Permanent modifiers for electrothermal atomization atomic absorption spectrometry

by

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SUMMARY

The technique of electrothermal atomization atomic absorption spectrometry (ETA-AAS) is widely used for the analysis of samples originating from many sources, such as from the industry and from the environment. Many of these analyses which are performed, are vital for the operation, quality control and monitoring of the products produced in the industry, as well as the byproducts and effluents produced by these processes. Unfortunately, many of these analyses are prone to interferences, which lead to troublesome, inaccurate and costly analyses. Traditionally, chemical modifiers were used to overcome these interferences, but owing to certain limitations of these modifiers, a need arose for a new type of modifier. The envisaged modifier must be able to improve the quality of analyses by improving the sensitivity, detection limits and versatility of the conventional chemical modifiers. This investigation involves the use of a low pressure argon glow discharge. The discharge will sputter a solid metal chemical modifier, such as iridium or rhodium, onto the inside of a graphite tube to produce a permanent modifier. To begin with, the operational characteristics and optimization of the sputtering process for each of the modifiers were investigated. Secondly, the ashing curves and other analytical performance characteristics were determined for Pb and As in three matrices, namely sulphate, nitrate and chloride using the permanent modifiers.. The analytical characteristics of the permanent modifiers were compared to the performances of the conventional chemical modifiers and comparisons and conclusions were drawn as to the performance and effectiveness of the permanent modifiers.
OPSOMMING

Die tegniek van elektrotermiese atomisering atoomabsorpsiespektrometrie (ETA-AAS), is 'n gewilde tegniek wat gebruik word vir die analise van 'n verskeidenheid monsters vanaf verskeie oorspronge, soos die industrie en die omgewing. Baie van hierdie analises is noodsaklik vir die optimale bedryf en beheer van die produkte van die prosesse asook die analises van die byprodukte en afvalstowwe van sulke prosesse. Ongelukkig is baie van hierdie analises onderworpe aan steurings wat na foutiewe, duur en onakkurate analises kan lei. In die verlede is van chemiese modifiseerders gebruik gemaak om van hierdie steurings ontslae te raak, maar beperkings in hulle doeltreffendheid het gelei na die behoefte vir 'n nuwe modifiseerder. Die hoofdoel van hierdie modifiseerder sal wees om die kwaliteit van sekere analises te verbeter deur die sensitiwiteit, deteksie limiete en meerdoeligmheid van die modifiseerders te verbeter. Hierdie ondersoek behels die gebruik van 'n laedruk argon gloeiontlading. Die gasontlading se doel is om die chemiese modifiseerder, soos iridium of rodium, aan die binnewand van 'n grafiet buis te verstuif om 'n permanente modifiseerder te produseer. Die eienskappe en optimale werkskondisies van die gloeiontlading is ondersoek vir elke modifiseerder. Die analitiese eienskappe van die permanente modifiseerders is getoets in sulfaat, nitraat en chloried matrikse vir Pb en As. Die analitiese eienskappe van hierdie permanente modifiseerders is vergelyk met dié van sekere konvensionele chemiese modifiseerders, en die doeltreffendheid daarvan is bespreek.

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CHAPTER 1

INTRODUCTION

The routine analysis of many elements at very low levels in many different samples and compounds have been simplified by the use of spectroscopic methods such as: atomic absorption spectrometry (AAS), atomic emission spectrometry (AES) and atomic fluorescence spectrometry (AFS). These methods are very popular in the industry and research circles and play a vital role in quantitative elemental analysis.

In this work, the technique of electrothermal atomization atomic absorption spectrometry (ETA-AAS) will be focussed on. The technique of atomic absorption spectrometry was developed as an analytical tool for the analysis of several elements in 1955 by Walsh [1], who proposed this method as an alternative to the popular atomic emission spectroscopic methods in use at that time. The atomic absorption method originally made use of high temperature flames to produce a population of neutral free atoms so that absorption of radiation by these neutral free atoms could be measured. This was called flame atomic absorption spectrometry (FAAS).

In 1961, L’vov [2] proposed an alternative to the popular, yet troublesome method of flame atomic absorption, namely, electrothermal atomization atomic absorption spectrometry (ETA-AAS). This method did not involve the use of flames, so it was dubbed a “flameless” technique. The method used by L’vov relied on the resistive heating properties of graphite to bring about heating of the sample and atomization of the analyte element so that absorption of the neutral free
atoms could be measured. This method showed tremendous promise with respect to greatly improved detection limits, but as with any analytical technique, it also had certain disadvantages, of which interferences were the most troublesome and elusive.

From the early stages in the development of the technique, several problems regarding interferences were noted and reported in the literature. Several attempts were made to either understand, reduce or eliminate these interferences, which were different to those experienced in flame atomic absorption methods, but to a large extent these attempts failed. That is, until Ediger [3, 4] introduced the technique of chemical or matrix modification to electrothermal atomic absorption techniques, which allowed vast reductions in interferences for several elements.

The use of chemical modifiers in ETA-AAS have greatly reduced interferences previously experienced and have improved the quality and detection limits of many analyses. Since the introduction of the technique of chemical modification, much work has been carried out to expand on the use of these chemical modifiers and the literature on the usage and performance of literally hundreds of chemical modifiers is vast [5].

This last point brings us to the aim of this project, the investigation of the analytical performance of a new chemical modifier for ETA-AAS, namely a permanent chemical modifier.

The pioneering work of this project was carried out by Rademeyer et al [6], and this work aims to expand and extend on the observations made therein.
The ultimate aims of the permanent modifiers are:

i. To further reduce interferences encountered in ETA-AAS.

ii. To bring about an improvement over the analytical performances of the conventional chemical modifiers in routine usage.

iii. To overcome some of the general disadvantages encountered with the use of these conventional chemical modifiers.

The process of glow discharge sputtering was used in this project as a tool for the production of these permanent modifiers. The characteristics of the sputtering process in a low pressure argon discharge were investigated and the parameters controlling the process were optimized. The procedures followed for the production of the permanent modifiers and the investigation of the performance of the permanent modifiers are outlined and discussed. The analytical performances of the prepared permanent modifiers are tested against those of the conventional chemical modifiers using the test analytes arsenic (As) and lead (Pb). The advantages gained, problems experienced and proposed future uses of these permanent modifiers are also presented and discussed.
1.1 References


CHAPTER 2

A BACKGROUND OF ELECTROTHERMAL ATOMIZATION
ATOMIC ABSORPTION SPECTROMETRY AND PROBLEMS
ENCOUNTERED WITH THE TECHNIQUE

2.1 Atomic absorption spectrometry—principles and basic instrumentation

2.1.1 Introduction

Atomic absorption spectrometry (AAS) is one of the most important techniques in daily use for the analysis and characterisation of the elemental composition of a vast number of materials and samples. Many research projects and essential analyses were only made possible with the advent of atomic absorption techniques. AAS is one of the branches of analytical spectroscopy that derives analytical information from atomic spectra in the optical region of the electromagnetic spectrum. This optical region includes the ultraviolet (UV), the visible and the infrared regions.

2.1.2 The principle of atomic absorption spectrometry

One of the most important advances in the study of atomic spectra was made by Bohr in 1914, who postulated the following [1]:

i. Atomic systems exist in stable states without radiating electromagnetic energy.
ii. Absorption (or emission) of electromagnetic energy occurs when an atomic system changes from one state to another.

iii. The absorption process corresponds to a photon of radiant energy, \( hv = E_1 - E_2 \), where \( E_1 - E_2 \) is the difference in energy between the two states of an atomic system.

These points simply imply that an atom is only allowed certain discrete and characteristic energy values and that absorption, or emission of radiation by an atom, occurs only when it undergoes a transition between these states or energy levels. The frequency \( (\nu) \) of radiation corresponding to the transition of an atom from a higher energy level, \( E_m \), to a lower energy level \( E_n \), can be given by equation 2.1 below, (by rearrangement of \( hv = E_m - E_n \))

\[
\nu = \frac{(E_m - E_n)}{h}
\]

Equation 2.2 shows equation 2.1 in terms of wavelength (\( \lambda \)),

\[
\lambda = \frac{c}{\nu} = \frac{hc}{\Delta E}
\]

where \( h \) is Planck's constant, \( c \) is the velocity of light and \( \Delta E \) is \( (E_m - E_n) \).

Thus, electronic transitions can be discussed in terms of the frequency, \( \nu \), energy, \( E \), and wavelength, \( \lambda \). These parameters have unique values for a given electronic transition. Each element can undergo several electronic transitions, resulting in a series of sharp lines called a spectrum, which is uniquely characteristic for each element. The visible region of the
electromagnetic spectrum extends from about 770 nm (red) to 380 nm (violet), although the optical spectra can be studied for a considerable range on either side of this visible range, namely the infrared and ultraviolet regions of the spectrum.

In the process of atomic absorption, electrons of an atom in its lowest energy state, the ground state, can absorb a quantum of energy and undergo a transition to a low-lying excited state. Spontaneous atomic emission occurs when this quantum of energy is released and the electron returns to the ground state. A transition to and from the ground state is called a resonance transition, illustrated as follows:

\[ \text{ENERGY} + \text{GROUND STATE ATOM} \rightarrow \text{EXCITED STATE ATOM} \rightarrow \text{ENERGY} + \text{GROUND STATE ATOM}. \]

Spectral lines originating from resonance transitions are also known as resonance lines. These lines are the most useful analytical lines for atomic absorption spectroscopy.

The properties of the excited state atoms compared to the ground state atoms at a given temperature can be determined with the aid of the Boltzmann relation, given by equation 2.3,

\[ N_m = N_n \left( \frac{G_m}{G_n} \right) \exp \left( \frac{(E_m - E_n)}{kT} \right) \quad \ldots \ldots 2.3 \]

where \( N \) is the number of atoms in the first excited state, \( m \), or ground state, \( n \), and \( G_m \) and \( G_n \) are the statistical weights of the excited and ground states, respectively. \( T \) is the absolute temperature, and \( k \) is the Boltzmann constant. Walsh [1] calculated the ratio \( N_m/N_n \) for the most populated energy states of several elements as a function of temperature. His findings showed that there were only a small proportion of atoms in the first excited state (even at 3000 K), indicating that the absorption of radiation other than that which originates from a transition
involving the ground state, would be very small. This is one of the reasons why the atomic absorption technique is so selective.

2.1.3 The measurement of atomic absorption

The transmitted intensity of the radiation source after absorption has taken place, is governed by the Beer-Lambert law, given by equation 2.4,

\[ I_t = I_0 \cdot 10^{-abc} \]  ...2.4

where \( I_t \) and \( I_0 \) represent the transmitted and incident intensity of radiation, respectively, \( a \) is the absorptivity, \( b \) is the optical path length and \( c \) is the concentration. This expression can be expressed in a number of ways, but the expression of note is the one involving the absorbance term. Rearrangement of 2.4 gives 2.5,

\[ \log \frac{I_0}{I_t} = abc \]  ...2.5

where \( \log \frac{I_0}{I_t} \) can be replaced by \( A \) (absorbance) to give 2.6, which is the general form of the Beer-Lambert law:

\[ A = abc \]  ...2.6

2.1.4 Basic instrumentation

An atomic absorption spectrometer is used to measure atomic absorption. The system generally consists of the following parts or devices:
1. **The radiation source** - The radiation source is chosen according to the element and spectral range under investigation. Some of these sources include hollow cathode lamps, and electrodeless discharge lamps.

2. **The sampling system** - The sample can be in the form of a liquid, solid or a gas and manual or automated samplers can be used, depending on the system.

3. **Monochromator** - Monochromators are essentially frequency analysers. The analysis is accomplished by varying the incidence angles of prisms or diffraction gratings with respect to the incident radiation. Optical filters are also often employed in monochromators.

4. **Detector** - Detectors can be divided into two categories: **selective** and **non-selective**. With **selective** detectors, the response varies with the frequency of the incident radiation. In the case of **non-selective** detectors, the response does not vary with the frequency of the incident radiation.

5. **Recorder** - The recorder can be any printout device, computer or data recorder, which is able to keep a record of the absorbance data.

### 2.1.5 Background of atomic absorption spectrometry

The atomic absorption technique as an analytical tool for chemical analysis was introduced by Walsh [1] and Alkemade and Milatz [2], around 1955. It was Walsh who suggested that the
measurement of absorbance at the peak of the absorption line profile would provide a linear relationship with concentration over a wide range of absorbance values, in accordance with the Beer-Lambert law. He demonstrated the advantages of the atomic absorption technique over the well-established emission spectroscopy method for elemental analysis, such as, more reliable sources of resonance radiation, modernised instrumentation and the use of high temperature flames.

It was believed that the sensitivity of the analyses could be improved if the atomic vapour formed in the process could be made to remain in the radiation beam for a longer period of time. Following this, many attempts were made to produce the atomic vapour in a completely neutral or unreactive medium and to provide the necessary heat energy into the system for atomization.

