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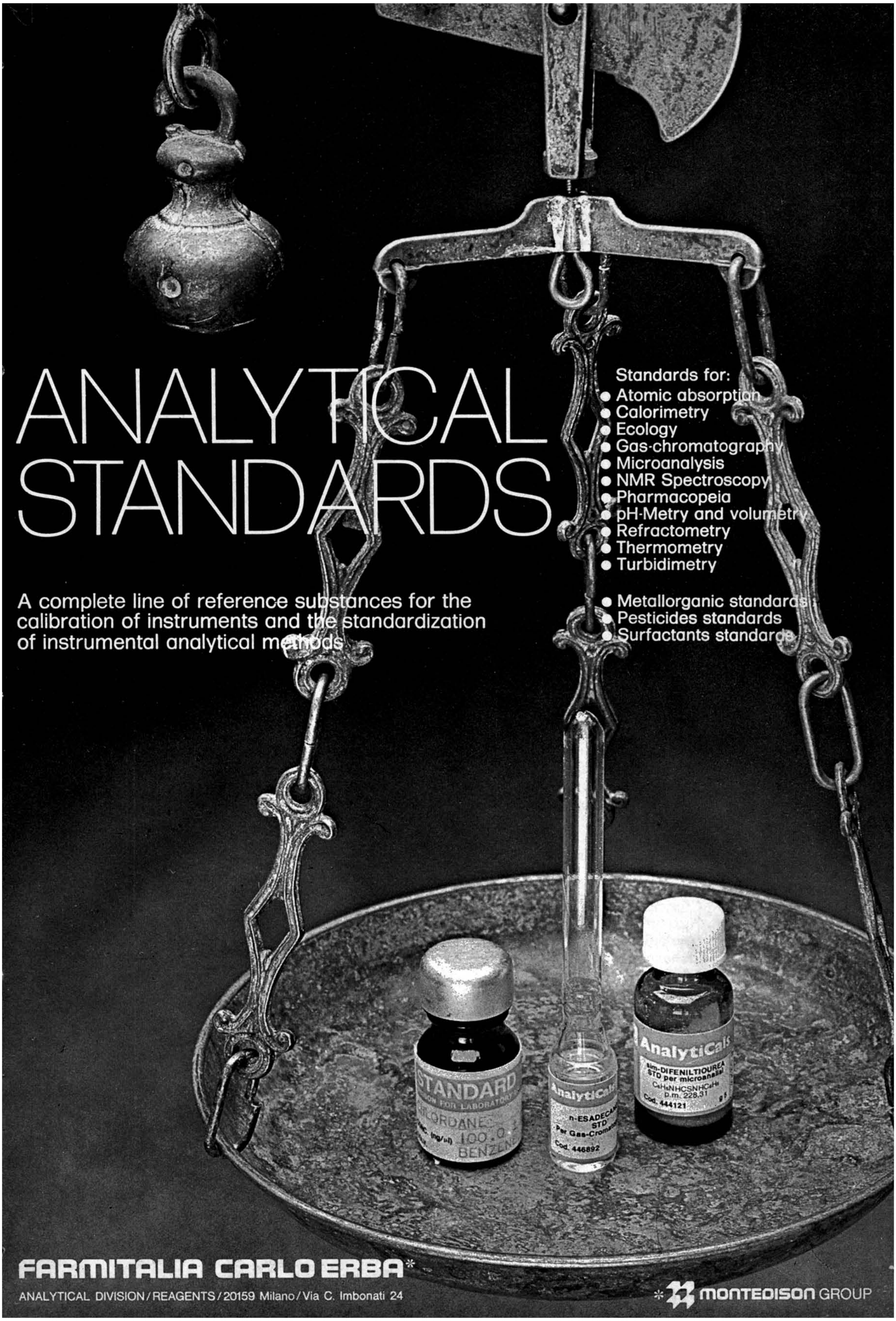
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Generation of Covalent Hydrides in Atomic-absorption Spectroscopy

A Review

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Keywords: *Review*; *atomic-absorption spectroscopy*; *covalent hydride generation*

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Analyst, 1980, **105**, 1137–1156.

Simultaneous Determination of the Noble Metals in Geological Material by Radiochemical Neutron-activation Analysis

A simple procedure is described for determining the noble metals in geological samples rich in chromium and copper. Powdered rock samples (0.1–0.3 g) are irradiated in an epithermal neutron flux, under a cadmium filter, to reduce interference from ^{51}Cr and ^{64}Cu. After digestion with a peroxide fusion, the noble metals are separated on Srafion NMRR ion-exchange resin. Activity from chromium(VI), retained on the resin, is eliminated by reduction to chromium(III) with iron(II) sulphate before separation. The gamma-ray activity is measured with a lithium-drifted germanium detector for palladium (^{109}Pd), platinum (^{199}Au), iridium (^{194}Ir) and gold (^{198}Au). The separation yield (iridium 40%, palladium 80%, gold 90%) is determined for each sample by irradiating the resin to activate a stable noble metal carrier. Multi-element noble metal standards (0.1–8 μg) are prepared from dilute solutions (100 μl) evaporated on resin (1 ml). The practical detection limits are 2.5 ng of palladium and platinum, 0.1 ng of iridium and 0.01 ng of gold. The reliability of the procedure was confirmed by analysing sulphide standards (PTM, PTC) and standard rocks (PCC-1, DTS-1). The method has been applied to the analysis of chrome-spinels.

Keywords: *Noble metal determination*; *epithermal neutron-activation analysis*; *ion-exchange separation*; *reference rocks*; *chrome-spinel*

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Analyst, 1980, **105**, 1157–1162.

Determination of Aluminium in Wood Pulp Liquors Using Graphite Furnace Atomic-absorption Spectrometry

A graphite furnace atomic-absorption spectrometric method for the determination of 0.5–100 μg ml^{-1} of aluminium in matrices containing chlorine and high concentrations of sulphur is described. The precision of the over-all procedure was 4%. Graphite tube conditions and the composition of the matrix were found to change the sensitivity for aluminium.

Keywords: *Aluminium determination*; *graphite furnace atomic-absorption spectrometry*; *sulphur interference*; *chlorine interference*; *graphite tube conditions*

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Analyst, 1980, **105**, 1163–1170.

Determination of 2-Aminobutane in Potatoes using High-performance Liquid Chromatography

Development work on the use of 2-aminobutane to control certain potato-tuber diseases necessitated the development of a convenient and sensitive analytical method for residue determination. The amine was distilled from potatoes, dansylated and determined using reversed-phase high-performance liquid chromatography with fluorescence detection. Recovery of 2-aminobutane by distillation was about 95% from standard solutions and 92% from treated potatoes. The lower limit of detection is below 0.2 μg kg^{-1}.

Keywords: *2-Aminobutane determination*; *potatoes*; *residues*; *high-performance liquid chromatography*; *fluorescence detection*

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Analyst, 1980, **105**, 1171–1175.

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Generation of Covalent Hydrides in Atomic-absorption Spectroscopy

A Review

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Keywords: *Review*; *atomic-absorption spectroscopy*; *covalent hydride generation*

Introduction

Covalent hydrides are a series of compounds whose elements are of the C, N and O groups, where the number of valency electrons is equal to, or greater than, the number of orbitals. These elements include As, Al, B, Bi, Ge, P, Pb, Se, Sb, Si, Sn, Te and Ti. Of these thirteen elements, eight have been induced to form covalent hydrides in sufficient amounts to be of practical analytical use; these are As, Bi, Ge, Pb, Se, Sb, Sn and Te.

The basic design of a hydride generation system, with subsequent atomic absorption, may conveniently be considered as four steps. First, generation of the hydride; second, collection of the hydride (if necessary); third, transfer of the hydride to the atomiser; and fourth, decomposition of the hydride to the gas-phase metal atoms within the optical axis of the atomic-absorption spectrophotometer. The measured atomic-absorption signal is directly proportional to the number of free metal atoms per unit optical axis cross-section at a given instant. In order to increase this signal it is necessary to generate the hydride quickly, or collect it and then transfer it as quickly as possible to the atomiser. This reduces dilution of the hydride by the carrier gas.

Historical

Arsenic is both extremely toxic and an indicator of precious metals, even at low concentrations. The poor sensitivity of this metal makes the application of conventional atomic absorption rather difficult. The arsenic resonance lines lie in the far ultraviolet region of the spectrum where flame absorption can produce an unfavourable signal to noise ratio (Fig. 1). With the application of the argon - hydrogen - entrained air flame to atomic-absorption spectroscopy in 1967 a much improved signal to noise ratio was obtained. This flame, usually referred to as the argon - hydrogen flame, when used with conventional hollow-cathode lamp sources, absorbs about 15% of the available light compared with 62% for the air - acetylene flame at 193.7 nm.[1]

Interferences are encountered when the argon - hydrogen flame is used to determine microgram amounts of arsenic in real samples. The argon - hydrogen flame is cooler than the air - acetylene flame, and interferences due to incomplete salt dissociation and molecular absorption are common.

In order to overcome this problem, modifications of the Gutziet method, utilising the generation of arsine, have been applied to atomic-absorption spectroscopy.

Holak[2] collected the arsine in a liquid nitrogen trap, which was then warmed, and the evolved arsine was swept into the flame with a flow of nitrogen. By removing the arsenic from the sample matrix, interferences in the flame are minimised.

Madsen[3] collected the arsine in dilute silver nitrate solution and aspirated the resulting solution directly into an argon - hydrogen flame of the type described by Kahn and Schallis.[1]

A spectrophotometric method, which involves reaction of arsine with silver diethyldithiocarbamate to form a red complex, has also been proposed for the determination of arsenic. Hundley and Underwood[4] applied this method to the determination of arsenic in a wide

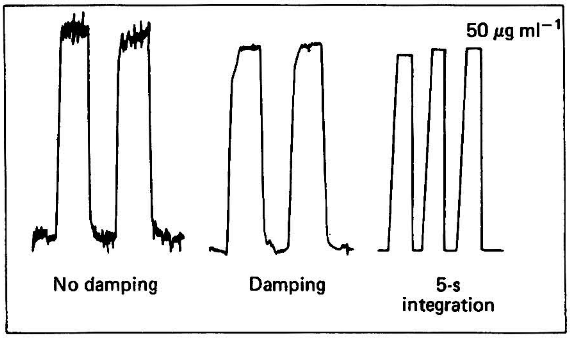

Fig. 1. Arsenic trace at 193.7 nm using the air - acetylene flame.

variety of food products. Spectrophotometric methods have the disadvantage of requiring large amounts of sample in order to obtain sufficient sensitivity.

Dalton and Malanoski[5] were the first to report the direct aspiration of arsine into a flame without the use of a collection device. This work utilised an argon - hydrogen flame, and the liberated arsine was carried to the nebuliser by the released hydrogen. A detection limit of 0.1 μg of arsenic was obtained by this method.

The sensitivity was further improved by Fernandez and Manning,[6] who collected the arsine in a balloon reservoir before introducing it into an argon - hydrogen flame. The determination of selenium as hydrogen selenide (SeH_2) was also described. A detection limit of about 0.02 μg of arsenic was obtained by this method.

This apparatus was further improved by Manning,[7] and this design became the first commercially available attachment for atomic-absorption spectrophotometers. A total reaction time of 4–5 min using tin(II) chloride - hydrochloric acid - potassium iodide - zinc is normal for this method. It was suggested by Manning that the technique might also be applied to the generation of the gaseous hydrides of antimony and bismuth. The successful generation of stibine was accomplished by Pollock and West,[8] but they found that the commonly used tin(II) chloride - hydrochloric acid - potassium iodide - zinc reaction was not suitable. They obtained good results with titanium(III) chloride - hydrochloric acid - magnesium.

The first reference to the use of a tube detector, in this instance electrically heated, as an alternative to the argon - hydrogen flame appears in the work reported by Chu *et al.*[9] in 1972. A tin(II) chloride - potassium iodide - zinc reaction in an acidic matrix was employed together with a balloon collection device. A reaction time of 10 min was allowed before the arsine was swept to the heated tube by a flow of argon, and a sensitivity of about 5 ng was obtained for arsenic. No detection limit was quoted. A further interesting aspect of this work is that the reaction time necessary to complete the reduction of the sample is about 8 min and not 4–5 min as allowed in previous reports.

Also in 1972 the use of sodium tetrahydroborate(III) to produce arsine was reported by Braman *et al.*,[10] who also reported an emission in a d.c. arc discharge method.

In 1973 the use of sodium tetrahydroborate(III) was extended to the determination of Se, Sb and Bi by Schmidt and Royer[11] and to the determination of Ge by Pollock and West.[12] Fernandez[13] expanded this range to the determination of Sn and Te. All the above methods continued to use the argon - hydrogen flame.

In 1974 Thompson and Thomerson[14] published a report on the use of sodium tetrahydroborate(III) as a reducing agent, coupled with a flame-heated silica tube as a detection device. Fig. 2 shows the sensitivity obtained for arsenic (*cf.* Fig. 1). This paper also included a report on the generation of plumbane (PbH_4) for analytical purposes.

At this stage the various combinations of reducing agents, collection devices and detection systems had been established.

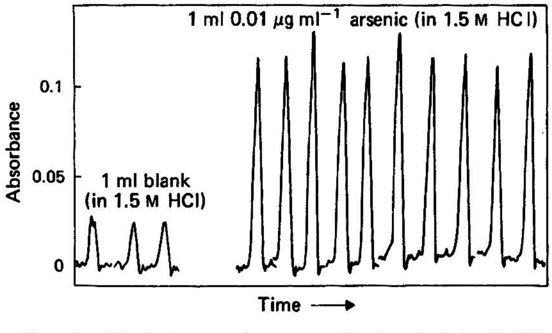

Fig. 2. Typical arsenic trace (2 ml of 1% $NaBH_4$ solution in the generator cell).

Methods of Reduction

Various reducing agents and sources of nascent hydrogen have been suggested in order to convert the element of interest into its hydride. The Marsh reaction, using zinc metal and dilute hydrochloric or sulphuric acid, was the most frequently used in the early methods.

A major drawback of this method is that it can only be used for arsenic, and the time taken for the completion of the reaction may be as long as 10 min. It is therefore necessary to store the evolved gas in some form of reservoir.

A mixture of dilute hydrochloric acid, 40% *m/V* potassium iodide solution, 40% *m/V* tin(II) chloride solution (using the dilute hydrochloric acid as a solvent) and granular zinc metal has been described.[5,6] This appears to give a faster reaction time as no collection vessel, or carrier gas, was found to be necessary. This mixture also appears to be usable for the determination of selenium.

Pollock and West[8] concluded that the above mixture was not suitable for the generation of stibine (SbH_3) from solutions containing antimony(III). However, they found that a magnesium - hydrochloric acid - titanium(III) chloride medium was entirely satisfactory. The advantage of this reduction mixture is that it can also be used for the determination of Bi and Te.

The use of sodium tetrahydroborate(III), reported by Schmidt and Royer,[11] is a landmark in the development of the technique. It has been applied successfully to the generation of the hydrides of As, Bi, Ge, Sb, Se, Sn and Te,[13] and subsequently Pb.[14] Collection times were reduced to 30 s for Bi and Te and 2–3 min for As, Ge, Sb, Se and Sn.[13] However, the system described by Thompson and Thomerson[14] requires no collection vessel, and complete reduction of most metals was obtained within 30 s.

The sodium tetrahydroborate(III) method offers several advantages over both the zinc - tin(II) chloride and magnesium - titanium(III) chloride procedures. Although sodium tetrahydroborate(III) was initially available only in powder form, the use of 0.25-g pellets soon became established. These are sufficiently uniform to eliminate the need for weighing, are easy to handle and are relatively inexpensive.

Although some problems were experienced with reagent purity in early determinations,[14,15] the quality of the sodium tetrahydroborate(III) supplied by the major companies in recent years has improved considerably.

The hydride generator described by Fernandez[13] requires a pellet of sodium tetrahydroborate(III) to be used for each measurement, whereas the system described by Thompson and Thomerson[14] requires one or two 0.25-g pellets to be dissolved in 25 ml of water and 1- or 2-ml aliquots of this solution are used. The latter system is obviously more economical with regard to consumption of reagent.

Several workers[16–18] have reported that sodium tetrahydroborate(III) solution is relatively unstable, and periods of several hours to 1 d have been quoted as the useful life. However, Knechtel and Fraser[19] reported the use of a 2% *m/V* solution of sodium tetrahydroborate(III) containing one pellet of potassium hydroxide per 100 ml of solution. The solution was filtered through a 0.45-μm membrane filter, and it was reported that this solution remained usable for 3 weeks.

A different reducing mixture, used by Goulden and Brooksbank,[20] consists of a mixture of tin(II) chloride, potassium iodide and aluminium powder. A heated packed stripping column was used to strip the selenium hydride generated from the reduced specimen so that atoms, and not molecules, would enter the optical path.

A further method, but one which has not gained wide usage, is the zinc column to which an acidic solution of the analyte is added.[14,21] This method is applicable only to the generation of arsine and stibine.

Design of Reaction Vessels/Collection of the Hydride

The speed of reaction of many of the reducing agents used is such that it can take several minutes for the reaction to reach completion. As peak-height measurements are normally made it is obviously advantageous to collect the liberated hydride and then sweep it to the detection system in the shortest possible time. Several methods of collection have been proposed and are outlined below. It should be noted that when sodium tetrahydroborate(III) is used as a reducing agent the need to collect the liberated hydride is often minimised.

Liquid Nitrogen Trap

This method was first proposed by Holak[2] and consists of an arsine generator connected to a U-tube via a calcium chloride drying tube. The U-tube was packed with glass beads and immersed in a Dewar flask containing liquid nitrogen. When all of the arsenic had been converted into arsine the generator outlet valve was closed. The rubber connecting hoses on each arm of the U-tube were sealed with pinch-clips and the U-tube was then removed from the liquid nitrogen and allowed to come to room temperature. Nitrogen at a flow-rate of about 50 ml min^{-1} was connected to one arm of the U-tube and the other arm was connected to the nebuliser capillary of an atomic-absorption spectrophotometer. The pinch-clamps were removed and the arsine was allowed to flow into the mixing chamber.

Several workers[22–24] have reported the use of a liquid nitrogen trap, but it is a specialised technique and seems to be slow and complex for routine use. However, Braman and Foreback[25] have shown that it is a useful method for the collection, and subsequent selective volatilisation, of methylated hydrides of arsenic generated from environmental samples.

Silver Nitrate Solution

This method was proposed by Madsen[3] and consists of an arsine generator constructed using a 125-ml conical flask, 6-mm glass tubing and a 10-ml graduated measuring cylinder. The end of the delivery tube was drawn to a fine tip and was arranged so that the tip of the delivery tube was placed against the bottom of the graduated cylinder, which contained 5 ml of 0.01 M silver nitrate solution. The evolution of the hydride was allowed to continue for 15 min and the delivery tube was then removed from the absorbing solution. This solution was aspirated into the argon - hydrogen flame of an atomic-absorption spectrophotometer.

The method is time consuming and later methods have found more widespread use.

Balloon Method

Probably the most popular collection device is the balloon attached to the side of the reaction vessel. This form of collection device was first described by Fernandez and Manning.[6]

The apparatus was modified by Manning,[7] who incorporated a dosing stop-cock so that zinc could be introduced into a closed system (Fig. 3).

A four-way valve permitted the system to be flushed with an inert gas, and the balloon was attached to a hose nipple, which it was not necessary to remove and replace for each sample. This was an improvement over the previous device. The system was connected to the burner in the same way as the previously described apparatus.

Various modifications of the balloon - reaction flask system have been proposed[9,21,26] in order to simplify the system. However, few, if any, commercially available systems continue to use a balloon as a collection device; the use of sodium tetrahydroborate(III) and silica detection tubes has almost eliminated the need to collect large amounts of hydride. A further drawback of balloons is the frequency of replacement; Chu *et al.*[9] mention 15–20 and Manning[7] 50 determinations per balloon.

Other Collection Devices

As an alternative to balloons several workers have advocated rigid or semi-rigid containers. Aggett and Aspell[27] used a 250-ml glass bottle and Pollock and West[12] employed a 450-ml plastic jar.

Direct Introduction

It is not always necessary to collect the liberated hydride, and most commercially available systems now allow direct introduction of the hydride to the atomiser. Several workers have reported systems that do not require collection of the hydride.[5,10,14,16,28–30]

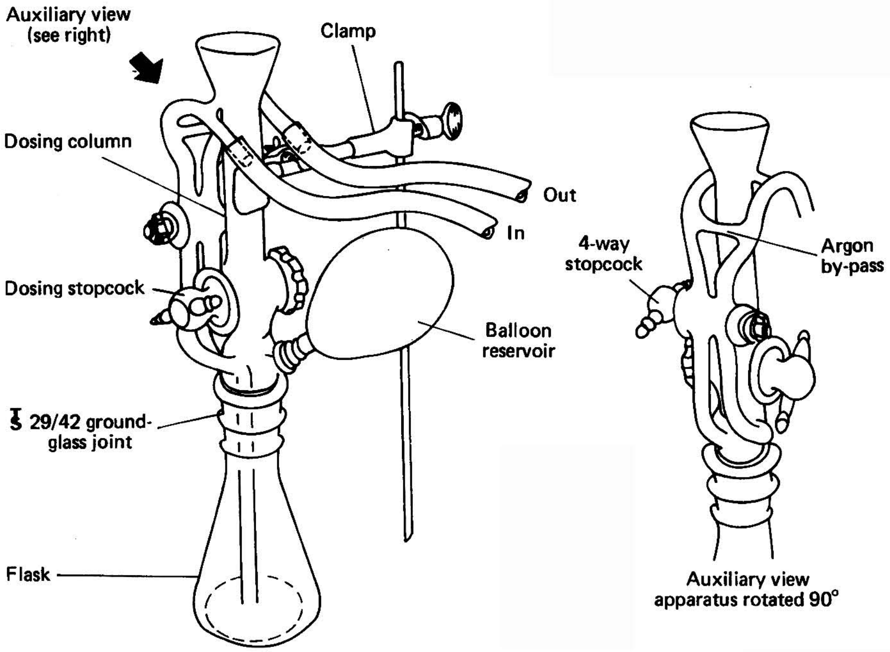

Fig. 3. System devised by Fernandez and Manning.

Automated Systems

Several workers have reported the design and application of automated and semi-automated systems.[31–37] The systems reported to date fall into two categories; the first uses a peristaltic pump and the second a pressurised reagent pumping system. The peristaltic pump system is the more automated of the two in that it requires less manipulation by the operator. However, the pressurised reagent pumping system appears to allow greater control over the reaction conditions.

A typical peristaltic system[33] employs a multi-channel pump to transfer sample and reagent, in suitable proportions [*e.g.*, 7.5 ml of hydrochloric acid and 7.5 ml of sodium tetrahydroborate(III) per 50 ml of sample]. The hydrochloric acid is mixed with the sample via a mid-feed coil. This acidified stream is allowed to react with a stream of sodium tetrahydroborate(III) solution in an expanded T-connector. The mixture of gaseous hydride and liquid then flows to a gas separator, where the gaseous portion is purged from the liquid phase with argon. This mixture of gaseous hydride and argon is introduced into the burner chamber via the supplementary oxidant inlet. An argon - hydrogen flame is employed.

The semi-automated system described by Fiorino *et al.*[38] consists of a single-stage gas regulator with a single nitrogen inlet and two outlets. One outlet is connected to a pressurised reagent bottle containing sodium tetrahydroborate(III) solution. The other outlet is connected to a pressurised reagent bottle containing distilled water. The outlet from each bottle passes through separate solenoid valves, which are controlled by a single four-cam motor-driven timer (90 s). The reagents are connected to PTFE metering valves contained within the reaction cell head.

Prior to the actual determination the duration and flow-rates of the sodium tetrahydroborate(III) solution and water wash, and the duration of the rest period, are adjusted to ensure complete reaction of the analyte and to maximise the absorption signal.

An aliquot of the sample is transferred to the 8-in test-tube reaction cell and diluted to 20 ml with acidic diluent. When necessary sodium iodide solution is added (0.5 ml of 10% *m/V* solution) to reduce As and Sb to the trivalent state. The test-tube is then connected to the cell head and the timer is actuated. Gaseous reaction products from the generator are delivered to the flame via a glass adaptor, which replaces the nebuliser.

Methods of Atomisation

Flames and Tubes

Air - acetylene flame

Holak[2] used a conventional air - acetylene flame supported on a three-slot Boling burner. Although the air - acetylene flame was used by many workers in the early stage of development of the technique it was soon superseded by the argon - hydrogen - entrained air flame (usually called the argon - hydrogen flame).

Argon - hydrogen flame

The use of this type of flame for the determination of arsenic in aqueous solution was first described by Kahn and Schallis.[1] They discovered that it absorbed about 15% of the light output from the hollow-cathode lamp, at 193.7 nm, compared with 62% absorbed by the air - acetylene flame. This resulted in a much better signal to noise ratio. The cooler flame also gives much better sensitivity, but it is more prone to interferences.

Dalton and Malanoski[5] introduced arsine directly into the argon - hydrogen flame, and Fernandez and Manning[6] collected arsine in a balloon before releasing the arsine into an argon - hydrogen flame.

This type of flame has remained one of the most popular detection systems, but there is a trend away from this flame and towards heated silica tubes.

Silica tubes

Electrically heated tubes. Chu *et al.*[9] first reported the use of an electrically heated tube as an alternative to a flame. The liberated hydride was swept into the tube by a stream of argon carrier gas and, as no flame was employed, the background absorption was reduced. The longer residence time of the arsenic atoms in the tube, compared with the flame, produced an improvement in sensitivity.

Vijan and Wood[28] have described the use of an electrically heated glass cell, which was used in conjunction with an automated system. Several workers[34,37,39] have published papers based on the use of this type of detector, and Thompson and Thoresby[40] reported its use in the determination of arsenic in soil and plant materials.

A novel adaptation of this form of atomiser was described by Robinson and co-workers.[41,42] They used spectrographically pure rods 10–20 mm in length heated with a 5000-W radiofrequency generator and a 10-turn copper coil. The quartz tube was heated by 700-W Nichrome resistance heaters.

One of the advantages of this form of atomiser is the ability to control its temperature, and achieve an optimum temperature for each element.

Flame-heated Tubes

Internal flame. A novel hydride generation atomic-absorption technique for the determination of selenium has been described by Siemer and Hagemann.[16] Sodium tetrahydroborate(III) was used as a reductant and hydrogen was used to carry the released hydride to the silica tube. A small amount of oxygen was added to the hydrogen to support combustion and atomisation of the hydride.

External flame. The first reported use of a flame-heated silica tube was by Thompson and Thomerson[14] in 1974. The liberated hydride was carried directly to a 17-cm silica tube mounted above an air - acetylene flame. The advantages claimed for the technique were that no collection vessel was required, flame background was virtually eliminated and better sensitivity was achieved than with the argon - hydrogen flame. One sample can be analysed every 40 s when this apparatus is used. The paper describes an apparatus that is still commercially available.

Similar systems have been described by various workers.[29,30,42,43]

Fig. 4 depicts the silica atomising tube used by Thompson and Thomerson.[14] The generated hydride, contained in a stream of nitrogen, is introduced through the side-arm (A) in the middle of the silica tube. Provision is made for cooling the outside of this side-arm via annulus B. An auxiliary nitrogen stream is injected into the transverse jets C and C′, which are designed to prevent the liberated hydrogen from igniting on the ends of the tube, but should instead burn on the ends of the jets D and D′. A schematic diagram of the apparatus used in this method[14] is shown in Fig. 5.

Graphite tube furnaces. McDaniel *et al.*[22] introduced the liberated hydride into a proprietary graphite tube furnace. This very comprehensive paper compares various sample pre-concentration techniques, including hydride generation, for concentrating selenium for its determination by heated-graphite atomiser. It is interesting that the authors conclude that published procedures (at least up to that date) may liberate as little as 10% of the total inorganic selenium from the solution.

Other workers[37,44] have reported the results of comparison studies between hydride generation techniques and heated graphite furnace determinations.

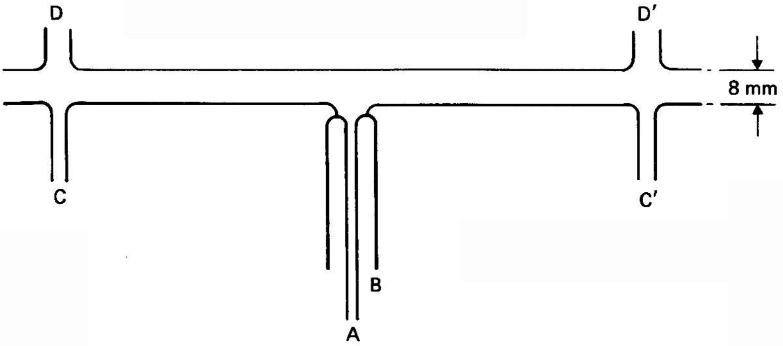

Fig. 4. Typical design of flame-heated silica tube.

Various

Although not strictly within the scope of this review, several non-atomic-absorption detectors are worth mentioning.

Molecular emission cavity analysis (MECA)

Belcher *et al.*[45] have described this technique, and subsequently how to eliminate interferences,[46] for the determination of arsenic and antimony.

In MECA the sample is placed within a small cavity at the end of a rod, which is then positioned in a hydrogen - nitrogen flame so that the flame gases flow almost vertically past the entrance of the cavity. The sample in the cavity is vaporised and emits band emissions characteristic of the elements in the sample.

Arsenic and antimony are reduced by sodium tetrahydroborate(III) to arsine and stibine, respectively, and a stream of nitrogen is used to sweep the gases into the MECA cavity, which is placed in a hydrogen - nitrogen diffusion flame.

