand, G. P., and Reilley, C. N., *Analyt. Chem.*, 1957, **29**, 258.
129. Ostertag, H., and Rinck, E., *C. R. Hebd. Séanc. Acad. Sci., Paris*, 1950, **231**, 1304.
130. Williams, K. T., and Wilson, J. R., *Analyt. Chem.*, 1961, **33**, 245.
131. Herrero-Lancina, M., and West, T. S., *Analyt. Chem.*, 1963, **35**, 2131.
132. Theobald, L. S., personal communication.
133. Pouget, R., *Rapp. CEA*, 1962, No. 2176.
134. Přibil, R., and Veselý, V., *Chemist-Analyst*, 1966, **55**, 82.
135. Jordan, D. E., and Monn, D. E., *Analytica Chim. Acta*, 1967, **37**, 42.
136. Beater, B. E., and Mand, R. R., *Chemist-Analyst*, 1959, **48**, 10.
137. Shapiro, L., *Chemist-Analyst*, 1959, **48**, 73.
138. Abbey, S., and Maxwell, J. A., *Analytica Chim. Acta*, 1962, **27**, 233.
139. Fletcher, W. W., *J. Soc. Glass Technol.*, 1959, **43**, 86T.
140. Society of Glass Technology Chemical Analysis Committee, *Glass Technol.*, 1973, **14**, 5.
141. Eardley, R. P., and Reed, R. A., *Analyst*, 1971, **96**, 699.
142. Billings, G. K., and Adams, J. A. S., *Atom. Absorption Newsl.*, 1965, **3**, 65.
143. Ohrdorf, R., *Geochim. Cosmochim. Acta*, 1968, **38**, 191.
144. Vosters, M., and Deutsch, S., *Earth Planet Sci. Lett.*, 1967, **2**, 449.
145. Nichol, A. W., *Editor*, "Physicochemical Methods of Mineral Analysis," Plenum, London, 1975.
146. Mulvey, T., and Webster, R. K., "Modern Physical Techniques in Materials Technology," Oxford University Press, London, 1974.
147. Kirkendale, G. A., "Analytical Methods for Materials Investigation," Gordon and Breach, New York, 1971.
148. Jackson, P. F. S., "Proceedings of the Third Ceramic Chemists Conference," British Ceramic Research Association, Stoke-on-Trent, 1968, p. 29.
149. Brown, R., "Proceedings of the Fourth Ceramic Chemists Conference," British Ceramic Research Association, Stoke-on-Trent, 1971, p. 49.
150. Fowkes, A. J., "Proceedings of the Fifth Ceramic Chemists Conference," British Ceramic Research Association, Stoke-on-Trent, 1974, p. 82.
151. Smales, A. A., "Proceedings of the Third Ceramic Chemists Conference," British Ceramic Research Association, Stoke-on-Trent, 1968, p. 41.
152. Ward, W., and Hartley, F., *J. Soc. Glass Technol.*, 1953, **37**, 113T.
153. Ward, W., and Innes, D. D., *J. Soc. Glass Technol.*, 1955, **39**, 156T.
154. Ahrens, L. H., "Spectrochemical Analysis," Addison-Wesley, Cambridge, Mass., 1954.
155. Mitchell, R. L., "Spectrographic Analysis of Soils, Plants and Related Materials," Technical Publication No. 44, Commonwealth Bureau of Soil Science, Harpenden, 1948.
156. Foster, R., *Proc. Br. Ceram. Soc.*, 1970, No. 16, 25.
157. Tingle, W. H., and Matocha, C. K., *Analyt. Chem.*, 1948, **30**, 494.
158. Eardley, R. P., *Proc. Br. Ceram. Soc.*, 1970, No. 16, 31.
159. Eardley, R. P., and Clarke, H. S., *Appl. Spectrosc.*, 1965, **19**, 69 and 186.
160. Greenfield, S., Jones, I. Ll., and Berry, C. T., *Analyst*, 1964, **89**, 713.
161. Greenfield, S., Jones, I. Ll., McGeachin, H. McD., and Smith, P. B., *Analytica Chim. Acta*, 1975, **74**, 225.
162. Elwell, W. T., and Gidley, J. A. F., "Atomic Absorption Spectrophotometry," Second Edition, Pergamon Press, Oxford, 1966.
163. Slavin, W., "Atomic Absorption Spectroscopy," Interscience, New York, 1968.
164. Price, W. J., "Analytical Atomic Absorption Spectrometry," Heyden, London, 1972.
165. Langmhyr, F. J., and Graff, P. R., *Analytica Chim. Acta*, 1959, **21**, 334.
166. Langmhyr, F. J., and Sveen, S., *Analytica Chim. Acta*, 1965, **32**, 1.
167. Langmhyr, F. J., and Paus, P. E., *Analytica Chim. Acta*, 1968, **43**, 397.
168. Langmhyr, F. J., and Paus, P. E., *Analytica Chim. Acta*, 1968, **43**, 506.
169. Langmyhr, F. J., and Paus, P. E., *Analytica Chim. Acta*, 1969, **44**, 445.
170. Langmhyr, F. J., and Paus, P. E., *Analytica Chim. Acta*, 1969, **45**, 173.
171. Langmhyr, F. J., and Paus, P. E., *Analytica Chim. Acta*, 1969, **45**, 176.

172. Langmhyr, F. J., and Paus, P. E., *Analytica Chim. Acta*, 1969, **45**, 157.
173. Langmhyr, F. J., and Paus, P. E., *Analytica Chim. Acta*, 1970, **50**, 515.
174. Rigby, J. H., "Proceedings of the Fourth Ceramic Chemists Conference," British Ceramic Research Association, Stoke-on-Trent, 1971, p. 39.
175. Thompson, K. C., and Thomerson, D. R., *Analyst*, 1974, **99**, 595.
176. L'vov, B. V., *Spectrochim. Acta*, 1961, **17**, 761.
177. Massmann, H., *Spectrochim. Acta*, 1968, **23B**, 215.
178. Price, W. J., "Proceedings of the Fifth Ceramic Chemists Conference," British Ceramic Research Association, Stoke-on-Trent, 1974, p. 51.
179. L'vov, B. V., *Talanta*, 1976, **23**, 109.
180. Philips Co., *X-ray News*, 1974, No. 2.
181. Vie le Sage, R., and Grubis, B., *X-ray Spectrom.*, 1973, **2**(4), 89.
182. Bennett, H., Oliver, G. J., and Holmes, M., *Trans. J. Br. Ceram. Soc.*, 1977, **76**, No. 1
183. Vie le Sage, R., Bacquillon, P., and Faucherre, J., *C. R. Hebd. Séanc. Acad. Sci. Paris, C*, 1974, **27**, 125.
184. Price, B. J., *Metals Minerals*, 1973, 140.
185. Hickson, K., "Proceedings of the Ceramic Chemists Conference," British Ceramic Research Association, Stoke-on-Trent, 1964, p. 37.
186. Orrell, E. W., "Proceedings of the Second Ceramic Chemists Conference," British Ceramic Research Association, Stoke-on-Trent, 1966, p. 70.
187. Lowe, R. S., "Proceedings of the Second Ceramic Chemists Conference," British Ceramic Research Association, Stoke-on-Trent, 1966, p. 79.
188. Ambrose, A. D., "Proceedings of the Fourth Ceramic Chemists Conference," British Ceramic Research Association, Stoke-on-Trent, 1971, p. 7.
189. Hutchison, C., "Laboratory Handbook of Petrographic Techniques," Wiley Interscience, New York, 1974.
190. Ambrose, A. D., Corporate Laboratories, Report No. MG/CC/565/72, British Steel Corporation, Sheffield, 1972.
191. Carr-Brion, K. G., "Proceedings of the Fifth Conference on X-ray Analytical Methods, Swansea, 1966," Philips, Eindhoven, 1967, p. 107.
192. Carr-Brion, K. G., *Analyst*, 1969, **94**, 177.
193. Hendry, G. L., "Proceedings of the Fifth Conference on X-ray Analytical Methods, Swansea, 1966," Philips Eindhoven, 1967, p. 72.
194. Gunn, B., *Adv. X-ray Analysis*, 1960, **4**, 382.
195. De Jongh, W. K., "Proceedings of the Sixth Conference on X-ray Analytical Methods, Southampton, 1968," Philips Eindhoven, 1969, p. 1.
196. Müller, R. O., "Spectrochemical Analysis by X-ray Fluorescence," Adam Hilger, London, 1972.
197. Berry, P. F., Futura, T., and Rhodes, J. R., *Advan. X-ray Analysis*, 1969, **12**, 612.
198. Anderman, G., and Allen, J. O., *in* Mueller, W. M., *Editor*, "Ninth Denver Conference on Advances in X-ray Analysis," Plenum, New York, 1960, Vol. 4, p. 414.
199. Adler, I., and Axelrod, J. N., *Spectrochim. Acta*, 1955, **7**, 91.
200. Claisse, F., *Norelco Reptr*, 1957, **3**, 3.
201. Blanquet, P., "L'Analyse par Spectrographie et Diffraction de Rayons X, Madrid, 1962," Philips, Eindhoven, p. 85.
202. Claisse, F., and Sampson, C., Province de Quebec Services des Laboratories, Report No. 67, 1962.
203. Claisse, F., *Prelim. Rep. Dep. Mines, Queb.*, No. 32, 1956.
204. Ambrose, A. D., "Proceedings of the Fifth Ceramic Chemists Conference," British Ceramic Research Association, Stoke-on-Trent, 1974, p. 25.
205. Sherman, J., *Spectrochim. Acta*, 1955, **7**, 283.
206. Ambrose, A. D., Rutherford, R., and Muir, S., *Metallurgia*, 1970, **82**, 119 and 491.
207. Hooper, P. R., and Atkins, L., *Mineralog. Mag.*, 1969, **37**, 409.
208. *Spectrogr. News Lett.*, 1954, **7**, 1.
209. Sastry, B. S. R., and Hummel, E. A., *J. Am. Ceram. Soc.*, 1959, **42**, 216.
210. Ashley, D. G., and Andrews, K. W., *Analyst*, 1972, **97**, 841.
211. Hermann, H., *Bull. Soc. Fr. Céram.*, 1974, **13**, 103.
212. Kroeft, U., *Keram. Z.*, 1974, **26**(8), 434.
213. Selman, G. L., Spender, M. R., and Darling, A. S., *Platin. Metals Rev.*, 1965, **9**(4), 130.
214. Norrish, K., and Hutton, J. T., *Geochim. Cosmochim. Acta*, 1969, **33**, 431.
215. Levin, E. M., Robbins, C. R., and McMurdie, H. F., "Phase Diagrams for Ceramicists," American Ceramic Society, Columbus, Ohio, 1964.
216. Bennett, H., and Oliver, G. J., *Analyst*, 1976, **101**, 803.
217. Tertian, R., *Spectrochim. Acta*, 1969, **24B**, 447.
218. Hughes, H., *Analyst*, 1972, **97**, 161.
219. Hughes, H., "Proceedings of the 24th BISRA Chemical Conference," BISRA, London, 1971, p. 9.
220. Rousseau, R., and Claisse, F., *X-ray Spectrom.*, 1974, **3**, 31.
221. Herbert, A. J., and Street, K., *Analyt. Chem.*, 1974, **46**, 203.
222. Bowie, S. H. U., *Min. Mag., Lond.*, 1968, **118**, 230.
223. Rhodes, J. R., *Spec. Tech. Publs Am. Soc. Test. Mater.*, 1970, No. 485, 243.
224. Bennett, H., and Brassington, P. H., *Trans. J. Br. Ceram. Soc.*, 1977, **76**, No. 1.
225. Ghonaim, S. A., *Proc. Soc. Analyt. Chem.*, 1974, **11**, 138.
226. Bogdanski, S. L., *Analytica Chim. Acta*, 1975, **77**, 53.

Stability of Iron(III) - Thiocyanate Complexes and the Dependence of Absorbance on the Nature of the Anion

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The dependence of the colour intensity of the iron(III) - thiocyanate complex formed at two different ratios of thiocyanate to iron on the nature and concentration of the acid anion was studied.   Four different acids were tested over the concentration range 0.05–1.0 N: perchloric acid, nitric acid, hydrochloric acid and sulphuric acid.   Fading of the iron(III) - thiocyanate colour was ascribed to a specific effect of the anion caused by progressive masking of iron(III) ions of the highly dissociated iron(III) - thiocyanate by the more strongly complexing anion ligand.   The results were interpreted in the light of the calculated values of side-reaction coefficients between iron(III) and the added ligand, as well as on the magnitude of conditional stability constants of iron(III) - thiocyanate in the various media.   That the order of effectiveness of the added anions towards complexing iron(III) ions is $SO_4^{2-} > Cl^- > NO_3^- \geqslant ClO_4^-$ was further substantiated.

Keywords: Iron(III) - thiocyanate complexes; stability constants; light absorbance; nature of anion

The spectrophotometric thiocyanate method[1] is still extensively used for the determination of minute amounts of iron, even though other reagents that may give better results have been discovered in recent years.[2]   Although it is widely used because of its high sensitivity and considerable colour intensity, the method suffers from some disadvantages.   The intensity of the red colour depends upon several factors, among which are the thiocyanate to iron ratio, the actual amount of thiocyanate present, the concentration of acid in solution and the nature of the anion.   Although ample work has been carried out in investigating these effects[3-8] much diversity of opinion still exists, especially if it is considered that these variables are inter-related.   Many of the inconsistencies result from the fact that the reaction mechanism of the coloration process is not simple and that more than one type of iron(III) - thiocyanate complex, along with other iron(III) complexes with interfering anions, may be formed.[9-20]

In the present work, a systematic study was carried out on the effect of acid concentration and nature of the anion on the intensity of the colour of iron(III) - thiocyanate developed at two different thiocyanate to iron ratios, namely 750:1 and 2:1.   Four different acids were examined over the concentration range 0.05–1.0 N; these were perchloric acid, nitric acid, hydrochloric acid and sulphuric acid.   In the light of the results obtained the role played by the acid anion as an interfering species on the colour reaction was clarified.

Experimental

All materials used were of AnalaR or CP grade and were therefore used without further purification.   Standard iron(III) nitrate or perchlorate solutions were prepared by dissolving a known amount of iron wire in the calculated least amount of hot concentrated nitric or perchloric acid.   The solutions were evaporated on a water-bath in order to expel any excess of acid; the directions of Snell and Snell[21] and Yoe[22] were followed during preparation of the nitrate solution.   Standard iron(III) sulphate solutions were prepared from ammonium iron(II) sulphate to which sulphuric acid was added and the solution then oxidised by continuous addition of potassium permanganate.   The iron solutions thus prepared were standardised by titration with EDTA at pH 2–3.[23]   The solutions contained 100 p.p.m. of iron(III) and were 0.03–0.05 N with respect to acid.   Stock solutions (4 N) of each of perchloric, nitric, hydrochloric and sulphuric acids were prepared with re-distilled water and standardised with sodium carbonate.

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Light-absorption measurements were carried out by using a double-beam spectrophotometer (Unicam SP700) with a range of 185–2 200 nm and scale divisions of 0.01 absorbance unit.

To 1 ml of the standard 100 p.p.m. iron(III) solution the calculated amount of acid required to give the requisite final normality was added, followed by 2 drops of 30% hydrogen peroxide solution and 1 ml of 10% ammonium thiocyanate solution. The volume of the solution was made up to 10 ml in a calibrated flask. The resulting solution was 1.7×10^{-4} M with respect to iron and 0.13 M with respect to thiocyanate, giving a thiocyanate to iron ratio of 750:1. For the preparation of the lower thiocyanate to iron ratio, the same procedure was followed except that the amounts of iron(III) and thiocyanate taken were 3.4×10^{-4} and 6.8×10^{-4} M, respectively. The absorbance of the solution was, in each instance, measured directly in a 1-cm glass cell at 480 nm, the wavelength of maximum absorbance.[24]

Results and Discussion

The results obtained for the various acids examined and for their corresponding sodium salts at the higher thiocyanate to iron ratio are shown graphically as absorbance - concentration curves in Figs. 1 and 2. Similar curves were obtained at the lower thiocyanate to iron ratio but these curves are not included. The dependence of the absorbance of the iron(III) - thiocyanate complex on the nature and concentration of the acid used is clearly shown by the shapes of these curves. In all instances, the lowest absorbance was observed with sulphuric acid and the highest values were obtained in perchloric or nitric acid media; the absorbance values in hydrochloric acid lay in between. Above a 0.05 N concentration of acid, and at the higher thiocyanate to iron ratio (Fig. 1), the absorbance in a sulphuric or hydrochloric acid medium was found to decrease rapidly with acid concentration, the effect being more pronounced with sulphuric acid. In perchloric and nitric acid media, however, the absorbance was nearly constant and appeared not to depend on acid concentration. Within the very low acid concentration range, 0.005–0.05 N, the absorbance increased with acid concentration, a result which is in accord with previous findings[2] for the optimum acidity that is necessary to develop the red colour. At the lower thiocyanate to iron ratio of 2:1 the interference effect became more clear and the decrease in absorbance was reflected even with perchloric or nitric acid.
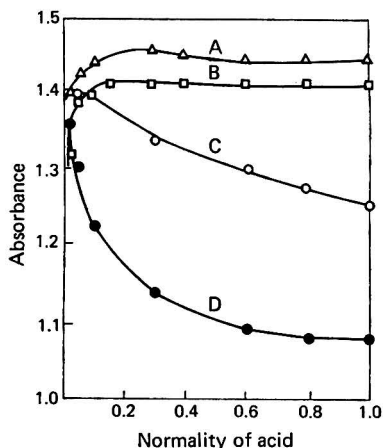

Fig. 1. Dependence of intensity of colour on nature of acid. $[Fe^{3+}]$ = 1.7×10^{-4} M; ratio CNS to Fe = 750:1. A, $HClO_4$; B, HNO_3; C, HCl; and D, H_2SO_4.
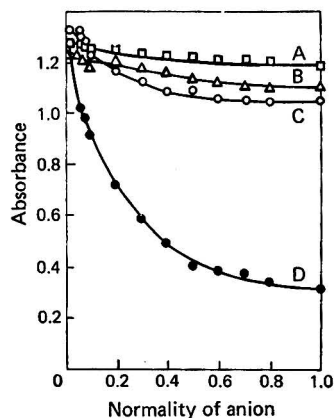
Fig. 2. Dependence of intensity of colour on nature of anion. $[Fe^{3+}]$ = 1.7×10^{-4} M; ratio CNS to Fe = 750:1. A, $NaNO_3$; B, $NaClO_4$; C, NaCl; and D, Na_2SO_4.

The dependence of absorbance on the acid used illustrates the specific influence of the added anion on the stability of iron(III) - thiocyanate in solution. This effect is further substantiated by consideration of the results for absorbance in the corresponding salt solutions,

over the same concentration range, for the higher thiocyanate to iron ratio (Fig. 2). Although the pH value of these salt solutions is low (pH = 2, corresponding to the natural acidity of the stock iron solution), the effect of sulphate is more noticeable than in sulphuric acid solution. This observation suggests that the species which complexes iron in sodium sulphate is SO_4^{2-} and not the hydrogen sulphate anion HSO_4^-, which is the principal ionic species in sulphuric acid solutions.[25,26] Similar conclusions can be arrived at by considering the absorbance *versus* log (concentration) graphs for sulphate and chloride media that are illustrated in Fig. 3. These are linear graphs with different slopes, which follow the simple relationship

$$\text{Absorbance} = \text{Constant} - b \log [\text{anion}]$$

The values of the slopes are 0.17, 0.66, 0.13 and 0.26 for sulphuric acid, sodium sulphate, hydrochloric acid and sodium chloride solutions, respectively.
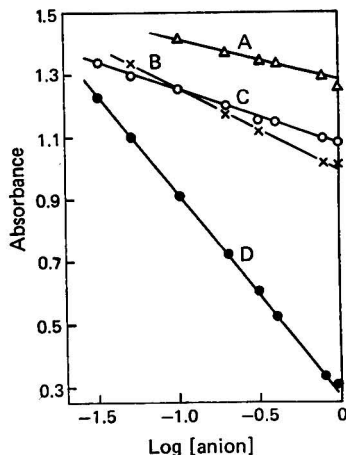
Fig. 3. Graphs of absorbance *versus* log (concentration of anion). $[Fe^{3+}] = 1.7 \times 10^{-4}$ M; ratio CNS to Fe = 750:1. A, HCl; B, NaCl; C, H_2SO_4; and D, Na_2SO_4.

