THE USE OF FLOW-INJECTION IN HYDRIDE-GENERATION ATOMIC-ABSORPTION SPECTROPHOTOMETRY

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The use of flow-injection in hydride-generation atomic-absorption spectrophotometry

by

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Synopsis

The method of analysis, where the generation of the gaseous hydrides of certain elements is used, has been thoroughly researched since its introduction in 1969. This technique is however, plagued with many interferences which necessitate cumbersome sample manipulation before accurate results are obtained. This has resulted in this technique being used only if all other options have failed.

Three methods of in-line sample manipulation were studied in an attempt to change the *status quo.*

The first method investigated was the simple in-line addition of reagents. Potassium iodide was added in this manner in order to overcome the interference resulting from the analyte being present in more than one oxidation state before generation of the hydride. Tellurium (IV) was used in the same manifold to extend the tolerance of noble metals in the determination of arsenic, selenium, and bismuth.

Secondly, a small column packed with ion exchange resin was included in a new manifold which enabled the base metal interferences and certain inter-hydride forming element interferences to be overcome.

Finally, the method of standard additions was automated in a flow-injection manifold which enabled the practice of this versatile approach without the usual sample preparation steps.

Die gebruik van die vloei-inspuittegniek in hidriedontwikkeling-atoomabsorpsiespektrofotometrie

deur

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Samevatting

Die ontwikkeling van die gasvormende hydriede van sekere elemente, is deeglik bestudeer sedert die metode van analise in 1969 voorgestel is. Die tegniek word egter gekniehalter deur steurings wat die metode tydroewend maak. As gevolg hiervan, is die tegniek, waar moontlik vermy.

Drie metodes van in-stroom monster hantering is bestudeer om die *status quo* te verander.

Die eerste metode wat ondersoek is, is die eenvoudige byvoeging van reagense in die draerstroom. Kaliumjodied is op die manier bygevoeg om die teenwoordigheid van meer as een stabiele oksidasietoestand van die analiet te voorkom. Tellurium (IV) is op dieselfde wyse gebruik om die steurende effek van edelmetale op die bepaling van arseen, selenium, en bismut te oorkom.

Tweedens, is 'n kort kolom, gepak met ioonuitruilingshars, ingesluit om die steuring van oorgangsmetale, en sekere van die onderlinge uitwerkings tussen hidriedvormende elemente, te oorkom.

Laastens is die metode van standaardtoevoeging geoutomatiseer. Standaard toevoeging, hoewel veelsydig, gaan gewoonlik gepaard met omslagtige monster hantering. Met die gebruik van die vloei-inspuitsisteem, is die' nadeel uitgeskakel.

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CONTENTS

Chapter 1

Introduction and Theory

1.1 Introduction

Eight elements from group IV, V, and VI of the periodic table have been induced to form gaseous covalent hydrides in sufficient amounts to be of practical analytical use.

The determination of one or more of these elements, i.e., antimony, arsenic, bismuth, germanium, lead, selenium, tellurium, and tin, at the lower or sub-parts-per-million level is increasingly being required in a wide variety of fields. Atomic-absorption spectrophotometry (AAS) using conventional flame atomization, (although sensitive for many elements), is not always sensitive enough for these elements. This lack of sensitivity may be attributed to the high signal-to-noise ratios[1] experienced at the wavelengths at which these elements are determined. Use of electrothermal atomization (ETA), usually results in an improvement in sensitivity of two to three orders of magnitude when compared to flame atomization, however, at the short wavelengths of interest, scattering by particulate matter, such as carbon, is severe. In addition, analyte loss of the more volatile elements can occur if matrix modification procedures are not instituted.

For these elements, there is a less expensive alternative to ETA-AAS, that is more sensitive than flame AAS. After conversion to their respective hydride, they may be introduced into the atomic reservoir of a spectroscopic instrument for the sensitive determination of the analyte concentration. AAS is the most commonly used spectroscopic technique for detection of these elements. However, atomic-fluorescence spectroscopy (AFS)[2] and atomic-emission spectrometry (AES), using inductively coupled plasma (ICP)[3,4], microwave induced plasma (MIP)[5], capacitively coupled microwave plasma (CMP)[6,7], or direct current plasma (DCP)[8] sources have been used as well. Sensitivities at least one order of magnitude better than those obtained when conventional sample introduction is used have been reported.

Many scientific papers and a number of reviews[9-15] have been devoted to this novel method of analysis. The interest shown may be attributed to the separation inherent in this highly efficient sample introduction system, and the corresponding superior sensitivity achievable compared to conventional sample introduction systems.

As in all analytical techniques, certain disadvantages must be overcome before successful analysis may be carried out. The greatest obstacle to simple utilization of this technique, is the numerous interferences encountered from the concomitant matrix. Strict control of the reagent concentrations is necessary in order to ensure optimum efficiency and in some hydride generators, collection devices are necessary. A disadvantage, which has been put to good use in speciation studies, is the fact that the different oxidation states of some of the hydride forming elements behave differently when treated with the reductant and thereby result in inaccurate analysis if precautions are not taken.

1.2. Aims of the investigation

A study of the literature reveals that the analysis of samples using hydride generation, is often fraught with problems. Interferences abound and special care is required in the execution of the analysis. Many authors recommend the use of the time consuming method of standard additions in an attempt to overcome interferences. Others insist on isolating the analyte from the sample before analysis. Hydride generation is often the only option at the low concentration levels required and so it is necessary to provide solutions to these problems.

Attention has been given to overcoming the interferences experienced when analyzing particular types using hydride generation. Most of the proposed methods have been applied to batch analysis. Batch analysis is the sequential treatment of a series of samples each in its own container. This treatment may simply be the addition of a particular reagent or a more complex set of steps such as the isolation of a particular element using ion-exchange chromatography. Each additional sample manipulation step lengthens the analysis time and increases the chance of experimental errors. Both of these factors reduce the usefulness of the technique being used.

Flow-injection analysis (FIA) has successfully been used to speed up analysis time, perform sample manipulation steps that require experienced analytical expertise, and improve the precision of such procedures.

In this study, existing batch methods of overcoming interferences have been automated using FIA principles. FIA manifolds have been constructed which allow the in-line execution of these previously manual procedures in a flow-injection hydride generator. The hydride generator used was designed, built, and tested as part of this investigation.

By using this approach, ease of operation is achieved without sacrificing the sensitivity or selectivity inherent to the method of hydride generation atomic-absorption spectrophotometry.

1.3. The gaseous hydride forming elements[16]

The method of hydride generation has been used for the routine analysis of certain group IV, V, and VI elements, for which the valence electron configurations are ns_2np_2, ns_2np_3, and ns_2np_4 respectively. The position of these elements in the periodic table is highlighted in figure 1.1. Indium and thallium have also been determined by hydride generation[17], however, the poor sensitivity achieved has precluded this technique as a possibility for routine analysis.

Hydrides are compounds formed by electropositive elements and contain the negatively charged hydride ion (H^-). Bonding with the hydrogen atoms to yield hydrides, is through the *p* orbitals and, for the elements that we are interested in, the bond has a covalent nature. From the valence configurations it is clear that elements in group IV will favour the II or IV oxidation state, those in group V will favour the III and V oxidation state while for the elements in group VI, the IV oxidation state predominates.

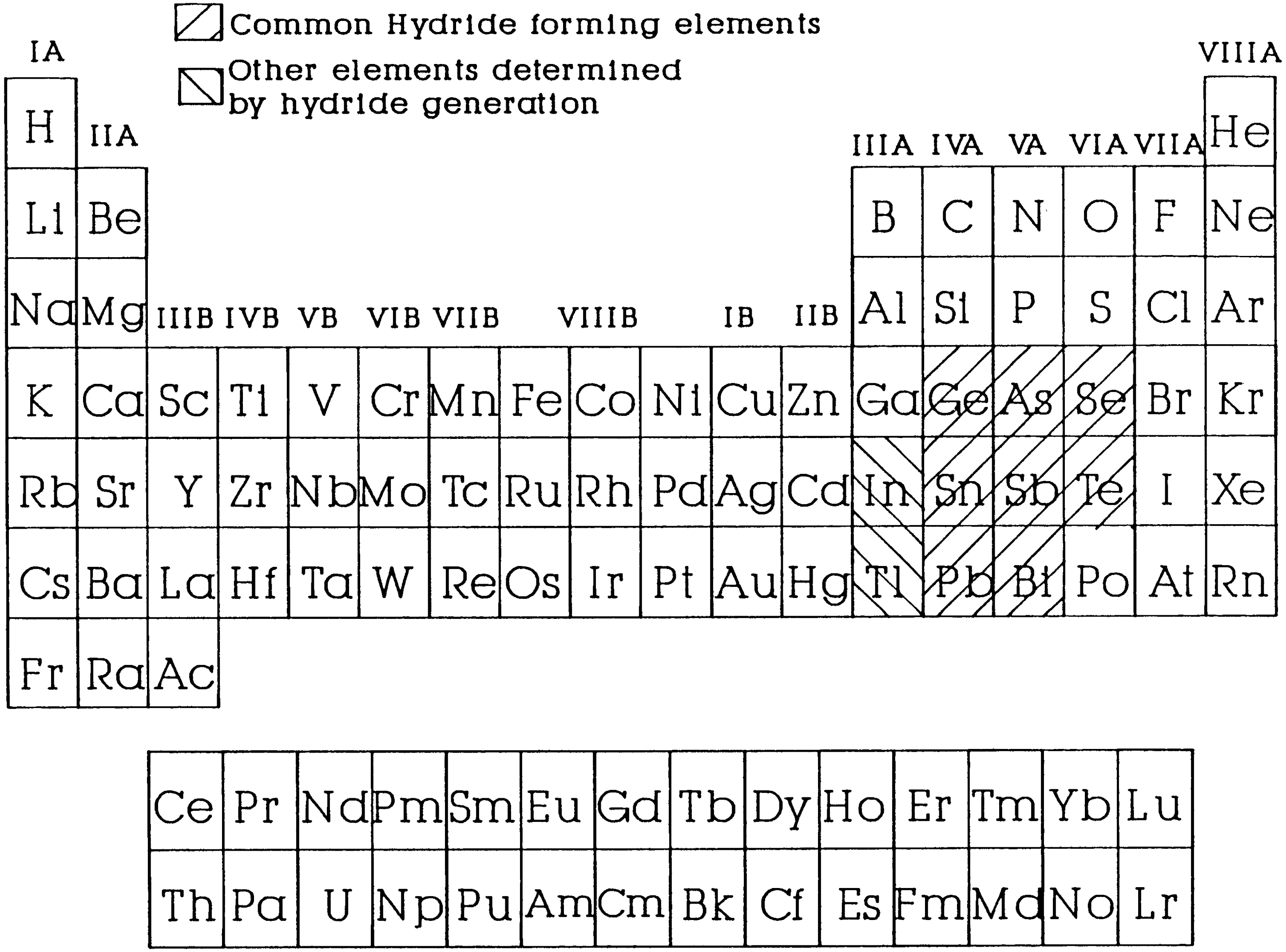


Figure 1.1: Periodic table showing gaseous hydride forming elements

Sensitive and accurate methods of analysis are required for these elements because of their dramatic and often deleterious affect even at trace levels. A brief resume' of the origin, uses, and toxicity of these elements will serve as an indication of the variety of sample types that must be analysed.

1.3.1. Antimony

Antimony is sometimes found native but usually as the sulphide, stibnite (Sb_2S_3). The element and many of its compounds are toxic and exposure even at trace levels is harmful. Because of this toxicity, analysis of samples such as urine, blood, tissue, leaves, air, and waters are often required.

Once purified to very stringent specifications, it is used in semiconductor devices such as infra red detectors, and diodes. It is also used extensively, up to concentrations of 20 per cent, in alloys. About half of the metal produced is used in flame-proofing compounds, paints, ceramic enamels, and glass. Hydrated potassium antimonyltartate has been used in medicine as an emetic.

Although in these applications, analysis at the trace level is not that important, during processing, analysis of tailing streams and wastes require monitoring.

1.3.2. Arsenic

Arsenic is found native, in the sulphides realgar and orpiment, as arsenides and sulfarsenides of heavy metals, as the oxide, and as arsenates.

Arsenic and many of its compounds are poisonous and cumulative in many living organisms. Although maximum tolerance levels have been set, these are under review with a probable reduction being eminent. Samples similar to those required for antimony will be required.

Arsenic is used in bronzing, pyrotechny, and for hardening and improving the sphericity of shot. It has also been used as an agricultural insecticide.

Its use in this role requires monitoring in order to ensure that it does not become an environmental hazard. Possibly its most important future use will be in the field of semi-conductors where there is an increasing tendency to use it as a doping agent. When used together with gallium in gallium arsenide crystals, it can convert electricity directly into coherent light and will therefore find application in the realm of optical data transfer.

1.3.3. Bismuth

The most important ores of bismuth are bismuthinite (Bi_2S_3) and bismite (Bi_2O_3).

Bismuth is the most diamagnetic of all metals, and its thermal conductivity is lower than any metal. It is used in alloys particularly for use in fire detection and extinguishing apparatus. In fact, bismuth's unique qualities ensure its use in a wide variety of applications, from medicine to thermocouples. Methods of analysis that are able to cope with such varied sample types are therefore required.

1.3.4. Germanium

This element is usually obtained from the flue dust of zinc smelters and in the combustion products of some coals. The extraction process is quite complex and requires stringent control in order to ensure adequate purity and enrichment, hence the need for sensitive and accurate methods of analysis in samples that vary depending on the stage in the extraction process.

Certain germanium compounds have a low mamalian toxicity, but a marked activity against certain bacteria. This makes germanium of particular interest as a chemotherapeutic agent. In this role accurate analysis is required in order to determine safe dosage levels and efficient activity against the bacteria.

Germanium is a very important semi-conductor material. Doped with arsenic or gallium it is used for components in thousands of electronic devices. It has also been used as an alloying agent, as a phosphor in fluorescent lamps, and as a catalyst. Its transparency to infra red radiation has made it useful in various optical devices.

1.3.5. Lead

Native lead occurs in nature but is rare. Lead is obtained mainly from galena (PbS). Anglesite ($PbSO_4$), and cerrusite ($PbCO_3$) are other common lead minerals.

Its resistance to corrosion has ensured its use for the storage of corrosive materials. A large amount of lead is used in storage batteries such as motor car batteries. It is also used in ammunition, as covering for cables and as an anti-knock compound (tetraethyl lead) in fuels. Because of its ability to absorb radiation, it is used as a shield in X-ray devices and in nuclear reactors.

In recent years, the use of lead in paints has been drastically reduced due to the health hazard it poses. Lead is a cumulative toxin and for this reason there has been a world wide drive to reduce the lead in petrol. Nevertheless, there are still numerous sources of lead and so the monitoring of lead in blood and other similar sample types is required.

1.3.6. Selenium

Most of the world's selenium requirements are obtained from the anode mud from electrolytic copper refineries.

Elemental selenium is claimed to be practically non-toxic and is even said to be an essential trace element. However, most selenium compounds are extremely toxic and resemble arsenic in their physiological effects.

Its photovoltaic and photoconductive characteristics have ensured its utilization in photocells and exposure meters. Its ability to convert alternating current to direct current has ensured its extensive use in rectifiers.

1.3.7. Tellurium

Tellurium is sometimes found native but is usually found as a telluride of gold. Most of the world's tellurium requirements are obtained from the anode muds obtained in the electrolytic refining of blister copper.

Tellurium and its compounds are probably toxic and further research in this area is required. Exposure to very low levels of tellurium results in 'tellurium breath' which has a garlic-like odour and is symptomatic of excessive tellurium exposure. In the study of this potentially harmful element, sensitive methods of analysis will be required for a variety of sample types.

Tellurium is used in blasting caps, as an alloying agent to improve lead's resistance to sulphuric acid corrosion, and in ceramics.

1.3.8. Tin

Tin is found mainly in cassiterite (SnO_2).

The small amount of tin (<300 mg/kg) used in canned food containers is harmless. Trialkyl and triaryl tin compounds are used as biocides and must be treated with care.

It may be highly polished and is used to improve resistance to corrosion in tin cans for storage containers. Alloys of tin are very important, a well known example being pewter. Stannous chloride is used as a reducing agent. Of recent interest is a tin-niobium alloy which is a super-conductor at low temperatures.

1.4. Atomic-absorption spectroscopy

1.4.1. Basic principles[18,19]

Atomic-absorption spectroscopy (AAS) is the term used to describe the analytical technique where energy absorbed by atoms is measured and related to the concentration of the atoms in a particular sample.

Atomic spectroscopy is made up of three main branches of analytical science; atomic-absorption spectroscopy (AAS), atomic-emission spectroscopy (AES), and atomic-fluorescence spectroscopy (AFS). The difference in the principles employed in each of these fields is given schematically in figure 1.2.

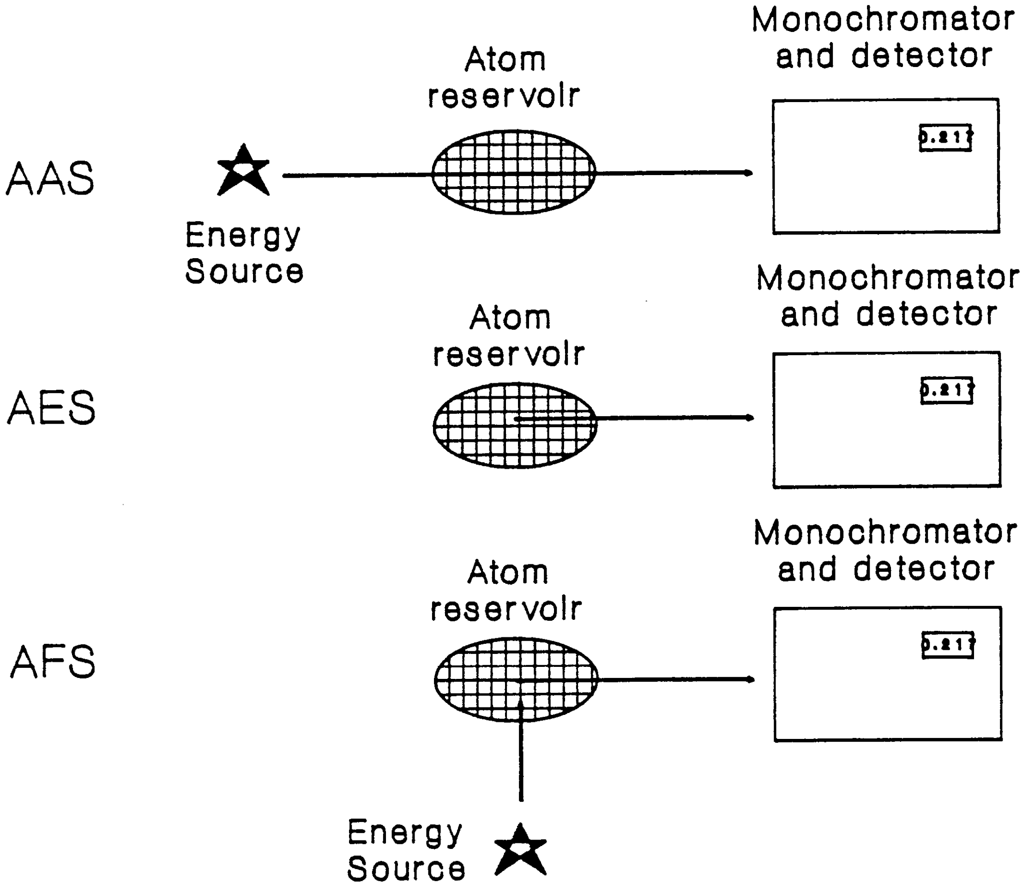


Figure 1.2: Schematic representation of AES, AAS, and AFS

In 1955, Walsh[20], the father of AAS, used a line source for the incident radiation. The width of this line was much narrower than the absorption band and overcame the need for a high resolution detector system to isolate the light of the desired wavelength. This opened the road to quantitative sensitive determination of analyte concentrations. Presently, most of the elements in the periodic table may be determined either directly or indirectly.

The principle of operation is set out as follows. Radiation from an external light source, emitting spectral lines that correspond to the energy required to excite a valency electron from the ground state to an excited state, is passed through an atom reservoir. The absorption of energy by the atoms in the atom reservoir is measured and related to concentration. The absorption is determined by measuring the decrease in light intensity in the presence of analyte atoms. In figure 1.3, a typical atomic-absorption incident is depicted.

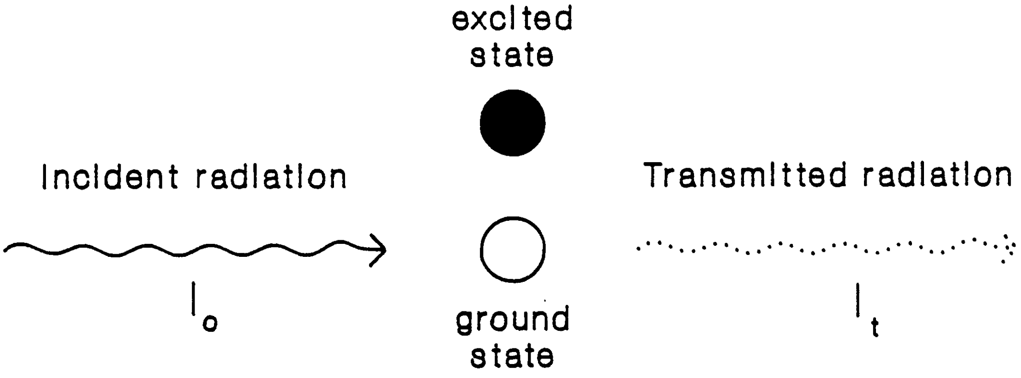


Figure 1.3: Atomic absorption process

The relationship between the intensity of transmitted radiation, I_t and incident radiation, I_o is given by the following equation.

$$\frac{I_\upsilon}{I_t} = e^{(k_\upsilon l)} \ldots\ldots\ldots\ldots (1)$$

where k_υ = absorption coefficient at frequency υ
l = absorption path length.

For spectroscopy in general, absorbance, A, is defined by equation (2).

$$A = \log (I_0/I_t) \quad \ldots\ldots \; (2)$$

Substitution of (1) in (2) results in equation (3).

$$\begin{aligned} A &= k_{\nu}l.\log e \;\ldots\ldots \; (3) \\ &= 0{,}4343\ k_{\nu}l \end{aligned}$$

k_{ν} is, in practical terms, proportional to the number of atoms in a particular unit volume i.e. concentration, and hence absorbance is linearly proportional to analyte concentration. This relationship is known as the Beer-Lambert law and it holds for molecular as well as atomic spectroscopy.

The measurement of the absorbance is achieved by instrumentation which in essence has not changed significantly since Walsh's first apparatus. The basic components of this instrumentation are depicted in figure 1.4. Each component is discussed in more detail below.

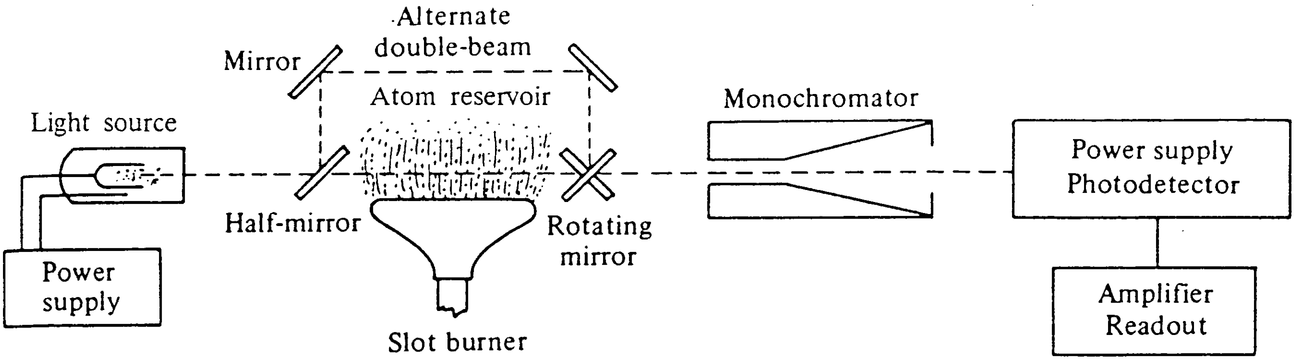


Figure 1.4: Components of an atomic-absorption spectrophotometer[18]

1.4.2. Light source[18,19]

In AAS the signal measured is the reduction in source radiation as a result of atomic absorption. For this reason it is important that the light source meets certain fundamental requirements to ensure sensitive reproducible measurement. These requirements are set out below:

- the spectral lines should be narrow compared to the width of the absorption line to be measured so that simple dispersion systems may be employed,
- the intensity should be bright against a very low background as a high signal-to-noise ratio reduces the sensitivity of measurement,
- the output should be stable after a warm-up time in order to enable reproducible measurement within a batch, and
- there should be no interference from other spectral lines that are not resolved by the spectrometer.

