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A CRITICAL SURVEY OF
HYDRIDE GENERATION TECHNIQUES IN
ATOMIC SPECTROSCOPY

(Technical Report)

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Abstract - Formation of the hydrides of antimony arsenic, bismuth, germanium, lead, selenium, tellurium and tin by reaction with sodium tetrahydroborate(III) affords an excellent method for the separation of these elements as gases from a wide range of matrices. Excellent low limits of detection are attained when this separation method is combined with atomisation of the hydride in a heated quartz tube in the optical axis of a conventional atomic absorption spectrometer but there are many interferences to contend with both at the hydride generation stage and in the atomisation process. Hydride generation is also used in conjunction with ICP emission spectrometers. It is particularly useful for the determination of arsenic and selenium which suffer considerable spectral interferences caused by radicals in flame AAS. Implications of recent advances in the application of this separation procedure for the determination of hydride forming elements by atomic absorption and also ICP atomic emission spectrographic techniques are discussed.

INTRODUCTION

The hydride generation technique which makes use of a separation of the analyte element from the matrix by conversion to its volatile hydride offers a route to the trace analysis of several important elements which have specific problems when analysed by conventional methods. The first to adopt this method for atomic absorption spectroscopy was Holak (ref. 1) who used the well known Marsh reaction to generate arsine which was atomised in an air acetylene flame. Since that time there has been a tremendous interest in this technique with a flood of publications. The technique comprises several distinct processes, namely hydride generation, hydride collection (optional) and atomisation but many variations of each of these components have been reported. The technique has been the subject of several reviews (ref. 2, 3, 4, 53, 134).

ATOMIC ABSORPTION

Hydride generation-atomic absorption spectroscopy is a measurement technique which is now applied to the determination of antimony, arsenic, bismuth, germanium, lead, selenium, tellurium and tin in a wide range of matrices. For example it is used for the determination of traces of these elements in biological samples and it is used in the analysis of alloys and environmental materials. Although the preparation of samples for analysis will receive little attention in this paper it must be stressed that no measurement technique can give accurate results unless the sample preparation/digestion process quantitatively releases bound analyte element and converts it to the appropriate valency state. This is well illustrated in the recent interlaboratory trial on the determination of selenium in biological materials by hydride generation atomic absorption spectrometry (ref. 6). Laboratories following a rigorous and precisely defined decomposition regime obtained results which show excellent agreement with values established in extensive trials using a number of independent techniques. However little consideration appears to have been given to the hydride generation procedure used but rather to establishing an efficient digestion regime as the key to success. Hydride generation is especially valuable for the determination of trace levels of arsenic and selenium because the useful resonance lines of these two elements are below 200 nm, a region where there is very considerable spectral interferences from radicals in flame AAS. Other advantages include the high efficiency of analyte introduction to the atomiser, ease of concentration of the analyte, and the possibility of speciation.

Reagents

In early work hydride generation was accomplished using a wide variety of reducing agents but the facile production of hydrides by reaction with sodium tetrahydroborate(III) (sodium borohydride) (ref. 7) introduced into analytical chemistry by Braman, Justin and Foreback (ref. 8), is now almost universally used for the synthesis of hydrides. The solid reagent in pelletised form was initially favoured but introduction of a solid into a reaction gives undesirable highly localised reagent concentrations. A freshly prepared solution of sodium tetrahydroborate(III) is more efficient (ref. 9) and now preferred and also is the obvious reagent for continuous flow systems. The concentration of this reagent must be optimised for the particular analyte element and for the equipment concerned. A variety of concentrations are recommended usually 5 to 50 g L^{-1} aqueous solution made alkaline with potassium or sodium hydroxide. After filtration through a 0.45 μm membrane filter this is sufficiently stable for up to three weeks (ref. 10).

The rapid reaction between sodium tetrahydroborate(III) and hydrochloric acid may generate a troublesome foam particularly when undigested biological fluids such as urine and blood plasma are analysed. In these cases the addition of an antifoaming compound is useful. Welz and Melcher (ref. 11) recommend Antifoam 110A Emulsion (DB 110A, Dow Corning, USA) which does not form a long lasting silicone film on the surface of the reaction flask.

The purity of all reagents is important and all new reagents should be checked in blank determinations. Also regular checks for contamination and for loss of sensitivity must be included in each series of determinations. Both the hydride generation reaction and the atomisation process when using the quartz tube atomiser are easily affected by small variations in conditions and it is wise to institute a full quality assurance system. Where possible acids used in trace analysis should be purified by sub-boiling point distillation. The concentration of acid (usually hydrochloric) has a considerable effect on the yield of hydride but the optimum concentration for a particular element and matrix is best established in trials (ref. 9).

Equipment

One of the attractions of the original hydride generation method was the simplicity of the equipment which allowed the method to be used with a conventional atomic absorption spectrometer. Subsequent developments, some arising from a desire to automate the system and others to help overcome interferences or enable the ultimate in trace analysis to be accomplished, have led to a wide variety of equipment now being used. The original papers must be referred to for construction details. Several units (ref. 12, 13) are manufactured for use with standard atomic absorption spectrometers.

There are three variations of the batch type operation. In its simplest form the generated hydride and hydrogen are transported immediately to the atomiser normally in a carrier gas. In equipment of the "stopped flow" type (ref. 12) the sweep of the hydride from the reaction vessel is delayed for a few seconds to allow the generation reaction to proceed to completion but the inherent instability of the hydride must be taken into consideration when this technique is contemplated. Others use a low temperature trapping device to concentrate the hydride so that it may be transported to the atomiser without dilution with the large volume of generated hydrogen (ref. 9).

Continuous flow equipment, with peristaltic pumps for sample and reagent as in the auto-analyser systems, has been used for hydride generation both with (ref. 14) and without (ref. 13) air segmentation and the hydride has been separated with conventional gas-liquid separators (ref. 14) or by membrane separation (ref. 15). These systems have the advantage of intimate mixing of reagents with better pH control and also they appear to be much more tolerant of elements which normally interfere in the hydride generation. However they usually have a lower detection limit compared to batch systems. Sturman (ref. 13) designed a special gas liquid separator for his system in which sample, acid and sodium

tetrahydroborate(III) are mixed continually using a peristaltic pump. This method has been shown to tolerate nitric acid in the sample digest when applied to the determination of arsenic and selenium in a variety of matrices (ref. 16) and to give good analyte recoveries in the presence of many of the metals which normally interfere in hydride generation. The good control over reaction conditions using a peristaltic pump was used to generate arsine selectively from various arsenic derivatives allowing an estimation to be made for As[III], As[V], monomethylarsonic acid and dimethylarsinic acid in aqueous solution (ref. 17).