That the decolorising action observed is caused by a specific effect of the anion rather than by a change in the hydrogen-ion concentration was confirmed by carrying out the following experiments. Two sets of mixtures of constant ionic strength ($\mu = 0.1$ and 1.0, respectively) were prepared, containing various amounts of the acid under study and its corresponding sodium salt but all having the same thiocyanate to iron ratio of 750:1 and an iron content of 1.7×10^{-4} M. By use of this system each solution contained the same concentration of the anion but various concentrations of hydrogen ions. The absorbance of the iron - thiocyanate complex formed in each mixture was instantaneously measured at 480 nm and the results obtained are collected in Table I. In another series of experiments solutions of constant ionic strength ($\mu = 0.1$ and 1.0, respectively) containing the same concentrations of hydrogen ions and various concentrations of the anion under examination were prepared. The sulphuric acid - perchloric acid couple was chosen in this instance because of the vast difference in behaviour of the respective anions toward complexing iron(III) ions. The absorbance values obtained are given in Table II.

The results included in Tables I and II indicate that at a fixed anion concentration the absorbance of the iron(III) - thiocyanate complex is nearly constant regardless of the hydrogen-ion concentration. Further, the absorbance is mainly determined by the concentration of the anion itself and decreases with increase in sulphate- or chloride-ion concentration. The relatively low absorbance values in solutions of low acidity (Table I) may be caused by hydrolysis of iron(III) salts, an effect which appreciably lowers the concentration of iron(III) ions in solution.[15]

TABLE I

ABSORBANCE OF IRON(III) - THIOCYANATE COMPLEX IN SOLUTIONS OF CONSTANT IONIC
STRENGTH WITH A CONSTANT CONCENTRATION OF ANION AND VARIOUS
CONCENTRATIONS OF HYDROGEN IONS

Concentration of iron(III) ions, 1.7×10^{-4} M; ratio of thiocyanate to iron(III), 750:1.

Mixture	$\mu = 0.1$			$\mu = 1.0$		
	Normality of salt	Normality of acid	Absorbance	Normality of salt	Normality of acid	Absorbance
NaCl - HCl	0.00	0.10	1.45	0.00	1.00	1.32
	0.02	0.08	1.41	0.20	0.80	1.28
	0.04	0.06	1.41	0.40	0.60	1.29
	0.06	0.04	1.45	0.60	0.40	1.25
	0.08	0.02	1.44	0.80	0.20	1.25
	0.10	0.00	1.40	1.00	0.00	1.24
NaNO$_3$ - HNO$_3$	0.00	0.10	0.96	0.00	1.00	0.98
	0.02	0.08	0.94	0.20	0.80	0.95
	0.04	0.06	0.93	0.40	0.60	0.95
	0.06	0.04	0.92	0.60	0.40	0.95
	0.08	0.02	0.90	0.80	0.20	0.94
	0.10	0.00	0.80	1.00	0.00	0.85
NaClO$_4$ - HClO$_4$	0.00	0.10	0.99	0.00	1.00	1.00
	0.02	0.08	1.00	0.20	0.80	0.98
	0.04	0.06	1.00	0.40	0.60	0.99
	0.06	0.04	1.00	0.60	0.40	0.98
	0.08	0.02	1.00	0.80	0.20	0.97
	0.10	0.00	0.96	1.00	0.00	0.94
Na$_2$SO$_4$ - H$_2$SO$_4$	0.00	0.10	0.85	0.00	1.00	0.78
	0.02	0.08	0.83	0.20	0.80	0.71
	0.04	0.06	0.77	0.40	0.60	0.64
	0.06	0.04	0.75	0.60	0.40	0.57
	0.08	0.02	0.68	0.80	0.20	0.40
	0.10	0.00	0.58	1.00	0.00	0.18

Stability constants for $FeSO_4^+$ and $FeCl^{2+}$ are well documented in the literature,[27–30] and the values vary widely according to the ionic strength of the medium. In a solution with an ionic strength of unity a value of 174 is given for k_1 of $FeSO_4^+$. Whiteker and Davidson[25,27] gave a lower value (107), while a markedly higher value, 1.04×10^3 at $\mu = 0.066$, was reported by Sykes.[31] For the chloride complex a value of 3.89 is given, which agrees well with a previous value of 4.2 reported by Rabinowitch and Stockmayer.[19] Perchlorate and nitrate ions, on the other hand, possess either no tendency, or only a weak tendency, to bind iron(III) ions.[32–34] The presence of excess of thiocyanate in solution appears to delay the interfering action of chloride or sulphate. In this connection, it is to be noted that at the lower thiocyanate to iron ratio studied the presence of perchlorate or nitrate in solution also leads to a noticeable decrease in absorbance.

TABLE II

ABSORBANCE OF IRON(III) - THIOCYANATE COMPLEX IN SOLUTIONS OF CONSTANT IONIC
STRENGTH WITH A CONSTANT CONCENTRATION OF HYDROGEN IONS AND
VARIOUS CONCENTRATIONS OF ANION (SULPHURIC - PERCHLORIC ACID MIXTURES)

$\mu = 0.1$			$\mu = 1.0$		
Normality of H$_2$SO$_4$	Normality of HClO$_4$	Absorbance	Normality of H$_2$SO$_4$	Normality of HClO$_4$	Absorbance
0.00	0.10	1.33	0.00	1.00	1.30
0.02	0.08	1.23	0.20	0.80	1.22
0.04	0.06	1.22	0.40	0.60	1.17
0.06	0.04	1.16	0.60	0.40	1.07
0.08	0.02	1.10	0.80	0.20	0.95
0.10	0.00	0.85	1.00	0.00	0.78

The results of the present investigation can be interpreted in a quantitative manner if the effect of interfering side reactions on the main equilibrium of the iron(III) - thiocyanate is considered. This investigation is usually carried out by calculation of the conditional stability constant, K', of the complex. As has been indicated by Ringbom,[35] this constant is not a real one but depends upon the experimental conditions. Common side reactions to be considered in this instance are those caused by hydrogen ions, hydroxyl ions, anions and other interfering metal ions. Formation of the iron - thiocyanate complex (FeCNS) occurs according to the reaction scheme
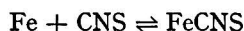
$$Fe + CNS \rightleftharpoons FeCNS$$

Therefore,

$$K_{FeCNS} = \frac{[FeCNS]}{[Fe][CNS]} \qquad .. \qquad .. \qquad .. \qquad .. \qquad (1)$$

The brackets [ ] indicate active masses and K_{FeCNS} is the apparent stability constant of the 1:1 complex. In this treatment the sign of the reacting species is usually omitted. The conditional stability constant K' is defined in a similar manner as

$$K' = K_{Fe'CNS'} = \frac{[FeCNS]}{[Fe'][CNS']} \qquad .. \qquad .. \qquad .. \qquad (2)$$

where [Fe'] denotes the concentration not only of free iron(III) ions but also of all iron(III) ions in solution that have not reacted with the complexing ligand (CNS). In a similar manner [CNS'] represents not only the concentration of free ligand (CNS) but also the concentration of all other species of complexing agent not bound to the metal.

In the system under study, involving complex compound formation between iron and thiocyanate in an acidic medium, the SO_4^{2-}, for example, will enter into side reactions with Fe^{3+}, whereas H^+ will enter into side reactions with thiocyanate; hence

$$[Fe'] = [Fe] + [Fe(SO_4)] + \ldots + [Fe(SO_4)_n] \qquad .. \qquad .. \qquad (3)$$

where n represents the co-ordination number ($n = 6$ for iron) and

$$[CNS'] = [CNS] + [HCNS] \quad .. \qquad .. \qquad .. \qquad .. \qquad (4)$$

The relationship between the stability constant (K_{FeCNS}) and the conditional constant ($K_{Fe'CNS'}$) for a 1:1 complex can be calculated by using the mass action equation (2) and from a knowledge of the side-reaction coefficient, α, introduced by Schwarzenbach,[36] which measures the extent of side reactions, *viz.*,

$$\alpha_{Fe} = \frac{[Fe']}{[Fe]} \text{ and } \alpha_{CNS} = \frac{[CNS']}{[CNS]}$$

If iron reacts with thiocyanate in accordance with the reaction scheme above $\alpha_{Fe} = 1$, but if Fe is involved in side reactions with other species $\alpha_{Fe} > 1$. In an analogous manner a value of α_{CNS} greater than unity indicates that the CNS reacts in some other way not assumed in the main reaction. Substituting for [Fe'] and [CNS'] in equation (2) in terms of α values, we obtain:

$$K_{Fe'CNS'} = \frac{[FeCNS]}{[Fe]\alpha_{Fe} \times [CNS]\alpha_{CNS}}$$

$$= \frac{[FeCNS]}{[Fe][CNS]} \times \frac{1}{\alpha_{Fe} \times \alpha_{CNS}}$$

$$= K_{FeCNS} \times \frac{1}{\alpha_{Fe} \times \alpha_{CNS}} \qquad .. \qquad .. \qquad .. \qquad .. \qquad (5)$$

When an interfering ligand, *e.g.*, sulphate, combines with iron, we have:

$$\alpha_{Fe(SO_4)} = \frac{[Fe']}{[Fe]} = \frac{[Fe] + [Fe(SO_4)] + \ldots + [Fe(SO_4)_n]}{[Fe]}$$

$$= 1 + [SO_4]\beta_1 + [SO_4]^2\beta_2 + \ldots + [SO_4]^n\beta_n \qquad .. \qquad .. \qquad (6)$$

where β_1, β_2 and β_n represent stability products according to the following relationships:

$$\beta_1 = \beta_{\text{FeCNS}} = K_1 = \frac{[\text{FeCNS}]}{[\text{Fe}][\text{CNS}]} \qquad \cdots \qquad \cdots \qquad \cdots \qquad \cdots \qquad \cdots \qquad (7)$$

$$\beta_2 = \beta_{\text{Fe(CNS)}_2} = K_1 \times K_2 = \frac{[\text{Fe(CNS)}_2]}{[\text{Fe}][\text{CNS}]^2} \qquad \cdots \qquad \cdots \qquad \cdots \qquad (8)$$

$$\beta_n = \beta_{\text{Fe(CNS)}n} = K_1 \times K_2 \times \ldots K_n = \frac{[\text{Fe(CNS)}_n]}{[\text{Fe}][\text{CNS}]^n} \qquad \cdots \qquad \cdots \qquad (9)$$

Similarly, with an interfering cation, such as hydrogen ion, we have

$$\alpha_{\text{CNS(H)}} = 1 + [\text{H}]\beta_1 + [\text{H}]^2\beta_2 + \ldots [\text{H}]^m\beta_m \qquad \cdots \qquad \cdots \qquad (10)$$

where β_m is the stability product of the proton ligand, *i.e.*, the reciprocal of the product of the dissociation constants of the acid (HCN in this instance), according to

$$\beta_m = \frac{1}{K_1 \times K_2 \times K_3}$$

As in fairly acidic solutions the tendency of iron to combine with hydroxyl ions is very weak, side reactions of this type do not occur and α_{Fe} with respect to OH$^-$ can be neglected; the conditional stability constant of the iron(III) - thiocyanate complex at such an acidic pH will be determined mainly by the nature and concentration of the added anion (sulphate or chloride) in solution. In the example under discussion $\alpha_{\text{Fe(SO}_4)}$ was obtained by substitution of five different concentrations of the ligand in equation (6), *viz.*, 0.02, 0.04, 0.06, 0.08 and 0.1 N. The values of log β_1 and log β_2 for iron(III) sulphate or chloride complexes were taken as 4.0, 5.4 and 0.6, 0.7, respectively.[37] Substitution in equation (10) enables the evaluation of $\alpha_{\text{CNS(H)}}$ to be carried out. The hydrogen-ion concentration was considered to be equivalent to 0.1 N in all solutions. As data for the stability constant of thiocyanic acid were not available the value for cyanic acid itself was taken instead, for which log β_1 is given the value 3.66.[37] From the results of $\alpha_{\text{Fe(SO}_4)}$ or $\alpha_{\text{Fe(Cl)}}$ and $\alpha_{\text{CNS(H)}}$ thus obtained at the five ligand concentrations selected, values of the conditional stability constants, K', for the 1:1 iron(III) - thiocyanate complex in sulphate or chloride media were obtained by substitution in equation (5). The value of 215 for the stability constant of FeCNS was chosen for these calculations.[8] The results obtained are summarised in Table III.

TABLE III

VALUES OF SIDE-REACTION COEFFICIENTS AND CONDITIONAL STABILITY CONSTANTS FOR THE IRON(III) - THIOCYANATE COMPLEX

$\alpha_{\text{CNS(H)}} = 458.1$.

Medium	Concentration of anion/N	$\alpha_{\text{Fe(SO}_4)}$	$\alpha_{\text{Fe(Cl)}}$	K'	Absorbance (Table II)
Sulphate	0.02	301.5	—	15.6×10^{-4}	1.23
	0.04	802.9	—	5.9×10^{-4}	1.22
	0.06	1 505.3	—	3.1×10^{-4}	1.16
	0.08	2 408.6	—	1.9×10^{-4}	1.10
	0.10	3 512.9	—	1.3×10^{-4}	0.85
Chloride	0.02	—	1.08	4.3×10^{-1}	—
	0.04	—	1.17	4×10^{-1}	—
	0.06	—	1.26	3.7×10^{-1}	—
	0.08	—	1.35	3.5×10^{-1}	—
	0.10	—	1.45	3.2×10^{-1}	—

A correlation study between the conditional stability constant values or the values of $\alpha_{\text{Fe(SO}_4)}$ calculated in sulphate solutions of varying concentrations and the corresponding absorbance results obtained in the present work is easily made. The results given in columns 3 and 6 in the sulphate medium section of Table III can easily be compared and can be plotted together on an inverse scale, where the two curves would be expected to run parallel

with each other. Based on the magnitude of the side-reaction coefficient values or the conditional stability constants, the order of complexation of iron(III) with the anions studied, $SO_4^{2-} > Cl^- > NO_3^- \gg ClO_4^-$, is further substantiated.

References

1. Ossian, H., *Pharm. Centralbl.*, 1837, **13**, 205.
2. Sandell, E. B., "Colorimetric Determination of Traces of Metals," Third Edition, Interscience, New York, 1965, p. 525.
3. Ovenston, T. C. J., and Parker, C. A., *Analytica Chim. Acta*, 1929, **3**, 277.
4. Szegoe, L., and Cassoni, B., *Chimica Ind. Appl.*, 1933, **15**, 281.
5. Shakhkeldian, A. B., and Skkitov, M., *Zav. Lab.*, 1937, **6**, 1083.
6. Woods, J. T., and Mellon, M. G., *Ind. Engng Chem. Analyt. Edn*, 1941, **13**, 551.
7. Peter, C. A., and French, C. L., *Ind. Engng Chem. Analyt. Edn*, 1941, **13**, 604.
8. Sandell, E. B., "Colorimetric Determination of Traces of Metals," Third Edition, Interscience, New York, 1965, p. 526.
9. Magnanini, G., *Z. Phys. Chem.*, 1891, **8**, 1; *J. Chem. Soc.*, 1891, **60**, 1150.
10. Krüss, G., and Moraht, H., *Ber. Dt. Chem. Ges.*, 1889, **22**, 2061; *J. Chem. Soc.*, 1889, **56**, 1129.
11. Krüss, G., and Moraht, H., *Z. Anorg. Chem.*, 1892, **1** 399; *J. Chem. Soc.*, 1893, **64**, 185.
12. Rosenheim, A., and Cohn, R., *Z. Anorg. Chem.*, 1901, **27**, 280; *J. Chem. Soc.*, 1901, **80**, 455.
13. Bray, W. C., and Hershey, A. V., *J. Am. Chem. Soc.*, 1934, **56**, 1889.
14. Moller, M., *J. Phys. Chem.*, 1937, **41**, 1123.
15. Lamb, A. B., and Jacques, A. G., *J. Am. Chem. Soc.*, 1938, **60**, 977.
16. von Kiss, Á., Ábrahám, J., and Hegedüs, L., *Z. Anorg. Allg. Chem.*, 1940, **244**, 98.
17. Schlesinger, H. I., and Vajkenburgh, V., *J. Am. Chem. Soc.*, 1941, **63**, 1765.
18. Bent, H. B., and French, C. L., *J. Am. Chem. Soc.*, 1941, **63**, 568.
19. Rabinowitch, E., and Stockmayer, W. H., *J. Am. Chem. Soc.*, 1942, **64**, 335.
20. Babko, A. K., *C. R. Acad. Sci. U.R.S.S.*, 1946, **52**, 37.
21. Snell, F. D., and Snell, C. T., "Colorimetric Methods of Analysis," Volume 1, Van Nostrand, New York, 1936, p. 283.
22. Yoe, J. H., "Photometric Chemical Analysis," Volume 1, John Wiley, New York, 1928, p. 218.
23. Flaschka, H., *Mikrochim. Acta*, 1954, 361.
24. Charlot, G., "Colorimetric Determination of Elements," Elsevier, Amsterdam, 1946, p. 271.
25. Whiteker, R. A., and Davidson, N., *J. Am. Chem. Soc.*, 1953, **75**, 3081.
26. Sykes, K. W., *Spec. Publs Chem. Soc.*, No. 1, 1954, 64.
27. Sillén, L. G., and Martell, E., "Stability Constants of Metal Ion Complexes," *Spec. Publs Chem. Soc.*, No. 17, 1965, and (Supplement No. 1) No. 25, 1971.
28. Bachmann, K., and Lieser, K. H., *Ber. Bunsenges. Phys. Chem.*, 1936, **67**, 802.
29. Maslowska, J., *Roczn. Chem.*, 1967, **41**, 1857.
30. Heistand, R. N., and Clearfield, A., *J. Am. Chem. Soc.*, 1963, **85**, 2566.
31. Sykes, K. W., *J. Chem. Soc.*, 1952, 124.
32. Walker, W. B., *Analyst*, 1925, **50**, 279.
33. Sutton, J., *Nature, Lond.*, 1952, **169**, 71.
34. Ibers, J. A., and Davidson, N., *J. Am. Chem. Soc.*, 1951, **73**, 476.
35. Ringbom, A., *J. Chem. Educ.*, 1958, **35**, 282.
36. Schwarzenbach, G., "Complexometric Titrations," Interscience, New York, 1957.
37. Ringbom, A., "Complexation in Analytical Chemistry," John Wiley, New York, 1963, pp. 313 and 315.

Determination of Selenium in Blood and Plant Material by Hydride Generation and Atomic-absorption Spectroscopy

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A method is described for the routine determination of selenium in blood and plant samples at concentrations in the range 0.01–0.50 μg g^{-1}. Samples of mass 1 g are digested with nitric and perchloric acids and then selenium hydride is generated from diluted digests by the controlled introduction of a solution of sodium borohydride. The selenium is subsequently atomised in a nitrogen - hydrogen - entrained air flame. Digests can be analysed at a rate of four per minute. For a pasture sample, which contained a 0.038 μg g^{-1} concentration of selenium, and a blood sample, which contained 0.029 μg g^{-1} of selenium, relative standard deviations of 7.9 and 4.3%, respectively, were obtained. The mean recovery of added selenium was 100.5%, with a relative standard deviation of 4.7%. The efficiency of hydride generation was 95%.

Keywords: Selenium determination; blood; plant materials; atomic-absorption spectrophotometry; hydride generation

Selenium deficiency in soils is widespread in New Zealand, particularly in the South Island,[1] and it is standard practice in such areas to dose animals with selenium in order to correct this deficiency. Selenium-responsive diseases can appear when the level of selenium is lower than 0.03 μg g^{-1} in the blood.[2] Levels of selenium in pasture plants associated with deficiency symptoms in animals are in the range 0.01–0.03 μg g^{-1}.[3] Such low levels of selenium have been determined satisfactorily by fluorimetry,[4] but it was hoped that atomic-absorption spectroscopy could provide a more rapid technique to cope with the analysis of the large numbers of samples associated with extensive field experimental work.