Hollow cathode lamps (HCLs) and electrodeless discharge lamps (EDLs) satisfy these requirements.

A typical HCL is shown in figure 1.5. The lamp is evacuated and filled with a monoatomic filler gas, usually neon or argon, at 150 to 600 Pa. When a high potential (of the order of 500 V) is applied across the electrodes, a low pressure discharge between the two electrodes takes place. Positive ions are formed through ionization of the carrier gas atoms. These ions accelerate through the electrical gradient and collide with the metal of the cathode thereby sputtering cathode material into the discharge region. Atoms of the metal are then excited by collision with gas ions and electrons. On reverting to ground state atoms, energy is emitted in a characteristic line spectrum which is utilized as a light source for atomic-absorption measurement.

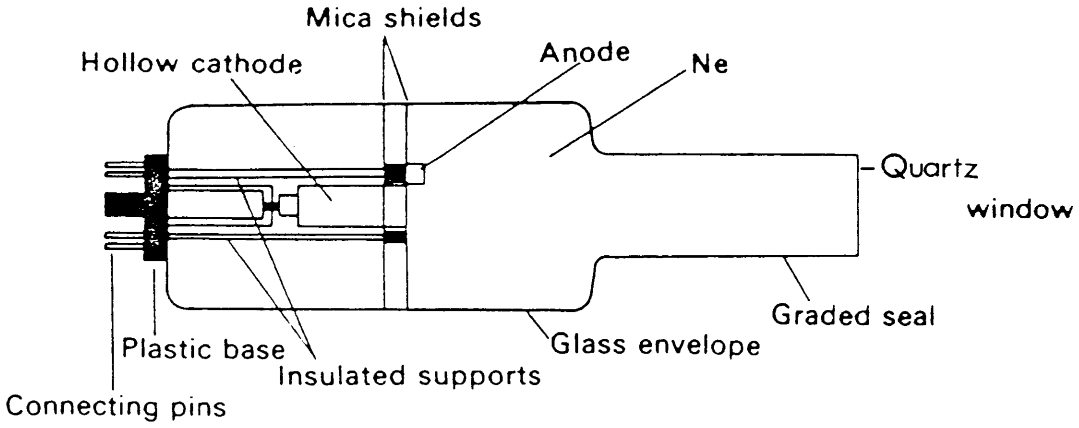


Figure 1.5: Schematic representation of a Hollow Cathode Lamp[18]

Recent improvements in methods of manufacture and the materials used have resulted in extensive and almost exclusive use of the HCL as light source. However, because certain cathode materials are not sputtered as easily as others, the intensity of some HCLs is low. In these cases, the EDL is the preferred light source.

EDLs were first developed for use in atomic-fluorescence spectroscopy (AFS) and emit higher intensity radiation. Their disadvantage is their lower stability. A cutaway diagramme of an EDL is given in figure 1.6.

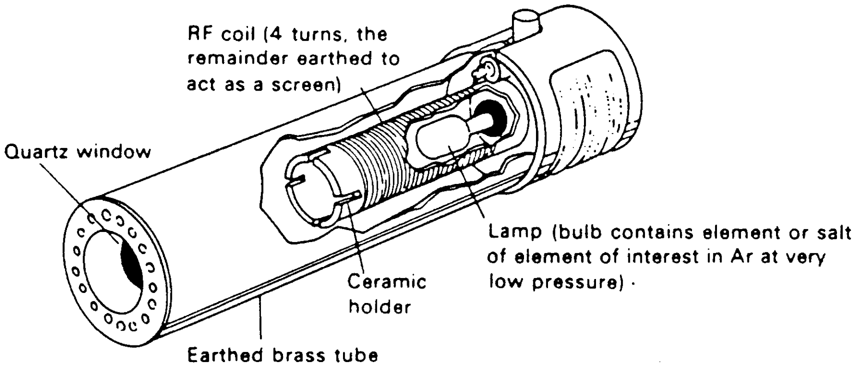


Figure 1.6: Cutaway diagramme of an Electrodeless Discharge lamp[18]

1.4.3. Atom reservoir[18,19]

For absorption of the radiation from the light source to take place, a reservoir of atoms positioned in the light path is necessary.

The prerequisites of the atom reservoir are:

- the analyte atom population in the reservoir should be representative of the analyte atom population in the sample,
- the analyte population should predominantly be in the ground atomic state in the atom reservoir,
- the residence time in the atom reservoir should be long enough for the detector to register the absorption by the atoms, and
- the conditions in the atom reservoir should be stable and constant enough to ensure precise analysis.

Various atom reservoirs meet these requirements and have been utilized, the most common being:

- the flame together with pneumatic nebulization,
- the miniature graphite furnace or electrothermal atomizer, and
- the quartz T-tube for the hydride generation or cold vapour methods of analysis.

1.4.4. Monochromator and Read out system[18,19]

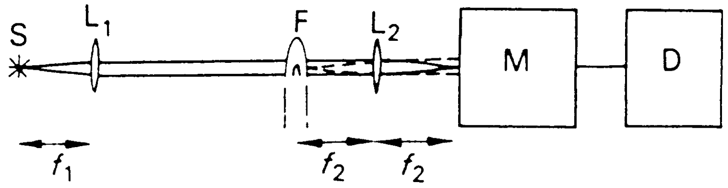
The purpose of the monochromator is simply to select the desired measurement line from the other source emission lines, and to reduce the total light flux reaching the detector system. The monochromator achieves this by dispersion of the incoming radiation with a grating.

Because emission and absorption occur at the same wavelength, it is necessary to incorporate a system of discriminating between the two effects in order to ensure maximum absorption sensitivity.

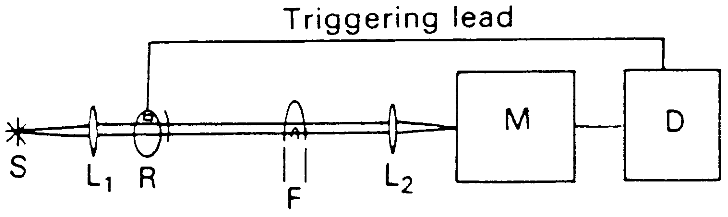
In Walsh's original system[20] (figure 1.7.1), the light from the lamp was passed through the flame in a parallel beam which was focussed on the entrance slit of the monochromator a second lens. The flame was placed at the focus of the second lens, so that the flame and atomic emission was exactly defocussed at the monochromator. Thus, the atomic-absorption signal was maximized and the atomic-emission signal was minimized.

In most modern instrumentation, the emission signal is eliminated electronically by spinning a rotating sector in the light path (figure 1.7.2) or modulating the light source (figure 1.7.3). This results in a modulated absorption signal while the emission signal is continuous. An AC amplifier, triggered by the same modulating signal that pulses the source, amplifies the absorption signal alone thereby eliminating the emission signal.

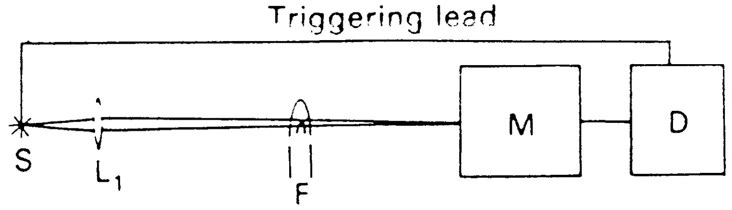
In all cases a photomultiplier is used as the detector, and, after amplification, a variety of read-out systems may be used. The photomultiplier measures the intensity of the transmitted radiation.



1.7.1



1.7.2



1.7.3

L_1 = First lens; L_2 = Second lens; f = focal length; F = Flame;
R = Rotating disk; S = Light source; M = Monochromator; D = Detector

Figure 1.7: Optical and instrumental arrangements for AAS

According to equation 2 above, absorbance is logarithmically proportional to the ratio of transmitted intensity to incident intensity and so it is common to use a logarithmic amplifier in order to obtain a linear signal on the read-out system. The electronics of the read-out systems usually enable some form of signal damping which decreases the noise resulting from the source, flame, and electronics. Most instruments also offer a scale expansion feature which allows the signal (but also the noise) to be amplified electronically. This option is useful when work at low concentrations is required, more so if the element being determined has a stable light source.

1.4.5. Background correction[18]

The absorption measured in AAS is a combination of true atomic absorption, absorption from molecular species present in the atom reservoir, and scattering of the incident radiation by particles in the light path. The latter two, known as non-specific absorption, have a particularly adverse effect at the lower wavelengths (<300nm). There are three methods of overcoming this non-specific absorption. These methods have recently been reviewed by Sotera and Khan[21] and are:

- the deuterium arc system which was introduced by Koirtyohann and Pickett[22] and is discussed in more detail below,

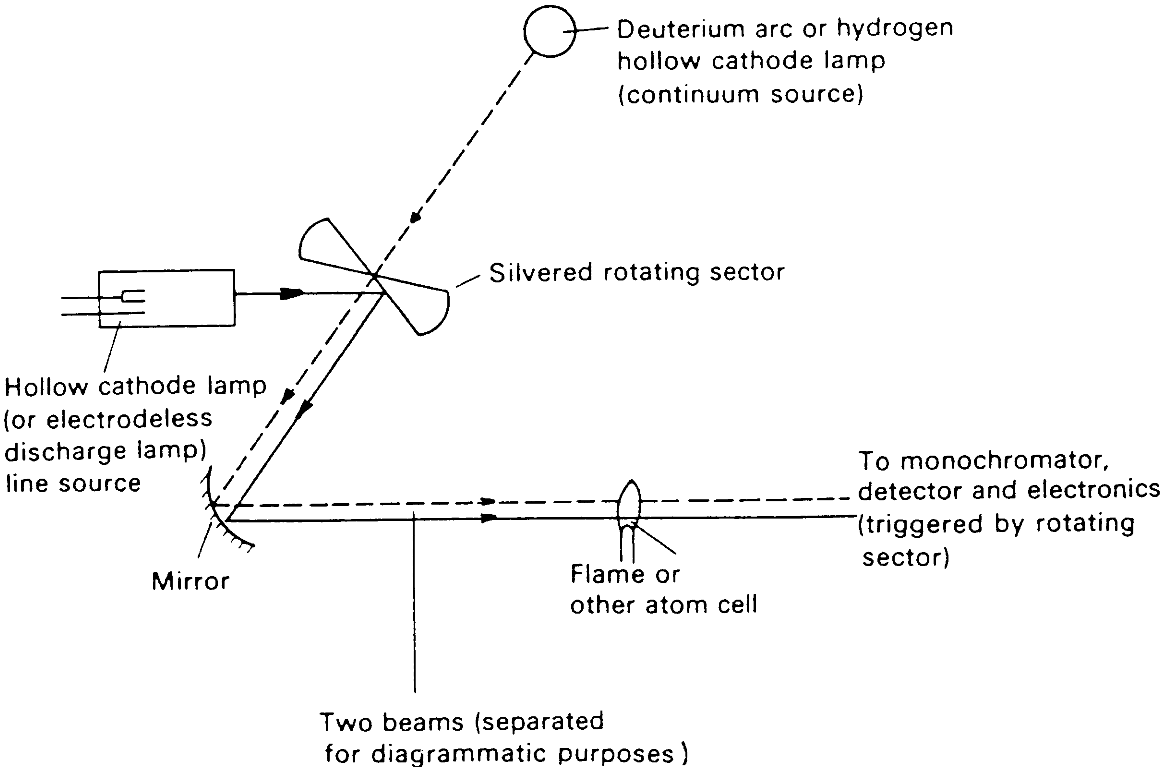
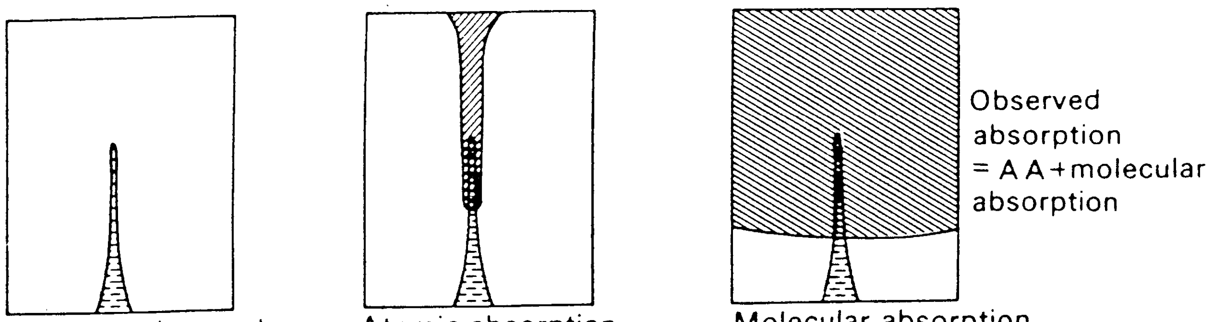


Figure 1.8: Instrumental set-up for deuterium arc background correction

- the Zeeman background correction system as described by de Loos Volbrecht and de Galan[23] which relies on the splitting of the spectral line into at least three components by a strong magnetic field, and



Radiation detected using a line source, e.g. hollow cathode lamp

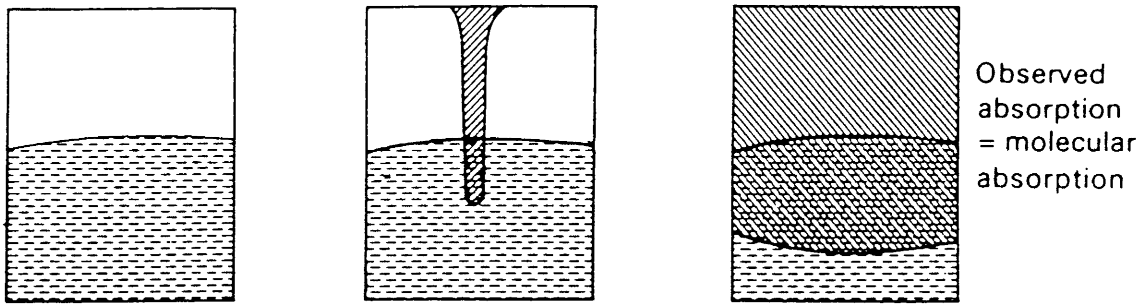
1.9.1

Atomic absorption of line source ~30%

1.9.2

Molecular absorption of the line source ~50%

1.9.3



Radiation detected using a continuum source, e.g. deuterium arc or hydrogen hollow cathode lamp

1.9.4

Atomic absorption of continuum source ~0.01%

1.9.5

Molecular absorption of continuum source ~50%

1.9.6

Corrected absorbance = Absorbance observed using line source
- Absorbance observed using continuum source

Figure 1.9: Principles of operation for deuterium arc background correction

- the Smith-Hieftje System[24] which relies on pulsing the HCL at a high current which results in the emission line being broadened and the relative atomic-absorption signal being greatly reduced. Subtraction of the absorption measured at the high lamp current, from that obtained at the normal lamp current, results in a background corrected signal.

Deuterium arc background correction system is the one most often used in modern instrumentation. The instrumental set-up and principle of operation for this background correction method is given in figure 1.8. The half-silvered mirror allows radiation from the HCL and the deuterium lamp to reach the monochromator. By modulating the signals from these two sources it is possible to isolate them electronically.

The radiation from the HCL is a line source (figure 1.9.1) while that from the deuterium lamp is a continuum (figure 1.9.4). The observed absorption for each source is the sum of the non-specific or molecular absorption and the atomic absorption (figure 1.9.2 and 1.9.5). However, when the continuum is monitored, the atomic absorption component (figure 1.9.5) is negligible and so the measured absorption (figure 1.9.6) is essentially only the non-specific absorption. By using the values given in figure 1.9 this fact is illustrated. For the line source, the measured absorption is 80 per cent (30 + 50), while for the continuum source, the measured absorption is 50,01 percent (50 + 0,01). The corrected atomic-absorption is then 29,99 percent (80 - 50,01) which is sufficiently close to the actual atomic-absorption of 30 percent to be of analytical use.

1.5. Hydride generation

1.5.1. Historical development

Although the design of hydride generators has undergone changes since Holak[25] first generated arsine in 1969, the basic principles established by Holak's method still pertain.

Hydride generation, as a method of sensitive analysis, was developed to solve a problem encountered in the sensitive determination of arsenic. The determination of arsenic is required because of its high toxicity, and also because it is an indicator of precious metals in geological formations. The sensitivity required was not achievable by conventional flame AAS measurement. The arsenic resonance lines lie in the far ultra-violet region of the spectrum where flame absorption produces an unfavourable signal-to-noise ratio. Attempts to overcome this by using the cooler (air entrained) argon - hydrogen flame, although resolving the problem of the poor signal-to-noise ratio, suffered from interferences resulting from incomplete salt dissociation and molecular absorption.

Holak[25] provided a solution to this problem by introducing the arsenic into the nebulizer assembly as arsine, a gas. He collected the arsine, that was generated when an acidic arsenic containing sample was treated with zinc, in a cryogenic trap. After ten minutes, the cryogenic trap was warmed and the arsine was swept into the nebulizer assembly where it was mixed with the flame gases.

Fernandez and Manning[26] used a balloon as the collection device and extended the method to the determination of selenium.

Dalton and Malanoski[27] were the first to do away with the collection device and the generated hydride was carried to the argon - hydrogen flame by the released hydrogen.

The next major improvement to the technique occurred when Chu *et al*[28] introduced the generated hydride into an electrically heated quartz tube. This tube was mounted above the burner assembly in the light path of the spectrophotometer. This resulted in a great improvement in the range of interference free determination possible for some of the hydride forming elements and overcame the disadvantage of dilution by the flame gases. These workers used a tin(II) chloride - potassium iodide - zinc reaction together with a balloon collection device. A reaction time of 10 minutes was allowed before the arsine was swept into the quartz tube by a flow of argon.

The method was still cumbersome because of the slow reaction rate and the resultant need for a collection device.

When Braman *et al*[8] introduced the use of sodium borohydride as the reductant in 1972, it was possible to do away with a collection device. The superior reaction rates experienced when this reductant was used enabled the direct introduction of the generated hydride into the atom reservoir. The method was extended by Schmidt and Royer[29] to the determination of selenium, antimony, and bismuth. Pollock and West[30] determined germanium and Fernandez[31] analysed samples containing tin and tellurium. Reagent blanks were also found to be lower when sodium borohydride was used. All of these workers continued to introduce the generated hydride directly into the nebulizer assembly and the hydride was atomized by an argon (air-entrained) - hydrogen flame.

It was not until 1974, when Thompson and Thomerson[32] published a report on the use of sodium borohydride as the reductant and the heated quartz tube as the atom reservoir, that hydride generation really became a viable routine method of analysis. Instead of directing the generated hydride into the nebulizer these workers alligned a quartz tube in the light path above the flame and flushed the generated hydride into this tube. By doing this, they were able to overcome the interference from non-specific absorption associated with flames at the wavelengths used for analysis.

Sodium borohydride was initially used in pellet form. But because of the resultant vigorous localized reaction and the generation of an excess of hydrogen McDaniel *et al*[33] proposed the use of sodium borohydride solution and reported an improved efficiency and more economic use of this expensive reagent. The use of sodium borohydride solution was also found to be advantageous when some workers[34-36] sought to automate the method. It was found that the stability of the sodium borohydride was improved if the reductant was prepared in an alkaline medium[33,36,37] (0,1 to 2 per cent sodium hydroxide or potassium hydroxide) and filtered through a 0,45 μm membrane filter[38].

1.5.2. The chemistry of measurement

The actual chemistry involved in the hydride generation process using the different reduction systems and the subsequent dissociation of the hydride to yield analyte atoms has not been neglected by analytical chemists in their search for a better understanding of this technique.

The simple covalent hydrides of the carbon, nitrogen, and oxygen groups are well known. The generation of the hydrides of some of these elements such as antimony, arsenic, bismuth, germanium, lead, selenium, tellurium, and tin has been used for the assay of these elements. Each of these hydrides are volatile (table 1.1) and once generated are suitable for effective sample introduction into an atomizer or excitation source of a spectroscopic instrument.

Table 1.1
Boiling points of the gaseous hydrides
of practical analytical importance(16)

Element	Hydride	B.p.,(°C)
Se	H_2Se	-41,3
Te	H_2Te	-2,3
As	AsH_3	-62,5
Bi	BiH_3	-22
Sb	SbH_3	-18,4
Ge	GeH_4	-88,5
Sn	SnH_4	-51,8
Pb	PbH_4	-13

Initially, these hydrides were formed using the principles of the classical Marsh reaction[39]. Acidified samples were treated with zinc granules, pellets or dust in order to reduce them to their covalent hydrides. This reduction reaction was successfully used for arsenic, antimony, and selenium determination. The following reaction equation depicts how the hydride is formed[25]:-

$$Zn + 2\ HCl \rightarrow ZnCl_2 + 2\ H\cdot \xrightarrow{E^{m+}} EH_n + H_2\ (excess)$$

where E is the hydride forming element and m may be equal to n.

Other metal-acid reactions have been investigated. Goulden and Brooksbank[40] tried an aqueous slurry of aluminium powder. A faster reaction time was reported. Pollock and West[30,41] employed a mixture of magnesium metal and titanium(III) chloride and were able to generate H_2Te and BiH_3 as well.

The time necessary for these reactions to proceed to completion and the fact that they could only be used for some of the hydride forming elements prompted researchers to look for an alternative reducing agent.

Sodium borohydride had traditionally been used by the organic chemists in their synthesis. But in 1972, Schmidt and Royer[42] used sodium borohydride as a reductant for the determination of antimony, arsenic, bismuth, and selenium. Since then, sodium borohydride has been used for the determination of germanium[30], tin and tellurium[31], and lead[32]. This reductant has also been used by Yan *et al*[17] to generate the hydrides of indium and thallium, however, the sensitivity of analysis was comparable to conventional flame AAS and has not found wide acceptance. The reaction by which the metal hydrides are formed is given by the following reaction:-

$$NaBH_4 + 3\ H_2O + HCl \rightarrow H_3BO_3 + NaCl + 8\ H\cdot \xrightarrow{E^{m+}} EH_n + H_2\ (excess)$$

The sodium borohydride-acid reaction was found to be superior to the metal-acid reduction system with respect to the reaction yield, reaction time, lower blank contamination, and applicability to more elements. The shorter reaction times opened up the possibility for automation of the method.

Having formed the hydride, the next step in the process is to transfer it to the quartz tube where atomization takes place. Some controversy exists about the atomization mechanism.

Initially it was believed that the decomposition of the hydride to the atomic state was by means of a thermal decomposition reaction; Thompson and Thoresby[43] refer to the 'electrothermal atomization' of arsenic in a heated quartz tube and Verlinden *et al*[44] used an electrically heated quartz tube for the 'thermal decomposition' of arsenic in an argon atmosphere.

There are however, a number of inconsistencies which cast doubt on such a mechanism.

- Optimum temperatures for the quartz tube are around 800°C whereas for thermal atomization in an electrothermal atomizer, temperatures of 1700-1800 °C are required, furthermore,
- the addition of oxygen increases the sensitivity[45], and finally
- the surface of the quartz tube appears to play an important role in the atomization process[46].

Dedina and Rubeska[47] studied the atomization of selenium hydride in a cool hydrogen oxygen flame burning in an unheated quartz tube. They showed that this process relies on the presence of free radicals present in the flame employed in their system. Welz and Melcher[48,49] concluded that the same mechanism holds for atomization in an electrically heated tube. These workers conducted experiments which support each of the three observations listed above. They proposed the reactions given below as being the mechanism for the atomization of, certainly arsenic, and probably, the other hydride forming elements as well. Collisions with free hydrogen radicals result in the atomization of metal hydrides.

$$MH_x + H\cdot \rightarrow MH_{x-1} + H_2$$

where M is the metal
hydride forming element

$$MH + H\cdot \rightarrow M + H_2$$

The hydrogen radicals are believed[47] to be formed as follows:-

$$H\cdot + O_2 \rightarrow OH\cdot + O\cdot$$
$$O\cdot + H_2 \rightarrow OH\cdot + H\cdot$$
$$OH\cdot + H_2 \rightarrow H_2O + H\cdot$$

This proposed mechanism supports all the observations made with respect to atomization of the hydride.

The proposed reactions occur at temperatures found to be necessary for optimum hydride atomization. The role of oxygen in the improvement of sensitivity is evident as it is one of the reactants in these reactions. The importance of a clean quartz surface may be explained by the fact that, if it is not clean, it presents sites for the recombination of the radicals and thereby reduces the population of available radicals.