One of the first designs of such a system was proposed by L’vov [3], who proposed an electrothermal atomizer for the atomic absorption method of analysis. The sample was placed on a special electrode, whereafter the electrode was introduced into the preliminary heated tube, which was heated by direct current (DC). Fuller [4] and L’vov [5] have reviewed this technique extensively.

The introduction of the electrothermal atomization method for AAS has had a great impact on analytical chemistry. The method is ideal for ultra trace determinations of many elements and requires only a few micro litres or micrograms of sample. Essentially, the operation of the system is as follows:

i. The sample is prepared (digested, homogenised, diluted or preconcentrated), usually in
the form of a solution, although solid samples can also be analysed.

ii. A sample aliquot is placed inside the graphite tube either manually or with the aid of a sampler system, which then normally uses a calibrated micro pipette.

iii. The heating programme is initiated and the sample is dried, charred and atomized within the graphite tube. (A description of these processes are given under 2.1.6)

iv. Absorbance is measured and the absorbance data is recorded.

The resulting effect is that detection limits are dramatically improved and are typically 100 to 1000 times more sensitive than conventional flame AAS.

2.1.6 Flame AAS compared to graphite furnace atomization

The generation of neutral free atoms by means of an electrically heated graphite furnace is a technique which is complementary to conventional flame AAS, rather than a technique which replaces it. For example, many trace metal analyses are only possible by means of electrothermal atomization using the graphite furnace. The atomic absorption method remains one of the most specific yet versatile analytical methods for the measurement of a wide range of elements.

The advent of “flameless” atomization, in particular the graphite tube furnace and the carbon rod atomizer, greatly reduced certain physical and chemical limitations imposed by the flame AAS method.

Some of the limitations of flame AAS are:

♦ The low efficiency of the nebulizer or spray chamber. This efficiency is typically 10% and
much of the sample solution is wasted.

- The production of atoms in the ground state is governed by many variables such as (i) the flame temperature, (ii) interactions between the flame gases, matrix components and analyte, (iii) chemical interferences and (iv) the degree of dissociation of molecular species of the analyte.

- The zone of the flame in which absorption occurs is only a small section of the whole flame. The residence time of the ground state atoms in the flame is also very short, typically $10^{-4}$ seconds [6] and depends greatly on the velocity of the flame gases.

- Flame gases also produce distinct absorption and emission bands which can cause interferences and increased background noise.

The *advantages* gained by the use of graphite furnace atomization include:

- A discrete volume of sample is vaporized and wastage is virtually eliminated.

- Although the ground state atoms are still subject to interferences, they are of a different nature to flame AAS and are controllable by the proper choice of analytical conditions and/or by chemical pre-treatment.

- The graphite furnace forms a confined chamber where vaporization of the sample takes place by raising the temperature with a programmed sequence of electrical power. Thus, a dense, localised population of ground state atoms is produced for a longer time interval, in comparison with the low atom density and short residence time of the flame.
The overall effect is that the analytical sensitivity is greatly enhanced using graphite furnace atomization. Another distinct advantage of the electrothermal atomization technique is that solid samples can also be analysed directly without prior dissolution or chemical pre-treatment.

2.1.7 Electrothermal atomizer design and principles of operation

The graphite furnace is an electrothermal atomizer that can be used with almost all types of atomic absorption spectrophotometers. The energy required for atomization is supplied by the application of a high electrical current through a graphite tube where the sample has been placed. The furnace is located in the sample compartment so that light from the light source passes through the graphite tube. A diagram of the graphite tube and the path of the radiation through the tube can be seen in figure 2.1 [7].

![Diagram of graphite tube](image)

Figure 2.1. The path of light through the graphite tube [7].

When the furnace is fired, the generated atomic vapour absorbs light from the radiation source. The absorbance signal obtained is transient, and a Gaussian-shaped signal is produced as the atom
concentration within the furnace rises, and then falls as the atoms diffuse from the furnace.

It must be noted that several terms such as flameless, non-flame, electrothermal atomization (ETA), graphite furnace atomic absorption spectroscopy (GFAAS) and furnace atomic absorption spectroscopy (FAAS) have been used in the literature in the past by many authors for this technique. In order not to confuse this technique with other flameless techniques such as hydride generation, cold vapour methods and sampling boat methods, in this work the term electrothermal atomization atomic absorption spectroscopy (ETA-AAS) will be used throughout.

The graphite furnace system consists of an atomizer compartment where the graphite tube is placed, a power supply, electrodes delivering power to the graphite tube, a casing providing water-cooling and an inert gas sheathing the graphite tube. A generalized atomizer design is given in figure 2.2.

![Graphite furnace atomizer design](image)

**Figure 2.2. Generalized graphite tube atomizer design [6].**

The function of the graphite tube is to generate a population of ground state atoms so that atomic
absorption can be measured. This, in general is achieved in three (3) steps, namely the drying, charring and atomization steps.

1. **Drying stage**
   
   The purpose of this step is to evaporate low-boiling liquids from the sample matrix. Rapid evaporation should occur, without any spattering of the sample, which will lead to loss of analyte. The drying time is dependent on the sample volume. Therefore, a longer drying time is necessary for larger sample volumes.

2. **Charring stage**
   
   This thermal pre-treatment or ashing step is necessary to remove any components of the sample matrix which are more volatile than the element of interest before atomization. This step decreases the possibilities of interferences during atomization. In order to prevent the loss of the analyte during this step, the ashing temperature must be carefully chosen after suitable investigation.

3. **Atomization step**
   
   This is the stage where an atomic vapour of ground state atoms are produced, and absorption is measured as the analyte atoms in the vapour phase absorb characteristic radiation from the radiation source.

The temperature of the furnace is raised by the heating effect of the current carrying graphite tube and the electrodes of the atomizer. In order to protect the incandescent graphite from excessive oxidation and corrosion, there is a flow of an inert gas (usually argon or nitrogen) which sheaths
the hot graphite tube. The inert gas also serves to sweep away the ashing products from the light path before atomization. In general, argon is the preferred gas due to the fact that with the use of nitrogen, cyanides and cyanogens are formed with the graphite at high temperatures. Although nitrogen is cheaper, an expensive ventilation system is required to remove the toxic nitrogenous products. The furnace itself is normally cooled with the aid of a water-cooled system.

2.1.8 Essential components of an electrothermal atomizer system

2.1.8.1 Optical system

The most important requirement of a light source for AAS, is that it must emit a steady, uniform level of radiation to obtain an analytical signal of a low noise level. The most commonly used light sources are electrodeless discharge lamps (EDL) and hollow-cathode lamps (HCL). The HCL is the most popular light source, as it produces a bright and stable light with a fine line spectrum. The HCL chosen for the analysis will correspond to the analyte(s) of interest. Either a single element or a multi-element lamp can be used.

The use of a single element lamp is generally preferred, owing to the fact that in multi-element lamps, the different elements in the lamp comprising the hollow cathode have different sputtering rates, thus depleting one or more element(s) faster than others. The multiple element lamps are, as can be expected, more expensive.
2.1.8.2 Background correction system

Background correction is essential in AAS, since it subtracts non-atomic absorption signals from the total absorbance signal generated.

The most common background correction system used is the continuum background correction system. This system emits light over a broad spectrum of wavelengths and corrects for broadband non-atomic absorption. This background correction system is limited to background absorption that is constant with wavelength over the spectral range of interest. The deuterium lamp is commonly used.

More recent work has seen the use of the Zeeman effect for background correction. The Zeeman effect splits atomic lines into three or more polarized components by using a strong magnetic field [7]. In a normal Zeeman pattern, the single pi (\(\pi\)) component remains at the original analyte wavelength. The sigma (\(\sigma\)) components are shifted away from the central analyte wavelength. The pi components are linearly polarized in a direction parallel to the magnetic field, while the sigma components are polarized in a direction perpendicular to the magnetic field.

Use of the Zeeman effect background correction system enables one to correct for nonspecific absorption, continuous background and structured or line background. The disadvantages of the method are that it causes slight delinearity of calibration curves and a loss in sensitivity is seen for some elements.
2.1.8.3 Graphite tubes

There are two (2) types of graphite tubes available on the market:

(1) Normal graphite
This is made from spectrally pure, high density graphite. These graphite tubes are relatively coarse and have a layered, porous surface. This allows certain materials such as gases, elements and solvents to penetrate the graphite lattice and thus react with the graphite at high temperatures. These tubes are uncoated and have limited lifetimes and applications. Strong oxidizing agents, such as acids, cause rapid deterioration of the graphite surface during analyses. Severe interferences can be encountered when the graphite retains some species and then releases these at higher temperatures. The use of normal graphite is thus not recommended for most analyses.

(2) Pyrolytic coated graphite
These tubes are made of the same graphite as the normal tubes, but have a thin coating of pyrolytic graphite covering the surface. These tubes have significantly longer lifetimes than the normal graphite tubes. The use of these tubes is recommended especially for the elements that form refractory carbides such as: V, Ti and Mo. In the manufacturing process, the pyrolytic graphite is deposited on the substrate graphite from the vapour phase after thermal decomposition of a simple hydrocarbon, such as methane. A dense, hard layer of graphite is deposited on top of the normal graphite. The crystals of the pyrolytic graphite lie virtually parallel to the surface and it is highly anisotropic, both electrically and thermally. These properties of the pyrolytic graphite coating explain the long lifetimes of these graphite tubes.
Some advantages of the pyrolytic coating are [6]:

i. The coating is relatively impermeable to hot atoms, compounds and gases.

ii. It is more resistant to oxidation and corrosion than normal graphite.

iii. It is significantly less reactive than normal graphite and the tendency of the refractory elements to form carbides are significantly reduced.

Several other coatings and materials have been investigated for use as alternative atomizers in the past, but few, if any other materials or coatings have all the desirable properties of pyrolytic graphite, and the pyrolytic graphite remains the most popular choice for analyses. The different coatings and materials investigated will be discussed in section 2.3.3.

2.2 Interferences in ETA-AAS

2.2.1 The nature, sources and causes of interferences

Interferences are a major cause of problems encountered in analyses in ETA-AAS. During the early years in the development of the technique of ETA-AAS, countless interferences were observed and reported. Analytical interferences can have severe effects on the accuracy and precision of a determination. These interferences are sometimes difficult to identify and are not always attributable to a single factor, or to an absolute effect. In many cases interferences can be dependent on a variety of factors or parameters. These factors will be discussed in detail in the following section. Many authors have emphasised the fact that many of the observable problems leading to interferences arise from specific analytical parameters that are selected when an analysis
is carried out. This has been observed even when similar or identical instrumentation is being used.

In general, two types of interferences can be distinguished, namely physical and chemical interferences.

2.2.1.1 Physical interferences

Physical interferences are those arising from the physical characteristics of the sample, atomizer and instrumentation employed in analyses. The factors contributing to physical interferences are discussed briefly.

a) Solid phase effects

The sample-drying process can lead to solid phase effects. When a sample is placed inside the graphite tube, the shape and size of the crystals formed during the drying and ashing stage affects the efficiency and reproducibility of the atomization process. In many cases, the use of a calibrated automatic pipette will overcome this problem as the calibrated pipette will ensure repeatable droplet formation on the inside of the graphite tube as well as ensure that a constant volume is dispensed each time, which is not always possible when using manual methods.

b) Vapour phase effects

The analytical results of an analysis are dependent on the type and condition of the analyte in the sample. If temperature equilibrium does not exist during atomization, different compounds or states of the analyte could exist, which require different atomization temperatures.
Production of the atomic vapour also contributes to the vapour phase effects. This involves the mechanism of atom formation from the graphite surface. The effects are noticeable since different mechanisms will require different conditions where atomization will take place. Three general mechanisms (steps) for atom formation have been put forward by Chakrabarti [8]:

1) carbon reduction of the oxide followed by sublimation of the metal,
2) dissociation of the metal oxide and
3) dissociation of the metal halide.

It was found that for the volatile metals, gas expansion rather than analyte diffusion controls the removal of the analyte from the furnace.