Atomic fluorescence

Tsuju and Kuga[47] described a non-dispersive system, employing a solar-blind photomultiplier, for the atomic-fluorescence determination of arsenic. Liberated arsine was carried to an argon - hydrogen flame by a stream of argon. The same workers subsequently reported a modification of this apparatus[48] for the determination of arsenic and antimony. They employed a modification of the reaction cell described by Thompson and Thomerson,[14] and used sodium tetrahydroborate(III) to liberate the hydrides. An argon - hydrogen flame was employed, but instead of storing the liberated hydrides they were carried directly to the flame by a stream of argon.

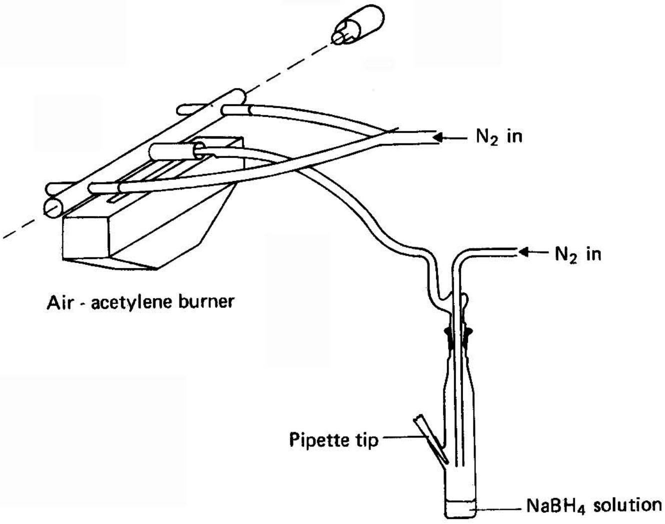

Fig. 5. Schematic diagram of apparatus used in flame-heated silica tube method.

Kobayashi *et al.*[49] reported the use of a non-dispersive system for the atomic-fluorescence determination of bismuth. Sodium tetrahydroborate(III) was used to generate the gaseous hydride of bismuth, which was then carried to an argon - hydrogen flame by a stream of argon. The authors reported a detection limit of 5 pg ml^{-1} or 0.1 ng of bismuth, but the reagent blank in a 20-ml sample was approximately 2 ng of bismuth. Analytical working graphs were drawn using both peak-height and peak-area measurements. The calibrations were found to be linear over a range of about four orders of magnitude from the detection limit. The presence of silver, gold, nickel, palladium, platinum, selenium and tellurium in a 1000-fold ratio to the bismuth caused pronounced depression of the signal. Mercury and tin slightly enhanced the atomic-fluorescence signal.

Nakahara *et al.*[50] have also described a non-dispersive system for the determination of antimony, with particular reference to waste waters and lead. The system is identical with that described by Kobayashi *et al.*[49] An improvement in sensitivity of at least one order of magnitude is claimed for non-dispersive atomic fluorescence compared with that of a dispersive system at the 217.6-, 231.1- and 259.8-nm antimony lines. The report includes a comprehensive comparative study of the zinc and sodium tetrahydroborate(III) reduction systems, and of the interference effects of acids and diverse elements on the fluorescence signal of antimony. As a follow-up to this report, the same workers[51] described the application of the same apparatus to the determination of antimony in phosphoric acid.

Thompson[52] has advocated a dispersive system whereby the hydrides of antimony, arsenic, selenium and tellurium were swept by a stream of argon into an argon - hydrogen flame supported on a 10-mm i.d. Pyrex tube. The top of this tube was mounted 2.5 cm below the bottom of a microwave cavity window. The microwave cavity was positioned so that the axis of the microwave lamp was 5 cm from the axis of the flame, which was positioned on the optical axis. The hydride generation system described by Thompson and Thomerson[14] was used to produce the hydrides.

Plasmas

The idea of coupling a hydride generator to a plasma arc was first proposed by Lichte and Skogerboe.[53] This technique makes it possible to determine simultaneously several elements in a single solution.

Thompson *et al.*[54,55] subsequently published a comprehensive study which showed that many of the operating parameters were critical to set up, and many interference effects were encountered. They generated the hydrides of arsenic, antimony, bismuth, selenium and tellurium by means of sodium tetrahydroborate(III) and detected them simultaneously in an inductively coupled plasma by measuring the atomic line emission intensities. Many of the more severe interferences were overcome by separating the matrix from the elements to be determined, the matrix being precipitated with lanthanum hydroxide. A comprehensive study of the interference effects of a large number of elements was tabulated, as were the percentage recoveries after separation with lanthanum hydroxide. This technique was then applied to the analysis of geological samples.

Other papers have described methods using plasma sources for the analysis of waste and sea waters,[23] whole blood, flour and orchard leaves.[56]

D.c. arc discharge

Braman *et al.*[10] reported a system whereby arsenic and antimony compounds were converted into arsine and stibine, respectively, in 1% sodium tetrahydroborate(III) solution. Arsine and stibine are swept out of the solution using helium carrier gas, passed through a calcium sulphate drying tube, then through a d.c. discharge detector. Modifications of this system have been reported.[24,57]

Light Sources

Perhaps the most popular light source is the hollow-cathode lamp, and certainly it is commonly used where the light beam is required to pass through a silica tube rather than a flame. Because of the relatively low output of hollow-cathode lamps in the ultraviolet region, they tend to give better signal to noise ratios with single-beam instruments with "straight through" optics.

Fernandez[13] reported the determination of arsenic and selenium using electrodeless discharge lamps (EDLs) as alternatives to hollow-cathode sources, and obtained better detection limits and sensitivities. The system used was sodium tetrahydroborate(III) - acid with balloon collection and an argon - hydrogen flame. A deuterium EDL was used as a background corrector.

McDaniel *et al.*[22] reported the use of a special design of demountable hollow-cathode lamp, and claimed an energy output ten times that of conventional hollow-cathode lamps. Robinson *et al.*[42] used a commercially available demountable hollow-cathode lamp.

Obviously the plasma and MECA systems require no light source; the fluorescence techniques use EDLs but not as atomic-absorption sources.

Interferences

The interferences associated with this technique are many and various and may be conveniently broken down into five sections.

Background Absorption

This is a problem that occurs more often when a collection device is used in conjunction with the argon - hydrogen flame. When the collected hydride is released to the flame, the flame transparency decreases, and therefore a non-specific absorption signal is obtained. It is necessary to subtract this signal from the total signal, by either continuous or sequential background correction. Fernandez and Manning[6] first reported the use of a deuterium background correction system, described by Kahn,[58] applied to this technique. The reduction in light throughput caused by automatic background correction systems has led to the common use of electrodeless discharge lamps with this type of system.

Thompson and Thomerson[14] reported that their system was free from this type of interference unless liberated hydrogen was allowed to ignite in the optical path of the spectrophotometer.

The increasing use of tube devices and the specificity of the method have reduced the need for background correction systems.

Valency

Several workers[6,9,25] have reported that arsenic must be present in the trivalent form for the evolution of arsenic, whereas others[10,15,27] reported that arsenic and antimony may be present in the trivalent or pentavalent form. Thompson and Thomerson[14] reported that by increasing the borohydride concentration from 1 to 4% *m*/*V* the arsenic(V) signal was 90% of that obtained for arsenic(III). However, they found that solutions of selenium(VI) and tellurium(VI) gave a negligible response compared with equal amounts of selenium(IV) and tellurium(IV). The selenium(VI) and tellurium(VI) solutions were simmered with an equal volume of aqua regia (3 + 1 *V*/*V* hydrochloric acid - nitric acid) for 15 min, allowed to cool and then diluted to twice the volume of sample originally taken. It was then possible to add 1 ml of the resulting solution directly to the generator cell containing 2 ml of 2% *m*/*V* sodium tetrahydroborate(III) solution. Under these conditions tellurium(VI) was reduced quantitatively to the tellurium(IV) state, but less than 50% of the selenium(VI) was reduced. For solid samples they recommend dissolution in aqua regia followed by suitable dilution with distilled water. This technique should ensure that the resulting solution contains arsenic(V), selenium(IV) and tellurium(IV). It was assumed that all dilute tin solutions (concentrations of less than 0.1 μg ml^{-1}) would be in the tin(IV) oxidation state.

Fernandez and Manning[6] state that during wet digestion of samples the arsenic must be maintained in the quinquevalent form at all times to avoid losses. A method is given.

Aggett and Aspell[27] have produced a method that allows the selective determination of arsenic(III) and arsenic(V) by carefully adjusting the pH of the solution before addition of sodium tetrahydroborate(III). A similar method has been described by Nakashima.[59]

Acid Concentration

The relationship between hydrochloric acid concentration [using sodium tetrahydroborate(III) as reducing agent] and sensitivity was studied by Fernandez.[13] He reported that signal size, with increasing acid concentration, remained almost constant for As, Bi, Sb and Te. The optimum acid strength for Ge is 1–3 M, for Sn 0.2 M and for Se 6–7 M.

Thompson and Thomerson[14] reported similar results except that a slight increase in signal size for tellurium was noted over the range 1–4 M. For lead the sodium tetrahydroborate(III) and acid concentrations were critical, and the optimum concentration was found to be 0.2 M. Miyazaki *et al.*[23] confirmed the data for arsenic and selenium.

By maintaining the solution at pH 4–5, Aggett and Aspell[27] reported that it was possible to determine arsenic(III) and arsenic(V) selectively. Total arsenic was determined by increasing the acidity of the solution to 5 M hydrochloric acid. This tends to confirm the earlier work of Knudson and Christian.[15,60]

Organic Binding

Fernandez and Manning[6] reported that if the sample to be analysed contained organically bound arsenic, prior oxidation is necessary and a method reported by Howitz[61] is cited. Braman and Foreback[25] reported that methylarsenic acid, $CH_3AsO(OH)_2$, and dimethylarsenic acid, $(CH_3)_2AsO(OH)$, are reduced to methylarsine, CH_3AsH_2, and dimethylarsine, $(CH_3)_2AsH$, respectively, by sodium tetrahydroborate(III) at pH 1–2. The liberated hydrides were collected in a U-tube, which was cooled by liquid nitrogen. After the liquid nitrogen had been removed, the cold trap was warmed gently and the arsines were volatilised from the trap in order of their boiling-points: arsine (−55 °C), methylarsine (2 °C) and dimethylarsine (55 °C).

Improvements to this technique have been published subsequently.[24,57] The possibility of organic binding within the sample should always be borne in mind when environmental and biological samples are to be analysed, and the reader is referred to the section Applications.

Inter-element Effects

Perhaps the most important and widespread difficulty occurs with inter-element effects, which suppress, or enhance, the true signal. Braman *et al.*[10] mention that copper and silver interfere in the generation of arsine and stibine when these hydrides are generated from alkaline solution using sodium tetrahydroborate(III). They also state that iron interferes with antimony but not arsenic, and that aluminium, cadmium, chromium, mercury, manganese, nickel, lead and zinc do not interfere with either antimony or arsenic. Dalton and Malanoski[5] determined arsenic using a zinc - hydrochloric acid reduction after prior treatment with tin(II) chloride - potassium iodide. They reported interference by nitric acid and antimony. Landsford *et al.*[62] found that mercury, arsenic and nitric acid interfered in the determination of selenium. They used a zinc - hydrochloric acid reduction. Roulet *et al.*[63] reported that arsine and stibine were decomposed by gold complexes.

A major contribution to the documentation of interferences has been made by Smith,[64] who undertook a general study of the effects of 48 elements on the determination of arsenic, bismuth, germanium, antimony, selenium, tin and tellurium. This work was carried out using sodium tetrahydroborate(III) and an argon - hydrogen flame. Certain trends in the interference effects were observed. For example, there was no interference on the six metals studied from the alkali metals, alkaline earths, boron, aluminium, gallium, titanium, zirconium, hafnium, mercury, lanthanum, manganese, vanadium and yttrium. However, there was always some interference on the six metals from copper, silver, gold, platinum, rhodium, ruthenium, nickel and cobalt. It was also found that nearly all of the volatile hydrides formed from the elements interfered with all the other volatile hydrides.

Maruta and Sudoh[65] used various reducing agents for the generation of arsine, and studied the interferences of various anions and cations.

Bédard and Kerbyson[66] reported the determination of bismuth in copper by precipitation of the bismuth with lanthanum hydroxide and subsequent conversion of the bismuth into its hydride with sodium tetrahydroborate(III). The same authors[67] have reported a separation technique for As, Se, Sn and Te in the presence of copper.

Kirkbright and Taddia[68] have described a novel method of masking the interference of large amounts of Cu, Ni, Pt and Pd on the determination of arsenic in the argon - hydrogen flame. They used thiosemicarbazide and 1,10-phenanthroline as masking agents, and effectively eliminated the strong suppression of the arsenic signal caused by a 1000-fold amount of nickel and 100-fold amounts of platinum and palladium. The effect of hydrochloric acid concentrations between 1 and 4.5 M was also studied.

Pierce and Brown[37,69] undertook a study to compare the interfering effects of several anions, cations and acids on arsenic and selenium. Three sample preparation - sample atomisation techniques were employed: manual hydride generation with argon - hydrogen flame; automated hydride generation with heated quartz tube; and graphite furnace atomisation. The study showed significant differences in interfering effects between the three techniques.

The papers by Smith[64] and Pierce and Brown[37,69] are the most useful reference sources of interferences for workers wishing to obtain background information before embarking on a new analysis.

Detector Temperature

Chu *et al.*[9] have shown that the temperature of the detector has a significant effect on the size of the signal produced by arsenic. The optimum temperature of their electrically heated tube appears to be in excess of 700 °C. It is reasonable to assume that the detector temperature will have an effect on at least some of the other hydride-forming elements. However, it is obviously not possible to control the temperature of flames and flame-heated tubes over a wide range, and the innate temperature of these devices must be accepted. Nevertheless, it is important that they are allowed to reach a constant temperature before introducing the sample, and an optimum fuel to oxidant gas ratio may be found by experiment.

The conclusion to be drawn from the above is that the generation of covalent hydrides, with subsequent determination by atomic-absorption spectroscopy, is subject to many interferences. These interferences may depend upon the method of reduction and the type of detector employed (*e.g.*, flame or tube). No determination should be carried out without checking that the sample under analysis does not contain a potential interferent and, if it does, that interference must be determined and allowed for (*e.g.*, by the method of standard additions).

Detection Limits and Sensitivities

Typical detection limits and sensitivities for the different methods are given in Tables I–IV.

TABLE I

TYPICAL DETECTION LIMITS FOR DIFFERENT METHODS

Values are given in micrograms

Element	Method*					
	A	B	C	D	E	F
As	0.0012	0.01	0.003	0.0008	0.0001	0.002
Bi	0.0032	0.005	0.008	0.0002	—	0.002
Ge	—	0.2	—	0.5	—	—
Pb	—	—	—	0.1	—	—
Sb	0.0041	0.005	—	0.0005	0.0001	0.005
Se	0.0017	0.005	0.003	0.0018	0.00006	0.002
Sn	—	0.004	—	0.0005	—	—
Te	0.0044	0.005	0.015	0.0015	0.00008	—

* See Table II.

TABLE II

KEY TO TABLE I

Column	Reducing agent	Collection vessel	Detector	Light source*	Reference
A	$TiCl_3$ - Mg	Balloon	Ar - H_2 flame	HCL	12
B	$NaBH_4$	Balloon	Ar - H_2 flame	HCL	13
C	$NaBH_4$	Balloon	Ar - H_2 flame	EDL	13
D	$NaBH_4$	None	Flame-heated silica tube	HCL	14
E†	$NaBH_4$	None	Ar - H_2 flame	EDL	52
F	$NaBH_4$	None	Electrically heated silica tube	EDL	Manufacturer's literature

* HCL = hollow-cathode lamp; EDL = electrodeless discharge lamp.
† Atomic-fluorescence method.

Applications

Waters and Effluents

As usual in atomic-absorption spectroscopy the analysis of waters and effluents is one of the most straightforward applications because the sample is already in a liquid form and matrix interferences are not usually severe.

Schmidt and Royer[11] used the sodium tetrahydroborate(III) reduction method on all types of water, from drinking water to heavily polluted water, including raw sewage, to determine arsenic and selenium. Analyses were compared of spiked samples (i) after digestion with sulphuric acid and nitric acid and (ii) untreated. The untreated samples gave a slightly larger response for both arsenic and selenium, and a blank for the arsenic of one third of the value for the digested sample. The blanks in all determinations appear to be very large (when compared with more recent methods) and no attempt was made to explain or to rectify this. The usual cause of high blanks is impurities in the sodium tetrahydroborate(III) and this has been found to vary between chemical manufacturers.

Shaikh and Tallman[70] found that a large portion of the arsenic in potable waters was organically bound because results for samples digested in sulphuric and nitric acids were higher than for untreated samples. They used a 50-ml sample volume and sodium tetrahydroborate(III) to reduce the arsenic to arsine, which was then trapped in a small volume of a chloroform - ephedrine solution of silver diethyldithiocarbamate. The arsenic content was then determined by graphite furnace atomic-absorption spectroscopy.

TABLE III

TYPICAL SENSITIVITIES FOR DIFFERENT METHODS

Values are given in micrograms

	Method*				
Element	A	B	C	D	E
As	0.006	0.01	0.005	0.0005	0.005
Bi	0.015	0.008	—	0.00004	—
Ge	—	0.27	—	1.0	—
Pb	—	—	—	0.08	—
Sb	0.02	0.01	—	0.0006	—
Se	0.008	0.011	0.009	0.002	0.0015
Sn	—	0.007	—	0.0004	—
Te	0.021	0.014	—	0.002	—

* See Table IV.

TABLE IV

KEY TO TABLE III

Column	Reducing* agent	Collection vessel	Detector	Light source†	Reference
A	$TiCl_3$ - Mg	Balloon	Ar - H_2 flame	HCL	12
B	$NaBH_4$	Balloon	Ar - H_2 flame	HCL	13
C	$NaBH_4$	Balloon	Ar - H_2 flame	EDL	13
D	$NaBH_4$	None	Flame-heated silica tube	HCL	14
E‡	$NaBH_4$	None	Electrically heated silica tube	HCL	38

* Acid must be added in all instances.
† HCL = hollow-cathode lamp; EDL = electrodeless discharge lamp.
‡ Automated system.

An automated system has been described[20] for the simultaneous determination of arsenic and selenium, based on reduction of the sample with tin(II) chloride, potassium iodide and aluminium. The hydrides were decomposed in an electrically heated silica tube. Spiked samples gave recoveries of 98–101% for levels of arsenic between 2 and 10 μg l^{-1} and levels of selenium between 0.5 and 5.0 μg l^{-1}.

This method was found to be unsuccessful by Pierce *et al.*,[34] who replaced the aluminium reduction method with sodium tetrahydroborate(III).

The determination of selenium in natural waters using a tin(II) chloride reduction system was subject to severe interference from arsenic and mercury, which were overcome only by using a tedious digestion process.[62] Most methods now favour the sodium tetrahydroborate(III) reduction process, which suffers from fewer interferences. Recent methods[71–73] have produced good results, mainly due to careful study of the possible interference effects and calibration by the method of standard additions.

The determination of selenium(IV) in sea water was found to be straightforward by Thompson[52] when using a fluorescence detection method. Samples were acidified with hydrochloric acid before reduction with sodium tetrahydroborate(III). A negligible "background" signal was reported when checked at the 216.5 -nm selenium non-resonance line and the concentration was reported as less than 0.0001 μg ml^{-1}.

Metallurgical

Probably the most severe interferences encountered for any application in hydride generation occur with metallurgical samples. For example, the interference of copper on selenium is very severe, almost completely suppressing the selenium absorption signal unless the copper is first removed.

The determination of As, Bi, Se, Sn and Te in copper alloys has been achieved after precipitation of the bismuth with lanthanum hydroxide.[66,67] A 10% m/V solution of the sample, dissolved in nitric acid, is treated with lanthanum nitrate and ammonia solution, filtered and re-dissolved in nitric acid. The hydrides are then generated in the usual way. In this way the serious interference from copper is removed, and results for bismuth obtained by this method agree well with those from spectrographic methods.

A less severe interference is caused by nickel on the absorption of bismuth and arsenic, where a 50% reduction in sensitivity occurs with a 1% m/V sample matrix. Nevertheless, the sensitivity for bismuth and arsenic is still sufficient to enable them to be determined by the method of standard additions in some alloys.[74] However, the addition of EDTA[75] to the sample solution completely overcomes the matrix interference for the determination of bismuth in nickel alloys at low concentrations. The alloy was dissolved in hydrochloric and nitric acids, and an addition of 0.27 M EDTA solution was made. The EDTA solution had previously been adjusted to pH 9 with 30% m/V sodium hydroxide solution to prevent loss of hydrogen when the EDTA solution was mixed with the sodium tetrahydroborate(III) reagent.

There is negligible interference by iron or lead (using a 1% m/V matrix) on the absorption of arsenic, selenium and tin. Therefore, the determination of these metals in iron and mild steels can be carried out after dissolving the sample in a mixture of hydrochloric and nitric acids. Calibration is carried out using acidified aqueous standards of the metals.[76] Table V shows some results for arsenic in steels using this method.

The determination of arsenic, selenium and tin in a complex lead alloy is more difficult because of the problems associated with maintaining a stable solution of lead or tin. In this instance a method based on the use of fluoboric acid and hydrogen peroxide is the most suitable.[77]

A thorough evaluation of the interference effects of most of the elements present in steels on the absorption of antimony, arsenic, bismuth, selenium, tellurium, tin and lead showed that many interferences occurred. However, by using a standard additions method for calibration good results could be obtained for most of the elements in a range of steels.[78] Of particular interest was the ability to make use of the plumbane generated after reduction with sodium tetrahydroborate(III). Plumbane had previously been detected using this technique[14] but the sensitivity was insufficient to be of any practical value. The addition of potassium dichromate in a tartaric acid medium gives a useful enhancement of the lead absorption signal. This allowed lead in seven steels to be determined, and the reported values showed very good agreement with certified values.

TABLE V

DETERMINATION OF ARSENIC IN STEELS BY HYDRIDE GENERATION AND ATOMIC-ABSORPTION SPECTROSCOPY

BCS No.	Result, %	Certified value, %	Range, %
260/4	0.010, 0.009	0.009	0.008–0.011
149/2	0.0005, 0.0006	<0.001	—
324	0.080, 0.085	0.084	0.079–0.085
321	0.003, 0.003	0.003	0.002–0.003
218/3	0.038, 0.035	0.0035	0.032–0.038

Arsenic and antimony can be determined in zinc powder by utilising the reducing power of the sample itself.[79] Hydrochloric acid at 80 °C is added to 1 g of the powdered sample in the reaction flask and the evolved hydrides are measured in the usual way.

Foods

The hydride generation technique has found wide application in the determination of toxic metals in food and drink products. The analysis of wine, sherry and beer samples presents no serious analytical problems. However, acidification and degassing of the samples must be carried out before the analysis. Water-soluble foods such as sugar, coffee and some organic food colourings can also be analysed directly once a suitable solution has been prepared.

For other food samples a digestion process is usually necessary before reduction to the hydride, and most of the published work deals with these methods. Typically 2–5 g of food sample is digested in a conical flask with 5 ml of concentrated sulphuric acid and 50% *m*/*V* hydrogen peroxide on a hot-plate until a clear digest is obtained.[80] Alternatively, the sample can be treated in a Kjeldahl flask with a 4 + 1 + 1 mixture of concentrated nitric, sulphuric and perchloric acids.[38] Reduction of the metal with sodium tetrahydroborate(III) then gives excellent recoveries for both methods after calibration with standards that have been treated in the same way as the samples. The choice of acid digestion appears to be due to the particular authors' preference rather than the type of foodstuff to be analysed.

As many laboratories analysing foods often determine mercury in addition to some of the hydride-forming metals, one of the digestion methods developed was suitable for retaining both mercury and selenium in solution.[81] The digestion mixture used was 1 + 1 concentrated nitric and sulphuric acids plus 0.1% *m*/*V* of vanadium(V) oxide added as a catalyst. The digested sample was divided into two parts; the portion for the selenium determination was acidified with hydrochloric acid and then reduced with sodium tetrahydroborate(III) in the usual way. Recoveries for selenium determined by this method were 99.5–101.0%. The aliquot retained for the mercury determination was treated with potassium permanganate before reduction to elemental mercury by means of hydroxylammonium chloride and tin(II) chloride. Detection was by the cold-vapour method.

Evans *et al.*[43] produced an extremely thorough paper on the determination of antimony, arsenic and tin in foodstuffs using the silica tube detection technique. Detailed information is given on both dry- and wet-ashing procedures, calibration ranges, interferences, recoveries and reproducibilities. As no review could do justice to the amount of information contained in this paper, we recommend that anyone faced with this type of analysis should read it for themselves.

Clinical

Arsenic is not a normal constituent in body tissue and fluids although no real information exists as to its toxic levels. A level of 0.05 μg ml^{-1} in human urine is considered "significant."[82]

All existing work on the determination of any of the hydride-forming metals in body tissue and fluids agrees that the metal hydrides cannot be generated from the untreated sample because of severe signal depression and poor recoveries. The samples must therefore be wet ashed before reduction.

Orheim and Bovee[83] favoured a reduction using concentrated nitric and sulphuric acids, followed by addition of hydrogen peroxide, for the determination of selenium in blood, milk, hair, tissue, fat and urine. The method of standard additions was used for calibration, and the analysis of spiked samples gave recoveries of 95–105%.

An alternative digestion method for blood, before the determination of selenium, involves the use of nitric and perchloric acids.[84] Levels of selenium in the range 0.01–0.50 μg g^{-1} were reported with a relative standard deviation of 4.3% and a mean recovery of 100.5%.

Bismuth compounds are currently used in the treatment of indigestion and stomach ulcers. As a result, the determination of bismuth in blood and urine is required. Natural levels of bismuth in blood are quoted as being between 0.009 and 0.012 μg ml^{-1}, but the anticipated level after bismuth therapy would be much higher. Rooney[18] compared the techniques of spectrophotometry and polarography with flame, electrothermal and hydride atomic-absorption methods for blood and urine and found that the hydride generation method, with detection using a heated silica tube, was the most satisfactory. A digestion using nitric and perchloric acids was also used in this method and recoveries of bismuth from both blood and urine were good.

Agricultural

Because of the widespread occurrence of arsenic in minerals and pesticides, its dispersal in the environment requires monitoring in soils and plants. Most current methods deal only with arsenic and selenium, although there seems no reason why the methods could not be extended to the other hydride-forming metals if required.

Several sample digestion methods have been proposed. Vijan and co-workers[35,36] used a mixture of perchloric and nitric acids for soil and vegetation. After reduction with sodium tetrahydroborate(III) and detection using an electrically heated quartz cell, results and interferences were reported for the determination of arsenic and selenium. Many of the interferences (by now commonly reported) were confirmed. Results were obtained using the standard additions technique. Recoveries for arsenic using this method were 86.7–126.7%. Wauchope[39] compared the results obtained on solutions of samples prepared by two different methods. The first method was simply to soak the samples in hydrochloric acid for 24 h. The second method involved the digestion of the samples in a mixture of nitric and perchloric acids. Both methods gave similar results. Thompson and Thoresby[40] treated soils by leaching with a mixture of nitric and sulphuric acids, or by fusion with potassium pyrosulphate followed by oxidation to arsenic(V) with potassium permanganate. Plants were wet oxidised with nitric and sulphuric acids. Samples of the digests thus produced were reduced with sodium tetrahydroborate(III). An electrically heated tube was used as a detection device. The results obtained were consistently higher than those obtained with a molybdenum blue spectrophotometric method. However, the authors believed the atomic-absorption method to be the most accurate, as collaborative reports had indicated erratic recoveries with the spectrophotometric method.

The determination of both arsenic(III) and total arsenic in waters and orchard leaves has been reported.[27] The leaves were digested in nitric acid at 70 °C for 5 min and the mixture was cooled, treated with dilute sulphuric acid and heated at 70 °C for 15 min. The acidity of the solution was then adjusted with 5 M hydrochloric acid, from which the total arsenic was determined, or with a citrate buffer at pH 4.5–5.0, for the arsenic(III) determination. The arsine was then evolved from the particular solution by means of sodium tetrahydroborate(III) and atomised in an argon - hydrogen flame.

The determination of germanium, arsenic, selenium, tin and antimony in orchard leaves and flour,[56] carried out on acid-digested samples, showed good recoveries and close agreement with certified values.

The determination of selenium in feed and forage samples was carried out by drying the samples at 200–300 °C for 30 min followed by dissolution in concentrated hydrochloric acid.[16] Selenium recoveries averaged 101% with a relative standard deviation of 5.0% using this method. It was reported that attempts at wet ashing with mixtures of nitric and sulphuric acids and sulphuric acid and hydrogen peroxide resulted in a loss of selenium.

The sensitivities for antimony, arsenic, selenium and tellurium by hydride generation, with detection by atomic absorption, are still inadequate for some samples. Thompson[52] linked the hydride generation technique with atomic fluorescence, and showed that not only were calibration graphs more linear, but that sensitivities were improved by factors of between 5 and 30. This method was also applied to the determination of selenium in animal feedstuff and sea water.

This technique was then applied to the determination of selenium in soil digests obtained by an overnight treatment with concentrated nitric acid and followed by the addition of perchloric acid and heating.[85] The detection limit of this method is 10 ng of selenium.

Geological

Rocks and minerals are complex samples chemically, and dissolution methods are often tedious and time consuming. The improved sensitivity of the hydride generation method for arsenic, selenium and tellurium has found applications with these samples.

Arsenic is used to indicate the presence of some precious metals in rocks and minerals, and several methods for the determination of arsenic have been proposed. As flame and electrothermal atomisation methods for these metals suffer from several interferences, the hydride generation method is favoured by most workers.[26,72,86] Sample digestion procedures vary, but one of the most popular is treatment with concentrated hydrochloric and nitric acids, followed by reduction with sodium tetrahydroborate(III).

