REACTIVE GASES IN ELECTROTHERMAL ATOMISATION ATOMIC ABSORPTION SPECTROMETRY

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ABSTRACT

Reactive Gases in Electrothermal Atomisation Atomic Absorption Spectrometry

by

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A variety of gases and vapours of organic compounds have been used as matrix modifiers in electrothermal atomic absorption spectroscopy (ETAAS). Oxidising gases such as air or nitrous-oxide, introduced during the charring stage, both thermally stabilised analytes such as lead, and improved the efficiency of pyrolysis by converting the normal charring into an ashing step. A number of interferences eg. magnesium chloride on lead determinations and non-specific absorbance interferences, decreased when air was introduced.

Hydrocarbon gases (< 5% v/v) introduced during charring improved sensitivity (up to 89%) for certain refractory analytes (eg. Al, Ca, Mg, Si and V), prolonged tube life and improved precision.

Introduction of hydrogen, just prior to atomisation, decreased non-specific absorbance interference produced by organic samples. Although a concomitant decrease in sensitivity of the analytes was observed, this was considerably less than for the background signal. When introduced during charring, hydrogen produced a slight improvement in sensitivity for some analytes (eg. Al and V). An attempt to decrease the interference of sodium chloride on lead determinations by removal of hydrogen chloride by volatilisation proved unsuccessful.

Organophosphorus vapours such as tri-ethyl phosphite were successfully used to thermally stabilise cadmium to temperatures comparable with those obtained by 'wet chemical' modifiers but without the accompanying contamination problems.

Halogenated compounds were unsuccessfully used to decrease the appearance temperature of some refractory analytes. Freon 23 (Tri-fluoromethane, 2% v/v) thermally stabilised cadmium to 750°C. The freon was successfully used in the clean stage to decrease memory effects.

An unsuccessful attempt was made to remove by volatilisation nickel contaminants as the carbonyl by the introduction of carbon monoxide. Leaching of nickel from the gas lines, prevented extended use of carbon monoxide.

Hydrogen sulphide (10% v/v) introduced during the drying stage both thermally stabilised mercury to 300°C, and improved the sensitivity of the analysis.

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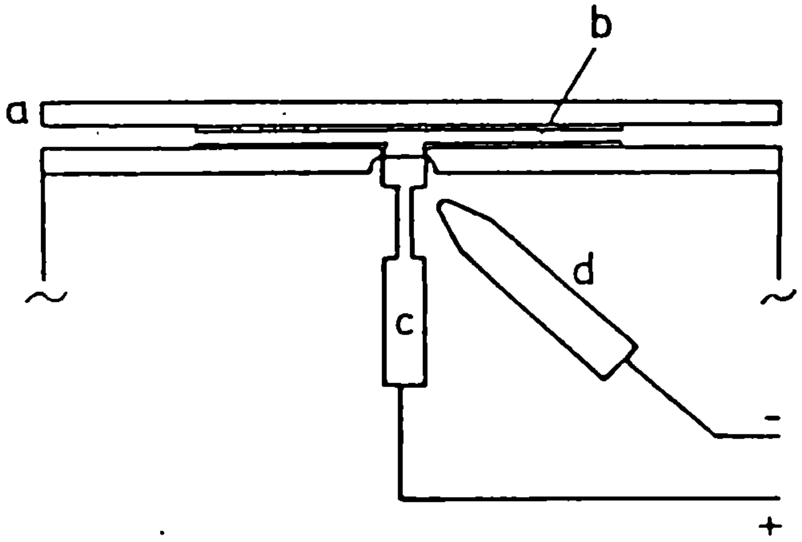
CHAPTER 1 - INTRODUCTION

1.1 Historical Development

The first worker to utilise a carbon furnace to study atomic emission spectra was King (1) (2). The apparatus in reference 1 was an arc-heated furnace which consisted of a carbon rod with a hole drilled longitudinally through it, held in a carbon block by an insulating asbestos pad at either end. A hole was drilled through the carbon block through which a carbon electrode could be inserted. Sample was placed within the furnace and the electrode was then raised until an arc formed with the furnace wall. Temperatures of up to 2200°C were obtained. The apparatus in (2) consisted of a carbon tube fitted within a brass cylinder and held by two supports. The tube was supplied with power via two upper leads. This was the first resistively heated carbon furnace. Although King used these pieces of apparatus to investigate the emission spectra of many elements, the technique was not used quantitatively for a further fifty years when L'Vov began to publish work on quantitative atomic absorption spectrometry (3).

L'Vov's apparatus was similar in design to King's arc heated furnace. It consisted of a carbon tube lined with tantalum foil to prevent diffusion of analyte vapour through the porous graphite, a carbon sample electrode, and an auxiliary electrode to arc with the sample electrode. The apparatus is shown schematically in Figure 1.1. The carbon furnace was heated resistively to the desired temperature and then



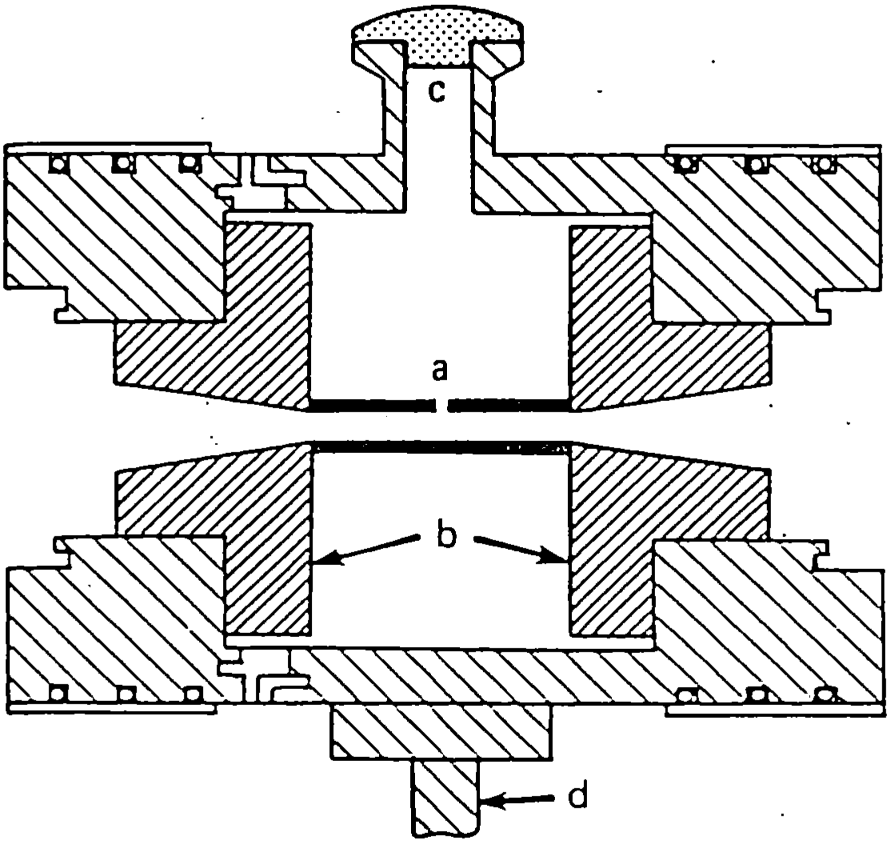
a. graphite tube
b. Tantalum liner
c. Sample electrode
d. auxiliary electrode

Fig. 1.1: The Arc Atomiser Designed by L'Vov.

as the sample electrode entered the furnace, a d.c. arc was struck between the sample and auxiliary electrodes. In a later design, L'Vov dispensed with the auxiliary electrode and simply heated the sample electrode resistively too.

In 1968 Massmann (4) designed an electrothermal atomiser that could be used for routine analyses with commercially available spectrometers. This was the first design (Fig. 1.2) into which liquid samples could be placed at ambient temperature and then raised via a temperature programme to atomisation. It consisted of a graphite tube with a small hole drilled through the wall at the centre. The tube was supported between two water cooled steel cones, and encased in a metal housing. The Massmann style furnace has become the most common commercial design due to its more rapid sample throughput, its size and its ease of operation. However, the detection limits obtained on such furnaces may be up to an order of magnitude poorer than those obtained from a L'Vov style furnace.

Other types of electrothermal atomiser have also been developed. The carbon filament atomiser described by West and Williams in 1969 (5) proved to be popular for a while, although very little work has been published more recently. Its advantages included the simplicity of its design, low power requirements and a fast heating rate. It did, however, suffer from severe interference effects caused by the rapid cooling of the atoms once they had left the



a. graphite tube
b. steel holders
c. sample inlet port
d. mounting holder

Fig. 1.2: The Massmann Style Atomiser.

graphite surface (6), and the poor precision associated with pipetting volumes of 5 μl.

The Woodriff style furnace (7), was similar in design to that of L'Vov. The furnace could be heated to temperatures of up to 3000°C before liquid samples were nebulised into it by a stream of argon via a side-arm. The furnace design was too large to fit into conventional spectrometers, and has therefore not received the acceptance of the Massmann style furnace.

The material used to manufacture the atomiser must satisfy some basic requirements (8). It must have:

i. good thermal and electrical conductivity;
ii. chemical inertness;
iii. very low levels of metallic impurities;
iv. low porosity;
v. good machinability;
vi. low thermal expansion and high rigidity;
vii. high melting point.

Although graphite satisfies many of these requirements other atomiser materials have been used. Donega and Burgess (9) developed an electrically heated tungsten or tantalum boat. This could reach temperatures of up to 2200°C using only 0.5 kW of power. However, since it was an enclosed system, the samples vaporised from the atomiser and condensed on the silica windows which made measurements difficult. Metal foils within graphite tube atomisers have been used by some workers (10). L'Vov discovered that of forty analytes tested, thirty two had improved sensitivity or decreased appearance temperature when a tantalum liner was used compared with an unlined graphite tube. Since metallic atomisers may be attacked by certain acids, and also become brittle and distorted after prolonged use at high temperatures, their use has been far less common than the graphite atomisers. Their main advantage over graphite tubes is that stable carbides cannot be formed with analytes such as molybdenum, silicon etc.

Since atomisation efficiency is far from optimal (11) it would seem likely that further modifications to furnace designs will occur.

1.2 Advantages and Disadvantages of Electrothermal Atomic Absorption Spectroscopy

Electrothermal atomic absorption spectroscopy (ETAAS) has several advantages over flame spectroscopy. An increase in sensitivity of typically 2-3 orders of magnitude is obtained for many analytes. The increase in sensitivity arises due to a combination of poor nebulisation efficiency, and the high velocity of the flame gases leading to a very short residence time of atoms within the analytical zone of the flame. In ETAAS, the atoms are confined within the tube for a considerably longer time, and hence increased sensitivity results. The increased sensitivity is obviously highly desirable for ultra-trace analyses since it negates the need for time-consuming pre-concentration techniques. Sample volumes of between 1-100 µl (typically 20-25 µl) may be used in ETAAS compared with a minimum of about 500 µl required for conventional flame AAS. This is obviously a considerable advantage if only a limited amount of sample is available. The capability of analysing solids directly removes contamination prone digestion steps and also decreases sample preparation time. However, the precision of such determinations is not particularly good, and accurate analytical balances are required to weigh the sample into specialised boats. Other less important advantages include in situ sample treatment, cheapness of operation and the ease of automation.

Electrothermal AAS does however suffer from several important disadvantages. Poor precision is a common problem especially when using manual pipetting. Precisions of typically 3-5% are obtained by manual injection, and of about 1% using an autosampler (8). This does not compare particularly favourably with the precisions obtained in flame AAS which are often below 1%. The time required for an analysis is also a disadvantage. A typical furnace cycle lasts 1-2 minutes compared with the 5-10 seconds required for flame analyses. However, recent work has substantially decreased the time required to obtain a result for a real sample (12, 13), where a programme lasting 45 seconds was used to analyse a slurry. The complicated temperature programmes required to achieve optimal performance require a degree of operator skill. The construction of ash/atomise plots may be necessary for all real samples since the volatility of the analyte may vary between matrices. Initially the process of analysis may therefore be operator intensive. Once optimum conditions have been determined, the process may be automated. Since samples may be very small and determination of analytes present in ng ml^{-1} levels are frequent, contamination may become a problem. This may be controlled by stringent use of ultra-pure chemicals, clean rooms, acid washed glass ware etc. The main disadvantage associated with ETAAS is that of interferences. Electrothermal AAS is generally acknowledged as being far more prone to interferences than is flame spectroscopy. There are several distinct types of interference that occur in ETAAS. These include memory effects, anion and cation interferences, condensation, carbide and nitride formation, non-specific absorption (smoke), and matrix interferences eg. loss of analyte as a volatile salt (6).

1.3 Overcoming Interferences in ETAAS

For many years ETAAS was plagued by interference problems. Several excellent guides to the literature governing interferences have been published (14-16). The most severe effects in graphite tube atomisers are normally observed in the Massmann-style furnaces. This is because the analyte often vaporises into an atmosphere with an insufficiently high temperature to promote complete atom formation (17).

Massmann-style furnaces have a temperature gradient throughout the tube, the ends being 200-300 degrees cooler than the middle and the atmosphere in the centre of the tube is cooler than that closer to the walls (18). This non-isothermality may result in losses of analyte by condensation on cooler tube parts, gas phase interference effects due to low vapour temperatures and memory effects. These effects may be ameliorated to some extent by isothermal operation ie. the atomisation of the sample into a hot environment. This may be achieved by the use of platforms (19) or probes (20) (21) to delay the vaporisation of the analyte from the graphite surface, or by capacitive heating (19). Another approach has been to use tubes heated from the sides (22). This decreases the temperature gradient along the tube, but so far has not gained wide popularity.

Other interference effects are more easily overcome. Refractory elements that form stable nitrides or carbides should be determined using argon as the inert purge gas, and either totally pyrolytic carbon tubes (TPC's), or pyro-coated tubes. Memory effects may frequently be diminished by the use of a clean stage at the end of a furnace cycle. Spectral interferences may be largely overcome by specialised background correction systems such as Zeeman effect and Smith-Hieftje. These are particularly useful when structured background is present, or if the matrix is involatile and hence a large background signal is obtained during atomisation.

Matrix modification was an expression first coined by Ediger in 1975 (23). It was a collective term for any chemical manipulation of the matrix that would either decrease the volatility of the analyte, (and hence allow more efficient ashing), or increase the volatility of the matrix. In that first paper, several matrix modifiers were investigated, the majority of which concentrated on the thermal stabilisation of the analyte. The use of ammonium nitrate to eliminate interferences by saline matrices via the reaction

$$NaCl + NH_4NO_3 \rightarrow NaNO_3 + NH_4Cl$$

was the major exception. Refractory chloride ions may be readily removed at 335°C as volatile ammonium chloride. This has without doubt, become the most common example of matrix modification by increasing matrix volatility. Since these preliminary results were published, a large number of matrix modifiers have been used. Table 1.1 shows several of them. Many papers use a combination of matrix modifiers. A mixture of palladium and magnesium nitrates has become a very popular matrix modifier for volatile analytes such as the metalloids (47). Other workers have mixed palladium and ascorbic acid, as a reducing agent (48). Various other mixtures of matrix modifiers of varying amounts of success have been reported.

The mechanisms of action of many of these modifiers are not

TABLE 1.1: EXAMPLES OF MATRIX MODIFIERS

Matrix Modifier	Analyte	Reference
$Al(NO_3)_3$	Be	24
$(NH_4)_2Cr_2O_7$	Bi	25
Citric Acid	Cd, Zn	26
$K_2Cr_2O_7$	Hg	27
	Al	28
La	Pb, Cd, Tl, Zn	29
	Pb	30
$Mg(NO_3)_2$	Cr, Ni, Co	31
	Be	32
Mo	Se	33
	Al	34
Oxalic Acid	Pb	35
Phosphoric Acid	various	36
Pd	Ge, Sb, As, Bi, Hg, Se, Te, Sn	37
	Mo, V	38
Pt	As, Se	39
Cu	Se	40
	Se	27
KI	Se	41
H_2SO_4	Tl	42
$(NH_4)_2HPO_4/NH_4H_2PO_4$	Pb, Cd, Zn	43
BaF_2	Mo	44
Alkali metal fluorides	Si	45
Ni	As	46

fully understood, although there has been a considerable amount of work recently that has thrown light on several. It is generally accepted that magnesium nitrate retains analytes by decomposing to magnesium oxide and trapping the analytes within its crystal matrix by occlusion (49). In addition to being a stabilising agent, magnesium nitrate has also been used as a dry ashing aid (49). It is believed that its mechanism of reaction is similar to that when it acts as a stabilising agent. Metalloids such as arsenic and selenium have been thermally stabilised by the addition of many transition elements, eg. nickel and palladium. This is due to the formation of involatile arsenides and selenides. This was confirmed by the use of x-ray photo electron spectroscopy which detected Pd-Se and Pd-As bonds (50). Other examples of matrix modifiers that thermally stabilise analytes by the formation of less volatile salts are the mono and dibasic forms of ammonium phosphate. It has been discovered that phosphate modifiers form thermally stable lead phosphate species, eg. $Pb_2P_2O_7$ (51). A different style of modifier is represented by carbide forming elements such as thorium, tantalum, molybdenum, zirconium and tungsten. These have been used to coat graphite tubes and occupy active sites, thereby preventing loss of sensitivity and increased memory effects by refractory analytes such as barium (52) (53), aluminium (34) and silicon (45), which also form stable carbides. The coating is achieved by soaking the graphite tubes in solutions of the modifier, eg. thorium nitrate, and then drying before use.