For the involatile metals, diffusional processes control their removal from the furnace. The distribution of the atoms across the cross-section of the graphite tube was shown not to be uniform and was due to the fact that atomization was a rate-limited desorption process from the graphite surface. All these factors contribute to interferences in the vapour phase.

c) Spectral interferences

A spectral interference is observed when the absorbing wavelength of an element, other than the analyte of interest, falls within the bandwidth of the absorbance line of the analyte. This is often observed in the form of a line overlap or shoulder overlap.

d) Sample introduction

Owing to the steep temperature gradient along most atomizers, any variation in the sample size,
viscosity or position in the tube could give rise to a variation in signal response, causing a reproducibility interference. Several authors [9, 10] have quoted advantages regarding reduced background signals when solid samples are analysed, rather than solutions. The sample can also be placed in the graphite tube in the form of an aerosol spray, which reduced interferences [11].

e) \textit{Background signals}

Large concentrations of the matrix vaporized during the atomization stage can cause scattering of the incident light beam and lead to spurious results. Molecular species which are vaporized during atomization can cause molecular absorption due to their broad band spectra and line spectra. Light emission from the heated atomizer can, in some cases, reach the detector and cause distortion of the baseline signal. These effects can be overcome in most cases by the use of suitable background correction.

f) \textit{Memory effects}

The incomplete atomization of an element will cause an enhancement in the analytical signal of subsequent analytical determinations. This effect will continue as long as the element accumulates on the atomizer and the error will become progressively greater. This is seen mostly for the elements that form stable refractory oxides (V, Mo, W etc.). Memory effects can be diminished by the use of longer atomization times or higher atomization temperatures, as long as the atomizer surface is not affected or deteriorated by the high temperatures.

The memory effect is also due to the effect of the graphite surface. The pyrolytic coating overcomes a lot of the problems encountered in earlier years, but the problem of intercalation still persists. Intercalation occurs when atoms of the analyte are bound between the planes of the
sheets of carbon that make up the crystal structure of graphite. The alkali metals, halogens and metal chlorides are particularly prone to intercalation. The intercalated product will be retained by the graphite and will appear at a later stage, giving rise to a memory effect.

g) Instrumental parameters/conditions

Several interferences are also largely due to the instrumental design or configuration used, as well as the analytical conditions chosen for the analyses. Some of the interferences reported in the literature reflect particular design problems in the earlier furnaces. In many cases, the radiation source is a source of problems, as many determinations have detection limits that are dependent on the brightness of the light source. In a lot of cases, the electrodeless discharge lamp, (EDL), have been used to improve the detection limits.

Another instrumental parameter which can also lead to interferences is the background correction system. Background correction is needed to correct for non-atomic absorption and scattering effects in ETA-AAS. The Zeeman effect has been used increasingly for improved background correction over the conventional continuum background correction systems.

2.2.1.2 Chemical interferences

The degree of chemical interferences depends on both the sample matrix and the analyte to be determined. If the analyte is not volatile, high temperatures can be employed to remove any matrix components which could lead to interferences during atomization. If on the other hand, the analyte is volatile, the use of high temperatures will cause loss of the analyte. The number of atoms in the light path will subsequently be reduced due to the compounds in the sample matrix.
and the signal is thus reduced. A brief outline of the factors contributing to chemical interferences are given below.

a) **Loss of analyte on ashing**

Losses of the analyte element can occur during the ashing stage for two reasons: *firstly*, the element may be present in the sample in such a form that it is volatile at the ashing temperature employed, and *secondly*, the element may be converted into a volatile form by association with the sample matrix. Therefore, a thorough study of the ashing temperature and composition of the matrix is required before starting an analysis in order to avoid unwanted loss of analyte.

b) **Carbide and Nitride formation**

Some elements form stable compounds with the graphite surface, such as carbides. These carbides cause the slow release of the element from the graphite atomizer, because the atoms are “held” by the graphite by the process of intercalation. For some elements, the analytical signals obtained are very dependent on the physical condition of the atomizer surface. Thus, the atomizer must be kept in a reproducible condition, ensuring the pyrolytic coating stays intact throughout the analyses.

Nitride formation is observed when nitrogen is used as the inert sheath gas. These are also stable species, which reduce the analytical sensitivity. This effect is usually minimal though, since it affects both samples and standards.

c) **Condensation**

Sometimes when the atomized element leaves the hot atomizer surface, it can be transported into
a much cooler region, where condensation of the element takes place. This also reduces the analytical signal and can lead to memory effects.

d) **Anion/Cation interferences**

Cation interferences are complex, and no general theory has been accepted to explain the interferences observed, except that excesses of certain cations have a suppressing effect on the analytical signals of several elements.

Anions, on the other hand, have several theories explaining their action of interferences [4]. The presence of oxyanions (SO₄²⁻, NO₃⁻, PO₄³⁻) in samples are normally preferred to the presence of halides (Cl⁻, Br⁻, I⁻), as the molecular halide species have the tendency to vaporize at low temperatures, thus leading to the loss of the analyte and reduction in the analytical signal. The oxyanionins, on the other hand normally pose fewer interference problems, as they decompose to simpler compounds such as SO₂ and NO₂, which are driven off at moderate temperatures.

### 2.3 Reduction of interferences

Over the years, many methods have been proposed and successfully employed in the reduction of interferences. Some of these methods are:

i. Reactive gases.

ii. Acid additions and extractions.

iii. Organic compound additions.

iv. Matrix / chemical modification.

v. Coating of graphite tubes.

vi. Platform atomization.
Methods iv. and v. are of interest in this work and are discussed in the following section.

2.3.1 Matrix / chemical modification

Owing to the inability of electrothermal atomizers to accommodate high matrix concentrations during atomization, the selective volatilization and matrix modification within the atomizer has become a necessity for the electrothermal atomization technique. This is vital for the reduction of interferences caused by the matrix components.

Ediger [13, 14] introduced the concept of “matrix modification”, suggesting that the drying or charring properties of the analyte or matrix be deliberately altered by chemical additions. The use of the term “chemical modification” refers to the same procedure. Ediger observed that if NaCl was a major matrix component, it produced a large background signal at certain wavelengths in his analysis, unless it was driven off in the ashing cycle. However, many analyte metals are lost at temperatures which are lower than that which will drive off the NaCl, leading to subsequent analyte loss. In view of this problem, Ediger suggested the addition of NH₄NO₃, to convert the NaCl to NH₄Cl and NaNO₃. These two compounds could then be driven off in the ashing step, below a temperature of 500° C, where volatilisation of the analyte element starts taking place. This is an example of a chemical addition which facilitates the removal of interfering matrix components by conversion to a more volatile substance.

Since the introduction of the chemical modifier by Ediger, literally hundreds of elements and compounds have been proposed and used as chemical modifiers for a vast number of elements in various sample matrices.
The use of chemical modifiers in ETA-AAS is a technique which has become routine procedure for the determination of many elements in various sample matrices. The aims of these modifiers are to minimize the effects of the matrix on the analyte, and to reduce interferences. This can be achieved in a number of ways, but in general, the chemical modifier is added to the sample containing the analyte of interest, and modifies the thermochemical behaviour of either the analyte or the matrix or both.

The overall effect the chemical modifier displays is the reduction of interference effects, such as molecular absorption, background absorption and vapour phase effects.

In general the chemical modifier achieves this in one of two ways:

I. The chemical modifier enables the formation of a more thermally stable analyte-modifier compound, which facilitates the separation of the matrix from the analyte, by removal of the matrix components prior to atomization.

II. The chemical modifier alters the thermochemical behaviour of the analyte so as to delay the atomization until a more stable thermal environment is achieved.

The chemical modifier also undergoes, as does the analyte, reactions and interactions with the graphite tube surface. This can either reduce or increase the reactions of both the analyte and the matrix with the graphite surface.
2.3.2.1 Chemical modifiers past to present

The literature abounds with references, procedures and chemicals to be used as chemical modifiers. Each element has its specific chemical modifiers for several matrices [15]. Since the introduction of chemical additions by Ediger [13, 14], an enormous amount of time and research has been spent on the role and mechanism of modification by several chemical modifiers on many elements. The chemical modifiers can be employed in any number of ways and many different methods and modifiers have been investigated. These methods generally differ in the form in which the chemical modifier is added, or is present in the graphite tube. Some of the methods employed are given below.

1. The chemical modifier can be mixed with the sample/analyte solution prior to analysis, usually in the form of a solution, using an inorganic salt of the modifier.

2. The chemical modifier can be added, in the form of a solution, before or after the sample aliquot has been placed in the graphite tube.

3. The chemical modifier may be added to the sample aliquot at a specific time during the heating program.

4. The chemical modifier may be placed in the graphite tube and undergo a heating-cycle, where the modifier is pre-reduced by heat or by a reducing agent.

5. The chemical modifier may be added in the gaseous form, during a certain stage of the
heating program, called reactive modification.

6. The chemical modifier may be added in the form of a solid.

Furthermore, in the cases where the modifiers have been used in the form of a solution, the modifier can be added as the individual (single-element) chemical modifier, as a mixed modifier solution, or as a composite chemical modifier [15].

2.3.3 Coatings on atomizer surfaces

Several authors have investigated the use of coatings on the graphite tube, to serve as chemical modifiers. Many methods have been employed in the production of these coatings on the graphite tubes, and some of these are given briefly.

i. Carbide coatings (W, Zr, Ta, Mo etc.)

The chemical modifier is present as a metal carbide coating on the surface of the graphite [16, 17, 18].

ii. Pre-reduced surfaces

The chemical modifier (Such as Pt or Pd) is present in the graphite tube in the reduced metal form. This is brought about by a heating program or by the use of reducing agents in the form of a solution or a gas [15,19].

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iii. **Electroplated surfaces.**

The chemical modifier is present in the graphite tube in the metallic form. The metal is deposited by electroplating or electrodeposition from solution [16].

iv. **Soaking methods.**

The chemical modifier is in the form of a solution and the graphite tube is immersed in this solution. After soaking, the graphite tube is removed from the solution and the graphite tube undergoes a heating program, leaving a coating of the modifier on the graphite surface [20]. The graphite tube is in effect impregnated and coated by the modifier, which becomes an integral part of the tube.

v. **Sputtered coatings**

The pure metal modifier is sputtered onto the graphite surface from a solid metal cathode. The chemical modifier is then present as a solid deposit in the reduced (metallic) form [21].

### 2.4 Conclusions

In view of the successes noted with the use of coatings of chemical modifiers on graphite tubes, the sputtered coatings method as listed in the last point (v) above, was under investigation in this work, where a solid, thin coating of a chemical modifier in the metallic form was deposited on the inside of graphite tubes. The graphite tubes prepared in this way were investigated for proposed use as permanent thermochemical modifiers for the analysis of As and Pb in sulphate, nitrate and chloride matrices.
The suitability and efficiency of the prepared modifiers were judged according to several analytical performance parameters and these results were judged against the performance of selected conventional chemical modifiers.
2.5. **References**


CHAPTER 3

LOW PRESSURE ARGON GLOW DISCHARGE SPUTTERING

3.1 Introduction to gas discharges

3.1.1 The gas discharge tube

Normally, a gas is a poor conductor of electricity, and in its normal state it is an almost perfect isolator, but if a sufficiently high electrical field is applied, conduction can occur and an electrical discharge results. This discharge occurs in a low pressure gaseous environment, where atoms and molecules of the gas break down electrically and give rise to electron-ion pairs. This is normally made to occur in a closed vessel or tube, called an electron tube or gas discharge tube.

In gas discharges, the ions and electrons initially formed are accelerated towards the electrodes, with the electrons causing further ionisation along their paths. The electrons are produced by ionisation of the gas as well as by secondary emission processes at the electrodes. Electrons and positive ions are removed at the anode and the cathode respectively, as well as by the process of recombination within the tube. After some time, a stable state can be reached where the rate of production of ions and electrons is equal to the rate at which they are being removed. In a glow discharge, the potential drop across the tube is independent of the current and does not vary uniformly down the length of the glow discharge. Most of the potential drop occurs between the
cathode and the negative glow, and is called the cathode fall.

The characteristics of the discharge depends on a number of factors such as the type of gas, the pressure in the discharge, the electrical field applied and the shape, condition and type of material employed in the electrodes. The most common type of discharge is the glow discharge, which is characterised by several distinct luminous regions in the tube, which are depicted in figure 3.1. The shaded areas in the diagram represent the glow regions and the light areas represent the so-called “dark” spaces.

![Figure 3.1. The gas discharge tube [1].](image)

The regions between the anode and the cathode differ with respect to factors such as light intensity, potential, electric field distribution and current density [1].