A continuous reagent flow system combined with continuous sample flow has the advantage that it provides a constant output signal as soon as equilibrium is reached. However use of the very successful and readily available flow injection type equipment has given methods in which discrete samples are introduced repeatedly with a resultant transient signal. Using this type of system Pettersson et al. (ref. 18) attained a limit of detection of 0.1 μg L^{-1} for selenium but they do report that copper will interfere if present at levels greater than about 1 mg L^{-1}. Pacey et al. (ref. 19) combined a flow injection system with intermittent sample introduction into a continuous reagent flow, microporous membrane separator with carrier gas on the outside of the membrane for hydride recovery and the Dĕdina quartz flame-in-tube type atomiser (ref. 20) in their automated system for the determination of arsenic. When determining As[V] with this equipment introduction of potassium iodide from the manifold gives the same analytical signal as that of an equivalent quantity of As[III] without potassium iodide. Others (ref. 14, 15) introduce the sample into a segmented reagent flow which is claimed to enhance sensitivity for arsenic by minimising the broadening of the sample zone. With this system the carrier gas (argon) is introduced into the reaction mixture of sample and reagents before separation in a PTFE microporous membrane tube separator. Here a short reaction time before separation of the hydride favours better tolerance to interfering elements such as copper(II) and nickel(II).

Frequent reference to the conditioning of equipment before analysing test samples would suggest that absorption of the analyte element (or derivative) on the surface of equipment is a problem. Reamer et al. (ref. 21) used ^{75}Se as a radiotracer to check adsorption. They report considerable retention of selenium hydride on polypropylene, glass and teflon (variable). Repeated treatment of glass with dimethyldichlorosilane was the most effective way to reduce these losses. Parisis and Heyndrickx (ref. 22) also report that gas transfer lines of silanised glass tubing gave the best sensitivity and reproducibility whereas silicone rubber and nylon gave poor reproducibility and variable blanks. They found that losses on untreated glass tubing decreased with time but returned on washing which obviously renewed active absorption sites. Quartz reaction vessels and traps are recommended (ref. 23) for work at very low levels of analyte concentration. All equipment must be maintained scrupulously clean and condensation of moisture on tubing surfaces must be avoided as this may give rise to peak broadening and memory effects. Rinsing the batch type generation equipment with 2 mol L^{-1} hydrochloric acid and distilled water after each determination is recommended (ref. 22).

Carrier gas

Both argon and nitrogen (less frequently) are now used as the carrier gas and under most circumstances either may be used without loss of sensitivity. However to avoid condensation of liquid argon, helium (ref. 24) or nitrogen is the preferred carrier gas when using a liquid nitrogen trap particularly if the trap is of the U tube type. A mixture of 1% V/V oxygen in argon is reported (ref. 22) to give enhanced optical absorbance compared to nitrogen. A trace of oxygen increases the efficiency of atomisation.

Desiccants

The generation of hydrides takes place with considerable effervescence and it is easy to get carryover of reagent mist into the atomiser particularly when using the batch type equipment with an immediate transfer of generated hydride to the atomiser. Condensation of water vapour and/or reagent mist on the transfer lines must be avoided because this moisture can

trap the hydride and release it slowly in the gas stream giving low results and high blank values. McDaniel et al. (ref. 9) used ^{75}Se as a radiotracer to show that anhydrous calcium chloride is effective as a desiccant and reports hydride losses no more than 4%. Other desiccants which have been used include anhydrous calcium sulfate ("Drierite"), a quartz tube cooled in a slurry of dry ice and methanol (ref. 23, 24) and sulfuric acid (ref. 25, 26) but magnesium perchlorate and silica gel cause considerable losses (ref. 24). In a continuous flow system Sturman (ref. 13) diluted the gas stream from the hydride generator with pure nitrogen to avoid condensation in the transfer lines and improve baseline stability but method sensitivity will be reduced if the volume of added nitrogen is large.

Preconcentration

The commonly described trap for the condensation of hydrides is a U tube (i.d. about 6-7 mm) cooled in liquid nitrogen (ref. 9). However the large volume of such a trap is disproportionate to the quantity of hydride being trapped and large surfaces favour adsorption losses. The trapping equipment of Piwonka, Kaiser and Tölg (ref. 24) appears to be a very significant development particularly for low analyte levels (in the pg range). Isotope tracer studies using ^{75}Se have confirmed a 99% recovery of hydrogen selenide trapped in a straight quartz tube (h. 65 mm; i.d. 3.5 mm) packed with silanised Chromosorb W which is retained by silanised quartz wool plugs. The cooling (liquid nitrogen) and heating phases of this trap have been refined further (ref. 23).

Hydride generation

Detailed studies of the hydride generation-atomic absorption technique have revealed several interference effects both in the hydride generation and in the atomisation process and it would appear that in many cases the cause of the signal change (usually a decrease) has not been attributed correctly. In general certain metals interfere in the hydride generation reaction but concomitant hydride forming elements are more likely to interfere in the atomisation process although Petrick and Krivan (ref. 27) report that the interference of bismuth and tellurium on antimony, arsenic, selenium and tin tends to occur in the hydride generation stage.

Macpherson, Sampson and Diplock (ref. 28) found no significant difference in the selenium content of biological fluids analysed by hydride generation AAS, fluorometry involving the use of 2,3-diaminonaphthalene or by electrothermal atomisation AAS. Also an interlaboratory trial (ref. 6) for the determination of selenium in serum, blood and urine has clearly demonstrated that careful experimental protocol affords results in good agreement with values established by alternative methods. In these cases the effect of any interferent element naturally present is adequately masked by the adopted procedure but many authors refer to the damaging effect of copper(II), cobalt(II) and nickel(II) on the formation of arsine (ref. 29) and hydrogen selenide (ref. 30, 31). However explanations to account for this phenomenon have been many and varied. Increasing the concentration of the sodium tetrahydroborate(III) appears to enhance the capture of hydrogen selenide by a matrix containing transition metal ions (ref. 16). and it is well documented (e.g. ref. 30, 32) that in batch type equipment selenium hydride generation in 5 mol L^{-1} hydrochloric acid is much more tolerant of interfering elements than solutions of lower acid concentrations. Also the extra reaction time afforded in equipment of the stopped flow type appears to favour good yields of hydride (ref. 12). One of the techniques least susceptible to heavy metal interference is that of McDaniel et al. (ref. 9) who used ^{75}Se radio tracer studies to show that when the sodium tetrahydroborate(III) was added over a period of 3 minutes with selenium hydride collection in a cold trap there was no interference from a wide range of cations and anions even at the 100 mg L^{-1} level. Also Åström (ref. 132) using a non segmented continuous flow system to determine bismuth, obtained improved yield of hydride by decreasing the length of the reaction coil.