The low levels of selenium involved are well beyond the analytical range of conventional flame atomic-absorption spectroscopy, which has a detection limit of about 0.5 μg ml^{-1} in solution when an air - hydrogen flame is used.[5] Although deficiency levels are slightly above the best reported concentration detection limits obtained with the carbon furnace atomisation technique,[6] the matrix interference problems to be overcome appear formidable for this element.[7,8]

The sensitivites attained by various workers with the hydride generation technique appeared likely to satisfy our requirements.[9,10] As well as adequate sensitivity, this technique, as a separation process, apparently suffers no matrix interference problems during atomisation and does not necessarily require background correction for non-atomic absorption. Preliminary investigations into the generation of selenium hydride prior to atomisation led to a preference for the rapid method of generation[10] rather than the collection and storage method.[9] The use of sodium borohydride solution rather than zinc powder slurry was preferred, as the solution was easier to inject reliably and a preliminary reducing step was not required. The apparatus and procedure described by Duncan and Parker,[10] with some modifications, was eventually chosen for this work.

A number of publications concerned with the development and application of the hydride generation technique for elements that readily form volatile hydrides have appeared in recent years. However, very few methods have been published in which this technique has been used for the determination of selenium in biological samples.[11–14]

Experimental

Apparatus

A controlled-temperature aluminium block was used for sample digestion. Holes were

drilled in the block to a depth of 38 mm with diameters of 24 mm to accommodate up to 60 borosilicate glass tubes, 150 × 19 mm in size.

The Varian Techtron accessory Model 64, with the following modifications, was used for hydride generation. The reaction vessel was replaced with a glass expansion adaptor to which a digestion tube could be attached, thus allowing it to act also as a reaction vessel. The syringe was replaced by a Fisons dispenser hand set (LFA 16), which was firmly attached to the apparatus. The probe passed through the septum and was carefully aligned in order to ensure that the sodium borohydride solution was dispensed into the centre of the sample solution in the digestion tube. This hand set allowed 2 ml of the sodium borohydride solution to be added at a controlled fast rate by means of the motorised 10-ml syringe of the dispenser (LFA 10). The rate of injection was such that the reagent solution jet penetrated to the base of the solution in the tube. This arrangement greatly improved reproducibility by eliminating the need for considerable skill in the operation of the hand-held syringe supplied with the original apparatus.

The Varian accessory Model 64 allowed 50% of the nitrogen that is used to stabilise the flame to be diverted through the reaction vessel in order to flush out any air and subsequently to carry the generated hydride to the burner. The generated hydride was swept into a nitrogen - hydrogen - entrained air diffusion flame on a standard propane burner (slot 100 × 1.5 mm) via a glass-wool filter and nebuliser chamber. This burner was preferred to the three-slot, Boling-type burner, because the flame on the propane burner was less susceptible to disturbance by air currents. Gas flow-rates of $8 \, l \, min^{-1}$ for nitrogen and $4 \, l \, min^{-1}$ for hydrogen were used. The top of the burner was positioned 8 mm below the centre of the beam of light from the selenium hollow-cathode lamp and was aligned horizontally to obtain maximum transmission of light, at a wavelength of 196 nm, through the flame. The width of the light beam passing through the flame was reduced by means of 4-mm lens diaphragms.

Measurements of the peak heights resulting from atomic-absorption spectroscopy were made with a selenium hollow-cathode lamp operated at 7 mA, a Uvispek monochromator with a slit width of 0.2 mm to isolate the selenium resonance line at 196 nm, a Varian Techtron AA5 power supply and amplifier and a Varian A25 high-speed chart recorder. Scale expansion × 2 has occasionally been used for sample solutions known to contain low levels of selenium.

Reagents

Digestion acid. Add 200 ml of analytical-reagent grade perchloric acid, 72% m/V, to 500 ml of redistilled nitric acid, 68% m/V.

Hydrochloric acid. Redistilled, 20% m/V.

Sodium borohydride solution. Dissolve 5 g of laboratory-reagent grade sodium borohydride in 100 ml of 0.1% m/V sodium hydroxide solution.

Standards. Dissolve elemental selenium in a small amount of redistilled nitric acid and dilute this solution with redistilled hydrochloric acid to provide a stock solution that contains 10 $\mu g \, ml^{-1}$ of selenium. Prepare standard solutions that contain 0, 0.05, 0.10, 0.15, 0.20 and 0.25 $\mu g \, ml^{-1}$ of selenium by dilution of the stock solution with redistilled hydrochloric acid.

Preparation of Samples

Blood samples

Weigh 1-g aliquots of blood into 150 × 19 mm borosilicate test-tubes and to them add 7 ml of the digestion acid mixture. Also add a few pieces of glass frit to prevent bumping. In order to reduce initial frothing, add 2 drops of kerosene to each tube. Next transfer the tubes to the cold aluminium digestion block and allow the block temperature to rise to 210 °C. This should take at least 20 min if the possibility of charring is to be avoided. Allow digestion to continue at this temperature until the fuming stage of perchloric acid is reached and then allow the tube contents to simmer for 15 min. Remove the tubes from the digestion block, allow them to cool, add 2 ml of redistilled hydrochloric acid to each and mix. The total time required for the digestion of 60 blood samples is about 1.5 h.

Plant samples

Plant samples should be dried, ground and then re-dried for 4 h at 90 °C before analysis.

When they are cool, place 1-g portions of the dried samples into 150 × 19 mm borosilicate glass test-tubes and to them add 7 ml of the digestion acid and a further 5 ml of redistilled nitric acid. Add 2 drops of kerosene to each tube in order to reduce frothing. Allow the tubes to stand overnight, or for at least 3 h, then transfer them to the cold aluminium digestion block and connect a 110-mm air condenser (CNB 19 conical joint) to each tube. When the block temperature has reached 130 °C allow the samples to reflux for 1 h, then remove the condensers and allow the block temperature to rise to 210 °C. Digest the mixtures to the fuming stage of perchloric acid and allow them to simmer for 15 min. Next remove the tubes from the digestion block, allow them to cool, add 2 ml of redistilled hydrochloric acid and mix. The presence of undissolved salts, such as potassium perchlorate, has no effect on the subsequent release of selenium hydride. The total time required for the digestion of a set of 60 plant samples is about 2.5 h.

Standard Solutions

Prepare a series of working standards in duplicate for each set of sample digests as follows. Place 2 ml of the standard solutions into digestion tubes, followed by 2 ml of 72% *m/V* perchloric acid, and mix. The working standards thus contain 0, 0.1, 0.2, 0.3, 0.4 and 0.5 μg of selenium and are comparable in acidity with the sample digest solutions.

Operation

With the instrumental and flame conditions optimised, attach a digestion tube containing a sample solution to the hydride generation apparatus. Switch the changeover valve to the "sample" position in order to flush out air from the apparatus. This process takes about 5 s. When the recorder pen has returned to the zero position, press the hand set button. After the peak absorbance has been recorded, remove the digestion tube. In routine operation it was found convenient to leave the changeover valve in the "sample" position throughout a set of determinations. Solutions can be processed at the rate of about four per minute.

Results and Discussion

A typical calibration graph, prepared from a duplicate set of standard solutions, is shown in Fig. 1. If the curvature obtained is characteristic of the selenium hollow-cathode lamps used for this work some improvement in linearity would be expected with an electrodeless discharge lamp as the source. An absorbance reading of 0.038, with a relative standard deviation of 0.004, for the blank solution was shown to be non-atomic by measurement with a hydrogen continuum lamp as the source, and is probably a result of hydrogen enrichment of the flame by the extra hydrogen evolved during hydride generation. It will therefore be constant for all of the solutions that are to be analysed.

The absolute sensitivity, defined as the amount of selenium required to give 1% absorption and calculated from the slope of the graph shown in Fig. 1, is 2.5 ng of selenium. The detec-
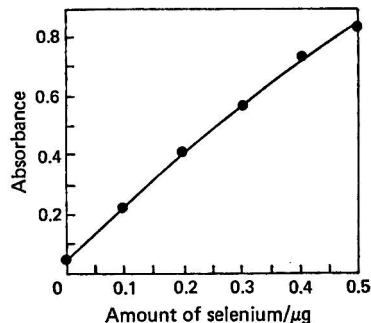
Fig. 1. Typical calibration graph. Each point is the average of duplicate standards.

tion limit, defined as the amount of selenium required to give an absorbance equal to twice the standard deviation of the blank absorbance, is 5.0 ng of selenium.

The results of the analyses of whole blood and plant samples by the method described in this paper are in close agreement with the results obtained for the same samples when determined by fluorimetry with 2,3-diaminonaphthalene (Table I). The sample digestion procedure was similar for both methods.

TABLE I

COMPARISON OF RESULTS

		Amount of selenium/μg g^{-1}	
Sample		By fluorimetry	By hydride generation and atomic-absorption spectroscopy
Blood	1	0.357	0.372
	2	0.276	0.275
	3	0.151	0.152
	4	0.091	0.092
	5	0.061	0.059
	6	0.029	0.032
	7	0.012	0.011
Pasture	1	0.048	0.050
	2	0.082	0.081

Recoveries were determined by the addition of known amounts of selenium in redistilled nitric acid to 1-g samples of blood and pasture prior to digestion. The results are given in Table II and show a mean recovery of 100.5% with a relative standard deviation of 4.7%.

Ten replicate digestions of a pasture sample that contained 0.038 μg g^{-1} of selenium, and nine replicate digestions of a blood sample that contained 0.029 μg g^{-1} of selenium, were analysed and gave relative standard deviations of 7.9 and 4.3%, respectively. The lower relative standard deviation for the blood sample is thought to be a result of the greater homogeneity of this sample.

TABLE II

RECOVERY OF ADDED SELENIUM

Sample	Amount of selenium added*/μg	Amount of selenium found†/μg	Recovery, %
Blood 5	—	0.057	—
	0.050	0.110	103
	0.100	0.156	99
	0.200	0.240	94
Pasture 1	—	0.050	—
	0.050	0.103	103
	0.100	0.146	97
	0.200	0.268	107

* Added as selenium in concentrated nitric acid prior to digestion.
† Averages of duplicate digestions.

The use of nitric acid - perchloric acid mixtures for the destruction of organic matter in biological samples has been shown to be reliable in that no loss of selenium occurs through volatilisation, provided that charring of the sample does not take place.[4,15] It is therefore not necessary for the standard solutions used for calibration to be digested. The effective generation of selenium hydride by sodium borohydride is dependent on the selenium in the acid solution being present as selenium(IV).[11,16] It is known that prolonged and vigorous boiling of a perchloric acid digest can effect the oxidation of selenium(IV) to selenium(VI).[4] For this reason, it is usually recommended that the final digest be heated with a small amount of concentrated hydrochloric acid in order to reduce any selenate that may be present to selenite.[4,11] The digestion procedure described here does not involve either vigorous or prolonged boiling of the perchloric acid digest. A comparison of selenium absorbances obtained for sample digests processed with and without boiling in hydrochloric acid showed no significant differences.

No measurable absorbances were obtained for standard solutions prepared from sodium selenate when sodium borohydride was used for hydride generation. When ascorbic acid or potassium iodide was tried as a reductant for selenate in acidic solution the subsequent generation of selenium hydride was both erratic and less than 20% efficient. It was thought that such pre-treatments may have reduced the selenium beyond the selenium(IV) state. Solutions of elemental selenium, when processed, also gave very erratic and low absorbances, which confirmed the inefficiency of sodium borohydride for the reduction of selenium, in elemental form, to its hydride.

A method to distinguish between the two oxidation states, selenium(IV) and selenium(VI), in the same solution has resulted from this work. As the generation of selenium hydride by means of sodium borohydride is specific for selenium(IV), the determination of selenium(VI) by difference can be achieved by the measurement of selenium(IV) with and without boiling with hydrochloric acid.

Two solutions containing 0.5 ml of a 1 $\mu g\ ml^{-1}$ selenium standard that was known to contain selenium(IV) and selenium(VI) in the ratio of 1:10 were prepared in digestion tubes in the same way as for normal standards. One of the prepared solutions was brought to the boil and cooled, then both were processed in the usual way. The concentration of selenium(VI) in the original solution was calculated by difference and it agreed with the known concentration within the limits of experimental error.

Flame Conditions

Optimum conditions for stability and reproducibility, as well as sensitivity, were highly dependent on gas flow-rates, the optical aperture and the horizontal burner position in relation to the optical beam. A steady flame was produced with a nitrogen flow-rate of $8\ l\ min^{-1}$ and a hydrogen flow-rate of $4\ l\ min^{-1}$. The horizontal position of the burner was adjusted to obtain maximum transmission of light at 196 nm with the flame present. The flame was found to be 100% transparent to light at 196 nm when 4-mm lens diaphragms were used to reduce the optical aperture and when the burner top was positioned 12 mm below the centre of the light beam. However, optimum sensitivity and stability were obtained when the burner was 8 mm below the light beam, and the latter height has been used throughout this work.

Efficiency of Hydride Generation

The optimum concentrations and volumes of hydrochloric acid and sodium borohydride were found to vary with the size of the reaction vessel. Early work with the original Varian Techtron apparatus confirmed the optimum concentrations and volumes used by Duncan and Parker.[10] However, with a 200 × 25 mm reaction tube, a size commonly used for plant digestion, and a 10-ml volume of sample solution, the sensitivity was increased by 35%. A further reduction in the size of the reaction vessel to that of the digestion tubes used here gave rise to a further increase in sensitivity when acid strength, total volume and strength of sodium borohydride reagent were optimised.

The efficiency of hydride generation from selenium(IV) in an acidic solution was determined by measurement of the residual selenium present in processed standard solutions. The residual selenium was determined by fluorimetry and it was found that an average of 5% of the original concentration was still present. The efficiency of hydride generation for this method is therefore about 95%.

The purity of the sodium borohydride reagent affects both the efficiency and reproducibility of hydride generation. An impure reagent is indicated by a loss in sensitivity, particularly at the higher concentrations of selenium, which cannot be corrected by an increase in the volume or concentration of the inferior reagent. In addition, a loss of precision is indicated by poor agreement between duplicate determinations. However, sodium borohydride powder reagents from both Sigma Chemical Co. and BDH Chemicals Ltd. have proved to be satisfactory, and have remained stable over a period of several months. These reagents are always stored in a desiccator. The 5% sodium borohydride solution prepared in 0.1% m/V sodium hydroxide solution has been found to remain stable for up to 4 h, but it is normally freshly prepared immediately before each set of digest solutions and standards is analysed.

Interferences

The most severe interference effect expected during hydride generation with sodium borohydride is that due to the presence of nitric acid.[10–12] With the sample preparation procedures described here it is very unlikely that sufficient nitric acid would be present in the digested samples to cause interference. The presence of 1% V/V nitric acid in a standard solution that contained 200 ng of selenium depressed the absorbance by only 7%.

Several elemental interferences in the generation of selenium hydride by using sodium borohydride have been reported.[17,18] Of these elements, only copper could be present in plant digest solutions in sufficient concentration to cause interference. The addition of increasing amounts of copper to a standard solution containing 200 ng of selenium showed no suppression effect up to 30 μg of copper. The presence of 50 and 100 μg of copper depressed the absorbance obtained by 5 and 9%, respectively. Because the level of copper found in agricultural plants is seldom above 20 μg g^{-1},[19] it was not considered necessary to develop a procedure in order to eliminate this interference. However, one should be aware of the possibility of interference from high concentrations of copper in horticultural plant samples, which may also be contaminated with copper spray residues.

Conclusion

The hydride-generation and atomic-absorption technique described has been applied to the determination of nanogram amounts of selenium in blood and agricultural plants. This method is simple to carry out and can be conveniently used for the analysis of large numbers of samples on a routine basis. Accurate results can be obtained only if the selenium in solution is present as selenium(IV). The precision of the analyses is very dependent on source-lamp stability, optical alignment and flame conditions, and it is essential that the method of addition of the borohydride solution should be reproducible. No significant interference effects have been encountered when analysing blood and plant material. The two oxidation states selenium(IV) and selenium(VI), in acidic solution, can be differentiated, as this analytical method is specific for selenium(IV).

References

1. Watkinson, J. H., *Trans. Jt Meet. Comm. IV V Int. Soc. Soil Sci.*, 1962, 149.
2. Hartley, W. J., *in* O. H. Muth, *Editor*, "Symposium on Selenium in Biomedicine," Avi Publishing Co., Westport, Conn., 1967, pp. 79–96.
3. Andrews, E. D., Hartley, W. J., and Grant, A. B., *N.Z. Vet. J.*, 1968, **16**, 3.
4. Watkinson, J. H., *Analyt. Chem.*, 1966, **38**, 92.
5. Allan, J. E., Paper presented at Fourth Australian Spectroscopy Conference, Canberra, 1963 (reported in Coogan, C. K., Morrison, J. D., Walsh, A., and Wilmshurst, J. K., *Nature, Lond.*, 1963, **200**, 319).
6. Baird, R. B., and Gabrielian, S. M., *Appl. Spectrosc.*, 1974, **28**, 273.
7. Ihnat, M., and Westerby, R. J., *Analyt. Lett.*, 1974, **7**, 257.
8. Mesman, B. B., and Thomas, T. C., *Analyt. Lett.*, 1975, **8**, 449.
9. Fernandez, F. J., *Atom. Absorption Newsl.*, 1973, **12**, 93.
10. Duncan, L., and Parker, C. R., "Varian Techtron Technical Topic, September 1974," Varian Techtron Pty., Springvale, Victoria, Australia, 1974.
11. Ng, S., and McSharry, W., *J. Ass. Off. Analyt. Chem.*, 1975, **58**, 987.
12. Siemer, D. D., and Hagemann, L., *Analyt. Lett.*, 1975, **8**, 323.
13. Fiorino, J. A., Jones, J. W., and Caper, S. G., *Analyt. Chem.*, 1976, **48**, 120.
14. Thompson, K. C., *Analyst*, 1975, **100**, 307.
15. Gorsuch, T. T., "The Destruction of Organic Matter," International Series of Monographs in Analytical Chemistry, Volume 39, Pergamon Press, Oxford, 1970.
16. Thompson, K. C., and Thomerson, D. R., *Analyst*, 1974, **99**, 595.
17. Smith, A. E., *Analyst*, 1975, **100**, 300.
18. Fleming, H. D., and Ide, R. G., *Analytica Chim. Acta*, 1976, **83**, 67.
19. Gladstones, J. S., Loneragan, J. F., and Simmons, W. J., *Aust. J. Agric. Res.*, 1975, **26**, 113.

Loss of Trace Elements During Dehydration of Marine Zoological Material

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Possible losses of trace elements during dehydration of marine zoological material with a high water content were studied by means of radioactive tracers, using the oyster *Crassostrea gigas* as an example. It is probable that no losses occurred with chromium, iron, manganese, cobalt and zinc, but serious losses of selenium, cadmium and lead were observed, both during freeze drying and oven drying at low temperatures. The analytical applicability of dehydration techniques in general thus requires re-assessment.

Keywords: Trace element loss; dehydration; marine zoological material; radiotracers

The accurate determination of trace elements in marine zoological species, important as it may be in itself for academic reasons, has indisputably attained a more urgent practical importance with the increased awareness of the dangers of marine pollution. In particular, this is true for those species that are used as biological indicators to reflect local changes in the elemental composition of coastal waters. In order to be classified as an indicator species, organisms have to meet established criteria.[1]

These criteria are met by seaweeds and some marine species, especially filter feeders, that accumulate metals through the food chain. Among the organisms that have been studied are the seaweed *Laminara digitata*,[2] the crab *Carcinus maenas*,[3] the mussels *Mytilus*[4-6] and the oyster *Crassostrea virginica*.[7] In this work a known indicator organism, the oyster *Crassostrea gigas*, was studied.

It is a characteristic of marine zoology that the body flesh of the animals has a very high water content. Dehydration is therefore a necessary preliminary to trace element analysis. However, the conditions under which dehydration is effected vary greatly from one instance to another, as is shown by the abbreviated survey of methods given in Table I. From this survey three approaches are evident.