In general, the glow discharges used in analytical chemistry are relatively small and sometimes do not contain all the regions discussed in the following points [2].
a. *The Aston dark space* - In the cathode region of the discharge the electrons are emitted from the cathode as a result of secondary electron emission caused by ion bombardment. The electrons are accelerated towards the anode and for a short distance do not have sufficient energy to ionise or excite the gaseous atoms. The positive ions moving towards the cathode have high velocities in this region and the probability of recombination with electrons is low. This region does not emit any radiation and appears dark.

b. *The cathode glow* - The cathode glow is a luminous region near the cathode where positive ions that have been excited by electrons return to their ground state, with the emission of radiation.

c. *The Crookes dark space (Cathode dark space)* - This is a thin, dark layer in front of the cathode and this zone is essential for sustaining the electrical discharge. Electrons leaving the cathode are accelerated by the electrical field in front of the cathode. When the electrons have gained sufficient energy, they can cause ionisation of atoms and create new electrons, but the electrons produced in this region do not have sufficient energy to excite further atoms. Consequently, this region produces little or no radiation and appears dark.

d. *The negative glow* - This is the large, bright region adjacent to the cathode dark space. The electrons are no longer accelerated in this region and are slowed down by collisions with gaseous species. By the time the electrons reach this region, the electrons have gained sufficient energy to cause excitation, which leads to the emission of radiation as the excited atoms return to their ground state. This zone is characterised by a bright,
luminous glow, the colour of which depends on the discharge gas used. In the case of argon, the glow is dark blue [2].

e. **The Faraday dark space** - In leaving the region of the negative glow, the electrons have lost much of their energy and in this region they do not have sufficient energy to excite or ionise the gas. This region is very similar to the Aston dark space and thus does not produce any distinctive radiation. This region is often not observed in analytical discharges.

f. **The positive column** - This region is rather luminous, but not as bright as the negative glow region. The electrons gain energy from the electrical field and possess sufficient energy to cause ionisation and excitation of the gas atoms. Thus, radiation is emitted as the atoms return to their ground state. The colour of the positive column is also characteristic for the type of discharge gas used, but differs from the colour of the negative glow and is also less intense [2]. This region is commonly not observed in analytical discharges.

g. **The anode dark space** - No excitation of the gaseous atoms takes place and the region appears dark.

h. **The anode glow** - Positive ions that have been excited by electrons return to their ground state with the emission of radiation, creating the glow in this region of the anode.
The characteristics of the two anode zones, the anode glow and the anode dark space respectively, differ according to whether the anode is in contact with the positive column, the Faraday dark space or the negative glow.

The actual position and occurrence of the regions in the discharge tube depend on several discharge parameters, and these are discussed briefly.

**Pressure**

As the pressure increases, the cathode dark space, negative glow and Faraday dark space are compressed towards the cathode, and the positive column takes up the major part of the discharge volume. A decrease in pressure has the opposite effect, i.e. the positive column, Faraday dark space and the negative glow will compress at the anode. If the pressure becomes too low, the discharge will extinguish.

**Voltage**

If the voltage increases, the cathode dark space becomes smaller, and the negative glow becomes longer.

**Current**

The current has no influence on the size or position of the regions, but it does affect the light intensity. The higher the current applied, the more intense will the glow discharge regions appear.
Cathode-anode distance
The effect seen in this region is similar to the pressure effect. As the distance increases, the positive column becomes longer and the positive column, the Faraday dark space and the negative glow appear closer to the anode.

Discharge gas
The discharge gas determines the colour of the negative glow and the positive column. The cathode dark space is affected by the type of gas used. The cathode dark space is seen to shorten when the discharge gas used is easily ionizable.

Cathode material
The cathode material influences the length of the cathode dark space. If the cathode material emits secondary electrons easily, the discharge is more easily sustained and a small cathode dark space is sufficient to sustain the discharge.

3.1.2 Analytical applications of glow discharges
In glow discharges used for analytical purposes, the cathode of the discharge consists of the material to be analyzed. Due to the bombardment of the cathode by the species present in the discharge, atoms of the cathode material are sputtered away from the cathode and enter the glow discharge where they are subject to a wide range of collisions, especially ionisation and excitation. Due to these sputtering and collisional processes, the discharge is filled with atoms, ions and photons of the material to be analysed, namely the cathode material.
This property of the glow discharge makes it useful for a wide variety of analytical techniques, including glow discharge mass spectrometry (GDMS) [3], glow discharge atomic fluorescence spectrometry (GDAFS) [4], glow discharge atomic absorption spectrometry (GDAAS) [4], glow discharge atomic emission spectrometry (GDAES) [5] and glow discharge sputtering [6]. This work will focus on the use of a low pressure argon glow discharge for sputtering the cathode material onto the inner surface of graphite tubes, which are to be investigated for use as permanent thermochemical modifiers in ETA-AAS.

3.2 Glow discharge sputtering

3.2.1 The glow discharge sputtering phenomenon

Sputtering is defined as the process whereby ions, either positive or negative, bombard a solid or liquid surface and bring about the ejection of atoms or clusters of atoms from these surfaces [7]. Sputtering is often referred to as cathode sputtering because it is the cathode material that is sputtered.

The phenomenon was observed at the cathodes of glow discharges in 1852 by Grove and in 1858 by Plücker [8], but the process was not fully understood at the time. Since then several theories on glow discharge sputtering have been put forward, but few actually clarify the physical process of sputtering occurring in the discharges. The main theories of note will be given briefly.

The theoretical model of Kingdon and Langmuir [8] suggested that sputtering was a simple mechanical collisional process, whereby ions striking the cathode surface caused depressions in
the surface of the cathode. These depressions were a few atoms deep and subsequent ions could be reflected in these depressions, retaining enough energy to knock out atoms of the cathode material. They derived an expression for the maximum energy transmitted from an incident ion of energy $eV$, mass $m$ to a metal atom mass $M$, given in equation 3.1.

$$E_{\text{max}} = 4ev \frac{mM}{(m+M)^2} \quad \ldots(3.1)$$

According to this model, at least two collisions are required to eject an atom, which in turn must first acquire the energy of evaporation before it can escape. The theory also predicts a minimum ion energy below which no sputtering will occur. This energy is called the threshold energy and is given in electron volts. The theoretical calculations according to this model are in reasonable agreement with experimental results, but only for the ions of the light gases.

Von Hippel, Blechschmidt and Townes [8] regarded sputtering as a process due to evaporation from small local regions where the impact of the ions produced a very high temperature for a very short time. It is believed that the ion delivers its energy in a very short time, approximately $10^{-12}$ seconds [9], and atoms lying on the surface can obtain some energy larger than their surface binding energy and can escape from the surface. The rise in temperature at the point of impact was derived from the standard equations of heat flow. However, it seems doubtful whether it is legitimate to apply the macroscopic concepts of heat flow and temperature to regions that only consist of a few atoms. Taking all these factors into account, the validity of this theory is also questionable.

More recently, Ecker and Emeleus [8] pointed out that sputtering in a glow discharge can only
be understood by considering three interdependent problems:

i. How the atoms are released from the cathode surface.

ii. How the sputtered atoms move through the gas discharge.

iii. How the sputtered atoms are deposited.

They believe that the inadequacy of the previous theories arose from the neglect of the following factors:

a. The differences in mass between the metal and the gas atoms.

b. The high velocities of the sputtered atoms.

c. The radial variation of the discharge current.

By taking these factors into consideration, Ecker and Emelius then concentrated on the motion of the sputtered atoms through the gas. Their theory describes the density distribution of the metal atoms in the gas as a function of the distance from the cathode. The density distribution shows a maximum at a short distance in front of the cathode, the position of which is dependent on the velocities of the ejected atoms. This then suggests that the thickness of the deposit, \( d \), should vary according to equation 3.2,

\[
    d = \exp \frac{z}{r} \quad \text{....(3.2)}
\]

where \( z \) is the distance from the cathode and \( r \) is the radius of the gas discharge tube.
Two different types of sputtering can be distinguished, namely physical sputtering and chemical or reactive sputtering.

Reactive sputtering arises from chemical reactions between the bombarding ions and the target material, giving rise to other chemical species in the discharge. If oxygen is added to the discharge gas, for example, the reactive sputtering process can yield thin films of the oxides of a large range of metal cathodes (NiO, TiO₂, Bi₂O₃ and WO₃), which are normally difficult to deposit by other conventional means [7].

Physical sputtering normally refers to the process of cathode sputtering, where the cathode material is sputtered away from the cathode by the process of ion bombardment.

3.2.2 Characteristics of glow discharge sputtering

Sputtering can be regarded as an undesirable effect in gas discharge tubes because it causes metal deposits on insulators and tube walls and disintegration of cathodes. The cathode surface is left in abraded and roughened condition due to the loss of atoms from the surface layers.

Although glow discharge sputtering is known to occur at relatively low pressures, the discharge is normally maintained at pressures in the region of 0.1 to 10 Torr (13.3 to 1330 Pa). The process normally occurs in inert gases such as He, Ar or Ne, unless reactive sputtering is employed, where oxygen or hydrogen or other reactive gases can be used.

In order to maintain the necessary ions, a gas discharge is held at a potential of 100 to 2000 volts
between an anode, consisting typically of brass, iron or aluminium, and a cathode consisting of the material to be sputtered.

Experimentally established results [7,8] for the sputtering process exist and some of the findings are as follows:

♦ Sputtering sets in appreciably at ion energies of about 50 electron volts (depending on the type of material, the type of ion and angle of incidence), and rises almost proportionally with increasing ion energies to a maximum value and finally decreases with increasing penetration of the ions into the target lattice.

♦ It was observed that most of the material sputtered away from the cathode was in the form of neutral atoms or clusters of atoms. This was verified by the spectrum they emit when excited using different cathodes. The spectra obtained were those of the neutral atoms and the paths of the sputtered particles through a gas at low pressures were not bent by a magnetic field.

♦ In some cases ionic compounds are sputtered away from the cathode, but owing to the very strong electrical field in front of the cathode, any positive ions will be attracted back to the cathode and will not enter the discharge. Any negative ions that are produced will be accelerated with great velocity towards the anode.

The control and characteristics of the sputtering process was the next topic of investigation. The sputtering rate and the sputtering yield are the most important quantities with respect to sputtering. The sputtering rate increases linearly up to a point with increasing voltage, whereafter a decrease is noted. The rate was seen to be directly proportional to the energies of the
The sputtering yield is defined as the number of sputtered atoms per incident ion. Many authors have derived analytical expressions for the sputtering process [10]. In effect, what can be concluded from these expressions is that the sputtering process is a complex function of the incident energy of the bombarding particles, the mass and atomic numbers of the bombarding particles and the mass and atomic numbers of the target material. Several factors affect the sputtering yield and these will be discussed briefly.

*The kind of discharge gas*

Inert gases are normally used due to their high sputtering efficiencies, coupled with the fact that they do not undergo chemical reactions with the cathode material.

*The masses of the bombarding particles*

The sputtering yield is seen to increase more or less with increasing mass of the bombarding particles. (This is not true for $\text{H}_2^+$, as $\text{H}_2^+$ has the ability to undergo chemical reactions with many cathode materials and thus leads to exceptionally high yields).

*The energies of the bombarding particles*

The threshold energy must first be overcome before sputtering can set in. The particles of the cathode material must also overcome their surface binding energy to be able to escape from the surface of the cathode. It has been suggested that the sublimation energy of the cathode material is a good approximation of the surface binding energy to be overcome in order for sputtering to occur. Above these constraints, the sputtering yield increases with increasing energy of the
bombarding particles, reaches a maximum and decreases as the penetration into the cathode metal lattice increases.

**The angle of incidence of the bombarding particles**

The sputtering yields reach a maximum at incident angles of between 60-80° relative to the surface [11]. At low incident angles the sputtering yield increases with increasing angle due to the increased probability of the collisional cascade to result in sputtering. At incident angles higher than 80°, the yield decreases as the incident particles are more likely to reflect off the surface than to cause penetration.

**The cathode material**

In general the sputtering yield increases with increasing atomic number of the cathode material within each row of the periodic table [2]. It has been found that as the penetration depth increases, a large fraction of the energy is expended in collisions which do not lead to sputtering. The increase in the sputtering yield is attributed to the filling of the electron shells, especially the d-shells of the transition metals. As the shells become more filled, thus higher atomic numbers, the surface becomes less “penetrable” and the incident particles are not able to penetrate deeply, which leads to a higher sputtering yield.

**The condition of the cathode surface**

It was thought that Al, Zn and Mg had very poor sputtering yields, but this was in fact due to the oxide layers formed on the surface. When the oxide layers were removed, a significant improvement in sputtering was observed. In the case of Mo, sputtering yields were poor at the onset of sputtering, increased with time until a constant value was reached, whereafter the yield
decreased due to penetration effects [8]. This implies that the surface layer contaminants were first removed by ion bombardment, leaving the surface atomically clean and free from contaminants, whereafter sputtering could then occur normally. Therefore, the sputtering yield is seen to be retarded in the following cases: if surface contaminants are present, if protective oxide layers cover the metal surface or if adsorbed gas layers are present on the surface of the cathode.

3.2.3 The applications of sputtering

Taking into account the parameters which have an influence on sputtering and using the correct configurations, sputtering can then be used in a wide range of applications:

- The removal of surface layers and the production of atomically clean surfaces.
- The preparation of colloidal solutions, if the discharge is through a liquid.
- The deposition of oxide layers through reactive sputtering when oxygen is added to the discharge gas.
- The hollow cathode lamp and hollow cathode plume.
- The production of thin metallic films on substrates placed near the cathode.