Another type of modifier has been developed recently. The very high temperatures required to atomise refractory analytes can take a serious toll on the state of the graphite tube. By increasing the volatility of these analytes, tube life-time may be extended. The use of barium fluoride (44) or alkali metal fluorides (45) have been reported to increase the volatility of analytes such as molybdenum and silicon.

Matrix modification has therefore become almost a prerequisite for the successful determination of many analytes in difficult matrices.

To obtain analytical results as free as possible from interferences, Slavin et al. (54) gathered together several recommendations under the collective title of the Stabilised Temperature Platform Furnace, or STPF concept. The recommendations of the STPF concept include (i) a platform to provide isothermal operation; (ii) a matrix modifier; (iii) an integrated absorbance signal rather than peak height measurements; (iv) a rapid heating rate during atomisation; (v) fast electronic circuits to follow the rapid transient furnace signals. The use of Zeeman effect background correction was also encouraged. Virtually all analyses undertaken by ETAAS nowadays includes some or all of the STPF concept recommendations in their protocols. As a result, interferences have been considerably reduced, and time-consuming extraction or precipitation procedures to extract the analyte from the matrix are now frequently unnecessary (49).

1.4 The Use of Gaseous Matrix Modifiers

The majority of matrix modifiers used over the last fifteen years have been 'wet chemical' modifiers, ie. they have to undergo a dissolution stage before they can be used. Successful matrix modifiers must meet a number of requirements (37). These include:

(i) applicability to as many analytes as possible;
(ii) availability in a high state of purity;
(iii) freedom from significant quantities of elements that may have to be determined in the future;
(iv) not reducing the lifetime of graphite tubes;
(v) not producing excessive background signals.

Wet chemical modifiers suffer from a few important disadvantages. They are frequently unavailable in a pure enough state, and must therefore be purified before they can be used. Purification of diammonium hydrogen phosphate has been achieved by APDC-$CHCl_3$ extraction (55) and of ammonium dihydrogen phosphate by passing a solution of it through a column of chelex 100 resin (56).

Modifiers containing metal ions, eg. nickel and copper, may contaminate the graphite tube and hence prevent its use for their analyses in the future. Other chemical modifiers have deleterious effects on the graphite tube. Examples include lanthanum and dichromate (37). Such disadvantages are obviously undesirable since they are either time consuming or result in large costs for extra tubes.

After preparation, the matrix modifier must still be added to the samples and standards. This also used to be a time consuming process but since the advent of programmable autosamplers this has become less of a problem. High non-specific background signals may also be encountered using wet chemical modifiers (34). In this particular example the tube had been coated with ammonium molybdate and several tube firings were required to eliminate the background signals.

The use of gaseous matrix modifiers should exhibit the same advantages proffered by the wet chemical modifiers, but not many of the concomitant disadvantages. Many modern commercial instruments provide an alternative gas inlet, and for those that do not, a simple switching system should enable an alternative gas to be used. A gaseous modifier may readily be used as an integral part of a furnace programme, and hence complex, time-consuming and contamination prone sample preparation procedures may be greatly reduced. In addition, gases are much less likely to contain metallic impurities and hence complex purification procedures are unnecessary.

1.5 Aims and Objectives

The aim of this work was to develop the use of gaseous matrix modifiers for ETAAS. Gases that decrease the volatility of the analyte, decrease background signals and increase the sensitivity of the analysis will all be investigated. Mechanistic aspects will also be examined for some of the gases to enable better understanding of the processes.

CHAPTER 2 - USE OF AIR IN THE ASHING STAGE

2.1 Introduction

Air or oxygen has been used by a number of workers as an ashing aid during the analysis of solid samples or samples that have a highly carbonaceous matrix. Examples of such matrices include the analysis of blood (57) serum (58), pine needle slurries (59), soil slurries (60), spinach slurries (61), coal slurries (62) and oil (63). The presence of air or oxygen in the ash stage leads to an oxidative decomposition process rather than the normal charring process that occurs in the presence of an inert gas. The result is much more efficient ashing, with the concomitant reduction in background signal and a reduction in the amount of carbonaceous residue left in the tube after each firing. In the absence of air or oxygen, the level of this residue gradually rises, and will eventually begin to obscure the light beam, resulting in a greatly increased background signal.

Recently there has been growing interest in the use of slurries as a means of introducing solids into a graphite furnace (59-62). This is because slurries are relatively simple to prepare, need no aggressive chemical pretreatment, and are thus less susceptible to contamination. The possibility of calibration using aqueous standards is also a major advantage. Due to the high matrix signals produced by such samples, air or oxygen ashing has become almost a pre-requisite where the matrix is predominantly organic.

In addition to being an ashing aid, oxygen has also been shown to exert a stabilising effect on volatile analytes such as lead (64, 65). Oxygen may therefore be classed as a gaseous matrix modifier because it both reduces matrix interferences, and stabilises some analytes.

2.2 Experimental

2.2.1 Reagents

High purity water was obtained by using reverse osmosis (Milli-RO 4, Millipore, Harrow, Middlesex, UK) followed by adsorption, de-ionisation and ultra-filtration (Millipore, Milli-Q system).

Nitric acid (S.G. 1.42) Pronalysar grade (May and Baker Ltd. Dagenham, UK) and hydrochloric acid (S.G. 1.18) AnalaR grade (BDH, Poole, Dorset, UK) were used. Stock standards (1000 $\mu g\ ml^{-1}$) of Co, Cr, Mn and Pb were made in the following manner:- Cobalt and iron metal powder (0.100 g) (BDH) was dissolved in the minimum of aqua regia, and diluted with water to 100 ml. Potassium dichromate (0.2829 g, BDH) was dissolved in water and made up to 100 ml. Manganese metal (0.100 g, BDH) was dissolved in HCl, and diluted to 100 ml using water. Lead nitrate (0.1598 g, BDH) was dissolved in water to a volume of 100 ml.

All stock standards were stored in acid washed polythene bottles. The working standards were prepared by serial dilution of these stock standards on a daily basis.

2.2.2 Instrumentation

An atomic absorption spectrometer (SP9, Philips Scientific, York Street, Cambridge) fitted with a video furnace programmer (PU 9095, Philips Scientific) was used. Additionally an alternative AA spectrometer (PU 9400, Philips Scientific) fitted with an electrothermal atomiser (PU 9390, Philips Scientific) was also used for repeat analyses of some certified reference materials slurries. The two furnaces differ in that the gas flow in the SP9 fills the entire furnace head, and only enters the graphite tube by diffusion, whereas in the PU 9390 the gas flows directly down the inside of the tube.

Pyrolytically coated tubes were used throughout. Both standards and slurries were introduced to the graphite furnace by micropipette (Gilson Medical Electronics, Villiers-le-Bel, France). All the work reported used conventional wall atomisation and gas stop mode. The slurries were agitated manually before pipetting.

2.3 Preliminary Experiments

2.3.1 Sample preparation

Approximately a 1% slurry of bovine liver (NIST SRM 1577, NIST, Washington, USA) was made by accurately weighing about 0.2 g of sample into a 30 ml capacity polypropylene bottle.

Zirconia beads (10 g) and de-ionised water (3 ml) were placed in the bottle, and the bottle shaken for 2 hours on a mechanical flask shaker (Gallenkamp, Loughborough, UK). After shaking the slurry was diluted to 20 ml by the addition of more water.

2.3.2 Results and Discussions

Initial experiments were performed in which investigations were made into the advantages of incorporating an air-ashing stage into the furnace cycle. Originally the temperature programme depicted in Table 2.1 was used to construct an ash curve for lead in the bovine liver slurry. However, the residual air present in the tube during atomisation very rapidly degenerated the graphite tube by oxidation to CO and CO_2 and, after as few as 4-5 firings, the tube snapped. It was therefore necessary to add a second ash stage during which the air could be flushed from the atomizer by inert nitrogen. The resulting temperature programme used for the ash plots is detailed in Table 2.2.

The ash plots obtained using varying amounts of air are shown in Fig. 2.1. It can be seen that as the amount of air bled into the inert gas flow increased, it was possible to ash at progressively higher and at lower temperatures than in the absence of air. The lower ash temperatures could be used because of the increased efficiency of pyrolysis eliminating non-specific absorbance interference (smoke). As yet, the mechanism whereby the air thermally stabilises

TABLE 2.1: FURNACE PROGRAMME INITIALLY USED FOR THE ASH PLOTS OF BOVINE LIVER SLURRY

Phase	Temp/°C	Hold time/s	Ramp/°C s^{-1}	Gas	Gas Flow /l min^{-1}
dry	110	40	10	N_2	3.5
ash	varied	20	50	N_2 + air	3.5
atomise	2200	3	*FP	gas stop	0
clean	2500	4	*FP	N_2	3.5

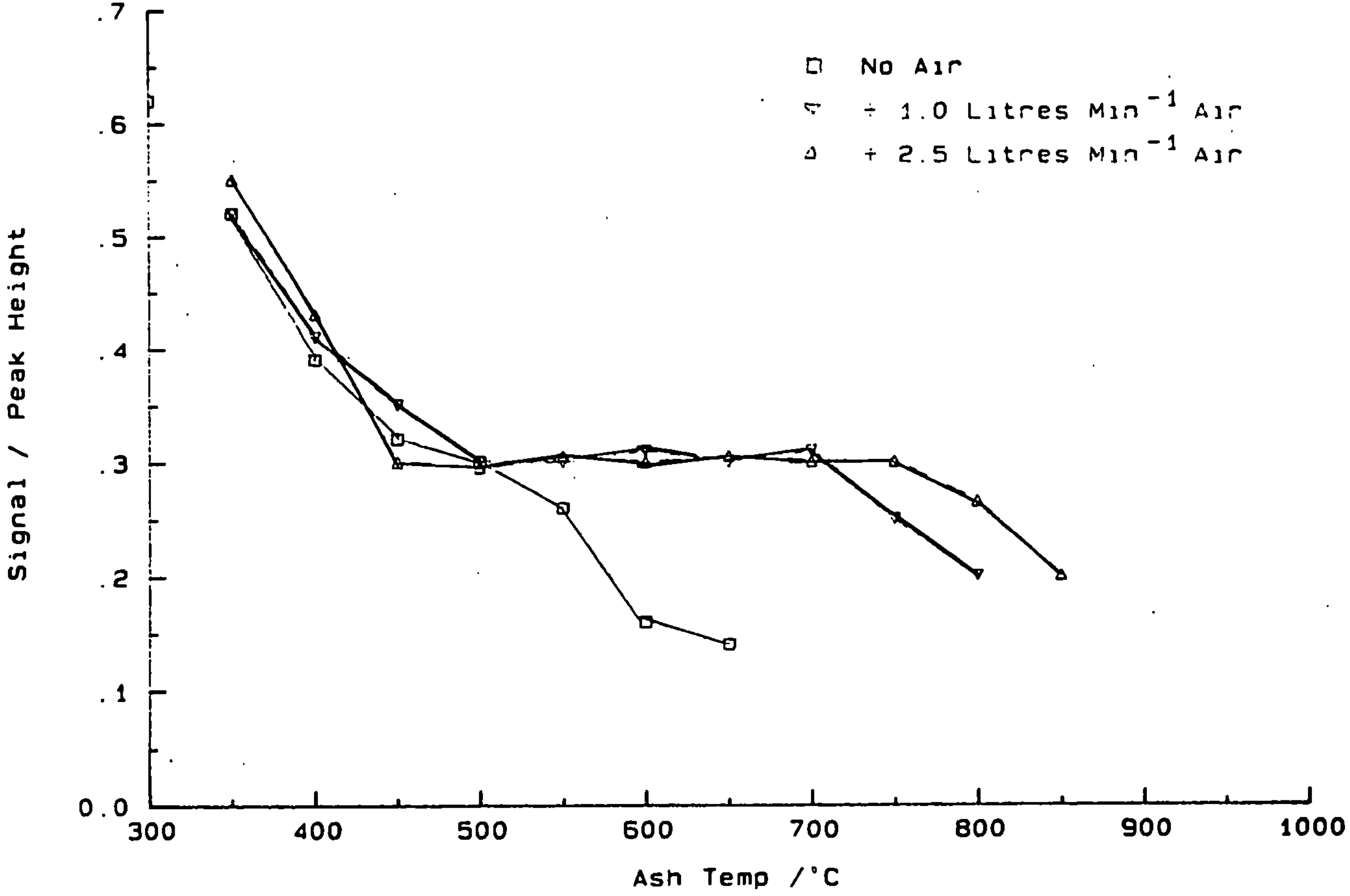
*FP = Full Power (2000°C s^{-1})

TABLE 2.2: FURNACE CONDITIONS USED FOR THE ASH PLOTS OF BOVINE LIVER SLURRY

Phase	Temp/°C	Hold time/s	Ramp/°C s^{-1}	Gas	Gas flow /l min^{-1}
dry	110	40	10	N_2	3.5
ash 1	varied	20	50	N_2 + air	3.5
ash 2	varied	20	0	N_2	3.5
atomise	2200	3	*FP	Gas stop	0
clean	2500	4	*FP	N_2	3.5

*FP = Full Power (2000°C s^{-1})

Fig. 2.1 Ash Plots For Pb In Bovine Liver. Using Varying Amounts Of Air.



the lead, is not fully understood. It was hypothesised (64) that the oxygen becomes adsorbed to the active sites on the graphite surface forming a C-O bond. The active sites are therefore blocked, and are incapable of reducing lead oxide to lead. The adsorbed oxygen is not released from the graphite until 950°C, and therefore it is at this temperature that the active sites become available again. In the absence of air, the active sites would reduce the lead oxide at a temperature of about 500°C, and therefore, the presence of air allows ashing at temperatures of 400-500°C higher than usual. In a later report (65), it was concluded that the above model was erroneous, but that the adsorbed oxygen did control the $CO:CO_2$ ratio, which in turn governed the appearance temperature of lead.

Examination of the ash curve in which no air was added shows that there is no plateau region, and hence it is impossible to determine a temperature at which smoke interference had ceased, but analyte loss had not begun. Using ash temperatures less than 500°C a very large signal was obtained. This was attributed to excessive smoke interference causing the deuterium background correction system to under-correct. To test this hypothesis, the signal obtained at the lead non-absorbing line at 280.1 nm was measured using the furnace programme in Table 2.2. At this wavelength there is no absorption by atomic lead, but excessive smoke would cause absorption or scattering of the incident light, and hence produce a signal. Signals were obtained at temperatures below 500°C, but decreased in magnitude as the ash temperature increased. At 500°C there was no significant signal, and hence there was no longer sufficient smoke to cause under correction.

Similar shaped ash plots were obtained, with and without air, when the bovine liver slurry was analysed for cadmium. Again the use of lower ashing temperatures, due to more efficient pyrolysis, and use of higher ashing temperatures were possible. Similar results were obtained for lead and cadmium in a milk powder slurry (BCR SRM 63, European Community Bureau of Reference, Rue de la Loi, Brussels, Belgium).

Ash plots were also constructed for some less volatile elements. Cobalt exhibited the same increase in the efficiency of pyrolysis, but higher ashing temperatures were not advisable when air was used. The boiling points of the species of interest are Co = 2870°C, $CoCl_2$ = 1049°C and CoO = 1795°C, indicating that the maximum ash temperature used should be 900-1000°C. In the presence of air, significant degeneration of the tube should not occur below temperatures of 950°C, since this is the temperature at which chemisorbed oxygen is released as carbon monoxide or dioxide from the active sites on the graphite surface. The presence of air at this temperature or above would therefore lead to oxidative chemical attack of the active sites, which would then expand throughout the graphite causing a large increase in porosity and fragility of the tube, and a decrease in tube lifetime. It was therefore decided that there was no point in extending the ash plots for cobalt above 950-1000°C. Very similar results were obtained for iron (Fig. 2.2).