Glass samples were dissolved in a mixture of hydrochloric, hydrofluoric and nitric acids in a sealed polyethylene bottle at 70 °C. After cooling, boric acid was added and hydrogen selenide generated with sodium tetrahydroborate(III).[87] The results showed good agreement with standard values, and the detection limit was 0.030 μg of selenium.

Tellurium, at concentrations down to 5 ng g^{-1}, has been determined in silicate rocks by treating the sample with hydrofluoric acid and evaporating the resulting solution to dryness. The residue was dissolved in a mixture of hydrochloric, nitric and perchloric acids.[17] The samples were reduced with sodium tetrahydroborate(III) and atomised in an electrically heated tube. Calibration was effected by the method of standard additions.

Tobacco

Arsenic has been determined in tobacco after a wet-ashing procedure. A 4-g amount of tobacco was treated with nitric acid before refluxing with a mixture of nitric and perchloric acids.[88] Detection was by reduction with potassium iodide and tin(II) chloride, followed by collection of the arsine (as a white solid) in a U-tube immersed in liquid nitrogen. When the reduction was complete the liquid nitrogen was removed and the evolved arsine measured by atomic-absorption spectroscopy.

A method for the determination of antimony, arsenic, bismuth, selenium and tellurium in tobacco and cigarette smoke was proposed by Spincer.[89,90] Samples are digested in nitric acid and diluted with EDTA, followed by reduction with sodium tetrahydroborate(III) and detection using the silica tube method.[14]

The maximum levels observed by this method were arsenic 500 ng g^{-1}, antimony, bismuth and tellurium 50 ng g^{-1} and selenium 90 ng g^{-1}. The metal content of smoke from 40 cigarettes was trapped at -80 °C and extracted with nitric acid.

Environmental

Air particulates, after collection on a fibre-glass filter and digestion with a $1 + 2$ mixture of nitric and sulphuric acids, were treated with sodium tetrahydroborate(III) to reduce the arsenic.[28] Recoveries for actual samples were 99.5–103%. Studies showed that the presence of either selenium, cobalt, nickel or copper at 200 μg ml^{-1} causes severe interferences but as they were seldom present at levels greater than 5 μg ml^{-1} in the prepared solutions no interferences occurred in practice.

Petroleum Products

No published work exists in which atomic-absorption detection has been used for hydride-forming metals in petroleum products. However, it is worth recording that arsenic has been determined in stocks and catalysts by generation of the arsenic as arsine.[91] The pre-treatment method for the stocks involved refluxing samples with sulphuric acid and hydrogen peroxide. The catalysts were fused with sodium peroxide. A spectrophotometric determination was used to measure the arsenic, but there seems to be no reason why atomic-absorption spectroscopy could not be applied to this method.

Future Trends

The technique appears to have reached a plateau, and no major improvements are likely in the near future.

Most commercial manufacturers offer hydride kits as accessories for their atomic-absorption spectrophotometers. As might be expected, there is a wide variety in the designs offered, some employing the argon - hydrogen flame and others flame-heated or electrically heated silica tubes. The simplest design is a reaction cell, which is coupled to the spray chamber of the instrument, to supply liberated hydride to an argon - hydrogen flame. The most sophisticated has an electronic control box which, at the touch of a button, purges the system with inert gas, starts a stirrer, initiates the recorder chart drive and adds the reducing agent to the reaction cell. An electrically heated silica tube detector is employed.

Two possible areas of future development are improved automation and methods of lowering detection limits. These may improve as commercial manufacturers introduce successive designs, but the really major improvements to sensitivity and detection limits may lie in the combination of hydride generation and techniques such as atomic fluorescence, inductively coupled plasmas and d.c. arc discharges. Although these techniques have already been mentioned they are not yet in widespread use.

A further area in which much useful work may yet be done is in the reduction or elimination of interference effects.

The development of an inexpensive specific detector system could be a useful idea for the future. This would release the more expensive atomic-absorption spectrophotometers for other purposes, and eliminate the time wasted in fitting and dismantling the hydride accessory.

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Simultaneous Determination of the Noble Metals in Geological Material by Radiochemical Neutron-activation Analysis

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A simple procedure is described for determining the noble metals in geological samples rich in chromium and copper. Powdered rock samples (0.1–0.3 g) are irradiated in an epithermal neutron flux, under a cadmium filter, to reduce interference from ^{51}Cr and ^{64}Cu. After digestion with a peroxide fusion, the noble metals are separated on Srafion NMRR ion-exchange resin. Activity from chromium(VI), retained on the resin, is eliminated by reduction to chromium(III) with iron(II) sulphate before separation. The gamma-ray activity is measured with a lithium-drifted germanium detector for palladium (^{109}Pd), platinum (^{199}Au), iridium (^{194}Ir) and gold (^{198}Au). The separation yield (iridium 40%, palladium 80%, gold 90%) is determined for each sample by irradiating the resin to activate a stable noble metal carrier. Multi-element noble metal standards (0.1–8 μg) are prepared from dilute solutions (100 μl) evaporated on resin (1 ml). The practical detection limits are 2.5 ng of palladium and platinum, 0.1 ng of iridium and 0.01 ng of gold. The reliability of the procedure was confirmed by analysing sulphide standards (PTM, PTC) and standard rocks (PCC-1, DTS-1). The method has been applied to the analysis of chrome-spinels.

Keywords: *Noble metal determination*; *epithermal neutron-activation analysis*; *ion-exchange separation*; *reference rocks*; *chrome-spinel*

Methods for the determination of the noble metals have been reviewed by Beamish and Van Loon.[1] The most common method for geological samples is atomic-absorption spectrometry with a fire-assay pre-concentration step. Emission spectrography and spectrophotometry are also useful techniques for ore analysis, where representative samples of up to 50 g are measured, and therefore sensitivity is not a problem. One of the most sensitive methods for the analysis of rock samples for which the supply of material is limited is neutron-activation analysis. Instrumental activation analysis has been applied successfully to the determination of iridium and gold in ores,[2] but generally it is necessary to separate the noble metals from interfering activity of the rock matrix. There are many examples of radiochemical separation schemes to isolate one or more of the noble metals in the neutron-activation analysis of geological samples. These schemes include solvent extraction, distillation, ion exchange and precipitation.[3–5] A relatively rapid method has been described by Nadkarni and Morrison,[6] based on the ion-exchange separation of the noble metals as a group. The resin Srafion NMRR is an anion exchanger that exhibits quantitative retention of the noble metals.[7] The resin has been used for the separation of gold,[8–11] iridium,[12,13] silver,[14] copper,[15] molybdenum[16] and mercury.[17] It has been shown, in addition, to adsorb vanadate and chromate ions.[18]

Nadkarni and Morrison[6] found that the noble metals were collected quantitatively on Srafion NMRR but that the solution had to be passed through a second column for complete collection of iridium. It has been demonstrated that iridium is not easily removed from the resin once adsorbed[13] and preliminary studies in this work confirmed this to be the case for the other noble metals. The high background activity due to the retention of copper on the resin was a problem in ore material and solvent extraction was introduced for its removal prior to the separation step.[19] Chromium was not considered to be an interferent in the analysis of silicates and ores[19] but this study showed that, following an oxidising fusion, the chromate ions on the resin caused interferences in samples containing high concentrations of chromium, such as chrome-spinels. Previous workers[20] have used epithermal irradiations to enhance the activation of the noble metals and reduce background interference from the matrix. In this work a cadmium filter reduced the activity from copper and chromium by a factor of 30. This paper describes a modified procedure of Nadkarni and Morrison[6] to overcome these problems, applied to the determination of platinum, palladium, iridium and gold. After an alkaline peroxide fusion and dissolution in acid, the sample solution is reduced with iron(II) sulphate to convert chromium(VI) into chromium(III), which is not collected by the resin. As it is difficult to remove the noble metals from the resin, they are counted on it and the yield of the separation is measured for each sample by re-irradiating the resin to activate the carrier. The yields were 90–100% of gold and platinum, 80–90% of palladium and 40% of iridium.

Experimental

Apparatus

The samples were irradiated in the University of London reactor at Silwood Park, Ascot. The 30-h irradiations were made in the core-tube (10^{12} n cm^{-2} s^{-1}), in an irradiation can lined with cadmium 1 mm thick (R_{Cd} Au = 2.8). The 5-min irradiation to determine the yield was made in a pneumatic irradiation system in the reactor core (2×10^{12} n cm^{-2} s^{-1}).

The gamma-ray analyses were performed with a high-resolution lithium-drifted germanium detector (nominal active volume, 42 cm^3; resolution, 1.81 keV FWHM at 1.33 MeV; peak to Compton, 36.3 at 1.33 MeV; Princeton-Gamma Tech), and a 4096-channel analyser (Link, Model 290). The lead shielding surrounding the detector was covered with cadmium sheet to avoid interference from lead X-rays.

Reagents

Analytical-reagent grade materials were used unless specified otherwise.

Hydrochloric acid, 12, 1 *and* 0.05 M.

Nitric acid, 16 M.

Ammonia solution, 15 M.

Sodium peroxide, powder.

Sodium hydroxide, pellets.

Scandium oxide. Specpure.

Iron(II) sulphate.

Ammonium tetrachloropalladate(III). Specpure, Johnson Matthey Chemicals Ltd.

Tetrammineplatinum(II) dichloride. Specpure, Johnson Matthey Chemicals Ltd.

Ammonium hexachloroiridate(IV). Specpure, Johnson Matthey Chemicals Ltd.

Potassium dicyanoaurate(III) solution. Specpure, Johnson Matthey Chemicals Ltd.

Srafion NMRR ion-exchange resin. Ayalon Water Conditioning Co., Haifa, Israel.

Noble Metal Solutions

Dissolve accurately weighed amounts of the noble metal complexes in 1 M hydrochloric acid to give stock solutions of 1–5 mg ml^{-1}. Dilute the stock solutions with 1 M hydrochloric acid to give a carrier solution containing 10 µg ml^{-1} of iridium and gold and 500 µg ml^{-1} of palladium and platinum. Further dilute these solutions 100-fold to give standards containing 0.1 µg of iridium and gold and 5 µg of palladium and platinum in 100 µl of solution.

Ion-exchange Resin

Equilibrate the Srafion NMRR resin in 0.05 M hydrochloric acid for several hours before packing in columns (120 mm × 7 mm i.d.) (5-ml disposable plastic pipettes) with a glass-wool plug.

Irradiation

Prepare the standards for quantitative analysis by evaporating exactly 100-µl aliquots of the standard solution on to 1 ml of Srafion NMRR resin, in a size 2 polythene irradiation capsule (15 mm diameter × 10 mm high). Weigh the powdered rock samples (0.1–0.3 g) into size 1 polythene irradiation capsules (15 mm diameter × 6 mm high). Place four rock samples, two multi-element standards and one reference rock sample in the cadmium-lined irradiation can and irradiate it for 4 d in the reactor core-tube. When the samples have been unloaded count the multi-element standards immediately and digest the rocks for separation of the noble metals.

Radiochemical Separation

Transfer 0.1 ml of carrier solution into a new nickel crucible (capacity 25 ml) and leave the solution to evaporate. Add a few milligrams of solid scandium oxide hold-back carrier and 2 g of sodium hydroxide pellets. Transfer the active rock sample into the crucible and cover the contents with 5 g of sodium peroxide powder. Heat the mixture with an electrothermal Bunsen burner and keep it at red heat for 15 min, swirling the mixture occasionally to ensure isotopic equilibration between the carrier and the sample, and allow the melt to cool to below 100 °C. Add 10 ml of de-ionised water to the melt while it is still hot. The melt dissolves violently and, in order to avoid losses from effervescence, the crucible should be placed in a glass filter-funnel over a round-bottomed flask and covered with a watch-glass. Transfer the solution into the flask and repeat the dissolution step several times. Rinse the nickel crucible with 12 M hydrochloric acid and the watch-glass and funnel with de-ionised water, and transfer all washings into the round-bottomed flask. Add 12 M hydrochloric acid to the dissolved sample until the solution is clear green. Add glass beads to the flask and boil the solution for 5 min. If the sample is rich in copper, add 2 ml of 16 M nitric acid before boiling. The solution will effervesce as any excess of peroxide boils off. Cool the flask in cold water and, if the sample contains more than a few micrograms per gram of chromium, add 1 g of solid iron(II) sulphate. Adjust the solution to pH 1–2 with ammonia solution, taking care not to precipitate the iron(II) ions. Make the solution up to 100 ml with de-ionised water and transfer the sample to the ion-exchange system. In this work an automated system was used but the separation can be carried out manually. Pass the sample solution on to the column at 2 ml min^{-1} and subsequently wash the resin with 0.05 M hydrochloric acid. Then transfer the resin sample into a plastic counting vial (5 cm diameter × 4 cm high). Repeat for the remaining samples.

Counting

Transfer the standard-loaded resin into a disposable plastic counting vial immediately after it has been unloaded from the reactor. Add 4 ml of fresh Srafion NMRR resin and mix well to give a uniform distribution of the activity. Count the standards for 1 h on the lithium-drifted germanium detector with the sample as close to the detector as possible in the Perspex sample holder of the sample changer. Determine the counts from the gamma-ray energies of ^{109}Pd, ^{199}Au, ^{194}Ir and ^{198}Au, given in Table I, using the total peak-area method. When the first rock sample has been processed, transfer the resin to the sample changer and count for 3 h. Repeat for the remainder of the samples, including the reference rock.

TABLE I

NUCLEAR DATA FOR THE NOBLE METAL NUCLIDES MEASURED IN THIS WORK[21]

Nuclide	Half-life	Gamma-ray energy/keV	Interferences
^{109}Pd	13.4 h	88.1	Pb X-rays at 87 keV from photon interaction with detector shielding
^{199}Pt	30.8 min (decays to ^{199}Au)	—	—
^{199}Au	3.14 d	158.3	^{47}Sc at 159.5 keV from ^{47}Ti(n,p); ^{199}Au from ^{198}Au(n,γ) where gold content $\gg$ platinum content
^{194}Ir	19.2 h	328.0	—
^{198}Au	2.70 d	411.8	—

Yield Determination

Leave the resin samples to decay for 1 week before re-irradiation to determine the yield. Transfer the resin to polythene capsules (15 mm diameter × 60 mm high) and dry at 80 °C. Place the capsules in outer irradiation capsules (18 mm diameter × 70 mm high). Prepare standards for the yield determination by evaporating 1.0 ml of carrier solution on 5 ml of

Srafion NMRR resin in the polythene capsules used for the resin samples, packed in outer irradiation capsules. Irradiate the samples and standards for 5 min in the pneumatic irradiation system at 10-min intervals sequentially. Leave them to decay overnight in order to remove the ^{38}Cl activity from the resin. Transfer the samples and standards to plastic counting vials and count them on the lithium-drifted germanium detector for ^{109}Pd, ^{194}Ir and ^{198}Au for 5 min each. Platinum is separated on the resin as ^{199}Au and therefore the yields for both gold and platinum are derived from the measurement of ^{198}Au.

Results and Discussion

Analysis of Sulphide Standards

The accuracy of the method was checked with reference material that had recommended values for palladium, platinum and gold and experimental values for iridium. PTC[22] and PTM[23] are produced by the Canadian Certified Reference Material Project. PTC is a noble metal-bearing sulphide concentrate containing 5.16% of copper, 9.42% of nickel, 23.5% of sulphur and 26.9% of iron. PTM is a noble metal-bearing copper - nickel matte containing 30.2% of copper, 44.8% of nickel, 1.58% of iron and 21.6% of sulphur. The activity that resulted from the copper content of the sulphides was reduced by epithermal neutron activation. The active sample solution was left in the oxidised state, as preliminary experiments showed that the retention of copper on the Srafion NMRR resin was 1% of copper(II) compared with 25% of copper(I). The noble metals are present in the sulphides at the micrograms per gram level and therefore the sensitivity was not a problem in the determination. Table II shows that the analyses of the reference material gave good agreement with the recommended values for the noble metals except for gold and platinum in PTC, which were low. This may be attributed to inhomogeneities, which are enhanced by the small sample size used, reflected by the large standard deviation on the results. Low results can be caused by losses due to incomplete decomposition of the sample, but it would be expected that if such a problem occurred it would also be seen in the analysis of PTM.

TABLE II

DETERMINATION OF THE NOBLE METALS IN STANDARD SULPHIDES

		Concentration/μg g^{-1}			
Sample	Parameter	Pd	Pt	Ir	Au
PTM	Mean value (this work)	8.8	5.97	0.38	1.78
	Standard deviation	1.6	0.53	0.07	0.32
	Recommended value[23]	8.1	5.8	0.25, 0.36, 0.81*	1.8
	95% confidence interval	7.4–8.8	5.5–6.2		1.6–1.9
PTC	Mean value (this work)	11.8	1.8	0.20	0.39
	Standard deviation	1.8	1.1	0.06	0.23
	Recommended value[22]	12.7	3.0	0.12, 0.24, 0.01, 0.19*	0.65
	95% confidence interval	12.0–13.0	2.8–3.2		0.55–0.72

* For information (not recommended).

Analysis of US Geological Survey Standard Rocks

The US Geological Survey reference rocks PCC-1 and DTS-1 were also analysed to determine both the sensitivity and the accuracy of the technique. There are no certified values for the noble metals in these rocks but they have been measured by other workers and the values are comprehensively listed in the literature.[5] Palladium and platinum could not be measured below the detection limit of 12 μg kg^{-1}, determined from 2.3 standard deviations on the background. Table III shows that the values obtained for iridium and gold were within the range of results obtained by other workers. An unexpected source of error was found to be due to ^{47}Sc interference at 159.5 keV, which contributed to the 158.3-keV peak of ^{199}Au, used in the determination of platinum. The ^{47}Sc is the result of an n,p reaction on irradiation of ^{47}Ti, which is enhanced by the epithermal neutron activation. The interference was removed by the addition of scandium oxide hold-back carrier. The detection limits for iridium and gold were 1 and 0.1 μg kg^{-1}, respectively.

TABLE III

DETERMINATION OF THE NOBLE METALS IN STANDARD ROCKS

		Concentration/μg kg^{-1}			
Sample	Parameter	Pd	Pt	Ir	Au
PCC-1 ..	.. Mean value (this work)	<11	<20	4.2	1.0
	Standard deviation			2.2	0.3
	Results of other workers	3.0–7.2	3.5–15	2–6.7	0.63–3.4
DTS-1 ..	.. Mean value (this work)	<12	<12	2.4	1.1
	Standard deviation			1.0	0.5
	Results of other workers	1.8–6.1	4.7–11	0.3–4.5	0.45–1.4

Analysis of Chrome-spinels

The method was then applied to the analysis of chrome-spinels, containing about 30% of chromium. The reduction step with iron(II) sulphate converted the chromate ions, which gave 75% retention on the resin, into chromium(III), which was collected at only the 1% level. However, the further reduction of the chromium activity by a factor of 30 with epithermal irradiation was essential before the noble metals could be determined in the chrome-spinels. The spinels were separated and purified prior to analysis and in most instances the sample size was limited to less than 0.1 g. Table IV shows that the detection limits for palladium and platinum in chrome-spinels are about 40 μg kg^{-1}. The noble metal concentrations in the chrome-spinels are presented as the means of three determinations in most instances. The large variation of the values reflects the inhomogeneity of their distribution within the sample.

TABLE IV

DETERMINATION OF THE NOBLE METALS IN CHROME-SPINELS

			Concentration/μg kg^{-1}			
Type of sample	Location	Code	Pd	Pt	Ir	Au
Stratiform complexes ..	Bushveld	1930, 66(17)	64 ± 40	215 ± 7	74 ± 18	2.4 ± 0.5
	Stillwater	1970, P20(1)	<60	<110	18 ± 7	2.2 ± 1.4
	Rhum	RWR9	137 ± 86	55,435	30 ± 10	2.1 ± 1.7
		RWR13	118 ± 49	147 ± 92	34 ± 3	23 ± 7
	Rhodesia (Zimbabwe)	RWRh2	150 ± 56	330 ± 180	140 ± 26	2.2 ± 2.7
	Oregon	RWTh1	85 ± 50	<30, 83	47 ± 11	2.2 ± 1.6
Alpine-type deposits ..	Greece	RWGR2	<20	<30	27 ± 8	0.29 ± 0.20
		RWGR3	430	170	540	5.7
	Pakistan	RWP1	<40	<40	26 ± 17	0.97 ± 0.49
		RWP3	<60,350	<40	39 ± 6	2.3 ± 3.8
	Turkey	RWT14	<30,140	190	49 ± 23	1.1 ± 0.8
		RWT16	170	<30	59	4.1
	Unst	SU11	3.7	<14	23 ± 4	1.5 ± 0.6

Conclusions

A rapid and simple procedure has been established for the routine determination of the noble metals in geological samples. Palladium, platinum, iridium and gold are measured simultaneously in five samples within 18 h of being unloaded from the reactor. Except for the initial digestion of the samples, the procedure can be automated for unattended operation. The precision of the method has been confirmed by analysis of standard rocks and the sensitivity is adequate for samples containing iridium and gold at the micrograms per kilogram level and platinum and palladium at levels above 50 μg kg^{-1}. The scheme is particularly suited to the analysis of samples that contain very high concentrations of copper and chromium.

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Determination of Aluminium in Wood Pulp Liquors Using Graphite Furnace Atomic-absorption Spectrometry

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A graphite furnace atomic-absorption spectrometric method for the determination of 0.5–100 μg ml^{-1} of aluminium in matrices containing chlorine and high concentrations of sulphur is described. The precision of the over-all procedure was 4%. Graphite tube conditions and the composition of the matrix were found to change the sensitivity for aluminium.

Keywords: *Aluminium determination*; *graphite furnace atomic-absorption spectrometry*; *sulphur interference*; *chlorine interference*; *graphite tube conditions*

Cellulose pulp is produced by cooking wood in a solution of sodium sulphite and sodium hydrogen sulphite. In order to minimise emissions and production costs, the chemicals used in the process have to be recycled as much as possible. The recycling of the cooking liquor includes neutralisation and evaporation. Part of the condensate is removed from the process in order to prevent accumulation of compounds originating from the raw materials. The remaining part is combusted and re-used in the process. The wood used as raw material contains calcium and oxalate compounds at such levels that severe problems caused by calcium oxalate incrustations arise during condensation in the evaporation plant. These problems can be avoided by adding small amounts of aluminium to the liquors before neutralisation. The added aluminium forms strong complexes with oxalate ions, thus preventing calcium oxalate depositions. The concentration of aluminium in the liquors has to be controlled carefully, as high concentrations will lead to precipitation of aluminium silicate and aluminium hydroxide.

At the Domsjö plant, aluminium was determined in wood pulp liquors by precipitation followed by colorimetry[1] or flame atomic-absorption spectromety[2] and by a procedure involving extraction of aluminium as a chelate followed by flame atomic-absorption spectrometry.[3] These methods are laborious and time consuming. The high sensitivity of graphite furnace atomic-absorption spectrometry has been exploited to develop simple and rapid methods for the direct determination of aluminium in a variety of matrices, *e.g.*, steels,[4,5] aerosols,[6] petroleum products[7] and biological materials.[8,9] The purpose of this work was to develop a graphite furnace atomic-absorption spectrometric method for the direct determination of aluminium in wood pulp liquors.

Experimental

Apparatus

A Perkin-Elmer 372 atomic-absorption spectrometer provided with background correction and a research spectrophotometer were used. Both instruments were equipped with HGA-74 graphite furnaces. The HGA-74 furnaces were connected to home-made power supplies with facilities for temperature-controlled heating of the graphite tubes.[10] Temperature settings referring to the inner surface of the graphite were calibrated with an NiCr - Ni thermocouple below 1000 °C and with an optical pyrometer (Keller Spezialtechnik Pyro Werk GmbH, Model PB06AF3) at higher temperatures. Samples were injected with a Perkin-Elmer automatic sampler, Model AS-1, or manually with Oxford micropipettes. The recorder output of the spectrometer was connected to a peak-reader module[11] which provided simultaneous recordings of the peak height and the peak area. The results given in this paper are based on the peak-height absorbance values because better precision was obtained in this way. The peak reader was connected to a printer (Newport Laboratories Inc., Model 810) and a strip-chart recorder (Perkin-Elmer, Model 56). The instrumental parameters are given in Table I.

TABLE I

INSTRUMENTAL PARAMETERS

	Time/s	Temperature/°C
Drying	35	100
Ashing	60	1200
Delay	4	—
Atomisation	6	2400
Clean-out	6	Maximum

Wavelength/nm	309.3
Slit/nm	0.7
Metal lamp current/mA	7
Deuterium lamp	On
Hydrogen lamp/mA	20*
Sample volume/μl	1–100†
Argon flow-rate/l min^{-1}—	
Internal	0.35‡
External	1.3

* Only used with research spectrophotometer for the determination of the background.

† Depending on the concentration of aluminium. The same volumes have to be used for standards and unknown samples.

‡ Gas-stop during atomisation.

Dry Ashing of Evaporated Liquor and Dried Pulp Samples

One gram of evaporated liquor was transferred into a platinum crucible. The sample was dried at 100 °C for 4 h and then placed in a furnace at 1000 °C for 4 h. After cooling the residue was dissolved in 2 ml of concentrated nitric acid and diluted to 100 ml with water.

Reagents and Materials

Nitric acid (65% *V*/*V*) and sodium chloride were Merck Suprapur grade products. Aluminium metal, sodium sulphide, sodium sulphate and sodium carbonate were Merck analytical-reagent grade materials. Sodium thiosulphate and sodium sulphite were obtained from Riedel de Haen (analytical-reagent grade) and sodium hydrogensulphite from Mallinkcrodt (analytical-reagent grade). All absorbance values obtained in the investigation of matrix components were corrected for blank values. Solutions were stored in polyethylene bottles.

All apparatus was washed with 4 M nitric acid.

Stock aluminium solution, 100 μg ml^{-1} *of aluminium.* Dissolve 0.100 g of aluminium in 5 ml of concentrated nitric acid, transfer the solution into a 1-l calibrated flask and dilute to volume with water.

Stock artificial matrix solution. Transfer 40 g of sodium sulphate, 10 g of sodium carbonate and 2 g of sodium chloride into a 1-l calibrated flask, adjust to pH 1 with nitric acid and dilute to volume with water.

Artificial solutions of sulphide liquor and green liquor. Prepare solutions containing the salt concentrations given in Table II. Transfer 1 ml of each solution into two separate 100-ml calibrated flasks and dilute to volume with water.

TABLE II

APPROXIMATE COMPOSITION OF THE LIQUORS ANALYSED

Green liquor		Sulphite liquor from scrubber		Evaporated liquor	
Component	Concentration/g l^{-1}	Component	Concentration/g l^{-1}	Component	Concentration/g l^{-1}
Na	80	Na	50	Na	50
Total sulphur	40	Total sulphur	35	Total sulphur	60
Na_2S	85	$NaHSO_3$	19	NaCl	2
Na_2CO_3	45	Na_2CO_3	3	Organic material	580
Na_2SO_4	7	Na_2SO_4	10		
$Na_2S_2O_3$	5	$Na_2S_2O_3$	8		
NaCl	2	Na_2SO_3	102		
NaOH	1	NaCl	1		

Procedure

Preparation of Sample Solutions

Liquors containing 0.5–10 μg ml^{-1} *of aluminium*

Evaporated liquor. Weigh 1 g of sample into a 100-ml calibrated flask, add 0.5 ml of nitric acid (65%) and dilute to volume with water.

Sulphite liquor from scrubber. Transfer 1 ml of sample into a 100-ml calibrated flask and add 0.5 ml of nitric acid (65%). Dilute to volume with water.

Green liquor. Transfer 1 ml of sample into a 100-ml calibrated flask and dilute to volume with water.

Liquors containing 10–100 μg ml^{-1} *of aluminium*

Proceed as described above but dilute the samples to 1 l instead of 100 ml.

Preparation of Standard Solutions

Aluminium standard solutions

Transfer 0, 2.0, 5.0, 7.0 and 10.0 ml of stock aluminium solution into 100-ml calibrated flasks. Add 0.5 ml of nitric acid (65%) and dilute to volume with water.

Standards prepared in an artificial matrix for determination of aluminium in the range 0.5–10 μg ml^{-1}

Transfer 1.0-ml aliquots of each of the aluminium standard solutions into 100-ml calibrated flasks each containing 1 ml of the stock artificial matrix solution. Dilute to volume with distilled water. These solutions contain 0, 0.02, 0.05, 0.07 and 0.1 μg ml^{-1} of aluminium.

Standards prepared in distilled water for determination of aluminium in the range 10–100 μg ml^{-1}

Transfer 1.0-ml aliquots of the aluminium standard solutions into 100-ml calibrated flasks and dilute to volume with distilled water. These solutions contain 0, 0.02, 0.05, 0.07 and 0.1 μg ml^{-1} of aluminium.

Measurement

Use the instrumental parameters given in Table I and determine the aluminium contents of green liquor, sulphite liquor from the scrubber, standards and blank solutions, at least in duplicate. For evaporated liquor, samples have to be run in triplicate. For every fourth sample a standard should be run. The aluminium concentration in green liquor and sulphite liquor from scrubbers is determined by evaluating the mean of the peak-height absorbances of standards, blanks and samples. For evaporated liquor samples, only the mean of the second and third determinations is evaluated.

Results and Discussion

The composition of the liquor changes during the processing of wood pulp. As the aluminium concentration has to be monitored during the whole process, determinations have to be made in solutions representing different matrices. Mean values of the main constituents of the different types of liquors involved in the processing of wood pulp are given in Table II. Depending on the composition of the raw materials used and the processes involved, the contents of sulphur and chloride in the different liquors may also vary from day to day. The effect of this variation on the graphite furnace atomic-absorption spectrometric determinations had to be investigated in detail in order to obtain an accurate procedure. In previous publications[12,13] it was shown that the determination of aluminium by the graphite furnace technique suffers from interferences in the presence of both sulphur and chloride.