The last point was of interest in this work as a thin film of the cathode material was deposited on the inside of a graphite tube. The cathode material can thus be varied in order to deposit different thin metallic layers on the inside of the graphite tube. In this way, the investigation of various permanent modifiers was made possible.
3.3 Experimental

3.3.1 Sputtering apparatus

Utilising the fact that sputtering can be used to prepare thin metallic coatings on substrates, an apparatus was constructed which could sputter solid metal modifiers onto the inner surface of pyrolytic coated graphite tubes. This metal modifier will be present as a permanent, thin film of the modifier (metal wire cathode) and will, in effect form an integral part of the tube. The sputtering apparatus is shown in figure 3.2.

The sputtering apparatus used in this work is a modified form of the system used by Rademeyer et al [6] where Perkin-Elmer tubes were sputtered. The new modified system was adapted in order to sputter the Varian type graphite tubes.
Figure 3.2. Sputtering apparatus (side-on cross sectional view).

The apparatus consists of a brass body (A), into which the graphite tube is slide-fitted. The graphite tube is represented by the shaded areas on either side of the wire cathode. The inner portion of the brass body is equipped with Viton O-rings, which insulate the graphite tube from the brass body. Glass plates (B) are fitted onto both ends of the brass body and have holes drilled at appropriate positions so that the metal wire cathode can fit through the glass plates. The glass plates fit tightly onto the ends of the brass body and a seal is provided via the Viton O-rings. Brass plates (C), fit tightly onto the glass plates, with Viton O-rings providing a seal once again. A hole is drilled into each brass side plate to provide an opening from where a vacuum can be drawn. The brass holder also has holes drilled in it, one on the top where the argon is introduced for the discharge, and a second hole drilled at the bottom, from where the vacuum is drawn.

The metal wire cathode is indicated by the thick, dark line on the inside of the apparatus. Iridium, rhodium and tungsten (99.99% pure, Goodfellow metals, Cambridge, UK) wires were 1.0 mm in diameter and cut in lengths of 42 mm. The brass side plates have protrusions into which the
metal wire cathode tightly fits, ensuring good contact between the cathode and the brass side plates. The brass side plates are connected to the negative pole of a high voltage, current limited direct current source. The metal wire making contact with the brass end plates thus forms the cathode from where the sputtering will occur. The brass body is connected to the positive pole of the direct current source, thus forming the anode.

The argon flow was finely controlled by a micro needle valve (Balzers RME010), coupled to a valve control unit (Balzers RVG040). The pressure in the system was monitored by the use of an Alcatel API201 piranimeter.

3.3.2 Experimental Method

3.3.2.1 Optimization of sputtering

The sputtering process was seen to occur over a wide range of voltages and at varying gas pressures. Consequently, in order to control the rate and efficiency of sputtering, optimum values for the parameters affecting sputtering were determined. This would also then ensure the reproducibility and dependability of the process. As was reported by Rademeyer et al [6], approximately 10 mg of the metal modifier proved to be sufficient in order to function as a permanent thermochemical modifier. In order to accurately sputter milligram quantities of the metals onto the graphite tubes, the system had to be optimized and the characteristics of the system had to be determined.

The same strategy for each metal was followed for the optimization procedure and the results of
the optimization are as follows:

1) It was noted that the current and the voltage were affected by changes in the gas pressure.

2) If the gas pressure was increased, the current and voltage were seen also to increase, up to a certain point, from which the current remained constant and any further increase in the gas pressure would result in the voltage decreasing. Thus, the voltage could be varied at this point where the current remained constant by slight changes to the gas pressure.

3) When the gas pressure became too high for the system, the current was seen to drop drastically and control of the voltage in the system was not possible. Conversely, if the gas pressure was too low, the voltage would assume a maximum value and the current would decrease to a minimum, which was caused by the very low pressure in the system.

From these observations, it was decided that the current must be set to an arbitrary value (14 mA) and the voltage was manipulated to give various values in order to determine where the optimum voltage and pressure values lied. This method was followed for each of the metal modifiers in turn.

### 3.3.3 Results

The discharge was seen to be most stable and useful in the range 580 to 740 V, and the optimum values of the voltage were sought within this range. The pressure of the system was seen to be useful in the range 3 to 8 torr and the optimum gas pressure was determined using this range. To determine the optimum voltage in the system, graphs of voltage versus mass of metal sputtered onto the graphite tubes were constructed. The results of voltage versus mass of metal sputtered onto the graphite tube in 10 minutes were plotted, and the results are given in figures 3.3, 3.4 and
3.5. A constant time span was used in each case so that the graphs could be directly compared and an optimum value obtained.

The graphite tube and the wire metal cathode were weighed before and after sputtering. The difference in mass before and after sputtering would yield the absolute mass of metal sputtered from the wire cathode as well as the mass of metal sputtered (deposited) onto the tube. The voltage in the system was controlled by varying the gas pressure. The voltage was varied between 580 and 700 V in increments of 20 V. A constant time span of 10 minutes was chosen.

![Graph showing the relationship between voltage and mass sputtered](image)

**Figure 3.3. Voltage optimization for iridium:** Mass of iridium deposited on the graphite tube at various voltages for 10 minute runs at 14 mA.
Figure 3.4. **Voltage optimization for rhodium**: Mass of rhodium deposited on the graphite tube at various voltages for 10 minute runs at 14 mA.

Figure 3.5. **Voltage optimization for tungsten**: Mass of tungsten deposited on the graphite tube at various voltages for 10 minute runs at 14 mA.
In order to use the system for the accurate deposition of a specific mass of the metal, one must be able to predict the mass of the metal deposited in a given time span at the optimum voltage. Therefore, plots of mass of metal deposited on the tube versus time were plotted, and the results are given in figures 3.6, 3.7 and 3.8.

Figure 3.6. Sputtering rate for iridium at the optimum voltage of 680 V.

(At 4.0 torr argon and 14 mA)

Figure 3.7. Sputtering rate for rhodium at the optimum voltage of 670 V.

(At 4.6 torr argon and 14 mA)
Figure 3.8. Sputtering rate for tungsten at the optimum voltage of 660 V.

(At 5.1 torr argon and 14 mA)

Using the optimum values from these graphs, one could then operate the system for a specific metal at the optimum voltage of that metal, for a given time span and accurately predict the mass sputtered in that time span. This knowledge of the mass sputtered onto the graphite tube is essential to this work, where a specific amount of the metal is required to be sputtered on the tube. This method of optimization and characterisation was repeated for each of the metals, and the optimum values for each metal are given in Table 3.1.
Table 3.1. Optimum values and characteristics of the sputtering system for Ir, Rh, W.

<table>
<thead>
<tr>
<th></th>
<th>Optimum Voltage (Volts)</th>
<th>Argon Pressure (Torr)</th>
<th>Current (mA)</th>
<th>Sputtering time for 10 mg (minutes)</th>
<th>Mass sputtered in 10 Minutes (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Iridium</strong></td>
<td>680</td>
<td>4.0</td>
<td>14</td>
<td>72</td>
<td>1.576</td>
</tr>
<tr>
<td><strong>Rhodium</strong></td>
<td>670</td>
<td>4.6</td>
<td>14</td>
<td>85</td>
<td>1.014</td>
</tr>
<tr>
<td><strong>Tungsten</strong></td>
<td>660</td>
<td>5.1</td>
<td>14</td>
<td>146</td>
<td>0.674</td>
</tr>
</tbody>
</table>

The values, as shown in table 3.1, were used throughout for the production of the coated graphite tubes.

The procedure followed for the preparation of the system for sputtering was as follows:

1. The graphite tube is inserted inside the brass body, using tweezers, ensuring no contact with hands or other possible contaminants.
2. The metal wire cathode is placed firmly in the space provided in one of the brass side plates, again ensuring no contact with the hands or other objects.
3. The brass side plates are attached to the sides of the brass body, covering the glass side plates and the metal wire cathode is pushed firmly in place.
4. The system is evacuated for 5 minutes and the system is inspected for vacuum leaks.
5. The argon gas flow is turned on and the system is flushed for 2 minutes, maintaining a pressure of about 5 Torr.
6. The power source is switched on and sputtering is initiated.
7. The final gas pressure adjustments are made to obtain the required optimum voltage for the specific metal being sputtered.

3.3.4 Discussion

It was noted that a two (2) minute rinse time for the preparation of the system was necessary in order to ensure that an inert argon atmosphere existed and that all the air was removed from the system. Air in the system was undesirable and lead to an unstable discharge. Figures 3.6, 3.7 and 3.8 showed that the minimum time used for sputtering to be 5 minutes.

The reasons for this were:

Firstly, during the first few minutes when sputtering was initiated, the discharge was unstable and the sputtering had not yet reached a maximum. This was due to the fact that the bombarding ions first produced an atomically clean surface where sputtering occurred freely and any contaminants or impurities were removed from the cathode wire surface.

Secondly, it was noted that the masses sputtered onto the tube in the first 5 minutes varied drastically from one run to the next. This can also be explained by the fact that the sputtering process had not yet reached a stable state each time and the reproducibility of runs under 5 minutes were poor.

In order to determine whether or not the sputtering process was running at an optimum, a calculation was made after each sputtering run. This simply involved pre-weighing the graphite tube and the metal wire cathode before and after each run and then determining the "sputtering
efficiency”. This is the mass sputtered onto the graphite tube, divided by the mass sputtered from the metal wire cathode, expressed as a percentage. A percentage of 85% was decided on as the minimum value which was acceptable. The metal not sputtered onto the graphite tube was accepted as being lost due to deposition on the glass side plates. By determining the efficiency for each run, the reproducibility of the process could be monitored.

From the time versus mass graphs (figures 3.6, 3.7, and 3.8), a series was derived showing the trend in the sputtering rate of each metal. This series, W < Rh < Ir, implied that in a given time span, iridium will sputter more material than rhodium, and rhodium in turn will sputter more material than tungsten.

3.4 Conclusions

Following the optimization of the experimental conditions for each metal modifier, the results showed that the inside of graphite tubes could effectively be sputtered with solid metal modifiers to form a solid coating of these metals on the graphite surface. The sputtering process could also be controlled by manipulation of certain experimental parameters and exact amounts of metal modifiers could be deposited on the graphite surface.

Several graphite tubes were sputtered with the metals, to function as permanent thermochemical modifiers, and the analytical performances of the coated graphite tubes were investigated.
3.5 References


CHAPTER 4

EVALUATION OF PERMANENT MODIFIERS

4.1 Problems encountered with the use of conventional chemical modifiers

Conventional chemical modifiers which are in use for routine analyses pose several distinct problems and limitations on these analyses. One of the most important of these limitations is interferences. In some cases, the chemical modifiers themselves are the cause of these interferences, which complicates the use of these modifiers.

Some of the problems associated with the general use of chemical modifiers will be given briefly.

1. The modifiers are normally added to the sample solution in the form of a solution before or during the analysis, as described in chapter 2, and in the case of ultra-trace determinations, the modifier solution itself can contain impurities, which can cause interferences during the analysis. Thus, the preparation and use of chemical modifiers is critically dependent on the purity of the commercially available modifiers. Also, the process whereby the modifier is added to the sample solution can bring about contamination.

2. The time for analysis when using a chemical modifier in the form of a solution is considerably lengthy. The sample and the modifier must either first be mixed, or the modifier must be placed inside the graphite tube along with the sample aliquot. Both these methods increase the time of analysis.
3. The mixing process of the modifier and sample solution is sometimes ineffective, leading to changes in the reproducibility of the analysis and inefficient chemical contact between the modifier and the analyte in solution. This ultimately reduces the sensitivity of the analysis and the performance of the chemical modifier.

4. In the case where the chemical modifier undergoes a pre-reduction step in the graphite tube, the graphite tube lifetime is decreased due to the heating cycle and new tubes have to be employed frequently. Some chemical modifiers also have a corrosive effect on the graphite surface, decreasing the lifetime and performance of the tube.

5. The distribution of the chemical modifier on the surface of the graphite has also been known not to be homogeneous when in the form of a solution or a deposit [1, 2, 3]. The analyte and modifier solution can spread along the length of the graphite tube, or in the case of more viscous solutions, can cause droplet formation, reducing the homogeneity of the modifier on the graphite surface and thus reducing the chances for effective modification.

Owing to these limitations and disadvantages encountered with the use of conventional chemical modifiers, as described above, the solid metal coatings produced by sputtering the metals on the inside of graphite tubes were investigated for their suitability as permanent modifiers. The use of these permanent modifiers intended to overcome some of these problems.

As and Pb are used as analyte elements to test the analytical performances of the permanent modifiers. The analytical performance parameters investigated were: maximum ashing
temperatures, atomization temperatures, tube lifetimes, analytical precision and detection limits.

The ultimate aims of the permanent modifiers in ETA-AAS were to simplify the use of modifiers for routine analyses, to increase the speed of analyses, to improve detection limits, to improve analytical precision and to increase the lifetimes of the graphite tubes for analyses.

If all, or most of these criteria can be met or improved upon, the use of different types of permanent modifiers can be investigated and extended for future use in routine and specific analyses. The suitability of the permanent modifiers in several different sample matrices will be investigated. This is necessary if the modifiers are intended for use in routine analyses, where a variety of sample matrices are encountered. This should then, hopefully help in the search for a more convenient and more universal modifier.