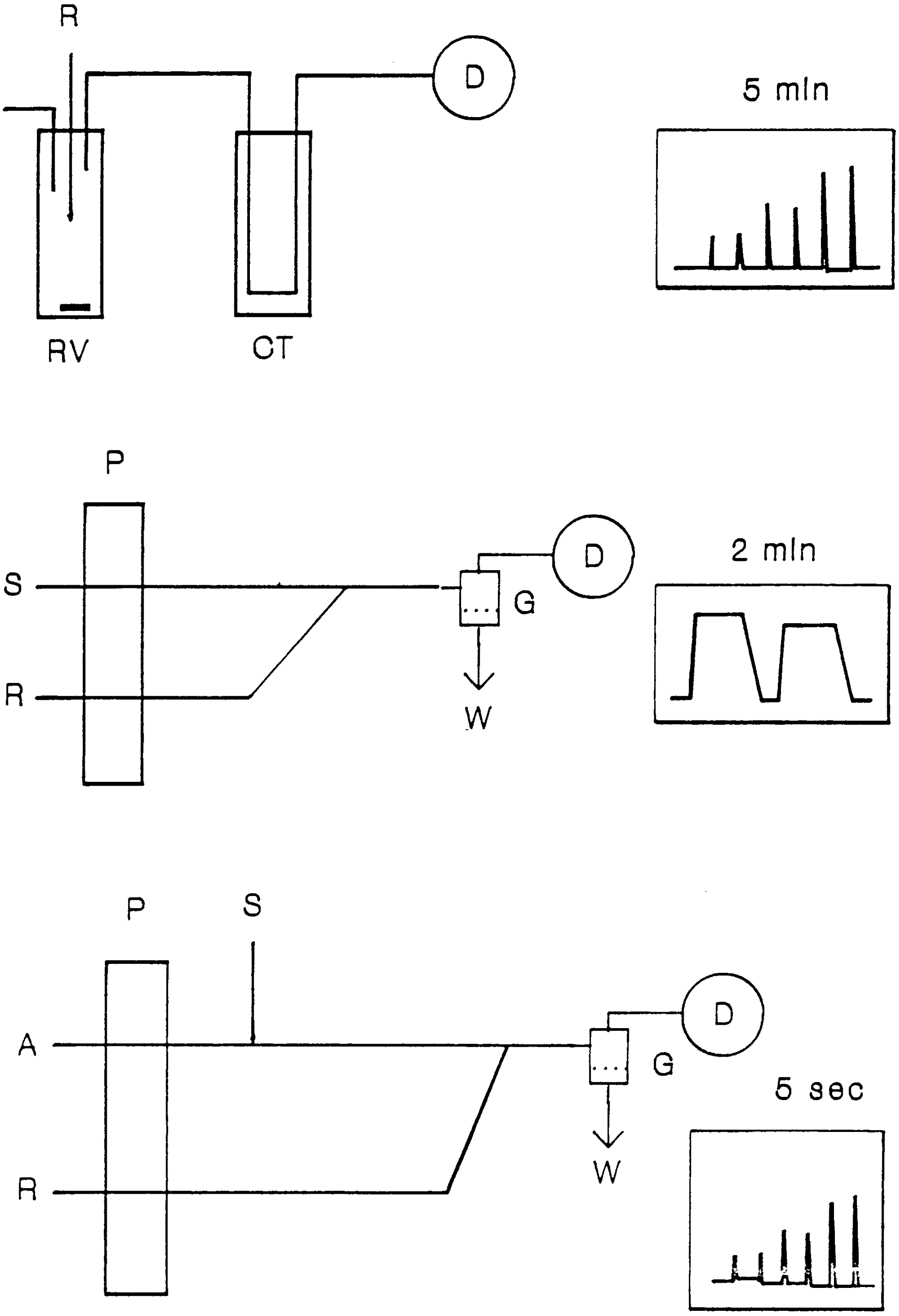
Welz and Melcher[49] finally concluded that thermal decomposition of the hydride occurs only in the absence of hydrogen and then it is not to yield atomic arsenic but rather one of the polymers, As_2 or As_4.

1.5.3. Hydride generators

Hydride generators may be divided into one of three groups depending on their mode of operation. These modes are listed below:

(1) batch-wise in a reaction flask (figure 1.10.1)[26]
(2) continuously in a continuous flow system where the sample stream is merged with the reductant stream (figure 1.10.2)[50], and
(3) intermittently by injection of the sample into an acidic carrier stream which is merged with the reductant stream (figure 1.10.3)[51].

In *batch methods*, each sample is processed separately in a vessel where different analytical procedures are performed (e.g. dilution, reagent addition, mixing, heating). Once all the sample manipulation steps have been completed, the sample is taken to the detector where the analysis is carried



R = Reductant; RV = Reaction vessel; CT = Cryogenic trap (or other collection device); D = Detector; S = Sample; P = Pump; G = Gas / liquid separator; W = Waste; A = Acid

Figure 1.10: Modes of measurement using hydride generation and typical recorder output with measurement times (per sample)

out on the sample or an aliquot of the sample. In hydride generation, an aliquot of the prepared sample is transferred into a reaction vessel to which acid and finally sodium borohydride are added. After completion of the measurement, the reaction vessel is drained and rinsed out before the next cycle begins.

The term *continuous-flow methods* applies to analytical procedures in which the analyte concentration is measured without stopping the flow of solution or gas through the detector. Successive samples are introduced into the carrier stream continuously. The resulting signal is a steady state signal which may either return to a base line corresponding to no analyte element present or alter to represent the concentration of the next sample.

There are two variations of the continuous flow system; segmented and unsegmented. The segmented-flow method as commercialized by Technicon was first described by Skeggs[52] in 1957. Many modern commercial hydride generation systems rely on this approach.

Flow-injection analysis (FIA), defined in 1974 by Ruzicka and Hansen[53], has been applied to a large number of analytical operations. The main differences between this new approach and segmented systems are that the streams are not segmented, the sample is injected rather than aspirated, and neither physical nor chemical equilibrium is a prerequisite for analyte detection. Hydride generators utilizing this approach are still in the prototype stage and are showing tremendous potential for improving analysis time, providing fundamental data on the chemistry taking place, and reducing interferences.

All commercial instruments and most home made apparatus fall into one of these groups. The basic components of a batch type apparatus are a reaction vessel and in some cases a collection device. In continuous flow systems, the reaction takes place in the apparatus tubing and some sort of phase separating system is required. Both systems require an atomization cell.

Reaction vessels vary in size and shape from fairly large 200 cm^3 beakers to miniaturized containers with a volume less than 10 cm^3. In most batch type apparatus, magnetic stirring is utilized to ensure that the reaction is not localized and the generated hydride is stripped from the liquid as quickly as possible. In continuous flow systems, the reaction takes place in the flow lines, reaction coils, or single bead string reactors (SBSRs).

A number of different *collection devices* have been used usually when the metal-acid method of reduction was used. Of these, rubber balloons appear to be the most popular[26,54-56]. However, they have the disadvantage that, in the acidic environment in which they are used, they tend to perish very quickly and loose their elasticity. Some workers have bubbled the reaction gas through a solution of silver nitrate[57] or some other collector[58,59] solution and then introduced the collector solution into a normal flame nebulizer or graphite furnace. Pressurized chambers have also been used to collect the generated hydride. Aggett and Aspell[60] used a 250 cm^3 glass bottle while Pollock and West[30] used a 450 cm^3 plastic container. The collected hydride was then flushed from the pressure chamber with an inert gas.

In automated systems, the sample is either injected into an acidic carrier stream or it acts as the carrier stream itself. This stream is merged with a stream of reductant. The various streams are either pumped by a peristaltic pump[50] or by a pressurized reagent pumping sytem[61].

Once the reaction has taken place the generated hydride and hydrogen gas are stripped from the liquid effluent in a gas / liquid separator and flushed through to the spectrophotometer by a stream of inert gas. The effluent is drained to waste. The *gas / liquid separator* described by Kan[34], and small variations of it, have been used to strip the gaseous hydride from the liquid phase. In some cases, smaller dimensions have been used and the effluent is then pumped to waste. Some workers[36,62] have used separators with a porous poly-tetrafluoroethylene (PTFE) membrane or, recently, a PTFE tube[63] where the increased surface area is claimed to be more efficient in stripping the gas.

The *atomization cell* most often used is the quartz tube introduced by Chu *et al*[28]. The improvement in sensitivity achievable compared to the previously used argon - hydrogen flame may be attributed to the increased residence time of the analyte in the light path, a smaller dilution by support gases, and improved signal-to-noise ratios.

Since the use of the quartz tube became established as the atomization cell, a number of different schemes have been proposed to ensure maximum sensitivity and minimum interference. Siemer and Hagemann[64] used the hydrogen generated in the reaction to carry the hydride to the atomization cell where they supported combustion by adding a small amount of oxygen into the generator. the combustion of these gases ensured the atomization of the metal hydrides. Dedina and Rubeska[47] investigated the so-called flame in tube atomizer and concluded that the mechanism for hydride atomization involved radicals rather than simple thermal decomposition.

Schmidt and Royer[29] were the first to use a flame heated quartz tube. The normal flame assembly of the AAS was used with the quartz tube mounted above it. These workers used a argon - hydrogen flame while others[32] used a stoichiometric air - acetylene flame. The hydrogen generated in the reaction was prevented from igniting at the ends of the tube by a transverse flow of nitrogen.

The main criticism against the quartz tube is the gradual decrease in sensitivity experienced as the tube ages. This may be attributed to traces of sodium hydroxide in the carrier gas, and burnt-in metals on the surface of the quartz. This problem can be overcome by rinsing the tube in dilute nitric acid and hydrofluoric acid. Parisis and Heyndrickx[65], in an investigation of different gas transfer tubing, reaction flasks and quartz tubes, found that silanization of the quartz tube greatly improved the sensitivity and reproducibility of measurement.

A variety of different shaped quartz tubes[66-70] have been described. Some of these are depicted in figure 1.11. Of these, the T-shaped quartz tube with a restriction in the middle has been found to give excellent sensitivity.

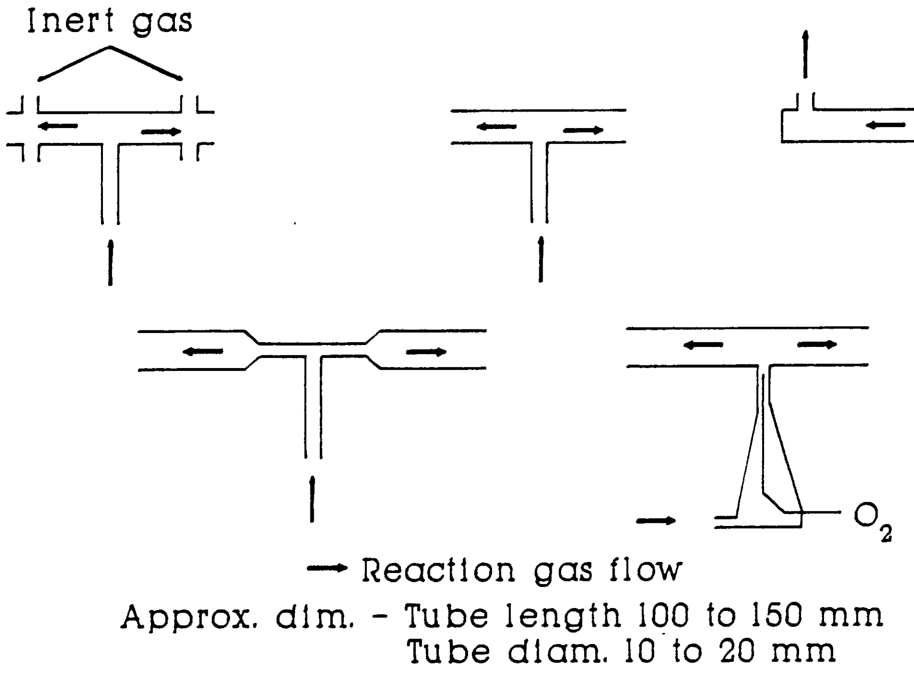


Figure 1.11: Schematic representation of some quartz tube atomizers

Sturgeon *et al*[71] have recently described the introduction of the generated hydride into a graphite furnace. Improved sensitivity and a reduction in interferences are claimed for this approach.

Although papers continue to appear on hydride generation apparatus design, attention in recent years has rather been on interferences, their mechanisms, and ways of overcoming them.

1.6. Interferences

1.6.1. Classification

Interferences may loosely be defined as '*any factor that changes (increases or decreases) the signal obtained from a particular analyte population*'. Hydride generation, although a sensitive technique, is fraught with numerous interferences. Even a cursory look at the literature reveals that overcoming interferences has commanded the greatest share of investigator's time. These interferences may be grouped into two groups, *viz.*,

(1) factors affecting the rate or efficiency of hydride generation or the subsequent atomization, and
(2) non-specific absorbance in the atom cell.

Interferences resulting from the second group have largely been overcome by the use of the quartz tube atomizer together with background correction.

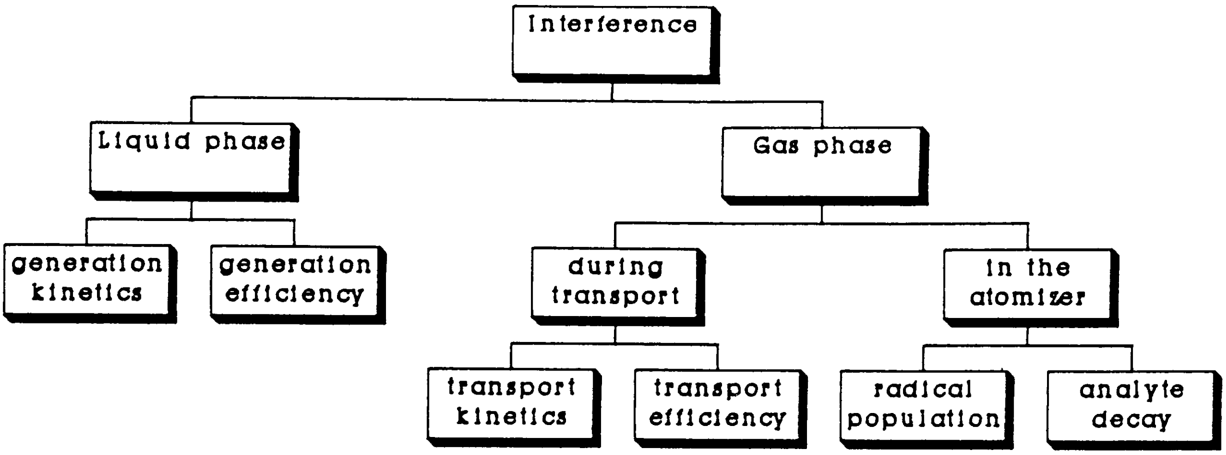


Figure 1.12: Classification of interferences

Dedina[69] has provided a scheme for the classification of interferences (figure 1.12) which fall into the first group. A classification of this kind enables the researcher to overcome new interferences based on experience gained with other interferences in the same partition.

Smith[72] conducted an extensive study into the effect of 48 elements on the analysis of arsenic, antimony, bismuth, germanium, selenium, tin, and tellurium. This work was carried out using sodium borohydride as the reductant and an argon - hydrogen flame. Certain trends are observable in this study. There is no interference on the seven elements studied by the alkali metals, alkaline earths, boron, aluminium, gallium, titanium, zirconium, hafnium, mercury, lanthanum, manganese, vanadium, and yttrium. Some interference was always encountered from copper, silver, gold, platinum, palladium, rhodium, ruthenium, nickel, and cobalt. Mutual interferences between hydride forming elements were also found in most cases.

Many other workers[70,73,74] have conducted investigations on interferences in a wide variety of hydride generator designs. Significant work was carried out by Pierce and Brown[36,75] who showed that the severity of the interference was dependent on the apparatus design. This conclusion supports the lack of agreement between investigators on the extent of interferences. It also means that interference handling strategies for each apparatus design must be undertaken.

Little is understood about the mechanism of these interferences and most publications are devoted to simply overcoming the interferences rather than understanding their mechanism. However, some workers have investigated the mechanisms involved in order to better overcome the influence of these interferences.

1.6.2. Mechanisms

Of all the publications on interference mechanisms, Welz and Schubert-Jacobs (*nee* Melcher)[48,49,76-79] have surely published the most thorough studies and come up with the most feasible experimentally proven mechanisms.

In one of their earliest publications[48], they reported on the results of an investigation into the influence of selenium on arsenic determination. Little previous work had been devoted to the mutual interference of hydride previous work had been devoted to the mutual interference of hydride forming elements. In this study they showed that competition for the reductant was an unlikely reason for the interference but rather that gas phase interference was taking place. Based on the work of Dedina and Rubeska[45], they assumed that atomization of the metal hydride occurs via free radicals generated in the reaction zone of the heated quartz furnace. Hydrogen selenide forms quicker than arsine and competes more successfully for the small population of radicals present in the quartz tube thereby suppressing the atomization of the arsenic.

Their solution to this problem was to add an element which would, at a carefully chosen concentration, suppress the formation of hydrogen selenide but have no effect on the reduction to arsine. Copper was found to be successful. This supported the mechanism for copper interference proposed by Meyer *et al*[46], *viz.*, the selenium hydride reacts with the copper to form insoluble selenides.

In a later publication, Welz and Melcher[49] investigated gas phase effects in the atomization of arsine. They concluded, after a very elegant set of experiments, that the mechanism for arsine atomization was indeed via reaction with radicals as had been proposed by Dedina and Rubeska[47], thereby supporting their earlier work on mutual interference mechanisms.

Welz and Melcher then took a close look at transition metal interferences[76-79]. First they investigated the influence of cobalt, copper, iron, and nickel on selenium determination[76]. After an evaluation of the existing theories and some experimental work, they concluded that the most likely mechanism for the interference from the studied metals on selenium determination was the one proposed by Kirkbright and Taddia[80], *viz.* the interferent is reduced to a finely dispersed metal which reacts with and absorbs the gaseous hydrogen selenide rendering it unavailable in the gaseous form.

Having looked at selenium, Welz and Melcher[76] turned their attention to the effect of copper, nickel, and iron on the reduction of arsenic from different oxidation states. Their findings further supported their proposed mechanism for transition metal interferences.

In the next area of study, Welz and Melcher[78] made a closer study of the mechanism of the nickel interference on selenium and an explanation for the observed releasing effect of iron (III) was offered. Again, finely divided nickel metal formed by the reduction of the nickel by the sodium borohydride was cited as the culprit for the nickel interference. Iron was found to have a releasing effect because it was preferentially reduced to iron (II) and thereby suppressed the reduction of nickel to metallic nickel.

There is no reason to doubt that the noble metal interferences occur by the same mechanism because we have observed the formation of a fine precipitate of metallic noble metal when solutions with high levels of noble metals are treated with sodium borohydride. The severity of these interferences may be attributed to the fact that these elements are well known hydrogenation catalysts which have the ability to absorb large amounts of hydrogen and related compounds.

Any previous proposals of competition for the reductant being the mechanism whereby certain base metals and noble metals interfere were ruled out by the final stage of Welz and Scubert-Jacobs[79] study where again, further evidence for their precipitated-metal / stable-hydride-forming-element combination mechanism was forthcoming.

Recently[81] new findings have raised the possibility of the hydride forming elements being absorbed by the interferents as borides rather than hydrides. No doubt this theory will be subjected to rigorous testing before it is accepted.

1.7. Overcoming interferences

Having established the extent of interferences, workers began to publish methods of overcoming these interferences. The approaches adopted fall into one of three categories.

- Optimization of experimental conditions.
- Addition of matrix modifiers and complexing agents.
- Use of a separation technique.

1.7.1. Optimization of experimental conditions

An interesting phenomenon was highlighted by Pearce and Brown[75]. The extent of the interference from different cations and anions was found to depend quite dramatically on the method of hydride generation and atomization. Astrom[51] described a flow-injection hydride generator for bismuth analysis. He showed how the severity of some interferences was decreased by the use of this flow-injection hydride generator when compared to the more conventional batch type apparatus. He attributed the improvement to the shortness of the reaction time which not only ensured that a minimum amount of bismuthine had decomposed, but also, the bismuthine was stripped from the reaction mixture before serious interference could take place. In a batch type apparatus where the reaction times are generally longer, interferences were found to be more severe.

Welz and Schubert-Jacobs[79] investigated the effect of acid and sodium borohydride concentration on the recovery of selenium and arsenic in the presence of cobalt, nickel and copper. Greater tolerance of the interferent was achievable by increasing the acid concentration and decreasing the sodium borohydride concentration. It must be noted that this had a negative effect on the overall sensitivity but improved the range of interference free analysis. However, it is important to note that improved interference tolerance may be achieved by optimization of the reagent concentrations.

The design of the quartz tube and the method of heating it, were found[69], to have an effect on the extent of the mutual interference of hydride forming elements.

From these findings it may be concluded that, it is necessary to investigate the design of the apparatus and the experimental conditions used and sensitivity may have to be sacrificed at the expense of an increased tolerance of interferences.

1.7.2. Addition of matrix modifiers and complexing agents

The method of reagent addition for the purpose of extending the range of interference free analysis has been used by many investigators. A study of the mechanism of the interference has enhanced the usefulness of this approach.

The oxidation state of the analyte in the sample material has been found to play a role in the efficiency of hydride formation. For example, antimony must be in the (III) oxidation state before hydride generation will take place. In order to ensure this, some workers[82,83] have added potassium iodide to the sample solution prior to hydride generation.

Kirkbright and Taddia[80] investigated the interference of copper, nickel, platinum and palladium on arsenic determination and found that the addition of thiosemicarbazide and 1,10-phenanthroline as masking agents, extended the range of interference free determination. Later, these same workers[84], having found their earlier complexing agents unsuitable for overcoming interferences in selenium determination, proposed the use of tellurium (IV) as a matrix modifier and interferent suppressor. The tellurium (IV) is believed to be reduced to Te^{2-} which can form very stable tellurides with many interfering ions and thereby remove their influence as interferents. Bye *et al*[85] disputed the findings of Kirkbright and Taddia as far as tellurium is concerned but, stated that the difference in conclusions made by the two groups could have originated from the different apparatus that they were using. They proposed[86] thiourea as a suitable matrix modifier. De Doncker *et al*[87] subsequently used 1,10-phenanthroline for the minimization of nickel interference in bismuth and antimony analysis. Other modifiers such as citric acid[88], EDTA[89], and iron (III)[90] have been used in various situations for the suppression of interferences.

Mutual interferences between hydride forming elements is believed to be a gas phase interference. Therefore, any factor which prevents the interfering hydride forming element from reaching the atomizer would overcome this interference. Welz and Melcher[48] used this fact to overcome the interference of selenium on arsenic determination.

1.7.3. Separation techniques

Separation techniques are used in order to either separate the analyte from the interfering matrix or to separate the interferent from the sample solution. Both methods are equally suitable. The approach adopted depends entirely on the availability of specific methods of separation. This approach, although being extremely successful tends to be rather cumbersome as a number of additional sample manipulation steps are introduced. Nevertheless, a number of researchers have described successful separation methods for overcoming interferences in hydride generation.

Jin and Taga[91] found that in the analysis of lead, the only solution to certain interferences was an extraction with dithiozone and chloroform followed by a back extraction before reduction to the hydride.

Ikeda[92] applied the hydride generation method of analysis to selenium determination in standard copper alloys and nickel sponge in a hydride generator which enabled the in-line removal of interferents using a mini-column of a chelating resin with iminodiacetate groups.

Bedard and Kerbyson[93] used the co-precipition of certain hydride forming elements with lanthanum to separate them from the interferents.

1.7.4. Standard additions

In addition to some of these methods of overcoming the interferences, many workers have advocated the use of the method of standard additions in order to ensure accurate results. Nakahara[15] in his review on hydride generation insists that the method of standard additions should be used as matter of routine and that the standard spike should be carried through the sample digestion, pretreatment, masking, and final reduction-detection stages.

The method of standard additions compensates for matrix effects. If the detector response is not linear or the suppression is so intense that the slope of the graph is small, large errors in extrapolation of the obtained graph can lead to errors. This method is therefore not a panacea for all interference problems. Judicious use of it though, may overcome many of the problems encountered in hydride generation.

Analysts avoid using this method as it requires additional sample manipulation which is time consuming and prone to errors. This means that this method is usually only used as a last resort rather than as a matter of routine.