Optimisation of Ashing Temperature

Fig. 1 shows the effect of the ashing temperature on the sensitivity for aluminium in the three types of liquors investigated (upper curves) and the magnitude of the non-specific

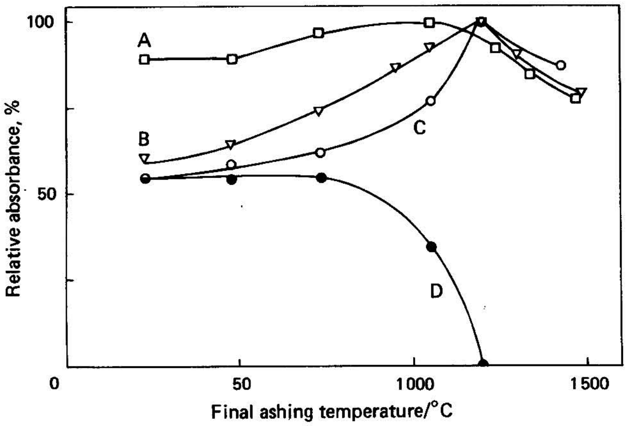

Fig. 1. Relative peak absorbance for aluminium as a function of the final ashing temperature: A, evaporated liquor; B, sulphite liquor from scrubber; C, green liquor; and D, the background in green liquor. All samples were diluted 1 + 99. The aluminium contents for evaporated liquor, sulphite liquor from scrubber and green liquor were 0.2, 0.3 and 0.14 μg ml^{-1}, respectively.

absorbance for green liquor (lower curve). The high salt concentration of the liquors gave rise to a disturbing non-specific absorbance at temperatures below 800 °C. For example, the non-specific absorbance for a green liquor sample diluted 1 + 99 and charred at 500 °C was 0.4. The background can be removed almost completely by ashing at 1100–1250 °C and in addition optimum sensitivity for aluminium is obtained. As the sensitivity with the evaporated liquor is only slightly decreased at 1200 °C, this temperature was used for all matrices. An ashing time of at least 60 s was needed to obtain these optimum conditions.

At the ashing temperature chosen the reproducibility was found to be typically about 3% compared with 5% at 500 °C. The impaired reproducibility and the lower sensitivity at 500 °C are probably caused by a time overlap in the furnace between the volatilisations of analyte atoms and the interfering species thereby increasing the number of gaseous aluminium molecules formed.

Sensitivity and Graphite Tube Conditions

During this work it was found that the sensitivity for aluminium varied from tube to tube. The magnitude of this variation was normally 25% but could be as much as 100%. However, the relative change in sensitivity between tubes was found to be equal in the liquors and aqueous solutions. In order to be able to compare results obtained with different tubes, all solutions had to be run relative to 0.01 M nitric acid. However, for a particular tube the sensitivity changed only slightly during its lifetime. This is illustrated in Fig. 2, in which the results of determinations of aluminium in 0.01 M nitric acid as well as in a sulphide liquor sample are shown. The useful lifetime for a graphite tube was found to be dependent on the type of solution determined. For liquor samples diluted 1 + 99, a tube could be used for 50–60 determinations. With more dilute solutions, up to 100 determinations could be performed. Before use each graphite tube was conditioned by three blank firings at maximum temperature.

Interferences from Sodium Sulphate and Sodium Sulphide

The sensitivity of the graphite furnace atomic-absorption spectrometer made it possible to dilute samples 100- to 1000-fold. After these dilutions samples contained less than 0.35 mg ml^{-1} of sodium sulphate and less than 0.85 mg ml^{-1} of sodium sulphide. Table III gives the relative sensitivity for aluminium in the presence of various concentrations of sodium sulphate. It can be seen that the signal for aluminium was enhanced in 0.01 M nitric acid solution for increasing salt concentrations.

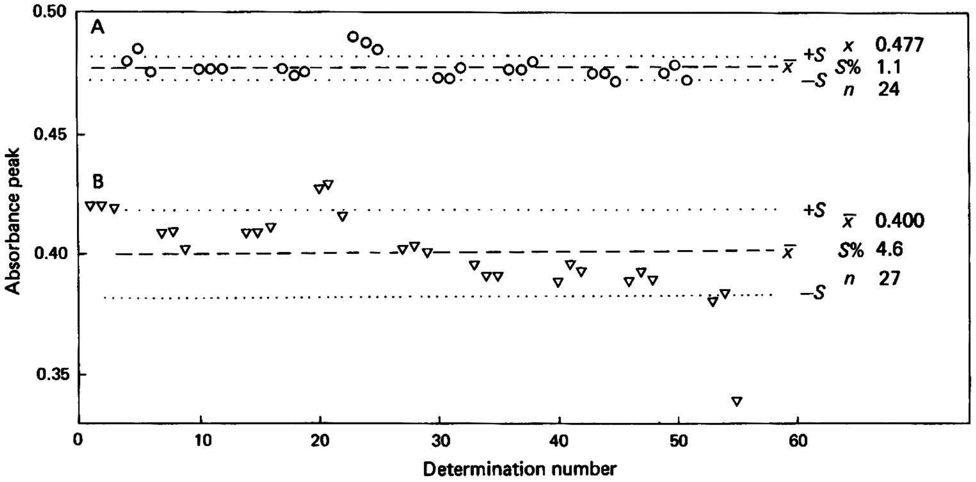

Fig. 2. Sensitivity for aluminium during the lifetime of a graphite tube. A, 0.1 μg ml^{-1} of aluminium in 0.01 M nitric acid; and B, 0.07 μg ml^{-1} of aluminium in a sulphite liquor from scubber sample diluted 1 + 99.

However, in the liquors and liquor-like matrices the aluminium signals decreased at the corresponding sulphate concentrations. With sodium sulphide similar interferences were obtained. The results are given in Table IV. These results show the importance of investigating interferences in solutions with compositions matching the samples as closely as possible. Tables III and IV also show that the magnitude of the interference effects obtained is dependent on the type of sulphur compound, as the effect of sodium sulphate is larger than that of sodium sulphide. However, the sensitivity for aluminium is decreased by a maximum of 15% in the presence of the highest tested concentrations of these sulphur compounds. Minor variations in the concentration of sodium sulphate and sodium sulphide in the liquors will therefore have a negligible effect on the analytical results provided that the procedure given above is followed.

TABLE III

RELATIVE INTERFERENCE EFFECTS OF SODIUM SULPHATE ON THE SENSITIVITY FOR ALUMINIUM IN DIFFERENT MATRICES

Relative absorbances corrected for reagent blank values are given.

Na_2SO_4 added to sample/mg ml^{-1}	0.01 M HNO_3	Evaporated liquor*	Green liquor*		Sulphite liquor from scrubber*	
			Artificial	Sample	Artificial	Sample
0	100	100	100	100	100	100
1	105	94	91	94	99	96
2	109	93	87	86	95	94
4	112	90	85	85	95	92

* Evaporated liquor was diluted 1 + 649, green liquor 1 + 49 and sulphite liquor from scrubber 1 + 199.

Interferences from Sodium Chloride

The effect of 0–1.5 mg ml^{-1} of sodium chloride on the determination of 60 ng ml^{-1} of aluminium was first investigated in artificial solutions of green liquor and sulphite liquor from the scrubber. No interferences were observed in these solutions. The experiment was repeated with real samples diluted 1 + 99 and the results are shown in Fig. 3. It can be seen that the sensitivity for aluminium is unaffected by chloride in green and evaporated liquor samples, whereas in the sulphite liquor sample from the scrubber the sensitivity for

TABLE IV

RELATIVE INTERFERENCE EFFECTS OF SODIUM SULPHIDE ON THE SENSITIVITY FOR ALUMINIUM*

Relative absorbances corrected for reagent blank values are given.

Na_2S added to sample/ mg ml^{-1}	0.01 M HNO_3	Green liquor	
		Artificial	Sample
0	100	100	100
1	95	97	101
2	105	96	95
4	106	95	96

* For the dilution factors used, see Table III.

aluminium is decreased by 50%. The interference with the sulphite liquor is probably caused by a combined action of the chlorides added and some minor component not listed in Table II. The minor component is assumed to form stable chlorides which cannot be removed by ashing at 1200 °C. During atomisation these chlorides must be volatilised simultaneously with aluminium in order to favour the formation of gaseous aluminium monochloride molecules. In this way the free atom concentration will be decreased, resulting in lower absorbance signals.

Liquor samples diluted 1 + 99 will contain 0.01 mg ml^{-1} of sodium chloride. From the results given in Fig. 3 it can be seen that even a 10-fold variation in the sodium chloride concentration will change the sensitivity for aluminium by only 5%. This means that the analytical results are relatively unaffected by large variations in the sodium chloride content.

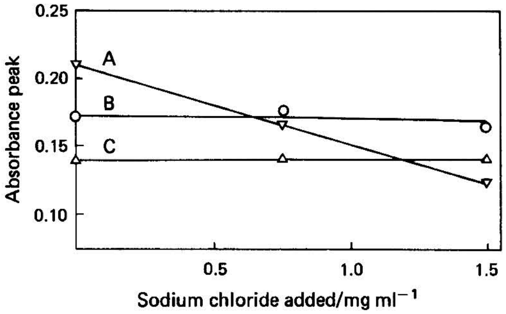

Fig. 3. Interference effects of sodium chloride on the peak absorbance of aluminium. A, Sulphite liquor from scrubber; B, green liquor; and C, evaporated liquor.

Combined Effects

For the determination of aluminium the green and sulphite liquors using the instrument parameters given in Table I, typical relative standard deviations of 3% were obtained whereas for the evaporated liquor a typical value was 10%. The reason for this poor precision can be understood by studying the peak height signals given in Fig. 4. After conditioning the tube, triplicate determinations of aluminium were made alternately in 0.01 M nitric acid (thin peaks) and evaporated liquor (thick peaks). Initially aluminium was determined in the nitric acid solution. The precision was better than 2%. The evaporated liquor was then tested. It can be seen that the sensitivity is markedly decreased after the first determination of the evaporated liquor after which the sensitivity is stabilised. In 0.01 M nitric acid the signal is depressed for the first determination and the original sensitivity is then regained. It is also shown in Fig. 4 that these variations in sensitivity were reproducible. For both solutions the over-all precision is poor; however, if the first determination in each series is excluded, relative standard deviations of about 3% are obtained. The evaporated

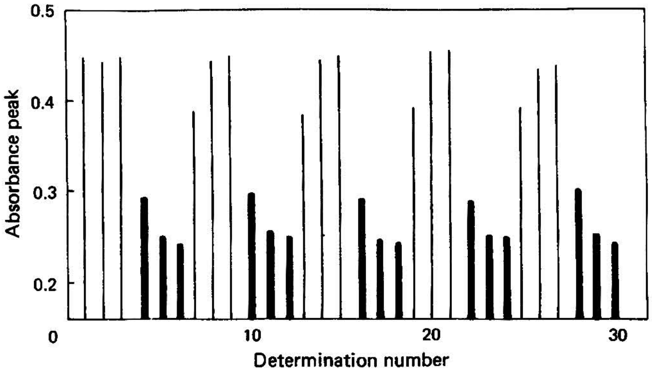

Fig. 4. Illustration of memory effects on the determination of aluminium caused by evaporated liquor. Thin peaks, 0.1 μg ml^{-1} of aluminium in 0.01 M nitric acid; thick peaks, 0.07 μg ml^{-1} of aluminium in evaporated liquor.

liquor contains a much greater amount of organic matter than the other liquors investigated and this was initially assumed to cause the irregularities described above; however this was shown not to be the case because results similar to those shown in Fig. 4 were obtained for evaporated liquor samples in which the organic matter had been removed by ashing.

The relative sensitivities obtained in the three types of liquors, an artificial standard solution and 0.01 M nitric acid were also investigated. This was accomplished by using the standard-addition technique. The slopes obtained in the linear range were taken as a measure of the sensitivity. Table V shows the slopes for samples diluted 1 + 99 and the artificial standard solution relative to 0.01 M nitric acid. As can be seen in the table the ratios are 10% less than unity and hence calibration against standards in 0.01 M nitric acid will give results that are too low. It was also shown that correct analytical results for the three types of liquors would be obtained by standardisation against the artificial standard solution. No interferences were observed in samples diluted 1 + 999 and therefore aqueous standards could be used for calibration.

TABLE V

SENSITIVITY FOR ALUMINIUM IN THE DIFFERENT SAMPLE TYPES RELATIVE TO 0.01 M NITRIC ACID

Sample	Slope of sample graph / Slope of graph for 0.01 M HNO_3
Green liquor	0.89
Evaporated liquor..	0.88
Sulphite liquor from scrubber	0.92
Artificial standard solution	0.88

Analytical Results

No liquor samples with certified values for aluminium were available. In order to test the validity of the proposed method, determinations of aluminium in sulphite liquor from scrubber, green and evaporated liquor samples were made by two other methods. In addition a number of liquor samples from other stages in the processing of wood pulp were included. The results obtained for the different methods can be seen in Table VI and the agreement is acceptable. The typical precision of the over-all graphite furnace atomic-absorption spectrometric procedure is 4%.

Table VI

COMPARISON OF RESULTS OBTAINED FOR THE DETERMINATION OF ALUMINIUM BY GRAPHITE FURNACE ATOMIC-ABSORPTION SPECTROMETRY WITH RESULTS OBTAINED BY OTHER METHODS

Sample	Graphite furnace atomic-absorption spectrometric method/μg ml^{-1}	Flame atomic-absorption spectrometric method/μg ml^{-1}
Green liquor I	72	66†
Green liquor II	22	24*
White liquor	106	100†
Evaporated liquor	33§	32*§
Sulphite liquor from scrubber I ..	4.5	4.5*
Sulphite liquor from scrubber II ..	3.9	3.9*
Spent sulphite liquor I	7.9	7.8*
Spent sulphite liquor II	3.5	2.8*
Hot water from scrubber	0.5	0.6*
Water from chloride scrubber ..	3.6	3.1*
Dried pulp‡	9.6§	9.1*§

* Determination of aluminium by atomic-absorption spectrometry with dinitrogen oxide - acetylene flame after precipitation.[2]

† Extraction of aluminium as a chelate followed by flame atomic-absorption spectrometry.[3]

‡ Dry ashing of the sample.

§ Concentration in micrograms per gram.

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Determination of 2-Aminobutane in Potatoes Using High-performance Liquid Chromatography

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Development work on the use of 2-aminobutane to control certain potato-tuber diseases necessitated the development of a convenient and sensitive analytical method for residue determination. The amine was distilled from potatoes, dansylated and determined using reversed-phase high-performance liquid chromatography with fluorescence detection. Recovery of 2-aminobutane by distillation was about 95% from standard solutions and 92% from treated potatoes. The lower limit of detection is below 0.2 μg kg^{-1}.

Keywords: *2-Aminobutane determination; potatoes; residues; high-performance liquid chromatography; fluorescence detection*

The control of decay in citrus fruits by treatment with an aqueous solution of 2-aminobutane was described by Eckert.[1] Later, application of the compound as a vapour was found to control the potato-tuber diseases gangrene, skin spot and silver scurf[2,3] and a method for the treatment of small bulks of potatoes in fumigation chambers was developed.[4] The Ministry of Agriculture, Fisheries and Food and the Department of Agriculture and Fisheries for Scotland have prepared recommendations for safe and efficient use of 2-aminobutane for fumigation of potatoes.[5] Recently, more extensive trials have shown that large bulks of up to 1000 tons or more of potatoes can be treated successfully *in situ* in store. Heavy sorption of 2-aminobutane vapour occurs particularly in the peel.[3,6] Residues, mainly in the form of amine salts, can persist for lengthy periods. However, achievement of a certain residue level is necessary for protection of the potatoes from disease. Sampling and analysis of 2-aminobutane in potatoes in bulk fumigations can give an indication of the likely success of the treatment as well as the safety of the process. Investigation of these factors in relation to the residue contents during storage and processing has necessitated the development of a simple and sensitive analytical method for their determination.

Day *et al.*[7] described a method for steam distillation of 2-aminobutane from fruit and this was later found to be equally applicable to potatoes.[3] In the method described here distilled amine extracts are dansylated and determined using high-performance liquid chromatography (HPLC) with a fluorescence detector.

Experimental

Distillation

Take four potato tubers from the bulk sample and quarter them. Finely chop one quarter of each potato and mix the four bulked portions thoroughly. Transfer 50 g of the bulked potato sample into a 500-ml round-bottomed flask and add 50 ml of distilled water, 40 ml of 1 M calcium chloride solution, 5 g of magnesium oxide slurried with 25 ml of water and a drop of anti-foaming agent. Use a further 50 ml of water to wash down the sides of the flask. Attach a distillation head and water condenser to the flask and heat the mixture to boiling. Collect the first 70 ml of the distillate in 10 ml of 0.3 M sulphuric acid. Pour the whole into a 250-ml beaker and adjust the pH to 9.0 using 0.5 M sodium hydroxide solution. Transfer into a 100-ml calibrated flask and make up to volume with distilled water.

Derivatisation

Reagents

Borate buffer, pH 9.0. Add 12.4 g of boric acid to 100 ml of 0.1 M sodium hydroxide solution and dilute to 1 l with distilled water. Mix 85 ml of this solution with 15 ml of 0.1 M hydrochloric acid.

Dansyl chloride (*1-dimethylaminonaphthalene-5-sulphonyl chloride*). A 3 mg ml^{-1} solution in dry analytical-reagent grade acetone. Store in the dark at 0 °C.

Standard solutions of 2-aminobutane in water, 20, 40 *and* 100 μg ml^{-1}.

Solution of analytical-reagent grade aniline (0.2 g) *in analytical-reagent grade acetone* (50 ml).

Hydrochloric acid, 1 M.

Preparation of dansylated aniline stock solution

Add 1 ml of the aniline in acetone solution to 5 ml of borate buffer and 10 ml of dansyl chloride in a 100-ml calibrated flask. Shake and leave for 4 h in darkness at room temperature. Add 1 ml of 1 M hydrochloric acid to hydrolyse excess of dansyl chloride. Make up to volume with acetone and store in the dark at 0 °C. Under these conditions the dansylated aniline stock solution has been found to be stable for at least 3 months.

Preparation of dansyl 2-aminobutane standards

Mix 2-ml aliquots of the different standard solutions of 2-aminobutane with 2 ml of borate buffer and 2 ml of dansylated aniline stock solution, as an internal standard, in a 10-ml calibrated flask. Add 2 ml of dansyl chloride solution and leave for 1 h at room temperature in darkness. Destroy excess of chloride by the addition of about 0.1 ml of 1 M hydrochloric acid and make up to volume with acetone.

Dansylation of samples

Derivatise 2-ml aliquots of the sample distillates as in the previous section, adding 2 ml of dansyl aniline to each as an internal standard.

Chromatography

Set any suitable isocratic constant-flow HPLC system to deliver a de-gassed solvent mixture of methanol (doubly distilled or ultra-pure grade) and water, 65 + 35 $\% V/V$, at a flow-rate of 0.8 ml min^{-1} to a 10 cm × 4.6 mm i.d. column packed with Hypersil 5 SAS. Inject 1–20 μl aliquots of standards and samples. Measure the fluorescence of eluting peaks with a suitable fluorescence detector. A Gilson Spectra GLO fitted with a broad-band 390 mm cut-off input filter and a 460 nm cut-on output filter was used in this work. Feed the output signal to a recording integrator or recorder. Under these conditions dansylated aniline elutes at 3.2 min and dansyl 2-aminobutane at 3.9 min. Area counts or peak heights obtained for the samples are compared with those for 2-aminobutane standards using internal standards correction.

Calculation

$$\text{2-aminobutane/mg kg}^{-1} = \frac{A_p \times N_s \times V_s \times 100}{A_s \times N_p \times I \times W \times M}$$

where A_p = area count (peak height) for potato sample; A_s = area count for 1 ng of 2-aminobutane standard; N_s = area count for aniline in the standard; N_p = area count for aniline in the sample; V_s = nominal volume of derivatised solution in millilitres; I = injection volume in microlitres; W = mass of potato sample in grams; and M = volume of sample distillate taken for derivatisation in millilitres.

Results and Discussion

The rate of formation of the dansyl derivative of 2-aminobutane is shown in Fig. 1. Two solutions containing 103 and 51.5 μg ml^{-1} of 2-aminobutane were derivatised as described below. Aliquots of these solutions were taken during the reaction period and injected directly into the chromatograph. After 2 h a further 1 ml of dansyl chloride solution was added and further aliquots were taken for analysis. The amount of derivatised product reached a maximum value within 1 h and then remained constant. The addition of further dansyl chloride did not increase the relative size of the derivative peak, taking into account changes in total solution volume, compensated for by use of the internal standard. A logarithmic plot of detector response against amount of dansyl 2-aminobutane (Fig. 2) shows that a linear calibration was obtained over the range 0.5–200 ng of dansyl 2-aminobutane

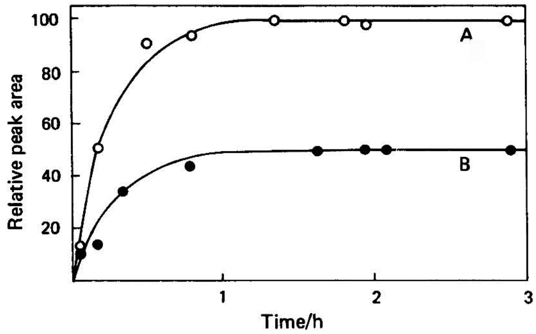


Fig. 1. Rate of dansylation of 2-aminobutane solution at room temperature: A, 103 µg ml^{-1}; and B, 51.5 µg ml^{-1}.

using either peak-area or peak-height measurements. Although no absolute standards were available, the evidence presented in Figs. 1 and 2 indicates that all the amine has reacted, or at least a very consistent percentage of it.

Both the dansyl derivatives of 2-aminobutane and that of aniline were stable for several months when stored at 0 °C in the absence of light. When two derivatised solutions from distilled potato extracts were stored for 3 months at 0–2 °C in darkness, the peak-area ratio of dansyl 2-aminobutane to internal standard changed by only 1 and 4%, respectively, over the period.

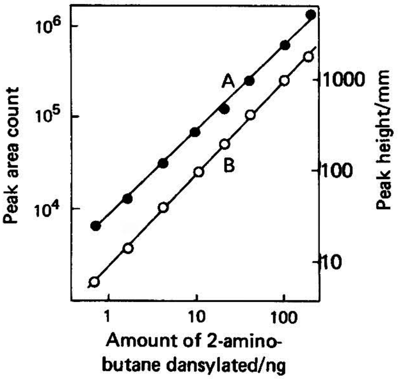
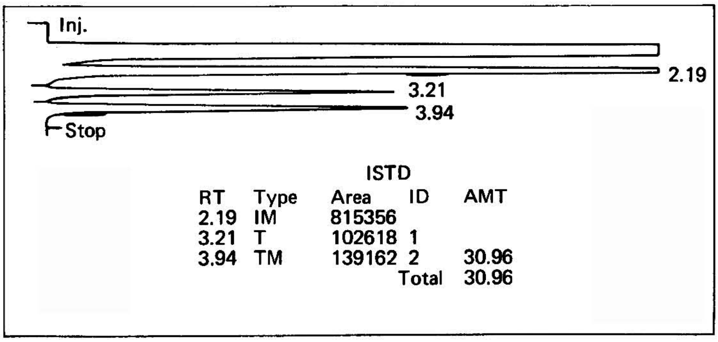


Fig. 2. Relationship between detector response and amount of 2-aminobutane dansylated: A, peak area; and B, peak height.

A print-out obtained from a computing integrator of a typical chromatogram for a derivatised sample of distilled potato extract is shown in Fig. 3. The printed report gives peak retention times (RT), the method of integration used (Type), peak area, a peak-reference number (ID) and the residue of 2-aminobutane in potatoes in milligrams per kilogram (AMT).

No additional peaks, other than that due to the 2-aminobutane derivative, are seen when compared with the pattern obtained with a sample of untreated potatoes. The peak at 2.19 min produced by both treated and untreated samples was shown to correspond, in retention time, to the dansyl derivative of ammonia (1-dimethylaminonaphthalene-5-sulphonamide). The peak heights shown represent injection of approximately 100 ng of aniline internal standard (3.21 min) and 20 ng of 2-aminobutane (3.94 min).



```
                    ISTD
RT    Type    Area    ID    AMT
2.19  IM      815356
3.21  T       102618  1
3.94  TM      139162  2     30.96
                   Total    30.96
```

Fig. 3. Reversed-phase liquid chromatography of dansylated 2-aminobutane (3.94) extracted from fumigated potatoes. Internal standard (ISTD), dansylated aniline (3.21).

Although the method as described will determine residues below 1 mg kg^{-1}, sensitivity may be further increased, if necessary, by using a larger sample of potato, *e.g.*, 100 g, by increasing the volume taken for derivatisation up to 5 ml or by evaporating the derivatised solution to dryness and re-dissolving in as little as 200 μl of methanol. Recoveries from standard solutions of 2-aminobutane through the distillation and derivatisation stages averaged 95% (Table I). This rate of recovery remained unaffected by the presence of 50 g of chopped potatoes in the distillation flask. On several occasions a further 30 ml of distillate were collected but no 2-aminobutane could be detected in this, confirming that all the compound is distilled over in the initial 70 ml, as outlined in the procedure. In further recovery experiments, 2–5 ml of 2-aminobutane in water were dripped on to 50 g of chopped potatoes in 500-ml distillation flasks. The flasks were stoppered and stored for 24 h at room temperature, after which time no excess of liquid was visible. The standard reagents were then added and the 2-aminobutane was distilled out and determined. No drop in recovery was recorded at the 5 mg kg^{-1} level and above (Table I). However, recovery was somewhat lower at the 1 mg kg^{-1} level but this might be due in part to loss of 2-aminobutane from the

TABLE I

RECOVERY OF 2-AMINOBUTANE BY DISTILLATION

2-Aminobutane added/mg	Residue equivalent/mg kg^{-1}	Recovery, %	Mean, %
Standard solutions—			
5.15	103	95.7, 92.0	93.8
4.65	3	101.0, 94.8, 91.8	95.9
2.06	43	96.2, 99.0	97.6
1.86	37	96.5, 99.9, 94.8	97.3
0.93	18.6	85.3, 89.5, 94.5	89.6
		Mean of 13 samples	94.9
Standard solutions + potatoes—			
4.65	93	98.5, 93.4, 92.4	94.8
0.93	18.6	99.9, 99.0, 90.2	96.4
0.51	10.2	92.2, 95.1, 96.5	94.6
0.256	5.1	99.9, 98.9, 93.2	97.3
0.068	1.4	94.7, 87.6, 88.2	90.2
		Mean of 15 samples	94.6
Treated potatoes—			
4.65	93	99.2, 93.5, 93.5	95.9
0.256	5.1	96.7, 95.1, 93.6	95.1
0.068	1.4	88.1, 84.0, 82.6	84.9
		Mean of 9 samples	92.0

apparatus during the treatment period. Typically, a potato sample could be prepared, distilled, derivatised and chromatographed in about 3 h and in practice 4–5 samples could be handled together.

Table II gives results showing the disappearance of 2-aminobutane from two 30-ton bulks of treated potatoes stored below 10 °C for 8 months in two metal bins. Samples were taken from three positions in each bin. In bin A the residue dropped from 24 to 2 mg kg^{-1} but in B only from 28 to 9 mg kg^{-1}. However, in A intermittent through-ventilation was carried out while in B a system using continuous re-circulation of air was in operation.

TABLE II

LOSS OF 2-AMINOBUTANE RESIDUES FROM POTATOES DURING STORAGE

		Residue/mg kg^{-1}	
Bin	Sampling position	October	June
A	1	27	2
A	2	18	1
A	3	28	3
B	4	27	11
B	5	29	7
B	6	28	9

During development of the method both normal-phase and reversed-phase systems were used. The short alkyl chain reversed-phase packing material was found to give better separation of the dansyl 2-aminobutane peak from dansyl aniline than on the octadecasilyl packing materials used. With normal-phase operation the elution order of these peaks is reversed. Reversed-phase separations were found to be more reproducible and did not suffer from the interference experienced with normal-phase packings owing to the late emergence of the peak for the sulphonamide derived from ammonia present in all distilled potato samples. Columns were found to have a long life, but were occasionally flushed out with 100% methanol to remove any impurities that had accumulated on the packing. Although dansyl derivatives also absorb in the ultraviolet region, fluorescence detection is more selective. It also gives a better signal to noise ratio and hence better sensitivity.

Conclusions

The analytical technique described provides a quick and sensitive method for determination of 2-aminobutane in distillates from potatoes. The dansylation of 2-aminobutane in acetone and water solution at pH 9.0 has been shown to be completed in 1 h at room temperature, providing the basis for a convenient analytical method for studying residues in potatoes after treatment.

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Pyrolysis - Gas Chromatography of Proline, Hydroxyproline and Related Peptides*

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On pyrolysis using a Curie point analyser at 770 °C proline and hydroxyproline (*cis*- and *trans*-) yielded as their major products a previously unreported fragment, tentatively identified as 1-pyrroline, and pyrrole, respectively. A number of dipeptides and a tripeptide containing these heterocyclic amino acids were also examined. All the degradations were found to be dependent on the pH of the solution that was examined.

Keywords: *Proline*; *hydroxyproline*; *pyrolysis - gas chromatography*; *dipeptides*

Pyrolysis - gas chromatography is increasingly being used to compare peptides and proteins as it is a convenient, direct method, avoiding the hydrolysis and derivatisation required by conventional gas - liquid chromatography (GLC).[1,2] The pyrograms formed are often complex and are used as fingerprints, few of the components being identified. As part of an investigation to examine the feasibility of identifying the amino acids in a peptide from characteristic pyrolysis fragments, we have previously examined histidine and 3-methylhistidine.[3] In this paper we report our studies on proline, *cis*- and *trans*-hydroxyproline and on a number of peptides containing these amino acids, and show that the free amino acids have distinctive pyrograms, contrary to earlier reports.