Following a very detailed study of these interference effects for copper(II), cobalt(II) and nickel(II) Aggett and Hayashi (ref. 33) conclude "that the most likely cause of the interference of copper(II), cobalt(II) and nickel(II) on the analysis for arsenic by arsine generation AAS is

the formation of a specific chemical species between arsenic and the interferent in lower than normal oxidation states". A similar explanation to account for the suppression of the selenium signal by the divalent ions of copper, cobalt and nickel is proposed by Bax et al (ref. 34). Their findings indicate that the interference is not due to any appreciable extent to the divalent ions but arises from elimination of hydrogen selenide through reaction with the products formed on reduction of the respective ions with sodium tetrahydroborate(III), i.e. the metal in a lower oxidation state or a metal boride. This proposal gives an explanation for the increase in interference found at higher sodium borohydride concentrations. It also accounts for a decrease in interference with flow systems where the hydride is rapidly separated from the matrix. Further they suggest that catalysis of the decomposition of sodium tetrahydroborate (III) by metal ions or their reduction products also plays an important role in the interference. Perhaps catalysis of the decomposition of sodium tetrahydroborate(III) by iron(III), cobalt(II) and nickel(II) (ref. 35) and platinum metals (ref. 36) has not received sufficient attention from analytical chemists. The black precipitate of approximate composition Co_2B formed by reacting cobalt(II) salts with sodium tetrahydroborate(III) is a very effective catalyst for the promotion of the formation of hydrogen from sodium tetrahydroborate(III) as also are the finely divided platinum metals formed on reduction of their salts and there can be no doubt that these must be taken into account when studying interference effects.It would seem that many interferences are strongly influenced by reaction conditions. Signal suppression by transition (including platinum) metals is much less marked when the sodium tetrahydroborate(III) concentration is kept low and reagent addition is relatively slow. Also there appears to be an advantage in ensuring good mixing as in continuous flow equipment (ref. 16). Perhaps this greater tolerance to interferents arises because at no time is there an extremely high concentration of the reducing agent or its reduction products present.

Although many claim to have obtained high yields of hydrides (usually arsenic or selenium) from standard solutions at extremely low levels (e.g. 0.1 mol L^{-1}) of hydrochloric acid when using sodium tetrahydroborate(III) as the reducing agent there is considerable evidence to support the use of higher concentrations. Several studies have indicated optimum yields at acid concentrations of at least 3 mol L^{-1} and transition metal interferences are much less damaging at even higher concentrations (e.g. 4-5 mol L^{-1}) (ref. 32, 37). Welz and Melcher (ref. 38) when analysing for hydride forming elements in steels overcame the transition metal problem by adding nitric acid to the sample solution to avoid the precipitation of damaging transition metal reduction products but the presence of nitric acid in the sample solution may give rise to other problems particularly with the batch type apparatus. Continuous flow methods appear to be much more tolerant of nitric acid. Following a very comprehensive study of anions and cations on the determination of arsenic and selenium Pierce and Brown (ref. 39) report much less interference from oxidising anions including nitric acid when the sample solution is acidified before the addition of sodium tetrahydroborate(III). Brown et al. (ref. 40) believe that the nitric acid problem is really due to oxides of nitrogen arising from reduction products of nitric acid which is frequently used in the decomposition of organic materials by acids. They found oxides of nitrogen present in a cryogenic trap used for hydride collection but overcame the problem by adding a large excess of sulfamic acid to the sample digest. Agterdenbos et al. (ref. 41) also report the successful use of sulfamic acid to eliminate "nitric acid" interferences when determining selenium in coal wastes. They report that halide enhances the generation of hydrogen selenide. Their values for selenium in sample solutions containing only sulfuric or nitric acid were lower than those obtained from solutions containing hydrochloric acid but if either chloride or bromide was added to the sulfuric or nitric acid containing sample solutions then absorbances similar to those in the presence of hydrochloric acid were obtained.

There are many reported examples of the use of separation techniques to eliminate interferences. In order to be able to recognise possible matrix effects it is essential to analyse certified reference materials to check the validity of equipment and protocol for a particular application. The method of standard additions will also assist in locating matrix effects. Branch and Hutchison (ref. 42) found their system to give results for arsenic and selenium consistent with those obtained by other spectroscopic techniques when analysing geological materials for

arsenic and selenium, but others (ref. 43) have found it necessary to remove copper(II) and nickel(II) by absorption on a chelating resin column when determining arsenic and selenium in copper and nickel powders. In a method (ref. 44) which is claimed to give improved sensitivity and eliminate interferences for the determination of lead in steels and air particulates lead(II) is separated as its pyrrolidine-1-carbodithioate in chloroform and the hydride is generated from this extract by reaction with sodium tetrahydroborate(III) in dimethylformamide. The same method has also been applied to the determination of antimony in steels (ref. 45). Lanthanum chloride and ammonia have been used to precipitate the salts of arsenic and selenium to effect a separation of these elements from interferents in a coal digest (ref. 46) and Maher (ref. 47) has applied a similar interferent removal technique for the determination of tin in marine organisms. The filtrate is discarded and the precipitated analytes are then redissolved and determined by conventional hydride generation techniques.

The complexing reagent thiourea has been shown to be effective in reducing the interference of copper(II) on selenium determinations in zinc-copper-lead ores (ref. 48) but adding a further potential interferent such as iron(III) (ref. 49, 50, 51) or tellurium(IV) (ref. 52) to suppress this effect is likely to have restricted application and introduce further complications. Addition of cystine to the sample solution is another method which has been used to reduce the effect of transition and platinum metals on the generation of hydrides when determining arsenic in steels (ref. 53) or tin (ref. 54).

Hydride atomisation

The useful resonance lines for arsenic and selenium are below 200 nm in a region where interferences from flame radical absorption is very damaging. Even radicals from the relatively transparent nitrogen (or argon)/hydrogen entrained air flame give rise to considerable absorption in this area and also its low temperature leaves many molecular species in the flame. The heated quartz tube (ref. 55) avoids many of the disadvantages of the flames and gives considerable signal enhancement. However those who have studied the heated quartz tube atomisation process in detail are aware that there are also many problems associated with the use of this simple device particularly when dealing with solutions containing more than one hydride forming element.