1.7.5. Disadvantages

While all the methods discussed above have been shown to be successful, and in many cases are in routine use, they not only add to an already lengthy method of analysis but also introduce additional areas where experimental errors can be made. This has lead to the prerequisite that only skilled analytical staff are used for these determinations thereby increasing the cost of analysis. Other simpler methods are often extended beyond their capabilities in an attempt to avoid the use of hydride generation.

This investigation will seek to provide a simple alternative which will raise this method of analysis to the status of the routinely implemented methods of flame AAS and FIA analysis using spectrophotometric detection while still making use of its features of sensitivity and selectivity.

Chapter 2

Development and optimization of a flow-injection hydride generator

2.1. Choice of the mode of measurement

In the initial stages of this project, the experimental conditions for a batch hydride generator were optimized and an evaluation of the generator was carried out. The system was found to be sensitive, versatile, and simple to operate. However, analysis times were long, (typically 2 to 5 minutes per analysis), and all sample clean-up steps had to be executed before the sample was presented to the generator.

Tests carried out on a continuous flow apparatus similar to the one described by Thompson *et al*[3] showed that this generator arrangement has the disadvantage of a large dead volume in the gas / liquid separator and generator tubing which results in the need for long flush times between determinations in order to achieve a 'zero' base line.

In view of the limitations experienced with these generators and the difficulty experienced in overcoming interferences in a quick, error-free manner a new generator was sought which would satisfy as many of the following specifications as possible:

- it should be easy to operate,
- analysis times should be short,
- in-line sample manipulation should be possible, and
- it should provide a sensitive means of analysis for most, if not all, of the hydride forming elements.

A flow-injection system similar to the one described by Astrom[51] was believed to meet all of these requirements. It was therefore decided to design and test a flow-injection type hydride generator.

2.2. The principles of flow-injection analysis (FIA)

Air-segmented flow systems for performing discrete chemical analysis is a technique that has been used for many years. It was believed that air segmentation and the attainment of a *'steady-state'* signal were prerequisites for performing continuous flow analysis. The introduction of flow-injection analysis (FIA), as described in the books authored by Ruzicka and Hansen[94], as well as Valcarcel and Luque de Castro[95], has introduced a new approach to chemical analysis.

FIA is based on the use of *non-segmented streams* and, contrary to the segmented continuous flow principles used by Technicon Auto-analysers, this technique utilizes the *controlled dispersion pattern* resulting from non-segmentation of the sample carrier stream for analytical purposes. The FIA approach constitutes a combination of the following three principles:

- the introduction of a well defined sample zone into a continuously moving stream,
- reproducible timing, and
- controlled dispersion.

These qualities together with unique possibilities of miniaturization offered by such systems imply that FIA techniques have intrinsically greater flexibility. Furthermore, unlike most modern instrumental analytical techniques, modification of the FIA manifold may be carried out by the analyst in order to obtain the best possible solution for a particular analytical problem.

The principles described above have been applied to the sample manipulation and presentation, for a large number of analytical techniques.

Astrom[51] foresaw that a FIA approach could be applied to hydride generation and be used to gain fundamental knowledge about the chemistry involved in this measurement technique. Furthermore, he believed that the short contact times between hydride and interferent carrying solution would result in a decrease in interferences experienced if this mode of operation was used.

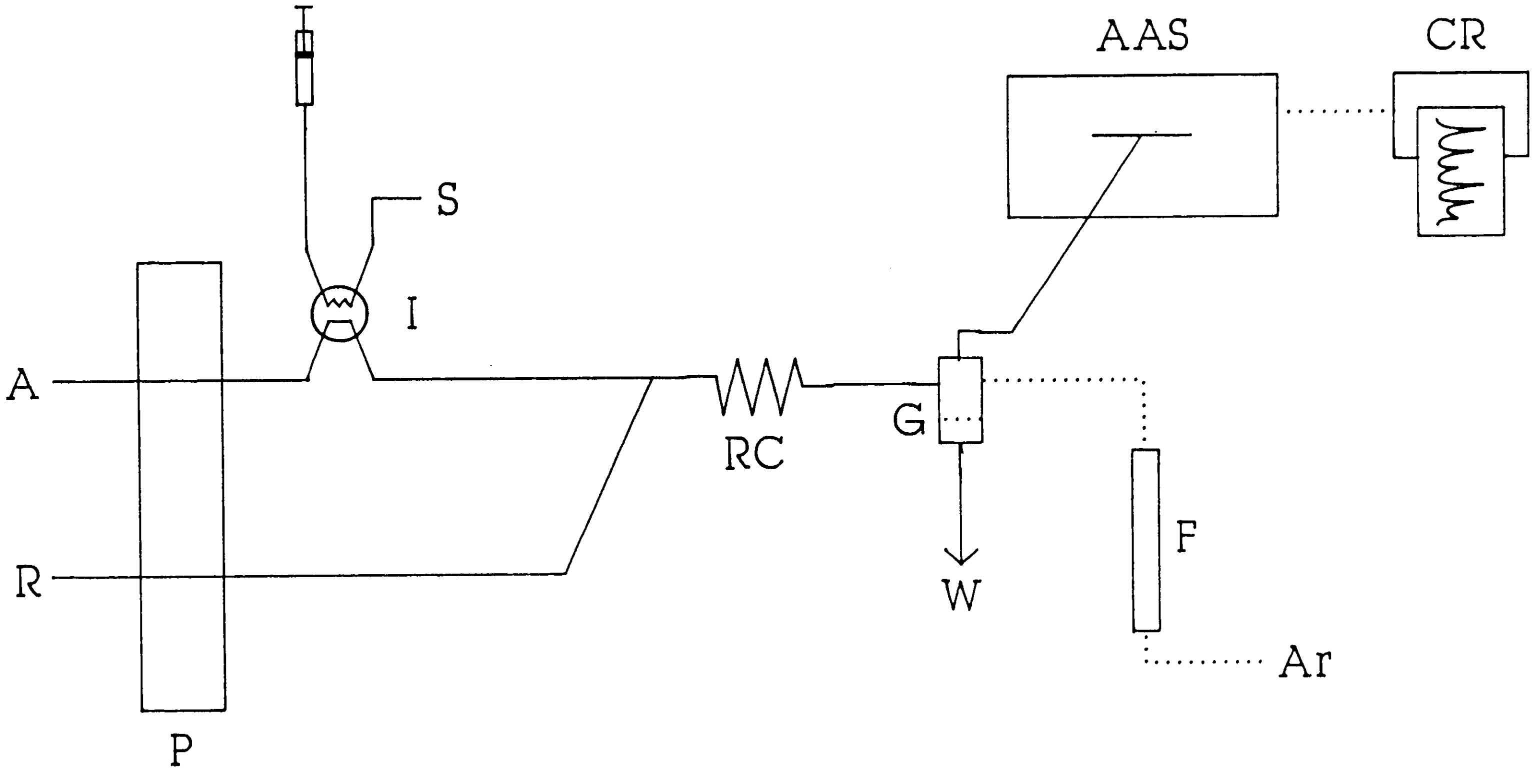
2.3. The hydride generator

One of the advantages of a FIA approach is that manifolds may be designed and constructed to meet the specific demands of a particular problem. In this investigation, the approach was adopted whereby tried and tested batch methods were converted into FIA systems by construction of a suitable manifold. This approach facilitates the use of the theory of proven methods in the more versatile flow-injection environment.

The basic flow-injection manifold used is depicted schematically in figure 2.1 and consists of the following basic components:

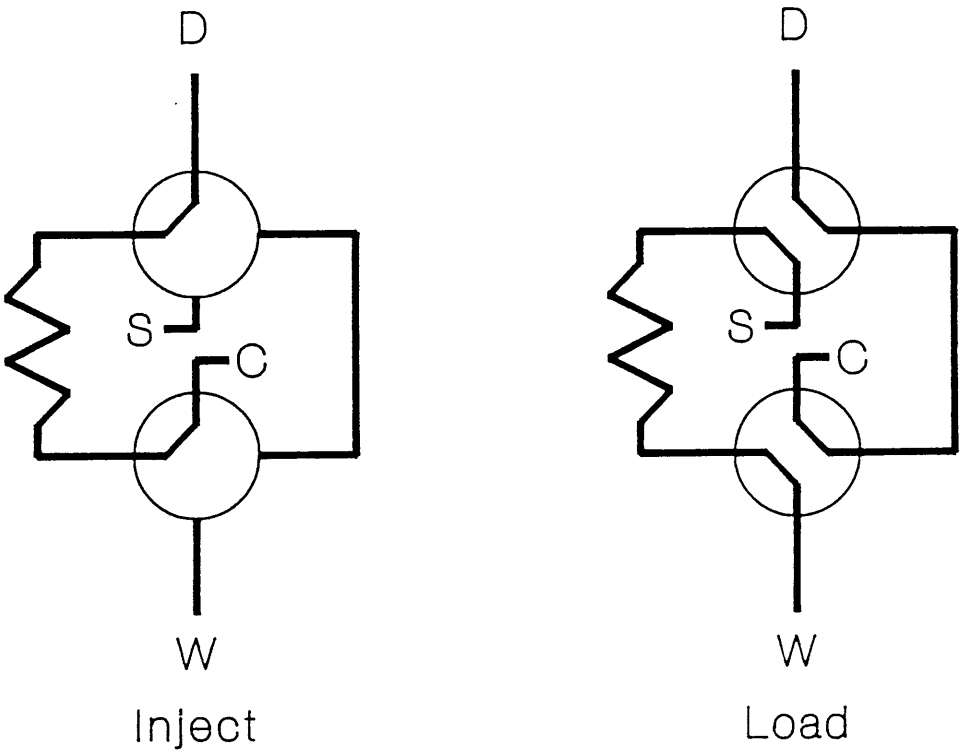
i. Peristaltic pump - Gilson Minipuls with 6 channels operating at variable speed
ii. Air-actuated injection valve - Dionex (Part No. 035913) with variable volume sample loop. This valve and its operation are depicted schematically in figure 2.2.
iii. Humphries air toggle switch - Dionex (Part No. 30070)
iv. Gas / Liquid separator - In-house design and construction (figure 2.3)
v. Quartz T-tube - (figure 2.4)
vi. Teflon tubing - 0,5 mm i.d.
vii. Teflon tubing - 3 mm i.d. (for the reaction tube)
viii. T-pieces for merging streams (figure 2.5.1)
ix. Peristaltic pump tubing
x. Gas flow-meter

The peristaltic pump propels the various streams through 0,5 mm i.d. tubing. The sample is injected into an acidic carrier stream which is then merged with the reductant stream by means of a T-piece. The connector configuration depicted in figure 2.5.2 was used to join the various components together. The hydrides are generated in a length of tubing which may be varied in length and diameter to allow the necessary reaction time. The mixture of gas and liquid is then introduced into the gas / liquid separator where the hydride and hydrogen gas is stripped from the effluent solution and flushed into the quartz tube by a carefully metered flow of inert gas.



A-Acid; R-Reductant; P-Pump; S-Sample; I-Injection valve; RC-Reaction coil; G-Gas/liquid separator; W-Waste; F-Flow-meter; Ar-Argon; AAS-Atomic-absorption spectrophotometer; CR-Chart recorder

Figure 2.1: Basic Flow-injection hydride generator manifold



D = To detector; S = From sample; C = From carrier; W = To waste

Figure 2.2: Diagrammatic representation of the sample injection valve

The quartz tube is heated by an air - acetylene flame and in this environment, the hydride is atomized and detected by the spectrometer. The output from the spectrometer was directed to a chart recorder. The actual setup used is depicted photographically in figure 2.6.

The concentration of the acid in the carrier stream was the same as in the sample. It was therefore unnecessary for mixing to take place between the sample and the carrier stream, in fact any mixing only resulted in dilution of the sample and a drop in sensitivity. For this reason, measures were taken to ensure that dispersion was kept to a minimum. Mixing between the sample and the other reagents was achieved by merging the sample bearing stream with the reagent stream.

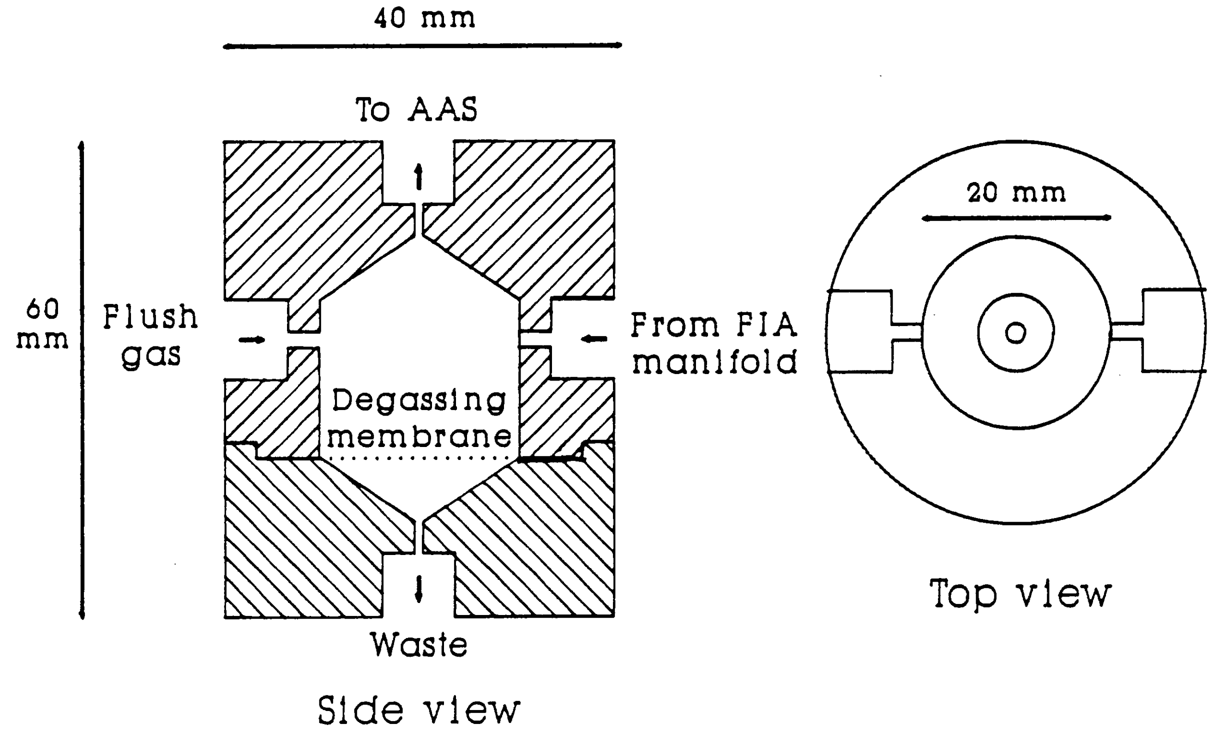


Figure 2.3: Gas / liquid separator

2.3.1. Tubing diameter

Dead volume is reduced to a minimum by using teflon tubing with a 0,5 mm i.d. for all reagent streams. In most instances, teflon tubing with an i.d. of 1,5 mm was used for the reaction coil. It was found that when tubing with an i.d. of 0,5 mm was used, pressure build up by the generation of hydrogen gas caused excessive back pressure. The reaction tube was coiled in order to minimize dispersion of the sample. This phenomenon has been described in detail by Tijssen[96]. The length of the reaction tube was varied to facilitate optimization of the reaction time.

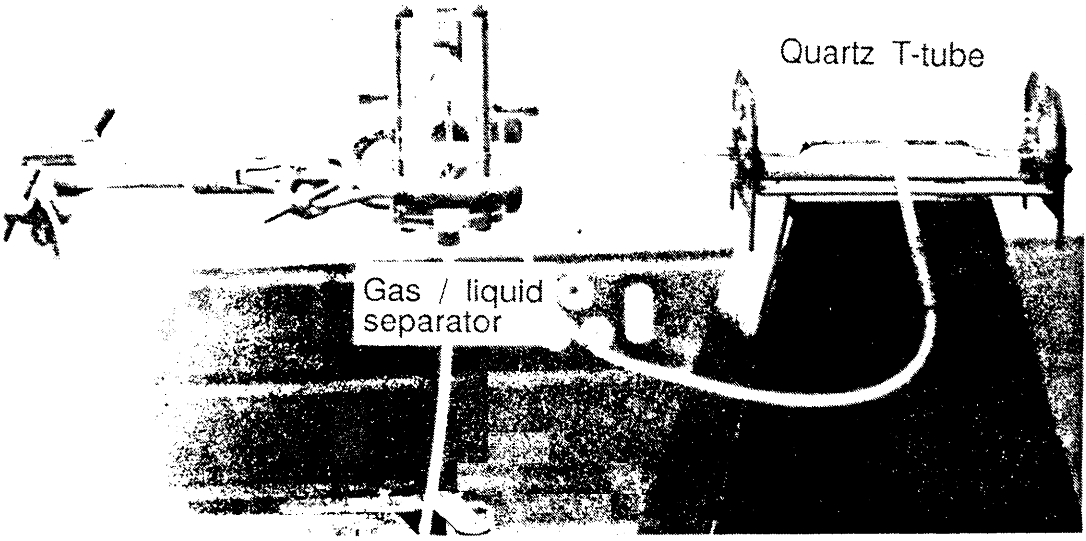


Figure 2.4: The gas / liquid separator and quartz tube

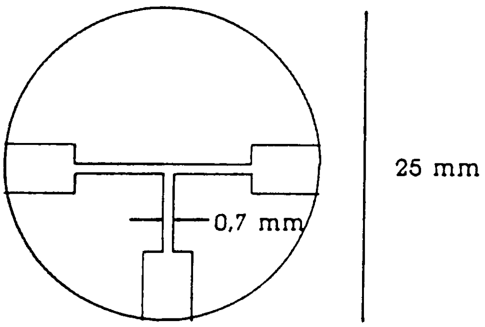


Figure 2.5.1: T-piece for stream merging

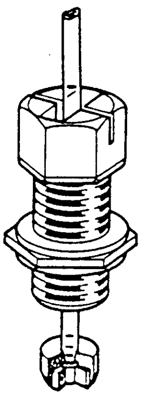


Figure 2.5.2: Tubing connectors

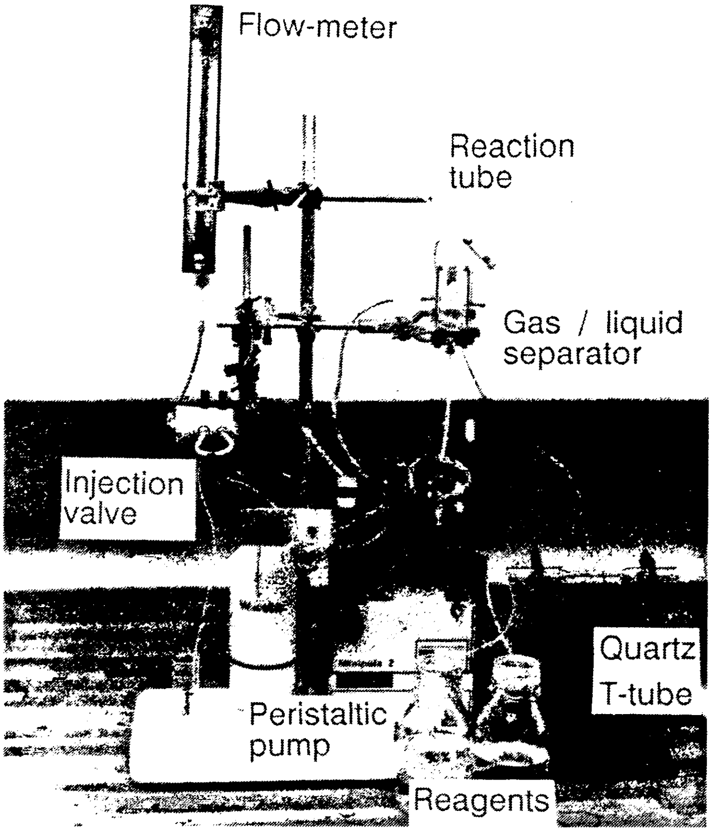


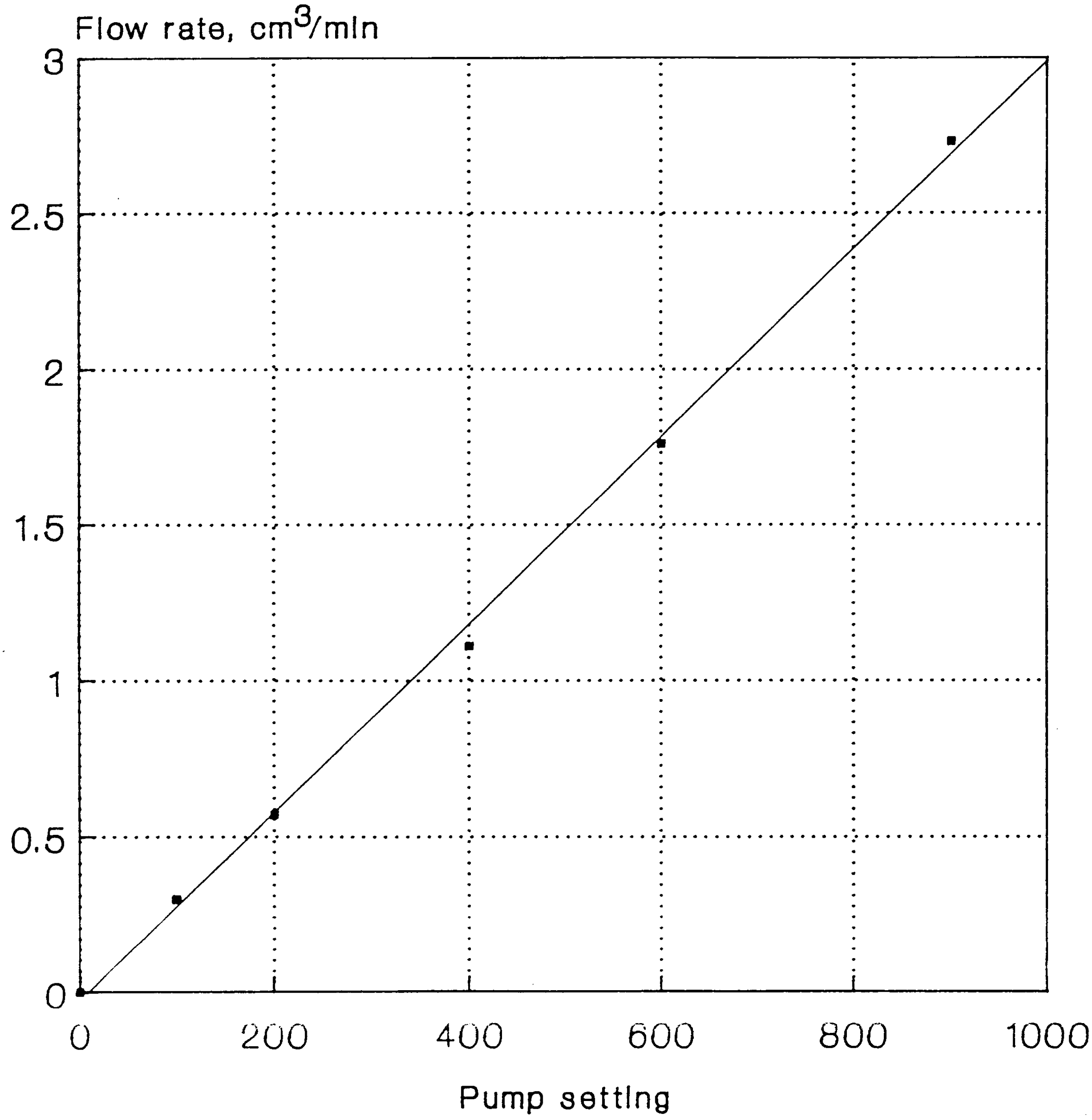
Figure 2.6: The flow-injection hydride generator

In order to improve the gas stripping procedure, a short (30 mm) length of 0,5 mm i.d. teflon tubing was inserted between the reaction tube and the gas liquid / separator.

The peristaltic pump tubing for reagent supply was coded grey / grey (Technicon Instruments Corp. Part No. 116-0549P11) and delivered a particular flow-rate dependent on the pump speed setting. The flow-rate for a particular pump speed setting may be read from the linear graph of pump-speed versus flow-rate (figure 2.7).

The effluent was pumped to waste. The peristaltic pump tubing used to achieve this was coded purple / purple (Technicon Instruments Corp. Part No. 116-0549P15) and two tubes connected in parallel were used to ensure that the gas / liquid separator did not flood. The actual flow-rate for this stream was not critical. The only prerequisite was that it should keep the gas / liquid separator from flooding.

The flush gas tubing and tube between the gas / liquid separator and the quartz T-tube had an i.d. of 3 mm.