These amino-acids are of particular interest because of the presence of a high percentage of hydroxyproline in collagen and as a marker of the metabolic disorders hydroxyprolinaemia and hyperprolinaemia. As a result a range of alternative analytical methods have been reported including spectrophotometry[4,5] and gas - liquid chromatography following derivatisation.[6]

A number of previous workers have examined the pyrolysis of proline and hydroxyproline using different conditions. The first studies were by Winter and Albro, who used filament pyrolysis and reported peaks from proline corresponding to ammonia, methyl or dimethylamine and tripropylamine or benzene.[7] In 1964 Simon and Giacobbo found pyrrolidine to be the major product from proline,[8] although in a later paper both proline and hydroxyproline were reported to give similar pyrograms at 700 °C with pyrrole as the major product.[9] This conclusion was confirmed by Völlmin *et al.* in a pyrolysis - GLC/MS study.[10] If large sample sizes were used *N*-alkylpyrroles were also formed. However, in 1967 Merritt and Robertson, again using GLC - MS (gas - liquid chromatography - mass spectrometry) and a Barker - Coleman pyrolyser, reported the unique products to be pyrrole and *N*-methylpyrrole from proline and hydroxyproline, respectively.[11]

Some previous work has also been carried out on proline containing dipeptides, including glycylproline[10,11] and prolylphenylalanine,[10] and Slack[12,13] reported that low temperature (280–320 °C) pyrolysis of collagen gave a large pyrrole peak due to the presence of proline and hydroxyproline.

Experimental

Apparatus

Pyrolyses were carried out by using a Pye Unicam 104 gas chromatograph fitted with a Philips PV 4080 Curie point pyrolysis unit; except where stated iron pyrolysis wire (maintained at 770 °C for 5 s) was used. The fragments were separated on glass columns (1.5 m × 4 mm i.d.) packed with either Chromosorb 103 (100–120 mesh) at 155 °C or 10% Carbowax 20M with potassium hydroxide on Chromosorb W (100–120 mesh) at 75 °C. The carrier gas was nitrogen, flowing at a rate of 60 ml min^{-1}, and the peaks were detected by using a flame-ionisation detector at an attenuation of ×500.

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* Presented at the 5th SAC International Conference on Analytical Chemistry, Lancaster, July 20–25th, 1980.

Pyrolysis - mass spectra were measured on a direct-insertion probe Curie-point pyrolyser with VG mass spectrometer system.

Reagents

Amino-acids and dipeptides. The materials were supplied by Sigma (London) Chemical Company Ltd., Poole, Dorset.

Procedure

The pyrolysis wires were cleaned before use by heating to a red heat. The standard poly(methyl methacrylate) in acetone (1 or 2 μl, 0.1% m/V) and samples in aqueous solutions (1% m/V) were applied by use of a microlitre syringe and dried in air.

The pH values of the aqueous solutions were adjusted to 2 or 9 (pH paper) before application by using 1 M hydrochloric acid or aqueous sodium carbonate solution (10%).

Results and Discussion

Trial pyrograms suggested that although hydroxyproline yielded pyrrole, proline gave a very different pattern with a major peak similar to pyrrolidine. As these results differed from previous reports, it was decided to undertake a detailed study of these two amino acids and related compounds. In order to be able to make accurate retention time comparisons with possible pyrolysis products it was necessary to use a pyrolysable internal standard, which would yield a single major product that would be used in direct chromatograms. After a number of trials poly(methyl methacrylate) was selected, methyl methacrylate, its single major pyrolysis product,[14] having a suitable retention time on Chromosorb 103. However, it could not be dissolved in the aqueous solutions used to apply the amino acids to the Curie point wire, and was therefore applied separately in acetone.

The relative retention times of methyl methyacrylate and pyrrole, and a number of related compounds, are given in Table I. In all the following examples runs were carried out both with and without the standard in order to check that peaks were not being masked. In the limited studies using Carlowax 20M with potassium hydroxide the pyrrole peak had such a long retention time that it could not be readily observed.

Although initial studies made use of aqueous solutions of the amino acids (denoted by pH 7 in the tables) we found that adjustment of the pH to approximately 2 or 9 with hydrochloric acid or sodium carbonate solution, respectively, usually resulted in more reproducible chromatograms, particularly with the dipeptides.

TABLE I

RETENTION TIMES OF POTENTIAL PYROLYSIS FRAGMENTS FROM PROLINE AND HYDROXYPROLINE

Relative retention times (relative to methyl methacrylate).

	Column	
Compound	Chromosorb 103, 155 °C	Carbowax 20M - KOH, 75 °C
Acetaldehyde	0.13	0.23
Acetone	0.28	0.37
Acetonitrile	0.37	1.02
Pyrrolidine	1.00	0.83
3-Pyrroline	1.02	1.26
(1-Pyrroline)*	1.12	—
Pyrrole	1.91	6.27
3-Hydroxypyrrolidine	3.65	—
Methyl methacrylate†	1.00	1.00

* Major fragmentation peak from proline; tentative identification.

† Typical retention times: Chromosorb 103 6.9 min and Carbowax 20M - potassium hydroxide 5.4 min.

TABLE II

PYROGRAMS OF PROLINE AND *cis*- AND *trans*-HYDROXYPROLINE ON CHROMOSORB 103 AT 155 °C

			Peak areas of major components to pyrrole* (relative retention time†)			
Sample	Approximate pH	Number of runs	Acetonitrile (0.37)	Unknown (0.54)	Pyrroline (1.12)	Pyrrole (1.91)
Proline	2	4	12 (3)	—	469 (59)	100
	7	4	70 (8)	—	225 (23)	100
	9	4	>80	6 (1)	123 (22)	100
trans-Hydroxyproline ..	2	3	1 (1)	—	8 (4)	100
	7	6	12 (7)	—	10 (6)	100
	9	3	7 (1)	1 (<1)	1 (<1)	100
cis-Hydroxyproline	7	7	12 (7)	—	11 (3)	100
Proline + *trans*-hydroxyproline (1:1) ..	7	1	7	—	81	100
Polyhydroxyproline ..	2	3	11 (5)	2	1	100
	9	3	>20	3	3	100
	7	3	4 (1)	1	10 (2)	100

* Pyrolysis at 770 °C for 5 s (standard deviation).
† Relative to poly(methyl methacrylate) pyrolysate. Typical retention time 6.9 min.

The pyrograms of a number of runs of proline and *cis*- and *trans*-hydroxyproline are reported in Table II with typical examples given in Fig. 1. Pyrrole presumably formed by dehydration and decarboxylation was the major product from the hydroxyprolines and the orientation *cis*- or *trans*- of the hydroxy and carbonyl groups did not appear to affect the results, suggesting a lack of interaction. In all the later studies only the more readily available *trans*- form was used.

The pyrogram of proline was very different, pyrrole being a minor component (Fig. 1(*a*)). The major peak (RRT 1.12) was unexpectedly not pyrrolidine [relative retention time (RRT) 1.00], nor the commercially available 3-pyrroline (RRT 1.02), and was clearly resolved from the standard peak.

We can postulate that the expected product should be 1- or 2-pyrroline, formed by decarboxylation. However, both of these compounds are unstable as 2-pyrroline spontaneously rearranges to the 3-isomer and the 1-isomer condenses to a trimer in the liquid phase[15];

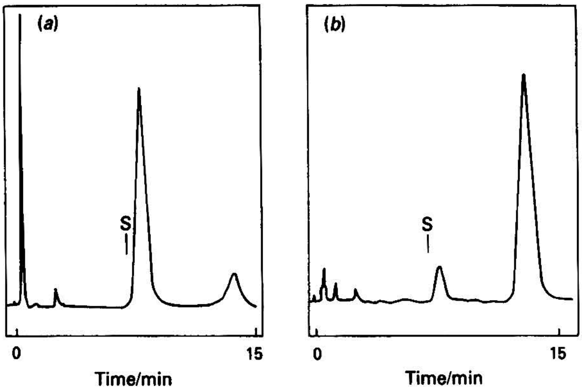

Fig. 1. Pyrograms of: (*a*), L-proline at pH 2; (*b*), L-hydroxyproline at pH 2. Sample (20 μg) pyrolysed at 770 °C for 5 s and products separated on Chromosorb 103 at 155 °C. Position of standard peak from poly(methyl methacrylate) marked by S.

thus, direct comparisons cannot be made. Electron impact mass spectrometry (EIMS) of proline yields a major fragment ion at m/z 70 corresponding to the loss of CO_2H but no peak at m/z 69 for a pyrroline,[16] although Posthumus has suggested that EIMS may be a poor guide to pyrolysis fragmentation pathways.[17] However, pyrolysis - mass spectrometry using a Curie point pyrolyser in the direct inlet source yielded a spectrum with m/z 69 (30%), 68 (21%), 67 (50%) and 41 (100%) as the major peaks, suggesting the possible presence of a pyrroline. Because of the instability of the 2-isomer to isomerisation, this peak and hence the pyrolysis - gas chromatographic product was tentatively assigned to 1-pyrroline.

The use of the solid chromatographic phase Chromosorb 103, rather than the more usual liquid phase, may be one reason why this peak from proline has not previously been observed. Confirmatory studies using a Carbowax 20M - potassium hydroxide column (Table I) were inconclusive because although 3-pyrroline (RRT 1.26) and pyrrolidine (0.83) were now separated, the only major pyrolysis peak (1.00) was unresolved from that of acetonitrile (1.02), which was also present in the pyrolysis.

The pH of the sample had little effect on the hydroxyprolines but low pH increased the proportion of 1-pyrroline from proline. The proportion and yield of the two major products from proline and hydroxyproline at different pyrolysis temperatures were determined (Table III). This determination showed a maximum yield at 770 °C, the highest temperature examined. The decrease in yield of the standard at the higher temperatures is in agreement with previous reports.[14]

Although most amino acid pyrolysis studies have been qualitative, the potential of this method for quantitative analysis was examined using the internal standard as reference (Table IV). The major peaks, 1-pyrroline from proline and pyrrole from hydroxyproline, showed a reasonable correlation with relative peak areas and suggest that with care direct pyrolysis could give satisfactory results but that further work needs to be carried out to evaluate the effects of matrices and sample application techniques.

In order to be able to use this technique to examine the composition of peptides it is necessary to determine whether the same pyrograms are obtained when these amino acids are pyrolysed as a mixture of individual compounds or when bound by peptide links. Although a mixture of proline and hydroxyproline gave a pyrogram very similar to the sum of their individual patterns, the peak assigned to the 1-pyrroline was very small in the pyrogram of prolylhydroxyproline (Table II). This is a surprising result as the prolyl ring is unsubstituted and might have been expected to behave as in the free acid. Polyhydroxyproline behaved very much as the free amino acid (Table II).

In order to explore these relationships further a series of dipeptides and one tripeptide with glycine and alanine were studied (Table V). In separate studies neither glycine nor alanine yielded peaks on pyrolysis with retention times longer than that of acetonitrile.

TABLE III

VARIATION OF PEAK AREAS OF THE MAJOR COMPONENTS OF PROLINE AND HYDROXYPROLINE WITH PYROLYSIS TEMPERATURE

Sample	Pyrolysis temperature/°C	Peak areas relative to the standard poly(methyl methacrylate) peak at 770 °C*		
		Standard	1-Pyrroline	Pyrrole
Proline	480	52	17	2
	510	105	27	3
	610	109	146	14
	770	100	202	35
trans-Hydroxyproline.. ..	358	4	1	24
	480	79	4	53
	510	90	5	61
	610	101	18	133
	770	100	18	191

* 1 μg of poly(methyl methacrylate) and 20 μg of amino acid, pH 7.

TABLE IV

QUANTITATIVE ANALYSIS OF PROLINE AND HYDROXYPROLINE*

Amino acid/μg	Proline: peak area ratio 1-pyrroline to standard	*trans*-Hydroxyproline: peak area ratio pyrrole to standard
0	0	0
5	—	1.21
5	—	1.35
10	2.65	2.09
10	2.52	1.33
15	3.85	4.24
15	4.49	4.54
20	5.57	5.31
20	4.87	5.31
Slope	0.265	0.275
Intercept	0.007	−0.208
Correlation coefficient	0.991	0.971
Standard deviation	0.281	0.504

* Pyrolysis at 770 °C for 5 s and separation on Chromosorb 103; standard poly(methyl methacrylate) (1 μg).

Glycylhydroxyproline yielded only pyrrole but the proline-containing dipeptides showed variable results, depending both on the position of the linkage and the pH of the solution. Glycylproline, alanylproline and glycylprolylalanine gave low yields of 1-pyrroline. In contrast, pyrolysis of prolylglycine and prolylalanine yielded a significant peak for 1-pyrroline. The formation of 1-pyrroline from these dipeptides was enhanced by low pH in a similar way to the fragmentation of proline (Table II). However, the results showed great variability, which was unrelated to sample storage or drying time on the wire before pyrolysis. A consistent feature of all the peptide pyrograms was an extra peak (RRT 0.54) which could not be identified.

TABLE V

PYROGRAMS OF DIPEPTIDES AND TRIPEPTIDES CONTAINING PROLINE AND HYDROXYPROLINE ON CHROMOSORB 103 AT 155 °C

			Peak areas of major components relative to pyrrole* (relative retention time†)				
Sample	Approximate pH	Number of runs	Acetonitrile (0.37)	Unknown (0.54)	Unknown (1.00)	1-Pyrroline (1.12)	Pyrrole (1.91)
Prolylglycine	2	4	84 (27)	18 (7)	—	102 (64)	100
	9	3	63 (15)	7 (1)	3 (2)	17 (13)	100
Glycylproline	2	6	39 (10)	6 (2)	—	11 (7)	100
	9	4	>64	5 (1)	1 (1)	13 (10)	100
Glycylhydroxyproline	2	4	26 (10)	4 (1)	—	0	100
	9	4	26 (2)	4 (1)	2 (1)	0	100
Prolylalanine	2	3	102 (27)	63 (10)	—	140 (98)	100
	9	4	>37	28 (32)	—	78 (74)	100
Alanylproline	2	3	>100	41 (34)	5 (5)	16 (9)	100
	9	4	>65	15 (2)	2 (1)	9 (7)	100
Glycylprolylalanine	2‡	2	>200	73	—	[52]	100
	9	5	>200	28 (14)	2 (1)	7 (3)	100

* Pyrolysis at 770 °C for 5 s (standard deviation).

† Relative to methyl methacrylate.

‡ Results poorly reproducible, peak at a relative retention time of 1.10 has an anomalous shape and is possibly not due to 1-pyrroline.

Thus, it appears that although the ratio of 1-pyrroline to pyrrole could be used to determine the proportion of proline in a mixture of free amino acids, once the proline is bound in a peptide its individuality is lost unless it is at an *N*-terminus and a low pH is used.

We thank Mr. G. Solabi for initial trials and Mr. B. B. Wheals and Mr. I. Jane of the Metropolitan Police Forensic Science Laboratory for pyrolysis - mass spectra.

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Use of a Sulphur Dioxide Gas Sensing Membrane Probe in Wines and Juices at Their Natural pH

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A sulphur dioxide gas sensing membrane probe has been used to determine the concentration of "free" sulphur dioxide in aqueous solutions of pH 3–4 in the concentration range 10^{-2}–10^{-4} mol l^{-1}. The accuracy and reproducibility suggested that this was a new non-destructive method suitable for the analysis of sulphur dioxide in juices and beverages.

Keywords: *Sulphur dioxide determination; gas sensing membrane probe; juice and beverage analysis; wine analysis*

The theory and use of gas sensing membrane probes for the determination of sulphur dioxide in solution has been previously described.[1,2] These probes use a membrane permeable to sulphur dioxide to separate a hydrogen ion sensing electrode immersed in an aqueous hydrogen sulphite solution from the aqueous sample under test. In order to elevate the concentration of sulphur dioxide in solution to its maximum, measurements are usually made at or below pH 1. This is because of the equilibria associated with the hydrolysis of sulphur dioxide in aqueous solutions [equations (1)–(3)]

$$SO_2 + H_2O \rightleftharpoons H_2O.SO_2 \quad \ldots \quad (1)$$

$$H_2O.SO_2 + H_2O \rightleftharpoons HSO_3^- + H_3O^+ \quad \ldots \quad (2)$$

$$HSO_3^- + H_2O \rightleftharpoons SO_3^{2-} + H_3O^+ \quad \ldots \quad (3)$$

Fig. 1 includes a diagrammatic representation of the proportion of the total sulphur species present that exist as molecular sulphur dioxide ($H_2O.SO_2$) at various solution pH values. For clarity, the sum of the concentrations of all sulphur species represented by equations (1)–(3) will be referred to as the S(IV) concentration.

As sulphur dioxide is a major food preservative most of the expected applications of the probe are for sulphur dioxide determinations in foodstuffs and beverages.[3,4] The adjustment of the pH to very low values makes this, of necessity, a destructive analytical method.

A sulphur dioxide sensing membrane probe offers the possibility of continuous, automatic monitoring of free sulphur dioxide in a flow system through which a beverage is being passed during its preparation. This in turn allows a constant concentration of free sulphur dioxide in the beverage to be maintained by automatic sulphur dioxide additions to the beverage flow in response to the probe signal. Measurements in the absence of added acid are therefore essential if they are to be made within the beverage flow itself.

It should be emphasised that this investigation refers only to the possibility of measuring free sulphur dioxide in beverages. The techniques for measuring bound sulphur dioxide and hence total sulphur dioxide are destructive to the sample and cannot be made otherwise by the proposed use of the probe.

The use of the sulphur dioxide probe in basic research involving aqueous sulphur dioxide solutions would be enhanced if the solution pH did not require adjustment prior to measurement. There is no theoretical reason why the sulphur dioxide probe may not operate at pH values in excess pH 1, the only limitation being the concentration of free sulphur dioxide in solution. Guthrie[5] has calculated that a solution 1×10^{-3} mol l^{-1} in hydrogen sulphite contains 8×10^{-4} mol l^{-1} of free sulphur dioxide at pH 1, which decreases to 6×10^{-6} mol l^{-1} at pH 4. A typical lower limit of detection for sulphur dioxide with the probe is about 10^{-6} mol l^{-1}.[1] An upper limit of solution pH for sulphur dioxide detection in many samples is probably 4 although this may be higher at high S(IV) concentrations. Many of the beverages and fruit juices for which the sulphur dioxide probe could be used

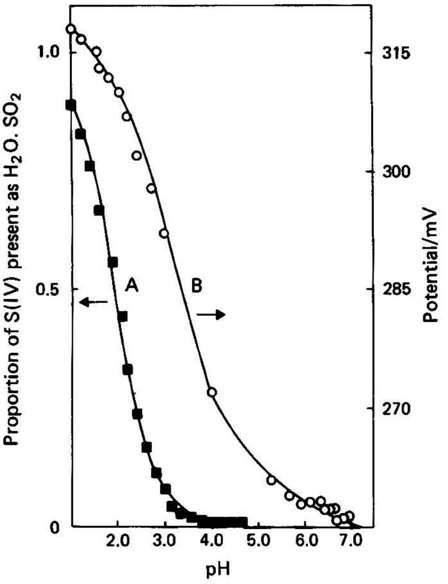

Fig. 1. Effect of pH changes on a sodium sulphate - sodium sulphite solution 0.095 mol l^{-1} in S(IV) at 33 °C (for details see text). A, Proportion of S(IV) solution present as $H_2O.SO_2$ (scale on left side of figure) and B, sulphur dioxide electrode potential (scale on right side of figure).

have a pH in the range 3–4; this upper pH limit therefore does not exclude these major areas of use. This paper describes experiments to determine the potential of a commercial sulphur dioxide sensing membrane probe for the determination of sulphur dioxide in aqueous solutions with pH values up to 4.

Experimental

Apparatus

The sulphur dioxide sensing membrane probe used was an Orion sulphur dioxide electrode, Model 95-64. This was connected to a Radiometer 26 pH meter having an expanded scale capable of being read to ±0.5 mV when operated in the millivolt detection range. All determinations were performed on 50-ml aqueous samples in a 100-ml beaker, the contents being stirred by means of a magnetic stirrer with a PTFE-coated follower. A Radiometer 28 pH meter with a combination pH electrode (Jena, Model N61) was used for all pH measurements.

Chemicals

Solutions of sulphur dioxide were prepared fresh daily from analytical-reagent grade sodium sulphite, which was standardised against a standard iodine solution. All other chemicals were of analytical-reagent grade and aqueous solutions were prepared using distilled water.

Results and Discussion

Effect of pH

A solution approximately 0.1 mol l^{-1} in S(IV) was prepared by dissolving sodium sulphite in distilled water. To 50 ml of this solution was added 1.9 g of anhydrous sodium sulphate.

The pH and potential of the sulphur dioxide probe were measured continuously as sulphuric acid was added dropwise to give the graph illustrated in Fig. 1. It can be seen that the response of the probe closely parallels the concentration of molecular sulphur dioxide in solution. A more detailed graph for the pH range 2.5–5 (Fig. 2) indicates an essentially linear relationship between potential and pH up to pH 4 in these solutions. Theory predicts[1] a linear relationship between potential and the logarithm of the sulphur dioxide concentration. When the free sulphur dioxide concentration at each pH in the S(IV) solution shown in Fig. 2 is calculated this is found to be so (Fig. 3).

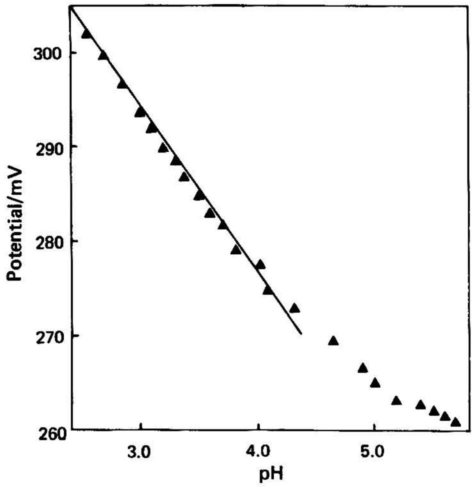

Fig. 2. Sulphur dioxide electrode potential *versus* solution pH for a 0.074 mol l^{-1} S(IV) solution at 25 °C.

The work described here was initiated to test the efficiency of the sulphur dioxide probe in the study of oenological problems. As wines are essentially aqueous solutions containing

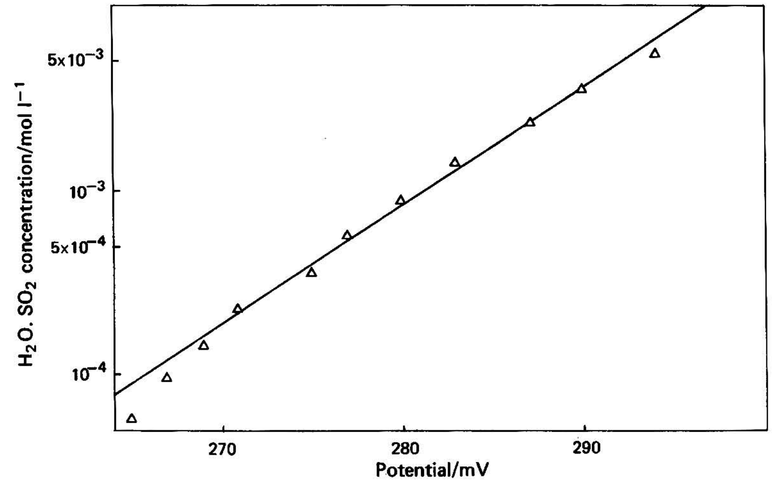

Fig. 3. Logarithm of the concentration of $H_2O.SO_2$ in a 0.074 mol l^{-1} S(IV) solution at different solution pH *versus* sulphur dioxide electrode potential at 25 °C.

approximately 10% of ethanol, such a solution was used in place of distilled water. Satisfactory probe responses were obtained with solutions of pH 2–4, containing 10^{-2} or 10^{-3} mol l^{-1} of S(IV) and 10 ± 2% of ethanol. It was also found that the addition of sodium sulphate was unnecessary, the osmotic properties of the ethanolic solutions being suitable for adequate operation of the probe. Variations in the standard graph were less than 5% for measurements in aqueous solutions containing between 8 and 12% of ethanol.

Response at Constant pH

Aqueous solutions containing 10% of ethanol were adjusted to pH 3.0 or 4.0 by the addition of sulphuric acid. Weighed portions of solid sodium sulphite were added, the pH re-adjusted to the same value and the potential of the sulphur dioxide probe recorded. Graphs of these potentials against the logarithm of the S(IV) solution concentration are shown in Fig. 4. It can be seen that these graphs are linear and that determination of S(IV) in solutions of pH as high as 4 is possible.

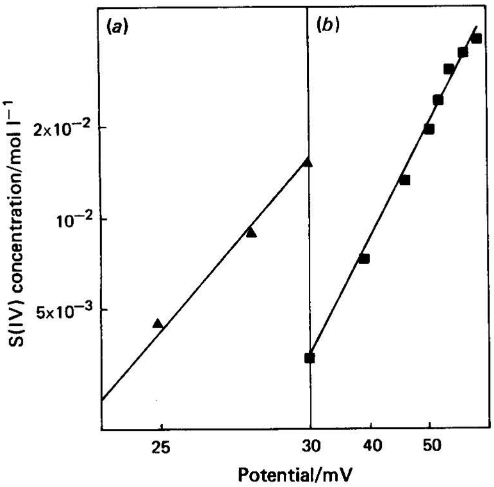

Fig. 4. Logarithm of the concentration of S(IV) in a 10% ethanol - water solution *versus* sulphur dioxide electrode potential at 25 °C when the solution pH was (*a*) 4.0 and (*b*) 3.0.

Effect of Temperature Changes

Temperature effects on the potential measured by the sulphur dioxide probe have been discussed in detail by Bailey and Riley.[2] In this work their recommendations were followed and both sample and standard measurements were made at the same temperature. Solution temperatures ranged from 20 to 35 °C with the majority of measurements being made at about 25 °C.

Response Time

The response time of a gas sensing membrane probe is an important consideration for its routine laboratory use. Ross *et al.*[1] have suggested that an adequate electrode would reach 99% of its final reading in 2–3 min, after a 10-fold increase in concentration of the species sensed. When operating in solutions of pH 3–4 our electrode required about 5 min for such a change, but never more than 10 min elapsed before a steady potential was attained. A response time of 2–3 min for a sulphur dioxide probe in solutions as dilute as 10^{-4} mol l^{-1} at pH 1 has been found.[1] It is likely that the longer response time found at pH 3–4 is directly related to the lower concentration of molecular sulphur dioxide in solution. Whether or not the longer response time at higher pH is of any consequence in routine laboratory use will depend upon the alternative methods available for the determination.

Accuracy and Reproducibility

The use of the sulphur dioxide probe for the determination of sulphur dioxide in S(IV) solutions is dependent upon the reproducibility of the electrode potential with changing pH while using the same standard S(IV) solution. In order to test this reproducibility, solutions containing 10^{-3} and 10^{-4} mol l^{-1} of S(IV) were prepared and a graph of electrode potential *versus* pH was plotted for each solution. A straight-line graph was obtained for each solution by linear regression analysis and the 95% confidence shell was constructed about each line (Fig. 5). After 4 h, fresh S(IV) solutions of the same concentration were prepared and a further scan of electrode potential *versus* pH for each solution was obtained. Fig. 5 shows that each of the new measured points falls within the 95% confidence (twice the standard error) shell about the original data obtained 4 h previously. At the 95% confidence limit, therefore, the standard graphs are reproducible.

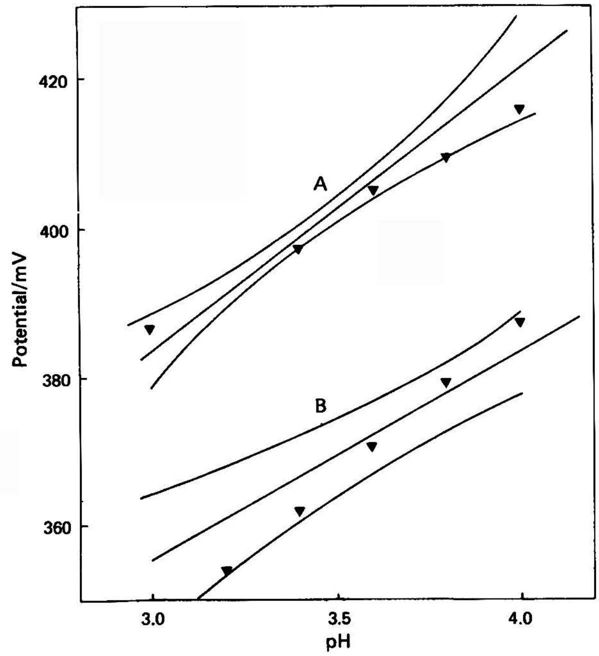

Fig. 5. Sulphur dioxide electrode potential at 25 °C *versus* solution pH for A, 10^{-4} and B, 10^{-3} mol l^{-1} of S(IV). Initial readings are represented as a straight line, obtained by linear regression analysis, surrounded by the 95% confidence limit shell. Readings obtained 4 h later are indicated by ▼.