Firstly, dry ashing is used at temperatures in the range 400-600 °C. This approach is justified if the trace elements are present in the biological system as inorganic salts, which have low vapour pressures at these temperatures. It may, however, be noted that possible losses during ashing were anticipated and thus yield determinations were often carried out. These checks invariably made use of the addition of inorganic salts to the biological material, followed by their subsequent re-determination. The possible presence of organically bound trace metals in compounds with different vapour pressures was not taken into account.

The second approach makes use of drying at relatively low temperatures of about 100–110 °C, followed by wet ashing with oxidising acids. Again it is noticeable that yield determinations are carried out only during the wet ashing stage, and even then by the use of inorganic compounds, as in the first approach. Once again it is implicitly assumed that possibly volatile, organically bound compounds are absent.

Thirdly, freeze-drying methods in vacuum are used. This approach is often regarded as being the absolute method and yield determinations are apparently not considered to be necessary. The implicit assumption is made that the vapour pressure of compounds of trace elements present will be so low at the effective drying temperature that loss through volatilisation is unlikely.

In the marine environment it can confidently be assumed that trace metal elements, originally present in the inorganic form, enter the food chain, where they can retain their

TABLE I

BRIEF REPRESENTATIVE SURVEY OF ANALYTICAL DRYING TECHNIQUES

Element	Material	Drying procedure	Yield determination	Reference
Cr	Blood, urine	Ashing at 550 °C	^{51}Cr	8
Cd	Fish	Ashing at 485 °C	$CdCl_2$	9
Zn	Fauna species	Ashing at 450 °C	*	10
Pb	Blood	Ashing at 400 °C	Inorganic Pb salt	8
As, Se, Hg, Cu	Cellulose (Whatman ashless tablets)	Ashing at >150 °C	Se(H$_2$SeO$_3$), As$_4$O$_6$ HgNO$_3$, CuSO$_4$	11
Cu, Mn, Zn, Fe, Pb, Co, Hg	*Tapes decussatus*	Drying at 105 °C, wet ashing	*	12
Co, Ni, Fe, Mn	Mussel (*Aplysia benedicti*)	Drying at 105 °C, wet ashing	*	13
^{65}Zn, ^{60}Co	Mussel (*Mytilus edulis*)	Drying at 105 °C, wet ashing	*	4–6
Review paper, ~40 elements	Seaweeds and marine organisms	105–110 °C	—	14
Fe, Zn, Mn, Co, Cr, Pb, Cd, Al, Sb, Bi, Cu, Ni	Marine fauna and flora	Freeze drying	None	1
Zn, Mn, Co, Fe	Mussel (*Mytilus edulis*)	Freeze drying	*	4–6

* Not reported.

inorganic character or be partly metabolised to other chemical forms. Because the established methods of yield determination take no account of these other chemical forms, losses during the drying processes will not be reflected in the analyses and apparent recoveries of the tracer compounds will not necessarily represent the behaviour of the corresponding metal in the animal. The purpose of this investigation was therefore to check existing analytical procedures by allowing an indicator species to accumulate, under near-natural conditions, selected trace elements administered as radioactive inorganic compounds.

Principles of the Investigation

The principles on which this investigation rests are that trace elements are made available to the indicator species, the oyster *C. gigas*, as soluble inorganic materials in the form of high specific activity salts of radioactive isotopes, that the oysters are allowed to accumulate and/or metabolise the trace elements under conditions which approximate as near as possible to those obtaining in nature, and that the accumulated radioactivity in the oysters is measured before any dehydration method is applied, and thereafter the activity of the same specimen is compared quantitatively at each following stage of dehydration. In this way the behaviour of the trace elements can be followed during the drying process, whether the elements have been accumulated in the original form or metabolised to some other chemical state, wholly or in part. The assumption is made here that the radioactively labelled trace element is present, after accumulation, in the same chemical form as would normally be the case with stable isotopes.

Experimental

Aquarium Conditions of Labelling

Oysters (*C. gigas*) of a similar size were collected from the Knysna estuary on the Indian Ocean coast of South Africa, where they were grown under controlled conditions. They were thoroughly cleaned and scrubbed in order to minimise the possible growth of algae, etc., in the aquaria. About 30 specimens at a time were placed in glass aquaria containing 30 l of sea water drawn from the same site, and filtered through a Millipore filter of 0.45 μm pore size. The aquaria were aerated by diaphragm pumps, which continuously and slowly bubbled air through the water. After allowing the oysters to acclimatise for 1 week, 60 μCi of high specific activity or "carrier-free" preparations of selected radionuclides were added to each aquarium (about 100 μCi for lead, or 200 μCi for cobalt). About 3 weeks were then allowed for the oysters to accumulate the radioactivity.

Selection of Radionuclides

The elements were selected with the following properties in mind[15]: the known ability of the organism to accumulate the trace element; the half-life of the tracer isotope and the relative intensity of its gamma-rays; the chemical properties of the compounds of these elements that could possibly lead to losses during dehydration; and the availability of high specific activity preparations of the radionuclide. Details of the selected nuclides and some of their properties are given in Table II.

TABLE II

RADIONUCLIDES USED FOR ACCUMULATION

Nuclide	Chemical form	Main γ-ray energy/keV	Half-life/d	Specific activity*/Ci g⁻¹	Number of oysters
^{51}Cr	$CrCl_3$	320	27.7	100–400	25
^{54}Mn	$MnCl_2$	835	303	>100	24
^{59}Fe	$FeCl_3$	1 095	45.6	3–20	40
^{58}Co	$CoCl_2$	810	71.3	>2 000	25
^{65}Zn	$ZnCl_2$	1 115	243.7	>100	24
^{76}As	As_4O_6	596	17.9	>1 000	10
^{75}Se	Na_2SeO_3	265	120	2–10	24
^{109}Cd	$CdCl_2$	88	453	>50	25
^{125}Sb	$SbCl_3$	427	989	>100	10
^{210}Pb	$Pb(NO_3)_2$	47	7 446	21–60	30

* Values supplied by Radiochemical Centre, Amersham, England.

Standardisation of the Measuring Equipment

A horizontally mounted 50-cm³ germanium (lithium) detector was used to measure the radioactivity. The detector head and the samples that were counted were shielded in a lead castle of dimensions $66 \times 66 \times 44$ cm. In order to ensure consistent geometry a permanent sample holder, slotted to take specimens at fixed distances from the detector face and parallel to the detector axis, was positioned in contact with the germanium-crystal holder. Specimen tubes were placed vertically inside specially constructed holders, the base of which formed an axle that fitted directly into a gear-driven motor that rotated the sample about its own axis at 6 rev min⁻¹. A diagrammatic representation of the counting arrangement is shown in Fig. 1.
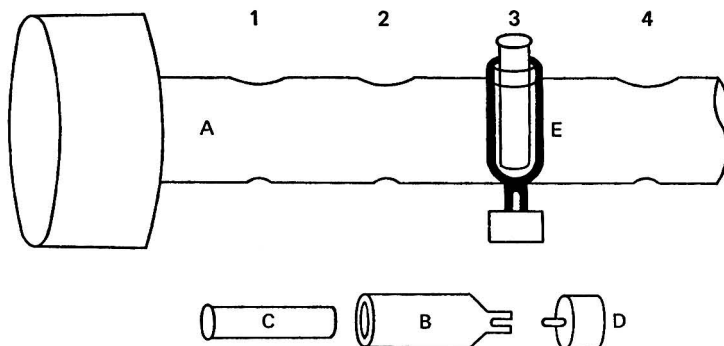
Fig. 1. Diagrammatic representation of the counting system: A, permanent sample holder slotted at positions 1, 2, 3 and 4, and mounted in contact with the germanium (lithium) crystal; B, rotating container for sample holder; C, sample holder; D, geared motor to drive rotating assembly; and E, assembled specimen in counting position.

During dehydration the biological specimen undergoes a marked change in shape and size. As this change would have affected the accuracy of measurement, the counting equipment was carefully standardised by using radioactive solutions in the same standard counting

tubes that were used for the specimens. By changing both the height of the solution in the tube and its distance from the detector, it was found that at distances greater than 10.5 cm a variation in height between 2 and 6 cm did not alter the count rate from the same amount of radioactivity by more than 1%. Afterwards the same solutions were evaporated to dryness and again counted under corresponding geometrical conditions. The results were then in agreement within the same statistical variation, provided that the samples were rotated about their own axes to compensate for uneven deposition of the residue.

As the oyster flesh samples have a high water content it is to be expected that activity measurements on the wet samples will differ from those on the same samples when dried because of absorption of the gamma-rays in water. The correction factors for absorption loss were measured as a function of gamma-ray energy with the aid of sealed standard radio-active sources obtained from the IAEA, Vienna. The results obtained are shown in Fig. 2. These correction factors were applied to all measurements.
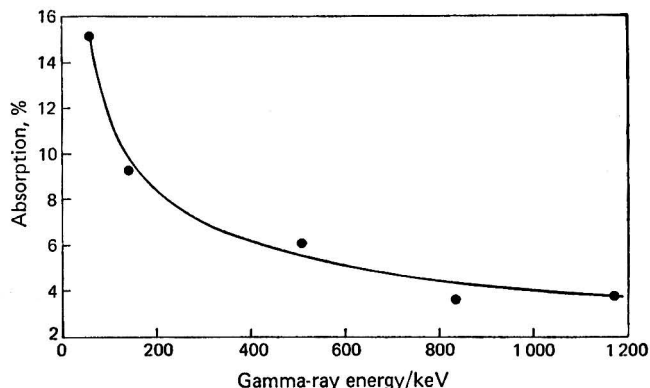
Fig. 2. Correction factor for absorption in water as a function of gamma-ray energy.

Methods of Dehydration

The material analysed in this investigation was the jelly-like flesh of the oyster. Wet samples weighed 2–4 g and filled the sample tube of 16 mm diameter to a height of 2–4 cm. The samples thus met the specifications required for optimum counting conditions (see above). When oven drying is used in order to dehydrate biological material, temperatures between 100 and 110 °C are commonly used. In this investigation oven drying from 50 to 120 °C was investigated.

Before heating at 50 °C, the radioactivity of the weighed sample was measured. Thereafter the sample was dried for 48 h at 50 °C. A test batch showed that constant mass was achieved after such a drying period. At this low temperature dehydration proceeded without sputtering. The dried specimen was then counted, after which it was re-heated for a further 48 h at 90 °C; this process was repeated at 105 and 120 °C. It should be noted that throughout all of the dehydration stages the same sample remained in the same sample tube entirely untouched. Oven temperatures were constantly monitored with calibrated thermistors.

Although dehydration at 50 °C accounted for losses of about 90% relative to the wet mass, losses on subsequent heating at the higher temperatures never exceeded an additional 2%. In order to provide a basis for comparison, freeze drying was also carried out on similar samples. As above, sample masses and radioactivity were recorded before and after drying. To ensure that water was removed by sublimation only, each specimen was frozen at −10 °C for 24 h before freeze drying.

Results and Discussion

Gamma-ray Spectrometry

The resolution of the gamma-ray measuring system was 6 keV. This, however, did not

detrimentally affect the results because when more than one radioactive tracer was added to the aquaria, they were chosen so that their gamma-ray energies were sufficiently different to be individually measurable without interference.

Mortality Rate of Oysters

In most instances few of the oysters died. However, two instances were encountered where the mortality rate was 70 and 100%, respectively. In these instances the radioactive tracers were iron-59 and a mixture of arsenic-74, antimony-125, mercury-203 and iron-59.

The natural concentration in sea water of the stable elements concerned[16] varies between 100 and 1 000 ng l^{-1}. The amount of tracer material added to the aquaria was, in general, of the order of 20 ng l^{-1}. The exceptions were cadmium (50 ng l^{-1}), lead (300 ng l^{-1}) and selenium and iron (1 000 ng l^{-1}). Only for the last two elements did the added radioactive tracer make an appreciable contribution to the total trace element concentration. However, in the aquarium labelled with radioselenium the mortality rate was negligibly low and comparable with that in the other aquaria. It may therefore be concluded that the high concentration of added iron played a role in poisoning the oysters.

Chromium

The relatively low error limits of the individual results reflect the appreciable extent of accumulation of chromium by the oysters. Variations between individual oysters are relatively small, which shows that accumulation is virtually uniform. In Fig. 3 the weighted values are shown plotted as a function of oven temperature and are compared with the value obtained by freeze drying. The errors shown are weighted standard deviations. From this figure it can be concluded that there was probably no loss during any drying stage, as the error limits are of the same order as the measured activity change. It can also be concluded that chromium is accumulated and retained in the inorganic state or, if metabolised to organometallic forms, that these forms are not volatile under the conditions investigated.

Manganese

Although radiomanganese was added to the aquaria in activities comparable with those of other radionuclides, all but a few of the oysters accumulated almost insignificant levels of radioactivity. As a result the statistical errors of the measurements are generally so great that the measured activity changes are meaningless.

The few instances in which appreciable accumulation occurred showed no change of activity during drying, within the statistical validity of the results.

Iron

As has been noted above, the mortality rate in aquaria labelled with radioiron was so high that relatively few oysters were available for analysis. Weighted values of the activity changes with drying temperatures are shown in Fig. 4. It can be concluded that no iron is lost either during freeze drying or oven drying up to 105 °C.

Cobalt

Because of the high specific activity of cobalt-58 the activity administered was about
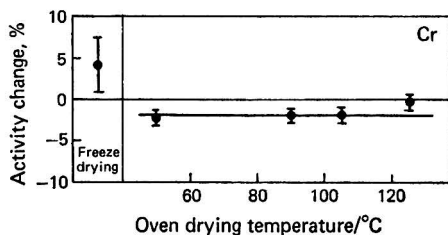
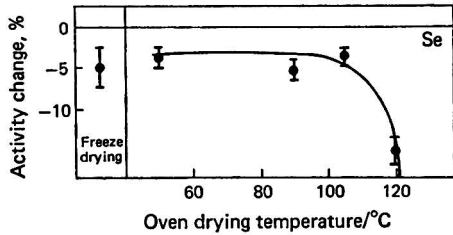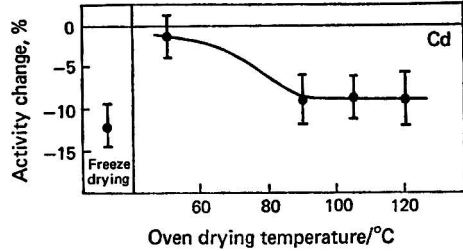Fig. 3. Weighted activity changes of accumulated chromium when freeze dried and dried at different oven temperatures.
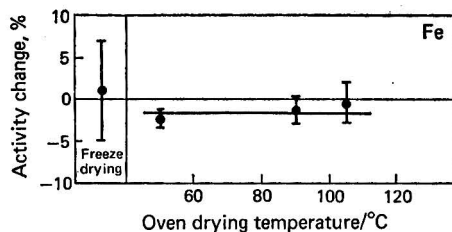
Fig. 4. Weighted activity changes of accumulated iron when freeze dried and dried at different oven temperatures.

three times that of the other nuclides. Despite this the activity accumulated by the oysters was relatively small. This result is in agreement with previous observations[17] on the mussel *Donax denticalatus* where it was found that ionic cobalt accumulated to about 20% of the accumulation of cobaltamine. Analytically, however, activity changes reflect little or no loss during drying, as shown diagrammatically in Fig. 5.

Zinc

The analytical results obtained for zinc are shown in Fig. 6. The results compare closely with those for chromium, except that a larger variation in uptake was observed between individual oysters.

It is known that only about 4% of accumulated zinc is metabolised,[18] implying that about 96% of the zinc is retained as inorganic compounds. If any of the metabolised zinc was formed in a volatile chemical form losses would have been within the error limits of the determinations and thus would not have been observed.
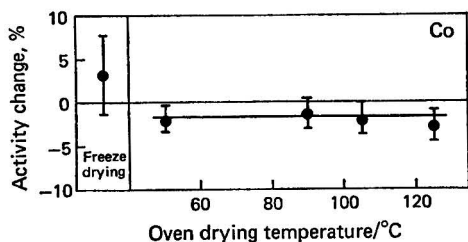
Fig. 5. Weighted activity changes of accumulated cobalt when freeze dried and dried at different oven temperatures.
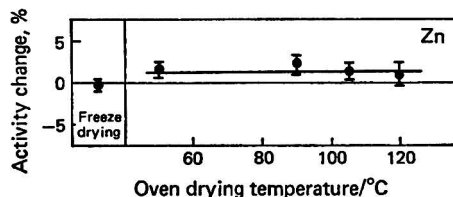
Fig. 6. Weighted activity changes of accumulated zinc when freeze dried and dried at different oven temperatures.

Selenium

The accumulation of selenium was again relatively uniform over all the oysters. The weighted analytical results are plotted in Fig. 7. Material oven dried up to a temperature of 105 °C showed slight losses, comparable with those obtained by freeze drying. This implies that the losses caused by oven drying are due to metabolised selenium compounds, which may be volatile under these conditions. The same volatility would explain the comparable loss by freeze drying.

However, at an oven temperature of 120 °C there is an appreciable loss of selenium activity. As the inorganic sodium selenite administered to the oysters is not volatile under these conditions, the loss of selenium may imply oxidation by air. If selenium oxide is formed from the original material, the most likely structure would be the chain structure
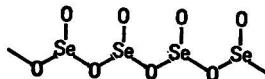
which is not volatile. However, if metabolised selenium in an organic form is oxidised to SeO_2, the selenium atoms would initially be separated from each other so that the most likely form would be molecular SeO_2, which readily distils. This assumption explains the observed result.

Cadmium

The amount of radiocadmium accumulated varied appreciably between individual oysters, as was the case with zinc. However, in contrast with zinc the measured losses on drying were appreciable. As the added radiotracer was in a non-volatile inorganic form, the observed losses (see Fig. 8) imply a relatively large degree of conversion to metabolised forms, which are themselves volatile under the conditions of drying, or which decompose to yield volatile products.

Fig. 7. Weighted activity changes of accumulated selenium when freeze dried and dried at different oven temperatures.

Fig. 8. Weighted activity changes of accumulated cadmium when freeze dried and dried at different oven temperatures.

It is remarkable that little, if any, radiocadmium was lost by oven drying at 50 °C but that virtually all losses occurred between 50 and 90 °C. This difference could be ascribed to the relatively low vapour pressure of cadmium compounds at the lower temperature. Above 90 °C the possibility of atmospheric oxidation to non-volatile compounds increases, so that total losses may be expected to be somewhat less than in the instance of freeze drying, in which all volatile compounds, even those with relatively low vapour pressures, will be removed. The above assumptions are consistent with the observed results.

The analytical implication of these results is that there now exists a doubt about the accuracy of cadmium analyses at the trace element level in marine zoological specimens, and possibly in other biological material as well, if these specimens have been dehydrated prior to analysis.

Lead

The amount of radiolead accumulated was relatively uniform over all the oysters. In addition, it was noted that the amount accumulated was high, particularly when it was considered that the intensity of the observed gamma-ray was only 4%. The high accumulation may partly be accounted for by the fact that three times as much activity was used here as in the other instances. The relatively high concentration of added lead also caused a visible colour change in the oyster flesh.

The weighted values of activity losses as a function of oven temperature and the comparable value obtained by means of freeze drying are shown in Fig. 9. Increasing losses were observed as the oven temperature increased and even with freeze drying losses were exceptionally high. As before, the added tracer was not volatile, so that the formation of volatile metabolised chemical forms can be inferred. The total amount of activity lost under freeze drying conditions probably indicates the proportion of lead with appreciable vapour pressure. As the losses encountered when using oven drying at the higher temperatures
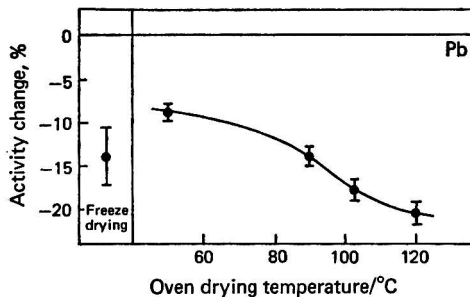
Fig. 9. Weighted activity changes of accumulated lead when freeze dried and dried at different oven temperatures.

exceed this value, it can be deduced that oxidation in air leads to the formation of decomposition products or oxides which are also volatile at these higher temperatures.

The losses encountered during freeze drying and oven drying at relatively low temperatures were marked.