(Instruments Corp. Part No. 116-0549P11 peristaltic pump tubing coded grey/grey)

Figure 2.7: Influence of pump setting on flow-rate

2.3.2. Factors affecting gas stripping

Various manifold arrangements were tested in order to improve the gas stripping capability of the system. In Astrom's[51] original design and some subsequent FIA systems[97-100], the flushing gas was introduced before the gas / liquid separator and in some cases even before the addition of the reductant. However, like Ikeda[92], it was found that optimum gas stripping was obtained if the flush gas was introduced into the gas / liquid separator. In addition, the most efficient stripping was obtained when the flush gas was introduced above the level of the liquid in the separator as apposed to being bubbled through the liquid.

The most significant improvement in stripping was achieved when a degassing membrane was introduced. Various materials were tested for permeability and durability. The results of these tests are given in table 2.1. A cotton gauze with 65 per cent polyester fibre content as is used in acid-resistant lab coats was found to be the most suitable material and was used throughout this study.

Table 2.1
Degassing membranes

Material	Disadvantages	Advantages
Whatman 540 filter paper	Poor durablity	Good permeability
Whatman 0,45μm celulose paper	Poor permeability	Average durability
Teflon tape	Bad permeablity	Good durability
Cotton gauze	None	Good permeability Good durability

Initially, the carrier stream inlet to the gas / liquid separator was directly opposite the inlet for the flush gas. This was found to be a disadvantage because the pressure with which the solution entered the separator was sufficient to propel some of the solution into the flush gas inlet orifice which, in time, clogged up. For this reason, the inlet from the FIA manifold was offset to the inlet for the purge gas while still maintaining it above the level of the solution in the separator.

The gas / liquid separator was machined in transparent perspex. This material proved to be resistant to all acids used, *viz.* hydrochloric acid, sulphuric acid, and acetic acid. Rinsing the separator in a solution containing nitric acid caused the perspex to become opaque and should be avoided.

2.3.3. The quartz tube

A number of different quartz tube designs have been used some of which are depicted in figure 1.11. In this study, a simple design was adopted (figure 2.8). The ends were left open to enable the spontaneous ignition of the reaction gases. The constriction in the middle of the T-tube, where the light from the light source is focused, was found to improve sensitivity as it helped to contain the atom cloud in a small volume. The tube was heated by means of the conventional air - acetylene flame.

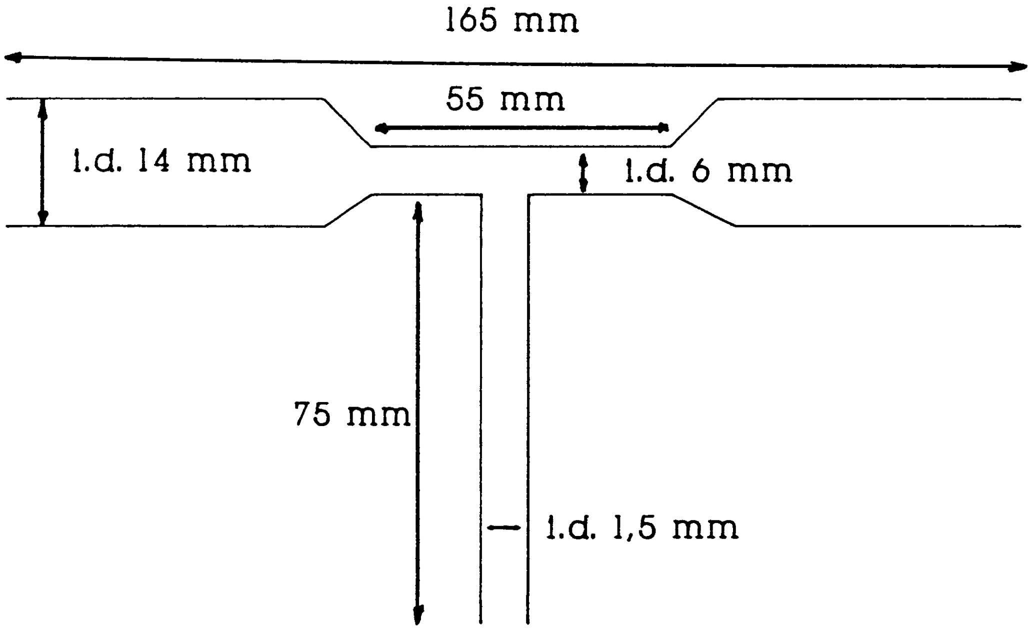


Figure 2.8: Schematic diagramme of the quartz tube

Vitrification of the glass with age resulted in a poorer sensitivity which could only be recovered by replacing the tube. This was only necessary after six months of continual use. Short term improvements in the sensitivity could be achieved by washing the tube in 40 per cent 3:1 *aqua regia*, followed by a soaking in 40 per cent hydrofluoric acid solution for 15 minutes.

The process of silanization descibed by Parisis and Hendrickx[65] was also found to result in a significant improvement in sensitivity. The process described below should be repeated on a weekly basis. After cleaning with acids as described, the tube is dried and submerged in a solution of 5 per cent by volume dimethyldichlorosilane, $(CH_3)_2Cl_2Si$, in toluene. The organic solvent is allowed to evaporate in a fume cupboard for 2 hours. Finally, the tube is dried in an oven at 110°C for 1 hour. The dimethyldichlorosilane reacts with the surface hydroxy groups and deactivates the glass surface. When not in use, the quartz tube should be kept in a desiccator as moisture destroys the silanized layer.

2.4. Optimization of experimental variables

A study of the literature soon reveals that the optimum values for the experimental variables are closely dependent on the particular generator design used. This fact is highlighted by the work published by Pearce and Brown[36]. This means that optimum conditions must be obtained for each generator design and, because the various hydride forming elements behave differently, for each element as well.

In this study, sensitivity of measurement was chosen as the factor to be maximized. Other factors which could also be considered are minimum interference or maximum signal-to-noise ratio.

The sample loop volume, was only optimized for the determination of bismuth and it was assumed that this variable was not dependent on the element determined. A chart recorder plot is given in figure 2.9 for the injection of different volumes of a bismuth standard solution. Maximum sensitivity was achieved for a sample loop of 500μl. The signal obtained when this sample volume was used was about the same magnitude as the continuous equilibrium signal obtained when the sample was pumped through the acid stream.

There were however, disadvantages in using this long sample loop. Not only was the reaction time 4 to 5 times longer than that achieved when a 50µl sample loop was used, but the precision was a lot poorer (s_r of 8 to 10 per cent). When a sample loop of 300µl was used, there was a marked improvement in precision (s_r of between 2 and 4 per cent) without a large reduction in sensitivity.

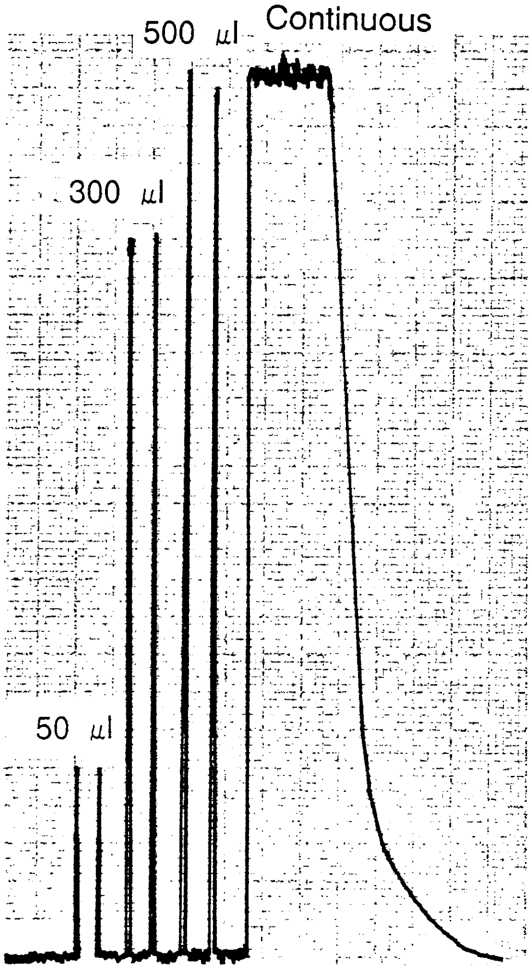


Figure 2.9: Recorder tracing for different sample loop volumes

During the various interference studies, a sample loop of 50µl was used. This practice held a two-fold advantage. Firstly, although a reduced sensitivity was obtained, analysis times were reduced enabling a much greater sample throughput. Because the purpose of these studies was to establish principles for the handling of interferences and not the development of an ultra-trace method of analysis, the sacrifice of sensitivity for speed of analysis was acceptable. Secondly, it ensured that the amount of interferent being introduced into the generator was kept to a minimum, so that long flush times were not necessary.

2.4.1. Method of optimization

Various methods of optimization have been proposed. The most common method used in analytical science is the univariant search method where each variable is optimized while the others are kept constant. Another method which has been applied to the optimization of experimental variables in hydride generation[68] where a batch-type apparatus was optimized, is the simplex method of optimization.

In this investigation, the univariant search method was used because response time was short and it was more convenient to vary some of the variables in fixed increments. The simplex method requires the possibility of continuous variations in the variable settings.

2.4.2. Experimental variables optimized

The experimental variables that were optimized for each element using the developed hydride generator, are listed below:

(1) Reactant concentration,
(2) Flush-gas flow-rate,
(3) Reaction-tube length and diameter,
(4) Flame conditions, and
(5) Flow-rates.

For acid concentration, three discrete acid concentrations (4,8 mol.dm^{-3}, 1,2 mol.dm^{-3}, and 0,12 mol.dm^{-3}) were tested. Having established the optimum acid concentration, three discrete reductant concentrations (0,5, 1,0, and 2,0 per cent by volume) were tested. Flush-gas flow-rates between 10 and 100 cm^3/min were investigated. For the reaction tube length, the sensitivity achieved when each of four reaction tubes were used, was compared in order to select the optimum length. The four options were 750 mm x 1,5 mm i.d., 500 mm x 1,5 mm i.d., 250 mm x 1,5 mm i.d., and 250 mm x 0,5 mm i.d. The flame conditions were varied continuously from a lean flame to a fuel-rich flame in order to achieve optimum heating conditions. The peristaltic pump has an adjustment knob which enables the pump speed, and thereby reagent flow-rate, to be varied. Flow-rates in the range 0,5 to 3 cm^3/min were tested.

2.4.3. Optimum conditions

1) Arsenic

A solution containing only arsenic (III) was prepared from sodium arsenite. Because there was no arsenic (V) present, it was not necessary to take any precautions against fluctuations in sensitivity resultant from the two stable oxidation states. (This phenomenon will be discussed in more detail in chapter 3).

Based on previous experience where arsenic had required longer reaction times than some of the other hydride forming elements, the basic flow-injection manifold was assembled with the 500 mm reaction tube with an i.d. of 1,5 mm.

The most critical variable appeared to be the flush gas flow-rate, this variable was optimized first for every element. Flow-rates that were to high reduced the residence time of the hydride in the atom reservoir and diluted the analyte hydride. Low flow-rates gave rise to broad shorter peaks. By optimizing this variable it was possible to achieve sharp sensitive peaks. The optimum gas flow-rate for arsenic determination was found to be 35 cm^3/min.

The effect of using the different reaction tubes was investigated next. No difference was detected between the signal obtained when the 750 mm and the 500 mm reaction tubes were used. Only an 8 per cent decrease in signal was observed when the 250 mm reaction tube was used. All the reaction tubes tested had an i.d. of 1,5 mm.

An optimum signal was achieved at a flow rate of 1,75 cm^3/min. Lower flow-rates resulted in smaller signals while faster flow-rates resulted in a decline in the precision without a significant improvement in sensitivity.

The effects of hydrochloric acid solution and sodium borohydride concentrations are depicted in figure 2.10. The combination of 1,2 mol.dm^{-3} acid and 2 per cent by volume sodium borohydride, although yielding the most sensitive reading, resulted in flooding of the gas / liquid separator because of the large volume of hydrogen that was generated and continued to evolve in the waste tubing. For this reason it was decided to use the compromise conditions of 1,2 mol.dm^{-3} HCl and 1 per cent by volume sodium borohydride.

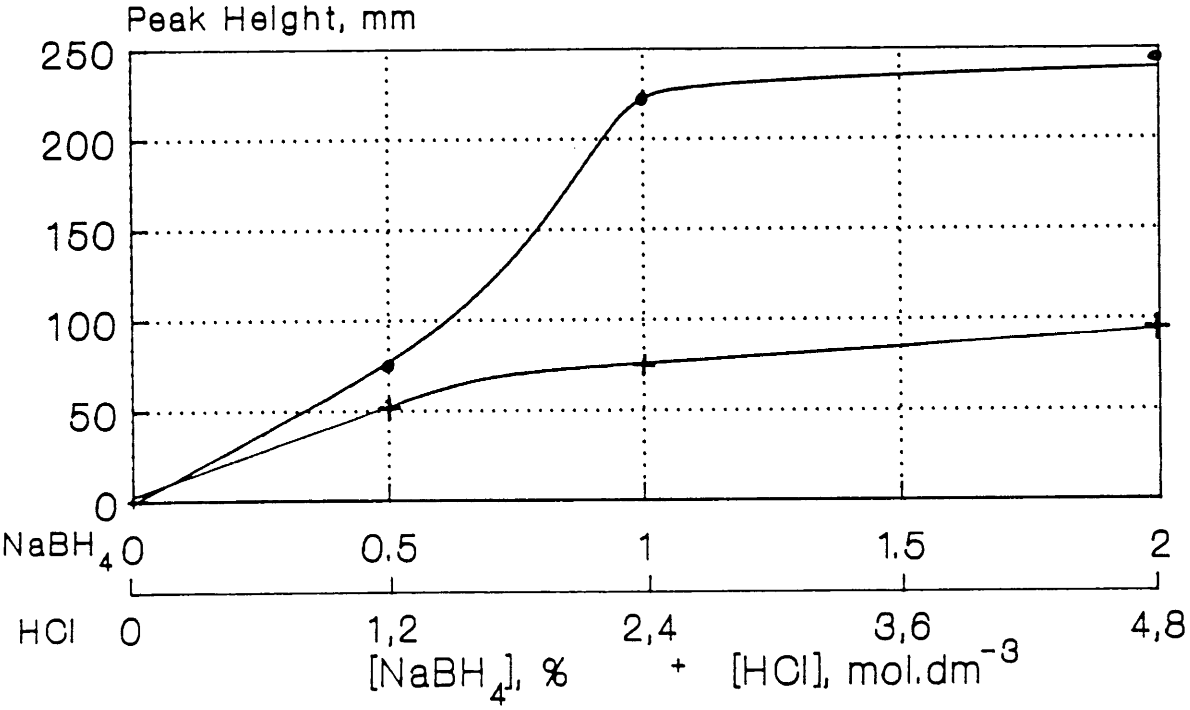


Figure 2.10: The influence of acid and reductant concentration on the sensitivity of arsenic determination

The sensitivity of measurement and shape of the calibration graph typically obtainable for hydride forming elements is depicted in the calibration graph obtained for arsenic (figure 2.11).

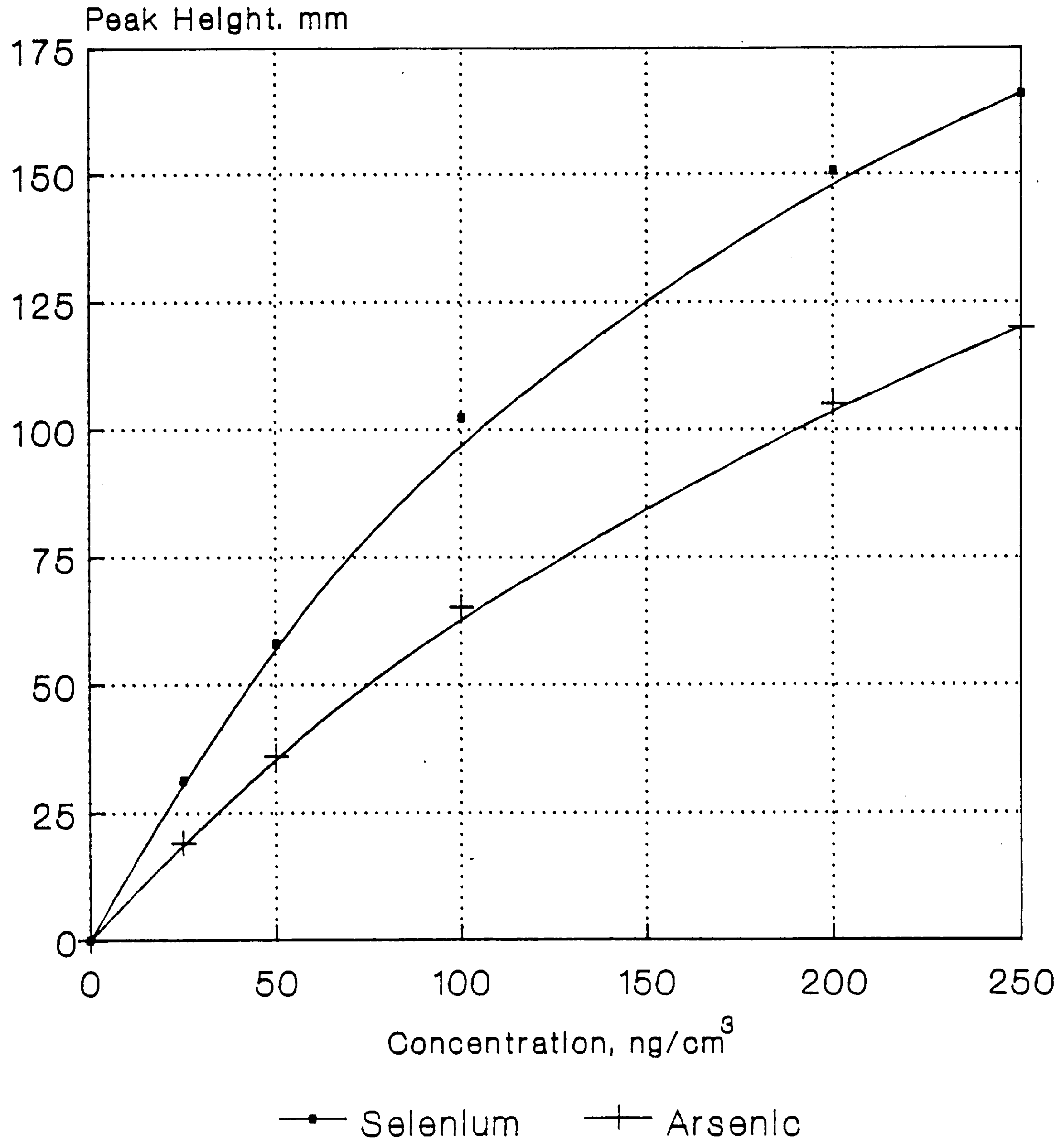


Figure 2.11: Calibration curves for arsenic and selenium determination

(2) Antimony

In order to ensure that the antimony was all in the (III) oxidation state before the generation of the hydride, a change was made to the flow-injection manifold in order to facilitate the in-line addition of a pre-hydride formation reducing agent. This change is discussed in detail in chapter 3. In this chapter the optimization of the pre-hydride formation reducing agent concentration together with the other reaction variables are discussed.

The gas flow-rate was found not to have as significant an influence on the sensitivity for antimony determination as had been found for the other hydride forming elements. After optimization, a flow-rate of 30 cm^3/min was used for further analysis.

Very little improvement in signal was attained by increasing the reagent flow-rate above 1,75 cm^3/min. Furthermore, at the higher flow-rate, the signal-to-noise ratio was found to be inferior.

In the optimization of acid concentration, it was found that increasing acid concentration resulted in increasing signal. The acid concentration was however, not increased above 4,8 mol.dm^{-3} for practical reasons.

The sodium borohydride concentration chosen, as for arsenic, was a compromise between sensitivity and the separator effluent draining capabilities of the generator. A concentration of 1 per cent by volume was settled for.

No benefit was found in using the 500 mm or 750 mm reaction tubes and so the 250 mm tube with an i.d. of 1,5 mm was used.

The concentration of the pre-hydride formation reducing agent, potassium iodide was also optimized. The results of this optimization are presented in table 2.2. A marked improvement in sensitivity was experienced even when only a 1,0 g/dm^{-3} solution was used. A plateau was attained at a potassium iodide concentration of 5,0 g/dm^{-3} and this concentration of potassium iodide solution was used for all subsequent measurements.

Table 2.2
Optimum potassium iodide concentration
for the determination of antimony

KI $g.dm^{-3}$	Peak Height mm
0	4
1,0	17
3,0	21
5,0	25
10,0	25

In the beginning it was difficult to reproduce the sensitivity achievable from day to day. On closer investigation, it was found that the ratio of combustion gases had a significant effect on the sensitivity. Use of a lean flame gave rise to virtually no signal when a sample containing 100 ng/cm^3 was injected into the generator. When a fuel-rich flame was used, an absorbance of 0,200 was achievable.

(3) Bismuth

The method for bismuth was found to be the most sensitive of the hydride forming elements. Bismuthine (BiH_3) is the most unstable of the eight gaseous hydrides determined using this technique. However, because of the rapid and reproducible nature of the flow-injection approach, the determination of bismuth is both sensitive and precise. Because of its instability, all measures to shorten the time delay between bismuthine generation and bismuth detection should be taken.

For this reason the 250 mm reaction tube with an i.d. of 0,5 mm was used and found to be superior to the other larger reaction tubes. Because of the short length of this tube there was no excessive build up of pressure in the reaction tube as the acid reacted with the sodium borohydride.

Flow-rate was also found to have a significant influence on the sensitivity. The signal obtained with a flow-rate of 2,75 cm^3/min was 2,5 times that achieved with a flow-rate of 1,5 cm^3/min.

A marginal improvement in sensitivity was observed when increasing borohydride concentration from 0,5 to 1,0 and then to 2,0 per cent by volume. One percent sodium borohydride was chosen for all further work as the difference in sensitivity attainable at the higher concentration did not warrant the extra reagent consumption.

Increasing the acid concentration above 1,2 $mol.dm^{-3}$ had no effect on the sensitivity of the analysis but, for acid concentrations below 1,2 $mol.dm^{-3}$, the sensitivity declined rapidly.

A gas flow of 60 cm^3/min was found to give the most sensitive signal. Gas flow-rate also had a significant effect on the sensitivity.

(4) Germanium

Attempts to improve the sensitivity of germanium determination beyond those of conventional flame AAS was not successful. Because analysis of germanium by ETA-AAS using matrix modification and solvent extraction is accurate and sensitive[110], further attempts to improve sensitivity were not pursued.

(5) Lead

Relatively little has been published on the determination of lead by hydride generation. The few papers that have covered the subject have all required the addition of an oxidizing agent to the sample solution before analysis[81]. It is believed that the formation of plumbane (PbH_4) proceeds preferentially from the higher oxidation state lead ion than from the lower. Furthermore, careful control of the acid concentration was also found to be necessary. In spite of lengthy and wide ranging attempts to improve the sensitivity attainable in the hydride generator for the determination of lead little improvement over conventional flame AAS sensitivity could be achieved. Sensitive interference-free methods exist for the determination of lead using electrothermal atomization (ETA-AAS). Consequently, it was decided not to pursue the determination of lead using this generator.

(6) Selenium

A much higher flush gas flow-rate was found to be necessary for the determination of selenium than any of the other hydride forming elements. No signal was attainable at a gas flow-rate of 35 cm^3/min. However, when the flow-rate was increased to 70 cm^3/min, a sensitive signal was obtained. Any increase above this resulted in suppression of the signal.

The effects of hydrochloric acid solution and sodium borohydride concentration on the sensitivity of selenium determination are portrayed in figure 2.12. An acid concentration of 3 mol.dm^{-3} and sodium borohydride concentration of 0,5 per cent by volume were chosen as optimum conditions. For hydrochloric acid concentrations above 2,4 mol.dm^{-3}, there is no improvement in the sensitivity.