Determination of Sulphur Dioxide in 10% Ethanol Solutions of pH 3–4

Initially the pH and potential of the sulphur dioxide probe in the unknown sample were measured. An estimate of the sulphur dioxide concentration in the sample was made and two fresh standard S(IV) solutions were prepared to bracket the estimated concentration. Each of these standards was separately tested for pH and sulphur dioxide electrode potential, as the pH was adjusted by stepwise addition of concentrated sulphuric acid, so that the unknown solution pH was bracketed. A graph of potential *versus* pH for each of the standards was plotted [Fig. 6(*a*)], enabling the potential of each standard at the unknown sample solution pH to be read off. Each of these potentials was plotted *versus* the logarithm of the S(IV) concentration [Fig. 6(*b*)] and a straight line drawn between the two points. The concentration of the unknown sulphur dioxide solution could then be obtained from the originally measured sulphur dioxide probe potential. Fig. 6 illustrates the use of this method for a wine sample of pH 3.51 with a free sulphur dioxide concentration, determined by the standard aspiration method, of 3.8×10^{-4} mol l^{-1}.

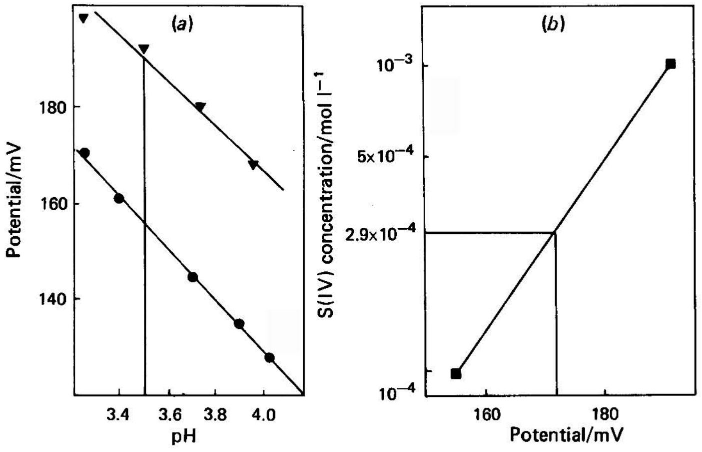

Fig. 6. (*a*) Sulphur dioxide electrode potential at 25 °C *versus* solution pH for standard S(IV) solutions of 10^{-4} and 10^{-3} mol l^{-1}. (*b*) Logarithm of S(IV) solution concentration *versus* sulphur dioxide electrode potential at pH 3.51. The wine sample had a sulphur dioxide electrode potential of 172 mV.

The method was further tested by using it to determine the S(IV) concentration arising from additions of known masses of solid sodium sulphite to a white wine. Table I shows that the sulphur dioxide electrode was able to determine the S(IV) concentration to within 5% of the known addition. Similar data were obtained with a red wine, but only after the sulphite binding capacity of the constituents of the wine had been satisfied.

The sulphur dioxide gas sensing membrane probe may thus be used for the determination of S(IV) present in aqueous solutions at concentrations above 10^{-4} mol l^{-1} and with pH values up to 4.0. The accuracy of the method is suitable for most beverage analyses and probably also for fruit juice analyses, but the response time may be a limiting factor in its routine operation.

TABLE I

ELECTRODE RESPONSE TO KNOWN S(IV) ADDITIONS TO A WHITE WINE

S(IV) added/ mol l^{-1} × 10^{-3}	Total S(IV) present/ mol l^{-1} × 10^{-3}	Measured S(IV)/ mol l^{-1} × 10^{-3}
0	2.7	2.7
3.0	5.7	5.8
5.0	7.7	7.4
6.5	9.2	8.8
8.1	10.8	10.5

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The Frequency Distribution of Analytical Error

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The widely held view that the frequency distribution of analytical error is log-normal at concentrations of analyte near the detection limit is examined in detail. It is argued that (*a*) there is no theoretical reason why such distributions should be log-normal and there is abundant evidence that they are not; (*b*) quasi-log-normal distributions can be produced as artifacts by data recording practices; and (*c*) inordinately large numbers of analytical results would be needed to distinguish a log-normal distribution from a normal distribution.

Keywords: *Analytical error*; *frequency distributions*; *normal curve*; *log-normal curve*; *chemometrics*

Statistical inference usually depends on the assumption that error conforms to a particular type of frequency distribution. It is usually assumed that analytical variation conforms to the Gaussian (normal) distribution.[1] This is a plausible assumption as the total error is made up of the combination of a large number of small independent random errors arising at the various stages of an analytical procedure. Such a combination tends to produce a normal distribution, regardless of the distribution of the individual components.

It is evident, however, that deviations from the normal distribution sometimes occur in practice, and the reasons for this have been discussed.[2,3] In brief, non-normal distributions arise when a skewed error component arising from a single stage in the analytical procedure forms a substantial proportion of the total error, or when artifacts are introduced by data recording practices. It must also be remembered that the approach of data to any continuous distribution can only be approximate, because analytical results are not a continuous variable, but have a limited digit resolution.

It is often maintained among geochemists that analytical error has a log-normal distribution,*[4] especially near the detection limit,[5] or for trace constituents generally.[6] When such claims appear in print, they seem to be unsupported by experimental evidence or cogent theoretical argument, or references to other works containing such evidence or argument. Because of its dubious provenance, and its effect on analytical thinking, the log-normal model of analytical error is examined more closely in this work.

The case against the log-normal model falls into four main areas, as follows:

(a) the log-normal model is argued by false analogy with the distribution of the concentrations of trace elements in suites of natural materials when there is, in fact, no logical connection;

(b) the log-normal model is associated with concepts of calibration and detection limit which seem to be fallacious when examined closely and which lead to data recording practices that artificially produce positively skewed distributions;

(c) genuine positively skewed distributions are wrongly identified as log-normal;

(d) inordinately large numbers of observations are required to distinguish between random samples from normal and log-normal populations with identical parameters by a statistical test.

These points will be discussed in turn.

Error Distribution and Geochemical Distribution

Frequency distributions of the concentration of a trace element in a large suite of natural samples of the same type (*e.g.*, a particular type of rock) are usually positively skewed, even when the sampling is unbiased. This is purely a feature of the samples and is not an artefact

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* A variate X is said to have a log-normal distribution when the logarithm (base e or 10) of X is normally distributed: $\log_{10}$ is used in this paper for convenience.

produced by analytical error. This type of distribution was identified as log-normal by Ahrens,[7,8] although this view has been strongly criticised by other workers.[9–13] Regardless of the arguments against it, it has become conventionally accepted that natural distributions of concentrations tend to be log-normal, and hence trace element data in geochemistry are commonly log-transformed before statistical processing.

This idea of the log-normal distribution of geochemical variation has been unjustifiably extended to analytical variation. Ahrens[5] argues that error is log-normally distributed near the detection limit because statements such as "the margin of error is 100%" are difficult to interpret. This argument is supported by an irrelevant citation of examples of positively skewed distributions of some trace element concentrations in suites of granite samples.

In fact, the two types of distribution are physically and conceptually unrelated. The connection is, perhaps, more psychological. As one author on the subject states; "one tends to think in a logarithmic manner." Additionally, because of the conventional log-transformation of trace element geochemical data, there is a tendency for workers to *want* analytical error to be log-normal also. If an originally log-normal analytical error were to be changed into a normal distribution by the transformation, then it would fulfill the theoretical requirements for an analysis of variance between geochemical variation, sampling error and analytical error, that all of the components have normal error distributions.[14]

Analytical Error, Calibration and Detection Limit

Positively skewed distributions can be produced artificially as a result of data recording practices based on an erroneous concept of detection limit. An obvious example of this is the reluctance of analysts to ascribe significance to analytical observations at or below zero. Typically, an analyst who sees a sub-zero reading on an instrument will repeat the measurement until a zero or positive result is obtained. Failing this, a zero reading will be recorded regardless. Many instruments that automatically record analytical results have hardware or software features that similarly censor negative observations. *Prima facie* this seems to be a sensible procedure: negative or even zero concentrations can hardly be conceived of as having physical reality, and must therefore be incorrect. This approach, however, overlooks the statistical nature of analytical observations. Analysts do not observe concentrations, they observe measurements of concentration. Any measurement has confidence limits, and some confidence limits on positive means may include negative values.

Fig. 1 illustrates the theoretical distribution of results obtained at low analyte concentrations by an unbiased analytical method with variance σ^2 and a normal error distribution. When the concentration (X) is zero, half of all of the observed results are less than or equal to zero. When $X = \sigma$, an average of 15.87% of observations are sub-zero. When $X = 2\sigma$ (the common definition of detection limit[1]), the proportion of sub-zero observations is still 2.27%.

Censoring values at zero concentration produces a folded normal distribution,[15] which, in some circumstances, can look to the eye very like a log-normal distribution. This may be simulated by drawing the primary results at random from the standardised normal distribution ($\mu = 0, \sigma^2 = 1$) [Fig. 2(*a*)]. This would correspond to repeated blank determinations by a method with a standard deviation of one unit. Half of the initially resulting observations are sub-zero, and are replaced by positive results from further random drawings. One hundred such untransformed results plotted as a histogram [Fig. 2(*b*)] could be mistaken on the basis of visual inspection for a log-normal distribution, as they exhibit marked positive skewness. However, log-transformation [Fig. 2(*c*)] results in a negatively skewed distribution and this difference from a normal distribution can be confirmed by using a goodness-of-fit test such as the Kolmogorov - Smirnov statistic (see below).

Censoring sub-zero observations can thus produce artificial distributions, which could be visually mistaken for log-normal in small data sets. It can also have the serious effect of underestimating analytical error by reducing the apparent range. The mean and standard deviation of the half-normal distribution derived from a normal distribution $N(0, \sigma^2)$ are $\mu_h = 0.7979\sigma$ and $\sigma^2_h = 0.3634\sigma^2$.[15] This means that a detection limit estimate based on censored data would be too low by a factor of about 0.6 ($\sqrt{0.3634}$). Thus censoring may be

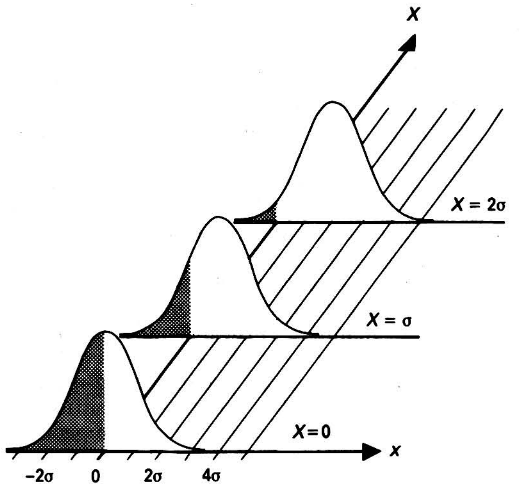


Fig. 1. Expected distribution of observations (x) for three known low analyte concentrations (X) as determined by an unbiased method with variance σ^2. Sub-zero observations are represented by the shaded parts of the curves.

one of the causes of optimistically biased detection limits, which is a serious fault in many reported analytical methods. Censoring values below the detection limit can have a similar although less marked effect.

It could be argued that the initial assumption of the normal distribution begs the question, and that log-normal distributions are more natural because they do not allow the inclusion of negative values that are *a priori* absurd. This argument is clearly refuted in practice. Negative observations are commonplace in low-level analysis, so long as some form of censoring is not applied to the results. An example of a distribution with a near-zero mean and about half of the observations negative is shown in Fig. 3.

An important fact that the log-normal argument overlooks is that all analytical methods have an in-built blank, or background, subtraction in their calibration. The observed response, whether a mass, an absorbance, an intensity or a voltage, is the difference between two measurements. Every calibration graph has a non-zero datum, rather than absolute

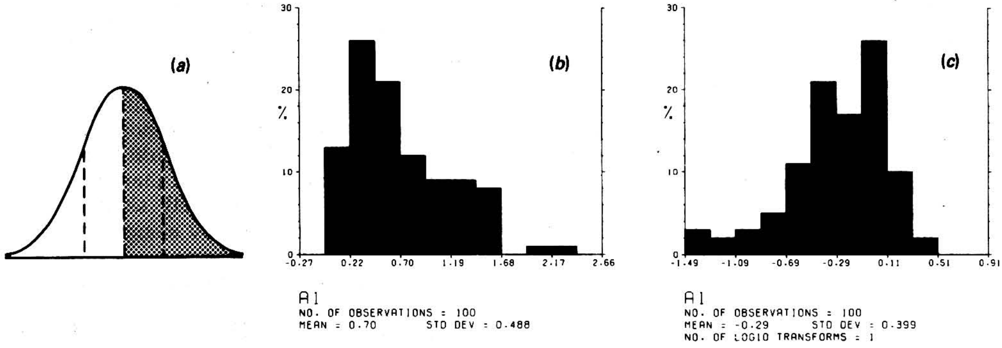


Fig. 2. A random sample drawn from the positive half of a normal distribution (a) simulates the censoring of negative observations when the analyte concentration is zero. The resulting distribution (b) is visually similar in shape to the log-normal, although the difference becomes clear after log-transformation (c).

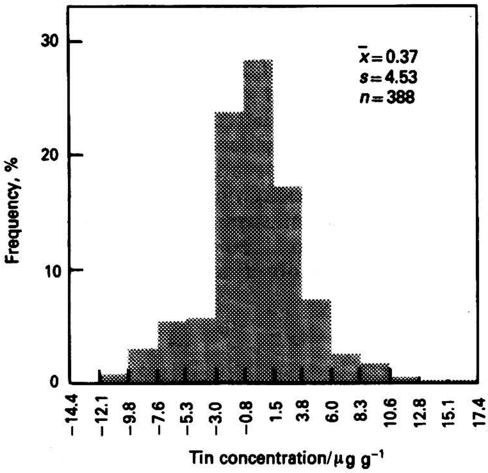


Fig. 3. Results obtained by repetitive analysis of a standard sample for tin by a direct-reading spectrographic method, with an almost symmetrical distribution centred at zero.

zero on the response axis. Calibrations that pass through the origin have had a blank subtraction previously made. The position of the intercept on the response axis is empirical; there is always error in ascertaining its mean position, there are always observations falling below its mean position and consequently the occurrence of negative estimates of concentration, which correspond to sub-datum responses, is an entirely natural phenomenon (Fig. 4).

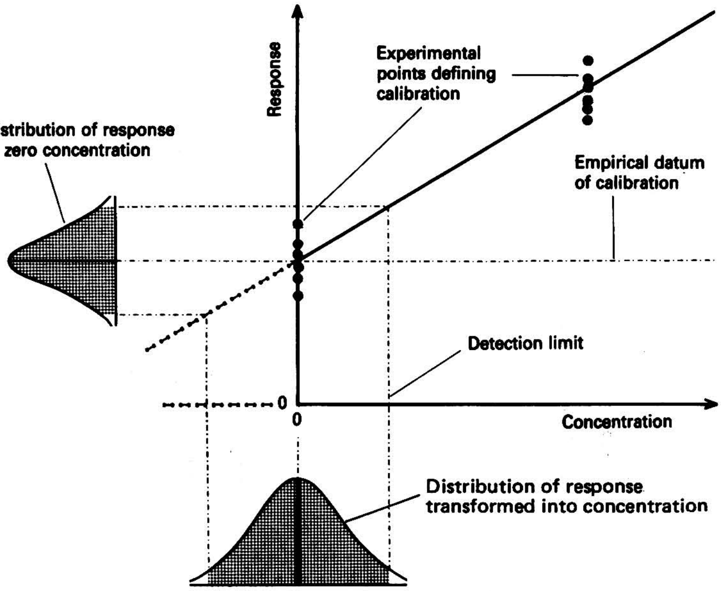
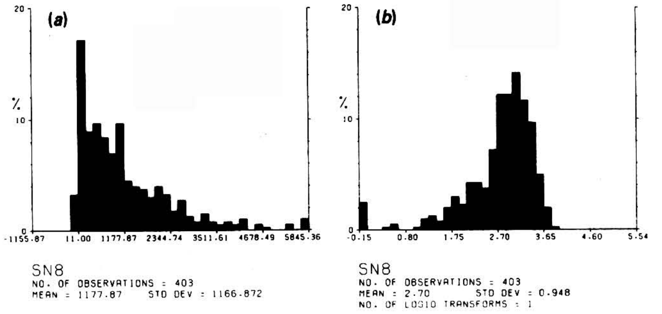


Fig. 4. A schematic calibration graph near the detection limit. The spread of points on the response axis gives rise in a natural way to negative observations on the concentration axis.

There is no validity in the argument that some calibrations (*e.g.*, spectrographic) are inherently logarithmic. The use of logarithmic axes for a calibration graph is a convention that allows several orders of magnitude of concentration to be presented visually with a uniform degree of relative precision, but it is by no means necessary. It is based on the prior assumption that the calibration is inherently linear for most of its range.[16] The use of the convention prejudices the issue: a log (concentration) axis automatically excludes the possibility of negative concentrations being read off. The use of a logarithmic response axis automatically requires that a blank or background reading has already been subtracted and also that negative differences have been suppressed. When direct-reading spectrometers are used logarithmic concentrations are avoided and, if there is no sub-zero censoring feature, symmetrical distributions with negative observations are commonplace, as in Fig. 3.



```
SN8
NO. OF OBSERVATIONS = 403
MEAN = 1177.87      STD DEV = 1166.872
```

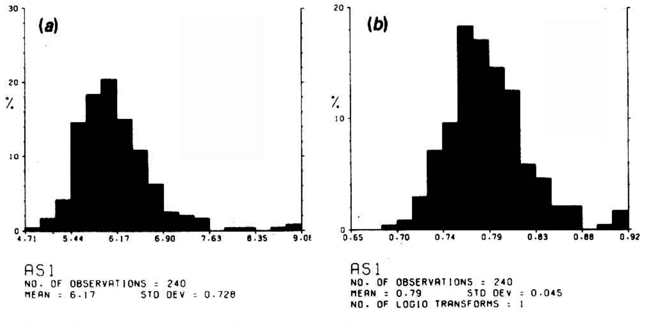
```
SN8
NO. OF OBSERVATIONS = 403
MEAN = 2.70         STD DEV = 0.948
NO. OF LOG10 TRANSFORMS = 1
```

Fig. 5. (*a*) Extremely skewed distribution produced by repetitive analysis of a standard sample for tin by a direct-reading spectrographic method. (*b*) Log-transformation of the data produces a strong negative skew. Concentrations in μg g^{-1}.

Positively Skewed Distribution Wrongly Identified as Log-normal

Genuine distributions of analytical error that are positively skewed can be encountered for a variety of reasons. Fig. 5 shows a distribution of results produced by the repeated analysis by a d.c. arc method of a standard sample for tin. In this extreme example the skew is a result of sub-sampling variations: the sample mass was small (15 mg) and the grain size of the material relatively large (—200 μm). In addition, the tin was exclusively in the grains of a separate mineral, cassiterite, which made up a small proportion of the sample. A single grain of cassiterite of maximum size could provide a tin concentration of about 2300 μg g^{-1}.*

Fig. 6 shows another example, of results obtained for arsenic on a standard sample analysed in many successive batches of samples by an inductively coupled plasma method. This



```
AS1
NO. OF OBSERVATIONS = 240
MEAN = 6.17         STD DEV = 0.728
```

```
AS1
NO. OF OBSERVATIONS = 240
MEAN = 0.79         STD DEV = 0.045
NO. OF LOG10 TRANSFORMS = 1
```

Fig. 6. (*a*) Skewed distribution of arsenic determinations produced on a standard sample by an ICPOES method. The data set is still skewed after log-transformation (*b*). Concentrations in μg g^{-1}.

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* This sub-sampling error is normally minimised by finely grinding the sample before analysis.

distribution is positively skewed mainly because of a proportion of outlying results: high "fliers" seem to be more common than low ones. Neither of these distributions corresponds closely with the log-normal; however, as can be seen from the distributions of the log-transformed data also shown. Observations far out in the positive tails are relatively much more frequent than in log-normal distributions with the same statistics.

Positively skewed results (*e.g.*, Fig. 7) are fairly common in direct-reading d.c. arc analysis of geological materials. They may be the result of non-linear calibration lines or of a systematic change in the mean value as a function of time, but again log-transformation does not make them normally distributed. Sometimes negatively skewed error distributions are observed (Fig. 8), but the reason for these remains obscure.

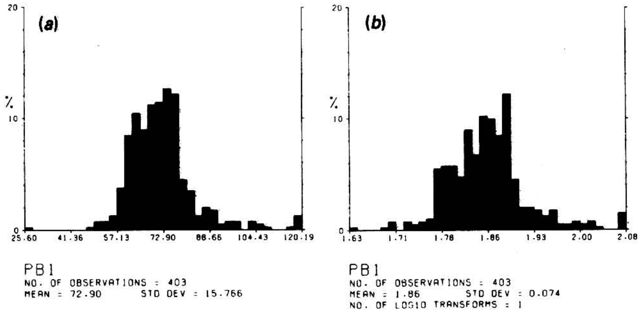

Fig. 7. (*a*) Spectrographic determinations of lead in a standard sample. The positive skew is a common feature in spectrographic data, but it is not log-normal, as shown by log-transformation (*b*). Results in µg g^{-1}.

The Problem of Distinguishing Between Normal and Log-normal Distributions

Any normal distribution is unaffected, except for scaling, by a linear transformation. Log-normal distributions, however, have different shapes depending on the coefficient of variation. At a coefficient of variation of 50%, which would be equivalent to the detection limit of an analytical method, log-normal curves are markedly positively skewed. Fig. 9(*a*) shows an ideal log-normal distribution with a coefficient of variation close to 50% and, for comparison, a normal distribution with identical parameters. The difference is clearly

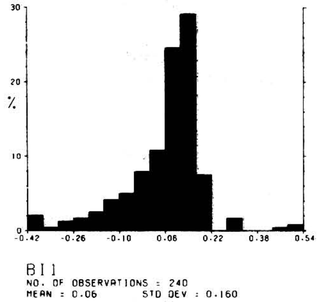

Fig. 8. A negatively skewed distribution produced by repeated analysis of a standard sample for bismuth by an ICPOES method. Results in µg g^{-1}.

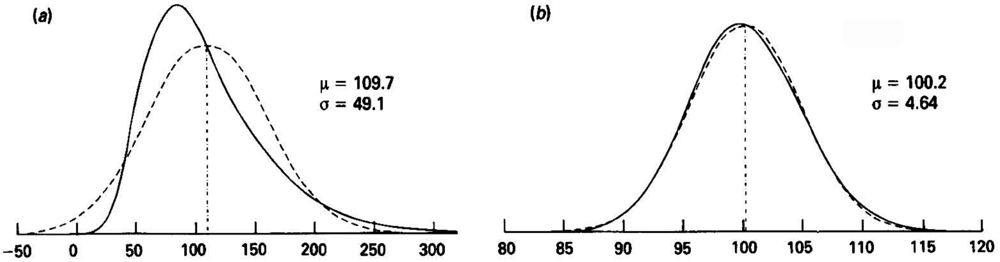

Fig. 9. (*a*) Log-normal and normal distributions with identical parameters and a coefficient of variation close to 50%. (*b*) A corresponding pair of curves with coefficient of variation close to 5%. Large "samples" are required to distinguish between the parent populations.

visible. At lower dispersions log-normal curves are much more symmetrical. Fig. 9(*b*) shows ideal normal and log-normal distributions, again with identical parameters, but with coefficient of variation close to 5%. In this instance the two curves are very close, and at lower dispersions still the two distributions resemble each other even more closely. These distributions however, represent infinite data sets, *i.e.*, "populations."

An experimentally observed distribution, on the other hand, consists of a finite (and usually small) "sample" of observations selected at random from such a population. Even "large" samples (*e.g.*, $n = 100$) tend to show only the broad-scale features of the parent distribution, so it is difficult to ascribe a "sample" to a particular type of distribution without a large number of observations.[1]

We have used the Kolmogorov - Smirnov statistic to estimate the minimum number of observations (*i.e.*, analytical replicates) in a "sample" required to enable a valid distinction at 95% confidence to be made between normal and log-normal populations with identical parameters. This has been undertaken over the range of coefficients of variation likely to be encountered in analytical practice, from 50% (at the detection limit) to 0.1%. The Kolmogorov - Smirnov statistic is the maximum difference between the cumulative frequency distributions of the two populations.[17] This maximum difference (d) has been calculated for large numbers of pairs of log-normal and normal curves with identical parameters, and related to the number of observations required to distinguish them at the 95% confidence level by means of the inequality $n > (1.22/d)^2$.

The results of this calculation are given in Table I, which shows the minimum number of observations required for a given precision. At the detection limit of a method (coefficient of variation = 50%) about 220 observations would be required, and at only slightly better precisions unrealistically large numbers of observations are needed. The Kolmogorov - Smirnov statistic is thought to be one of the most powerful tests available for distinguishing between distributions,[17] so it can reliably be deduced that very few studies have been based on sufficient data to justify the assertion that an analytical error distribution is log-normal rather than normal.

Conclusion

Experience suggests that most analytical error distributions approach the normal, but that small deviations, especially a positive skew, are common. However, there seem to be no theoretical grounds for assuming that a skewed distribution should necessarily be log-normal. It may be presumed that very few investigators would have accumulated enough data to make statistical tests that would objectively differentiate between log-normal and normal distributions. The assumption of log-normality is associated with the practice of censoring negative observations, which leads to optimistically biased estimates of detection limit. Even the assumption of normality should be regarded as no better than a useful rule-of-thumb, very likely to be invalidated by trends, "fliers" and other factors in real data sets.

TABLE I

MINIMUM NUMBER OF OBSERVATIONS REQUIRED TO DISTINGUISH BETWEEN NORMAL AND LOG-NORMAL POPULATIONS OF THE SAME ARITHMETIC MEAN AND VARIANCE BY MEANS OF THE KOLMOGOROV - SMIRNOV STATISTIC AT THE 0.05 LEVEL OF SIGNIFICANCE

Coefficient of variation, % ..	0.1	1.0	5.0	10.0	20.0	50.0	100.0
Number of observations ..	4.5×10^7	4.6×10^5	1.9×10^4	4.7×10^3	1.2×10^3	2.2×10^2	61

The analysis of variance on log-transformed geochemical data, however, is not likely to be rendered less valid by virtue of the more or less normal frequency distribution of analytical error. Only at near-detection limit concentrations are the differences between the normal and log-normal distributions marked. In any event, the effects of the violation of a different assumption (that log-transformed error is homoscedastic, *i.e.*, independent of concentration) are likely to be greater. More general transformations, such as the λ-transform of Box and Cox,[18] could be used for stabilisation of variance in an analysis of variance or regression context.[19] Alternative distribution types, such as the gamma, may be worthy of investigation, but in most applications the data will be too sparse to allow a rigorous choice between competing alternatives.

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SHORT PAPERS

Spectrophotometric Determination of Nickel with Diacetyl Monoxime Glycinimine

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Keywords: *Nickel determination*; *spectrophotometry*; *diacetyl monoxime glycinimine*

Diehl,[1] Egneus[2] and Singh *et al.*[3] have reviewed most of the dioximes available for the spectrophotometric determination of trace amounts of transition metals. Pfeiffer and Richarz[4,5] have shown that if one of the oxime groups in a dioxime is replaced with an imino or methylimino group, complex formation can occur in the same fashion. Mathur and Narang[6] used bisdiacetyl monoxime ethylenediimine and bisdiacetyl monoxime *o*-phenylenediimine as gravimetric reagents for nickel and palladium. As a result of their studies we decided to investigate oxime imines to determine their reactivity with metal ions. This paper presents the results of a study of the use of diacetyl monoxime glycinimine (BAMGI) for the spectrophotometric determination of nickel in the presence of aqueous bromine in ammoniacal medium.

Experimental

Reagents

Nickel stock solution. A 0.1 M solution was prepared by dissolving ammonium nickel sulphate (analytical-reagent grade) and was standardised by gravimetry.[7] The stock solution was diluted as required.

Concentrated ammonia solution, sp. gr. 0.91.

Saturated aqueous bromine solution. Freshly prepared.

Diacetyl monoxime glycinimine. The reagent was synthesised by condensing equimolar amounts of diacetyl monoxime and glycine on a water-bath (80–90 °C) for 3 h. The crude sample was recrystallised from aqueous ethanol (1 + 1).

Determination of the nitrogen content by Kjeldahl's method gave 17.68%; calculated for $C_6N_2O_3H_{10}$, 17.70%. The infrared spectrum (potassium bromide pellet) was as follows ($\upsilon_{max.}$, cm^{-1}): –N,OH-N (3250, b, s); –C–N (azomethine) (1650, sh); –C–N (oxime) (1475 m, s); $-COO^-$ (1400, s, s); –N–O (1160, m; 1000, s, s; 920, s, s); –CH (770, m, b; 725, m, s). The compound melts at 233–235 °C and is sparingly soluble in water and readily soluble in ethanol and acetone.

A 0.05 M solution of the reagent was prepared in aqueous ethanol (1 + 1).

Instrumentation

The absorbance was measured with a Beckman, Model B, spectrophotometer fitted with 10-mm borosilicate cells. All pH measurements were made with an Elico, Model LI-10, pH meter.

Recommended Procedure

To an aliquot of test solution containing 20–70 µg of nickel, add 2 ml of bromine solution and 1 + 1 ammonia solution dropwise until the bromine colour is discharged. Add a further 5 ml of 1 + 1 ammonia solution and 1 ml of the reagent solution. Make up the solution to 25 ml in a calibrated flask with distilled water. After 5 min, measure the absorbance at 450 nm against a reagent blank.

Results and Discussion

Absorption Spectrum

The absorption spectrum of the BAMGI complex of nickel from 320 to 625 nm was studied, and showed maximum absorbance at 420 nm. The reagent has negligible absorbance between 320 and 625 nm. All subsequent measurements were made at 420 nm against the reagent blank.

Rate of Reaction

Absorbance readings were made 2 min after the reagent solution was added and then every 5 min up to 60 min. The reaction was found to be instantaneous and after 2 min there was no appreciable increase in the absorbance.