Conclusions

In this investigation the indicator, *C. gigas*, was allowed to accumulate radiotracers of chromium, manganese, iron, cobalt, zinc, arsenic, selenium, cadmium, antimony and lead in order to use the oyster flesh to test the reliability of freeze drying and oven drying at temperatures between 50 and 120 °C as a preliminary analytical technique for subsequent trace element analyses. The results indicate the following: that for the elements chromium, manganese, iron, cobalt and zinc, where possibly no losses occurred during drying, the existing techniques are applicable and reliable; that for the elements selenium, cadmium and lead, where appreciable losses were detected, the application of existing techniques without additional precautions or corrections would probably lead to inaccurate results; that antimony and arsenic were not studied owing to 100% mortality among the oysters; and that although the results recorded here are applicable only to *C. gigas*, this study points to the need to re-investigate the analytical validity of dehydration processes in other biological systems.

References

1. Fourie, H. O., *S. Afr. J. Sci.*, 1976, **72**, 110.
2. Bryan, G. W., *J. Mar. Biol. Ass. U.K.*, 1969, **49**, 225.
3. Bryan, G. W., *Proc. Roy. Soc., B*, 1971, **177**, 389.
4. Brooks, R. R., and Rumsley, M. G., *Limnol. Oceanogr.*, 1965, **10**, 521.
5. Segar, D. A., Collins, J. D., and Riley, J. P., *J. Mar. Biol. Ass. U.K.*, 1971, **51**, 131.
6. Pentreatch, R. J., *J. Mar. Biol. Ass. U.K.*, 1973, **53**, 127.
7. Pringle, B. H., Hissong, D. E., Katz, E. L., and Mulawka, S. T., *J. Sanit. Engng. Div. Am. Soc. Civ. Engrs*, 1968, **94**, 455.
8. Hwang, J. Y., Ullucci, P. A., and Mokeler, C. J., *Analyt. Chem.*, 1973, **45**, 795.
9. Eisler, R., Zariogian, G. E., and Hennekey, R. J., *J. Fish. Res. Bd Can.*, 1972, **29**, 1369.
10. Carey, A. G., and Cutshall, N. H., "Radioactive Contamination of the Marine Environment," STI/PUB/313, IAEA, Vienna, 1973, p. 307.
11. Mulford, C. E., *Atom. Absorption Newsl.*, 1966, **5**(6), 135.
12. Geldiay, R., and Uysal, H., "Origin and Fate of Chemical Residues in Food, Agriculture and Fisheries," STI/PUB/399, IAEA, Vienna, 1975, p. 69.
13. Patel, B., Valanju, P. G., Mulay, C. D., Balani, M. C., and Patel, S., "Radioactive Contamination of the Marine Environment," STI/PUB/313, IAEA, Vienna, 1973, p. 307.
14. Fukai, R., and Meinke, W. W., *Limnol. Oceanogr.*, 1959, **4**, 398.
15. Fourie, H. O., and Peisach, M., *Radiochem. Radioanalyt. Lett.*, 1976, **26**, 277.
16. Van As, D., Fourie, H. O., and Vleggaar, C. M., *S. Afr. J. Sci.*, 1975, **71**, 151.
17. Shimizu, M., "Design of Radiotracer Experiments in Marine Biological Systems," STI/DOC/10/167, IAEA, Vienna, 1975, p. 121.
18. Robertson, D. E., Report BNWL-SA-4048, Battelle North West Laboratory, Richland, Wash., 1971

Detection of the Presence of BHA by a Rapid Spectrofluorimetric Screening Procedure

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A rapid screening procedure for detecting BHA in miscellaneous materials such as foodstuffs is presented. It is based on the sensitive fluorimetric detection of BHA following its isolation from complex sample matrices by steam distillation. Because of the sensitivity achieved, only small samples are required and time-consuming extractions of the antioxidant are eliminated. The rationale for the procedure, and some of its limitations, are discussed.

> *Keywords: Butylated hydroxyanisole detection; foodstuffs; steam distillation; spectrofluorimetry*

A satisfactory analytical procedure for the determination of butylated hydroxyanisole (2- and 3-*tert*-butyl-4-methoxyphenol, BHA) or, indeed, other antioxidants in foodstuffs must cover a wide range of concentrations extending from a few parts per million to an upper level of about 200–300 p.p.m. The upper limit is fixed in most instances by governmental regulation but the lower limit will be variable and time dependent because of the dynamic nature of the systems into which the antioxidants are incorporated. Existing methods for the lower range are not entirely satisfactory because of the time-consuming recovery measures often required for the more complex sample matrices, such as are represented by the great variety of foodstuffs.

The over-all simplicity of an analytical method based on the intrinsic fluorescence of BHA is an attractive feature. Although the quantum yield for BHA is probably small, it is, nonetheless, adequate for a simple, rapid and sensitive spectrofluorimetric procedure.

Little work has been reported that deals with the spectrofluorimetric analysis of antioxidants such as BHA. The first report of the luminescence properties[1] of the common food antioxidants was intended for the determination of propyl gallate in the presence of BHA and 2,6-di-*tert*-butyl-4-methylphenol (BHT). Chloroform was employed to quench the fluorescence of BHA and BHT, and as little as 0.000 5% of propyl gallate was determined in lard. In a later paper,[2] spectrofluorimetry was used for the measurement of BHA in lard, cereals and waxed liners. The procedure for each type of sample varied considerably. In the simplest procedures such as for lard, a standard-additions technique was employed, whereas for the more complex samples, including those giving high fluorescence background readings (such as certain packaging materials and glues), a chromatographic separation was necessary prior to spectrofluorimetry.

In this paper are presented the details of a spectrofluorimetric method suitable for the rapid screening and approximate determination of BHA in miscellaneous materials such as foodstuffs, following recovery of the antioxidant by steam distillation. Because of the sensitivity attainable, small samples are required and time-consuming extraction procedures eliminated.

Experimental

Apparatus

Glass distillation apparatus. Isolate the antioxidant from the sample by steam distillation in the all-glass apparatus shown in Fig. 1. It is important that the condenser be an efficient coiled type, as depicted, in order to avoid heating the condensate.

Spectrofluorimeter. A Perkin-Elmer, Model MPF2A, spectrofluorimeter was used at an excitation wavelength of 293 nm and emission wavelength of 323 nm with slit widths of 5–13 nm and detector sensitivity settings of 5–6.

Measure the fluorescence of the aqueous distillate in 1-cm silica cells at the wavelengths and

instrument settings found to give maximum sensitivity. A suitable concentration of BHA for establishing the analytical conditions was 2.5 p.p.m. in hexane.
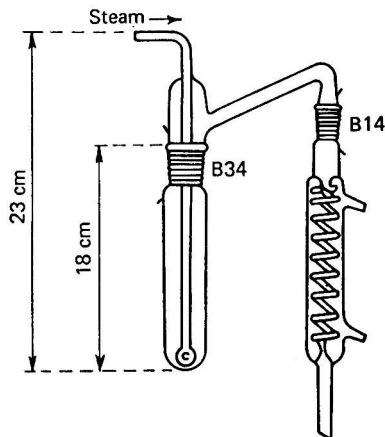

Fig. 1. Design of an all-glass distillation apparatus for the recovery of BHA.

Reagents

All reagents were of analytical-reagent grade.

Standard BHA solution. Dissolve 100 mg of pure BHA in re-distilled ethanol and dilute to 1 l with ethanol. Prepare a working solution (containing 1 p.p.m.) by diluting 10 ml of this solution to 1 l with water.

Ethanol, 95% V/V. Re-distilled in an all-glass apparatus.

Sulphuric acid, 0.2 M.

Calibration Graph

Prepare a calibration graph by plotting the fluorescence readings against the concentration of BHA (parts per million in a final distillate of 100 ml). This can be done by subjecting known volumes (between 1 and 10 ml) of the working solution containing 1 p.p.m. of BHA to steam distillation as described below. Determinations should be carried out at a minimum of four different concentrations of BHA.

Procedure

Attach a 100-ml calibrated flask as receiver below the condenser and seal the end of the delivery tube within the flask with a small volume of water.

Weigh 1 g of sample into the distillation tube. Add 5 ml of 0.2 M sulphuric acid and subject the mixture to vigorous steam distillation in the assembled apparatus at such a rate that, with condensation, the volume of liquid in the tube does not exceed 25–30 ml at the end of the distillation (approximately 8 min). Collect approximately 100 ml of distillate, dilute to the mark with water and measure the fluorescence intensity of the solution. Compare the reading with that of a 0.025 p.p.m. standard (obtained by the distillation of 2.5 ml of aqueous working standard and diluting to 100 ml, in the same manner as the sample) and using water condensed from the clean apparatus for the measurement of the fluorescence background. If the fluorescence readings exceed that of the background it is probable that BHA is present and the samples should be re-examined by an alternative method if required. An approximate value for the concentration of BHA can be obtained by comparing the fluorescence readings with a calibration graph prepared as described above and using the same instrument settings (see Results and Discussion and Fig. 4).

Results and Discussion

Isolation of BHA by steam distillation greatly simplifies the subsequent analytical procedure by excluding many compounds present in the sample matrix that interfere in spectrofluorimetric measurements or complicate the recovery steps, or both. Of the common antioxidants, BHT is probably the only important compound likely to be found in the distillate together with BHA. Its quantum yield is so much lower than that of BHA, however, that there is no serious interference problem.[1] Furthermore, the presence of BHT in the distillate can be confirmed by thin-layer chromatography or more satisfactorily by gas chromatography provided that the necessary extraction and concentration steps are introduced. Such additional measures do not invalidate the spectrofluorimetric screening procedure, but rather furnish supplementary data that are useful, for example, in such areas as regulatory control.

It appears that certain objections[3-6] to a steam distillation procedure for recovery of BHA can be related to the nature of the sample material itself and the actual amount of sample taken for analysis. High-fat types can be expected to be less amenable to steam distillation because of the affinity between BHA (or BHT) and the lipoidal substances present. We have found that this effect can be demonstrated readily by distilling known amounts of BHA from aqueous systems when the recoveries are quantitative in distillates of less than 100 ml. In contrast, recovery of the same amounts of BHA from oils (1–2 g) requires larger volumes (200 ml) of distillates for complete recovery of the last traces (approximately 5%) of the antioxidant.

The selection of analytical wavelengths was based on uncorrected spectroscopic results for BHA, which are given in Fig. 2. The excitation spectrum was recorded, as is common practice, with the fluorescence grating in the zero-order position. The limiting feature of the proposed method is the extent to which there is overlap of the Raman scatter peak with the fluorescence spectrum of BHA. The extent of this overlap can also be judged from Fig. 2. The overlap is unavoidable in the circumstances and is independent of the solvent. The limitation is not a serious handicap, however, as a detection limit (based on three times the noise level) of 0.01 p.p.m. of BHA in the aqueous distillate means that a concentration approaching 2 p.p.m. can be detected in a sample (1–2 g). No attempt has been made to reduce this concentration limit by extraction into an organic solvent in a concentration step.
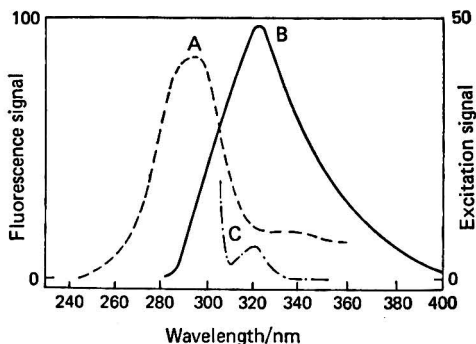
Fig. 2. Excitation (curve A, ordinate 0–50) and fluorescence (curve B, ordinate 0–100) spectra of BHA (2.5 p.p.m.) in re-distilled hexane (sensitivity setting 5, slits 10 nm) and the fluorescence spectrum of pure hexane (curve C, ordinate 0–100; sensitivity 6, slits 10 nm).

Calibration graphs for BHA, using different instrument settings, are shown in Fig. 3. Over the concentration range up to 5 p.p.m. the graph is linear but beyond this level there is distinct curvature. At concentrations greater than 35–40 p.p.m. quenching of fluorescence is evident and the graph passes through a maximum value in accord with theoretical predictions. Closer examination of the calibration graph at lower concentrations (see Fig. 4)

discloses the rationale for the proposed analytical procedure. At the low concentrations shown, each graph is linear but when extrapolated to zero concentration there is a significant background signal attributable, presumably, to the proximity of the excitation and fluorescence spectra. As the choice of instrument parameters markedly influences the detection sensitivity (as indicated by the gradient of each graph), an increase in sensitivity is accom-
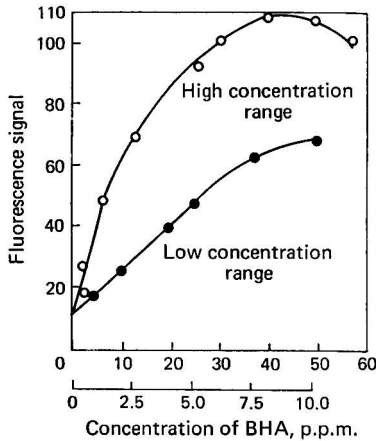

Fig. 3. Spectrofluorimetric calibration curves for BHA in hexane-ethanol $(1 + 1 \ V/V)$ measured at $\lambda_{\text{excitation}}$ 293 nm and $\lambda_{\text{emission}}$ 323 nm (sensitivity setting 3, slits 6 nm).
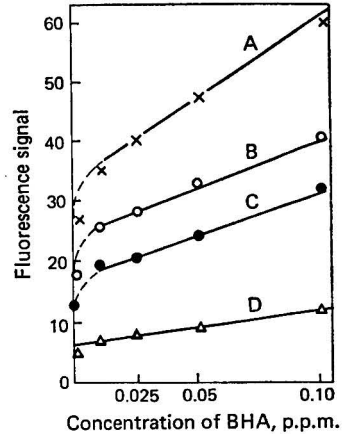
Fig. 4. Spectrofluorimetric calibration curves for BHA in water: A, $\lambda_{\text{excitation}}$ 283 nm, sensitivity setting 5, slits 13 nm; B, $\lambda_{\text{excitation}}$ 293 nm, sensitivity setting 5, slits 11 nm; C, $\lambda_{\text{excitation}}$ 283 nm, sensitivity setting 5, slits 11 nm; and D, $\lambda_{\text{excitation}}$ 293 nm, sensitivity setting 6, slits 6 nm.

panied by an appreciable increase in the corresponding background fluorescence signal. At concentrations close to the detection limit, the best compromise appears to be the use of wide slits and reduced amplifier gain (*i.e.*, instrument sensitivity setting) in spite of the large background fluorescence signal.

TABLE I

EXAMINATION OF SOME FOODSTUFF SAMPLES FOR PRESENCE OF BHA

No.	Sample	Fluorescence intensity*
1	Cooking margarine	18
2	Condensed milk	13
3	Groundnut oil	13
4	Sunflower oil, brand A	11
5	Sunflower oil, brand B	11
6	Sunflower oil	13
7	Groundnut butter	12
8	Sunflower oil, brand C	22
9	Sunflower oil, brand D	20
10	Vegetable cooking oil	12
11	Vegetable oil	12
12	Cheddar cheese	12
13	Chocolate (block)	12
—	Blank (fluorescence background)	12
—	Standard BHA (0.025 p.p.m.)	19

* Values obtained using $\lambda_{\text{excitation}}$ 293 nm, sensitivity setting 5 and 11-nm slits.

The value of this method is illustrated by the results for the analysis of a number of food-stuffs and cooking oils given in Table I. The results indicate the presence of BHA, consistent with labelling, in three samples (Nos. 1, 8 and 9) at a level not less than 2.5 p.p.m. The effectiveness of the steam distillation is illustrated in Fig. 5, where the fluorescence spectrum of distilled water at the analytical wavelength is identical with that of steam distillates from two antioxidant-free fats. Contrary to expectations, examination of steam distillates by thin-layer chromatography showed lipids to be totally absent.
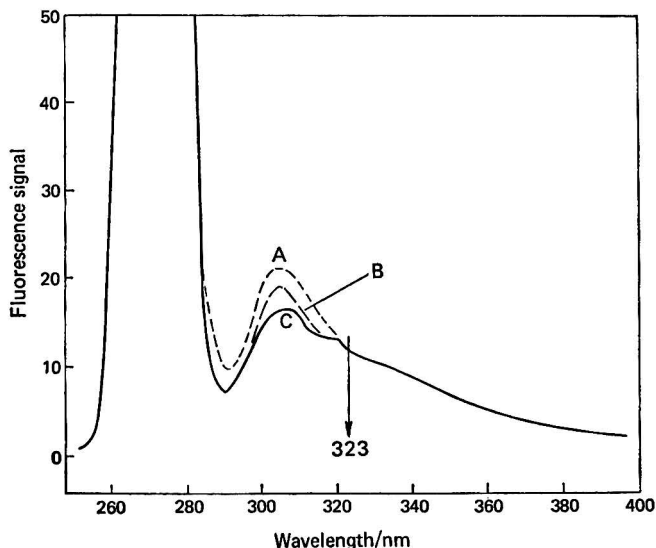
Fig. 5. Fluorescence spectra for steam distillates, measured at $\lambda_{excitation}$ 293 nm, sensitivity setting 6, slits 10 nm: A, steam distillate from sunflower oil; B, condensed steam; and C, steam distillate from crude tallow.

References

1. Latz, H. W., and Hurtubise, R. J., *J. Agric. Fd Chem.*, 1969, **17**, 352.
2. Hurtubise, R. J., and Latz, H. W., *J. Agric. Fd Chem.*, 1970, **18**, 377.
3. Buttery, R. G., and Stuckey, B. N., *J. Agric. Fd Chem.*, 1961, **9**, 283.
4. Sloman, K. G., Romagnoli, R. J., and Cavagnol, J. C., *J. Ass. Off. Agric. Chem.*, 1962, **45**, 76.
5. Anderson, R. H., and Nelson, J. P., *Fd Technol., Champaign*, 1973, **17** (July), 95.
6. Stuckey, N. B., and Osborne, C. E., *J. Am. Oil Chem. Soc.*, 1965, **42**, 228.

Analytical Methods Committee

REPORT PREPARED BY THE ANTIBIOTICS IN ANIMAL FEEDINGSTUFFS SUB-COMMITTEE

Microbiological Assay of Monensin in Animal Feeds and Pre-mixes

The Analytical Methods Committee has received and approved for publication the following Report from its Antibiotics in Animal Feedingstuffs Sub-Committee.

Report

The constitution of the Sub-Committee responsible for the preparation of this Report was: Mr. R. S. Hatfull (Chairman), Mr. M. Bentley, Mr. R. Goodey, Mr. A. F. Lott, Mr. G. S. Meadows, Miss F. N. Mulholland, Mr. G. H. Palmer, Mr. R. Ryden and Mr. L. D. Ward, with Mr. P. W. Shallis as Secretary and Mr. J. J. Wilson as Assistant Secretary.

Introduction

Monensin is an antibiotic proposed for use in poultry feeds because of its activity as a coccidiostat. The recommended level of inclusion of the antibiotic in feeds is 100 mg kg^{-1}. When the Sub-Committee began its work, some published methods for the assay of monensin were available, which included both microbiological plate and turbidimetric assays. To assist in this work the Sub-Committee co-opted members of the staff of the companies that manufactured the antibiotic in the UK, namely Eli Lilly and Company Ltd. and Dista Products Ltd. As a result of this co-operation, the Sub-Committee obtained access to a newly developed microbiological assay method for monensin and, after having been informed of the main difficulties associated with the previously published methods of assay, decided that the most profitable line of investigation would be to begin with this new method.

Experimental

Some of the members of the Sub-Committee carried out preliminary trials of the method and found it to be straightforward and capable of giving good results. However, at the time that this work was being undertaken it had become apparent to the Sub-Committee that there existed a basic difference between its approach to microbiological assay and that followed by the EEC in that the Sub-Committee favoured the two-level assay with statistical evaluation of the results, as employed in the UK for the assay of antibiotics for use in human medication, whereas the EEC favoured a four-level assay with the application of an arbitrary test for parallelism. It was decided, therefore, to attempt to convert the method under investigation into a four-level method, and this conversion introduced some further difficulties in that the lowest levels tended to give zones of inhibition that were too small to be measured. An attempt to concentrate the solutions by rotary evaporation was not particularly successful. Some members did find it possible to apply a four-level assay on occasions, whereas others found that for the most part only the two highest levels gave measurable zones of inhibition.