2.4 Using Air to Overcome Chemical Interferences

2.4.1 Introduction and Procedure

Air is rarely used in the atomization stage because of its deleterious effects on the tube. However, Katskov et al. (66) removed the interference of chloride upon indium, bismuth and lead. The presence of the air converted the analytes to their oxides. A molybdenum tube was used because of its greater resistance to oxidative attack. An experiment was performed to determine whether or not an air ashing phase could decrease the well documented (14) interference of magnesium chloride on lead determinations. Ash plots with and without air of an aqueous 2 ng ml^{-1} lead standard were constructed. The ash plots were repeated after the addition of $MgCl_2$ (0.15 g l^{-1}, AnalaR, BDH). The general furnace programme used is detailed in Table 2.2.

2.4.2 Results and Discussion

The results obtained are shown in Fig. 2.3. It can be seen that the air did decrease the amount of interference exerted by the $MgCl_2$. Presumably this may again be attributed to the formation of lead oxide, and the blocking of the active sites by chemisorbed oxygen. It has previously been found that the use of $NH_4H_2PO_4$ or the pre-treatment of the tube with 1% ammonium molybdate followed by the use of phosphoric

Fig 2.2 Ash Plots For Fe In Bovine Liver. With And Without Air.

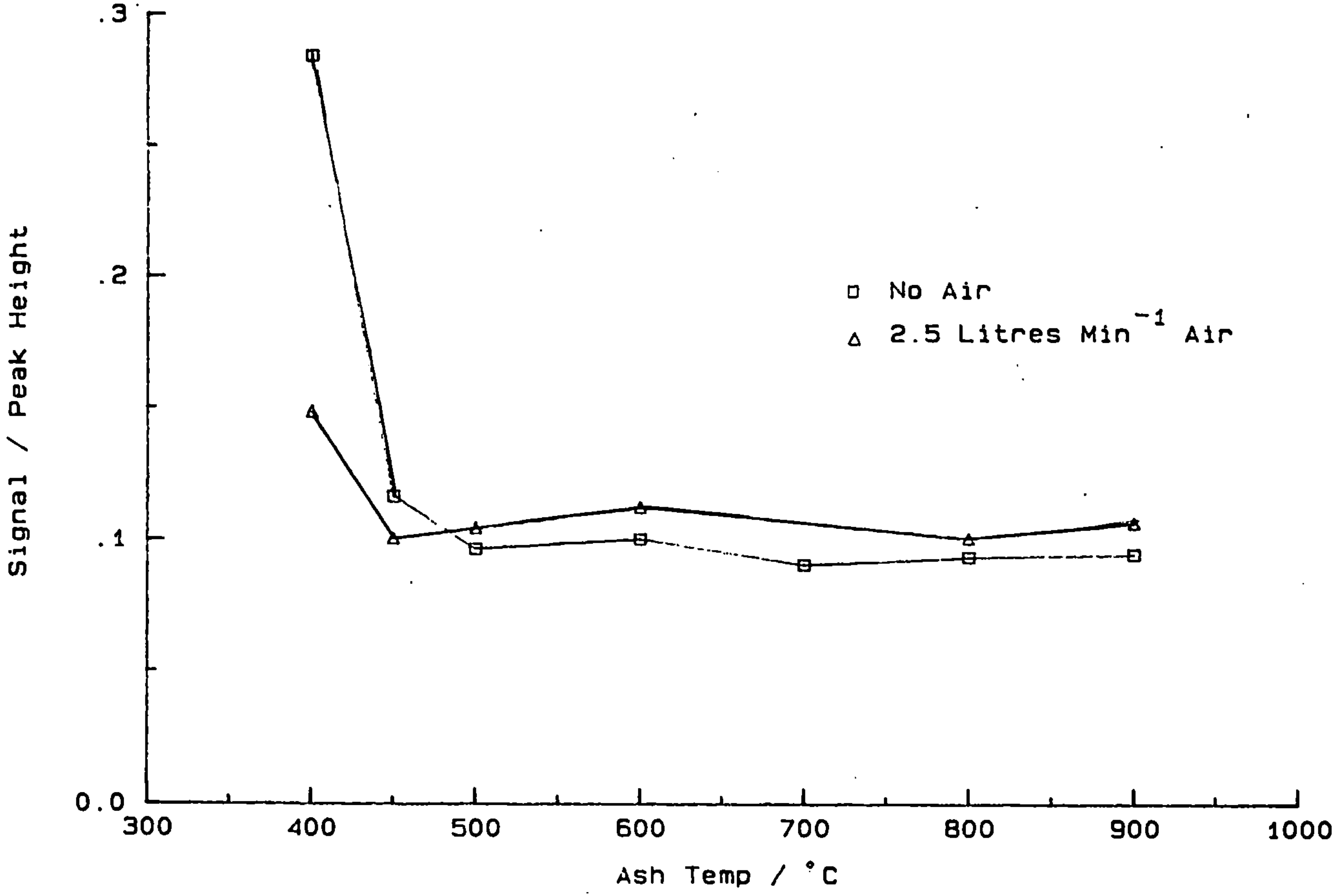
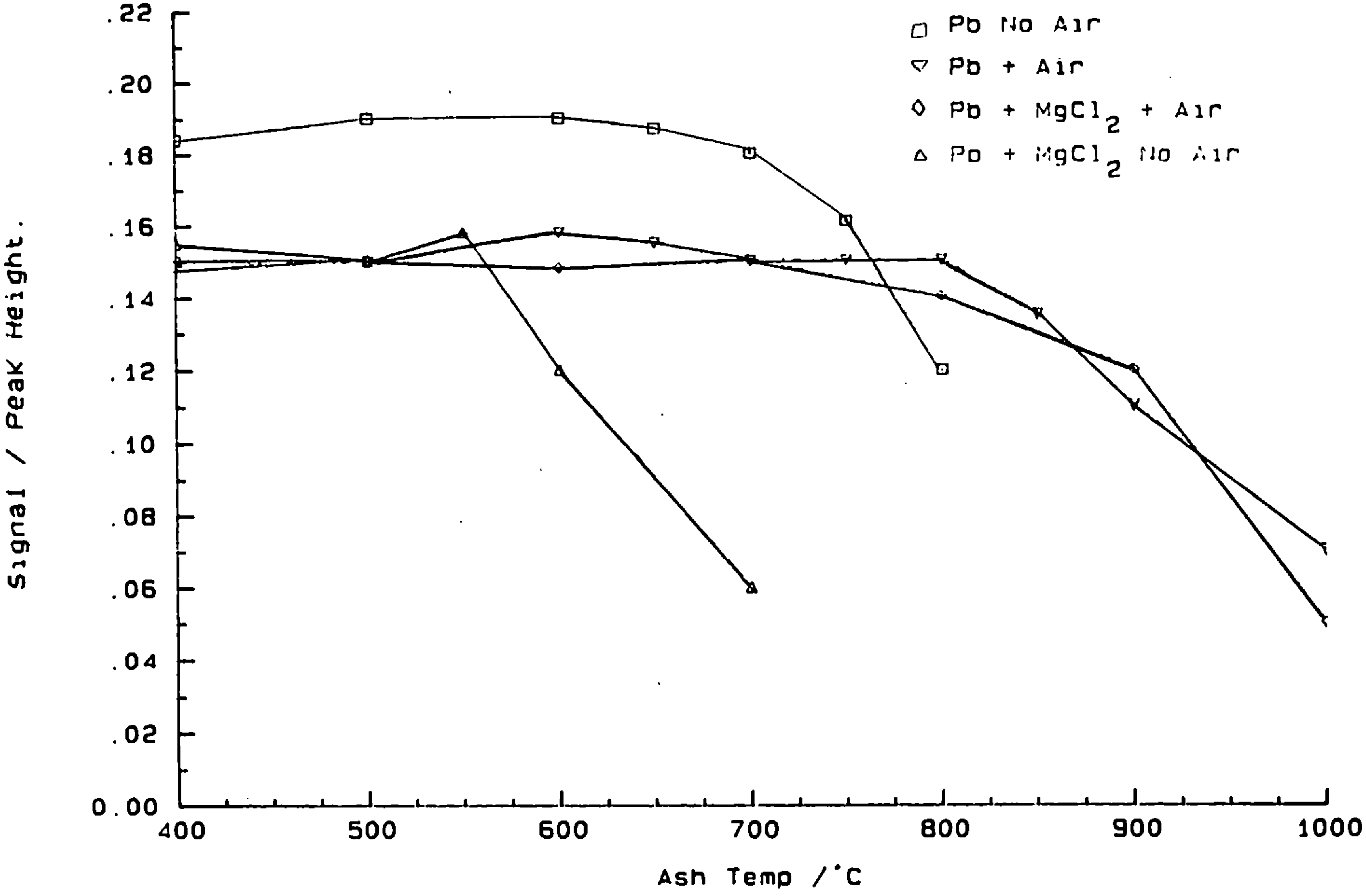


Fig. 2.3 Ash Plots For Pb And Pb With $MgCl_2$. With And Without Air.



acid as a matrix modifier (67), also decreased interference by $MgCl_2$. However, the use of an air ashing system may be quicker, is less prone to contamination than the use of 'wet' chemical modifiers, and is more readily automated. Probe atomisation (21) has also been used to decrease this interference.

The use of an air ashing phase was not found to have any significant adverse affect on the precision of the technique. An experiment was performed in which the lead signal from a bovine liver slurry was measured, and the relative standard deviation (RSD) calculated after every 5 firings. This continued over a period of 50 firings. The RSD was found to be below 4% in all cases. The experiment was repeated using a normal ashing stage in place of the air ashing stage. The RSD was again found to be less than 4% in all cases. The furnace programme used is as shown in Table 2.2, with an ash temperature of 500°C.

2.5 Evaluation of the Method

2.5.1 Introduction and Procedure

Certified reference materials (CRMs) were analysed for chromium, manganese, cobalt and lead. The CRMs chosen were CRM 1573 Tomato leaves (NIST, Washington DC, USA), NIES CRM 5 Hair, NIES CRM 6 mussel, NIES CRM 3 chlorella (National Institute for Environmental Science, Yatabe-Machi,, Tsukuba, Ibaraki, Japan), and BCR CRM 145 sewage sludge (European Community Bureau of Community Reference, Rue de la Loi, Brussels, Belgium). One per cent slurries of the CRMs were prepared using the bottle and bead method described in 2.3.1. The operating conditions and furnace parameters used for the analyses are shown in Table 2.3. The analyses were conducted on both SP9/PU 9095 (Philips Scientific), and PU 9400/PU 9390 (Philips Scientific) systems. From Fig. 2.1 it could be seen that the more air present, the more efficient the ashing. Therefore, for all the analyses performed on the SP9 system 3.5 l min^{-1} air was used, whereas the maximum of 200 ml min^{-1} was used on the PU 9390 electrothermal atomizer.

2.5.2 Results and Discussion

The results from the two furnace systems are shown in Table 2.4. In general, the results obtained were in reasonable agreement with the certified values. The precision of some analyses undertaken on the SP9 was poor. This corresponded to situations in which the high concentration of the analyte elements in the samples necessitated the use of lines of relatively poor sensitivity. Unfortunately these lines often showed poor signal to background ratios, and resulted in noisy signals. The particular continuum source background corrector used in the older SP9 design did not function well above 350 nm. Using the more modern PU9400 the alternative lines were easier to locate using the computerised peak search routine, and above 350 nm it was not necessary to use background correction. Thus for the Mn analyses at the 403.1 nm line and the Pb analyses at the 368.35 nm line, the background corrector was switched off.

TABLE 2.3: FURNACE PARAMETERS FOR THE ANALYSIS OF THE SLURRIES

Element	Wavelength (nm)	Matrix	Spectral band width (nm)	Lamp Current (mA)	Ash phases temp (°C)	time(s)	Atomise phase (°C)
Mn	403.1	Chlorella Mussel Hair	0.5	8	550	20	2400
	321.7	Tomato leaves Sewage sludge	0.1	8	550	20	2400
Cr	357.9	Tomato leaves Hair Mussel	0.5	8	550	20	2400
	520.5	Sewage sludge	0.1	8	550	20	2400
Co	240.7	Mussel Tomato leaves Chlorella	0.5	8	550	20	2400
	304.4	Sewage sludge	0.5	8	550	20	2400
Pb	283.3	Chlorella Mussel Hair Tomato leaves	0.5	5	550	20	2200
	368.3	Sewage sludge	0.5	5	550	20	2200

All analyses incorporated a drying stage at 110°C for 40 seconds. A tube clean stage at 2800°C for 3 seconds was also used for all analyses except lead.

TABLE 2.4: RESULTS FOR SLURRY ATOMISATION OF VARIOUS CERTIFIED REFERENCE MATERIALS

Element	Certified Value ($\mu g\ g^{-1}$)	Result Obtained (SP9) ($\mu g\ g^{-1}$)	Result Obtained (PU9400) ($\mu g\ g^{-1}$)
Tomato leaves (NBS 1573)			
Mn	238 ± 7	260 ± 17	216 ± 22
Cr	4.5 ± 0.5	4.24 ± 0.35	4.4 ± 0.25
Co	(0.6)	0.57 ± 0.03	0.56 ± 0.05
Pb	6.3 ± 0.3	6.1 ± 0.7	5.3 ± 0.6
Human Hair (NIES 5)			
Mn	5.2 ± 0.3	4.9 ± 0.6	5.6 ± 0.1
Cr	1.4 ± 0.2	1.3 ± 0.1	1.4 ± 0.16
Co	(0.1)	0.08 ± 0.03	-
Pb	(6.0)	5.8 ± 0.9	6.6 ± 0.6
Mussel (NIES 6)			
Mn	16.3 ± 1.2	16.5 ± 5.9	17.3 ± 0.4
Cr	0.63 ± 0.07	0.56 ± 0.05	0.59 ± 0.03
Co	(0.37)	0.35 ± 0.01	0.35 ± 0.02
Pb	0.91 ± 0.04	1.03 ± 0.14	0.96 ± 0.05
Chlorella (NIES 3)			
Mn	69 ± 5	65 ± 21	61 ± 3
Cr	-	-	-
Co	0.87 ± 0.05	0.91 ± 0.06	0.74 ± 0.03
Pb	(0.6)	1.2 ± 0.12	-
Sewage Sludge (BCR 145)			
Mn	241 ± 12	244 ± 15	229 ± 25
Cr	(105)	94.3 ± 6.3	120.9 ± 7.8
Co	8.38 ± 0.71	8.63 ± 0.62	-
Pb	349 ± 15	365 ± 22	330 ± 9

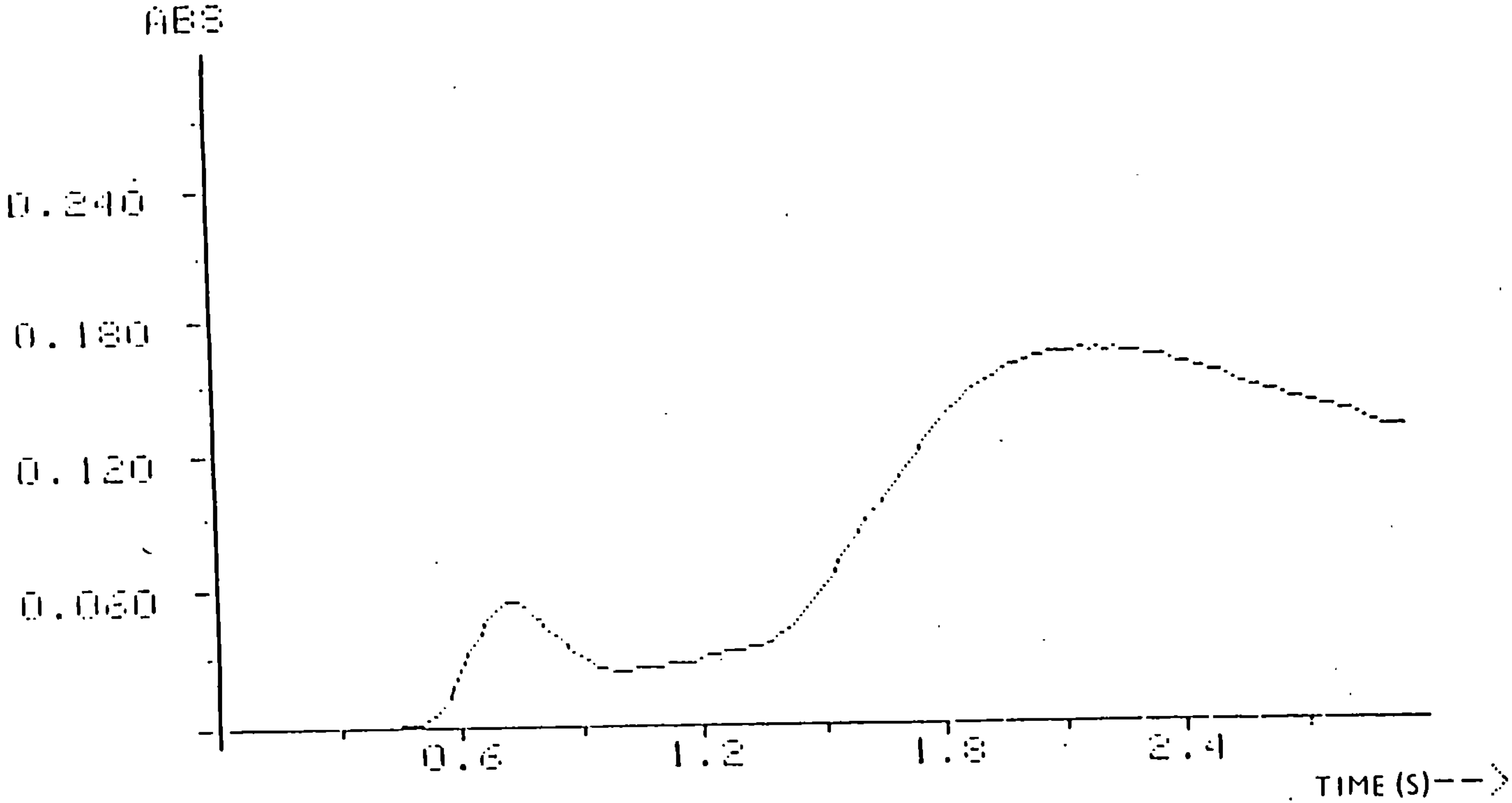
The signals obtained may therefore have included any background absorption. As Fig. 2.4 shows, the analyte peak precedes a large non-specific absorbance peak. By decreasing the read time to 1 second and by using peak height measurements, it was possible accurately to determine the analyte concentration before the onset of smoke interference.