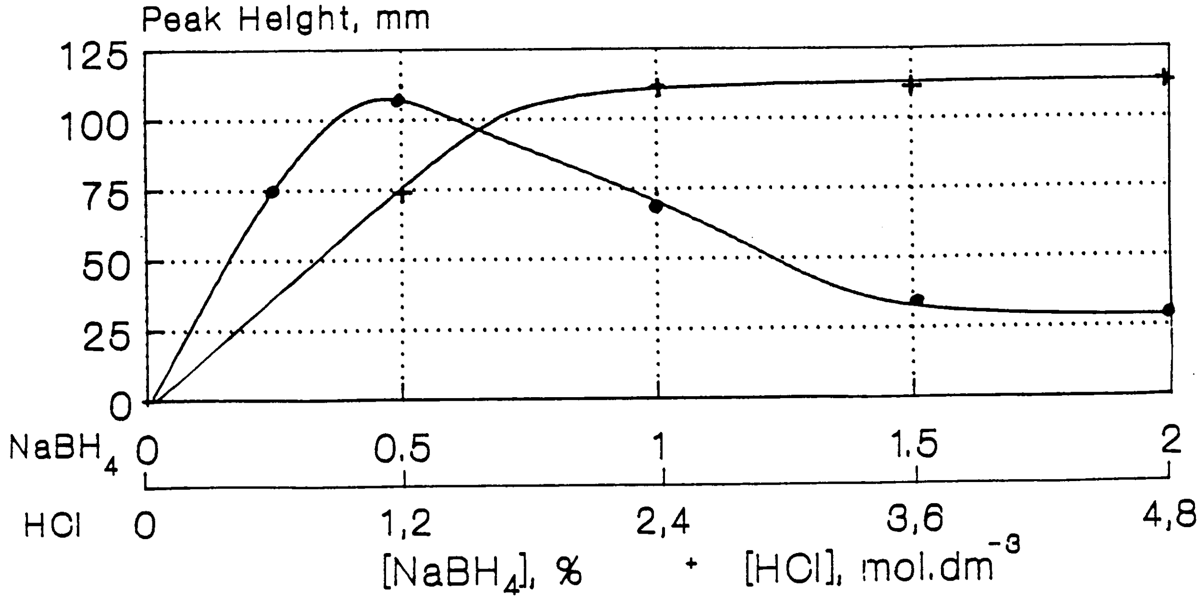


Figure 2.12: The influence of acid and reductant concentration on the sensitivity of selenium determination

When samples containing base metal are analysed, an increase in the acid concentration increases the solubility of the base metal. Although this does not effect the sensitivity, it ensures that a higher level of base metal may be tolerated.

A reagent flow-rate of 1,75 cm^3/min was found to give the most sensitive results.

Selenium, requiring a short reaction time, was found to give the most sensitive signal when the 250 mm x 1,5 mm reaction tube was used.

The calibration graph obtained for selenium illustrates the typical range of measurement achievable for hydride forming elements. Adequate calibration over one order of magnitude is possible with a small amount of curvature at the higher concentrations. This is clearly demonstrated in the calibration graph for selenium depicted in figure 2.11.

(7) Tellurium

Of all the hydride forming elements none form as rapidly as tellurium. For this reason the short 250 mm reaction tube with a 0,5 mm i.d. was found to be most suitable. In fact the longer reaction tubes with larger i.d. resulted in a decrease in the signal height. The advantage of being able to use the short reaction tube is that the resultant peaks are narrow and precise. This enables rapid reproducible analysis of samples containing tellurium.

Similar to the method for bismuth, the other rapidly hydride forming element, the pump speed setting had a dramatic affect on the signal sensitivity. Unfortunately the reproducibility deteriorated with flow-rates exceeding 2,5 cm^3/min and so this flow-rate was used in subsequent experiments.

Sodium borohydride concentration also had a dramatic effect on sensitivity, the higher concentrations giving superior results. However, because of problems encountered in draining the gas liquid separator when 2 per cent by volume reductant was used, 1 per cent by volume solutions were used in all further investigations.

At 1,2 $mol.dm^{-3}$ acid concentration the sensitivity attainable was about 40 per cent of that attainable when 4,8 $mol.dm^{-3}$ hydrochloric acid was used.

A high flush-gas flow-rate was found to be necessary and an optimum flow-rate of 60 cm^3/min was chosen.

(8) Tin

The determination of tin using this hydride generator did not enjoy the success of some of the other hydride forming elements. The problem of reagent blanks, encountered by other workers, is overcome by this generator design because the reagents are flowing continuously and the spectrophotometer is 'zeroed' on these conditions. Nevertheless, sensitivities comparable to conventional flame AAS were achieved once all the variables had been optimized.

A method described by Balls[101] stresses the importance of silanization of the surfaces that the stannane (SnH_4) comes into contact with. This worker used mainly glass and some teflon components. He silanized all the glass components but still found varying sensitivities dependent on the success of the silanization process. In our generator, the components that come into contact with the hydride are teflon (reaction tube), perspex (gas / liquid separator), plastic (tube between separator and quartz tube), and quartz (T-tube). When the quartz tube was silanized, a noticeable but not significant improvement was observed. A possible explanation for the poor sensitivity is that the hydride decomposes on the surface of the components of the generator and does not reach the atom cell. This theory was not pursued further.

The optimized conditions for the five elements for which sensitive analysis was achieved are summarized in table 2.3.

Table 2.3
Optimum conditions for some of the hydride forming elements

Element	HCl mol.dm^{-3}	$NaBH_4$ %	Flush gas flow rate cm^3/min	Reaction Tube mm	Pump Speed	Remarks
As	4,8	1,0	35	500 x 1,5	600	
Bi	1,2	1,0	60	250 x 0,5	900	Rich flame
Sb	4,8	1,0	30	250 x 1,5	600	KI added
Se	3,0	0,5	70	250 x 1,5	600	
Te	4,8	1,0	60	250 x 0,5	800	

2.5. The atomic-absorption spectrophotometer

2.5.1. Apparatus

In this investigation, the Philips SP-9 atomic absorption spectrophotometer was used. No particular feature of this instrument was used and any modern instrument would suffice. Data obtained from this instrument was found to be sensitive and stable.

The conventional air-acetylene burner was used to heat the quartz tube. The liquid trap was kept full of water in order to prevent a flash-back.

This instrument is equipped with the deuterium-arc background correction system and this was used as a matter of routine for all measurements. Careful care was taken in aligning the deuterium arc beam with that from the hollow cathode lamp (HCL).

Commercially available HCLs were used for each of the elements studied. No advantage was found in using electrodeless discharge lamps (EDL). In fact, EDLs were found to be less stable than HCLs.

2.5.2. Instrumental settings

Instrumental settings as recommended by the manufacturer were used for each of the elements determined. These are summarized in table 2.4. A damping of 0,5 sec was used in order to eliminate small fluctuations in the absorbance output. No scale expansion was used.

Table 2.4

Instrumental settings for the atomic-absorption spectrophotometer

Element	Lamp current mA	Slit width nm	Wavelength nm
As	8	1,0	193,7
Bi	6	0,2	223,1
Sb	12	0,2	206,8
Se	6	1,0	196,0
Te	6	0,5	214,3

2.5.3. Data output

Because of the transient nature of the signal resulting from the flow-injection hydride generator, it is important to be able to monitor and register such signals. Most modern instrumentation, particularly those which have an electrothermal atomizer accessory are equipped with the electronics necessary to register and store transient signals. Either the peak height or peak area of such signals may be accessed. In this investigation peak height measurements were found to be adequate. The use of a chart recorder further assisted in the diagnostics of results obtained.

The chart recorder plot for antimony is given in figure 2.13. Antimony determination gave rise to the noisiest signal. This is probably due to the fact that two reagent merging points were necessary for antimony, one for the addition of the potassium iodide and one for the addition of the reductant. The chart recorder plot for bismuth on the other hand gave a very stable baseline with sharp well defined peaks (figure 2.14). For the other elements, tracings between these two extremes were achieved.

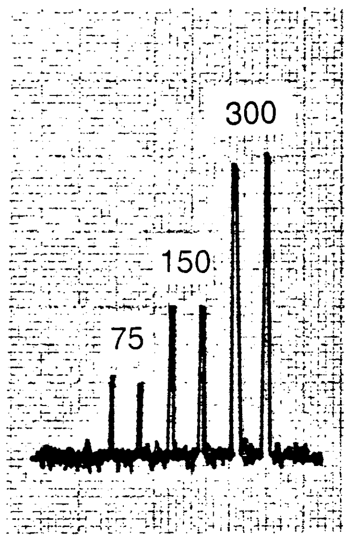


Figure 2.13: Chart recorder tracing for antimony determination

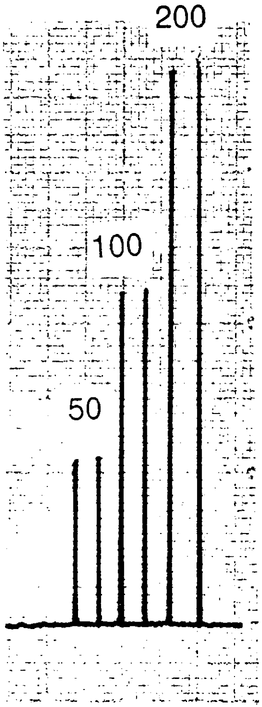


Figure 2.14: Chart recorder tracing for bismuth determination

2.6. Analytical performance

Once all the variables had been optimized for the determination of the hydride forming elements, work was done on the establishment of the working ranges and precision of measurement for those elements for which sensitive signals could be obtained *viz.* arsenic, antimony, bismuth, selenium, and tellurium.

For this experimental work, a 300μl sample loop was used. Although this gave a signal which was about 75 per cent of that achievable for continuous flow or very large sample loops, the precision was superior to that obtained with the larger sample volumes.

The working range and precision for each of the elements is given in table 2.5. The relative standard deviation, s_r, was used as a measure of precision. The precision is determined from 10 measurements of standard solutions giving a mean peak height absorbance of between 0,200 and 0,300. The working range represents the actual practical working range for analysis. The lower limit was calculated and corresponds to 10 times the variance in the baseline. The upper limit was set at a value where curvature of the calibration graph was minimal.

Table 2.5
Working range and precision for the determination of some of the hydride forming elements

Element	Working Range ng/cm^3	s_r %
As	40-500	2,9
Bi	10-250	2,2
Sb	50-500	3,7
Se	30-300	3,2
Te	15-300	2,5

It is clear from these working ranges and precision measurements that the constructed and optimized flow-injection hydride generator is a suitable accessory for the sensitive determination of arsenic, antimony, bismuth, selenium, and tellurium.

Chapter 3

In-line addition of reagents

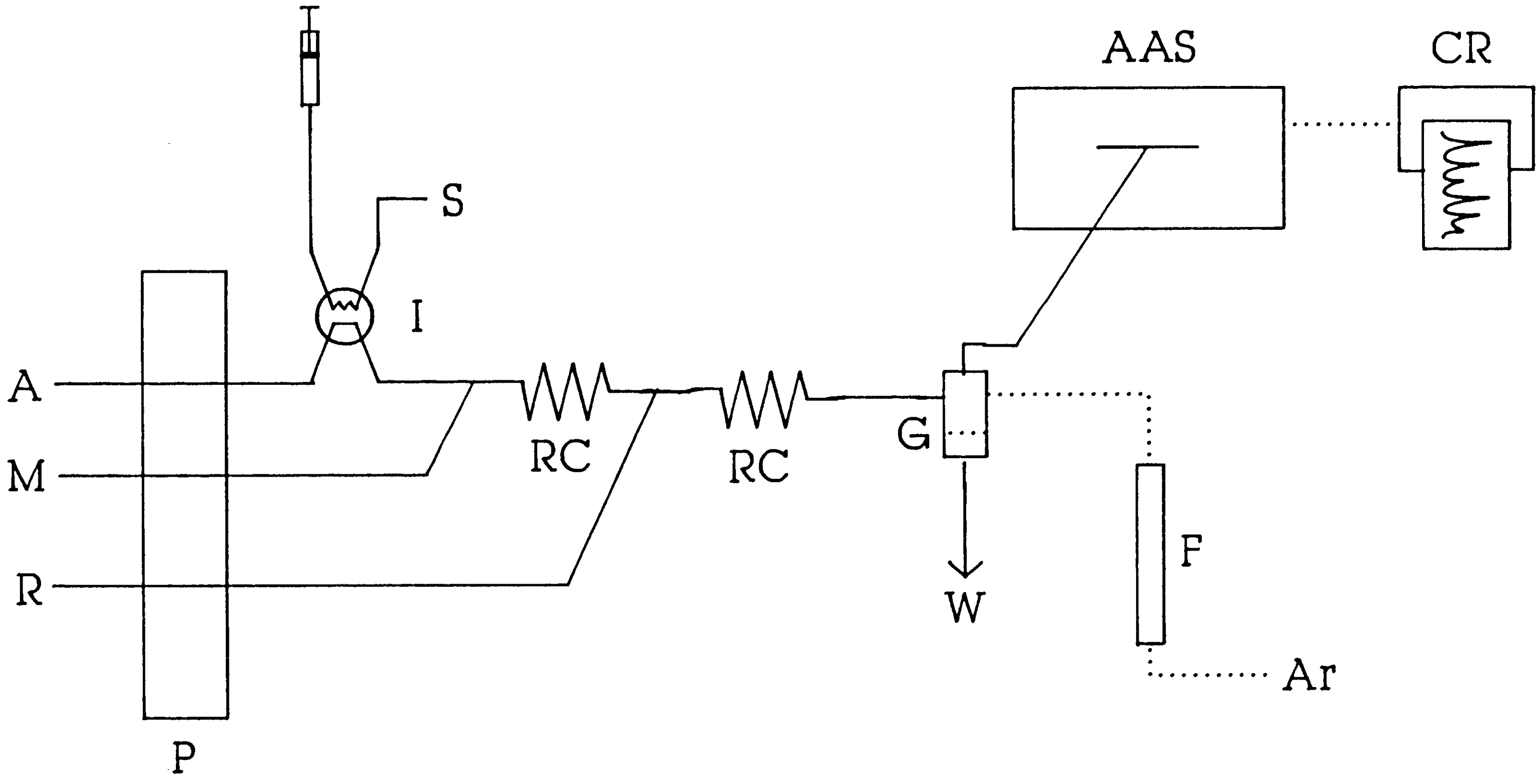
3.1. Introduction

Addition of matrix modifiers and complexing agents as a means of overcoming interferences in batch analysis has been described in chapter 1. This method has been used to overcome interferences resulting from the oxidation state of the analyte, interferences from other elements in the liquid phase, and mutual interferences between hydride forming elements in the gas phase.

Because of the versatility of FIA, all of these methods may be automated and accomplished on an in-line basis using a manifold such as the one depicted schematically in figure 3.1.

3.2. Overcoming 'oxidation state' interferences

Potassium iodide has been used to reduce all the analyte present to the oxidation state suitable for hydride generation before the sodium borohydride is added and the hydride generation step itself has been initiated. This method has found particular use in the analysis of arsenic and antimony. Although the respective hydrides are generated from arsenic and antimony in the (V) oxidation state, the rates of reaction from the (V) and (III) oxidation states are not the same. This difference is more noticeable in FIA hydride generation where no collection device is utilized particularly if peak height rather than peak area measurements are used. It is therefore, important that all the analyte present is in the same oxidation state so that the reduction to the metal hydride will take place at the same reaction rate.



A-Acid; R-Reductant; M-Modifier; P-Pump; S-Sample; I-Injection valve; RC-Reaction coil; G-Gas/liquid separator; W-Waste; F-Flow-meter; Ar-Argon; AAS-Atomic-absorption spectrophotometer; CR-Chart recorder

Figure 3.1: Flow-injection hydride generator manifold with in-line reagent addition

This effect is clearly evident from the experimental results depicted in figure 3.2, where the peak profile resulting from the analysis of a solution containing arsenic (III) and one containing arsenic (V) are superimposed. Not only is there a difference in the appearance time of the arsine, but the peak height resultant from the two solutions of equal arsenic content is different. The reason for this is that the rate of reaction for the reduction of arsenic (V) to the hydride is slower than for the reduction of arsenic (III).

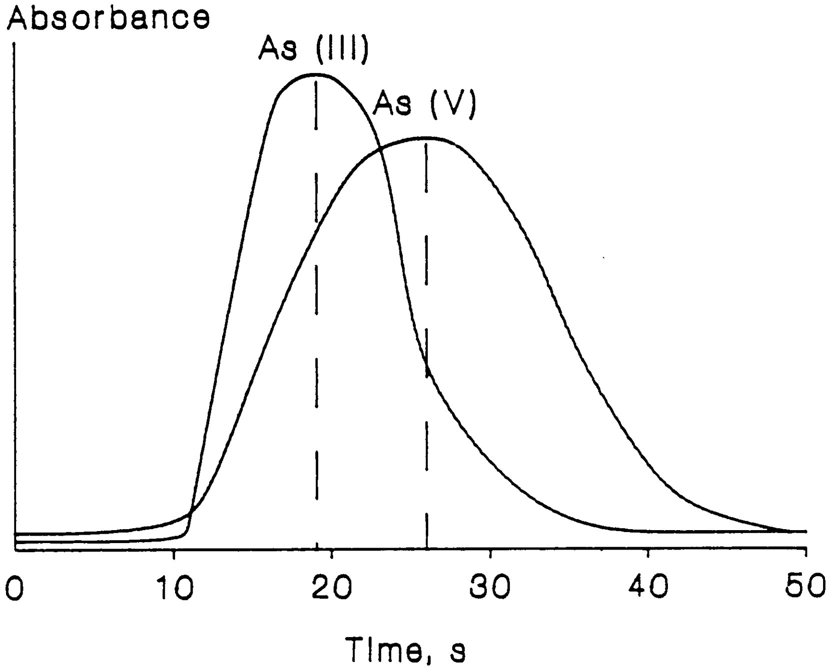


Figure 3.2: Absorbance peaks for arsenic (III) and arsenic (V)

In FIA, reaction time is fixed by the reaction tube length and no collection device is used, and so any factor which changes the reaction rate manifests itself as a change in peak height; hence an interference. The interference resultant from the different appearance times of the hydrides of the two oxidation states may be overcome by ensuring that the samples and standards used are all in the same oxidation state, i.e. the lower oxidation state. This is achieved by adding potassium iodide prior to addition of the sodium borohydride.

In batch analysis, the potassium iodide is added to an aliquot of the sample solution before pipetting the sample into the generator. In this investigation, a stream of 5 $g.dm^{-3}$ potassium iodide was merged with the sample carrying stream before merging with the sodium borohydride stream. Reduction to the (III) oxidation state was carried out in a reproducible manner for each sample.

3.2.1. Apparatus

The manifold depicted in figure 3.1 was constructed and the efficiency of the system was tested. The same basic components as described in chapter 2 were used. The additional stream consisted of 0,5 mm i.d. teflon tubing and merging with the carrier stream was achieved with a T-piece similar to the one used for merging of the reductant stream with the carrier stream. The additional reagent was introduced at right angles to the flowing sample carrier stream.

The same peristaltic pump tubing that was used for the carrier stream and reductant stream, viz. Technicon Instruments Corp., Part No. 116-0549P11, was used for the reagent stream.

A short coiled reaction tube was introduced between the merging point of the reagent and the reductant streams. Adequate mixing of the reagent with the sample plug was achieved by merging the two streams. The length of this tube was 250 mm.

The 50 µl sample loop was used for all the experiments carried out in this part of the investigation.

Optimum atomic-absorption spectrophotometer conditions as determined previously and listed in table 2.4 were used.

3.2.2. Experimental method

A sample containing a mixture of antimony in the (III) and (V) oxidation state was analysed without addition of potassium iodide. Potassium iodide was added to an aliquot of this sample and then analysed without further potassium iodide addition. Finally, the sample was analysed with in-line addition of potassium iodide.

3.2.3. Results and discussion

When this suite of tests was carried out, the chart recorder tracing depicted in figure 3.3 was obtained.

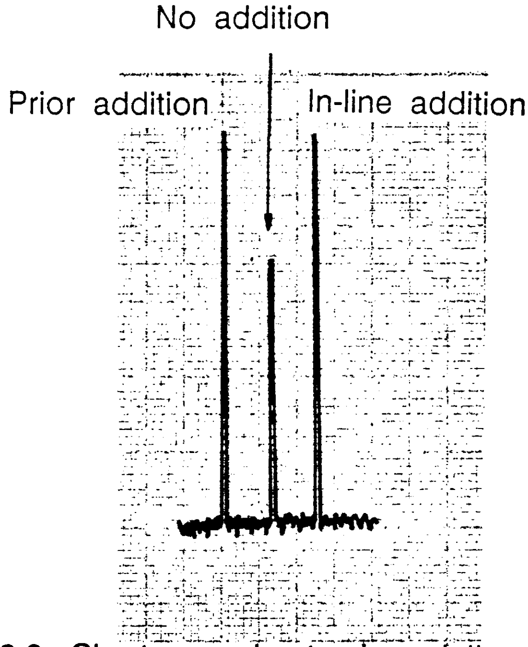


Figure 3.3: Chart recorder tracing of the effectiveness of in-line potassium iodide addition

It is clear from this data that the in-line addition of potassium iodide achieves the same result as the batch addition but, the sample manipulation required by the analyst is reduced. The absorbance obtained from a solution with in-line addition of potassium iodide is the same as that obtained from the solution where the potassium iodide was added before the hydride generation experiment was begun.

It is necessary to prepare fresh potassium iodide before use because the efficiency of the reduction decreases with the age of the potassium iodide solution. Use of the in-line method of analysis not only ensures that fresh potassium iodide is added, but the sample may be kept and re-analysed at a later date or analysed for other elements where the presence of potassium iodide may be unnecessary or even undesirable. It is also possible to vary the concentration of the potassium iodide should this be necessary.

3.3. Tellurium (IV) addition

Kirkbright and Taddia[84] first proposed the use of tellurium (IV) as a means of reducing the interference of some metal ions on the determination of selenium. They believed that the sodium borohydride reduced the Te^{4+} to Te^{2-} which forms very stable tellurides with many interfering metal ions.

These workers[84] have also described the addition of thiosemicarbazide as a means of overcoming numerous metal interferences. Kellerman[102] found that tellurium (IV) could also be used to overcome noble metal interferences on arsenic, antimony, and bismuth.

3.3.1. Apparatus

In order to test the adaptability of this approach to FIA hydride generation, the same FIA manifold that was used for the potassium iodide addition was used for the addition of tellurium (IV). The instrumental settings for the atomic-absorption spectrophotometer were, for each element, as had been determined and listed in chapter 2.

3.3.2. Experimental method

The interference by some of the noble metals on arsenic, selenium, and bismuth determination was investigated. In each case a sample containing a constant amount of analyte was spiked with different amounts of interferents. These solutions, as well as sample solutions containing no interferent, were injected into the manifold first with no tellurium (IV) addition and then with tellurium addition. The height of the various peaks were measured and the level of interference was determined by calculating the percentage recovery. Recovery is defined as the peak height achieved when the interferent is present divided by the peak height achieved in the absence of the interferent.

The tellurium (IV) was dissolved in a 4,8 mol.dm^{-3} hydrochloric acid solution. When tellurium (IV) was not added, a 4,8 mol.dm^{-3} hydrochloric acid solution was pumped through this stream in order to ensure constant dilution conditions and acid concentration.

3.3.3. Results and discussion

The interference by platinum and palladium on the determination of selenium was investigated. A sample containing 400 μg/cm^3 of selenium was spiked with each interferent. The results of this experiment are summarized in table 3.1 and 3.2.

Table 3.1
Effect of tellurium (IV) addition on platinum interferences in selenium determination

Pt μg/cm^3	Recovery, %		
	0μg/cm^3 Te	10μg/cm^3 Te	40μg/cm^3 Te
0	100	100	100
0,1	102	100	98
1,0	100	103	101
5,0	89	99	102
10,0	85	101	101
50,0	7	98	100
100,0	0	96	102
500,0	0	30	101

Table 3.2
Effect of tellurium (IV) addition on palladium interferences in selenium determination

Pd µg/cm³	Recovery, %		
	0µg/cm³ Te	40µg/cm³ Te	200µg/cm³ Te
0	100	100	100
0,1	100	102	101
0,5	102	103	104
1,0	86	103	104
5,0	0	97	98
10,0	0	102	102
50,0	0	50	101
100,0	0	11	100
500,0	0	0	8

For the study of the effect of platinum on selenium determination, it is clear that interference begins with levels of platinum as low as 5 µg/cm³. Once the platinum concentration in the sample solution has reached 50 µg/cm³, the signal is almost totally suppressed. By the addition of tellurium (IV) at a concentration of 10 µg/cm³, the tolerance of platinum has been increases to a level of 100 µg/cm³. Above this concentration, the 10 µg/cm³ tellurium (IV) solution can not cope with the interference. However, by increasing the tellurium (IV) concentration to 40 µg/cm³, platinum concentrations of as high as 500 µg/cm³ may be tolerated.

Palladium was found to be a more severe interferent than platinum. Trace levels of palladium as low as 1 µg/cm³ in the sample solution already showed signs of interfering with the selenium signal. However, by adding tellurium (IV) at a concentration of 40 µg/cm³, 10 µg/cm³ of palladium in the sample solution could be tolerated, and when the 200 µg/cm³ tellurium (IV) solution was added, even 100 µg/cm³ of palladium did not suppress the signal at all.