It was initially believed that atomisation arose from thermal decomposition of the hydride but this is extremely unlikely at temperatures around 800-1000 °C which are normally attained in the quartz tube. Those who use carbon furnace atomisation recommend a temperature of about 2000°C for the decomposition of hydrides (ref. 9, 56). The many reports of signal suppression due to devitrification of the quartz tube (ref. 32), to the sensitive catalytic surface on the quartz tube (ref. 57), to conditioning the equipment before use and to the damaging effect of dust on the atomisation process suggest that the mechanism is a catalytic one. Also the atomisation process is readily quenched by the presence of a trace of organic solvent vapour (ref. 58). Most of these phenomena can be explained by a mechanism involving hydride decomposition catalysed by radicals generated in the system such as that proposed by Dědina and Rubeška to account for atomisation of selenium hydride in a cool hydrogen-oxygen flame entering a quartz tube (ref. 20). The significance of this hydrogen radical mechanism with reference to the reaction in a quartz tube atomiser was noted by Welz and Melcher (ref. 59) who made an in depth study of the atomisation process. They find that hydrogen is an essential component in the quartz tube atomisation reaction. At 900 °C pure arsine in argon gives no absorption but the expected absorption is obtained if hydrogen is introduced into the carrier gas. Also the decomposition of the hydride is assisted by the presence of a small amount of oxygen (ref. 22, 29). It would appear that in the thermal decomposition reaction in the absence of hydrogen As_2 and As_4 are formed and retained as a deposit near the ends of the heated quartz tube but this material is largely atomised as soon as hydrogen is introduced into the gas stream (ref. 60). Antimony, bismuth, selenium and tin appear to behave similarly. Revolatilisation of the deposit and subsequent atomisation is unlikely to be accomplished by molecular hydrogen but it could be accounted for by a mechanism involving hydrogen radicals. The role of radicals and oxygen in the atomisation

process has recently come under further study by Agterdenbos et al. They find that both oxygen and hydrogen are necessary for the formation of selenium from hydrogen selenide in a heated quartz tube at temperatures above 700 °C (ref. 61) but the quantity of oxygen required is very small. There is little gain from anything but a trace of oxygen introduced into the carrier gas and there is probably sufficient present as an impurity in the nitrogen carrier gas or dissolved in the solutions. Although they find no arguments against the reaction $4AsH_3 + 3O_2 \rightarrow 4As + 6H_2O$ for the decomposition of arsine they agree that radicals play a role in atom formation in a heated quartz tube irrespective of the exact mechanism (ref. 62, 63).

Low carrier gas flow rates might be expected to give enhanced sensitivity but this is not always the case. Thermodynamic data would predict that, at the temperature of the heated quartz tube the formation of molecules of the type As_2, As_4 and Se_2 is possible. Agterbendos et al. find that for selenium (ref. 64) and arsenic (ref. 62) dimerisation is negligible providing the concentration of atoms is relatively low i.e. with high carrier gas flow rates. The wall of the quartz tube appears to favour dimerisation (ref. 63). Interferences from other hydride forming elements may also arise from interelement dimerisations (formation of chalcogenides) particularly when the concentration of interferant is high (ref. 65).

The heated quartz tubes currently in use vary in design from a simple quartz T to quite complex designs. Sturman (ref. 13) found that a 7 mm i.d. tube gave good sensitivity but recommends a stepped design about 7 mm i.d. over the centre portion with larger diameter ends to overcome problems associated with instrument signal attenuation caused by a full length tube of the narrower diameter. However this phenomenon may be related to the optical system of their particular instrument. For arsenic and selenium in particular increased noise levels at shorter wavelengths may be observed if the hydrogen escaping from the end of the quartz tube ignites and a tube with quartz end windows (ref. 12, 22) or a nitrogen flow screen across the ends of the tube (ref. 64) is desirable at high hydrogen flow rates. However this interference was not noted in the analysis of tin and is wavelength dependent (ref. 57, 66). The nature of the surface of the quartz tube is extremely important. Occasional cleaning with hydrofluoric acid is desirable and mist carry over from hydride generation must be avoided. A hydrofluoric acid cleaned quartz tube was observed to give slowly increasing results for about thirty determinations but then to remain stable in atomisation efficiency providing it was retained in a desiccator when not in use (ref. 22).

The quartz tube is heated either electrically or in a fixed position over a conventional laminar flow air-acetylene burner. Increased signal stability and less memory effect was observed with the shorter nitrous oxide-acetylene burner head but using air-acetylene as the fuel (ref. 67). Graham (ref. 58) introduced hydrogen flushing after each determination to eliminate the memory effect which was shown to be associated with the quartz tube atomiser when analysing for tin. Although the simple quartz tube atomiser is used extensively it has several serious disadvantages particularly when other hydride forming elements are present in the sample matrix. It is particularly valuable for the determination of arsenic and selenium because it avoids the very pronounced radical interferences experienced below 200 nm and it provides a method of very high sensitivity. However for elements other than arsenic and selenium and particularly where high sensitivity is not required the problems associated with the atomisation process in a quartz tube can be avoided by using a flame rather than the heated quartz tube for the decomposition of the hydride.

Some of the interferences which obviously arise from the formation of heat stable molecular species in the quartz tube can be alleviated by the use of higher temperature atomisation systems. The graphite tube of the conventional graphite atomiser has a length which gives relatively low sensitivity when used as the atomiser for a hydride in a gas flow but arsenic and selenium have been collected in a graphite tube at 600 °C and then atomised at 2600 °C with excellent sensitivity (detection limit 30 pg As and 70 pg Se) (ref. 68, 69). The use of a graphite furnace for atomisation of hydrides was recently reviewed by Dědina et al. (ref. 133) who used a continuous flow system with steady state signal output to study the mechanism of atomisation of selenium hydride in a graphite furnace. The mechanism for atomisation at

low temperatures required the presence of oxygen and is probably similar to that which applies to the atomisation in a flame in tube atomiser. However at high temperatures, e.g. above 2000 °C, the mechanism does not require the presence of oxygen and the sensitivity appears to be dependent on the quality of the graphite surface. Although the sensitivity of a flame in tube atomiser of similar tube dimensions to the graphite furnace is better than that attained with the low temperature graphite furnace the stability and reproducibility of the latter is superior and warrants further investigation for routine applications. Dittrich and Mandry (ref. 70, 71) designed an argon shielded graphite paper atomiser (92 mm h., 9 mm i.d.) which could be heated to 1850-2000 °C. This effectively eliminated the interferences of antimony in arsenic analysis and arsenic in antimony, selenium and bismuth determinations (ref. 65). An excellent low detection limit (0.2 ng cm^{-3}) has also been attained (ref. 72) using an alumina tube (190 mm h.) at temperatures above 1200 °C.