Since in the PU 9390 electrothermal atomizer the internal gas is directed through the tube, it is considerably more efficient than the SP9 furnace system which relies on air diffusing into the tube. The increased efficiency was demonstrated by the fact that it yielded similar results to the SP9 system, but used only a fraction of the gas.

2.6 Conclusions

The use of an air ashing phase in the analysis of slurries leads to more efficient pyrolysis. This has two advantages. First, it decreases the amount of carbonaceous residue left in the tube after an analysis, and second, it allows atomization that is more free from interferences after ashing at much lower temperatures. Interference from other species, such as $MgCl_2$, was also found to decrease. This was presumably due to the formation of less volatile lead species, and hence, reduced interaction with chloride ions in the vapour phase. Air-ashing was found to have no deleterious effect on either tube life-time, provided ash temperatures of less than 950°C, typically 600°C, were used,

Fig. 2.4: The signal obtained for a slurry at the lead 368.35nm line without background correction.



or on analytical precision. An air-ashing stage was then used in the determination of Co, Cr, Mn and Pb in some slurries of certified reference materials. The results showed good agreement with the certified values.

CHAPTER 3 - THE USE OF HYDROCARBON GASES IN THE ASH STAGE

3.1 Introduction

The advantages offered by total pyrolytic carbon (TPC) or pyrolytically coated tubes have been well documented (68). The low permeability to gases of pyrolytic graphite leads to improved vapour confinement and hence improved sensitivity. The low porosity; (0% compared with 17% for electrographite (68)) leads to less soaking of the sample into the graphite lattice, which in turn, leads to improvements in sensitivity, detection limits and precision, and a decrease in memory effects. Pyrolytic carbon has a higher sublimation point than standard graphite, and that combined with its higher resistance to oxidation, leads to increased tube life-time. Its high thermal conductivity leads to more uniform heating which results in an increase in the rate of atomisation, and increased efficiency of atomization (69).

The presence of oxidising acids or ions (70), oxygen (64) or water vapour (71, 72) at elevated temperatures rapidly leads to tube oxidation and degeneration. This is particularly prolific in uncoated electrographite tubes, but also occurs albeit more slowly, in coated tubes. The situation is exacerbated by analytes that require extremely high atomisation temperatures. The use of a hydrocarbon gas to replenish the pyrolytic coating is a concept that has been in use for many years. Methane (69, 71-79), acetylene (70, 75), propane (75, 80) and ethylene (75), have all been used for this purpose. Methane has been the most common hydrocarbon to be used. It thermally decomposes at a temperature of 607°C (81) according to the equation

$$CH_4 \rightarrow C + 2H_2,$$

but most workers use temperatures of 2000-2200°C to coat the tubes. Originally, the first workers used 100% methane, but this resulted in the formation of loose sooty deposits. Most workers have therefore invested in a commercial mix of 10% methane in argon, and diluted this with pure argon as necessary. The efficiency of the coating process has been calculated by Manning and Ediger (69) to be about 50% at 2200°C. By bleeding the methane into the inert gas atmosphere, it is possible to extend tube lifetime by the deposition of the liberated carbon as a robust, inert layer on the graphite surface.

The majority of workers have used the gaseous hydrocarbon during either the clean stage at the end of the furnace programme (76), as an initial pre-treatment before the tube is used (69, 77), continuously throughout the entire furnace cycle (71, 72, 77), or a combination of the last two (70). Few if any appear to have limited the use of the hydrocarbon to the ash stage. If the temperature of the ash stage is high enough, then all the advantages proffered by the use of hydrocarbons should be exhibited, while the amount of explosive gas used is minimised.

3.2 Experimental

3.2.1 Instrumentation

An atomic absorption spectrometer (PU 9100X, Philips Scientific) fitted with an electrothermal atomiser (PU 9390X, Philips Scientific) an autosampler (PU 9380X, Philips Scientific), and a data station (PU 9178X, Philips Scientific) was used. Additionally, an alternative spectrometer (SP9, Philips Scientific) fitted with a video furnace programmer (PU 9095, Philips Scientific) and an SP9 furnace, (Philips Scientific) was used. Pyrolytically coated tubes were used throughout. Samples were introduced manually to the SP9 system by precision micropipette (Gilson).

3.2.2 Reagents and Standards

Stock standards (1000 mg l^{-1}) of all analytes were obtained from BDH (Spectrosol, BDH). Working standards were prepared on a daily basis by serial dilution of the stock standards into clean plastic volumetric flasks. Methane (99%) and a subsequent mix of 5% methane in argon, were obtained from Air Products (Marsh Barton, Exeter, UK).

3.3 Initial Experiments

3.3.1 Procedure

Initial experiments were performed on the older SP9 furnace system. Methane (99%) was diluted by the inert argon gas by the use of rotameters. The first experiment performed involved the consecutive measurements, (peak height) of an aqueous aluminium standard (10 ng ml^{-1}) from the wall of a pyro-coated tube, in the absence of methane. After 12 firings, a 2% methane in argon mix was introduced during the clean stage, and the measurements continued. The furnace programme and the operating conditions used are detailed in Tables 3.1 and 3.2 respectively.

3.3.2 Results and Discussion

A plot of peak height against the number of firings is shown in Fig. 3.1. It shows that the signal obtained was initially fairly stable, but as the pyrolytic coating began to wear away and expose the more porous electrographite, the magnitude of the signal began to diminish. On addition of the methane to replenish the pyrolytic layer, the signal immediately increased again, although it did not reach its original size. This was probably due to insufficient carbon being deposited. If a second introduction of methane had been made during another clean stage, the analytical signal may have returned to its original size. This initial experiment showed the extent to which the pyro-coating governs the size of the signal, by preventing sample soaking into the tube and carbide formation.

3.4 Introduction of Methane During the Ash Stage

3.4.1 Introduction

For extremely refractory analytes such as V, Al, Si etc, ash temperatures of up to 1300-1500°C may be used without analyte loss. At temperatures above 600°C methane should start to thermally dissociate and hence produce reducing

TABLE 3.1: FURNACE PROGRAMME USED FOR Al

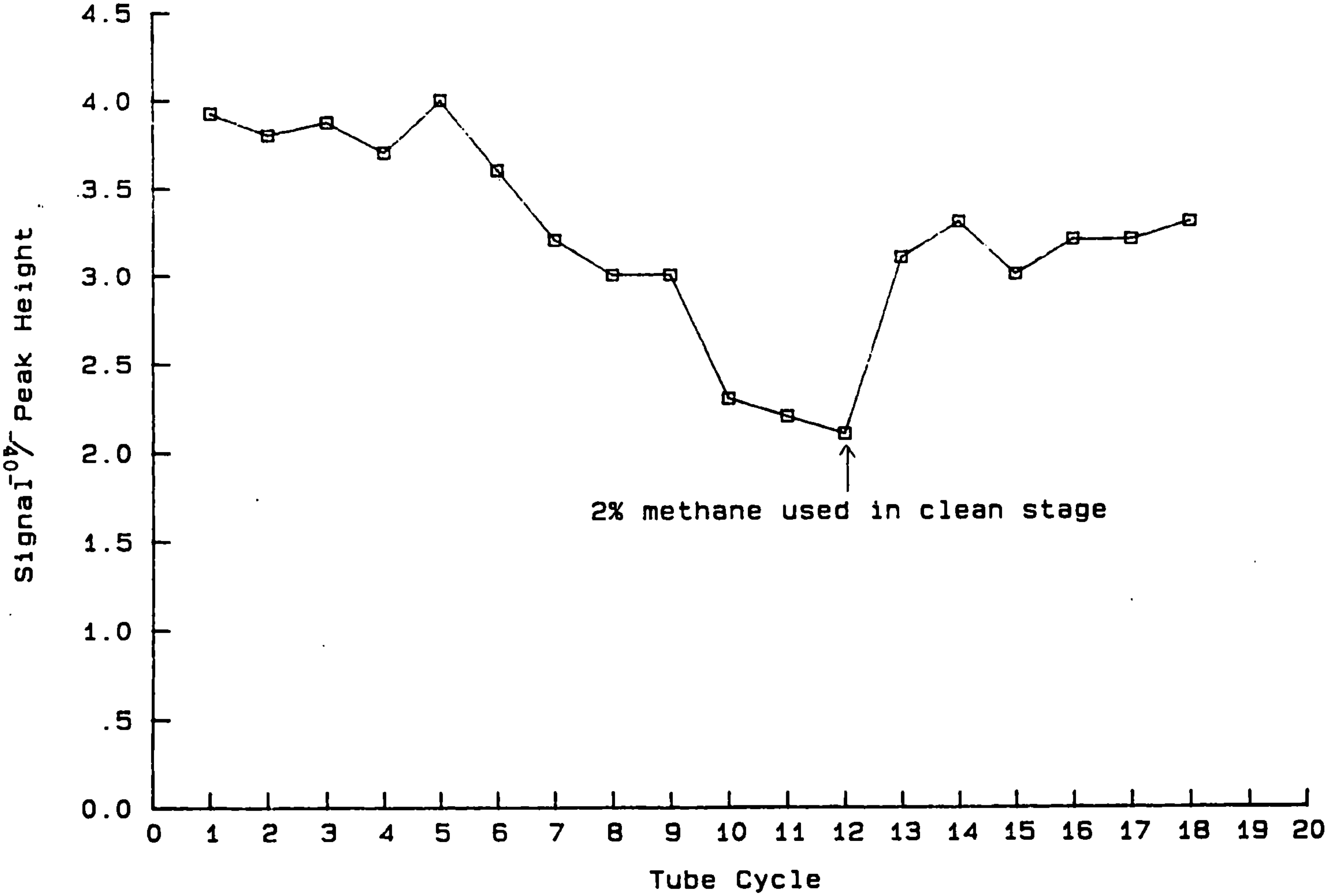
Phase	Temperature/°c	Hold time/s	Ramp/°c s^{-1}
dry	110	30	20
ash	700	10	100
atomise	2600	5	FP*
clean	2700	5	FP*

* Full Power

TABLE 3.2: OPERATING CONDITIONS FOR Al

bandpass	0.5 nm
lamp current	10 mA
wavelength	309.3 nm
injection volume	20 μl

Fig. 3.1 Signal Size For Al Against Tube Cycle



carbon and hydrogen. By introducing methane during the ash stage the pyrolytic coating on the tube should be preserved, but in addition to that, any residual oxygen present should be scavenged. This is obviously desirable for analytes such as these that form stable oxides.

3.4.2 Procedure

Analytes such as Al (10 ng ml^{-1}), V (50 ng ml^{-1}), Si (50 ng ml^{-1}), Mg (20 ng ml^{-1}), Ca (400 ng ml^{-1}) and Mo (10 ng ml^{-1}) were used to determine the affects of methane. An early experiment performed on the SP9 system showed that the optimum amount of methane for aluminium determination was about 2% (Fig. 3.2). At concentrations higher than that, the carbon liberated from the decomposition of methane, coated the electrical contacts, the inside of the furnace head and the quartz windows. However, in the more modern PU 9390X system, this problem was largely overcome. For the remaining analytes, the experiments were performed using the PU 9390X system and a commercial mix of 5% methane in argon. The operating conditions and furnace programmes used are detailed in Table 3.3.

3.4.3 Results and Discussion

The results obtained are shown in Table 3.4. The results shown are the averages of five replicate injections, and are based on peak height measurements. It can be seen that the presence of the methane in the ash stage led to sensitivity enhancements for most analytes which in some cases, eg. Si, Fig 3.2 Aluminium Signal Against Amount Of Methane Used.

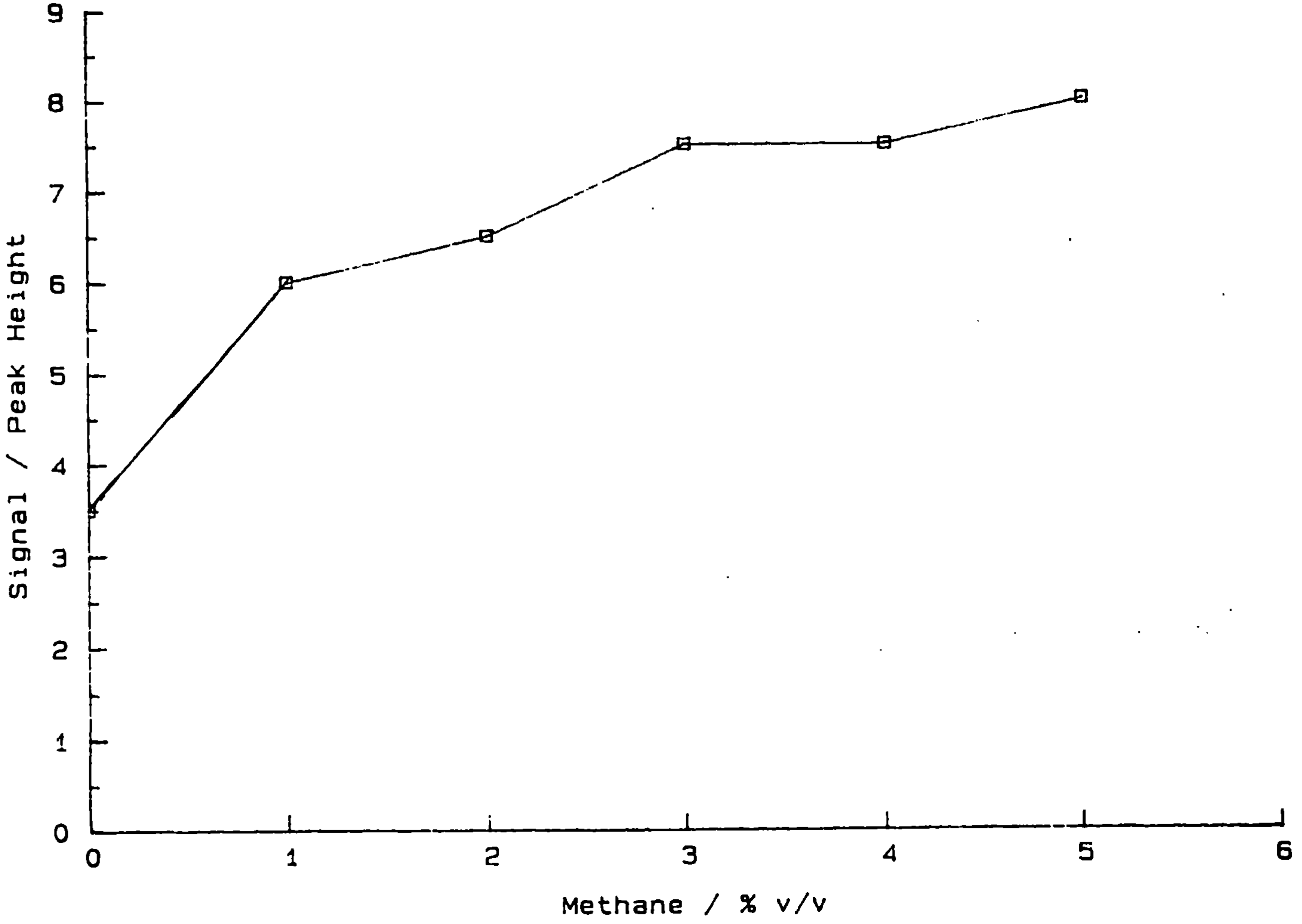


TABLE 3.3: OPERATING CONDITIONS AND FURNACE PARAMETERS USED FOR METHANE IN ASH STAGE EXPERIMENTS

Analyte	Stage	Temp/°C	Hold time/s	Ramp/ °C s^{-1}	Wave-length /nm	Lamp current mA	Band-pass/ nm
Al	dry	110	30	20	309.3	7	0.5
	ash	1100	30	50			
	atomise	2800	3	FP*			
	clean	2900	3	FP*			
Ca	dry	110	30	20	239.9	6	0.5
	ash	1000	30	50			
	atomise	2600	3	FP*			
	clean	2900	3	FP*			
Mg	dry	110	30	20	279.6	4	0.5
	ash	800	30	50			
	atomise	2400	3	FP*			
	clean	2900	3	FP*			
Mo	dry	110	30	20	313.9	12	0.2
	ash	1200	30	50			
	atomise	2800	3	FP*			
	clean	2900	3	FP*			
Si	dry	110	30	20	251.6	12	0.5
	ash	1100	30	50			
	atomise	2800	3	FP*			
	clean	2900	3	FP*			
V	dry	110	30	20	318.5	10	0.2
	ash	1200	30	50			
	atomise	2800	3	FP*			
	clean	2900	3	FP*			