4.2 **Experimental**

4.2.1 **Equipment and instrumentation**

A Varian AA-275 series atomic absorption spectrophotometer and a Varian GTA-95 graphite tube atomizer were used for the determinations. The spectrophotometer was connected to an EPSON LX 400 printer, where the absorbance data was recorded. Deuterium background correction was used throughout for all determinations.

The modified sputtering apparatus, as described in chapter 3, was used for the production of the permanent modifiers (W, Ir, Rh) and the "mixed" permanent modifiers, in the form of the
sputtered graphite tubes which are discussed under section 4.2.3.

**4.2.2 Reagents**

The Pb standard solution used was a commercially available standard, 1000 mg.l⁻¹, Univar, Saarchem, RSA. The As standard solution was also a commercially available standard, 1000 mg.l⁻¹, Spectrosol, BDH, Poole, England. The Pb and As stock solutions (both 10 mg.l⁻¹) were prepared from the 1000 mg.l⁻¹ standard solutions each day by dilution with deionized water (Continental water systems corp., Modulab modupure, San Antonio, TX). The Pb and As working solutions, 20 ng.ml⁻¹ and 100 ng.ml⁻¹ respectively, were prepared from the stock solutions each day by dilution with the deionized water.

All glassware and plasticware used in the preparation of standard solutions were leached in an acid bath, consisting of HNO₃ and HCl in the ratio of 1:1, for 24 hours before use. The glassware and plasticware were then rinsed at least three (3) times with deionized water before use. The chemical modifier solutions, containing Ni, Mg and Pd, were prepared from standard solutions of Ni(NO₃)₂, Mg(NO₃)₂ and Pd(NO₃)₂ by dilution with the deionized water. The final concentrations of the chemical modifiers were ten (10) times molar excess to those of the As and Pb working solutions respectively.

The chloride, sulphate and nitrate matrices were prepared from the mineral acids (Merck, pro analysis), namely hydrochloric acid (32%), sulphuric acid (95-97%) and nitric acid (65%) and were present as 1% matrices in the stock solutions.
All acids used were from Merck, and values of Pb and As were investigated in all the acids and were found to be negligible. Spectroscopic (instrument) grade argon was used throughout (Air products, 99.999% pure).

4.2.3 Experimental conditions

4.2.3.1 Spectrophotometer

The spectrophotometer was operated in the absorbance mode using single beam operation, with an absorbance expansion factor of one (1). The time for measurement of absorption was set to 3.2 seconds for both As and Pb, and peak heights were measured throughout.

A Pb hollow cathode lamp (Cathodeon Ltd., Cambridge, UK) was used for the determination of Pb, operating at a lamp current of 4 mA. The spectrophotometer was operated at a wavelength of 283.3 nm, using a slit width of 1.0 nm. The choice of the 283.3 nm line for Pb is preferred to the 217.0 nm line due to the fact that non-atomic absorption is lower at the 283.3 nm line, thus presenting fewer interferences [4].

An As hollow cathode lamp (Rank-Hilger, UK) was used for the determination of As, operating at a lamp current of 7 mA. The spectrophotometer was operated at a wavelength of 197.4 nm at a slit width of 1.0 nm.
4.2.3.2 Graphite tube atomizer

An argon gas flow rate of 3 l.min⁻¹ was employed during the analyses, except during the atomization stage and the ramp stage leading to the atomization stage, where the gas flow was stopped to extend the residence time of the atoms in the analytical zone.

The furnace operating parameters for As are given in table 4.1, and for Pb in table 4.2.

**Table 4.1. Graphite furnace operating parameters for the determination of As.**

<table>
<thead>
<tr>
<th>Step Number</th>
<th>Stage</th>
<th>Temperature (°C)</th>
<th>Time (seconds)</th>
<th>Gas Flow (l.min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Drying (Ramp)</td>
<td>75</td>
<td>5.0</td>
<td>3.0</td>
</tr>
<tr>
<td>2</td>
<td>Drying (Ramp)</td>
<td>90</td>
<td>5.0</td>
<td>3.0</td>
</tr>
<tr>
<td>3</td>
<td>Drying (Ramp)</td>
<td>120</td>
<td>10</td>
<td>3.0</td>
</tr>
<tr>
<td>4</td>
<td>Drying (HOLD)</td>
<td>120</td>
<td>15</td>
<td>3.0</td>
</tr>
<tr>
<td>5</td>
<td>Ashing (Ramp)</td>
<td>300*</td>
<td>5.0</td>
<td>3.0</td>
</tr>
<tr>
<td>6</td>
<td>Ashing (HOLD)</td>
<td>300*</td>
<td>20</td>
<td>3.0</td>
</tr>
<tr>
<td>7</td>
<td>Atomize (Ramp)</td>
<td>2300*</td>
<td>1.2</td>
<td>0.0</td>
</tr>
<tr>
<td>8</td>
<td>Atomize (HOLD)</td>
<td>2300*</td>
<td>2.0</td>
<td>0.0</td>
</tr>
<tr>
<td>9</td>
<td>Clean out</td>
<td>2400</td>
<td>2.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>

* The temperatures for the ashing and atomization steps used here are the literature reference values for As [4]. The optimization strategy for the ashing and atomization temperatures are given in section 4.3.
Table 4.2. Graphite furnace operating parameters for the determination of Pb.

<table>
<thead>
<tr>
<th>Step Number</th>
<th>Stage</th>
<th>Temperature (°C)</th>
<th>Time (seconds)</th>
<th>Gas Flow (l.min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Drying (Ramp)</td>
<td>75</td>
<td>5.0</td>
<td>3.0</td>
</tr>
<tr>
<td>2</td>
<td>Drying (Ramp)</td>
<td>90</td>
<td>5.0</td>
<td>3.0</td>
</tr>
<tr>
<td>3</td>
<td>Drying (Ramp)</td>
<td>120</td>
<td>10</td>
<td>3.0</td>
</tr>
<tr>
<td>4</td>
<td>Drying (HOLD)</td>
<td>120</td>
<td>15</td>
<td>3.0</td>
</tr>
<tr>
<td>5</td>
<td>Ashing (Ramp)</td>
<td>400*</td>
<td>5.0</td>
<td>3.0</td>
</tr>
<tr>
<td>6</td>
<td>Ashing (HOLD)</td>
<td>400*</td>
<td>20</td>
<td>3.0</td>
</tr>
<tr>
<td>7</td>
<td>Atomize (Ramp)</td>
<td>2000*</td>
<td>1.2</td>
<td>0.0</td>
</tr>
<tr>
<td>8</td>
<td>Atomize (HOLD)</td>
<td>2000*</td>
<td>2.0</td>
<td>0.0</td>
</tr>
<tr>
<td>9</td>
<td>Clean out</td>
<td>2200</td>
<td>2.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>

*The temperatures for the ashing and atomization steps used here are the literature reference values for Pb [4]. The optimization strategy for the ashing and atomization temperatures are given in section 4.3.

### 4.2.4 Experimental method

In order to evaluate the analytical performances of the permanent modifiers compared to those of selected conventional chemical modifiers, namely Ni(NO₃)₂, Mg(NO₃)₂ and Pd(NO₃)₂, the experimental conditions for each determination had to be kept identical in every respect so that direct comparisons could be made. This meant that precision was of utmost importance, and every day the experiments had to be carried out in exactly the same way as the previous day.
The experimental procedure followed for Pb and As differed slightly in that different instrumental conditions had to be used, so the two determinations will be dealt with separately. In brief, the experimental method common to both Pb and As will be outlined.

- The blank values of Pb and As in the deionized water and the acid solutions were determined and were found to be negligible, ruling out possible interferences from these.
- The optimum ashing and atomization temperatures for Pb and As in all three (3) matrices using pyrolytic coated graphite tubes without chemical modifiers were determined, whereafter the characteristic masses and analytical precision were determined for both analytes.
- The optimum ashing and atomization temperatures for Pb and As in all three (3) matrices were determined for each of the chemical modifiers (Ni, Mg, Pd) and the characteristic masses and analytical precision were determined for both analytes.
- The optimum ashing and atomization temperatures for Pb and As in all three (3) matrices were determined for all the permanent modifiers (W, Ir, Rh) and the characteristic masses and analytical precision were determined for both analytes.
- The optimum ashing and atomization temperatures for Pb and As were determined in all three (3) matrices for the "mixed" permanent modifiers (Ir/Rh, Rh/Ir) and the characteristic masses and analytical precision were determined for both analytes.
- The tube lifetime studies of the conventional chemical modifiers and the permanent modifiers were carried out for both analytes.
- The ashing curves and atomization curves for Pb and As in all three matrices using all the different types of modifiers were plotted graphically in order to determine the optimum ashing and atomization temperatures. The graphs are given in Appendix 1. Tabulated
values of maximum ashing and atomization temperatures are given under section 4.3.

The Ir/Rh and Rh/Ir notation denotes the two different methods used to prepare the mixed permanent modifiers. Ir/Rh denotes the case where first Ir was sputtered onto the graphite tube, followed by Rh, and Rh/Ir denotes the case where Rh was sputtered first and Ir afterwards.

The aim of the mixed permanent modifiers are to see if any advantages are gained by the use of a mixed noble metal permanent modifier over the single noble metal permanent modifiers. This is analogous to the use of conventional multi-element chemical modifiers.

4.3 Results

4.3.1 Characteristic masses and analytical precision for As and Pb

The tables which follow give the detection limits (expressed as characteristic masses) and analytical precision for the determinations of As and Pb in the different matrices using various chemical modifiers.

PCG in the tables represents determinations carried out on pyrolytic coated graphite tubes without the use of chemical modifiers.
Table 4.3. Characteristic masses (ng) of As in three different matrices using various chemical modifiers

<table>
<thead>
<tr>
<th>MODIFIER</th>
<th>PCG</th>
<th>Ni</th>
<th>Pd</th>
<th>Mg</th>
<th>W</th>
<th>Rh</th>
<th>Ir</th>
<th>Ir/Rh</th>
<th>Rh/Ir</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride Matrix</td>
<td>0.30</td>
<td>0.18</td>
<td>0.12</td>
<td>0.32</td>
<td>0.32</td>
<td>0.14</td>
<td>0.08</td>
<td>0.15</td>
<td>0.09</td>
</tr>
<tr>
<td>Nitrate Matrix</td>
<td>0.16</td>
<td>0.08</td>
<td>0.10</td>
<td>0.16</td>
<td>0.20</td>
<td>0.10</td>
<td>0.08</td>
<td>0.12</td>
<td>0.08</td>
</tr>
<tr>
<td>Sulphate Matrix</td>
<td>0.10</td>
<td>0.08</td>
<td>0.04</td>
<td>0.12</td>
<td>0.12</td>
<td>0.10</td>
<td>0.10</td>
<td>0.11</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Table 4.4. Analytical precision (%RSD) of the methods for the determination of As in three different matrices using various chemical modifiers

<table>
<thead>
<tr>
<th>MODIFIER</th>
<th>PCG</th>
<th>Ni</th>
<th>Pd</th>
<th>Mg</th>
<th>W</th>
<th>Rh</th>
<th>Ir</th>
<th>Ir/Rh</th>
<th>Rh/Ir</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride Matrix</td>
<td>7.5</td>
<td>4.5</td>
<td>3</td>
<td>8</td>
<td>8</td>
<td>3.5</td>
<td>2</td>
<td>4</td>
<td>2.5</td>
</tr>
<tr>
<td>Nitrate Matrix</td>
<td>4</td>
<td>2</td>
<td>2.5</td>
<td>4</td>
<td>5</td>
<td>2.5</td>
<td>2</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Sulphate Matrix</td>
<td>2.5</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>2.5</td>
<td>2.5</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>
Table 4.5. Characteristic masses (pg) of Pb in three different matrices using various chemical modifiers

<table>
<thead>
<tr>
<th>MODIFIER</th>
<th>PCG</th>
<th>Ni</th>
<th>Pd</th>
<th>Mg</th>
<th>W</th>
<th>Rh</th>
<th>Ir</th>
<th>Ir/Rh</th>
<th>Rh/Ir</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride Matrix</td>
<td>40</td>
<td>13</td>
<td>11</td>
<td>12</td>
<td>16</td>
<td>10</td>
<td>8</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>Nitrate Matrix</td>
<td>24</td>
<td>12</td>
<td>10</td>
<td>11</td>
<td>13</td>
<td>9</td>
<td>7</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Sulphate Matrix</td>
<td>18</td>
<td>14</td>
<td>10</td>
<td>11</td>
<td>11</td>
<td>8</td>
<td>8</td>
<td>9</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 4.6. Analytical precision (%RSD) of the methods for the determination of Pb in different matrices using various chemical modifiers

<table>
<thead>
<tr>
<th>MODIFIER</th>
<th>PCG</th>
<th>Ni</th>
<th>Pd</th>
<th>Mg</th>
<th>W</th>
<th>Rh</th>
<th>Ir</th>
<th>Ir/Rh</th>
<th>Rh/Ir</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride Matrix</td>
<td>5</td>
<td>1.6</td>
<td>1.7</td>
<td>1.6</td>
<td>2.8</td>
<td>1.5</td>
<td>1.5</td>
<td>2.5</td>
<td>1.8</td>
</tr>
<tr>
<td>Nitrate Matrix</td>
<td>3</td>
<td>1.7</td>
<td>1.5</td>
<td>1.4</td>
<td>2.6</td>
<td>1.6</td>
<td>1.4</td>
<td>1.7</td>
<td>1.4</td>
</tr>
<tr>
<td>Sulphate Matrix</td>
<td>2.5</td>
<td>1.8</td>
<td>1.6</td>
<td>1.4</td>
<td>2.5</td>
<td>1.5</td>
<td>1.2</td>
<td>1.7</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Nickel, magnesium and palladium chemical modifiers were used in ten (10) times molar excess to the arsenic and lead.