Because palladium had been found to yield the most severe interference affects, further experimentation concentrated on reducing the effect of this interferent. A sample solution containing a mixture of noble metals would certainly suffer most from the palladium interference. The same experiment that was conducted on the determination of selenium in the presence of palladium was repeated for arsenic spiked with palladium. The arsenic concentration was 1000 μg/cm^3. The results are presented in table 3.3.

Table 3.3
Effect of tellurium (IV) addition on palladium interferences in arsenic determination

Pd μg/cm^3	Recovery, %		
	0μg/cm^3 Te	20μg/cm^3 Te	200μg/cm^3 Te
0	100	100	100
1	97	102	102
5	33	100	100
10	28	98	96
50	0	42	91
100	0	10	41
500	0	0	14

It may be seen from the data that the effect of palladium on arsenic was similar to its effect on selenium. The presence of 5 μg/cm^3 palladium resulted in a reduced recovery. By the addition of 20 μg/cm^3 tellurium (IV), the level that could be tolerated was increased to 10 μg/cm^3, and by using the 200 μg/cm^3 tellurium (IV) solution, palladium interference at the 50 μg/cm^3 concentration level was just detectable.

Bismuth is also subject to interferences by the noble metals. The suitability of tellurium (IV) addition as a means of overcoming this interference was tested by spiking a 200 μg/cm^3 bismuth solution with varying amounts of palladium and repeating the experiments carried out for selenium and arsenic. The results of these experiments are summarized in table 3.4.

Table 3.4

Effect of tellurium (IV) addition on palladium interferences in bismuth determination

Pd µg/cm^3	Recovery, %		
	0µg/cm^3 Te	20µg/cm^3 Te	200µg/cm^3 Te
0	100	100	100
0,1	100	96	99
0,5	89	92	103
1,0	68	73	97
5,0	12	21	94
10,0	5	9	92
50,0	0	0	31

The effect of palladium on bismuth was more severe than on arsenic or selenium as can be seen from the fact that even 0,5 µg/cm^3 resulted in a detectable suppression of the bismuth signal. When the 20 µg/cm^3 tellurium (IV) modifier solution was used, only a minor improvement was detected. However, when the 200 µg/cm^3 tellurium (IV) solution was used, it was possible to tolerate 5 and possibly even 10 µg/cm^3 levels of palladium in the sample solutions.

The optimum concentration of tellurium (IV) is established by the level of interferent present. As can be seen from the above tables, the higher concentration of tellurium (IV) certainly enabled greater tolerance of noble metal interferences. However, for very high concentrations of tellurium (IV) (>200 µg/cm^3), a black precipitate formed which blocked the reaction lines and gas / liquid separator. Furthermore, the addition of tellurium (IV) was found to suppress the absorbance signal (table 3.5).

Table 3.5
Effect of tellurium (IV) addition on sensitivity
(Concentration of bismuth : 200 ng/cm^{-3})

Te µg/cm^3	Peak Height mm
0	73
4	75
20	65
100	11
·200	8

This phenomenon is worse at higher concentrations of tellurium (IV). Although it may be argued that the tellurium (IV) is then, in fact, an interferent itself, the suppression of the signal by the tellurium (IV) is reproducibly constant for samples and standards alike and it overcomes the unknown larger suppression resulting from the interference from the noble metals.

Chapter 4

In-line ion-exchange separation

4.1. Ion exchange chromatography

Ion exchange chromatography has been defined by Fritz *et al*[103] as *the separation of substances by their different migration on a sheet impregnated with an ion exchanger or on an ion-exchange column.* Ions are separated on the basis of ion exchange reactions that are characteristic for each ion. In recent years this phenomenon has been utilized for analytical measurement in high performance liquid chromatography (HPLC). This technique's origin lies in simple separation chemistry using ion exchange resin. Many clever useful ion exchange procedures have been described for removing interfering ions and separating mixtures of cations and anions.

In classical separation chromatography, resin that would pass through a 100 mesh sieve but be retained by a 200 mesh sieve is packed into a column with a bore of between 10 and 30 mm and a length of between 100 and 500 mm. In most cases, gravity flow of the eluent is relied on to carry the sample through the column. Separations are slow and fractions of sample are collected by some kind of fractioning device. Each fraction is analysed and the fractions containing the desired ion are combined for further sample manipulation or analysis.

Modern ion exchange chromatography has developed into a faster, convenient, and more selective technique. The improved performance stems from better chromatographic components, more efficient ion exchange resins and columns, and automatic detection of separated sample substances.

In this study we combined the miniaturization of modern techniques with the use of large resin bead ion exchange resins in a low pressure system that enabled the continuous separation of interfering ions from the sample solution on an in-line basis.

Ion exchange resins may be divided into one of three groups:

- cation exchange resins which are usually an organic polymer with sulfonic acid functional groups attached to most of the surface benzene rings of the polymer,
- anion exchange resins which usually consist of an organic polymer with quaternary ammonium functional groups, or a
- chelating ion exchange resin.

The resin bead are spherical, small, and uniform in size.

In cationic resins, the sulfonic acid groups are the active resin sites used for the exchange. The $-SO_3^-$ anionic group is chemically bound to the resin and its movement is thus severely restricted. However, the H^+ counter ion is free to move about and can be exchanged for another cation (say M^+) as follows:

$$\text{Res-}SO_3^-H^+ + M^+ \leftrightarrows \text{Res-}SO_3^-M^+ + H^+$$

Separations of metal cations is either based on differences in their affinity for the cation exchange resin or on selective complexation by the eluent.

The affinity of an ion for a particular resin is measured by the *Distribution coefficient*, K_d which is defined by the following equation:

$$K_d = \frac{\text{Amount of ion on resin, (mmol.dm}^{-3}\text{) x volume of solution, (cm}^3\text{)}}{\text{Amount of ion in solution, (mmol.dm}^{-3}\text{) x weight of dry resin,(g)}}$$

The value of this coefficient gives a measure of the volume of eluent required to elute a particular ion from a column. The larger the value of K_d for an ion, the more eluent will be required to elute that particular ion. In general, the affinity of an ion exchange resin for an ion increases with the charge on the ion.

The distribution coefficient is determined experimentally. A measured mass of resin is contacted with a solution of known strength until equilibrium is reached. The concentration of the desired ion is then measured in the remaining solution and the concentration of the ion absorbed onto the resin is determined by difference.

It is important to note though, that the reaction of the absorption of the ion onto the resin is reversible and an equilibrium exists between the ions in solution and those associated with the resin. This means that ions with different distribution coefficients will require different volumes of eluent to elute them from the resin and while a large volume of eluent is required for ions with large distribution coefficients, eventually these ions will be eluted from the resin.

Mayer and Tompkins[104] developed an equation for calculating the volume, υ, of eluent required to pass through a column to give rise to the maximum of the elution peak for a particular ion. This equation is only valid when the total amount of ion present is less than 3 per cent of the total column capacity.

$$\upsilon = K_d \text{ x (mass of dry resin in the column)}$$

If the distribution coefficient of the interferent is inserted into this equation, then for a particular resin column, the volume of eluent necessary to flush the interferent through the column may be calculated. Because the flow-rate is known, it is possible to determine how long interference free determinations could be carried out before the interferent breaks through the column.

4.2. In-line ion exchange separation

4.2.1. Apparatus

In order to execute the in-line removal of interferents using ion-exchange resin, the manifold was altered to include a small ion exchange column. This column, supplied by Anatech (Omnifit Part no. 416310) is depicted schematically in figure 4.1. The column is 50 mm long with an i.d. of 3 mm. The resin is retained in the column by the teflon frits.

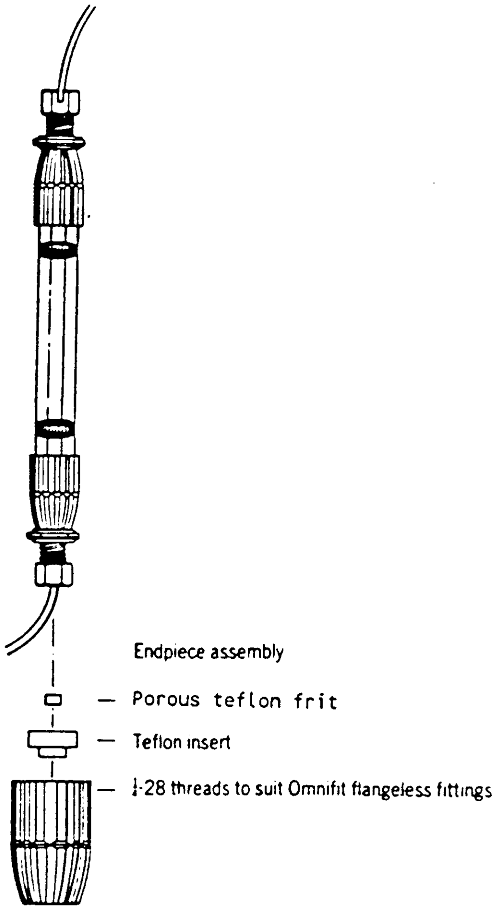
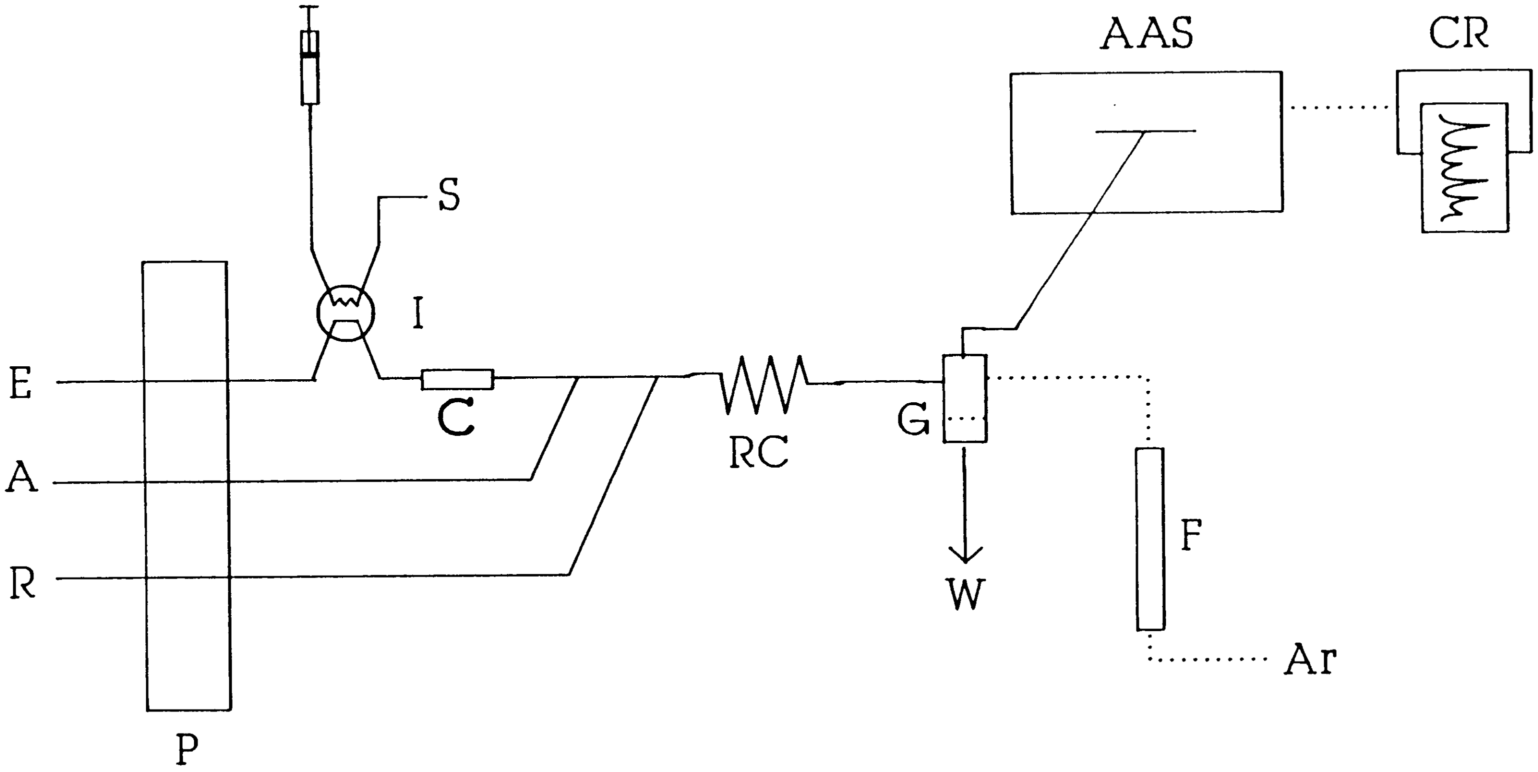


Figure 4.1: Schematic representation of in-line column

The flow-injection manifold which was constructed for this series of experiments is depicted in figure 4.2. It was necessary to introduce the additional stream of acid in order to attain the required acid concentration. Teflon tubing with an i.d. of 0,5 mm was used for all streams. Peristaltic pump tubing supplied by Technicon Instrument Corp. (Part No. 116-0549P11) was used for all streams. A 50 µl sample loop was used for this suite of experiments.



A-Acid; R-Reductant; E-Eluent; P-Pump; S-Sample; I-Injection valve; C-Column; RC-Reaction coil; G-Gas/liquid separator; W-Waste; F-Flow-meter; Ar-Argon; AAS-Atomic-absorption spectrophotometer; CR-Chart recorder

Figure 4.2: Flow-injection hydride generator manifold with in-line ion exchange column

4.2.2. Experimental method

The eluent solution is used as the matrix solution for the sample and standards. When the sample is injected into the manifold, the interfering ions, having a much higher distribution coefficient than the analyte for the resin used, is retained on the resin while the analyte passes through unhindered to be acidified and reduced to the relevant hydride. This approach requires that the resin be regenerated periodically to remove all the interferent ions before they break through the column.

Attempts to obviate this necessity by just retarding the interferent on the resin so that the hydride could be generated and stripped from the solution before the interferent could influence the process were not successful as can be seen from the chart recorder tracing depicted in figure 4.3. A sample containing 1,0 μg/cm^3 of arsenic and 1000 μg/cm^3 copper (II) was prepared. Copper (II) has a distribution coefficient of 128 and arsenic has distribution coefficient of <0,1 when 0,25 mol.dm^{-3} H_2SO_4 is used as the eluent.

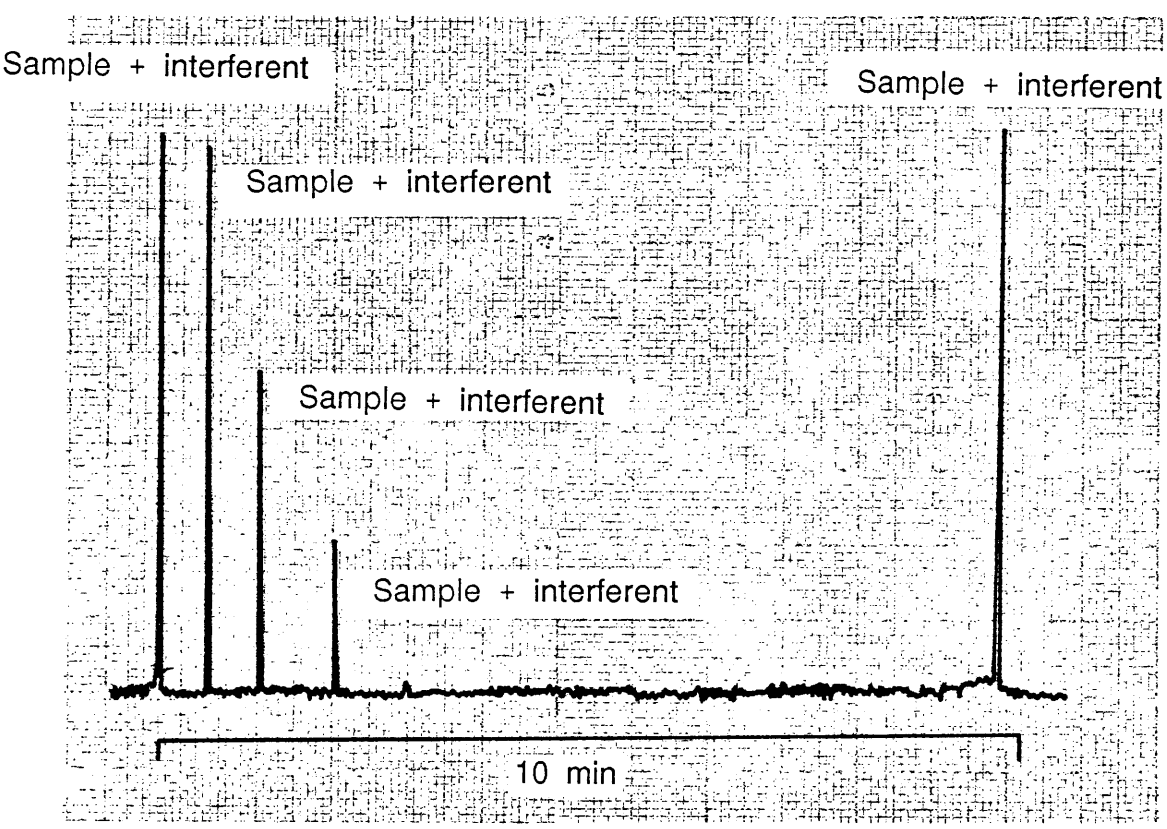


Figure 4.3: Chart recorder trace of interferent retarded

While for the first measurement recovery is good, subsequent measurements are increasingly suppressed. It would therefore appear that the base metal, that was retained on the column for the first sample, begins to elute from the column when the second sample passes. With subsequent injections more and more interferent is eluting from the column resulting in greater suppression of the analyte signal. When the system was allowed to flush for 10 minutes the original full recovery was achieved, thereby supporting this proposition. While flushing the system would be a solution to the problem of signal suppression it defeats the objective of speed of analysis.

Strelow and co-workers[105,106] produced tables of distribution coefficients for different acids at different concentrations for a cation exchange resin (AG50W-X8) supplied by Biorad. The values pertinent to this investigation are reproduced in table 4.1.

Table 4.1
Distribution coefficients for analytes and interferents

Ion	0,1 mol.dm^{-3} HCl	0,05 mol.dm^{-3} H_2SO_4
Bi (III)	-	$>10^4$
Fe (III)	9000	$>10^4$
Cr (III)	1130	198
Ni (II)	1600	1390
Co (II)	1650	1170
Fe (II)	1820	1600
Cu (II)	1510	1310
Se (IV)	1,1	<0,5
As (III)	1,4	<0,1

A simple empirical experiment showed that when a column was packed with AG50W-X8 resin of a 200 to 400 mesh size, the distribution coefficient of the analyte had to be less than 5. The smaller this value the quicker the analyte passed through the column giving rise to a sharp narrow peak. Larger distibution coefficients resulted in peak broadening and hence a drop in sensitivity. This is illustrated in figure 4.4 which is a chart recorder trace of an experiment where the analyte used was tellurium and the eluent was 0,25 mol.dm^{-3} H_2SO_4. The distribution coefficient under these conditions is 9,8. At such reduced sensitivities it would be easier to use conventional flame AAS where base metal interferences are nonexistent.

The interferent on the other hand had to have a distribution coefficient greater than 500 in order to ensure its removal from the system. If this was the case, it would require at least 120 cm^3 of carrier solution to elute the interferent. At a flow rate of 2 cm^3/min, a minimum of one hour interference free measurement was possible before column regeneration became necessary. Larger distribution factors for the interferent improved this situation. From table 4.1 it is clear that the only base metal interferent that does not conform to this constraint is chromium (III) when sulphuric acid is used as the eluent. This was confirmed experimentally.

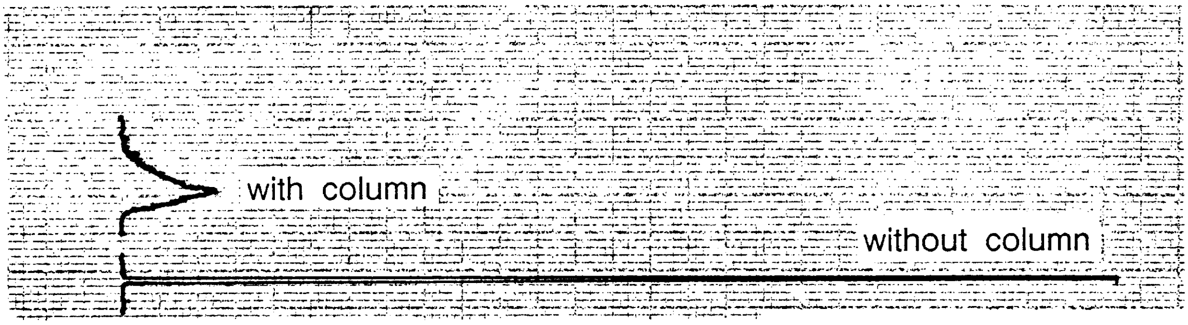


Figure 4.4: Chart recorder tracing of tellurium determination (K_d=9,8)

Of course other factors also affect this breakthrough time, the most important being resin capacity. Once the resin has become saturated with interferent, the interferent will pass through unhindered. This would however be picked up as a decrease in sensitivity in the standards and the column could be regenerated. In addition, many of these base metals are coloured and their progress through the column can be monitored visually.

Regeneration of the column is a simple process. The carrier stream used during measurement was either 0,05 mol.dm^{-3} H_2SO_4 or 0,1 mol.dm^{-3} HCl acid. By pumping 10 cm^3 of the relevant acid at a concentration of 2 mol.dm^{-3} through the column and then equilibriating the column by pumping 20 cm^3 of the carrier acid through, the column is regenerated.

4.2.3. Results and discussion

The influence of five base metals with a concentration of 1000 μg/cm^3 in solution on arsenic and selenium determination at interferent to analyte ratios of 1000 to 1 was investigated using this manifold. The results are given in table 4.2 and 4.3.

In the column headed 'With Column', the peak height obtained for each of the sample solutions for the manifold where the ion exchange column had been included, is given. For the data portrayed in the column headed 'Without Column', the same manifold configuration was used except that the column was omitted. All other tube lengths and merging points were maintained. Data are given for two different eluents, *viz.* 0,05 mol.dm^{-3} H_2SO_4 and 0,1 mol.dm^{-3} HCl.

The data given for the instance where no interferent was added (labelled 'None') is not the same for when the column was included and when it was omitted from the manifold. This is to be expected as the analyte is also slightly retained on the column and so instead of a sharp narrow peak, a slightly shorter broader peak is obtained.

Table 4.2
Effect of in-line base metal interferent removal
in the determination of arsenic with two different eluents

	Peak Height, mm			
Eluent	0,05 mol.dm^{-3} H_2SO_4		0,1 mol.dm^{-3} HCl	
Interferent	With Column	Without Column	With Column	Without Column
None	95	114	117	130
Ni (II)	94	12	112	13
Co (II)	95	88	114	113
Cu (II)	92	55	115	78
Fe (II)	95	110	113	131
Cr (III)	88	113	116	124

Table 4.3
Effect of in-line base metal interferent removal
in the determination of selenium with two different eluents

	Peak Height, mm			
Eluent	0,05 mol.dm^{-3} H_2SO_4		0,1 mol.dm^{-3} HCl	
Interferent	With Column	Without Column	With Column	Without Column
None	112	137	125	174
Ni (II)	113	3	117	3
Co (II)	115	7	123	108
Cu (II)	111	2	117	2
Fe (II)	109	94	118	174
Cr (III)	75	65	114	24
Cr (III)*	109	118	117	55

* 250 $\mu g/cm^3$ Cr (III)

By careful choice of the method of dissolution, all the arsenic and selenium in a sample can be made to occur as their respective anionic oxide, arsenate or selenate. As anionic species, they are poorly retained by the resin and therefore move through the column quickly. The other hydride forming elements occur as cationic species and are more strongly retained by the resin resulting in an unacceptable reduction in sensitivity. Furthermore, the base metals are strongly retained on the resin when low concentrations of acid are used for the eluent. Some of the hydride forming elements, like tellurium in H_2SO_4 and bismuth and antimony in HCl, form precipitates under these conditions.

For the determination of arsenic in the presence of the five base metals tested, no interference was detected for iron (II) or chromium (III) at the 1000 to 1 interferent to analyte ratio. Nickel (II), cobalt (II), and copper (II) all interfered to varying degrees. The interference experienced when H_2SO_4 was used as the eluent appeared to be more severe. Each of these interferences were overcome by using the in-line ion exchange column. The worst recovery obtained was for the sample containing chromium (III) where a recovery of 93 per cent was obtained when H_2SO_4 was used as the eluent. (Recovery is defined as in chapter 3.)