*FP = Full Power

TABLE 3.4: A COMPARISON OF THE SENSITIVITY OBTAINED FOR SEVERAL ELEMENTS IN ARGON AND 5% v/v METHANE IN ARGON

Analyte	$\frac{\text{Signal using 5\% methane in argon}}{\text{Signal using argon}}$
Al	1.26
Ca	1.53
Mg	1.46
Mo	1.01
Si	1.89
V	1.14

were significant. Figures 3.3 and 3.4 show the peaks obtained for silicon without, and then with methane. The background signal caused by residual methane is only slightly larger than that obtained in the absence of methane, indicating that any enhancement in sensitivity is not due to under-correction by the background correction system. The optimal amount of methane required for each analyte was not determined, and since each analyte has a different optimum (78), the enhancements in sensitivity may not be maximal. The results in general, and the rather disappointing result for molybdenum in particular, may have been greatly improved had the optimal methane mixtures been used.

The sensitivity enhancements may have a number of causes. It could be due to the formation of a non-porous pyrolytic carbon layer, thereby preventing soaking and memory effects, or the reduction of analyte oxide species, or the prevention of their formation by the reducing carbon or hydrogen formed. By using an electrographite tube and measuring the signal obtained by a vanadium standard (50 ng ml^{-1}) first without, and then with methane in the ash stage, it was shown that the pyro-coating did not cause the signal enhancement. The results obtained showed an increase in sensitivity similar in magnitude to that obtained in pyro-coated tubes, although the overall signal was smaller. Since an electrographite tube was used, sample soaking and carbide formation would occur. This explains the overall drop in sensitivity. The methane was introduced during the

Fig. 3.3: Signal obtained from 50 ng ml^{-1} silicon without 5% methane in Argon.

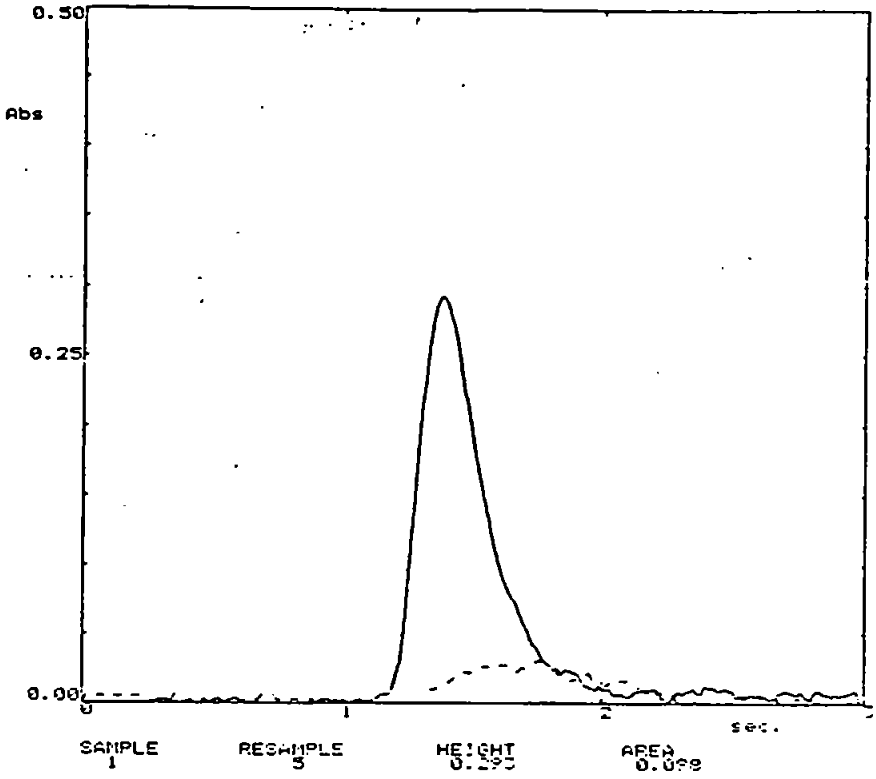
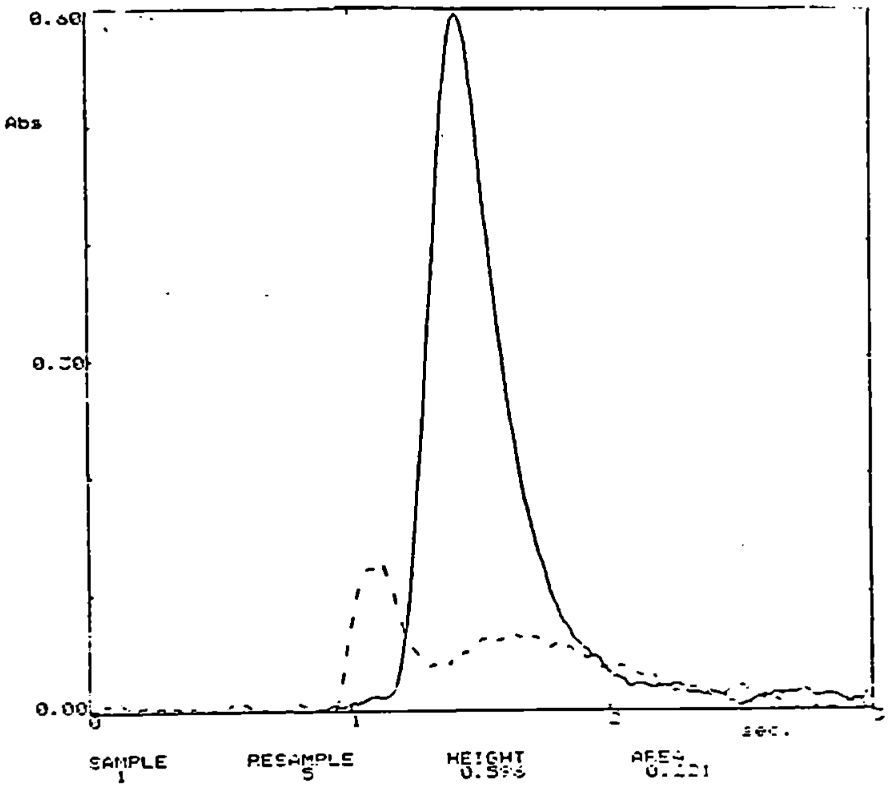


Fig. 3.4: Signal obtained for 50 ng ml^{-1} silicon with 5% methane in Argon.



ash stage and, therefore, sample soaking would already have occurred. Since the same sensitivity enhancement was obtained, it was deduced that signal enhancements were due to the presence of reducing carbon, hydrogen or perhaps hydrocarbon radicals. When a comparison of sensitivity was made between hydrogen and argon in the ash stage, it was found that in the presence of hydrogen, a very slight increase in signal was obtained for both peak area and peak height for analytes such as Al (7%) and V (3%). However, this increase was considerably smaller than that obtained in the presence of methane. This indicated that although the hydrogen may be partially responsible for the signal enhancement, the main cause is the reducing carbon or the hydrocarbon radical. This is in accordance with the results of Welz and Schlemmer (79). These workers also found increases in sensitivity when methane was used in glassy carbon tubes, and to a lesser extent in pyro-coated tubes (82).

3.5 Investigation of the Kinetics of Methane Dissociation

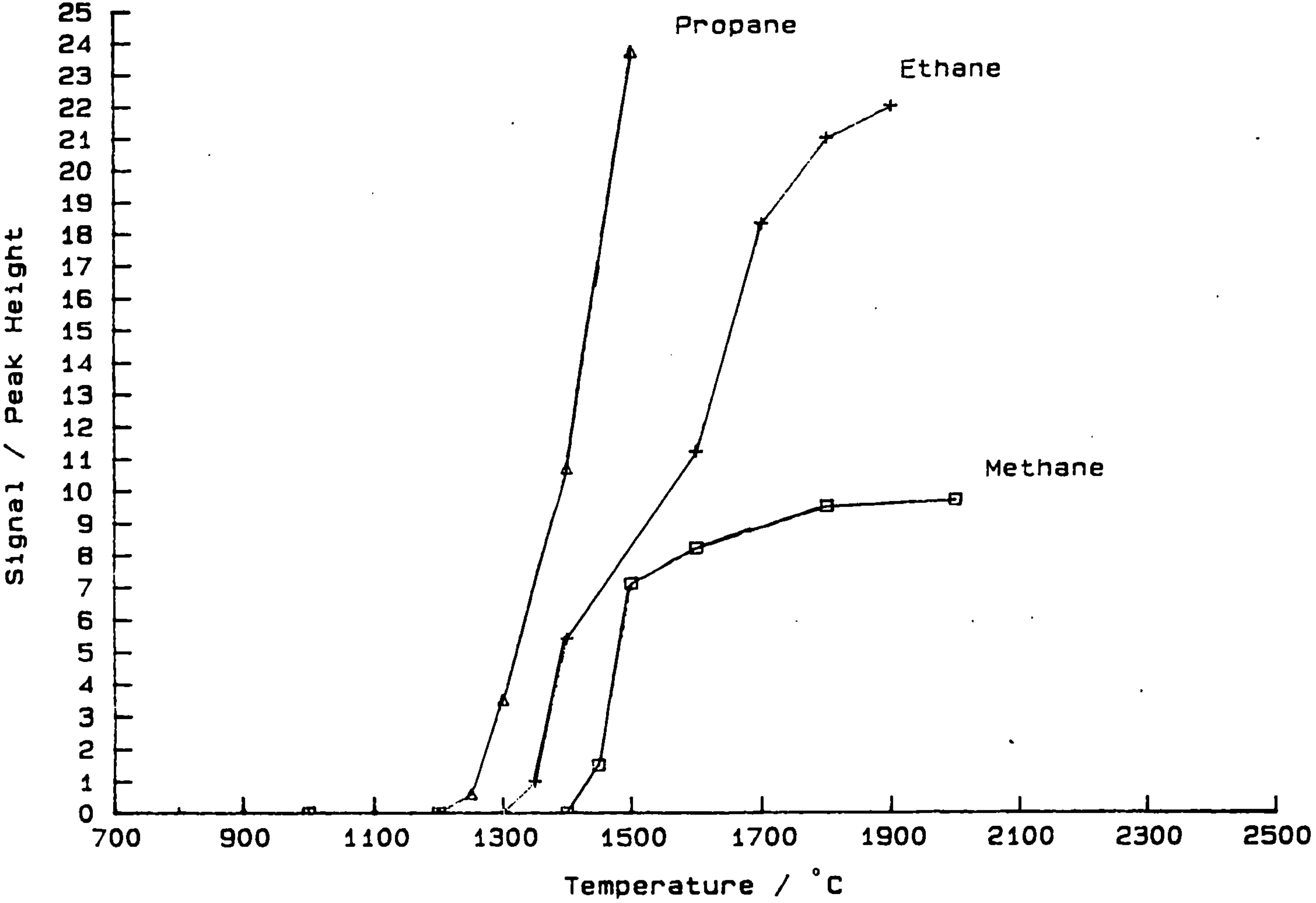
3.5.1 Introduction

The rate at which the hydrocarbon thermally dissociates is important considering that the temperatures used in the ash stage were lower than those recommended for pyrolytic coat formation found in literature. If the rate of dissociation is very slow, then longer ash times or higher ash temperatures may be required for optimal signal enhancement.

3.5.2 Procedure Results and Discussion

Using the copper non-absorbing line at 323.1 nm, and with the background correction lamp switched off, the signal obtained at different temperatures in the presence of 100% methane was measured. The signal was measured for 10 seconds at temperatures of between 1000 and 2000°C. The experiment was then repeated for the gases ethane and propane. The results are shown in Fig. 3.5. From Fig. 3.5 it can be seen that the kinetics are very slow. The literature (81) quotes a temperature of 607°C to be the point at which methane dissociates. However, in the 10 second measurement period no signal from the dissociating methane was observed until 1450°C. Had longer measurement times been used, then the dissociation of methane at lower temperatures would have become apparent. The ethane and propane dissociated at lower temperatures (1350°C and 1250°C respectively). The use of higher hydrocarbons might therefore enable lower ash temperatures or times to be used whilst still yielding the same results. However, the amount of hydrocarbon necessary is considerably less than methane. Other workers (75) have found that the amount of propane required is only 7% of that of methane. Figure 3.5 shows the much larger signals obtained from the ethane and propane which demonstrates the point. Obtaining mixes of gases that may be less than 1% in argon is extremely difficult experimentally unless specialised gas blenders are used, and may be expensive to purchase commercially. It was therefore decided that despite the obvious advantages offered by the higher hydrocarbons, methane should be used for all further

Fig 3.5 Decomposition Curves for Methane, Ethane and Propane.



investigations.

Having decided that the kinetics of methane dissociation were slow, it was necessary to determine whether or not the use of longer ash times would result in further signal enhancement. The use of higher ash temperatures was briefly tested, but the ash temperatures used originally were the maximum recommended for each analyte, and raising it further led to premature analyte loss, and a reduction in sensitivity. Increasing the ash time did not lead to any further enhancement in signal, indicating that a time of 20 seconds was sufficient to scavenge residual oxygen and reduce analyte oxides.

3.6 Evaluation of the Method

3.6.1 Procedure

In order to ensure the validity of the procedure, some certified reference materials (CRMs) were analysed for their aluminium and vanadium contents. Slurries (approximately 1% w/v) of the CRM NIES 9 Sargasso and NIES 8 vehicle exhaust particulates (National Institute for Environmental Science, Yatabe-Machi, Tsukuba, Ibaraki, Japan); coal, (NIST SRM 1635, NIST Washington DC, USA) and coal (South African Reference Material 20, Pretoria, RSA), were prepared using the bottle and bead method described in Section 2.3.1. In addition, the simulated fresh water CRM IAEA-W4 (National Atomic Energy Agency, Vienna, Austria) was prepared according to the instructions, and hair (0.1g NIES 5, Japan) was weighed accurately into a digestion bomb, nitric acid (2 ml) and perchloric acid (1 ml) added, and the bomb heated to 120°C for 3 hours. After cooling, the digest was diluted to 100 ml. If necessary, the moisture contents of the CRMs were determined according to the instructions on the certificate. The analyses were performed on the SP9/PU 9095 system using pyro-coated tubes. The slurries were agitated manually to ensure homogeneous suspension. The furnace parameters and operating conditions used for the analyses for Al and V are given in Tables 3.5 and 3.6 respectively.