The flame in tube atomiser of Dĕdina and Rubeška (ref. 20) has the advantage of combining hydride generation with measurement of absorption in a quartz tube with flame atomisation. In a detailed study of the effect of other hydride forming elements on the determination of selenium (ref. 73) this technique gave considerably less interference than electrothermal atomisation. However control of this flame system with hydrogen burning at an oxygen jet must be very critical for safety reasons.

Providing hydride generation is efficient it affords a useful separation technique for combination with other methods of analyte measurement. Interferences in the determination of antimony, arsenic, bismuth, germanium, selenium, tin and tellurium observed when using the relatively low temperature and interference prone argon/hydrogen flame for atomisation were extensively studied by Smith (ref. 113). Maher (ref. 74) trapped arsine in potassium iodide and then used a graphite furnace to estimate the arsenic.

INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

An obvious development is to combine the advantages of hydride generation with those of the plasma atomic emission spectrometers which are now relatively common in analytical laboratories. Unfortunately the plasma discharge is more sensitive to changes in operating conditions than a flame and initially the technique was restricted to instruments of relatively high power. However problems associated with the introduction of large volumes of hydrogen and also carbon dioxide into a plasma now appear to have been reduced to the extent that many recent publications refer to the use of instruments in the medium to low power range. Many hydride forming elements are found in concentrations too low for determination by conventional ICP and one of the main advantages of the use of hydride generation for sample introduction is the increase in sensitivity gained over liquid sample nebulisation techniques because of the high transport efficiency of the hydride and the possibility of preconcentration. Also atomisation and excitation of the hydride element is very efficient because it avoids the energy consuming desolvation and vaporisation phases associated with liquid samples. An improvement in detection limits over those found for conventional ICP nebuliser systems of the order of one or two orders of magnitude can be expected. However interferences in the actual hydride generation process such as those related to transition (including platinum) metals as discussed in the previous section will remain. Notable advantages of ICP spectrometers include the possibility of rapid simultaneous determination of multiple elements, a linear calibration over an extended range of concentrations and greatly reduced matrix effects.

Thompson et al. (ref. 75, 76) carried out an extensive study of both the hydride generation and the atomic emission phases using an ICP instrument of medium to high power. They report the simultaneous determination of arsenic, antimony, bismuth, selenium and tellurium but found that for multielement work some compromise of operating conditions is necessary. Hydride generation from 5 mol L^{-1} hydrochloric acid was selected after a study involving a wide range of acids and conditions but germanium, tin and lead could not be included with the above elements because of different acidity requirements. They eliminated transition metal

interference in the generation process by co-precipitation of the analyte elements with lanthanum nitrate and ammonia with subsequent dissolution of the precipitate in hydrochloric acid for analysis. Mutual interferences in the plasma from concomitant hydride forming elements were negligible. They report that for germanium and tin the acid concentration for maximum hydride generation is very critical (ref. 77). However using a near neutral sample solution containing hydrochloric and tartaric acids they obtained detection limits around 0.2 µg L^{-1} for these two elements. They have applied their method to the determination of arsenic antimony and bismuth in soils (ref. 78) and also in herbage (ref. 79) and to selenium in soils and sediments (ref. 80). Their system which enables test solution or blank reaction medium to be introduced into the generator alternately without the introduction of air aids in maintaining a stable plasma (ref. 79). Halicz and Russell (ref. 81) also used an instrument of relatively high power (4.75 kW) for the simultaneous determination of arsenic, antimony, selenium and tellurium in silicate rocks. They realize the importance of the oxidation state of the analyte element and reduce selenium(VI) and tellurium(VI) to selenium(IV) and tellurium (IV) by heating with hydrochloric acid before analysis but they stress that if arsenic(V) must be reduced to arsenic(III) with potassium iodide this must follow sodium tetrahydroborate(III) addition from the manifold, otherwise selenium(IV) is reduced to elemental selenium which is inert and will not form the hydride with sodium tetrahydroborate(III). When analysing silicate rocks containing gold and platinum metals and sulfide ores containing lead and transition metals they separated the hydride forming elements by co-precipitation with iron(III) hydroxide at pH 2.4 in the presence of ammonium chloride to reduce the effects of interfering elements on hydride generation.

Concentration of the generated hydride in a cold trap is one method which has been adopted to avoid introducing large volumes of hydrogen into the plasma of the emission spectrometer and it also provides a good method to increase sensitivity. Fry et al. (ref. 82) used a trap cooled in liquid argon to eliminate hydrogen before introducing the sample into a relatively low powered (1.2 kW) instrument for the determination of arsenic while Hahn et al (ref 83) also using a low powered instrument developed a method for the simultaneous determination of arsenic, antimony, bismuth, germanium, selenium and tin in foods. They used helium to transfer the hydride to a corrugated Teflon tubing trap cooled with liquid argon but introduced a brief argon purge to clear the helium before warming the trap. A long coil of Teflon tube between the trap and the plasma torch improved plasma stability by evening out switching induced gas surges. They also used their system to study the carbon dioxide interference in some detail. In another variation of the trapping system Eckhoff et al. (ref. 84) collected the hydrides in a Teflon U tube filled with Teflon shavings cooled in liquid nitrogen. The helium carrier gas was replaced by argon when the hydrides were swept to the spectrometer through a 3.5 ft column of Chromosorb 102 and the elements were determined in order of elution from the column. Although excellent detection limits were obtained for arsenic, antimony and germanium they found that selenium, tellurium, bismuth and lead hydrides were not transferred through the column quantitatively. The instability of the hydride would be an important factor with their system. Other devices used to aid plasma stability under hydride generation operating conditions include a larger than usual diameter plasma torch (19 mm) (ref. 85) and variations to the nebuliser system. In the tandem nebuliser system of Woinik et al. (ref. 86) sodium tetrahydroborate(III) from one nebuliser enters the second where acidic sample is nebulised while in another variation (ref. 87) sodium tetrahydroborate(III) is pumped into a cyclone sample nebuliser so that it reacts with sample droplets which do not pass to the plasma torch. In both of these variations some sample solution enters the plasma as an aerosol as also does the hydride from the analyte element in the condensed droplets which would normally pass to waste in a conventional system.