Effect of Ammonia

The function of ammonia is to eliminate the excess of bromine and to adjust the pH. Ammonia solution (1 + 1) was added dropwise until the yellow colour due to the excess of bromine disappeared. Then a further 5 ml were added, although the colour was unaffected by using any volume between 5 and 10 ml in a total volume of 25 ml. At pH values lower than those so achieved (pH 8.5–11), the colour intensity was less and the complex faded quickly.

Amount of Reagent

For attainment of maximum absorbance the complex required a reagent concentration 3.5 times greater than that of the nickel present. Excess of the reagent has no effect on the absorbance.

Nature of the Complex

Stoicheiometry

Job's method of continuous variation showed a stoicheiometric ratio of metal to ligand of 1:3.

Migration experiment

A Hittorf-type transference cell with platinum electrodes was used to investigate the influence of electric potential on the BAMGI complex of nickel. A coloured solution 0.01 M in the nickel complex, 1 M in potassium nitrate and 0.2 M in ammonia was placed in the centre compartment with a solution 1 M in salt and 0.2 M in ammonia in the electrode compartments. The centre compartment was isolated from the electrode compartments by a medium-porosity sintered-glass disc to minimise the transference by convection. An average current of 80 mA was applied for 1 h. Ferroin was studied as the reference system under identical conditions. The nickel complex migrated in a direction opposite to that of ferroin, indicating the anionic character of the nickel complex.

Conformity to Beer's Law

The BAMGI complex of nickel followed Beer's law with solutions containing 0.24–4.1 $\mu g\ ml^{-1}$ of nickel. As the absorbance readings show minimum error between 0.2 and 0.8, the optimum concentration range of nickel is between 0.7 and 2.8 $\mu g\ ml^{-1}$ ($\equiv$ 17.5–70 μg per 25 ml).

Sensitivity

The nickel complex showed a molar absorptivity of 17000 $l\ mol^{-1}\ cm^{-1}$, corresponding to a Sandell's sensitivity of 0.0035 $\mu g\ cm^{-2}$.

The standard deviation[8] of the proposed method was 0.0055 for 1.5 $g\ ml^{-1}$ of nickel in a series of ten determinations.

Interferences

The following ions did not interfere (within ±3% error) at a concentration 300 times greater than that of nickel: acetate, arsenate, arsenite, bromide, carbonate, chloride, citrate, cyanide, fluoride, formate, iodate, lactate, nitrate, nitrite, oxalate, phosphate, sulphate, sulphite, tartrate, barium, cadmium, calcium, caesium, lead, lithium, magnesium, potassium and sodium.

Owing to the presence of an excess of ammonia, many metals precipitated, *e.g.*, aluminium, beryllium, chromium, cerium, gold, manganese, thorium and uranium, when present at high concentrations. Table I gives results obtained for the determination of 1.5 μg ml^{-1} of nickel with smaller amounts of these elements present, which could be regarded as tolerable.

TABLE I

EFFECT OF METALS ON DETERMINATION OF NICKEL

Nickel present: 1.5 μg ml^{-1}.

Element	Amount added, p.p.m. (in 25 ml)	Error, %	Element	Amount added, p.p.m. (in 25 ml)	Error, %
Na(I)	400	+0.7	Bi(III)	50	+1.7
K(I)	400	+0.8	Au(III)	50	+1.5
Ba(II)	300	+2.3	Ti(IV)	50	+1.0
Cd(II)	300	+1.5	Pt(IV)	50	+1.2
Pb(II)	300	+2.3	Pd(II)	50	+3.5
Zn(II)	300	+1.8	Cr(III)	20	+1.2
Ca(II)	300	+2.1	Cr(VI)	10	+1.5
Mg(II)	300	+2.1	Ce(IV)	10	+0.3
Al(III)	200	+2.5	Fe(III)	5	+3.0
U(VI)	50	+2.4	Co(II)	5	+1.5
Hg(II)	50	0.0	Cu(II)	5	+2.0
Ag(I)	50	+2.0	Mn(II)	5	+1.5

Analytical Applications

The reagent is suitable for the determination of nickel in alloys and biological materials. Analyses were carried out on British Chemical Standards (BCS) alloys 233 and 266. About 0.2 g of the sample was dissolved in aqua regia and evaporated until fumes of nitrogen oxides were no longer evolved. The residue was dissolved in 5–10 ml of concentrated hydrochloric acid. Silica and other acid-insoluble materials were discarded. The sample was transferred quantitatively into a Dowex 1-X8 anion-exchange resin column (J. T. Baker Chemical Co.), approximately 2 cm in diameter and 18 cm long, attached to a vacuum suction arrangement. The nickel and aluminium were eluted with 9 M hydrochloric acid (50–75 ml), excess of the acid was expelled by boiling and the solution was made up to 1000 ml in a calibrated flask. An aliquot of the solution was treated with 5 ml of 5% potassium tartrate solution, followed by bromine water, ammonia and ligand solution, as mentioned above, and the absorbance was measured at 420 nm. The two samples were also analysed by the dimethyl glyoxime method[9] (spectrophotometrically, in the presence of an oxidising agent). The results are given in Table II.

TABLE II

ANALYSIS OF BCS ALLOYS BY PROPOSED METHOD AND DIMETHYL GLYOXIME METHOD[9]

			Nickel determined, %	
Alloy	Certified nickel content, %	Other components, %	BAMGI method	Dimethyl glyoxime method
BCS 233	11.22	Co 24, Mn 0.2, Fe 51, Si 0.6, Cu 5.1, Al 7	11.2	11.2
BCS 266	13.30	Co 23.4, Mn 0.3, Fe 50, Nb 1.2, Si 0.2, Cu 3.3, Al 8	13.3	13.3

Comparison with Other Dioximes

The reagent was compared with well known dioximes such as dimethyl glyoxime, furil dioxime, heptoxime and nioxime (Table III). It is evident that BAMGI is the most sensitive reagent.

TABLE III

COMPARISON OF RESULTS OBTAINED WITH DIFFERENT OXIMES

Method	Sandell's sensitivity/ $\mu g\ cm^{-2}$ Ni $\equiv \log I_0/I = 0.001$
Dimethyl glyoxime, $CHCl_3$ extraction of Ni(II)[10]	0.0170 (375 nm)
Heptoxime, $CHCl_3$ extraction of Ni(II)[10]	0.0130 (377 nm)
α-Furil dioxime, $CHCl_3$ extraction of Ni(II)[10]	0.0040 (435 nm)
Dimethyl glyoxime + oxidising agent[10]	0.0042 (445, 465 nm)
Nioxime + oxidising agent[11]	0.0043 (410 nm)
BAMGI + oxidising agent	0.0035 (420 nm)

The author is indebted to Prof. P. B. Janardhan for guidance and for providing the facilities for this work to be carried out.

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Determination of Total Nitrogen in Plant Material with Nessler's Reagent by Continuous-flow Analysis*

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Keywords: *Plant analysis; continuous-flow analysis; Nessler's reagent; Total nitrogen determination*

The advent of continuous-flow analysis techniques and sophisticated wet digestion equipment has permitted the analysis of large series of samples. As we are involved in the study of contamination of the food chain with radionuclides, personal contamination has to be considered carefully in our Institute. This is one of the reasons for the use of continuous-flow analysis.

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On account of its sensitivity and simplicity, we preferred to work with the Nessler method, although the commonly used continuous-flow method for the determination of total nitrogen, as ammonia, in plant digests is carried out by means of the indophenol blue method as described by Shuman *et al.*[1] Among the reasons for which an analyst may choose to use the automated Nessler method in preference to the indophenol blue method are that it is not pH dependent, the reagents required are less expensive and the Nessler cartridge is less complicated because thermostabilisation of the reaction coil is not necessary. The theory and history of the Nessler reaction have been described recently by Krug *et al.*[2] Continuous-flow analysis using Nessler's reagent was difficult because of a yellow - brown precipitate in the system. The purpose of this paper is to show the suitability of the Nessler method for continuous-flow analysis when a protective agent is used to prevent the deposition of precipitates.

Experimental

Reagents

All chemicals were of analytical-reagent grade and solutions were prepared with distilled water.

Nessler's reagent. Nessler's reagent is prepared by using the commercially available Nessler A [mercury(II) potassium iodide; Merck] and Nessler B (sodium hydroxide; Merck) solutions. A 28.22-g amount of the protective agent, potassium sodium tartrate, is dissolved in 800 ml of water, then 25 ml of Nessler B solution are added and the mixture is boiled gently for 15 min. After cooling, 25 ml of Nessler A solution are added and the solution is made up to 1000 ml with water. The final concentration of potassium sodium tartrate in the Nessler reagent is 0.1 M.

Standard ammonia solution. A stock solution containing 3.50 g l^{-1} of ammonium-nitrogen is prepared by dissolving 16.52 g of ammonium sulphate in 1000 ml of water. Suitable dilutions are made in order to obtain standard solutions containing 70, 140, 210, 280 and 350 mg l^{-1} of ammonium-nitrogen and with a final concentration of sulphuric acid of 1.65 N.

Distilled water. Containing 0.1% *V/V* of Teepol (Baker).

Sodium hydroxide solution, 1.25 M. Containing 0.1% *V/V* of Brij 35 (Merck).

Wet digestion solution. Sulphuric acid (30 N) containing 6% *m/V* of salicylic acid.

Hydrogen peroxide, 30%.

Plant Samples

The plant materials used were (1) orchard leaves No. 1571 from the National Bureau of Standards (Washington, D.C.) and (2) samples of dwarf bean plants grown by hydroponic culture at this institute.

The wet digestion method described by Novozamsky *et al.*[3] was slightly modified: 0.5 g of ground dry plant material is weighed in digestion tubes (75 ml), 5 ml of digestion solution are added and a thermo-stabilised digestion block is used. Digestion is effected by pre-heating at 100 °C for 1 h and then heating at 275 °C for 2.5 h. At regular intervals 5 drops of hydrogen peroxide are added until the resulting solution remains clear at full heat (275 °C) for 15 min.

Apparatus*

A Tecator digestion block (Tecator AB, Sweden) with a capacity of 40 digestion tubes (calibrated at 75 ml with a constricted neck), identical with the arrangement described by Shuman *et al.*,[1] is used. After digestion, the samples are adjusted to volume with water, shaken and a portion is transferred into polyethylene bottles and stored in a refrigerator at 10 °C. Storage periods of over 3 weeks did not affect the ammonium content.

A flow diagram of the ammonia determination based on the Nessler reaction is depicted in Fig. 1. All manifolds for the continuous-flow analysis were obtained from Breda Scientific, Breda, The Netherlands. The sample changer (BS 34517-700) has a capacity of 40 polyethylene sample cups (1.5 ml). The reagent streams are pumped by a 24-channel peristaltic pump (BS 34510-350). The light absorption of the colloidal solution is measured by means of a power supply (BS 34516-003) and a photometer (BS 34516-200) equipped with a Hellma flow-through cuvette with a built-in de-bubbler (BS 34514-010) and a 410-nm filter (BS 34514-410S). The peaks are recorded on a lin/log recorder (BS 34195-001).

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* Names of products do not imply endorsement or preferential treatment by the Association Euratom ITAL.

Procedure

The standard ammonia solutions and plant digests are transferred to the sample changer cups. Before analysing the samples, the continuous-flow analyser is flushed with all reagents for 30 min to equilibrate the system. During this period a standard ammonia solution (140 mg l^{-1} of ammonium-nitrogen) and a wash solution (1.65 N sulphuric acid) are passed alternately. A constant absorbance reading for the standard solution indicates that the system is ready for use. The wash and sampling times are usually set at 1 min each but can be shortened so that up to 80 samples per hour can be analysed.

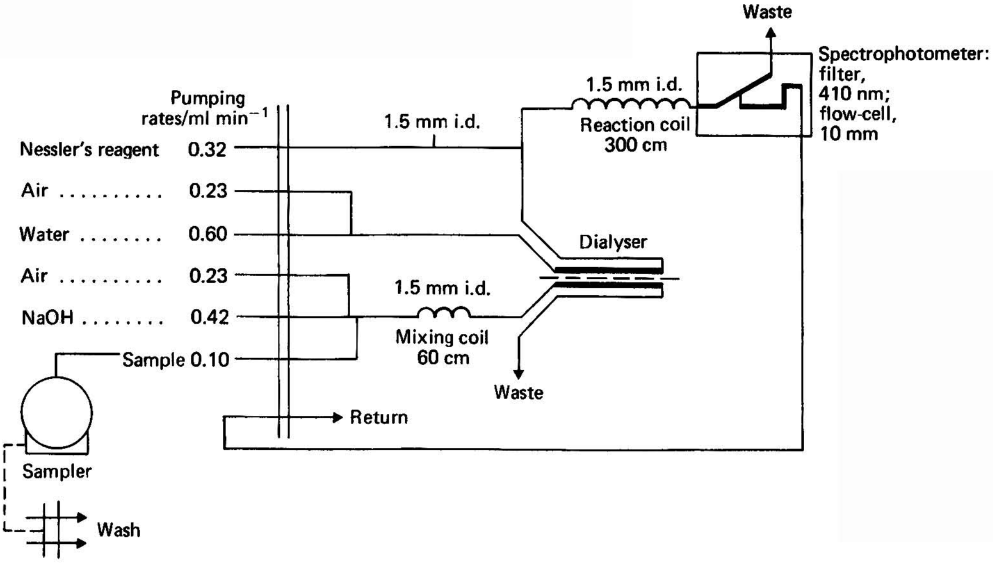

Fig. 1. Flow diagram for continuous flow analysis of ammonia using Nessler's reagent. Coil lengths are given in centimetres, internal diameters of coils and tubes in millimetres.

Results and Discussion

Dialysis Step

The high sensitivity of the Nessler method requires dilution of the plant digest in the system. A dialyser (path length 67.5 mm) is preferred to a pre-dilution step as it is much more effective in avoiding overlapping of absorbance readings. Further, calcium and magnesium, which are always present in plant digests, precipitate in the alkaline (1.25 M NaOH) understream of the dialyser and possible interference during the photometric measurement is avoided. The alkaline understream also contributes to minimising the influence of different acidities of the plant digests (see Acid Concentration of Plant Digests).

Protective Agent

Krug *et al.*[2] recently discussed an adaptation of the Nessler reaction to flow injection analysis for the determination of low ammonia concentrations (0.5–6 mg l^{-1} of ammonium-nitrogen) in water samples and soil extracts. They observed occasional deposition of a yellow - brown precipitate on the wall of the system and, in such an event, prescribed cleaning of the system with 5 M hydrochloric acid. They emphasised that it would be advantageous if a protective agent could be found that would prevent gradual deposition of precipitate. The same difficulty was encountered during our preliminary experiments. This deposition could not be avoided by modification of the flow-rates. Direct sealing of a glass T-piece to the reaction coil and preparation of Nessler's reagent, with a final concentration of potassium sodium tartrate of 0.1 M, prevented the deposition of the yellow-brown precipitate. Also, the stability of Nessler's reagent was much improved by using the tartrate solution instead of water.

Acid Concentration of Plant Digests

After digestion of the plant material, the acid concentration always differs between samples, usually varying around 1.65 N sulphuric acid. For this reason, the standard ammonia solutions are prepared with a final concentration of sulphuric acid of 1.65 N and washing is carried out with a 1.65 N sulphuric acid solution. As mentioned above, small differences in acid concentration are minimised by the alkaline understream of the dialysis step.

The influence of the acid concentration of the samples was investigated by varying the sulphuric acid concentration of the 280 mg l^{-1} ammonium-nitrogen standard solution between 1 and 2 N (increments of 0.1 N). Over this range a fairly constant absorbance reading was obtained (deviations less than 1% of the ammonium-nitrogen concentration).

Sensitivity of the Method

The sensitivity of the manifold was tested by analysing dilute ammonia solutions. It was found that the deviation from the real value is about 1% of the ammonium-nitrogen concentration in the normal concentration range (70–350 mg l^{-1}) and increases to 5% at 14 mg l^{-1} of ammonium-nitrogen.

The lowest threshold mass concentration for the arrangement depicted in Fig. 1 without changing the amplification factor is about 20 mg l^{-1} of ammonium-nitrogen, corresponding to 0.3% *m/m* of nitrogen in plant material.

Using the same manifold but with a higher amplification or a longer dialyser significantly lowers the threshold value.

Practical Application

The accuracy and reproducibility of the method are illustrated by comparing the continuous-flow method with the titration method as described by Schouwenburg and Walinga.[4] Table I gives the results obtained with both methods after digestion of different amounts of orchard leaf material. The amount of plant material digested does not influence the results significantly.

TABLE I

COMPARISON OF THE CONTINUOUS-FLOW METHOD AND THE TITRATION METHOD FOR THE DETERMINATION OF TOTAL NITROGEN IN ORCHARD LEAVES

Certified total nitrogen content, 2.76 ± 0.05% *m/m* after digestion of different masses of dry material. Mean values of total nitrogen (% *m/m*) and standard deviations (10 replicates) are given.

Tentative mass for digestion/mg	Total nitrogen, % *m/m*	
	Continuous-flow method	Titration method
300	2.72 ± 0.02	2.72 ± 0.03
400	2.75 ± 0.02	2.70 ± 0.03
500	2.73 ± 0.02	2.71 ± 0.03
600	2.74 ± 0.01	2.71 ± 0.03

Table II gives the results obtained after digestion of different plant materials (dwarf bean plants grown by hydroponic culture). These results again demonstrate the excellent numerical agreement between the two methods. The maximum absolute differences for root, leaf and fruit samples are 0.07, 0.13 and 0.20% *m/m*, respectively; the correlation coefficients are 0.98, 0.92 and 0.99, respectively.

TABLE II

COMPARISON OF THE CONTINUOUS-FLOW METHOD AND THE TITRATION METHOD FOR THE DETERMINATION OF TOTAL NITROGEN IN PLANT MATERIAL

Roots, leaves and fruits were digested separately.

	Total nitrogen, % m/m					
	Root samples		Leaf samples		Fruit samples	
Plant No.	Continuous-flow method	Titration method	Continuous-flow method	Titration method	Continuous-flow method	Titration method
1	1.67	1.61	1.22	1.20	2.22	2.19
2	1.79	1.75	1.28	1.24	1.86	1.81
3	2.11	2.17	1.43	1.40	2.01	1.97
4	2.10	2.05	1.24	1.24	1.75	1.76
5	1.89	1.84	1.37	1.36	2.09	2.07
6	1.81	1.78	1.48	1.43	2.03	2.00
7	1.58	1.52	1.22	1.09	2.14	1.94
8	2.23	2.22	1.44	1.40	2.67	2.63
9	2.11	2.06	1.31	1.32	2.74	2.72
10	1.89	1.89	1.54	1.61	2.48	2.46
11	1.82	1.89	1.52	1.51	2.3	2.45
12	2.01	1.98	1.41	1.45	2.3	2.32
13	1.96	2.00	1.21	1.29	2.58	2.59

Conclusion

The suitability of Nessler's reaction for the determination of total nitrogen in plant material, using the continuous-flow technique, has been demonstrated. The analysis is performed at a rate comparable to those usually achieved with such analytical techniques. The use of potassium sodium tartrate in Nessler's reagent prevents the gradual deposition of a yellow - brown precipitate on the walls of the apparatus. The use of a dialyser reduces the influence of slightly different acidities of the wet digests of plant samples.

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Automatic Determination of Ethylene Glycol in Anti-freeze Solutions with a Periodate-sensitive Flow-through Electrode

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Keywords: *Periodate flow-through electrode*; *automatic potentiometric analysis*; *ethylene glycol determination*; *anti-freeze solution analysis*

The response of the perchlorate ion-selective electrode toward periodate is known.[1] A detailed study of this electrode as a periodate activity sensor and its capability of monitoring periodate reactions have been reported.[2] New schemes of kinetic[3,4] and catalytic[5–7] analysis

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have been developed based on the high reactivity of periodate toward certain classes of compounds in conjuction with the capability of the perchlorate electrode to follow periodate activity during the course of these reactions.

Recently, a new type of flow-through ion-selective electrode unit operating with liquid ion exchangers has been developed in our laboratory. This electrode unit can be filled with almost any type of liquid ion exchanger, resulting in an excellent in-flow monitor for the corresponding ion, suitable for use in conjunction with automated flow systems of analysis. This paper describes the use of a periodate flow-through electrode of the aforementioned type for the determination of ethylene glycol in aqueous solutions. The analysis is completely automated and samples can be analysed at a rate of forty per hour. Amounts of ethylene glycol in the range 75–750 µg (0.4 ml of 0.003–0.03 M solution) were determined in synthetic samples with an average error of 1.9% and a coefficient of variation of 0.7%. The method has been applied to the analysis of anti-freeze solutions obtained from the cooling system of military vehicles. Comparison with the Fleury - Lange iodimetric method[8] gave satisfactory results.

Experimental

Equipment

The periodate flow-through electrode consists of a piece of porous glass (pore size 5–10 µm) with an equilateral triangular cross-section entrapped in a cylindrical time-cured plastic material (Epofyx resin, Struers Scientific Instruments, Copenhagen, Denmark). An axially drilled hole passing through the porous glass constitutes the pathway for the solution under measurement. Radially drilled holes reaching the porous glass serve as liquid ion-exchanger reservoirs. These holes are filled with small amounts (0.1–0.2 ml) of perchlorate liquid ion exchanger (Orion ClO_4^- ion exchanger, Cat. No. 92–81–01). This exchanger consists of an almost saturated solution of the complex Fe(4,7-diphenyl-1,10-phenanthroline)$_3$(ClO_4)$_2$ in 2-nitro-*p*-cymene. The porous glass is always kept wet with the liquid ion exchanger, acting as a solid support for the liquid membrane. One of the radially drilled holes is filled with 0.1 M sodium chloride - 0.1 M sodium perchlorate internal reference solution into which a silver - silver chloride wire is dipped. A detailed description of the flow-through electrode unit will be published elsewhere.[9]

The periodate-sensitive flow-through electrode is used in conjunction with a Technicon AutoAnalyzer II system consisting of a sampler and a proportioning pump. The potential of the flow-through electrode is measured against a saturated calomel electrode, and a Sargent-Welch, Model XKR, recorder is used. A Corning, Model 12, Research pH meter, acting as a voltage follower, is inserted between the electrodes and the recorder to match the high output impedance of the electrodes with the relatively low input impedance of the recorder. Fig. 1 shows a schematic diagram of the automated analysis system.

Reagents

All solutions were prepared from analytical-reagent grade materials using de-ionised, distilled water.

Sodium periodate working solution, 0.0200 M. Dissolve 4.28 g of sodium periodate in water and dilute to 1 l. This solution should be kept in an amber-glass bottle.

Composite phosphate buffer - EDTA solution, pH 7.0. Dissolve 69.0 g of sodium dihydrogen orthophosphate monhydrate ($NaH_2PO_4.H_2O$) and 7.44 g of EDTA (disodium salt) in about 800 ml of water. Adjust the pH to 7.0 with saturated sodium hydroxide solution and dilute to 1 l with water. This solution is 0.50 and 0.020 M in phosphate and EDTA, respectively.

Ethylene glycol stock solution, 0.30 M. Dissolve 18.6 g of ethylene glycol in water and dilute to 1 l. The exact titre should be determined iodimetrically with the Fleury - Lange method.[8] Standard ethylene glycol solutions of concentration 0.0030, 0.0100, 0.0200 and 0.0300 M are prepared from the stock solution by dilution.

Procedure

The samples of anti-freeze solutions are filtered through a Whatman No. 41 filter to remove particulate matter and oil spills. The filtrate is diluted to adjust its ethylene glycol concentration to the range 0.003–0.030 M (typical dilutions are 1:520 to 1:500). Sample cups are

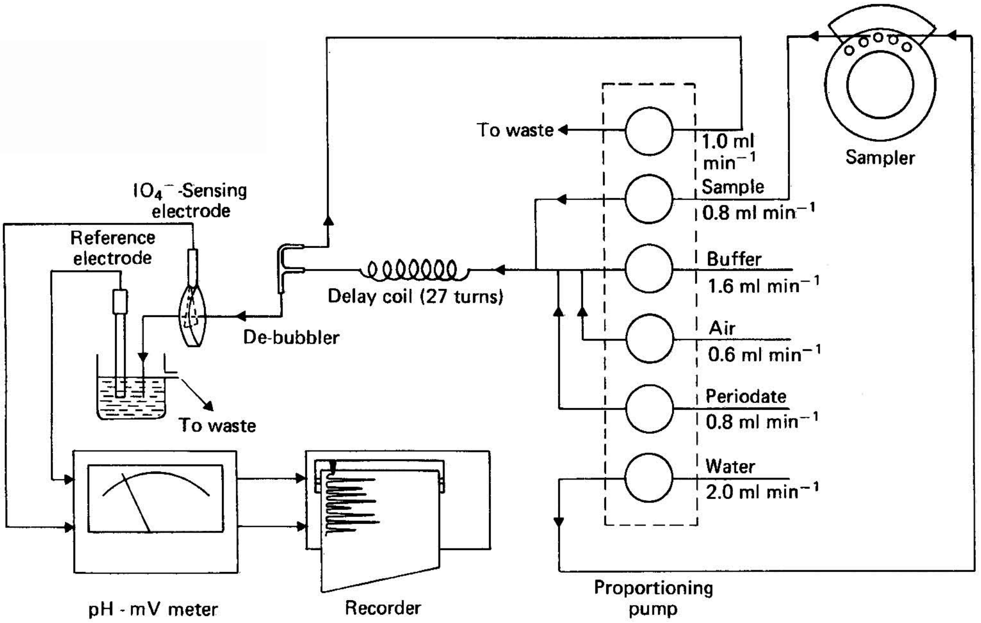

Fig. 1. Schematic diagram of automated analysis system.

filled with the samples and standard solutions. A cam is selected so as to run 40 samples per hour with a sample to wash ratio of 1:2. The instrument and the recorder are activated and he analysis proceeds automatically.

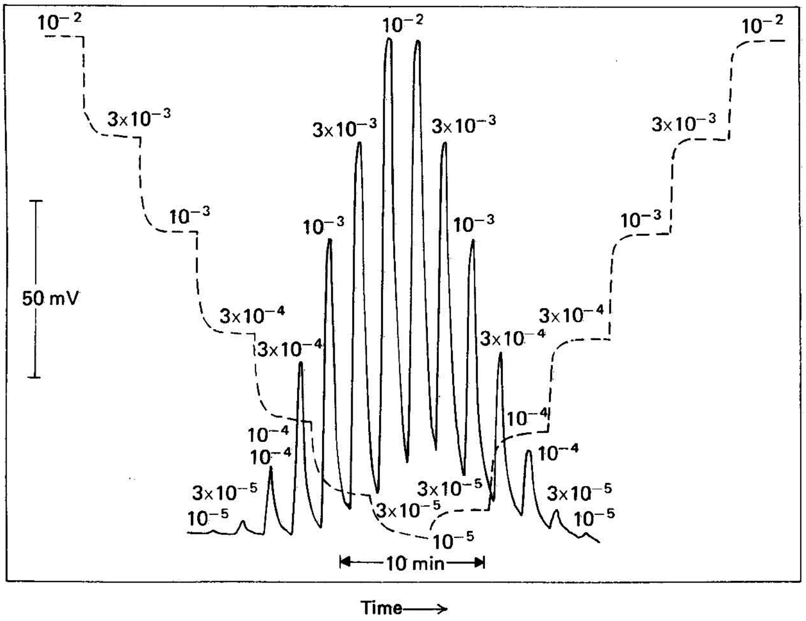

Fig. 2. Dynamic response (solid lines) and steady-state response (dashed lines) of the periodate sensitive flow-through electrode. Concentrations, in moles per litre, are shown at the corresponding peaks and plateaux.

Results and Discussion

Electrode Response

Fig. 2 shows the recorded signal (solid lines) obtained when the periodate solution of the manifold shown in Fig. 1 was replaced with water and various sodium periodate solutions were sampled (dynamic response). It should be noted that because of the dilution factor the final periodate concentration is one quarter of the initial concentration. Therefore, it is concluded from Fig. 2 that the electrode can detect periodate at concentrations of about 2.5×10^{-6} M. Fig. 2 also shows the recorded signal (broken lines) when the sampler is set permanently in the "wash" position and various sodium periodate solutions are pumped through the periodate channel (steady-state response).

The electrode steady-state potential is directly proportional to the logarithm of periodate activity at periodate concentrations down to 3×10^{-5} M, which is about the same as for the Orion 92–18 liquid membrane perchlorate electrode.[2] Steady-state potential values are equal to the dynamic peak potential values. The peak values show excellent reproducibility for initial periodate concentrations higher than 10^{-3} M.

The electrode response is stable provided that one drop of perchlorate liquid ion exchanger is added every 2–3 working days.

Calibration Graph

Calibration graphs are prepared by plotting peak-height values in millivolts against the ethylene glycol concentrations in the standard solutions. Linearity and reproducibility are improved at higher periodate concentrations, but the sensitivity is reduced. A 0.020 M initial sodium periodate concentration was chosen as a compromise.

Fig. 3 shows recorded tracings for a typical calibration sequence. It can also be seen that the final value for the 0.0010 M ethylene glycol peak is approximately equal to 93% of the steady-state value obtained under continuous sample flow conditions.

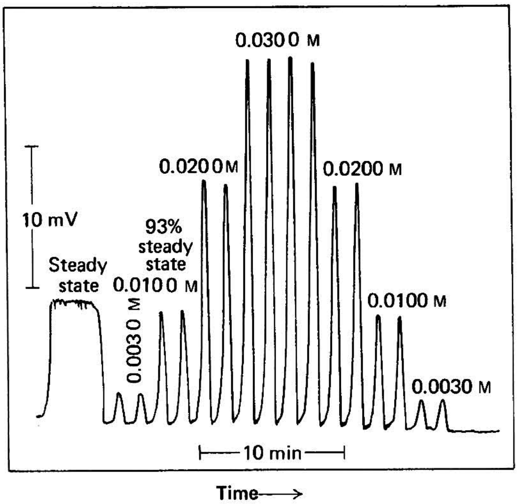

Fig. 3. Recorded tracings for a typical calibration sequence.