3.6.2 Results and Discussion

The results obtained are given in Table 3.7. In general, the results are in reasonable agreement with the certified values. As expected, the uncertainty values (expressed as $\pm 2\sigma$) are larger when methane was not used during the ash stage. In the case of the vanadium determination in the certified water sample, the low level present required determinations very close to the detection limit and therefore large uncertainty resulted. In the presence of methane, the resulting increased sensitivity allowed the levels to be determined more precisely. The result obtained for the analyses of coal SARM 20 for vanadium in the absence of methane was significantly lower than the certified value. It is not clear why this should be, although it has been reported (72) that different matrices affect the pyrolytic coating to different extents. The more accurate result obtained for the same matrix in the presence of methane may be a reflection of the extent to which it overcomes chemical

TABLE 3.5: FURNACE PROGRAMME AND OPERATING CONDITIONS FOR ALUMINIUM ANALYSES

Matrix	Wavelength /nm	lamp current /mA	bandpass /nm	Ash temp /°C	Atomise temp/°C
NIES9 Sargasso	256.8	10	0.5	800	2500
NIES5 Hair	256.8	10	0.5	800	2500
IAEA-W4 Water	309.3	10	0.5	800	2500

All analyses incorporated a drying stage at 110°C and a tube clean at 2800°C

TABLE 3.6: FURNACE PROGRAMME AND OPERATING CONDITIONS FOR VANADIUM ANALYSES

Matrix	Wavelength /nm	lamp current /mA	bandpass /nm	Ash temp /°C	Atomise temp/°C
NIES8 VEP	318.5	10	0.2	800	2700
NIST 1635 Coal	318.5	10	0.2	800	2700
SARM 20 Coal	306.6	10	0.2	800	2700
IAEA-W4 Water	318.5	10	0.2	800	2700

All analyses incorporated a dry stage at 110°C and a tube clean at 2800°C

TABLE 3.7: RESULTS* OBTAINED FROM THE ANALYSES OF CRMS

Matrix	Analyte	Certificate value/µg g^{-1}	Result-CH_4+ /µg g^{-1}	Result+CH_4ǂ /µg g^{-1}
Sargasso	Al	(215)	228 ± 22	239 ± 6
Hair	Al	(240)	235 ± 19	231 ± 13
Water	Al	50 ng ml^{-1}	52 ± 5	44 ± 3
	V	5.1 ng ml^{-1}	5 ± 2	4.9 ± 0.4
VEP	V	17 ± 2	16 ± 0.5	16 ± 0.4
NIST 1635 Coal	V	5.2 ± 0.5	6.2 ± 0.3	5.6 ± 0.5
SARM 20 Coal	V	47	35 ± 2	52 ± 2

(   ) = non certified result

* mean ± 2 σ n = 6

\+ Results obtained without 5% v/v methane in the ash stage

ǂ Results obtained with 5% v/v methane in the ash stage attack of the tube.

In addition to analysing certified reference materials, some samples of bovine liver serum (supplied by C. Fellows, Southampton General Hospital) were also analysed for their Al contents using the furnace parameters and operating conditions shown in Tables 3.3 and 3.7 respectively. The results obtained in this study are compared with those obtained from Southampton in Table 3.8. Again, the results are in reasonable agreement, indicating that the method provides results comparable with other methods.

3.7 Conclusions

The introduction of small amounts of methane, or another hydrocarbon gas into the ash stage of a furnace cycle produces an enhancement in sensitivity for a number of analytes that form refractory oxides or carbides. Excess hydrocarbon results in the formation of sooty deposits that coat the interior of the furnace head. Although each analyte has a different optimal amount of hydrocarbon, a standard mix of 5% methane in argon provided enhancements of between 14-89% for most analytes, the only exception being molybdenum. Lesser amounts of the higher hydrocarbons are required to produce the same effect. The enhancement was found to be caused by the amount of reducing carbon liberated during hydrocarbon pyrolysis, or perhaps a hydrocarbon radical reducing analyte oxide species or scavenging residual oxygen thereby preventing oxide

TABLE 3.8: RESULTS FOR THE ANALYSES FOR ALUMINIUM IN BOVINE LIVER SERUM

Matrix	Results Obtained	σ	Result from Southampton	σ
A	72.0	2.7	79.2	5.3
B	15.0	1.0	19.0	1.1

formation.

In addition to causing sensitivity enhancements, the pyrolysis of methane also extended tube lifetime by the formation of a robust, inert coating of pyrolytic carbon on the graphite surface.

The method was evaluated by the analysis of some certified reference materials. The results obtained were in reasonable agreement with the certified values.

CHAPTER 4 - USE OF HYDROGEN TO OVERCOME INTERFERENCES

4.1 Introduction

Hydrogen was first used in ETAAS by Amos *et al*. (23), who produced a hydrogen diffusion flame above a graphite rod which resulted in reduced interferences. It has since been used by several workers. Ohta *et al*. (84-91) have reported increased sensitivity for many analytes when hydrogen was introduced to various metal tube atomisers. The hydrogen had the effects of protecting the atomiser against oxidation by any residual oxygen, reducing the analyte oxide to analyte atoms

eg. $GeO_2 + 2H_2 \rightarrow Ge + 2H_2O$ (85),

and preventing atom loss by recombination *eg*. by atmospheric oxygen. Increases in sensitivity have also been reported by other workers (83, 92, 93).

Hydrogen has been used in graphite atomisers to reduce the spectral interference of the calcium oxide molecular band emission on the determination of barium, and strontium band emission on lithium determinations (94). Chloride interferences on lead determinations have also been eliminated by the addition of hydrogen (95, 96), however, other workers have reported that the hydrogen does not overcome this interference (97, 98). The inconsistent results obtained have been attributed to the use of different types of atomiser and by working under different experimental conditions.

It has been reported (96) that hydrogen is produced in very small amounts during any normal furnace programme. Graphite tubes, especially porous electrographite ones, allow the sample to soak through the surface and become trapped in the graphite lattice. The sample may therefore be only partially dried. During the ash phase, the trapped solvent (frequently water based) reacts with the graphite and produces small amounts of hydrogen. This process has been credited with the removal of chloride interference in some atomisers.

In graphite atomisers hydrogen has therefore been used primarily to overcome chemical and spectral interferences. In this work, hydrogen has been used in a graphite tube atomiser in an attempt to overcome these and other interferences.

4.2 Instrumentation

An atomic absorption spectrometer (PU 9100X, Philips Scientific) fitted with an electrothermal atomiser (PU 9390X, Philips Scientific) and a data station (PU 9178X, Philips Scientific) was used throughout. Gas mixtures were achieved, where necessary, by using a gas blender (series 800, Signal Instrument Co. Ltd., Camberley, Surrey, UK). Samples were introduced by a hand held precision micropipette (Gilson).

4.3 Introduction of Hydrogen during the Auto-Zero Stage

A cool down stage just before atomisation has been reported to lead to increased sensitivity for many analytes (99). The instrument used in this study has such a stage as an integral part of every furnace programme. It lasts ten seconds, during which the signal is auto-zerod. If hydrogen were to be introduced during this stage, its effects would appear in the atomise stage.

4.3.1 Procedure

NB: Before any experiments using hydrogen were performed, the instrumentation must be flushed with hydrogen at a low temperature to drive out any air present in the gas lines. Failure to do this may result in a damaging explosion.

Preliminary experiments were performed to assess the viability of using hydrogen in this stage. A mixed aqueous standard of 6 analytes was prepared by serial dilution of 1000 $\mu g\ ml^{-1}$ stock standards (Spectrosol, BDH). A comparison of the sensitivities obtained between argon and varying amounts of hydrogen was performed using the operating conditions in Table 4.1. Since the analytes were all fairly refractory, a general furnace programme could be used. This is shown in Table 4.2. All experiments were performed using pyro-coated tubes.

TABLE 4.1: OPERATING CONDITIONS FOR THE SENSITIVITY COMPARISON

Analyte	Lamp current (mA)	Wavelength (nm)	Bandpass (nm)	Concentration (ng ml^{-1})
Aluminium	8	309.3	0.5	15
Calcium	4	422.7	0.2	4
Magnesium	3	202.6	0.5	5
Silicon	8	251.6	0.5	80
Vanadium	8	318.5	0.2	50

Injection volume = 20 µl

TABLE 4.2: GENERAL FURNACE PROGRAMME USED FOR THE SENSITIVITY COMPARISON

Stage	Temperature /°C	Hold time /s	Ramp /°C s^{-1}	Internal Gas	Gas Flow /ml min^{-1}
Dry	110	35	20	Ar	200
Ash	800	30	100	Ar	200
Atomise	2800	4	FP*	Ar/H_2	0
Clean	2900	3	FP*	Ar	200

*FP = Full Power

4.3.2 Results and Discussion

The results obtained (table 4.3) indicate that the presence of hydrogen in the atomise stage leads to a significant loss of sensitivity. This is in accordance with another report (95) which ascribed this effect to diffusional losses. The addition of less hydrogen results in a smaller drop in sensitivity. The presence of hydrogen resulted in a small flame which emerged from the injection hole of the graphite tube, and was due to the hot hydrogen coming into contact with atmospheric oxygen. The flame was occasionally accompanied by a small 'pop'.

The introduction of hydrogen to the auto-zero stage appeared to markedly decrease the appearance temperature of several analytes. Figures 4.1 and 4.2 show the signal obtained for 15 ng ml^{-1} lead without and with hydrogen respectively. It was therefore decided to measure the gas phase temperature using the two line method (100, 101). Three thermometric species were used, namely tin, nickel and lead. The general operating conditions for each of the three elements is given in Table 4.4 and the furnace programmes for tin, nickel and lead are given in Tables 4.5, 4.6 and 4.7 respectively. The apparent tube wall temperature was measured using the infra-red fibre optic temperature control device located within the furnace head.

The vapour phase temperatures were calculated according to the equations below.

TABLE 4.3: RESULTS OBTAINED FOR THE COMPARISON OF SENSITIVITY BETWEEN ARGON AND HYDROGEN

Analyte	$\frac{\text{Signal in Hydrogen}}{\text{Signal in Argon}}$	$\frac{\text{Signal in 105 v/v Hydrogen}}{\text{Signal in Argon}}$
Aluminium	0.56	0.77
Calcium	0.96	1.04
Magnesium	0.67	0.84
Silicon	0.04	0.28
Vanadium	0.43	0.57

Fig. 4.1: Signal obtained for 15 ng ml^{-1} lead without hydrogen.

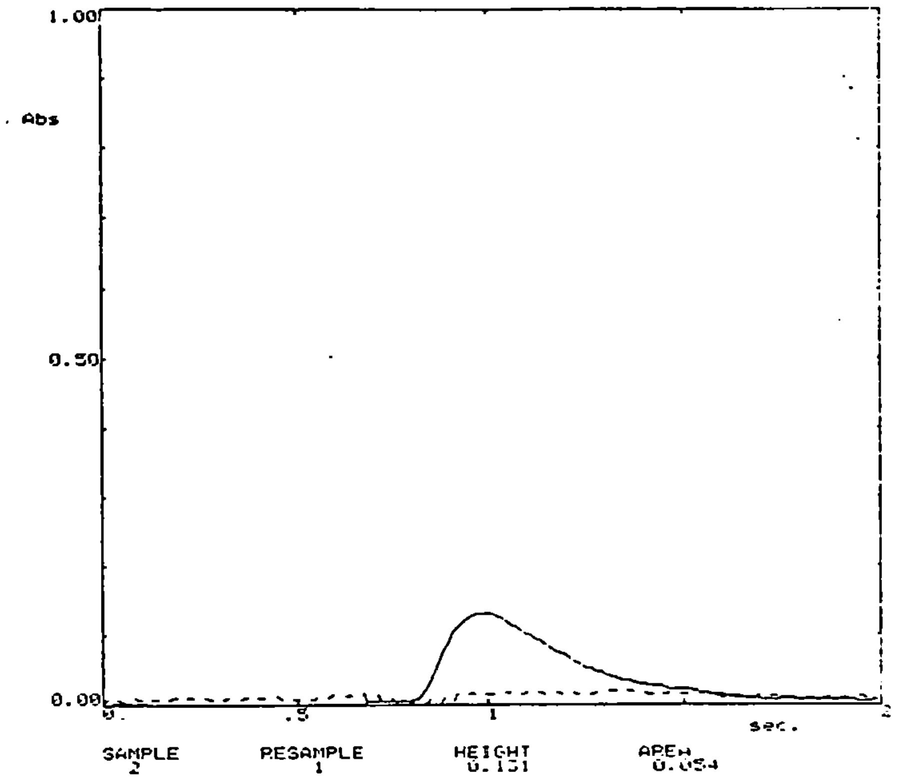


Fig. 4.2: Signal obtained for 15 ng ml^{-1} lead with hydrogen.

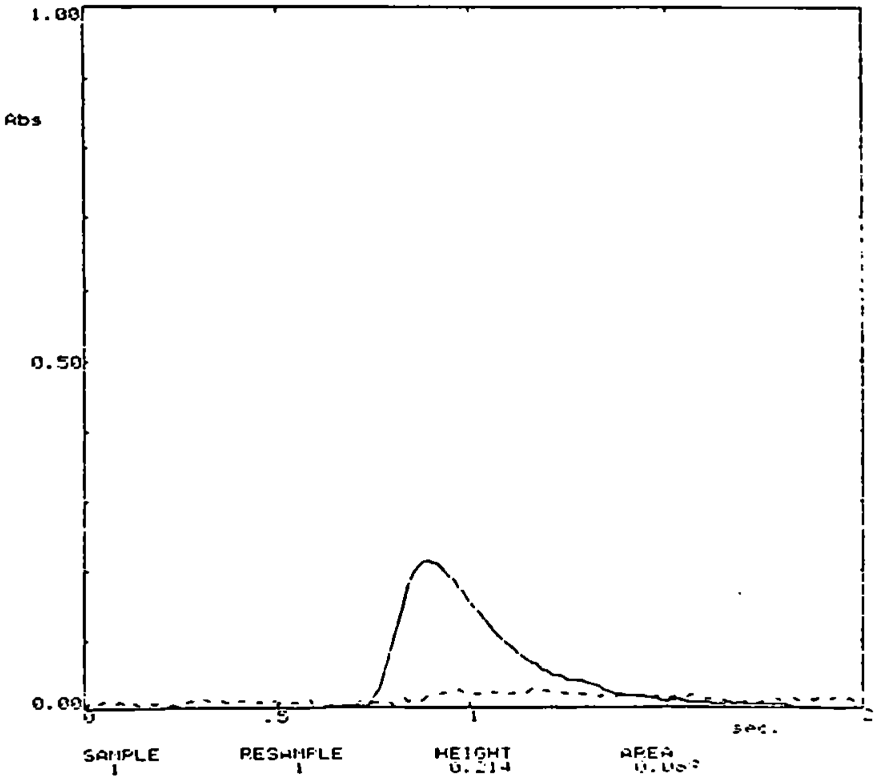


TABLE 4.4: GENERAL OPERATING CONDITIONS FOR THE VAPOUR PHASE TEMPERATURE MEASUREMENTS

Analyte	Lamp Current /mA	Bandpass /nm	Wavelength /nm	Concentration /ng ml^{-1}
Tin	5	0.5	286.3/284.0	100
Nickel	5	0.2	229.0/232.6	200/20
Lead	5	0.5	283.3/368.4	40/3000

20 µl injection

TABLE 4.5: FURNACE PROGRAMME FOR TIN

Stage	Temperature/°C	Hold Time/s	Ramp/°C s^{-1}
Dry	110	35	20
Ash	600	20	50
Atomise	2500	3	FP*
Clean	2700	3	FP*

*FP = Full Power

TABLE 4.6: FURNACE PROGRAMME FOR NICKEL

Stage	Temperature/°C	Hold Time/s	Ramp/°C s^{-1}
Dry	110	35	20
Ash	700	20	100
Atomise	2600	3	FP*
Clean	2700	4	FP*

*FP = Full Power

TABLE 4.7: FURNACE PROGRAMME FOR LEAD

Stage	Temperature/°C	Hold Time/s	Ramp/°C s^{-1}
Dry	110	35	20
Ash	450	20	50
Atomise	1800	3	FP*
Clean	2200	3	FP*

*FP = Full Power

$$\text{Tin: } T/^{\circ}\mathrm{C} = \frac{2143}{\log\left(4.9 \times \frac{\mathrm{ABS1}}{\mathrm{ABS2}} \times \frac{M2}{M1}\right)} - 273$$

where ABS1 and ABS2 are the absorbance readings obtained at 286.3nm and 284.0nm respectively, and M1 and M2 are the mass of the analyte injected for each measurement.

$$\text{Nickel: } T/^{\circ}\mathrm{C} = \frac{833}{\log\left(2.18 \times \frac{\mathrm{ABS3}}{\mathrm{ABS4}} \times \frac{M4}{M3}\right)} - 273$$

Where ABS3 and ABS4 are the absorbance readings obtained at 229.0 nm and 232.6 nm respectively, and M3 and M4 are the mass of analyte injected for each measurement.

$$\text{Lead: } T/^{\circ}\mathrm{C} = \frac{-\ 11259}{\ln\left(0.498 \times \frac{\mathrm{ABS5}}{\mathrm{ABS6}} \times \frac{M6}{M5}\right)} - 273$$

where ABS5 and ABS6 are the absorbance readings obtained at 283.3 nm and 368.4 nm respectively, and M5 and M6 are the mass of analyte injected for each measurement. All absorbance values used were the average of five measurements. The results shown in Table 4.8 show that the vapour phase temperature using argon is 60-150°C cooler than the indicated tube wall measurement. This is because the vapour temperature measurement is an average value, arising because of the thermal gradient along the tube (102). Since the tube has this temperature gradient, the vapour phase within it should also possess the gradient. Since the infra-red fibre-optic measures the tube wall temperature at its hottest part, ie. the middle, the value obtained for the

TABLE 4.8: THE EFFECT OF HYDROGEN ON THE GAS PHASE TEMPERATURE OF SEVERAL THERMOMETRIC SPECIES

Thermometric Species	Temperature without hydrogen/°C	Temperature with 100% hydrogen/°C
Sn	2329	1732
Ni	2492	2245
Pb	1738	1213

tube wall temperature is bound to be higher than the average gas phase temperature measured.