The carrier gas flow rate is one of the most critical factors in maintaining a stable plasma when an ICP instrument is coupled directly to a continuous hydride generator unit. Nygaord and Lowry (ref. 88) used an instrument of relatively low power (1.25 kW) with direct insertion of hydride to the plasma for the determination of arsenic, antimony and selenium in a range of industrial sludges. They made an extensive study of sample digestion procedures and obtained results in good accord with those found by electrothermal atomisatiom atomic absorption

spectrometry. More recently Watling and Collier (ref. 89) determined arsenic, antimony, bismuth and selenium simultaneously with detection limits around 1 µg L^{-1}. In their hydride generator which is linked directly to the plasma torch they pump sample solution and sodium tetrahydroborate(III) over a specially designed dual platinum screen through which argon flows to give nebulisation together with rapid release of entrained gases. A small amount of sample solution (up to 3%) enters the plasma as an aerosol but the remainder was pumped to waste. Detection limits 30-700 times better than those found with pneumatic nebulisation were obtained by Hwang et al. (ref. 90) who also used an instrument of low power (1 kW). Again it is apparent that the carrier gas flow rate is critical and very much less than for conventional ICP operation. However although their hydride generation conditions are similar for arsenic, antimony, bismuth and selenium (1:1 V/V hydrochloric acid) the optimum conditions for tin (5% hydrochloric acid) are very much different. Some compromise of optimum generation reaction conditions is necessary for multielement work if the advantages of a good ICP instrument are to be exploited to the full.

CHEMICAL SPECIATION

When studying toxicity and metabolism it is important to know the valency state and in many cases the organic form of the element under consideration. Of the hydride forming elements four exist in solution in two possible oxidation states (arsenic(III) and (V), antimony(III) and (V), selenium(IV) and (VI) and tellurium(IV) and (VI)) which can be distinguished by controlled sodium tetrahydroborate(III) reduction. Also the methyl derivatives of many of the hydride forming elements can be volatilised and determined following sodium tetrahydroborate(III) reduction.

It was recognised early that arsenic(III) and arsenic(V) reacted at different rates with sodium tetrahydroborate(III) in acid solution and some even recommended different calibration graphs for each oxidation state. For total arsenic it is now normal practice to add iodide to the acidified sample solution to reduce arsenic(V) to arsenic(III) which readily reacts with sodium tetrahydroborate(III) under a range of conditions. The reduction with iodide is very rapid and when using continuous flow equipment it is sufficient to add the iodide to the acidified sample solution from the manifold immediately before the sodium tetrahydroborate(III). Aggett and Aspell (ref. 91) were the first to exploit the difference in the rate of reduction of arsenic(III) and arsenic(V). They noted the reduction was Ph dependent and obtained a quantitative yield of hydride from both arsenic(III) and arsenic(V) in 5 mol L^{-1} hydrochloric acid but hydride corresponding to only arsenic(III) at Ph 4.5 in an acetic acid/sodium acetate buffer. However it must be noted that methyl derivatives of arsenic such as monomethylarsonic acid and dimethylarsinic acid if present, as they are likely to be in environmental samples, may also contribute to the apparent yield of hydride if the hydride generator is connected directly to the atomiser (ref. 92).

Following a very comprehensive review of methods used for the speciation of derivatives of arsenic Anderson, Thompson and Culbard (ref. 17) devised a system for the determination of arsenic(III), arsenic(V), monoethylarsonic acid and dimethylarsinic acid using continuous flow equipment but their methods require very rigorously controlled reaction conditions. It is more common, though possibly more time consuming, to use a separation technique to differentiate between the generated hydrides. arsine, monomethylarsine and dimethylarsine. The system of Comber and Howard (ref. 93) is a refinement of earlier equipment (ref. 94) which was based on the work of Andreae (ref. 95) and Braman et al. (ref. 96) and has been applied to the speciation of derivatives of arsenic in natural waters and in studies involving geological and biological processes. The hydrides are generated using continuous flow equipment connected to a gas liquid separator and collected in a U-tube packed with hydrofluoric acid etched glass beads cooled in liquid nitrogen. The hydrides are released sequentially by warming the trap and arsenic is determined by atomic absorption following atomisation in a heated quartz tube. This system has given detection limits of about 20-60 pg for arsenic derivatives and the performance of the method has been checked by standard additions. Mukai and Ambe (ref. 97) used a gas chromatograph for the separation of the hydrides when determining arsenic

derivatives in airborne particulates collected on a quartz fibre filter with a high volume sampler. They trapped the hydrides in a U-tube cooled in liquid nitrogen but then transferred the hydrides quickly into a helium gas flow connected to a column of 5% PEG-20M on Chromosorb 101. Hydrogen was added to the effluent gases from the gas chromatograph before determination by atomic absorption following atomisation in a ceramic alumina tube at 900-1000 °C. Detection limits are better than 100 pg arsenic derivative.

Experimental conditions normally used for arsenic are appropriate for the determination of antimony and this also applies to speciation of the inorganic forms. Campbell and Howard (ref. 98) adapted a method previously applied to the determination of arsenic (ref. 94) for the determination of antimony in estuarine and sea water. Reaction with sodium tetrahydroborate(III) at Ph 5 in a sodium acetate/acetic acid buffer gave a quantitative yield of stibine from antimony(III) but no hydride even from a 10 fold excess of antimony(V). However total antimony was readily obtained following reduction of antimony(V) to antimony(III) with iodide. Although they overcame nitrite interference with sulphanilamide and metal interferences and used trapping to concentrate the hydride their detection limit (240 ng L^{-1}) would suggest that the method is not suitable for very low levels of antimony.

Selenite, (selenium(IV)) is readily reduced to hydrogen selenide in 4 mol L^{-1} hydrochloric acid but it is necessary to reduce selenate, (selenium(VI)) by heating in hydrochloric acid (at just below the b.p. for several minutes) when determining total selenium using sodium tetrahydroborate(III) because selenium(VI) gives hydrogen selenide only from very strong acidic solution. This distinction was successfully exploited by Cutter (ref. 99) who adapted the gas chromatographic system of Chau et al. (ref.100) with the flame-in-tube detection system used by Andreae (ref. 95) to the determination of dimethyl selenide and dimethyl diselenide as well as selenite and selenate. Iodide should not be used to reduce selenium(VI) to selenium(IV) because this is likely to give elemental selenium which is inert to sodium tetrahydroborate(III).

Jin et al. (ref. 101) found that tellurium(IV) gave a quantitative yield of hydride on treatment with sodium tetrahydroborate(III) in 3 mol L^{-1} hydrochloric acid but tellurium(VI) was unaffected even when present at a 200 fold excess. They obtained hydride corresponding to the total tellurium following reduction of the tellurium(VI) with 5% titanium(III) chloride. A detection limit of 8 ng tellurium is reported. Heating with hydrochloric acid has also been used to reduce tellurium(VI) to tellurium(IV) (ref. 81).