Tungsten, rhodium and iridium were present as permanent modifiers in the form of sputtered deposits of approximately 10 mg on the inside of the graphite tubes.

The mixed permanent modifiers were present on the graphite tube as a total of 10 mg, 5 mg of the one modifier being sputtered first, followed by 5 mg of the other permanent modifier.

Chloride, nitrate and sulphate matrices were present as 1% in the arsenic and lead working solutions.

The injection volume used was 20μl for all samples and chemical modifiers in solution.

100 ng.m⁻¹ As and 20 ng.m⁻¹ Pb working solutions were used throughout for the determination of the detection limits and precision.

The detection limit is defined as the concentration of an element that will produce an absorbance equal to twice the standard deviation of a series of replicate measurements (at least 10) of a solution, the concentration of which is distinctly detectable above the baseline [4]. The characteristic mass is expressed as a mass, taking the concentration obtained multiplied by the volume used for the determinations.

The percentage relative standard deviation (%RSD) is an indication of the precision, the measure of agreement among replicate measurements and was calculated as follows:

\[
% \text{RSD} = \frac{\text{Standard deviation}}{\text{Mean of replicate measurements}} \times 100
\]
Twenty (20) replicate measurements were made for the determinations of the characteristic masses and the analytical precision in each case.

4.3.2 Optimum ashing temperatures for As.

The literature value of 300 °C [4] for the maximum ashing temperature for As was taken as a guideline temperature for the investigation of the optimum temperature for ashing. The method involved starting with an ashing temperature of 120 °C and increasing this in increments of 50 °C until a temperature is reached where a decrease in the absorbance signal is observed. The temperature prior to the decrease in the absorbance signal, is taken as the optimum ashing temperature.

Table 4.7. Optimum ashing temperatures (in °C) for As in three matrices using various modifiers. (Values extracted from Appendix 1.)

<table>
<thead>
<tr>
<th>MODIFIER</th>
<th>PCG</th>
<th>Ni</th>
<th>Pd</th>
<th>Mg</th>
<th>W</th>
<th>Rh</th>
<th>Ir</th>
<th>Ir/Rh</th>
<th>Rh/Ir</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride Matrix</td>
<td>250</td>
<td>300</td>
<td>400</td>
<td>250</td>
<td>350</td>
<td>250</td>
<td>300</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Nitrate Matrix</td>
<td>300</td>
<td>350</td>
<td>350</td>
<td>300</td>
<td>300</td>
<td>250</td>
<td>350</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Sulphate Matrix</td>
<td>200</td>
<td>200</td>
<td>300</td>
<td>300</td>
<td>350</td>
<td>300</td>
<td>400</td>
<td>350</td>
<td>400</td>
</tr>
</tbody>
</table>
4.3.3 Optimum atomization temperatures for As

The literature value of 2300 °C [4] for the atomization temperature of As was taken as a guideline temperature for the investigation of the optimum atomization temperature. The method followed for the determination of the optimum atomization temperature differs from that of the ashing temperature in that the optimum atomization temperature is taken as the lowest temperature giving the maximum absorbance signal. The atomization temperature was varied in 100 °C increments. This method ensures that excessively high temperatures are not used, which will only serve to reduce the lifetime of the tube, decrease the analytical precision and waste energy.

Table 4.8. Optimum atomization temperatures (in °C) for As in three matrices using various modifiers. (Values extracted from Appendix 1.)

<table>
<thead>
<tr>
<th>MODIFIER</th>
<th>PCG</th>
<th>Ni</th>
<th>Pd</th>
<th>Mg</th>
<th>W</th>
<th>Rh</th>
<th>Ir</th>
<th>Ir/Rh</th>
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<td>2100</td>
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</tr>
<tr>
<td>Nitrate Matrix</td>
<td>2200</td>
<td>2100</td>
<td>2100</td>
<td>2100</td>
<td>2200</td>
<td>2200</td>
<td>2200</td>
<td>2200</td>
<td>2200</td>
</tr>
<tr>
<td>Sulphate Matrix</td>
<td>2100</td>
<td>2100</td>
<td>2200</td>
<td>2200</td>
<td>2100</td>
<td>2200</td>
<td>2000</td>
<td>2200</td>
<td>2100</td>
</tr>
</tbody>
</table>

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4.3.4 Optimum ashing temperatures for Pb

The same procedure is followed as in the case of As and the literature value for Pb of 400 °C [4] is used as a guideline in the investigation of the optimum ashing temperature. A starting ashing temperature of 150 °C was used, increasing in 50 °C increments. The highest temperature giving the greatest signal is taken as the maximum ashing temperature.

Table 4.9. Optimum ashing temperatures (in °C) for Pb in three matrices using various modifiers. (Values extracted from Appendix 1.)

<table>
<thead>
<tr>
<th>MODIFIER</th>
<th>PCG*</th>
<th>Ni</th>
<th>Pd</th>
<th>Mg</th>
<th>W</th>
<th>Rh</th>
<th>Ir</th>
<th>Ir/Rh</th>
<th>Rh/Ir</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride Matrix</td>
<td>400</td>
<td>500</td>
<td>400</td>
<td>300</td>
<td>400</td>
<td>500</td>
<td>500</td>
<td>600</td>
<td>500</td>
</tr>
<tr>
<td>Nitrate Matrix</td>
<td>300</td>
<td>400</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>Sulphate Matrix</td>
<td>300</td>
<td>400</td>
<td>400</td>
<td>400</td>
<td>400</td>
<td>500</td>
<td>400</td>
<td>600</td>
<td>500</td>
</tr>
</tbody>
</table>

4.3.5 Optimum atomization temperatures for Pb

The same procedure is followed as in the case of As and the literature value for Pb of 2000 °C [4] is used as a guideline in the investigation of the optimum atomization temperature. The lowest temperature giving the greatest signal is taken as the optimum atomization temperature.
Table 4.10. Optimum atomization temperatures (in °C) for Pb in three matrices using various modifiers. (Values extracted from Appendix 1.)

<table>
<thead>
<tr>
<th>MODIFIER</th>
<th>PCG*</th>
<th>Ni</th>
<th>Pd</th>
<th>Mg</th>
<th>W</th>
<th>Rh</th>
<th>Ir</th>
<th>Ir/Rh</th>
<th>Rh/Ir</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride Matrix</td>
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<td>1900</td>
<td>1800</td>
<td>2000</td>
<td>1800</td>
<td>1800</td>
<td>1900</td>
<td>1800</td>
<td>1800</td>
</tr>
<tr>
<td>Nitrate Matrix</td>
<td>1900</td>
<td>1800</td>
<td>1900</td>
<td>2000</td>
<td>1800</td>
<td>1800</td>
<td>1900</td>
<td>1900</td>
<td>1800</td>
</tr>
<tr>
<td>Sulphate Matrix</td>
<td>1900</td>
<td>1900</td>
<td>1900</td>
<td>1800</td>
<td>1800</td>
<td>1800</td>
<td>1900</td>
<td>1800</td>
<td>1800</td>
</tr>
</tbody>
</table>

4.3.6 Tube lifetime studies

The analytical lifetimes of the graphite tubes when different modifiers were employed was the next topic of investigation. A sulphate matrix was chosen for the analytical lifetime studies of As and a nitrate matrix was chosen for the analytical lifetime studies of Pb.

It is believed that the analytical lifetimes will improve when using the permanent modifiers as was reported in the literature [2, 5]. The discussion of the analytical lifetimes is given in section 4.4. The graphite tubes were put through 600 atomization cycles (firings) each. The poor performances of some of the modifiers under investigation can be seen in the case where the absorbance values decreased after only a few firings. The modifiers that showed the best performances are those which maintained high, or relatively constant absorbance values for many hundreds of atomization cycles. Figures 4.1 and 4.2 show the results of the analytical lifetimes of the graphite tubes for As in a sulphate matrix and Pb in a nitrate matrix, respectively, using various modifiers.
Figure 4.1. Analytical lifetimes of graphite tubes using various modifiers for As in 1% sulphate matrix

Figure 4.2. Analytical lifetimes of graphite tubes using various modifiers for Pb in 1% nitrate matrix
4.4 Discussion

Each analytical performance parameter under investigation will be discussed for As and Pb in turn, and the performances of the permanent modifiers will be compared to the conventional modifiers.

4.4.1 Characteristic masses for As. (Table 4.3)

In the investigation of As, the permanent modifiers Ir and Rh/Ir show improved characteristic masses compared to those of the conventional modifiers in a chloride matrix. This can be explained by the fact that chlorides are normally quite volatile, but the permanent modifiers in this case seem to decrease the volatility of the chloride species, giving an improved signal.

In the nitrate matrix, the characteristic masses of the permanent modifiers, Ir and Rh/Ir, are comparable to that of the conventional Ni and Pd modifiers, but no noteworthy improvements in characteristic masses are seen. This is possibly due to the fact that the nitrate matrix is normally easily ashed, even when using basic chemical modifiers.

In a sulphate matrix, the permanent modifiers show no noticeable improvements over the conventional modifiers and in most cases, show poorer characteristic masses than the conventional Ni and Pd chemical modifiers.

4.4.2 Characteristic masses for Pb. (Table 4.5)

For the determination of Pb, in the chloride matrix, all the permanent modifiers, excepting W, give
lower characteristic masses than that of the conventional modifiers. This shows the effectiveness of the permanent modifiers in retaining the Pb so that it does not volatilise at lower temperatures.

The same trend is seen in the case of the nitrate and sulphate matrices. Thus, for the determination of Pb, the permanent modifiers Ir, Rh, Rh/Ir and Ir/Rh show an improvement over the conventional modifiers in all the matrices with respect to characteristic masses.

4.4.3 Analytical precision for the determination of As. (Table 4.4)

It can be seen that Ir and Rh/Ir give the best analytical precision in the chloride matrix, possibly due to the volatile chloride species, which are now modified so that volatilisation takes place at higher temperatures. The effectiveness of the permanent modifiers are comparable to the reproducibility of the conventional modifiers in the nitrate matrix, and no noticeable improvements are seen. In the case of the sulphate matrix, the permanent modifiers have poorer analytical precision than the conventional modifiers.

4.4.4 Analytical precision for the determination of Pb. (Table 4.6)

The W, Ir/Rh and Rh/Ir permanent modifiers in the chloride matrix show poorer reproducibility than that of the conventional chemical modifiers. Here, the permanent modifiers may be less effective in the case of lead than in the case of arsenic.

Besides these three cases in the chloride matrix, the permanent modifiers show improvements over the conventional modifiers in all the matrices with respect to analytical precision.
4.4.5 Optimum ashing temperatures for As. (Table 4.7)

In the chloride matrix, it is noted that the Pd conventional modifier gave the highest ashing temperature. The ashing temperatures in the chloride matrix for the other permanent modifiers are comparable to that obtained in the case of Ni and better than that of Mg.

In the nitrate matrix, the Ir permanent modifier has comparable ashing temperatures to that of Ni and Pd, but no improvements in ashing temperatures are seen. The ashing temperatures for the Rh/Ir and Ir/Rh permanent modifier are comparable to those of Mg and W.

In the case of the sulphate matrix, the Ir and Rh/Ir permanent modifiers are seen to have the highest ashing temperatures. The ashing temperatures of the Ir/Rh and W permanent modifiers are seen to be higher than that of the conventional modifiers. In the case of Rh, the ashing temperatures are comparable to Pd and Mg and better than that of Ni.

4.4.6 Optimum ashing temperatures for Pb. (Table 4.9)

In the chloride matrix, it is seen that the Ir/Rh permanent modifier has the highest ashing temperature. Rh, Ir and Rh/Ir permanent modifiers have similar ashing temperatures to that of Ni and higher than that of Pd and Mg.