When hydrogen was introduced the vapour phase temperature was found to decrease significantly. This was in agreement with the earlier finding that lead appeared to have a decreased appearance temperature in the presence of hydrogen (Figs. 4.1 and 4.2), and is to be expected, because of the thermal conductivities of the gases. Hydrogen has a much higher thermal conductivity (1.815 mW cm^{-1} k^{-1}) than argon (0.1772 mW cm^{-1} k^{-1}) at 298.2 K (103). It is unclear why the vapour temperature for nickel is influenced less by the hydrogen than were the other two thermometric species.

4.4 Elimination of Interferences by the Addition of Hydrogen

4.4.1 Introduction

The introduction of hydrogen to the auto-zero stage just prior to atomisation might result in decreases in interferences. It has been found (104) that the addition of hydrogen to the inert gas decreased the background signal obtained during molybdenum analyses. The background arose due to the very high atomisation temperature, required for molybdenum, volatilising carbon particles from the tube into the light beam. The reduction in the background signal when hydrogen was introduced was ascribed to the removal of the particles by the formation of hydrocarbons. It therefore seemed likely that, by the same mechanism, the addition of hydrogen would substantially reduce the background signal obtained from samples with a highly carbonaceous matrix.

4.4.2 Procedure

Preliminary experiments designed to determine the efficiency of the procedure were performed using industrial grease samples. Grease (1g) was dissolved in white spirit to 100 ml. The resulting solution was analysed for iron using the operating conditions shown in Table 4.9 and the furnace programme shown in Table 4.10. The integrity of the procedure was validated by the analysis of some certified reference materials. Certified reference materials BCR 145 sewage sludge (European Community, Bureau of Community Reference, Brussels, Belgium) and Canmet SO-2 soil (Canada Centre for Mineral and Energy Technology) were slurried (0.5% and 2% w/v respectively) using the bottle and bead method described in Section 2.3.1. No dispersant was used.

4.4.3 Results and Discussion

The analysis of the grease samples in an argon atmosphere proved to be virtually impossible. Figures 4.3 and 4.4 show the iron signal obtained by wall atomisation without and with hydrogen. The deuterium background lamp was incapable of overcoming the excessive non-specific absorbance interference caused by the matrix, and hence no reliable atomic signal was obtained. In the presence of the hydrogen the background signal was reduced to a level where an atomic signal could be obtained. The use of platform atomisation

TABLE 4.9: OPERATING CONDITIONS FOR IRON DETERMINATIONS IN GREASE

Wavelength/nm	248.3
bandpass/nm	0.2
lamp current/mA	10
injection volume/μl	20

TABLE 4.10: FURNACE PROGRAMME FOR IRON DETERMINATIONS IN GREASE

Stage	Temperature/°C	Hold time/s	Ramp/°C s^{-1}
dry	130	35	50
ash	700	20	100
atomise	2400	3	*FP
clean	2600	3	*FP

*FP = Full Power

Fig. 4.3: Iron signal obtained without hydrogen from wall atomisation of a grease sample.

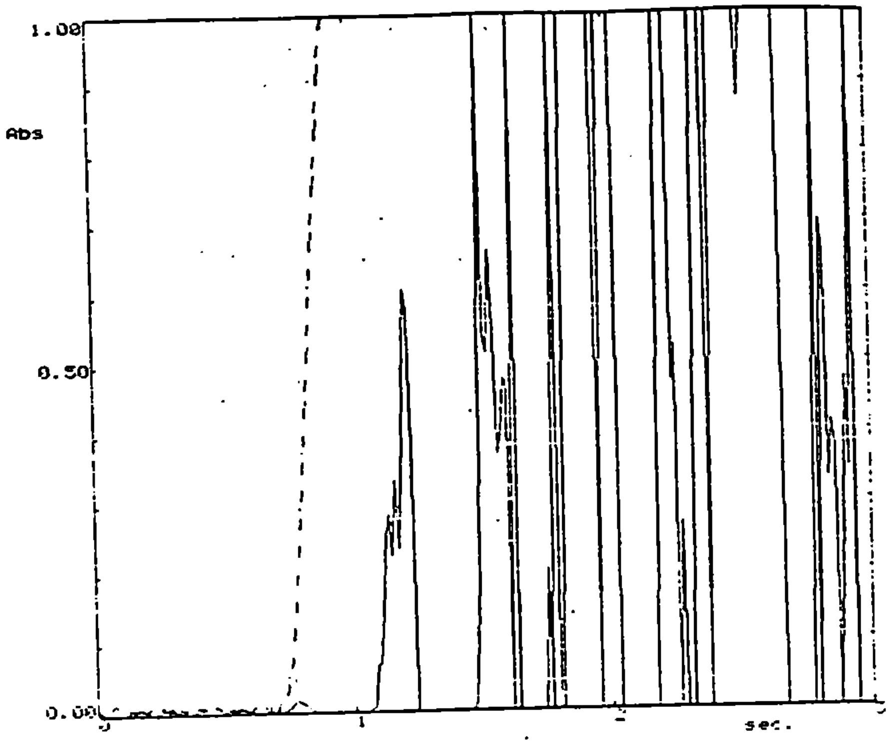
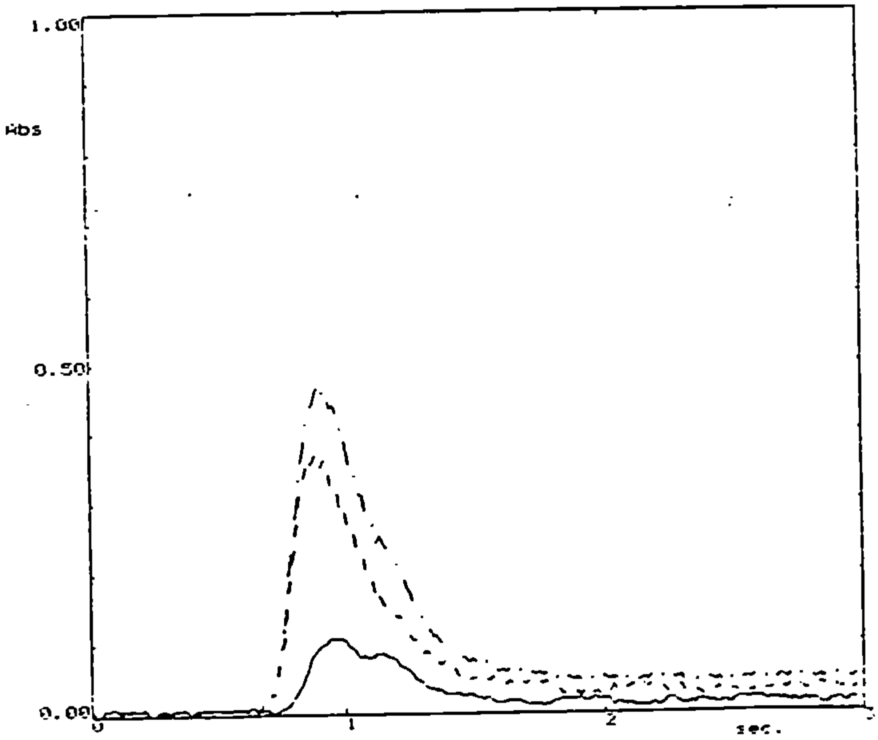


Fig. 4.4: Iron signal obtained with hydrogen from wall atomisation of a grease sample.



resulted in a further improvement in the signal to background ratio (Fig. 4.5). Without hydrogen the iron produced a very low, broad peak (Fig. 4.6). Comparing Figures 4.5 and 4.6 the extent to which the hydrogen decreased the smoke interferences, deceased the sensitivity of the analyte, decreased the appearance temperature and improved the peak shape becomes apparent. The improvement in peak shape may be readily explained in terms of the speed of diffusion of the atoms out of the light beam. Since in the presence of hydrogen the atoms diffuse out much faster than when they are in argon, the trailing edge of the peak, whose shape is diffusion controlled, returns to the baseline more rapidly.

The same decrease in background signal was found to occur when 10% v/v hydrogen in argon was used. The drop in sensitivity of the analytes was again found to be less severe than when 100% v/v hydrogen was used.

The certified reference materials were analysed for chromium, manganese and lead using the operating conditions shown in Table 4.11 and the furnace programmes shown in Table 4.12. As has been shown previously, air ashing removes many interferents. A comparison was therefore made between the use of argon, air and 10% v/v hydrogen. The results are shown in Table 4.13. The results indicate that air ashing was as efficient as hydrogen at overcoming smoke interferences in the sewage sludge but was far less efficient for the soil. The hydrogen would therefore seem

Fig. 4.5: Iron Signal obtained with hydrogen from platform atomisation of a grease sample.

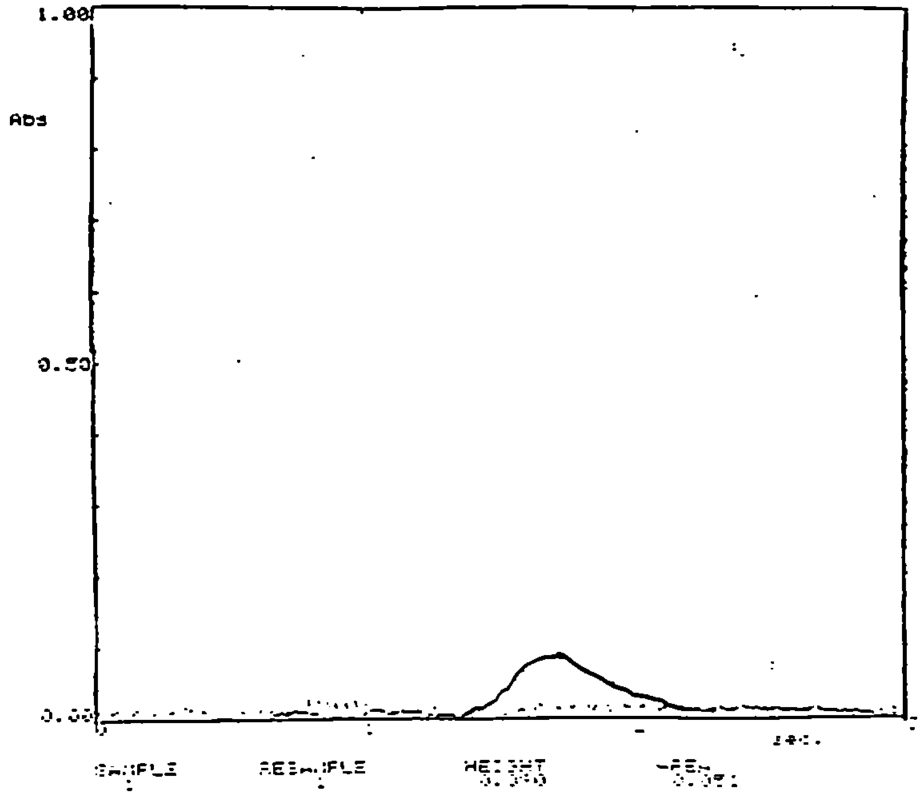


Fig. 4.6: Iron signal obtained without hydrogen from platform atomisation of a grease sample.

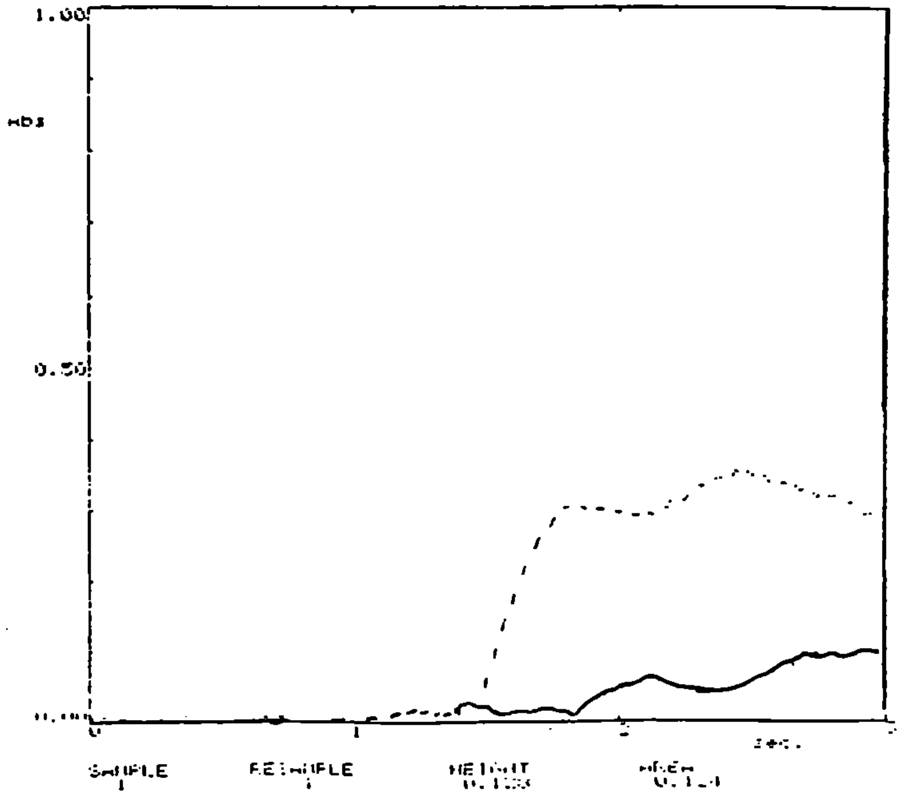


TABLE 4.11: OPERATING CONDITIONS USED FOR THE ANALYSIS OF SLURRIES

Analyte	Lamp Current /mA	Bandpass /nm	Wavelength /nm
Chromium	5	0.5	429.0
Manganese	5	0.5	403.0
Lead	5	0.5	368.4

injection volume = 20 μl

TABLE 4.12: FURNACE PROGRAMMES USED FOR THE ANALYSIS OF SLURRIES

Analyte	Stage	Temperature/°C	Hold time/s	Ramp/°C s^{-1}
Chromium	Dry	110	35	20
	Ash	800	30	100
	Atomise	2500	3	FP*
	Clean	2600	3	FP*
Manganese	Dry	110	35	20
	Ash	800	30	50
	Atomise	2400	3	FP*
	Clean	2500	3	FP*
Lead	Dry	110	35	20
	Ash	500	30	50
	Atomise	1800	3	FP*
	Clean	2200	3	FP*

*FP = Full power

For the air ash analyses, a second ash stage at the same temperature was used to remove air from the tube.

TABLE 4.13: RESULTS OBTAINED FOR THE ANALYSIS OF SLURRIES

Material	Analyte	Cert Value /µg g^{-1}	Result obtained with		
			Argon/µg g^{-1}	10% H_2/µg g^{-1}	Air ash/µg g^{-1}
BCR 145	Cr	(105)	131 ± 10	125 ± 8	131 ± 14
Sewage sludge	Mn	241 ± 12	212 ± 8	241 ± 12	235 ± 10
Canmet-SO-2	Cr	16 ± 2	38 ± 10	18 ± 2	35 ± 2
Soil	Pb	21 ± 4	15.5 ± 1	22 ± 7	18 ± 2

n = 5 Results ± 2σ ( ) reference value to be necessary to obtain an accurate result for these analytes, under these conditions, for these matrices.