Interest in the biological activity of organotin derivatives has stimulated the development of methods based on the production of volatile hydrides with sodium tetrahydroborate(III) for their determination at trace levels in sea and estuarine waters. Earlier analytical systems have been reviewed by Chamsaz, Khasawneh and Winefordner (ref. 102) who developed a method with a detection limit of 0.4 - 1.5 ng for tin derivatives in a 0.5 L sample. Following the relatively slow addition of sodium tetrahydroborate(III) to the sample acidified to pH2 with hydrochloric acid the hydrides are collected in a liquid nitrogen cooled trap similar to that of Valkirs et al. (ref. 103) and Donard et al. (ref. 104) who demonstrated the efficiency of a trap packed with a chromatographic grade stationary phase to facilitate good sequential volatilisation of the various hydrides on warming. When analysing methyl derivatives a dry ice/acetone cooled desiccant trap may be used to protect the hydride trap from moisture but butyl derivatives will also condense at this temperature. Although a heated quartz tube atomiser gives good sensitivity for tin (ref. 105) the surface of the tube deteriorates rapidly with consequential change in response. Valkirs et al. (ref. 103) and Donard et al. (ref. 104) used a flame-in-tube type atomiser but Chamsaz et al. (ref. 102) chose an alumina tube heated to 1400 °C inside an electrically heated inert gas protected graphite tube furnace. This atomiser did not deteriorate with samples containing tin. Andreae and Byrd (ref. 106) reported that it was not possible to distinguish between tin(II) and tin(IV) using hydride generation, both giving stannane under similar reaction conditions. Glass surfaces in contact with stannane and organic derivatives should be regularly treated with dimethyldichlorosilane to avoid loss of tin by adsorption (ref. 106, 107).

APPLICATIONS

Although the equipment used for hydride generation has wide application among the elements which form volatile hydrides with sodium tetrahydroborate(III) the reaction conditions for optimum yield of hydride are not universal and are best established for a particular system by experiment. For some elements such as germanium, tin and lead the reaction conditions which favour good hydride recovery are so different from what could be called standard conditions that they warrant separate treatment.

Germanium

Germane is a relatively stable gas which is readily produced by reacting germanium(IV) with sodium tetrahydroborate(III) although digermane and some polymeric material $(GeH)_x$ may also be formed (ref. 108). Reaction conditions are quite critical for the production of good yields of germane at the levels normally encountered in analytical chemistry, most authors adding the reductant to a slightly acidic (ref. 77) or buffered (ref. 109) sample solution. Many metals and also other hydride forming elements interfere seriously in the generation of germane (ref. 110). Co-precipitation of germanium with lanthanum or with iron is therefore not appropriate because these methods retain selenium and tellurium. Halicz (ref. 111) avoided interferences when analysing sulfide ores and silicate rocks by the very selective method of acidifying the sample digest to 9 mol L^{-1} with hydrochloric acid and extracting the tetrachlorogermanium in tetrachloromethane. Following a back extraction into water germane was generated with sodium tetrahydroborate(III) and atomised by direct introduction into a dinitrogen oxide/acetylene flame for analysis by atomic absorption spectrometry. Brindle et al. (ref.112) obtained greatly enhanced yields of germane when ammonium peroxydisulfate, which has been used to facilitate the formation of hydride from lead(II), was added to the generation reaction mixture. Also peroxydisulfate eliminated interferences from several metals up to quite high concentrations although it had limited effect on cadmium(II), cobalt(II), nickel(II) and zinc(II) even in the presence of thiourea. They attained a detection limit of 1 ng in their system in which the generated germane was introduced directly to a d.c. arc emission spectrometer.

Tin

When solution nebulisation atomic absorption spectrometry is applied to tin atomisation efficiency is low and as a result detection limits are unsatisfactory for trace analysis. However a survey of hydride generation methods applied to the determination of tin and organotin derivatives suggests that although there are many attractions, a low limit of detection and rapid sample throughput with automated systems, there are also many problems for the unwary particularly with interferences and reaction conditions. It is essential to optimise reagent concentrations and quantities (reagent flows for continuous flow equipment) for a particular set of equipment and apply frequent checks with reference samples and/or standard additions. High blank values have been reported for tin (ref. 113) and Hodge et al. (ref. 114) found it necessary to reduce tin contamination of their sodium tetrahydroborate(III) electrolytically.

The pH of the generation reaction is related not only to the initial acidity of the sample but also to the quantity of alkali used to stabilise the sodium tetrahydroborate(III) solution. Although a small amount of dilute acid or buffer solution may influence the initial reaction the final pH is more dependent on the quantity of usually much more concentrated reductant which is added. Several authors have compared hydride yields from samples acidified with various acids (ref. 77, 115, 116) but the results are inconclusive some finding all three, hydrochloric, sulfuric and nitric acid equally effective. Most common would be acidification with dilute hydrochloric acid (about 0.1 mol L^{-1}) (ref. 117, 118, 119, 120) but this was discarded in favour of sulfuric acid by De Doncker et al. (ref. 115) because of the reported catalytic effect of fumes or mist from hydrochloric acid on the devitrification of the quartz cell used for hydride atomisation (ref. 122). However Alvarez et al. (ref. 119) recommend hydrochloric acid

because they were unable to get consistent results with sulfuric acid. Likewise Thompson et al. (ref. 77) found nitric acid unsatisfactory even although it is used by others (ref. 54, 106, 116) Acetic acid has also been used (ref. 114). Factors giving these inconsistencies could be the purity of the reagents and also it is apparent that continuous flow equipment or slow generation of hydride from a large volume is much more tolerant of reaction conditions than the typical batch type systems with their associated vigorous reaction. For example Legret and Divet (ref. 116) recommend the removal of hydrofluoric acid before analysis in their batch type system but Chan and Baig (ref. 120) did not report any difficulty with acid with continuous flow generation equipment when analysing for tin in mineral samples following lithium metaborate fusion and a work up process involving sulfuric and hydrofluoric acids.