The method was re-written with the actual concentrations of the standard and sample solutions adjusted so that a rotary evaporation stage was unnecessary. An unmedicated sample of a poultry feed was circulated to six laboratories with instructions that it should be medicated with monensin at a level of 100 mg kg^{-1} by the addition of a dilution of a standard monensin pre-mix, which was to be accurately prepared in each laboratory. The assays were carried out collaboratively in the six laboratories in accordance with the method detailed in the Appendix. Assessment of the validity of the results obtained was effected as described under *Evaluation* in the Appendix.

Results and Discussion

The only difficulties encountered in the collaborative work were that some members did not obtain measurable zones of inhibition for the lowest level of test and standard. If this difficulty is experienced, a pre-diffusion of $1\frac{1}{2}$–2 h at room temperature is suggested. Adequate sporulation of the *Bacillus subtilis* was not readily achieved by the procedure originally specified, but the instructions have now been modified to overcome this problem.

Results obtained in the six laboratories for the microbiological assay of monensin present at a level of 100 mg kg^{-1} are given in Table I. The mean recovery of the 22 results was 97.2 mg kg^{-1} with a standard deviation of 9.22 mg kg^{-1} and a coefficient of variation of 9.49%.

TABLE I

DETERMINATION OF MONENSIN IN ANIMAL FEEDS AT A LEVEL OF
100 mg kg^{-1} BY THE RECOMMENDED METHOD

Laboratory	Monensin found/mg kg^{-1}	Assay levels used
A	94.7, 102.1, 99.8, 98.3	2*
B	102.0, 108.0, 103.0, 105.0	3
C	89.5, 87.5	4
D	98.6, 99.3, 96.3, 102.5, 100.2	4
	101.8	3
E	118.0	4
	82.1	3
F	88.4	3
	81.6, 79.7, 99.7	4

* Calculated from the upper two levels only by using the equation

$$\text{Log (potency ratio)} = \frac{u_8 + u_4 - s_8 - s_4}{u_4 - u_8 + s_4 - s_8} \times 0.301$$

The Sub-Committee recommends that the method in the Appendix should be used for the determination of monensin in animal feeds and pre-mixes.

APPENDIX

Recommended Method for the Determination of Monensin

Scope and Field of Application

The method is for the determination of the concentration of monensin in complete feeding-stuffs and pre-mixes. The lowest limit of the determination is 50 mg kg^{-1}.

Principle

The sample is extracted with 90% methanol and the extract is purified by passing it through a column of aluminium oxide. After dilution, the antibiotic activity is determined by measuring the diffusion of monensin in an agar medium inoculated with *Bacillus subtilis*. Diffusion is shown by the formation of zones of inhibition in the presence of the micro-organism. The diameters of these zones are taken to be in direct proportion to the logarithm of the antibiotic concentration. The sensitivity of the assay system is reduced in the presence of sodium ions.

Micro-organism

The micro-organism is *Bacillus subtilis* ATCC 6633 (NCIB 8054).

Maintenance of the parent strain

Inoculate *B. subtilis* on to an agar slope prepared from the culture medium. Incubate overnight at 30 °C. Store the culture in a refrigerator and re-inoculate on to agar slopes every 4 weeks.

*Preparation of the spore suspension**

Harvest the growth from a recently prepared agar slope with 2–3 ml of sterile distilled water (do not use physiological saline). Inoculate this suspension into 300 ml of culture medium contained in a Roux flask. Incubate for 6–7 d at 37 °C, harvest the growth in 15 ml of ethanol and mix. (Confirmation of sporulation can, if desired, be effected by microscopic examination.) This suspension is usable for at least 5 months if kept in a refrigerator.

Make preliminary tests on the assay plates using the assay medium to determine the amount of inoculum needed to obtain the largest possible clear zones of inhibition with the different concentrations of antibiotic used. Inoculate the culture medium at a temperature between 50 and 60 °C.

Culture Media

Culture medium.†

Glucose	1 g
Tryptic peptone	10 g
Meat extract	1.5 g
Yeast extract	3 g
Agar, according to quality	10–20 g
Water	to 1 000 g

Sterilise in 500-ml batches for 15 min at 15 lb in^{-2} pressure and then adjust the pH to 6.5 with 1 N hydrochloric acid.

Assay medium.

Dipotassium hydrogen orthophosphate, K_2HPO_4 ..	0.69 g
Potassium dihydrogen orthophosphate, KH_2PO_4 ..	0.45 g
Yeast extract	2.5 g
Glucose	10.0 g
Agar, according to quality	10–20 g
Water	to 1 000 g

Prepare freshly before use. Dissolve the ingredients and, if necessary, adjust the pH to 6.0 with 1 N hydrochloric acid. Sterilise in 500-ml batches for 15 min at 15 lb in^{-2} pressure (avoid overheating).

Reagents

Ethanol, 20% V/V aqueous solution.
Methanol, anhydrous.
Methanol, 90% V/V aqueous solution.
Methanol, 50% V/V aqueous solution.
Aluminium oxide, 100–200 mesh. It is necessary to carry out a preliminary test to ensure that the grade of aluminium oxide chosen is suitable for the purpose.
Standard substance. Monensin (sodium salt) of known activity. Dista Products Ltd., Speke, Liverpool.

Standard Solutions

Dissolve an accurately weighed amount of the standard substance in anhydrous methanol in a calibrated flask to give a solution containing 800 μg ml^{-1} of monensin. This solution can be kept for up to 2 weeks at 4 °C.

Prepare from this solution, by diluting it with 50% methanol, a standard working solution, S_8, containing 8 μg ml^{-1} of monensin. Then prepare solutions having the following concentrations of monensin by means of successive dilutions (1 + 1) with 50% methanol: S_4, 4 μg ml^{-1}; S_2, 2 μg ml^{-1}; and S_1, 1 μg ml^{-1}.

* A commercially prepared suspension of spores can be used.
† Any commercial preparation of the same composition can be used.

Procedure

Extraction

(a) *Feedingstuffs with a presumed monensin level of* 100 mg kg^{-1}. Take 12–14 g of the sample, weighed to the nearest 0.01 g, add 100 ml of 90% methanol and homogenise for 15 min. Prepare a column of aluminium oxide as follows. Take a glass tube 400 mm in length and of 25 mm i.d. tapered at one end to 2 mm i.d. Insert a plug of cotton-wool in the tapered end and, with gentle tapping of the tube, fill it with aluminium oxide to a depth of 75–80 mm. Place the homogenate on the prepared column of aluminium oxide and collect the effluent. Dilute a portion of the effluent with water so as to obtain an expected monensin concentration of 8 μg ml^{-1} (u_8). Then prepare solutions having the concentrations u_4, u_2 and u_1 by making successive dilutions (1 + 1) with 50% methanol.

(b) *Pre-mixes with a presumed monensin level of about* 250 g kg^{-1}. Take 2–3 g of the sample, weighed to the nearest 0.01 g, add 100 ml of 90% methanol and homogenise for 15 min. Filter the homogenate through a Whatman No. 1 or equivalent filter-paper and dilute the clear supernatant solution with 50% methanol so as to obtain solutions having the concentrations u_8, u_4, u_2 and u_1.

Determination

Diffusion through agar is carried out in plates, all four concentrations of the standard solution (s_8, s_4, s_2 and s_1) and of the sample extract (u_8, u_4, u_2 and u_1) being used. The four concentrations of sample extract and standard solutions must be used in each plate. For this purpose, select flat-bottomed plates that are large enough to allow at least eight holes of 10-mm diameter, with at least 30 mm between centres, to be punched out of the agar medium.

Inoculate with the spore suspension, at a temperature between 50 and 60 °C, an amount of the melted assay medium sufficient to give a layer approximately 2 mm thick in the assay plates to be used. Swirl to mix thoroughly, and pour into accurately levelled sterile assay plates (complete the pouring of one plate before proceeding to the next). With a sterile cork borer, remove agar plugs to form holes as described above. Pipette into each hole an exactly measured and equal volume (0.10 ± 0.025 ml) of, respectively, solutions S_8, S_4, S_2 and S_1 and U_8, U_4, U_2 and U_1.

Apply solutions of each concentration four times so that the determination is subject to an evaluation of 32 zones of inhibition. Incubate the plates for approximately 18 h at 35–37 °C.

Evaluation

Measure the diameters of the zones of inhibition, if possible to the nearest 0.1 mm. For each zone two measurements at right-angles should be made. Calculate the mean diameters (s_8, s_4, s_2 and s_1 and u_8, u_4, u_2 and u_1) for each of the concentrations of standard and sample. Plot the mean diameters against the logarithms of the concentrations for both standard and sample solutions. Determine the "best fit" lines for the standard and sample as follows. Determine the "best fit" point for the standard low level (*SL*) from the equation

$$SL = \frac{7s_1 + 4s_2 + s_4 - 2s_8}{10}$$

Similarly, determine the "best fit" point for the standard high level (*SH*) from the equation

$$SH = \frac{7s_8 + 4s_4 + s_2 - 2s_1}{10}$$

Similarly, calculate the "best fit" points for the sample low and high levels (*UL* and *UH*) by substituting u_1, u_2, u_4, u_8 for s_1, s_2, s_4, s_8 in the above equations.

Plot *SL* and *SH* on the same graph paper and join them to give the "best fit" line for the standards. Similarly, plot *UL* and *UH* to give the "best fit" line for the sample. In the absence of interference, the lines should be parallel. For practical purposes, the lines can

be considered to be parallel if the values $SH - SL$ and $UH - UL$ do not differ from their mean values by more than 10%.

Calculate the high-level concentration of the sample from the relationship

Sample high-level concentration = Standard high-level concentration × potency ratio

where the logarithm of the potency ratio is given by the expression

$$\text{Log (potency ratio)} = \frac{UL + UH - SL - SH}{UH - UL + SH - SL} \times 0.903\ 1$$

If the lines are found not to be parallel, either u_1 and s_1 or u_8 and s_8 can be discounted and SH, SL, UH and UL calculated from the equations

$$SL = \frac{5s_1 + 2s_2 - s_4}{6} \qquad \text{or} \qquad \frac{5s_2 + 2s_4 - s_8}{6}$$

$$SH = \frac{5s_4 + 2s_2 - s_1}{6} \qquad \text{or} \qquad \frac{5s_8 + 2s_4 - s_2}{6}$$

with similar equations for UL and UH.

The alternative "best fit" lines should be checked for parallelism as before. If parallelism is confirmed, calculate the high-level concentration of the sample as before, where the logarithm of the potency ratio is given by the expression

$$\text{Log (potency ratio)} = \frac{UL + UH - SL - SH}{UH - UL + SH - SL} \times 0.602\ 1$$

SHORT PAPERS

Spectrophotometric Determination of Iron(III) in Sulphuric Acid

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The concentration of iron, in particular iron(III), is a very important factor in the classification of the quality of commercial sulphuric acid. Iron(III) is usually a reaction product of hot (above 150 °C), concentrated sulphuric acid with metallic iron[1]:

$$2Fe + 6H_2SO_4 = Fe_2(SO_4)_3 + 3SO_2 + 6H_2O \qquad .. \quad .. \qquad (1)$$

As the usual hydrogen-forming reaction takes place in parallel with (1), another two subsequent trace reactions occur:

$$SO_2 + 2H_2 = S + 2H_2O \quad .. \qquad .. \qquad .. \qquad .. \qquad (2)$$

$$SO_2 + 3H_2 = H_2S + 2H_2O \ .. \qquad .. \qquad .. \qquad .. \qquad (3)$$
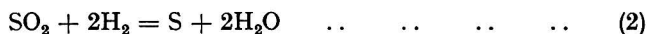
Colloidal iron(III) sulphate and elemental sulphur [reactions (1) and (2)] cause an amber colour and, in higher concentrations, turbidity in commercial sulphuric acid. The fact that the insolubility of iron(III) sulphate in sulphuric acid increases with concentration of the acid is well known.[2]

No convenient method has been described for the determination of iron(III) in sulphuric acid. Indirect methods involving the determination of iron(II) with the 1,10-phenanthroline family of reagents[3] or with potassium hexacyanoferrate(III)[4] fail because these reagents so increase the oxidation potential of the Fe^{3+} - Fe^{2+} ion redox couple by complexation as to permit the quantitative reduction of iron(III) by any sulphur dioxide present.

During our experiments to establish the reason for the amber colour and turbidity of some commercial sulphuric acid samples we found a very high ultraviolet absorbance for the iron(III) - sulphate complex. Bastian *et al.*[5] have already described a total iron determination based on the formation of the iron(III) - sulphate complex in diluted sulphuric acid. The formation of that complex can be the basis of a very convenient method for the determination of iron(III) in sulphuric acid.

Experimental

Reagents

Stock solutions containing 1 mg ml^{-1} of the appropriate substance were made up by using finely powdered sulphates of iron(III), iron(II), chromium(III), copper(II), aluminium and zinc, ammonium metavanadate, ammonium molybdate, selenium dioxide and tellurium dioxide, each suspended in 10 ml of water. Dissolution was effected by the subsequent addition of concentrated sulphuric acid and dilution with that acid to 100 ml. The exact volume was adjusted after cooling to 25 °C. Other solutions had been prepared by direct dilution with concentrated sulphuric acid. The concentration of sulphur dioxide was checked by iodimetric titration; the concentration of sulphuric acid was 96–98% *m/m*.

Instruments

The spectrophotometric measurements were made with a Cary 118C double-beam spectrophotometer (Varian Associates, Palo Alto, Calif.) and 1-cm silica cells.

Procedure

Dilute the sample of sulphuric acid with reagent-grade 96–98% acid so that it contains 20–200 μg of iron(III) per 25 ml. Measure the absorbance in 1-cm silica cells at 280 nm against a water blank. Then measure three or four standard solutions in the given range of iron(III) concentration and calculate the result by employing a linear regression programme on a calculator or by means of a calibration graph. The absorbance of solutions is infinitely stable.

Results and Discussion

The variation of the absorbance with concentration of sulphuric acid and wavelength is shown in Table I. Typical results for the determination and the effect of interferents are given in Table II.

TABLE I

ABSORBANCE VALUES OF IRON(III) AT VARIOUS WAVELENGTHS AND
SULPHURIC ACID CONCENTRATIONS

$[Fe(III)] = 1.77 \times 10^{-4}$ M; temperature, 25 °C.

Concentration of H_2SO_4/M	Wavelength/nm										
	200	220	240	260	280	300	320	340	360	380	400
18.34	0.982	1.252	1.290	1.271	1.309	1.191	0.742	0.342	0.136	0.048	0.018
17.76	0.981	1.252	1.289	1.271	1.309	1.191	0.741	0.342	0.135	0.047	0.018
17.09	0.980	1.250	1.288	1.270	1.308	1.191	0.740	0.341	0.135	0.047	0.017
15.20	0.945	1.209	1.167	1.080	1.160	1.041	0.699	0.311	0.100	0.028	0.008
13.30	0.984	1.206	1.092	0.971	1.049	0.988	0.695	0.329	0.124	0.043	0.004
11.40	0.955	1.147	0.976	0.820	0.910	0.913	0.666	0.346	0.156	0.059	0.023
9.57	1.162	1.331	1.210	0.947	1.061	1.117	0.848	0.444	0.168	0.063	0.020
7.69	0.940	1.079	0.881	0.644	0.690	0.754	0.593	0.324	0.142	0.064	0.028
5.81	0.890	0.983	0.817	0.564	0.565	0.631	0.508	0.280	0.115	0.050	0.023
3.94	0.911	0.974	0.850	0.565	0.511	0.574	0.474	0.266	0.126	0.069	0.045
2.07	0.857	0.858	0.773	0.476	0.393	0.455	0.373	0.201	0.078	0.025	0.006
0.19	0.846	0.905	0.814	0.477	0.393	0.486	0.422	0.445	0.115	0.058	0.036

The absorbing species is probably an adduct of sulphuric acid molecules and iron(III) ions. The dependence of absorbance on the concentration of sulphuric acid (Table I) shows that the adduct formation is a complicated reaction. Our attempts to interpret that dependence as the formation of species $Fe(H_2SO_4)_n$ were not successful. The possibility of the formation of polynuclear species is not excluded.

TABLE II

DETERMINATION OF IRON(III) IN THE PRESENCE OF VARIOUS
INTERFERING COMPONENTS

Results are expressed in terms of absorbance at 280 nm; 100 μg of iron(III) were
present throughout.

Interfering component	Amount of interfering component/mg		
	0.1	1.0	10.0
—	0.239*	0.478†	0.955‡
HNO_3	0.482	0.517	0.869
SO_2	0.518	0.878	—
Cr(III)	0.488	0.577	—
Cu(II)	0.516	0.860	—
Al(III)	0.734	—	—
V(V)	0.733	—	—
Se(IV)	0.478	0.477	0.481
Te(IV)	0.478	0.485	0.547
Mo(VI)	0.490	0.602	—
Zn(II)	0.477	0.482	0.525
HCl	0.478	0.477	0.476
H_3PO_4	0.478	0.478	0.477
$HClO_4$	0.478	0.477	0.478
Fe(II)	0.482	0.513	0.828

* 50 μg of iron(III).
† 100 μg of iron(III).
‡ 200 μg of iron(III).

Assuming that 100 μg of iron(III) are being determined and that the maximum acceptable deviation in absorbance is $\pm 5\%$, the greatest non-interfering amounts of other components are as follows: vanadium(V) 0.009, aluminium 0.01, copper(II) 0.06, sulphur dioxide 0.06, chromium(III) 0.20, molybdenum(VI) 0.20, nitric acid 0.60, iron(II) 0.68, tellurium(IV) 3.40, zinc 5.1, hydrogen chloride 340, orthophosphoric acid 1 200 and perchloric acid 2 000 mg.

Sulphur dioxide presents the most serious interference as it commonly occurs in commercial sulphuric acid. However, it is usually the subject of an independent iodimetric determination[6] so that the necessary correction can easily be performed according to the relationship that for each 100 p.p.m. of sulphur dioxide the concentration of iron(III) found should be decreased by 8.37 p.p.m.

Correction for iron(II) is usually unnecessary owing to the relatively high permissible concentration for this ion. However, it can be carried out by using the equation

$$Fe(III) = 7.369 \times 10^{-3} (28\,571A - Fe_{tot.})$$

where $Fe_{tot.}$ and $Fe(III)$ are the micrograms of total and trivalent iron in 25 ml of solution, respectively, and A is the absorbance at 280 nm. Total iron is determined by atomic-absorption spectrophotometry or by ultraviolet spectrophotometry with 1,10-phenanthroline.[6]

The deviation in the concentration of the 95% sulphuric acid, $\pm 3\%$, is negligible. The method of iron(III) determination described is almost four times more sensitive than the method of Bastian *et al.*[5]

References

1. Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Volume XIII, Longmans, New York and London, 1934, p. 328.
2. Seidell, A., "Solubilities of Inorganic and Organic Compounds," Van Nostrand, New York, 1919, p. 343.
3. Stephens, B. G., and Lindstrom, F., *Analyt. Chem.*, 1964, 36, 1308.
4. Fasullo, O. T., "Use and Handling of Sulfuric Acid," McGraw-Hill, New York, 1965, p. 159.
5. Bastian, R., Weberling, R., and Palilla, F., *Analyt. Chem.*, 1953, 25, 284.
6. "Standard Methods for Analysis of Sulfuric Acid," American Society for Testing and Materials, Philadelphia, Pa., 1968, E-223.

Limits of Detection of Gas-sensing Probes

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In this paper, we propose a method by which the limits of detection of gas-sensing probes can be derived and summarise the relevant experimental evidence.

Hansen and Larsen[1] recently described a graphical method for this purpose; this method is intended to apply equally to gas-sensing membrane probes and to gas-sensing probes without membranes ("air-gap electrodes"). We believe that their theory has been incorrectly applied, because the thin film of internal electrolyte should be considered as essentially separate from the bulk of the internal electrolyte, and that a substantial amount of experimental evidence has been ignored. Our theory is probably identical with that used by Midgley and Torrance[2] in their calculations.