In the nitrate matrix, all the permanent modifiers have the same maximum ashing temperatures as those of Pd and Mg, and better than that of Ni. No improvements in the maximum ashing temperatures in a nitrate matrix are seen when permanent modifiers are used.
In the sulphate matrix, the Ir/Rh permanent modifier shows the highest maximum ashing temperature. Rh and Rh/Ir show ashing temperatures higher than that of Ni, Pd and Mg. The Ir permanent modifier has a maximum ashing temperature comparable to that of the conventional modifiers.

4.4.7 Optimum atomization temperatures for As. (Table 4.8)

In the chloride matrix, it can be seen that all the permanent modifiers, excepting W, have atomization temperatures higher than that of the Pd modifier, with no improvements in atomization temperatures seen.

In the nitrate matrix, all the permanent modifiers show higher atomization temperatures than any of the other conventional modifiers, and no improvements are seen when permanent modifiers are used.

In the case of the sulphate matrix, the Ir permanent modifier is seen to have the lowest atomization temperature. The Rh/Ir and W permanent modifiers have atomization temperatures comparable to that of Ni, and Rh and Ir/Rh show atomization temperatures which are comparable to that of Pd and Mg.

Thus, the only improvement in atomization temperature is seen in the case of the sulphate matrix when the Ir permanent modifier is used.
4.4.8 Optimum atomization temperatures for Pb. (Table 4.10)

In the chloride matrix, the W, Rh, Ir/Rh and Rh/Ir permanent modifiers have atomization temperatures comparable to those of Pd. The Ir permanent modifier has an atomization temperature comparable to the case of the Ni modifier and the case of PCG, where no modifiers are used. Thus, no improvements in atomization temperatures are seen.

In the nitrate matrix, W, Rh and Rh/Ir permanent modifiers show atomization temperatures comparable to the case of the Ni modifier. The atomization temperatures for Ir and Ir/Rh are comparable to those of Pd and PCG. Again, no improvements are noted.

In the sulphate matrix, W, Rh Rh/Ir and Ir/Rh show atomization temperatures equal to those of Mg. The atomization temperature for Ir is comparable to those of Ni and Pd, but no improvements in atomization temperatures are seen.

4.4.9 Analytical lifetimes of graphite tubes

The two cases of As in a 1% sulphate matrix and Pb in a 1% nitrate matrix will be dealt with separately.

4.4.9.1 Tube lifetimes for As in a sulphate matrix (Figure 4.1)

It can be seen that the absorbance values in the case of PCG, where no modifiers are used, decreases from the onset and the PCG only lasts about 100 firings. The same is true for the cases
of the W permanent modifier and for the conventional Pd modifier added for each firing, except that these last longer, about 200 firings, before a drastic decrease in absorbance is seen.

Looking at the cases of Ir, Rh/Ir, Rh and Ir/Rh, one can see that the absorbance signal only decreases slightly, even at the end of 600 firings. This means that the permanent modifier coating stays intact for at least 600 firings before a decrease in absorbance is seen. One can also note that Ir and Rh/Ir give very high absorbance readings, compared to the slightly lower readings of the Rh and Ir/Rh cases. The conventional Pd modifier is shown to give a similar absorbance reading to that of the Ir and Rh/Ir permanent modifiers up to about 100 firings, but the signal decreases rapidly thereafter, implying that new tubes will have to be employed frequently if the same absorbance signal is required. Thus, the absorbance signal is increased in the case of the permanent modifiers and the analytical lifetimes of the graphite tubes are greatly extended, in comparison to PCG and the conventional Pd modifier.

4.4.9.2 Tube lifetimes for Pb in a nitrate matrix (Figure 4.2)

As in the case of As, it can be seen that the absorbance signal in the case of PCG decreases after about 100 firings. The tube employing the conventional Pd modifier, added for each firing, lasts about 150 firings in this case before a decrease in absorbance is noted. The W permanent modifier also lasts about 150 firings before displaying a decrease in absorbance. A more pronounced, earlier decrease in the absorbance signal is noted in the case of the other permanent modifiers compared to that of As in a sulphate matrix. For the Rh and Ir/Rh permanent modifiers, a decrease is seen after 350 firings. In the case if Ir and Rh/Ir, the decrease in absorbance is seen after 400 firings. This might be due to the effect of the nitrate matrix being more corrosive than
the sulphate matrix on the metal coatings, causing erosion or destruction of the layer, leading to
the noted decrease in absorbance signals.

Although the determinations for Pb in the nitrate matrix do not show such a drastic improvement
in analytical lifetimes as is the case of As, there is still, nevertheless, a marked improvement in the
analytical lifetimes of the tubes using the permanent modifiers.

4.5 Conclusions

Taking all the results into account and considering the discussions on the performances of the
permanent modifiers, one can clearly see that the permanent modifiers do offer certain
improvements over the conventional modifiers in specific matrices for a specific element. This
implies that the permanent modifiers do not appear to be as universal as was expected and have
specific noteworthy advantages only in certain cases.

The permanent modifiers show promise with respect to improved characteristic masses and
analytical precision over those of the conventional chemical modifiers and can be taken into
account when trace analyses are required.

The permanent modifiers showed drastic improvements in the analytical lifetimes of the graphite
tubes, making the use of the permanent modifiers worthwhile for routine analyses, where fewer
tubes will have to be employed to carry out analyses.
Thus, on the basis of the improved characteristic masses noted in several cases, better analytical precision, several improved ashing temperatures, and drastically improved analytical lifetimes, the use of the permanent modifiers should be taken into consideration for the analysis of Pb and As.
4.6 References


CHAPTER 5

FINAL CONCLUSIONS

The problem of interferences is one of the most serious in the technique of ETA-AAS. One of the methods employed to overcome this problem is to use matrix modifiers. Unfortunately, the use of the chemical modifiers led to other problems. Thus, the need for an improved chemical modifier became apparent. The permanent modifiers seemed to be the most promising prospect. In order to produce and test the new modifier, a process which could produce a thin layer of a specific metal on the inside of graphite tubes was required. This process, called glow discharge sputtering, was already in use for other applications and could be utilised for the purposes of the project, as was already shown by previous researchers.

The aims of the project were as follows: 1) To investigate the characteristics of the low pressure argon glow discharge for the production of permanent modifiers. 2) To investigate and optimise the parameters having an influence on the sputtering process occurring in the glow discharge. 3) To produce thin metallic coatings of iridium, rhodium, tungsten as well as mixtures of these, on the inside of graphite tubes. 4) To test the analytical characteristics of the prepared permanent modifiers. 5) To compare the obtained results with those obtained with the conventional modifiers.

It was found that these permanent modifiers proved to be homogeneous on the graphite surface and had lifetimes which spanned the normal useful lifetimes of the graphite tubes and most of
these coatings generally greatly improved the analytical lifetimes of the graphite tubes. The analytical performance parameters usually associated with ETA-AAS analyses, such as the detection limits, the analytical precision and the lifetimes of the graphite tubes were determined.

The analytical lifetimes of the graphite tubes coated with the permanent modifiers by the sputtering process, showed vast improvements over those of conventional pyrolytic coated graphite tubes for the cases where conventional chemical modifiers are used. In contrast, improvements noted for the permanent modifiers with respect to the atomization temperatures were not as drastic and noteworthy as those of the maximum ashing temperatures of the permanent modifiers. Improvements with respect to maximum ashing temperatures were seen to be largely dependent on the matrix employed and to some extent on the analyte element. It must be noted, however, that the permanent modifiers do show improvements with respect to maximum ashing temperatures for most of the matrices employed.

The permanent modifiers also showed great promise in the improvement of the analytical precision of analyses, as can be seen from the results of the determination of precision, where almost all the permanent modifiers displayed superior analytical precision compared to those of the conventional chemical modifiers used.

Another vast improvement seen with the use of the permanent modifiers is seen for the case of the detection limits (characteristic masses). The detection limits obtained for the permanent modifiers showed somewhat improved detection limits when compared to most of the conventional chemical modifiers.
More work and further investigations must be carried out into the utilisation of the mixed permanent modifiers. In some cases these “mixed” permanent modifiers displayed improved characteristics over those of the “single” permanent modifiers, and in other cases their performances were poorer than those of the conventional chemical modifiers.

The absolute masses of the permanent modifiers sputtered onto the tubes are important owing to the fact that the noble metals are very expensive and any savings that could be made without compromising the performance of the modifiers, should be taken into consideration. This could also be extended to include the ratio in which the metals are sputtered onto the graphite tube. In this study, the metals were sputtered in approximately the ratio 1:1, but if the ratios were varied, one could possibly improve on some of the aspects of the mixed permanent modifiers.

An interesting future project which might prove fruitful, could include the use of perhaps platinum and/or palladium, owing to the previous successes with the use of palladium and platinum as conventional chemical modifiers. If one or both of these are sputtered onto the graphite tubes, one would expect the permanent modifier in the form of solid palladium or platinum to act in much the same way as the conventional palladium or platinum chemical modifiers and perhaps improve on the performances of these conventional modifiers.

This project opens many doors and poses many questions on the use and feasibility of the permanent chemical modifiers and some work must still be carried out to elucidate the best possible permanent modifier.
Appendix 1

1.1 Ashing and atomization curves for arsenic

Figure 1.1.1 Optimization of ashing temperatures for arsenic without the use of a chemical modifier.

Figure 1.1.2 Optimization of atomization temperatures for arsenic without the use of a chemical modifier.
Figure 1.1.3 Optimization of ashing temperatures for arsenic using nickel as chemical modifier.

Figure 1.1.4 Optimization of atomization temperatures for arsenic using nickel as chemical modifier.
Figure 1.1.5 Optimization of ashing temperatures for arsenic using magnesium as chemical modifier.

Figure 1.1.6 Optimization of atomization temperatures for arsenic using magnesium as chemical modifier.
Figure 1.1.7 Optimization of ashing temperatures for arsenic using palladium as chemical modifier.

Figure 1.1.8 Optimization of atomization temperatures for arsenic using palladium as chemical modifier.
**Figure 1.1.9** Optimization of ashing temperatures for arsenic using a tungsten permanent modifier.

**Figure 1.1.10** Optimization of atomization temperatures for arsenic using a tungsten permanent modifier.
Figure 1.1.11 Optimization of ashing temperatures for arsenic using a rhodium permanent modifier.

Figure 1.1.12 Optimization of atomization temperatures for arsenic using a rhodium permanent modifier.
Figure 1.1.13 Optimization of ashing temperatures for arsenic using an iridium permanent modifier.

Figure 1.1.14 Optimization of atomization temperatures for arsenic using an iridium permanent modifier.
Figure 1.1.15 Optimization of ashing temperatures for arsenic using a mixed rhodium and iridium permanent modifier.

Figure 1.1.16 Optimization of atomization temperatures for arsenic using a mixed rhodium and iridium permanent modifier.
Figure 1.1.17 Optimization of ashing temperatures for arsenic using a mixed iridium and rhodium permanent modifier.

Figure 1.1.18 Optimization of atomization temperatures for arsenic using a mixed iridium and rhodium permanent modifier.
Figure 1.2.1 Optimization of ashing temperatures for lead without the use of a chemical modifier.

Figure 1.2.2 Optimization of atomization temperatures for lead without the use of chemical modifiers.
Figure 1.2.3  Optimization of ashing temperatures for lead using nickel as chemical modifier.

Figure 1.2.4  Optimization of atomization temperatures for lead using nickel as chemical modifier.
Figure 1.2.5 Optimization of ashing temperatures for lead using magnesium as chemical modifier.

Figure 1.2.6 Optimization of atomization temperatures for lead using magnesium as chemical modifier.
Figure 1.2.7 Optimization of ashing temperatures for lead using palladium as chemical modifier.

Figure 1.2.8 Optimization of atomization temperatures for lead using palladium as chemical modifier.
Figure 1.2.9 Optimization of ashing temperatures for lead using a tungsten permanent modifier.

Figure 1.2.10 Optimization of atomization temperatures for lead using a tungsten permanent modifier.
**Figure 1.2.11** Optimization of ashing temperatures for lead using a rhodium permanent modifier.

**Figure 1.2.12** Optimization of atomization temperatures for lead using a rhodium permanent modifier.
Figure 1.2.13  Optimization of ashing temperatures for lead using an iridium permanent modifier.

Figure 1.2.14  Optimization of atomization temperatures for lead using an iridium permanent modifier.
Figure 1.2.15 Optimization of ashing temperatures for lead using a mixed rhodium and iridium permanent modifier.

Figure 1.2.16 Optimization of atomization temperatures for lead using a mixed rhodium and iridium permanent modifier.
Figure 1.1.17 Optimization of ashing temperatures for lead using a mixed iridium and rhodium permanent modifier.

Figure 1.2.18 Optimization of atomization temperatures for lead using a mixed iridium and rhodium permanent modifier.