In the determination of selenium, interferences were experienced for each of the five base metals tested when H_2SO_4 was used as the eluent. When HCl was used as the eluent, all except iron (II) interfered. When the ion exchange column was included in the manifold and H_2SO_4 was used as the eluent, these interferences were overcome for nickel (II), cobalt (II), copper (II) and iron (II). However, for chromium (III), it was necessary to reduce the level of chromium to 250 $\mu g/cm^3$ before the column could cope with this interferent. All of the interferents tested were overcome by use of the column with HCl as eluent.

A study of the distribution coefficients suggests that for the AG50W-X8 resin using 0,05 $mol.dm^{-3}$ H_2SO_4, the interference of bismuth on selenium determination can also be overcome using this system. Indeed, by careful selection of resin and carrier stream many other interferences may also be overcome using this flow-injection manifold. For example, as noble metals occur as anionic species in hydrochloric acid, they will be retained on an anion exchange column while the cationic hydride forming elements would pass through unhindered. Such a scheme would solve the problem of tellurium analysis in the presence of noble metals.

Chapter 5

In-line standard additions

5.1. Introduction

The general principles of the *standard additions method* of overcoming certain interferences has been discussed by Bader[107]. This method is usually used to overcome sample matrix effects. Successive additions of known amounts of the analyte are added to the sample. If linear response of the detection system is assumed, linear regression calculation permits the original concentration to be evaluated regardless of the matrix effect. In addition, the magnitude of this effect is indicated by the deviation of the slope of the graph of absorbance versus concentration of added analyte from that obtained for the analyte in the absence of the matrix effect.

These principles are depicted graphically in figure 5.1. The curve is a plot of concentration versus absorbance for the sample plus successive amounts of the analyte. The concentration of the 'unknown' may be read directly from the graph and is equal to the intersect on the x-axis.

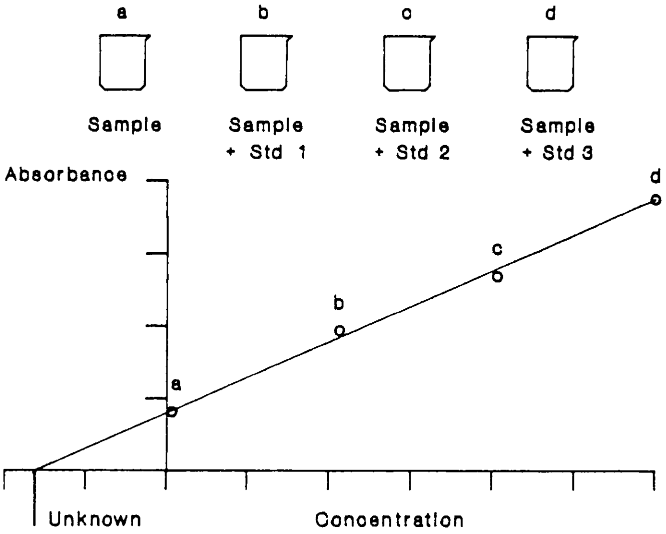


Figure 5.1: Graphical representation of standard additions procedure

Tyson[108] has described a simple FIA standard additions method and used it for the determination of chromium in steels by AAS. Araujo *et al*[109] have discussed a fast procedure for standard additions in FIA where a flame photometer was used as the detector. These workers also discussed various approaches to standard additions and finally settled on a method whereby a single standard is injected into a carrier stream consisting of the sample.

This approach has been termed reverse FIA[95]. Peak height measurements are taken at accurately determined time intervals after the peak maximum has been reached. Because of the controlled dispersion of the injected slug into the carrier stream achieved by a FIA system, each measurement is taken at an instant when there is a different ratio of sample solution to standard solution. When these measurements are compared to those obtained when a standard is injected into a stream containing a reagent blank, the concentration of the unknown may be calculated.

In this investigation, the approach used by Araujo *et al*[109] could not be used for two reasons. Firstly, accurate timing facilities were not available, and secondly, the signal peak shape was not as smooth as that obtained by Araujo *et al.* It was therefore decided, to a different approach in FIA to correct for matrix effects.

5.2. Principles

Matrix matching of standards is used extensively in routine analysis. For example, the same acid type and strength is used for sample and standards alike. In conventional batch analysis, it is seldom possible to match the matrix of the standards exactly to that of the samples. By spiking aliquots of sample solution with standards, improved matrix matching is achieved and this forms the basis of the method of standard additions.

The only disadvantage of this approach is that the analyte is still present in the sample. For this reason it is necessary to extrapolate the standard additions plot to the x-axis in order to determine the unknown concentration of the sample. Unless the standard additions plot is absolutely linear, this can lead to large errors. The standards should ideally be prepared in sample matrix solution from which the analyte has been removed. Alternatively, the signal resulting from the analyte in the sample must be distinguishable from the signal from the analyte in the standard.

This may be achieved using FIA principles. Consider the simplified FIA manifold depicted in figure 5.2. All measures to reduce dispersion have been implemented. There will be an equal mixing of the two streams provided that the peristaltic pump tubing used in each streams are identical.

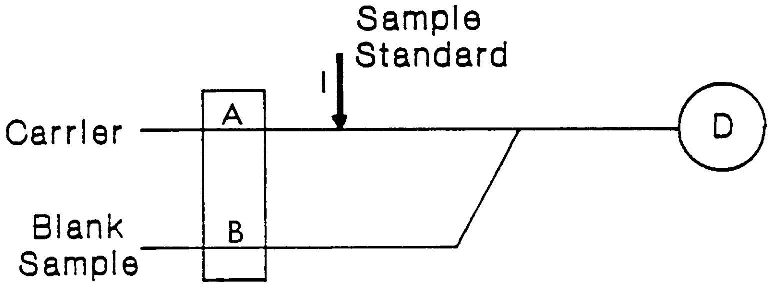


Figure 5.2: General flow-injection manifold for in-line standard additions

Two experiments are carried out. Firstly, blank solution is pumped through stream B and carrier stream A and the sample is injected at I. The output obtained (figure 5.3) by monitoring the analyte concentration at D is the characteristic transient peak. This peak results from the analyte in the sample which is mixed equally with the blank solution in stream B. In the second experiment, sample solution is pumped through stream B and the blank carrier stream is still pumped through stream A, a typical plateau type output (figure 5.3) is achieved if the analyte concentration is monitored at D. By injecting a standard solution into the system at I, an equal mixing will be achieved between the standard (in stream A) and the sample (in stream B) and the output will reflect a peak superimposed on the plateau (figure 5.3). It is now possible to distinguish between the signal from the sample and that from the standard.

By injecting several standards of differing concentration in a similar manner, and using the peak height, measured from the summit of the plateau to the peak maximum, it is possible to construct a calibration graph. This will be the calibration graph of standards that have been perfectly matrix matched to the sample without including the contribution from the analyte in the sample. Comparison of the peak obtained when the sample was injected into the system, with this calibration graph yields an accurate result for the sample.

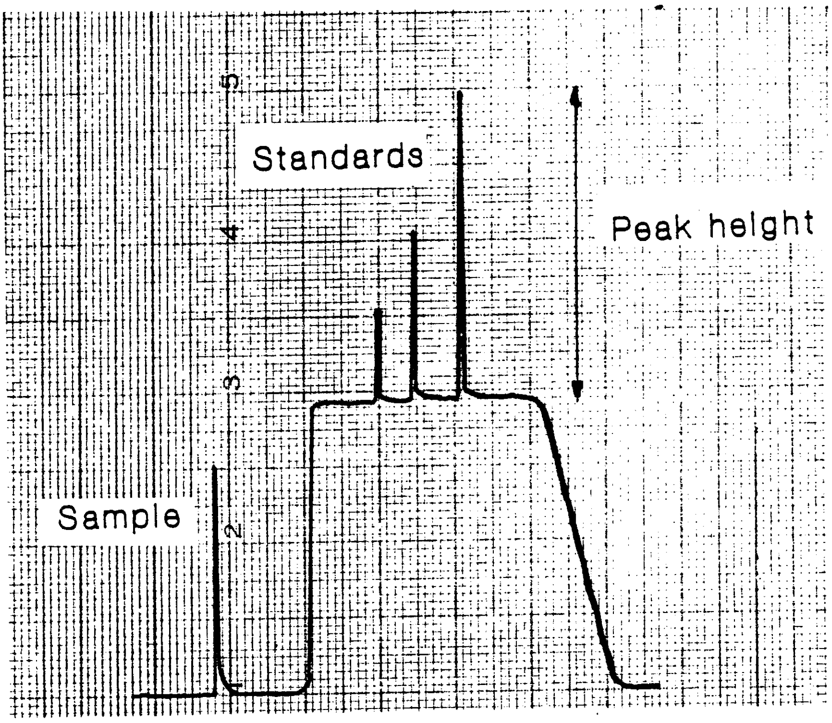


Figure 5.3: Recorder output for a standard additions experiment

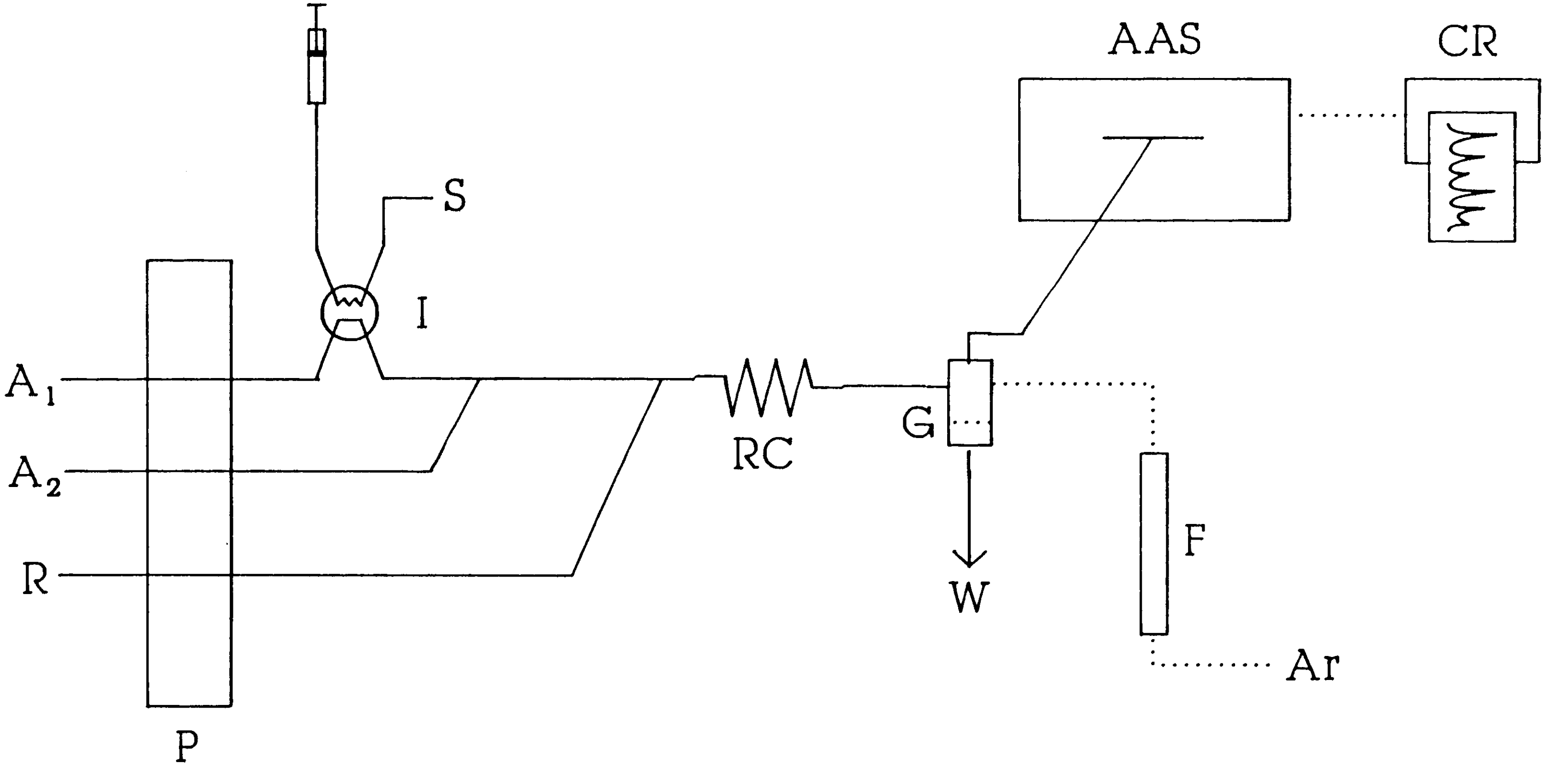
5.3. Experimental validation

5.3.1. Apparatus

In order to implement these principles in the hydride generator, the FIA manifold depicted in figure 5.4 was constructed. The sample loop has a volume of 300μl. This volume should be as close to the volume which yields the maximum signal obtainable with the manifold without sacrificing precision. The tubing between the injection valve and the merging point with stream A_2 and between the merging point with A_2 and the merging point with the reductant stream were kept as short as possible in order to minimize dispersion of the injected slug. Teflon tubing with an i.d. of 0,5 mm was used for both streams A_1 and A_2. The peristaltic pump tubing was supplied by Technicon Instruments Corp. (Part No. 116-0549P15). When either of the peristaltic pump tubes for stream A_1 or A_2 showed signs of excessive ware, both were replaced in order to ensure that the flow-rates in both streams was the same.

In order to test this method, bismuth was chosen as the analyte. A sample solution was prepared containing 25 ng/cm^3 bismuth and 75 ng/cm^3 palladium. The palladium was added to simulate an interference.

The atomic-absorption spectrophotometer and hydride generator were optimized to give a minimum signal to noise ratio. In this regard, flush gas flow-rate was found to influence this ratio. By sacrificing some sensitivity and reducing the flush gas flow-rate to 50 cm^3/min for bismuth determination, a more stable signal was achieved. The damping on the spectrophotometer was increased to 2,0 seconds. All other instrument settings were as set out in chapter 2.



A_1-Acid; A_2-Acid **or** *sample; R-Reductant; P-Pump; S-Sample* **or** *Standard;*
I-Injection valve; RC-Reaction coil; G-Gas/liquid separator; W-Waste;
F-Flow-meter; Ar-Argon; AAS-Atomic-absorption spectrophotometer; CR-Chart recorder

Figure 5.4: Flow-injection hydride generator manifold for automatic standard additions

5.3.2. Experimental method

The following series of experiments were carried out. The output portrayed on the chart recorder is given in figure 5.5.

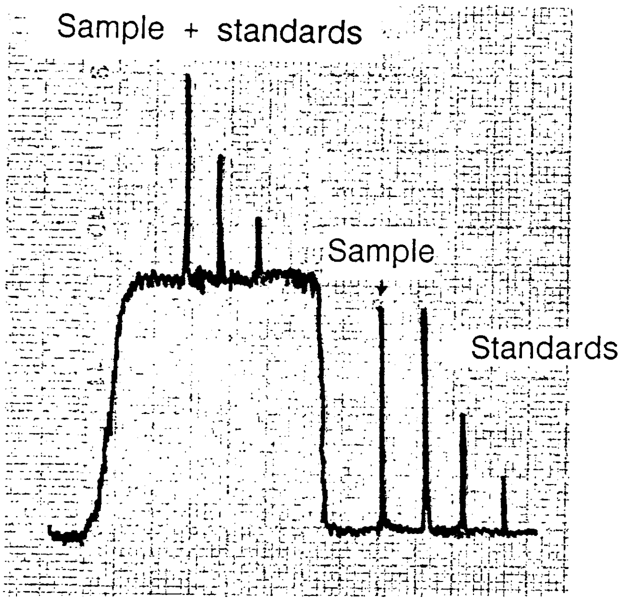


Figure 5.5: Chart recorder tracing for a standard additions experiment

(1) The usual acid carrier stream *viz.* 1,2 mol.dm^{-3} HCl, was pumped through both streams A_1 and A_2. The flow-rate of these streams were the same ensuring an equal mixing of the two streams. The standards and samples were injected into the carrier stream A_1. For the experiment resulting in the output depicted in figure 5.5, three standards and one sample were injected. The concentration of the standards were 10, 25, and 50 ng/cm^3. Stream A_1 is merged with stream A_2 before mixing with the reductant from stream R and the typical transient signal, which has characterised this investigation so far, was observed.

(2) The acid flowing through A_2 was then replaced with the sample solution. The signal output to the chart recorder increased to yield a plateau typical of continuous introduction of the analyte.

(3) While the sample solution was flowing through stream A_2, the same standards were injected into carrier A_1 via the injection port. These standards, on merging with the sample solution from A_2 are mixed intimately in a 1:1 ratio. This ensures that sample matrix has the same affect on the standards as it does on the sample itself and so the analyte in the standards experience the same interferences as the analyte in the sample.

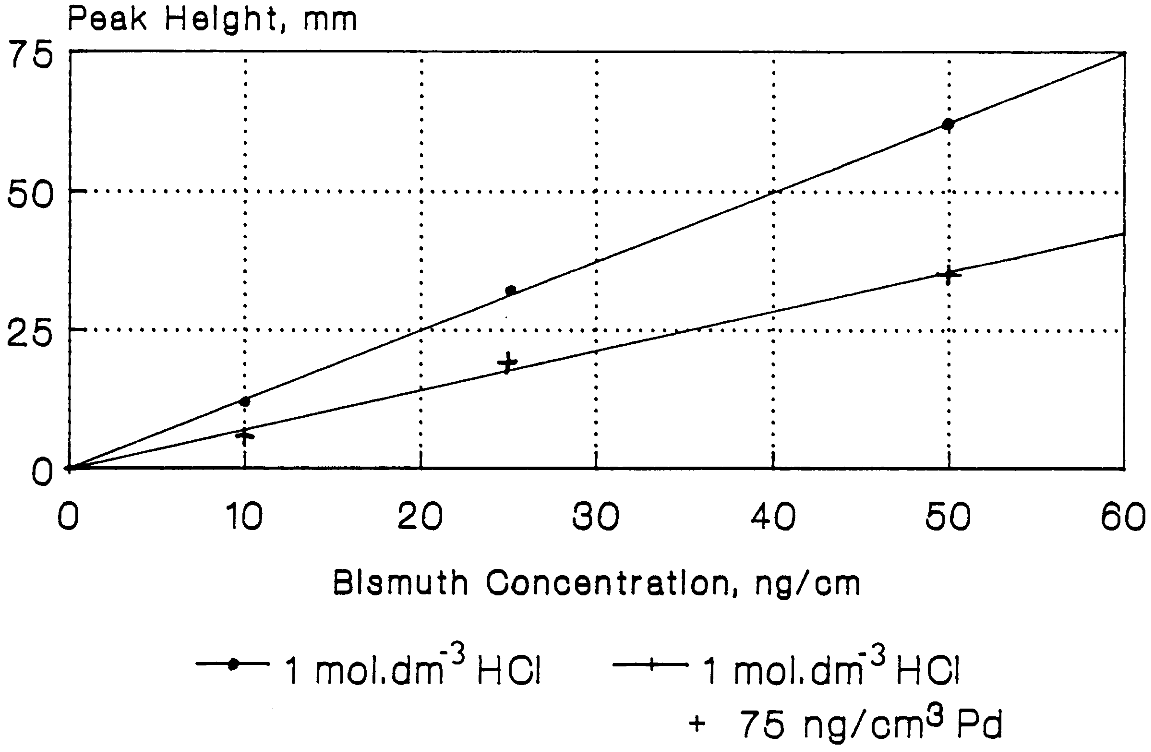


Figure 5.6: Calibration graph for standard additions method

(4) The standard peaks are measured from the plateau, resultant from the analyte in the sample, to the peak maximum, resultant from the analyte in the standard. Using these values, a calibration graph is constructed (figure 5.6). The concentration of the analyte in the sample is then determined as usual from the calibration graph by using the peak height obtained when the sample was injected into the manifold.

5.3.3. Results and discussion

Flow-rates from each stream were tested and it was found that it was important to introduce each stream at the arms of the T-piece and allow the mixed solution to exit via the stem of the T. This ensured that both streams experienced the same back pressure and helped to ensure equal flow-rates.

Having ascertained that the manifold was performing as required, the extent of interference was determined. A sample containing no palladium was analysed and compared to one containing 75 ng/cm^3 palladium. Addition of the palladium resulted in a 42 per cent suppression of the signal. The method was then tested by executing the procedure as described in §5.3.2. The concentration of the sample was determined by direct comparison to the the calibration graph constructed from the data obtained by measuring the peaks superimposed on the plateau. The other calibration graph, which corresponds to the standards injected into the system where no interferent was present, has a steeper gradient and indicates the extent of the suppression by the interferent.

The bismuth content of the sample was 25,0 ng/cm^3. The bismuth concentration was calculated to be 24,7 ng/cm^3. This value falls within the precision of 0,022 relative standard deviation as reported in chapter 2.

Although this approach to interference suppression is somewhat more tedious than the other methods investigated, it does present a quick method for standard additions and offers a solution to many matrix associated interferences.

Chapter 6

Conclusions

6.1. Introduction

In this investigation the approach was adopted whereby proven batch methods of sample manipulation for interference reduction were automated using FIA. Miniaturized FIA manifolds were constructed which enabled the simple generation of hydrides of five of the common hydride forming elements with sufficient sensitivity of measurement to offer an attractive solution to the problem of ultra trace analysis.

The simplicity inherent in the use of FIA principles raises hydride generation from a technique requiring skilled expertise to one for which automated handling may be considered. A number of methods of eliminating interferences are achieved by the use of this versatile approach to sample handling.

To illustrate this point three commonly used batch methods of interference suppression were automated by constructing suitable FIA manifolds. The conclusions to be drawn from each case are given below.

6.2. In-line addition of reagents

It has been shown that the in-line addition of reagents is indeed feasible for the suppression of interferences. Interferences originating from the analyte existing in different oxidation states once dissolved, have been overcome by the in-line addition of potassium iodide.

Noble metals have been classified as the most severe of interferences in hydride generation. The maximum amount of noble metals tolerable before interference is experienced has been extended by the in-line addition of tellurium (IV).

The literature cites other complexing agents which may be utilized to overcome interferences. Some of these were listed in chapter 1. Little doubt exists that any of these could be added, using the manifold described in chapter 3, with equal success.

The advantages of this approach are that the sample bulk solution is not contaminated by the interference suppressor, sample manipulation is reduced which results in a time saving, and the chance of experimental error is smaller.

6.3. In-line ion exchange removal of interferences

The development of selective ion exchange resin has received much attention in the past and this attention has not diminished with time. Ion exchange resins and eluent combinations have been proposed for the separation of many different element mixtures. In this investigation the versatile cation exchange resin, AG50W-X8 has successfully been used to overcome the base metal interferences on arsenic and selenium, thereby demonstrating the feasibility of this approach.

Interferent absorption on the resin has been shown to be necessary as opposed to simply retarding its progress. This necessitates the periodic regeneration of the resin column. This process has been shown to be a simple enough procedure to repeat even on an hourly basis. Of course, because no particular care needs to be taken in packing the column, simple replacement of the interferent loaded resin with fresh resin is also a possible solution to the problem of interferent breakthrough.

This method clearly enables the tolerance of higher interferent to analyte ratios for the base metal interference on arsenic and selenium determination thereby showing that, by careful choice of resin and eluent combinations, other interference suppressing systems are possible.

6.4. In-line standard additions

Many workers investigating the determination of hydride forming elements in various sample types conclude that the method of standard additions should be used to ensure that compensation is made for all interferences present. A simple method of achieving this has been developed which enables this approach to be adopted without having to perform the sample manipulation usually associated with the method of standard additions or the calculations necessary to arrive at results. The time necessary to complete the full set of measurements is less than 10 minutes per sample based on duplicate measurement of standards and sample alike. A sample volume of 25 cm^3 is adequate for analysis and one set of standards may be prepared for use with the whole batch of determinations. Sample and standard preparation time is greatly reduced and normal calibration routines can be used.

This investigation has shown that this approach makes standard additions a viable alternative for interference suppression rather than a last resort.

6.5. Closing comment

Hydride generation has survived as an analytical technique, in spite of many interferences. This is an indication of the fact that it does provide a method of analysis for certain analytes. Although electrothermal atomization may rival it as far as sensitivity is concerned, graphite furnace accessories are not always available. Nevertheless, the method of hydride generation is often used with reluctance. This investigation has shown that simple procedures may be utilized to overcome interferences thereby ensuring the continued usefulness of this technique.

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