Hansen and Larsen chose the ammonia probe system to illustrate their method. They predicted that for a 10^{-1} M ammonium chloride internal electrolyte, as commonly used in commercial probes, the lower limit of Nernstian response of the probe is approximately 10^{-4} M ammonia and the limit of detection 6×10^{-6} M ammonia. For comparison, experimental results with ammonia-sensing probes are presented in Table I; it can be seen that

TABLE I

RESPONSE LIMITS OF AMMONIA-SENSING MEMBRANE PROBES

Reference	Type of electrode*	Concentration of ammonium chloride internal electrolyte/M	Reported limits†	
			Limit of Nernstian response/M	Limit of detection/M
Hansen and Larsen[1]	b	0.1	10^{-4}	—
Midgley and Torrance[2]	a	5.9×10^{-2}	6×10^{-6}	3×10^{-6}
Gilbert and Clay[3]	a	0.1	10^{-6}	1.5×10^{-8}
Bailey and Riley[4]	a	0.1	10^{-5}	10^{-6}
Proelss and Wright[5]	a	0.1	5×10^{-6}	10^{-6}
Sanders and Thornton[6]	a	0.1	2×10^{-5}	—
Evans and Partridge[7]	a	0.1	1.5×10^{-5}	2×10^{-6}
Beckett and Wilson[8]	a	0.1	3×10^{-6}	—
Thomas and Booth[9]	a	0.1	10^{-6}	—
Mertens *et al.*[10]	a	0.1	6×10^{-6}	10^{-6}
Mertens *et al.*[11]	a	0.1	1.5×10^{-5}	10^{-6}
Dewolfs *et al.*[12]	a	0.1	10^{-5}	10^{-6}
Midgley and Torrance[13]	a	5.9×10^{-2}	6×10^{-6}	—
Hansen and Růžička[14]	b	0.01	1.6×10^{-5}	10^{-5}

* a, Gas-sensing membrane probe; b, gas-sensing probe without membrane.
† Where the limits have not been quoted in the reference cited, the figures have been derived from their results. Not all authors used the same method for deriving the limits but, nevertheless, the methods are sufficiently similar for the figures to be roughly comparable.

in practice the limit of Nernstian response for membrane probes is generally found to be 10^{-5} to 10^{-6} M and the limit of detection is less than or equal to 10^{-6} M.

The constructions of various gas-sensing probes have been described in detail in several papers (*e.g.*, references 4, 15 and 16). In the usual electrode assembly, where the internal ion-selective electrode is a pH-sensing glass electrode, the probes comprise a pH electrode with a convex tip covered by a thin film of internal electrolyte; a diagram of the sensing tip of a typical gas-sensing membrane probe is shown in Fig. 1. The gas being determined diffuses into the thin film from the sample, through either the membrane or an air gap, until the partial pressure of the gas in the film is equal to that in the sample. The equilibrium
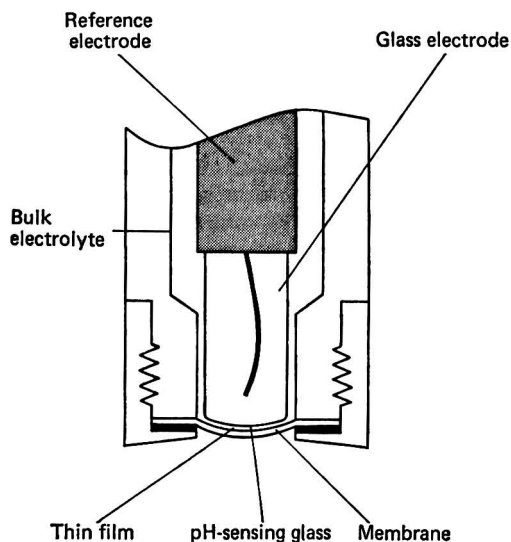
Fig. 1. Diagram of sensing tip of a typical gas-sensing membrane probe.

amount of determinand in the film gives rise to a characteristic pH that is measured by means of the pH electrode and an internal reference electrode immersed in the bulk of internal electrolyte. Thus, clearly, the response of the probe is dependent on the relationship between the equilibrium concentration (or partial pressure) of the determinand in the sample, and hence in the thin film, and the resultant pH. It is this relationship which Hansen and Larsen sought to explain; an alternative explanation is presented here.

Three assumptions can reasonably be made that simplify the calculation of the lower limit of detection; they are as follows.

(*i*) The sample volume is infinitely large with respect to the volume of the thin film. Thus the amount of determinand which diffuses into the thin film is assumed not to decrease the initial concentration of determinand in the sample.

(*ii*) The rate of equilibration of the thin film with the bulk of the internal electrolyte is negligible compared with the rate of equilibration of the thin film with the sample. This assumption fails only at extreme determinand dilution, as discussed later.

(*iii*) For probes sensing alkaline gases, the hydroxyl-ion concentration in the film is zero. Similarly, for probes sensing acidic gases, the pH is dependent only on $K_w/[OH^-]_f$. This assumption is not essential to the derivation of the lower limit of detection but does simplify the calculation.

Taking the ammonia probe as an example again, and using these three assumptions, the relationship between the pH of the thin film and the concentration of ammonia in the film, $[NH_3]_f$, can be derived as follows:

$$K = \frac{[NH_4^+]_f}{[H^+]_f [NH_3]_f} = 1.75 \times 10^9 \qquad .. \qquad .. \qquad .. \qquad (1)$$

where K is the stability constant for the formation of ammonium ions[17] by the reaction $NH_3 + H^+ \rightleftharpoons NH_4^+$, and the suffix f denotes concentrations in the thin film. The suffixes s and b will be used to denote concentrations in the sample and in the bulk of the internal electrolyte, respectively. If the internal electrolyte is a dilute solution of ammonium chloride, as is usual, and neglecting any effects due to the added silver chloride, which has been shown experimentally to have little or no effect on the practically determined limit of detection, the electroneutrality equation gives

$$[NH_4^+]_f + [H^+]_f = [Cl^-]_f + [OH^-]_f \qquad .. \qquad .. \qquad .. \qquad (2)$$

As $[OH^-]_f$ is assumed to be zero:

$$[NH_4^+]_f + [H^+]_f = [Cl^-]_f \qquad .. \qquad .. \qquad .. \qquad .. \qquad (3)$$

For a 0.1 M ammonium chloride internal electrolyte, $[Cl^-]_f$ remains constant at 0.1 M; thus

$$[NH_4^+]_f = 0.1 - [H^+]_f \qquad .. \qquad .. \qquad .. \qquad .. \qquad (4)$$

Substitution of equation (4) into equation (1) and rearrangement lead directly to

$$[H^+]_f = \frac{0.1}{1 + 1.75 \times 10^9 [NH_3]_f} .. \qquad .. \qquad .. \qquad .. \qquad (5)$$

Because at equilibrium $[NH_3]_s = [NH_3]_f$ (assuming that the Henry's law constants for ammonia in the two solutions are identical), this equation can be used to construct the ideal calibration graph shown in Fig. 2 (line A). $[NH_4^+]_f$ can also be calculated as a function of $[NH_3]_s$ by use of equations (4) and (5), giving the relationship shown graphically in Fig. 2 (line B). A more rigorous derivation of these relationships from equations (1) and (2), without assumption (*iii*), leads to the equations

$$[H^+]_f = \frac{[Cl^-]_f + \{[Cl^-]_f^2 + 4K_w (1 + 1.75 \times 10^9 [NH_3]_s)\}^{\frac{1}{2}}}{2 + 3.50 \times 10^9 [NH_3]_s} \qquad .. \qquad .. \qquad (6)$$

and

$$[NH_4^+]_f =$$

$$\frac{[Cl^-]_f [NH_3]_s + \{[Cl^-]_f^2 [NH_3]_s^2 + 7.0 \times 10^{-5} [NH_3]_s^2 ([NH_3]_s + 5.71 \times 10^{-10})\}^{\frac{1}{2}}}{2 ([NH_3]_s + 5.71 \times 10^{-10})} .. \qquad (7)$$

Substitution of figures into these equations shows that the error due to the simplification adopted in assumption (*iii*) steadily increases as $[NH_3]_s$ increases, reaching approximately 0.2% at 1 M $[NH_3]_s$. Thus the ideal calibration graph shown in Fig. 2, line A, would appear identical if constructed from equation (6).
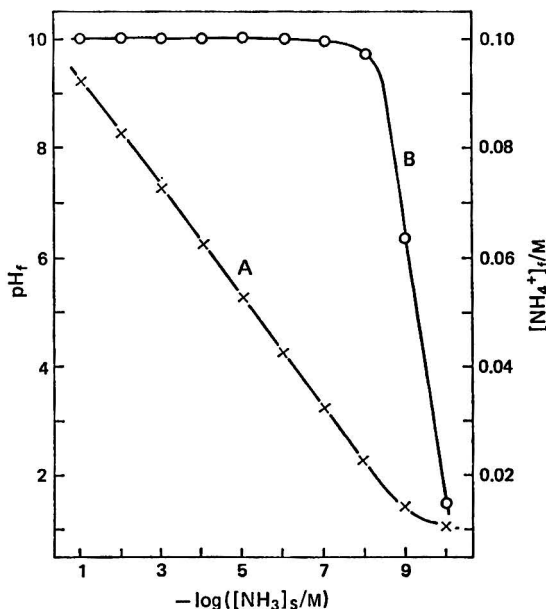
Fig. 2.   Graphs showing variation of pH_f and $[NH_4^+]_f$ with $[NH_3]_s$.   A, pH_f and B, $[NH_4^+]_f$ (0.1 M NH_4Cl internal electrolyte).

These equations enable the behaviour of a probe that has been immersed in samples containing different concentrations of ammonia to be predicted. If the probe is immersed in a solution in which $[NH_3]_s > [NH_3]_f$, ammonia diffuses from the sample into the thin film until equilibrium is reached when $[NH_3]_s = [NH_3]_f$; this process will result in a small concomitant increase in $[NH_4^+]_f$. Substitution into equation (7) shows that for a 0.1 M ammonium chloride internal electrolyte, if $[NH_3]_s = [NH_3]_f = 10^{-2}$ M, then $[NH_4^+]_f = 0.100\,001\,7$ M. Conversely, if the probe is immersed in a solution in which $[NH_3]_s < [NH_3]_f$, ammonia diffuses out of the thin film into the sample until equilibrium is reached; this process results in a decrease, via the reaction $NH_4^+ \rightarrow NH_3 + H^+$, in $[NH_4^+]_f$. The work of Emerson *et al.*[17] suggests that this reaction is sufficiently rapid that it will not slow the probe response. Again using equation (7), if $[NH_3]_s = [NH_3]_f = 10^{-7}$ M, then $[NH_4^+]_f = 0.099\,43$ M for a 0.1 M ammonium chloride internal electrolyte.

Comparison of the observations in Table I with the behaviour predicted by equation (5) clearly indicates that our theoretical predictions of the limits of detection are too optimistic. However, there are several reports of probes responding to concentrations of ammonia that would cause the pH of the thin film to be below that of the bulk of the internal electrolyte; this behaviour is contrary to the statement of Hansen and Larsen[1] that it is not possible to measure a pH (in the thin film) that is lower than the pH value in the electrolyte itself. There are two main reasons why our predictions are so optimistic. Firstly, the rate of interchange of ammonia between the thin film and the bulk of the internal electrolyte is not completely negligible; thus the limit of detection is the value of $[NH_3]_f$ when dynamic equilibrium has been achieved between the ammonia diffusing into the thin film from the bulk electrolyte (in which $[NH_3]_b = 6 \times 10^{-6}$ M for a 0.1 M ammonium chloride internal electrolyte) and the ammonia diffusing out of the thin film through the membrane into

a sample containing no ammonia. The more the diffusion between the thin film and the bulk electrolyte is restricted, the closer the limit of detection will be to the theoretical limit; conversely, the freer the interchange the more the limit of detection will tend to be set by $[NH_3]_b$. However, experiments to determine the effect of temperature on probes with microporous membranes have demonstrated that this interchange is relatively slow[4]; similar behaviour would be expected from probes with homogeneous membranes. A lower limit of detection should be achievable when using a more dilute internal electrolyte, because of of the smaller free ammonia content of such an electrolyte. However, the use of more dilute internal electrolytes is of limited practical value because, as pointed out by Hansen and Larsen, the upper response limit is drastically reduced. Secondly, the experimental determination of limits of detection of ammonia probes is complicated by the inevitable interference by trace amounts of ammonia in the reagents and the water used to make up solutions; this has been well illustrated by the work of Midgley and Torrance[2] with waters of different purities. The significantly lower limits obtained by Gilbert and Clay[3] can probably be attributed to the fact that their different method of measurement avoided this interference; in addition they allowed extremely long times for equilibrium to be reached.

References

1. Hansen, E. H., and Larsen, N. R., *Analytica Chim. Acta*, 1975, **78**, 459.
2. Midgley, D., and Torrance, K., *Analyst*, 1972, **97**, 626.
3. Gilbert, T. R., and Clay, A. M., *Analyt. Chem.*, 1973, **45**, 1757.
4. Bailey, P. L., and Riley, M., *Analyst*, 1975, **100**, 145.
5. Proelss, H. F., and Wright, B. W., *Clin. Chem.*, 1973, **19**, 1162.
6. Sanders, G. T. B., and Thornton, W., *Clinica Chim. Acta*, 1973, **46**, 465.
7. Evans, W. H., and Partridge, B. F., *Analyst*, 1974, **99**, 367.
8. Beckett, M. J., and Wilson, A. L., *Wat. Res.*, 1974, **8**, 333.
9. Thomas, R. F., and Booth, R. L., *Environ. Sci. Technol.*, 1973, **7**, 523.
10. Mertens, J., Van den Winkel, P., and Massart, D. L., *Bull. Soc. Chim. Belg.*, 1974, **83**, 19.
11. Mertens, J., Van den Winkel, P., and Massart, D. L., *Analyt. Chem.*, 1975, **47**, 522.
12. Dewolfs, R., Broddin, G., Clysters, H., and Deelstra, H., *Z. Analyt. Chem.*, 1975, **275**, 337.
13. Midgley, D., and Torrance, K., *Analyst*, 1973, **98**, 217.
14. Hansen, E. H., and Růžička, J., *Analytica Chim. Acta*, 1974, **72**, 353.
15. Ross, J. W., Riseman, J. H., and Krueger, J. A., *Pure Appl. Chem.*, 1973, **36**, 473.
16. Růžička, J., and Hansen, E. H., *Analytica Chim. Acta*, 1974, **69**, 129.
17. Emerson, M. R., Grunwald, E., and Kromhout, R. A., *J. Chem. Phys.*, 1960, **33**, 547.

Modified Packing for Absorption Tubes for Carbon Dioxide Produced by Combustion on the Semi-micro or Macro Scale

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The absorption of carbon dioxide evolved in the micro-determination of carbon is usually effected by means of sodium hydroxide granules. As the amounts of carbon dioxide evolved and water produced by secondary reaction during the combustion of 3–10-mg samples are relatively small, the packing of the absorption tube remains permeable to the flow of gases. When, however, samples of 30 mg or more, containing high percentages of carbon, *e.g.*, carbonised matter, are analysed, then the amounts of water produced become a serious problem.

With such samples the packing of the absorption tube becomes impermeable to the carrier gas after one or two analyses. Formerly, when liquid absorbents were used, the problem did not arise, but as it is more convenient to use solid absorbents, the solution to the problem given here offers a better alternative.

The filling has been used for the past 10 years for the analysis of samples that contain either high or parts per million carbon contents as well as the usual types of organic materials. The advantages of the packing are that it remains permeable to the carrier gas throughout its life. When exhausted the packing can be removed readily from the tube by washing with water with the assistance of a metal wire and the use of acid is unnecessary. The tube containing the absorbent for carbon dioxide is a conventional U-tube, 12.5 cm high and 15 mm i.d., provided with side-arms and two ground-glass stopcocks.

Method

Introduce a small plug of cotton-wool into the centre of the U-bend followed by a layer of Carbosorb - anhydrone mixture $(80 + 20 \ V/V)$ from a small glass scoop $(20 \times 10 \ mm)$ into one side of the U-tube. Next, add a layer of Carbosorb from a second glass scoop $(10 \times 10 \ mm)$ and make alternate additions until this side of the U-tube has been filled. Secure the packing with a small plug of cotton-wool and replace the greased stopcock in the "off" position. (This procedure will result in seven bands each of mixed and undiluted reagents.) Fill the other side of the tube with a 20- to 30-mm backing layer of Carbosorb. (This layer is not used for absorbent purposes but is merely a protective backing to the main absorbent.) Follow the Carbosorb by a plug of cotton-wool, a layer of anhydrone to the top of the tube and a plug of cotton-wool to hold the anhydrone in place, and finally replace the greased stopcock. When in use, the entrance end of the tube must be moistened with one or two drops of water (30–50 mg) before starting the daily routine of analysis.

An absorption tube filled as above weighs about 80–90 g and can be weighed on a good four-place balance. Such a tube will absorb 3.5–4 g of carbon dioxide so that if 120–130 mg of carbon dioxide are absorbed for each analysis, it can be used for 24–30 analyses.

For quantitative absorption of carbon dioxide, especially with newly filled tubes, a gas flow-rate of 20–25 ml min^{-1} is recommended during the initial combustion. Subsequent sweeping of the combustion train can then be carried out at 50–80 ml min^{-1}.

Communications

Sources of Interference in the Determination of Lactic Acid in Silage

Lactic acid is usually the major fermentation product present in silage and its accurate determination is therefore of importance in assessing silage quality. Under the conditions employed at this Institute for the quantitative gas - liquid chromatography of individual volatile acids and other components in aqueous acid extracts of silage (Chromosorb 101 at 160 °C), lactic acid is determined

only qualitatively. Quantitative gas - liquid chromatographic methods for lactic acid have been developed elsewhere,[1-3] but they are time consuming and not easily applicable to routine automated analysis of large numbers of samples. A method involving oxidation of lactic acid to acetaldehyde by periodic acid during the gas - liquid chromatographic procedure[4] is at present being investigated with a view to its application to the routine analysis of aqueous acid extracts of silage.

For a number of years a cerium(IV) sulphate oxidation method[5] has been employed at this Institute for the determination of lactic acid in silage. This method involves oxidation of the acid to acetaldehyde, which is steam-distilled into sodium hydrogen sulphite solution to form the acetaldehyde hydrogen sulphite compound in which the acetaldehyde is determined iodimetrically. This method has hitherto been considered to give reliable values for lactic acid. However, unexpectedly high values for lactic acid have on occasion been obtained from silage samples that have a pH of about 5, which would normally be expected to contain only small amounts of lactic acid and in which the presence of only small amounts has been demonstrated qualitatively by gas - liquid chromatography. A study of the gas - liquid chromatographic separation of volatile components from extracts of these particular silages revealed the presence of butane-2,3-diol. It has been suggested that this compound can arise from the action of lactobacilli during anaerobic fermentation processes[6] and its presence in silages made from crops treated with formaldehyde has been reported by Fennessy and Barry.[7] Although often present only in trace amounts, butane-2,3-diol has been found to comprise up to 5% of the dry matter of silages made from crops ensiled both with and without the addition of formaldehyde.

It has been demonstrated in this laboratory that butane-2,3-diol is oxidised to acetaldehyde by cerium(IV) sulphate. Therefore, if it is present in silage extracts it will lead to high values for lactic acid as determined by the cerium(IV) sulphate method. The gas - liquid chromatography of butane-2,3-diol by the periodic acid procedure has shown that one molecule is converted quantitatively into two molecules of acetaldehyde and it would therefore also interfere in the determination of lactic acid by this method.

Two other compounds closely related to butane-2,3-diol, namely 3-hydroxybutan-2-one (acetoin) and its oxidation product butane-2,3-dione (diacetyl), can occur as fermentation products of lactobacilli. Both are volatile in steam and form hydrogen sulphite compounds; in addition, acetoin yields acetaldehyde on oxidation with cerium(IV) sulphate. Hence both will interfere in the determination of lactic acid by the cerium(IV) sulphate method. Gas - liquid chromatography with periodate has shown that one molecule of acetoin yields one molecule of acetaldehyde and one of acetic acid, whereas diacetyl yields two molecules of acetic acid; only acetoin would therefore interfere in this procedure.