Formation of stannane is strongly influenced by the presence of many transition metals, platinum metals and other hydride forming elements with significant suppression when there is more than about 20 fold excess over tin of such elements as copper, cobalt, nickel, arsenic and antimony. Methods for countering this interference are many and varied. Thompson et al. (ref. 77) had some success in diminishing the effect of transition metals by using tartaric acid for acidification of the sample and tartaric acid has also been added in addition to mineral acids (ref. 116). Other reagents recommended include oxalic acid and o-phenanthroline (ref. 120) and EDTA (ref. 121) but one of the most successful is that of Brindle and Le (ref. 54) who found that nickel(II), cobalt(II), copper(II) and iron(II) could be accommodated up to about 1000 mg L^{-1} level if 0.4 g solid L-cystine was added to the reaction flask (batch type process) before sample addition. However interferences from platinum metals remain significant. Separation of tin by a co-precipitation technique must be adopted to completely remove interferences from high concentrations of many elements. When analysing for tin in marine organisms Maher (ref. 47) coprecipitated tin by adding lanthanum(III) followed by ammonia to pH9-10. The precipitate was redissolved in sulfuric acid for analysis. Vijan and Chan (ref. 117) used an alternative method involving co-precipitation with manganese dioxide when determining tin in air particulate matter. Their precipitate was dissolved in hydrogen peroxide/hydrochloric acid and analysed using an air segmented continuous flow system. Manganese did not interfere. Hydride generation from non-aqueous medium was used by Aznárez et al. (ref. 123) following extraction of tin into chloroform as its complex with N-nitrosophenylhydroxamic acid. Tin was then determined by reacting an aliquot of the chloroform extract with sodium tetrahydroborate(III) in N,N-dimethylformamide. These separation techniques also introduce an analyte concentration step into the analysis.

A wide range of methods have been used to measure tin in the generated hydride. Many use the conventional quartz T tube heated to about 850 °C for atomisation in an atomic absorption spectrometer (ref. 47, 115, 116, 117, 118, 120) because it is a method which gives excellent low limits of detection (e.g. 4 ng (ref. 115)) but it will also introduce signal variability with devitrification. The response of such a system should be checked with frequent reference samples. The useful analytical line for tin is at 224.6 nm which is clear of the area where flame radical absorbances predominate and an air/acetylene flame has been shown to be quite effective for atomisation (ref. 119, 123). Other methods used for final measurement are ICP (ref. 77), d.c. plasma emission spectrometry with a detection limit of 100 pg tin for a 5 ml sample (ref. 54) and MECA (molecular emission cavity analysis) (ref. 121).

To summarise, the hydride generation technique has been applied to the determination of tin in foods (ref. 119, 123), atmospheric particulate matter (ref. 115, 117), sediments and sludges (ref. 116), geological materials (ref. 118, 120) and metals and alloys (ref. 54, 123). (See also the section on tin under Chemical Speciation).

Lead

Lead(II) does not give a satisfactory yield of hydride when reacted with sodium tetrahydroborate(III) under conditions which would be standard for arsenic or selenium. The concentration of both acid and sodium tetrahydroborate(III) are very critical (ref. 66) but greatly improved yields of hydride are obtained if an oxidant such as dichromate (ref. 124) or

hydrogen peroxide (ref. 125) is introduced into the generator. However when the latter method was applied to the determination of lead in potable waters (ref. 126) it was necessary to separate the lead by coprecipitation with manganese hydroxide from acid solution particularly in the presence of both copper(II) and nickel(II) although some interferences were eliminated by potassium cyanide and citric acid. The value of several oxidants was assessed by Jin et al. (ref. 127) who found ammonium perdisulfate to be superior in their continuous flow system with hydride atomisation in a heated silica tube. However although ammonium perdisulfate could suppress interferences from low levels of several metals a separation process involving the extraction of lead as its complex with dithizone was necessary at higher concentrations of interferents. Further oxidants were studied by Castillo et al. (ref. 128) who related the oxidation potential to the oxidant to the yield of plumbane but they also concluded that ammonium peroxydisulfate was the best. Obviously it is desirable to convert lead(II) to lead(IV) for reaction with sodium tetrahydroborate(III). With their system in which the hydride was introduced directly into the nebuliser of an air-acetylene burner they attained a detection limit of 0.05 μg lead. This method has been the subject of a detailed study of interferences (ref. 129). Plumbane has also been generated in non aqueous systems using N,N-dimethylformamide as solvent. When determining lead in steel Aznárez et al. (ref. 44) avoided metal interferences by extracting the lead as its complex with sodium diethyldithiocarbamate in chloroform and generated the hydride from an aliquot of this extract directly by addition of sodium tetrahydroborate(III) in N,N-dimethylformamide. They then determined the lead by AAS using an air acetylene flame. A similar non aqueous solvent system has been used to determine lead in gasoline (ref. 130).

Although the limit of detection may be good for the determination of lead by atomic absorption spectrometry following atomisation of plumbane in a heated silica tube it is possible that there will be far fewer interference effects associated with techniques involving conventional solution nebulisation or electrothermal atomisation. The potential of the hydride generation method may be with its application to the speciation of alkyl derivatives of lead as recently reported by Forster and Howard (ref. 131). They separated alkyl derivatives of lead on a capillary column and sequentially determined the eluted derivatives by atomic absorption spectroscopy following a flame-in-tube type atomisation.

CONCLUSIONS

Hydride generation is widely used in the determination of low levels of those elements whose salts readily form hydrides with sodium tetrahydroborate(III). However those using this technique must be aware of the conditions which have been reported to give rise to interferences in the generation reaction and take steps to alleviate these. The technique has the advantage that it affords a concentration step and the analyte element is conveyed to the atomiser in a much higher yield than is ever attained in conventional solution nebulisation systems. Hydride generation also allows the determination of the speciation of many elements.

Although atomisation in a heated quartz tube for determination by atomic absorption spectroscopy is subject to some interferences from other hydride forming elements it affords a large increase in sensitivity over flame atomisation and is valuable for very low level determinations. The heated quartz tube atomiser is particularly useful for the determination of arsenic and selenium because absorption wavelengths for these two elements are below 200 nm in an area which is subject to intense interference from flame radicals. The elements other than arsenic and selenium with absorption wavelengths above 200 nm do not suffer serious flame radical interferences to the same extent. For them conventional flame atomisation using air/acetylene or hydrogen/entrained air flames may provide a more robust atomisation method than the heated quartz tube except when working at very low levels of analyte element.

Hydride generation also affords improved detection limits for hydride forming elements when used with plasma atomic emission spectrometers. For multielement analyses some

compromise of optimum reaction conditions may be necessary and generation reaction interferences must be considered although atomisation interferences should be negligible. It is important to adopt an experimental technique which eliminates or at least reduces the adverse effect on plasma stability of the large volume of hydrogen produced in the hydride forming reaction.

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