Effect of pH and Delay Time

pH has a moderate effect on the rate of the periodate - ethylene glycol reaction in the pH range 4–7.[3] A pH of 7.0 was chosen because at this pH higher sensitivity and better precision were observed. EDTA was added to the buffer solution to prevent reactions of periodate with other reducing substances, frequently catalysed by uncomplexed metal ions, and also the accumulation of insoluble salts in the sensing porous glass membrane of the flow-through electrode.

A delay coil with 27 turns was found to be suitable for achieving acceptable sensitivity and linear calibration graphs. The peak-height potential values obtained correspond to periodate concentrations that indicate that about 50% of the ethylene glycol is oxidised until the peak value is obtained.

Interfering Substances

Any substance that reacts with periodate would interfere and should be eliminated prior to the measurements. Peak heights relative to ethylene glycol for several interfering polyhydroxy compounds are given in Table I.

TABLE I

PEAK-POTENTIAL HEIGHTS RELATIVE TO ETHYLENE GLYCOL FOR VARIOUS INTERFERING COMPOUNDS

Compound	Peak height ratio*
Propylene glycol	1.6
Butylene glycol†	1.6
Potassium sodium tartrate.. ..	1.8
Glycerine	2.6
Glucose	5.9
Mannitol	7.3

* Ratio of peak height of interfering compound to that of ethylene glycol; all concentrations 0.0100 M.
† Mixture of *meso* and racemic form.

Precision and Accuracy

Fourteen replicate determinations were made with 0.0050 and 0.0020 M ethylene glycol solutions. The coefficients of variation were 0.78 and 0.71%, respectively. The accuracy of the method was checked with measurements on 18 samples of known ethylene glycol concentrations. The average error was 1.9%.

Analytical Application

Twenty samples of anti-freeze solution obtained from the cooling system of military vehicles were analysed according to the proposed method and also by the Fleury - Lange iodimetric method.[8] The correlation graph of both methods was linear, passing almost through the origin, with the equation $y = 1.004x + 0.27$, $r_{yx} = 0.998$ and $n = 20$ (concentration range of the samples = 0–50% m/V). There was satisfactory agreement between the results obtained with the two methods, the average relative difference of the results obtained being 1.9%.

Conclusion

The proposed method for the determination of ethylene glycol is a typical application of an ion-selective electrode in the field of automated analysis. The periodate-sensitive flow-through electrode provides an inexpensive, sensitive and reliable sensor with many possible applications in automated analytical schemes. The possible application of this electrode to the determination of other reducing substances and catalytically active species is under investigation.

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Determination of Fluoride Ions in Concentrated Sulphuric Acid with a Fluoride Ion-selective Electrode

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Keywords: *Fluoride determination*; *sulphuric acid*; *ion-selective electrode*

The manufacture of sulphuric acid usually results from thermal oxidation of sulphur compounds to sulphur dioxide and subsequent catalytic oxidation to sulphur trioxide. The lifespan of the catalyst is generally between a few years and 20 years. However, this lifespan is shortened by the presence in the gas stream of fluoride-containing compounds, which tend to break down the silicate binders of the catalyst.[1] Fluorides can be introduced into sulphur or sulphuric acid in many ways, for example during the phosphoric acid process, frequently carried out at or near sulphuric acid manufacturing sites. When phosphate rock is crushed, fluorides present in the dust can enter the sulphur product gas stream.[2] Fluorides can also be present in the raw sulphur used for acid production. The determination of fluoride in most materials requires careful separation of fluoride from the sample before measurement. In sulphuric acid this is difficult. The established method of separation is that of Willard and Winter[3,4] and requires a double distillation.[5,6] When using a solid-state fluoride ion-selective electrode a sample can be analysed quickly, simply and accurately. The need for distillation is eliminated and a large number of samples can be measured in a short period of time. Most important, accuracy is improved as possible losses during distillation are eliminated.

In acidic solution below pH 5, fluoride complexes with hydrogen to form undissociated HF and/or HF_2^-. At higher pH values, hydroxide ion interferes with the electrode response to fluoride. To avoid these undesirable effects the sample is buffered between pH 5.0 and 5.5. With sulphuric acid samples loss of fluoride during neutralisation is not a problem if the temperature is kept below that required to volatilise the hydrogen fluoride.

Experimental

Apparatus

An Orion fluoride ion-selective electrode, Model 94-09, was used with an Orion, Model 407A/L, ion-selective expanded scale meter. The reference electrode was an Orion single-junction electrode, Model 90-01, filled with equitransferent filling solution, Orion Cat. No. 90-00-01, comparable to a silver - silver chloride reference electrode.

Reagents

All chemicals used were of analytical-reagent grade. Distilled, de-ionised water was used throughout.

Standard fluoride solution. Dissolve 2.210 g of sodium fluoride in water and dilute to 1 l. This solution contains 1000 μg ml^{-1} of fluoride ion.

Total ionic-strength adjustment buffer. Dissolve 58 g of sodium chloride, 4 g of *trans*-1,2-diaminocyclohexane-*NNN'N'*-tetraacetic acid (CDTA) and 57 ml of glacial acetic acid in water and dilute to a final volume of 1 l. This solution is available commercially as TISAB II, Orion Cat. No. 94-09-11.

Sodium acetate solution, 15% *m*/*V.*

Potassium hydroxide solution, 45% *m*/*V.*

Determination of Fluoride

Because of the high salt concentration and possible hazard of neutralising large amounts of concentrated sulphuric acid, a 5.00-ml sample was chosen. This sample is combined with 45 ml of 15% *m*/*V* sodium acetate solution. TISAB II is added until the total volume is 80 ml. The solution is neutralised with 45% *m*/*V* potassium hydroxide solution and brought to the required pH, between 5.0 and 5.5. After cooling to room temperature, the sample is diluted with water to exactly 100 ml. The fluoride content is measured by immersing the electrodes directly in the sample. Readings are taken after allowing 1 min for equilibration. Readings are evaluated either by comparing the observed potential with a calibration graph obtained using solutions of known fluoride content or by a standard-addition method.

Results and Discussion

A series of samples containing known amounts of fluoride were prepared from fluoride-free, 70–80% *m*/*m* sulphuric acid and analysed for their fluoride content by the proposed method. The results are shown in Table I. Values presented in Table I were obtained using the standard-addition method with readings taken from the "Known addition" scale of the ion-selective meter. The potential response of the fluoride ion electrode to fluoride ions in 70–80% *m*/*m* sulphuric acid with increasing fluoride concentration is linear. The slope obtained from a graph of observed potential *versus* fluoride concentration is 55.5 mV from a least-squares analysis of the linear portion of the graph. This value agrees with that of the manufacturer for fluoride measurements in aqueous solutions. The theoretical slope of the graph from the Nernst equation is 59.2 mV at 25 °C. The data begin to deviate from linearity at about 1 μg ml^{-1} of fluoride ion (5.3×10^{-5} M) in concentrated sulphuric acid. The corresponding deviation in aqueous solutions begins at about 0.5 μg ml^{-1} (2.6×10^{-5} M).

TABLE I

POTENTIOMETRIC MEASUREMENT OF ADDED FLUORIDE ION IN 70–80% *m*/*m* SULPHURIC ACID

Fluoride ion added/μg ml^{-1}	2.0	5.4	6.1	7.6	9.3	9.8	15.2	19.2	48.0	99.0	200
Fluoride ion measured/μg ml^{-1}	2.0	5.3	6.2	7.6	9.3	10.0	15.3	18.9	48.0	98.7	196

The manufacturer reports a detection limit of 0.02 μg ml^{-1} of fluoride ion (1.1×10^{-6} M) for measurements in aqueous systems. In 70–80% *m*/*m* sulphuric acid the blank reading estimated from extending the potential *versus* log [F$^-$] data to zero fluoride ion concentration is about twice this value. Even though the calibration graph is not linear below 1 μg ml^{-1} of fluoride ion in sulphuric acid, concentration estimates can still be made from a calibration graph, provided that the standards from which the graph was prepared have a total acid concentration and total salt concentration approximately equal to those of the unknown solution. Different matrix conditions result in slight variations of the observed potential and, if not compensated for, erroneous fluoride ion values will be obtained from the calibration graph. The slight solubility of the electrode membrane in a sample solution is responsible for non-linear values at very low fluoride concentrations.

Table II illustrates the application of the proposed method to a series of actual samples containing known amounts of added fluoride ion. Samples 1–7 are spent sulphuric acid from a refinery aklylation process. Each sample contains approximately 90% *m*/*m* of sulphuric acid, 6% *m*/*m* of hydrocarbons and 4% *m*/*m* of water. Differences between added and measured fluoride ion content could be due in part to a slight hydrocarbon film on the electrodes after their removal from the sample. This effect is small and should be eliminated by the substitution of a small amount (5 ml) of methanol or ethanol in place of water in the final dilution step. However, the alcohol added may cause precipitation of potassium sulphate but it does not affect the fluoride concentration measurement. Samples 8–16 are technical-grade sulphuric acid, either 93 or 99% *m*/*m*. The iron content of these samples varied from 50 to 20 μg ml^{-1} for the 93 and 99% *m*/*m* acids, respectively. Iron interference is reduced by the TISAB II metal ion buffer.

Table III shows a typical range of fluoride ion concentrations present in spent sulphuric acid from various sources. Samples 1–3 are from different refinery processes. The fluoride ion content of sample 3 is greater than those from the other two sources. This may be due

TABLE II

DETERMINATION OF ADDED FLUORIDE ION IN INDUSTRIAL-GRADE SULPHURIC ACID

Sample	Fluoride ion added/μg ml^{-1}	Fluoride ion measured/μg ml^{-1}
1[*]	1.5	1.5
2	7.0	7.6
3	9.3	9.3
4	20.0	19.3
5	50.0	49.0
6	200	200
7	1000	1000
8[†]	2.0	2.0
9	5.0	5.4
10	7.0	7.6
11	10.0	10.0
12	15.0	15.3
13	20.0	19.6
14	50.0	48.0
15	100	98.7
16	200	200

[*] Samples 1–7 are approximately 90% *m/m* sulphuric acid from a refinery alkylation process.

[†] Samples 8–16 are technical-grade sulphuric acid, either 93 or 99% *m/m* and containing small amounts of iron.

TABLE III

DETERMINATION OF FLUORIDE ION IN INDUSTRIAL-GRADE SULPHURIC ACID

Sample number	1[*]	2	3	4[†]	5[‡]	6[§]	7	8
Fluoride ion content/μg ml^{-1}	0.93	0.82	2.92	0.69	1.16	1.10	0.73	1.90

[*] Samples 1–3 are approximately 90% *m/m* sulphuric acid from various refinery processes.

[†] Sample 4 is approximately 75% *m/m* sulphuric acid from an ion-exchange process.

[‡] Sample 5 is approximately 76% *m/m* sulphuric acid from reclaimed refinery acid.

[§] Samples 6–8 are 4–15% *m/m* sulphuric acid from gas scrubbers used in reclaiming spent sulphuric acid.

to the different processes employed, the first two samples being from similar manufacturing processes. Sample 4 is from an ion-exchange process and sample 5 is from re-used spent refinery acid. The remaining samples, 6–8, illustrate the amount of fluoride ion removed from gas scrubbing equipment following the thermal decomposition of spent sulphuric acid.

Conclusion

The method described permits the rapid, accurate determination of trace fluoride ion contamination in industrial sulphuric acid. The procedure is applicable to all grades and types of sulphuric acid. The procedure is simple and rapid and is recommended in place of the usual distillation procedure for fluoride determination.

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Book Reviews

AUGER ELECTRON SPECTROSCOPY. A BIBLIOGRAPHY: 1925–1975. Compiled by DONALD T. HAWKINS. Pp. viii + 11–297. IFI/Plenum. 1977. Price $54. ISBN 0 306 65168 8.

Receiving this book to review was something of a mystery for two reasons. Firstly, the book was published in 1977, and as the literature surveyed covers the period up to the end of 1975, it is thus seriously out of date in that, in the last four years, the literature in this rapidly growing field has doubled. Secondly, the first 11 or so pages of the review copy were missing, including the author's introduction and explanation of the organisation of the text and the first 220 references (out of a total of 2146).

The book consists of some 300 pp. of tarted up computer print-out divided into three main sections. The first section is sub-divided into six sections: (*i*) General Reviews and Miscellaneous (222 references); (*ii*) Theory, Physics of the Auger Effect (359 references); (*iii*) Apparatus, Technique (139 references); (*iv*) Auger Spectra of Materials, Spectral Line Energies (403 references); (*v*) Surface Analysis by Auger Spectroscopy (863 references); and (*vi*) Metallurgical Applications of Auger Spectroscopy (155 references). Each reference consists of the title, authors and source of the reference and in certain instances the language and *Chemical Abstracts* or *Science Abstracts A* reference. The second section is a permuted title index and occupies just over half of the book. The final section is an alphabetical list of all authors and takes up some 52 pp. These latter two sections have been produced by the Bell Laboratories computer system BELDEX.

Examination of our Library's copy of the book reveals that the author's introduction contains a brief explanation of the coverage and analysis of the literature (the "top" authors and journals are listed). The book undoubtedly fulfils a useful function in collating and indexing the literature, in this area, although a trend towards publication, as text books, of worker's personal computerised literature data banks is definitely not to be encouraged, a critical review is a much more valuable contribution. It is a great pity that the volume received for review was not a second volume covering 1976–1979.

J. F. TYSON

ANNUAL REPORTS ON NMR SPECTROSCOPY. Volume 9. Edited by G. A. Webb. Pp. x + 426. Academic Press. 1979. Price £25; $57.50. ISBN 0 12 505309 6.

Progress in NMR spectroscopy during the last five years has been characterised by the introduction and use of sensitive Fourier transform multinuclear spectrometers, which have facilitated routine measurements on less sensitive magnetic nuclei. These developments are reflected in the four authoritative essays contributed to this addition to a well established series of reports on NMR spectroscopy (cf., *Analyst*, 1978, **103**, 1007).

K. G. Orrell's essay (124 pp., 791 references) updates earlier reviews of the NMR spectroscopy of paramagnetic species and covers papers published between 1973 and the end of 1977. This period saw the general acceptance of paramagnetic materials as shift reagents in analytical work and as relaxation agents in biochemical studies. After a survey of the theoretical background and a discussion of applications of the technique in studies of electron distribution and bonding in transition metal complexes, organometallic compounds and free radicals, Dr. Orrell considers applications in dynamic, stereochemical and conformational problems and in studies of the formation and exchange reactions of metal complexes. He describes the use of lanthanide shift reagents in analysing strongly coupled spectra and in deducing the average solution geometries of adduct molecules, and finally, reviews biological applications of paramagnetic probes.

The upsurge of interest in chemical applications of NMR of less common, quadrupolar nuclei, which occurred during the period 1976 to mid-1978, is discussed by F. W. Wehrli (95 pp., 251 references). Quadrupolar nuclei constitute 75% of the magnetic nuclei in the Periodic Table, but because of their relaxation and line-broadening effects and as many quadrupolar nuclei have a low intrinsic NMR sensitivity, their investigation has, until recently, been restricted by the limited availability of sensitive multi-nuclear instruments. Dr. Wehrli describes the nuclear properties and chemical applications of less common, quadrupolar nuclei from each group of the Periodic Table and he shows how measurements on ionic nuclei can help to evaluate complexation and solvation equilibria. Full use of the equipment that is now available commercially should lead to new applications of NMR in inorganic, organometallic and bio-inorganic chemistry.

The NMR spectroscopy of silicon-29, a nucleus that has not been considered previously in these reports, is surveyed by E. A. Williams and J. D. Cargioli (99 pp., 252 references). Silicon-29 is a nucleus of considerable practical importance, but until the advent of sensitive Fourier transform spectrometers and of relaxation agents to shorten spin-lattice relaxation times it was a difficult nucleus to study. The authors list silicon-29 chemical shift and coupling constant values for a wide range of compounds and discuss spin-lattice relaxation and nuclear Overhauser effects.

W. McFarlane and D. S. Rycroft review advances in homo- and hetero-nuclear multiple resonance reported between 1971 and 1978 (96 pp., 570 references). After short sections on theory and instrumentation and longer ones on experimental procedures for INDOR, spin-echo and two-dimensional spectra and for the assignment of carbon-13 NMR spectra, the authors discuss the nuclear Overhauser effect, chemical exchange and chemical applications, such as the measurement of chemical shifts and the determination of the signs and magnitudes of coupling constants.

The volume maintains the high standards set by previous reports, but the subjects, which are of topical interest and indicate the direction of future developments, will be appreciated more readily by an NMR specialist than by an analytical chemist.

J. E. Page

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Notes on the Writing of Papers for *The Analyst*

Manuscripts should be in accordance with the style and usage shown in recent copies of *The Analyst.* Conciseness of expression should be aimed at: clarity is increased by adopting a logical order of presentation, with suitable paragraph or section headings.

Descriptions of new methods should be supported by experimental results showing accuracy, precision and selectivity.

The recommended order of presentation is as indicated below:

(*a*) *Title.* This should be as brief as is consistent with an adequate indication of the original features of the work. The analytical method used in the work should be mentioned in the title.

(*b*) *Synopsis.* A synopsis of about 100 words, giving the salient features and drawing attention to the novel aspects, should be provided.

(*c*) *Keywords.* Up to 5 keywords, indicating the topics of importance in the work described, should be included after the synopsis.

(*d*) *Aim of investigation.* An introductory statement of the object of the investigation with any essential historical background, followed, if necessary, by a *brief* account of preliminary experimental work.

(*e*) *Description of the experimental procedures.* Working details must be given concisely. Analytical procedures should preferably be given in the form of instructions; well known operations should not be described in detail.

(*f*) *Results.* These are best presented in tabular form, followed by any statistical evaluation, which should be in accordance with accepted practice.

(*g*) *Discussion of results.* This section will comment on the scope of the method and its validity, followed by a statement of any conclusions drawn from the work.

Nomenclature. Current internationally recognised (IUPAC) chemical nomenclature should be used. Common trivial names may be used, but should first be defined in terms of IUPAC nomenclature.

SI units. The SI system of units should be used. These units are summarised in the Appendix. The effect on current style of papers for *The Analyst* includes the following:

(*a*) dimensions should preferably be given in metres (m) or in millimetres (mm);

(*b*) temperatures should be expressed in K or °C (not °F);

(*c*) wavelengths should be expressed in nanometres (nm) (not mμ);

(*d*) frequency should be expressed in Hz (or kHz, etc.), not in c/s or c.p.s.; rotational frequency can be denoted by use of s^{-1};

(*e*) radionuclide activity will be expressed in becquerels (Bq) or curies (Ci); $1\ \text{Ci} = 3.7 \times 10^{10}\ \text{Bq}$;

(*f*) the micron (μ) will not be used; 10^{-6} m will be 1 μm.

Abbreviations. SI units should be used. Normality and molarity are generally expressed as decimal fractions (*e.g.*, 0.02 N, 0.375 M). Abbreviational full stops are omitted after the common contractions of metric units (*e.g.*, ml, g, μg, mm) and other units represented by symbols.

Abbreviations other than those of recognised units should be avoided in the text; symbols and formulae are not used instead of the names of elements and compounds in the text, but may be used in addition to names when they are necessary to avoid ambiguity, *e.g.*, to specify crystalline composition, as in $CuSO_4.5H_2O$, to show structure or in equations.

Percentage concentrations of solutions should be stated in internationally recognised terms. Thus the symbols "*m*" for mass and "*V*" for volume are to be used instead of "w" for weight and "v" for volume. The following shows the manner of expressing these percentages together with an acceptable alternative given in parentheses: % *m/m* (g per 100 g); % *m/V* (g per 100 ml); % *V/V*. Further implications of the use of the term "mass" are that "relative atomic mass" of an element (A_r) replaces atomic weight, and "relative molecular mass" of a substance (M_r) replaces molecular weight.

Concentrations of solutions of the common acids are often conveniently given as dilutions of the concentrated acids, such as "dilute hydrochloric acid (1 + 4)," which signifies 1 volume of the concentrated acid mixed with 4 volumes of water. This avoids the ambiguity of 1 : 4, which might represent either 1 + 4 or 1 + 3. Dilutions of other solutions can be expressed in a similar manner.

Tables and diagrams. The number of tables should be kept to a minimum. Column headings should be brief. Tables consisting of only two columns can often be arranged horizontally. No lines should be ruled in tables in the manuscript. Tables must be supplied with titles and be so set out as to be understandable without reference to the text.

Either tables or graphs may be used but not both for the same set of results, unless important additional information is given by so doing. The information given by a straight-line calibration graph can usually be conveyed adequately as an equation or statement in the text.

The style used in headings to tables and in labels on the axes of graphs, where the numbers represent numerical values, is, for example: Volume/ml. The diagonal line (solidus) will not be used to represent "per." In accordance with the SI system, units such as grams per millilitre are already expressed in the form g ml^{-1}. For a table (or graph), this would appear as: Concentration of solution/g ml^{-1}. It should be noted that the "combined" unit, g ml^{-1}, must not have any "intrusive" numbers. To express concentration in grams per 100 millilitres, the word "per" will still be required: Concentration/g per 100 ml. It may be preferable for an author to express concentrations in grams per litre (g l^{-1}) rather than grams per 100 ml.

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1. Wilson, H. N., and Duff, G. M. S., *Analyst*, **1967**, **92**, 723.
2. Mendoza, C. E., Wales, P. J., McLeod, H. A., and McKinley, W. P., *Analyst*, **1968**, **93**, 173.
3. Hanson, N. W., *Editor*, "Official, Standardised and Recommended Methods of Analysis," Second Edition, Society for Analytical Chemistry, London, 1974, p. 77.

For books, the edition (if not the first), the publisher and the place and date of publication should be given, followed by the volume or page number, or both if required.

Authors must, in their own interest, check their lists of references against the original papers; second-hand references are a frequent source of error. The number of references must be kept to a minimum.

Appendix

The SI System of Units

In the SI system there are seven base units—

Physical quantity	*Name of unit*	*Symbol for unit*
length	metre	m
mass	kilogram	kg
time	second	s
electric current	ampere	A
thermodynamic temperature	kelvin	K
amount of substance	mole	mol
luminous intensity	candela	cd

There are two supplementary dimensionless units for plane angle (radian, rad) and solid angle (steradian, sr). Some derived SI units that have special names are as follows—

Physical quantity	*Name of unit*	*Symbol for unit*	*Definition of unit*
energy	joule	J	$\mathrm{kg\ m^{2}\ s^{-2}}$
force	newton	N	$\mathrm{kg\ m\ s^{-2} = J\ m^{-1}}$
power	watt	W	$\mathrm{kg\ m^{2}\ s^{-3} = J\ s^{-1}}$
quantity of electricity	coulomb	C	A s
electric potential difference	volt	V	$\mathrm{kg\ m^{2}\ s^{-3}\ A^{-1} = J\ A^{-1}\ s^{-1}}$
electric resistance	ohm	Ω	$\mathrm{kg\ m^{2}\ s^{-3}\ A^{-2} = V\ A^{-1}}$
electric capacitance	farad	F	$\mathrm{A^{2}\ s^{4}\ kg^{-1}\ m^{-2} = A\ s\ V^{-1}}$
frequency	hertz	Hz	$\mathrm{s^{-1}}$
magnetic flux density (magnetic induction)	tesla	T	$\mathrm{kg\ s^{-2}\ A^{-1}}$
radionuclide activity	becquerel	Bq	$\mathrm{s^{-1}}$

Examples of other derived SI units are—

Physical quantity	*SI unit*	*Symbol for unit*
area	square metre	$\mathrm{m^{2}}$
volume	cubic metre	$\mathrm{m^{3}}$
density	kilogram per cubic metre	$\mathrm{kg\ m^{-3}}$
velocity	metre per second	$\mathrm{m\ s^{-1}}$
angular velocity	radian per second	$\mathrm{rad\ s^{-1}}$
acceleration	metre per second squared	$\mathrm{m\ s^{-2}}$
magnetic field strength	ampere per metre	$\mathrm{A\ m^{-1}}$

Certain units will be allowed in conjunction with the SI system, *e.g.*—

Physical quantity	*Name of unit*	*Symbol for unit*	*Definition of unit*
volume	litre	l	$\mathrm{10^{-3}\ m^{3} = dm^{3}}$
magnetic flux density (magnetic induction)	gauss	G	$\mathrm{10^{-4}\ T}$
temperature, *t*	degree Celsius	°C	$t/°\mathrm{C} = T/\mathrm{K} - 237.15$
radionuclide activity	curie	Ci	3.7×10^{10} Bq
energy	electronvolt	eV	1.6021×10^{-19} J

The common units of time (*e.g.*, minute, hour, day) and the angular degree (°) will continue to be used in appropriate contexts.

Decimal multiples and submultiples have the following names and symbols (for use as prefixes)—

10^{-3}	milli	m	10^{3}	kilo	k
10^{-6}	micro	μ	10^{6}	mega	M
10^{-9}	nano	n	10^{9}	giga	G
10^{-12}	pico	p	10^{12}	tera	T
			10^{15}	peta	P
			10^{18}	exa	E

Compound prefixes (*e.g.*, mμm) should not be used; 10^{-9} m = 1 nm.

Pyrolysis - Gas Chromatography of Proline, Hydroxyproline and Related Peptides

On pyrolysis using a Curie point analyser at 770 °C proline and hydroxyproline (*cis*- and *trans*-) yielded as their major products a previously unreported fragment, tentatively identified as 1-pyrroline, and pyrrole, respectively. A number of dipeptides and a tripeptide containing these heterocyclic amino acids were also examined. All the degradations were found to be dependent on the pH of the solution that was examined.

Keywords: *Proline*; *hydroxyproline*; *pyrolysis - gas chromatography*; *dipeptides*

ROGER M. SMITH, SANAA A. K. SHAWKAT and WILLIAM P. HAYES

Department of Chemistry, University of Technology, Loughborough, Leicestershire, LE11 3TU.

Analyst, 1980, **105**, 1176–1181.

Use of a Sulphur Dioxide Gas Sensing Membrane Probe in Wines and Juices at Their Natural pH

A sulphur dioxide gas sensing membrane probe has been used to determine the concentration of "free" sulphur dioxide in aqueous solutions of pH 3–4 in the concentration range 10^{-2}–10^{-4} mol l^{-1}. The accuracy and reproducibility suggested that this was a new non-destructive method suitable for the analysis of sulphur dioxide in juices and beverages.

Keywords: *Sulphur dioxide determination*; *gas sensing membrane probe*; *juice and beverage analysis*; *wine analysis*

D. J. SPEDDING and G. M. STEWART

Chemistry Department, University of Auckland, Auckland, New Zealand.

Analyst, 1980, **105**, 1182–1187.

The Frequency Distribution of Analytical Error

The widely held view that the frequency distribution of analytical error is log-normal at concentrations of analyte near the detection limit is examined in detail. It is argued that (*a*) there is no theoretical reason why such distributions should be log-normal and there is abundant evidence that they are not; (*b*) quasi-log-normal distributions can be produced as artifacts by data recording practices; and (*c*) inordinately large numbers of analytical results would be needed to distinguish a log-normal distribution from a normal distribution.

Keywords: *Analytical error*; *frequency distributions*; *normal curve*; *log-normal curve*; *chemometrics*

MICHAEL THOMPSON and RICHARD J. HOWARTH

Applied Geochemistry Research Group, Department of Geology, Imperial College of Science and Technology, London, SW7 2BP.

Analyst, 1980, **105**, 1188–1195.

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ANALYTICAL PROCEEDINGS

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Spectrophotometric Determination of Nickel with Diacetyl Monoxime Glycinimine

Short Paper

Keywords: Nickel determination; spectrophotometry; diacetyl monoxime glycinimine

P. RIYAZUDDIN

Department of Analytical Chemistry, University of Madras, A.C. College Campus, Madras 25, India.

Analyst, 1980, **105**, 1196–1199.

Determination of Total Nitrogen in Plant Material with Nessler's Reagent by Continuous-flow Analysis

Short Paper

Keywords: Plant analysis; continuous-flow analysis; Nessler's reagent; total nitrogen determination

J. H. VAN GINKEL and J. SINNAEVE

Association Euratom-ITAL, P.O. Box 48, 6700 AA Wageningen, The Netherlands.

Analyst, 1980, **105**, 1199–1203.

Automatic Determination of Ethylene Glycol in Anti-freeze Solutions with a Periodate-sensitive Flow-through Electrode

Short Paper

Keywords: Periodate flow-through electrode; automatic potentiometric analysis; ethylene glycol determination; anti-freeze solution analysis

E. P. DIAMANDIS, C. E. EFSTATHIOU and T. P. HADJIIOANNOU

Laboratory of Analytical Chemistry, University of Athens, Athens, Greece.

Analyst, 1980, **105**, 1203–1207.

Determination of Fluoride Ions in Concentrated Sulphuric Acid with a Fluoride Ion-selective Electrode

Short Paper

Keywords: Fluoride determination; sulphuric acid; ion-selective electrode

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Analyst, 1980, **105**, 1208–1210.

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December, 1980

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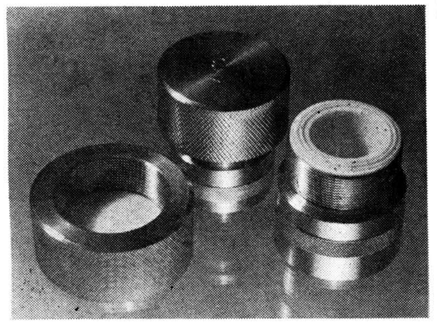

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