It can thus be seen that butane-2,3-diol and related compounds can be sources of error if present in mixtures in which lactic acid is to be determined. Although each interfering compound can be determined by gas - liquid chromatography and the lactic acid results corrrected accordingly, this procedure is clearly not convenient, especially on a routine basis. Methods of removing these sources of interference are therefore being investigated.

References

1. Salwin, H., and Bond, J. F., *J. Ass. Off. Analyt. Chem.*, 1969, **52**, 41.
2. Drucker, D. B., *J. Chromat. Sci.*, 1970, **8**, 489.
3. Jones, D. W., and Kay, J. J., *J. Sci. Fd Agric.*, 1976, **27**, 1005.
4. Hoffmann, N. E., Barboriak, J. J., and Hardman, H. F., *Analyt. Biochem.*, 1964, **9**, 175.
5. Elsden, S. R., and Gibson, Q. H., *Biochem. J.*, 1954, **58**, 741.
6. Whittenbury, R., McDonald, P., and Bryan-Jones, D. G., *J. Sci. Fd Agric.*, 1967, **18**, 441.
7. Fennessy, P. F., and Barry, T. N., *J. Sci. Fd Agric.*, 1973, **24**, 643.

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Determination of Ammoniacal Nitrogen in Fertilisers by Molecular Emission Cavity Analysis

Keywords: Ammoniacal nitrogen determination; fertilisers; molecular emission cavity analysis

Molecular emission cavity analysis (MECA)[1] has been used to determine many non-metals and metalloids.[2] This communication reports for the first time the direct determination of some nitrogen compounds by MECA. This determination is achieved by conversion of the compounds into ammonia, which is volatilised and transported to the MECA cavity by a stream of oxygen, wherein a white band emission ($\lambda_{max.} = 500$ nm) is produced. The spectrum is shown in Fig. 1. Similar MECA volatilisation systems have previously been designed for boron[3] (as methyl borate) and arsenic and antimony[4] (as their hydrides).
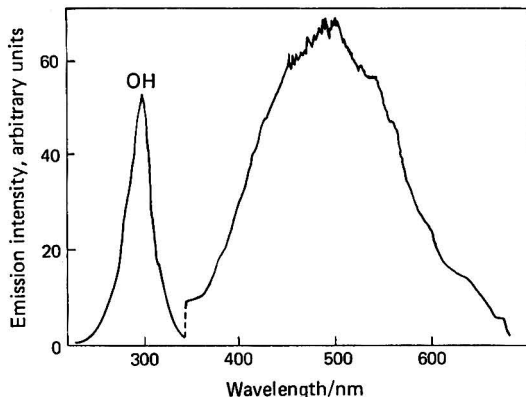
Fig. 1. Spectrum of emission obtained from ammonia introduced into a MECA oxy-cavity.

The volatilisation apparatus is shown in Fig. 2. It incorporates a 4-ml glass vial containing 0.5–0.6 g of solid sodium hydroxide (about three pellets). The vial is screwed into a Teflon cap fitted with a septum, which serves as an injection port for introduction of an 0.2-ml aliquot of aqueous sample solution. If the ammonia is being generated from ammonium ions, no other reagents are required. The heat generated by dissolution of the alkali speeds up the volatilisation of the ammonia. The stainless-steel wire around the oxygen inlet breaks up bubbles emerging from the
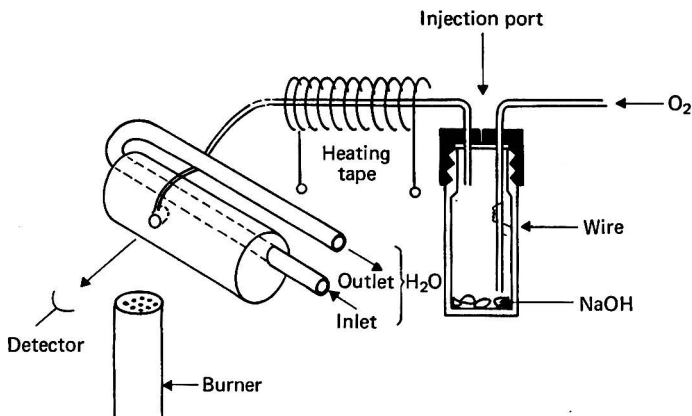
Fig. 2. System for determination of ammonia by MECA (not to scale).

alkaline solution, thereby eliminating obstruction of the vapour duct to the cavity by sodium hydroxide. Ammonia is carried by the oxygen flow (40 ml min^{-1}) through the stainless-steel tube, heated externally to prevent condensation of water, which would delay the transport of ammonia, to the MECA cavity (6 mm diameter) drilled in an aluminium, water-cooled cylinder. Water cooling prevents sodium atom emission in the cavity. The emission intensity is measured as a function of time at 500 nm (spectral slit width 68 nm), using a MECA 22 spectrophotometer (Anacon Instruments, Ashland, Mass., USA). The peak height is a measure of the amount of ammonia produced. The complete measurement takes about 5 min.

The method gives a linear calibration for 10 p.p.m.–1.0% m/V of ammonia in 0.2 ml of aqueous solution, with a reproducibility of $\pm2\%$ at the 100 p.p.m. level, and a detection limit of about 1 p.p.m. Larger concentrations (up to 10%) can also be determined, but the calibration graph curves towards the concentration axis. Identical responses are obtained from solutions of ammonium acetate, chloride and nitrate, and ammonia of equal molar concentrations. There were no interferences in the determination of 100 p.p.m. of ammonia from 9-fold amounts of Co^{2+}, Cd^{2+}, Cr^{3+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, Cu^{2+}, Hg^{2+}, Fe^{2+}, Ag^+, SO_4^{2-}, PO_4^{3-}, NO_3^- or urea. The procedure was applied to a selection of commercially available fertilisers. The results (Table I) compare well with those obtained by the classical distillation - titrimetric method.[5]

TABLE I

DETERMINATION OF AMMONIACAL NITROGEN IN FERTILISERS BY MECA

Ammoniacal nitrogen, %	
Classical method[5]	MECA
0.88	0.88
2.03	2.12
4.7	4.6
4.7	4.5
5.0	4.8
5.4	5.5
6.4	6.3
8.4	8.1
9.4	9.4
13.1	13.1

The system is also applicable to other nitrogen species which can be converted into ammonia. Addition of Devarda's alloy to the above system rapidly converts nitrate ions into ammonia, and enables nitrate ions down to parts per million levels to be determined.

References

1. Belcher, R., Bogdanski, S. L., and Townshend, A., *Analytica Chim. Acta*, 1973, **67**, 1.
2. Al-Abachi, M. Q., Belcher, R., Bogdanski, S. L., and Townshend, A., *Analytica Chim. Acta*, 1976, **86**, 139, and references cited therein.
3. Belcher, R., Ghonaim, S. A., and Townshend, A., *Analytica Chim. Acta*, 1974, **71**, 255.
4. Belcher, R., Bogdanski, S. L., Ghonaim, S. A., and Townshend, A., *Analytica Chim. Acta*, 1974, **72**, 183.
5. Belcher, R., and Nutten, A. J., "Quantitative Inorganic Analysis," Third Edition, Butterworths, London, 1970, p. 174.

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Book Reviews

PROGRESS IN ANALYTICAL CHEMISTRY. Volume 8. Edited by IVOR L. SIMMONS and GALEN W. EWING. *Proceedings of the Eastern Analytical Symposium held in New York, October, 1975.* Pp. viii + 336. New York and London: Plenum Press. 1976. Price $35.40.

This book is the latest in a series which gives selected papers from the annual Eastern Analytical Symposia; Volume 8 gives 14 papers from the 1975 Symposium.

One's first impression of the book is rather disappointing; it is produced by a photographic process on unglazed paper from the authors' original typescripts, and the use of different type-faces by the various authors produces a very patchy effect. I find this method of producing a book unsatisfactory, especially at this price. The usual reason is that it allows proceedings of this type to be produced more quickly; however, to have transcribed all the papers into the same type face could have been accomplished in a matter of days, and would have rendered the book more acceptable.

The impression created by the production disappears as one dips into the book, as the quality of most of the contributions, although naturally somewhat varied, is in general very high. The phrase "dip into" is used here deliberately, as the range of subjects covered is very varied, and one tends to select odd papers here and there. Indeed, the range is so wide as to make it difficult to decide at what audience it is aimed. Although in a widely ranging consultant laboratory, I found only half of the 14 papers to be of immediate usefulness, and it is hard to imagine a potential reader with an interest in all of them.

The papers found particularly useful were on trace metals in alloys, clinical samples and glasses, all using atomic-absorption techniques, on drinking-water pollution levels, on effluent characterisation, an extremely competent account of sampling problems in gas chromatography, and on fluorescence in drug analysis. The papers of less immediate interest were on biochemical separations on bonded microparticle ion exchangers, gas - solid chromatography, GC - MS in blood analysis for therapeutic agents, anti-Stokes Raman spectroscopy, nanosecond-lifetime fluorescence and vibrational spectroscopy.

This list of subjects will perhaps enable the reader to decide whether it is a book he wishes to buy; my own feeling is that it is one I would like an accessible library to have.

<div align="right">R. C. ROONEY</div>

HIGH-SPEED LIQUID CHROMATOGRAPHY. By PETER M. RAJCSANYI and ELISABETH RAJCSANYI. *Chromatographic Science Series, Volume 6.* Pp. x + 203. New York and Basle: Marcel Dekker Inc. 1975. Price SwFr55.

The most remarkable feature of this photocopied typescript is that 60 of its 203 pages are devoted to a list of 1008 references on high-speed liquid chromatography and an accompanying author index. The remaining pages comprise three review chapters: theory (22 pages), instrumentation (40), applications (62). Publishers do, I believe, have a responsibility to their public and to authors to publish only works of reasonable usefulness and quality. In this instance the responsibility has not been exercised and we have an embarrassing situation where the authors should have been encouraged to withdraw their text or revise it extensively before publication. It does neither publisher nor authors any good to bring out texts that are so ill-conceived as this. The first chapter on theory is almost unintelligible, except possibly to an expert who is already familiar with the background, because terms and symbols are not defined and virtually all equations are quoted without derivation. In the chapter on equipment, incredibly the only figure is a single block diagram of a chromatograph. Descriptions of individual components are far too uncritical and sketchy. Nowhere in the book are there proper descriptions of the major HPLC techniques—adsorption, partition, ion-exchange and exclusion chromatography. The final chapter on applications would have been more useful had it simply listed references with titles of papers instead of trying to describe each method individually.

Tragically, this book is a disaster and for this the publishers are entirely to blame. The volume is number six of Dekker's *Chromatographic Science Series*, of which two earlier members were Giddings' "Dynamics of Chromatography" and Snyder's "Principles of Adsorption Chromatography." Both of these books were masterpieces for which the scientific community will long be grateful and one would have expected a high standard to continue. How are the mighty fallen!

<div align="right">JOHN H. KNOX</div>

HANDBOOK OF ANALYSIS OF ORGANIC SOLVENTS. By VACLAV SEDIVEC and JAN FLEK. *Ellis Horwood Series in Analytical Chemistry.* Pp. 455. Chichester: Ellis Horwood Ltd. Distributed by John Wiley and Sons, Chichester. 1976. Price £18; $34.20.

Although organic solvents are widely used in so many different areas, this book appears to be the first which has gathered together, systematically, the available analytical methods, and which also provides all the essential physical data.

In Part I, sampling methods, the treatment of samples, classification procedures and the separation of the various constituents in mixed solvent systems are described. Methods are also provided for the determination of basic physical constants. Gas - liquid chromatographic and other separation methods are included. In Part II, full details of the properties of all of the common solvents are provided. Methods for identification and determination are detailed together with methods for the preparation of derivatives; tables of melting-points are included. Finally, there are some useful appendices that present tabulated data on the composition and boiling-points of azeotropes and the miscibility of solvents.

This is a concise and valuable compilation; it should be a very useful source book for all chemists, because of the wide applications of organic solvents in so many different processes. The author has collected together information and data that have been widely dispersed and would otherwise be difficult to obtain. There are some better methods available for the determination of certain physical constants than those described, but there is very little else to criticise in this well planned volume.

R. BELCHER

ACTUALITÉS DE CHIMIE ANALYTIQUE, ORGANIQUE, PHARMACEUTIQUE ET BROMATOLOGIQUE. 24e Série. Edited by J.-A. GAUTIER, P. MALANGEAU and F. PELLERIN. Pp. iv + 175. Paris, New York, Barcelona and Milan: Masson. 1976. Price Fr135.

This book contains five chapters, and each is considered separately below.

1. "Alcoométrie," by P. Jaulmes, S. Brun and Y. Tep. The authors review the history of alcoholometry, paying particular attention to the factors leading to the establishment of the internationally adopted alcohol tables published by the International Organisation of Legal Metrology. The authors' own contributions to the development of tables for the International Wine Office (OIV) are fully discussed and data are presented to demonstrate the small differences between these tables and those calculated by Osborne, McKelvy and Bearce, by the Japanese workers Kowasaki, Minova and Inamatsu, and the official table of the USSR. The authors describe their application of chemical and pyknometric techniques to establish and test the validity of their tables. A thorough bibliography is provided.

2. "Méthode d'Analyse des Polluants de l'Environnement Résultant de l'Incinération des Matières Plastiques," by M. Chaigneau and G. Le Moan. A broad review is presented of the increasing use of plastics in commerce and attention is drawn to the injuries that can result from the products of the combustion of these materials. Data are presented demonstrating the volumes of the principal gases produced from the complete combustion of 1 kg of the more common plastics. Experimental methods aimed at reproducing the conditions of incineration are described, as are the analytical techniques, both physical and chemical, that are employed in the identification and measurement of combustion products. Considerable emphasis is placed on the application of mass spectrometry to this field and a comprehensive bibliography is given.

3. Les Électrodes Spécifiques et Leurs Applications en Analyse Pharmaceutique, Bromatologique et Médicale (Partie 2)," by J. Mertens, H. Declereq, D. L. Massart, Y. Michotte, P. Van Den Winkel, L. Dryon and A. Henrion-Boeckstijns. The authors present a thorough literature survey of specific electrodes and their application to inorganic and organic materials. Among the inorganic cations, sodium, potassium, ammonium and calcium are considered in detail. Of the inorganic anions, fluoride ion electrodes are given special attention although the other halide and more common ions are also discussed. The second section is devoted to the application of specific electrodes to organic materials. The direct measurement of acetylcholine and of some detergents is described. Indirect methods using specific electrodes for amino-acids, urea and urease employing immobilised enzymes are discussed. The final section reviews miscellaneous applications of specific electrodes to the analysis of, for example, glucose, lactate ion and glucosidase.

4. "Méthodes Physicochimiques d'Analyse dans le Cadre de la Pharmacopée," by R.-C. Moreau. M. Moreau assures us that a pharmacopoeia sets a just and acceptable standard for each drug but leaves doubt whether this outweighs its damaging effect on analytical initiative. He considers the French Pharmacopoeia in terms of its mandatory and optional sections and discusses the merits of allowing a choice of methods for confirming purity and characteristics and the need for reference standards. The remainder of the article is devoted to an outline of the principles of the physicochemical methods employed, ranging from densitometry and polarimetry to spectrometric and chromatographic techniques.

5. "Rhéologie et Viscosimétrie: Principes Fundamenteaux," by L. Molle. M. Molle presents a comprehensive review of viscometry and rheology encompassing the ideal elastic behaviour of solids as defined by Hooke's law and the ideal behaviour of fluids displaying Newtonian flow. Between these extremes are a variety of states often found in nature. For example, there is the plastic flow exhibited by toothpastes and pomades and the phenomenon of thixotropy exhibited by certain paints and concrete. The author gives a concise account of the theory underlying these properties and reviews the various practical methods for the measurement of viscosity. A substantial bibliography is provided.

P. J. WAGSTAFFE

ANALISIS POR ACTIVACION NEUTRONICA, TEORÍA, PRÁCTICA Y APLICACIONES. By A. TRAVESI. Pp. xxxii + 727. Madrid: Junta de Energía. 1975. Price 1 500 pesetas.

During the early days of the development of neutron-activation analysis, books covering theory and application were relatively rare. However, in recent years, a number of authors have produced works that consider the technique in various levels of detail. This work by Travesi is clearly intended to treat the subject in some depth. It consists of 17 chapters, the first 12 of which describe various aspects of theory and technique and the last 5 applications. The Appendix provides information about nuclear reactions, some of which are likely to be of interest for analysis, radioisotope data and a means of calculating disintegration rates. The early chapters consider nuclear reactions, methods of neutron production, techniques for measuring neutron flux and the basic principles of neutron activation itself. Techniques of carrying out neutron activation, sample preparation and radiochemical separations are also considered separately. Considerable space is allocated to descriptions of gamma-ray spectroscopy with chapters covering theory, experimental methods and spectral interpretation; processes leading to interferences are also described. Uses are summarised in chapters on medicine, archaeology and fine art and forensic and environmental applications. The final chapter on miscellaneous applications covers uses in geochemistry, cosmochemistry and industry.

This volume is substantial, containing more than 700 pages, and includes a considerable amount of information that will be of interest to those who intend to apply neutron-activation analysis on a regular basis. The book is primarily concerned with traditional techniques of activation analysis but some mention is made of less widely used methods employing neutron generators, radioisotope sources and procedures based upon neutron capture. The book would perhaps have benefitted from expansion of the last two of these fields, reflecting the present increasing interest, but its omissions do not detract from the general usefulness of the work. T. B. PIERCE

EXPERIMENTELLE EINFÜHRUNG IN DIE POTENTIOMETRIE. By S. EBEL and W. PARZEFALL. Pp. 190. Weinheim Bergstr.: Verlag Chemie, GmbH. 1975. Price DM38.

Produced by offset litho from typewritten text, this softback is outrageously priced at DM38, and will have little appeal for the undergraduates at whom it is aimed, even if their native tongue is German. Nor are many teaching institutions likely to own the expensive and sophisticated equipment described. As an introduction to computer-aided digital autotitrimetry within a limited context it has some merit. E. BISHOP

Erratum

OCTOBER (1976) ISSUE, pp. v and 803, paper by H. Bennett and G. J. Oliver, synopsis, lines 7 and 8: *for* "A 1 + 4 mixture of metaborate and tetraborate" *read* "A 1 + 4 mixture of tetraborate and metaborate."

Microbiological Assay of Monensin in Animal Feeds and Pre-mixes

Report prepared by the Antibiotics in Animal Feedingstuffs Sub-Committee.

Keywords: Monensin assay; antibiotics; animal feeds; microbiological assay

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Spectrophotometric Determination of Iron(III) in Sulphuric Acid

Short Paper

Keywords: Iron(III) determination; sulphuric acid; spectrophotometry

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Limits of Detection of Gas-sensing Probes

Short Paper

Keywords: Gas-sensing probes; gas-sensing electrodes; limits of detection

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Modified Packing for Absorption Tubes for Carbon Dioxide Produced by Combustion on the Semi-micro or Macro scale

Short Paper

Keywords: Carbon dioxide; absorption tube; packing

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Sources of Interference in the Determination of Lactic Acid in Silage

Communication

Keywords: Lactic acid determination; silage; interferences

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Determination of Ammoniacal Nitrogen in Fertilisers by Molecular Emission Cavity Analysis

Communication

Keywords: Ammoniacal nitrogen determination; fertilisers; molecular emission cavity analysis

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Reprints of Review Papers

Reprints of the following Review Papers published in *The Analyst* since 1967 are available from the Publications Sales Officer, The Chemical Society, Blackhorse Road, Letchworth, Herts., SG6 1HN (not through Trade Agents). These reprints will be available only until June 1977, and their sale will then cease.

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"Properties and Uses of the Colorimetric Reagents 2-Nitroso-5-dimethylaminophenol and 2-Nitroso-5-diethylaminophenol for Cobalt," by Kyoji Tôei and Shoji Motomizu (July, 1976).

"Fibre Identification and Analysis of Fibre Blends," by H. M. Appleyard (August, 1976).

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CONTENTS

17 ⌒⌒ 2520