4.4.4 Conclusions

The addition of 100% v/v hydrogen to the auto-zero stage just prior to the atomise stage leads to a greatly decreased background signal from samples with an organic matrix. Unfortunately it also results in a loss of sensitivity, which for some elements is severe. The use of 10% v/v hydrogen also leads to a greatly reduced background signal, but the atomic signal is affected to a lesser extent. The introduction of 5% or 2% v/v hydrogen still resulted in a reduction of background signal, however, no further improvement in atomic signal was obtained.

4.5 Overcoming Chloride Interferences

4.5.1 Introduction

As was described in Section 4.1, there is some disagreement as to whether or not the introduction of hydrogen ameliorates the interference by chloride ions on lead determinations. Volatile lead chloride species are formed below 400°C, and species such as PbCl vaporise away at very low temperatures (23). A brief study was therefore performed to determine if the hydrogen alone would be sufficient to remove the chloride from the furnace in the form of HCl.

4.5.2 Procedure

A lead standard (15 ng ml^{-1}) prepared by serial dilution of 1000 μg ml^{-1} stock standard (Spectrosol, BDH) was injected into a graphite tube, and the absorbance measured using the temperature programme for lead given in Table 4.14. A lead standard prepared in the same way, but containing 0.05% m/v sodium chloride (AnalaR, BDH) was also analysed using this programme. Both analyses were repeated in the presence of hydrogen in the ash stage. Platform atomisation was used in all cases.

4.5.3. Results and Discussion

The peak profiles obtained without and with hydrogen and without and with sodium chloride, are shown in Figures 4.7 and 4.8, and 4.9 and 4.10, respectively. The background level was not significantly reduced in the presence of hydrogen, indicating that the chloride ions were not being removed as HCl. It has been reported (105) that the chloride may be removed as HCl at temperatures in excess of 600°C. Since the maximum recommended ashing temperature of lead is 600°C (106) it would seem necessary to prevent the volatilisation of lead by the addition of a thermal stabilising agent, eg. ammonium phosphate. It was therefore concluded that in the furnace system used, and under these operating conditions, hydrogen alone was not sufficient to eliminate sodium chloride interferences on lead determinations. Inspection of an Ellingham diagram for chlorides (107) shows that hydrogen is capable of reducing copper and silver chlorides at relatively low temperatures.

TABLE 4.14: FURNACE PROGRAMME USED TO INTRODUCE HYDROGEN TO DECREASE CHLORIDE INTERFERENCE ON LEAD DETERMINATIONS

Stage	Temperature/°C	Hold time/s	Ramp/°C s^{-1}
Dry	180	35	30
Ash	600	30	50
Atomise	2000	3	FP*
Clean	2000	3	FP*

*FP = Full Power

Fig. 4.7: Lead signal obtained from a platform without sodium chloride or hydrogen.

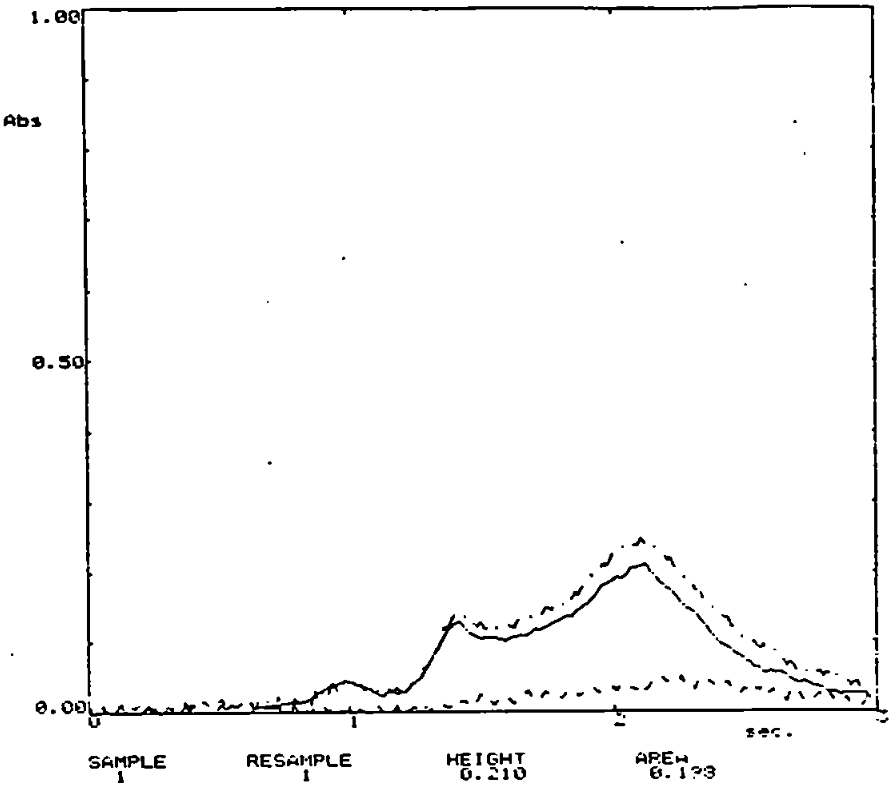


Fig. 4.8: Lead signal obtained from a platform without sodium chloride but with hydrogen.

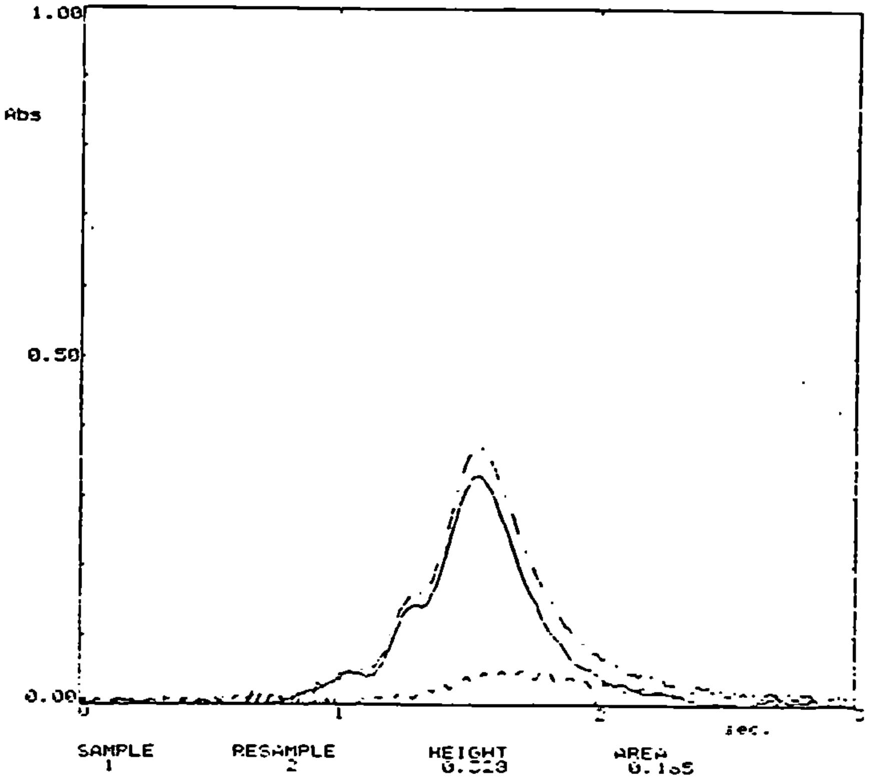


Fig. 4.9: Lead signal obtained from a platform with sodium chloride but without hydrogen.

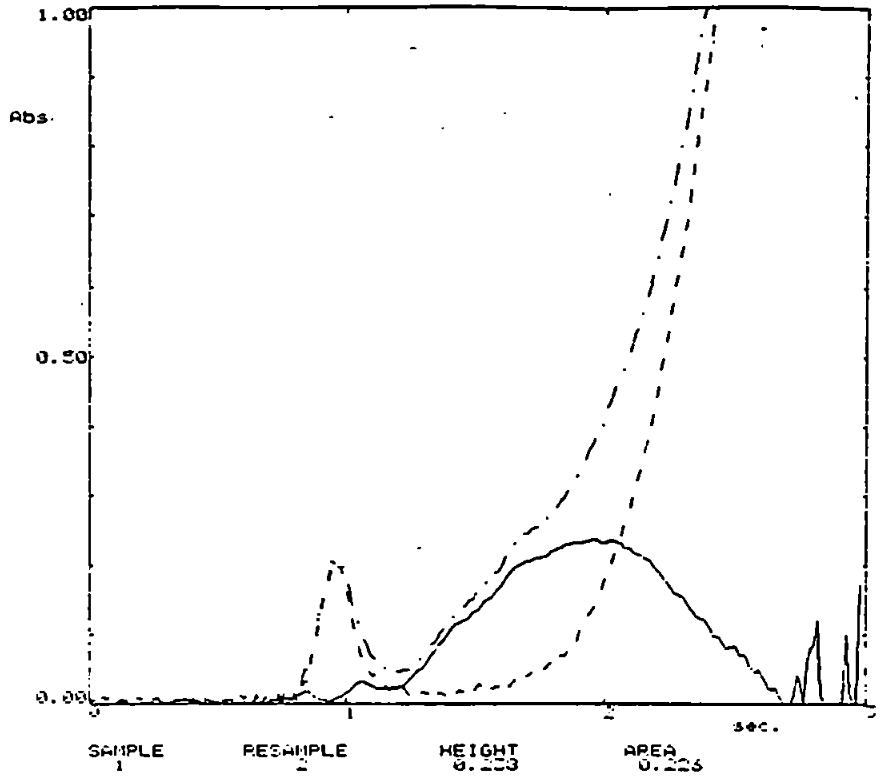
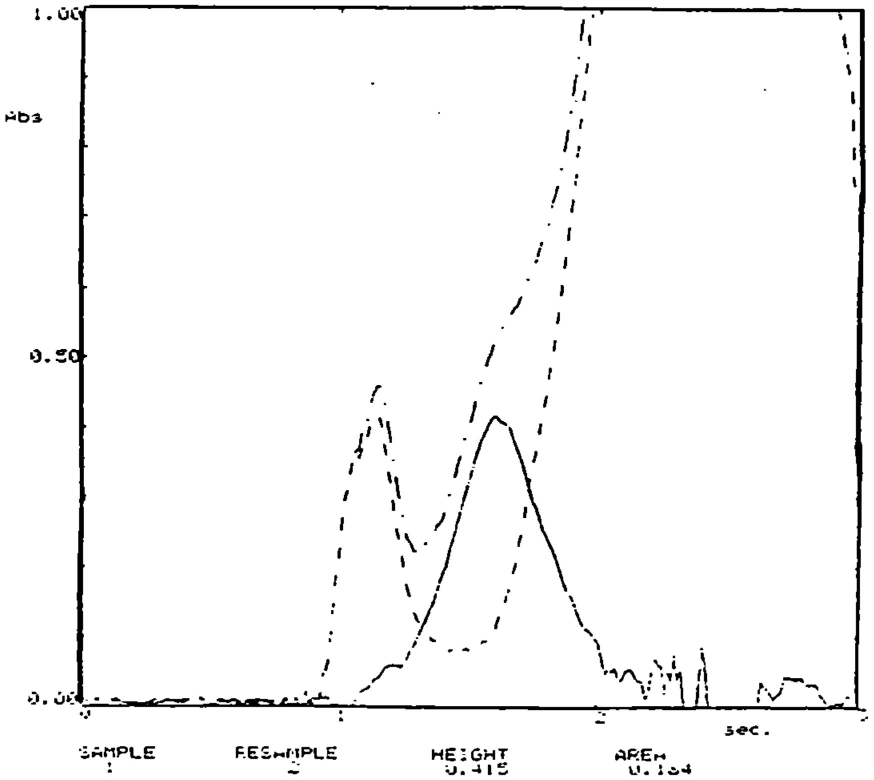


Fig. 4.10: Lead signal obtained from a platform with sodium chloride and hydrogen.



Other chlorides may be reduced at elevated temperatures eg. chromium and iron chlorides at about 1000°C. Sodium chloride appears not to be reduced by hydrogen until extremely high temperatures, and it would therefore seem unlikely that hydrogen should be capable of removing chloride interferences if they are present as the sodium salt. This is in agreement with the observations of Frech and Cedergren (96, 98).

4.6 General Conclusions

The use of hydrogen has been shown to have numerous advantages in ETAAS. It has been demonstrated that if used during the ash stage, it leads to a small signal enhancement for several refractory analytes and also for analytes such as lead. It has also been shown that it is extremely efficient at the removal of background signals arising from carbonaceous matrices, by a mechanism that may well involve the formation of hydrocarbons. It was, however, less successful in overcoming the inorganic matrix interference of chloride on lead; because insufficiently high ash temperatures could be used. Had chlorides, other than sodium chloride, been used, then the hydrogen may have been more successful.

CHAPTER 5: THE USE OF ORGANOPHOSPHORUS VAPOURS TO THERMALLY STABILISE CADMIUM

5.1 Introduction

Cadmium is known to induce toxic effects in certain organisms at low concentrations. Therefore, analyses for cadmium in a variety of matrices by electrothermal atomisation - atomic absorption spectrometry (ETAAS) has become common (57, 108-111). Serious problems may be encountered during the analyses due to the very high volatility of cadmium. This means that the matrix constituents may not be readily removed during the ash stage, and hence non-specific absorbance interference may seriously affect the analytical signal. To overcome this problem, a number of matrix modifiers have been used to thermally stabilise the cadmium. These modifiers include alcoholic potassium hydroxide (109), ammonium oxalate, to aid the volatilisation of chloride ions (110), lanthanum-nitric acid (112), magnesium nitrate (113), palladium-magnesium nitrate (114, 115) and palladium-ammonium nitrate (116). The most common matrix modifier used for cadmium has been ammonium phosphate (57, 117). Unfortunately, the use of many of these modifiers may give rise to several disadvantages. The lanthanum modifier has been found to have a corrosive effect on the graphite tubes, which curtails their useful lifetime (115). The palladium modifiers are expensive, and the ammonium phosphate is often not available in a state of high enough purity (115) and may give rise to elevated background signals (113). An inexpensive, contamination free, gaseous matrix modifier would go some way to ameliorating the disadvantages, while still possessing the thermal stabilising properties.

5.2 Experimental

5.2.1 Reagents and Standards

A 1000 µg ml^{-1} standard of cadmium, as the nitrate, (Spectrosol, BDH Chemicals Ltd), was used as the stock standard. Various organic liquids with a relatively high vapour pressures were used as prospective matrix modifiers. These were tri-ethyl phosphite (GPR, BDH), tri-ethyl phosphate (GPR, BDH), and tri-methyl phosphite (97% Aldrich).

5.2.2 Instrumentation

All analyses were performed using an atomic absorption spectrometer (PU 9100X, Philips Scientific), fitted with an electrothermal atomiser (PU 9390X, Philips Scientific) and a data station (PU 9178X Philips Scientific). A Dreschel bottle containing the modifier under investigation was placed in the gas line between an argon source and one of the alternative gas inlets of the electrothermal atomiser. Electrographite tubes were used throughout, and electrographite platforms used for some analyses. Sample introduction was used by hand-held micro-pipette.

5.3 Preliminary Experiments

5.3.1 Procedure

Initially, ash plots were constructed for a 1 ng ml^{-1} cadmium standard in the absence of any modifier, in the presence of tri-ethyl phosphite, then tri-ethyl phosphate and finally, tri-methyl phosphite. The furnace programme and the analytical operating conditions are shown in Tables 5.1 and 5.2 respectively. The vapours were introduced during the dry and ash stages.

5.3.2 Results and Discussion

Figure 5.1 shows the ash plots obtained for cadmium from wall atomisation in the presence of each modifier, and in the absence of any modifier. All three organic liquids stabilised the cadmium but to different extents. Without any modifier, the maximum ash temperature was only 450°C, but the use of tri-ethyl phosphite vapour stabilised the cadmium to temperatures of up to 700°C. The extent to which the cadmium was modified by the different vapours was determined by the hydrolytic properties of the vapour. Tri-ethyl phosphite hydrolyses in moist air, whereas the tri-ethyl phosphate hydrolyses only slowly in the presence of water (118). By introducing the vapours during the dry and ash stages of the furnace cycle, the tri-ethyl phosphite should readily hydrolyse, depositing modifying species in the graphite tube. These may then interact with the cadmium ions, which are consequently thermally stabilised. The tri-ethyl phosphate only partially hydrolyses and hence, it has less of a stabilising effect.

TABLE 5.1: FURNACE PROGRAMME USED FOR THE ASH PLOTS FOR CADMIUM BY WALL ATOMISATION

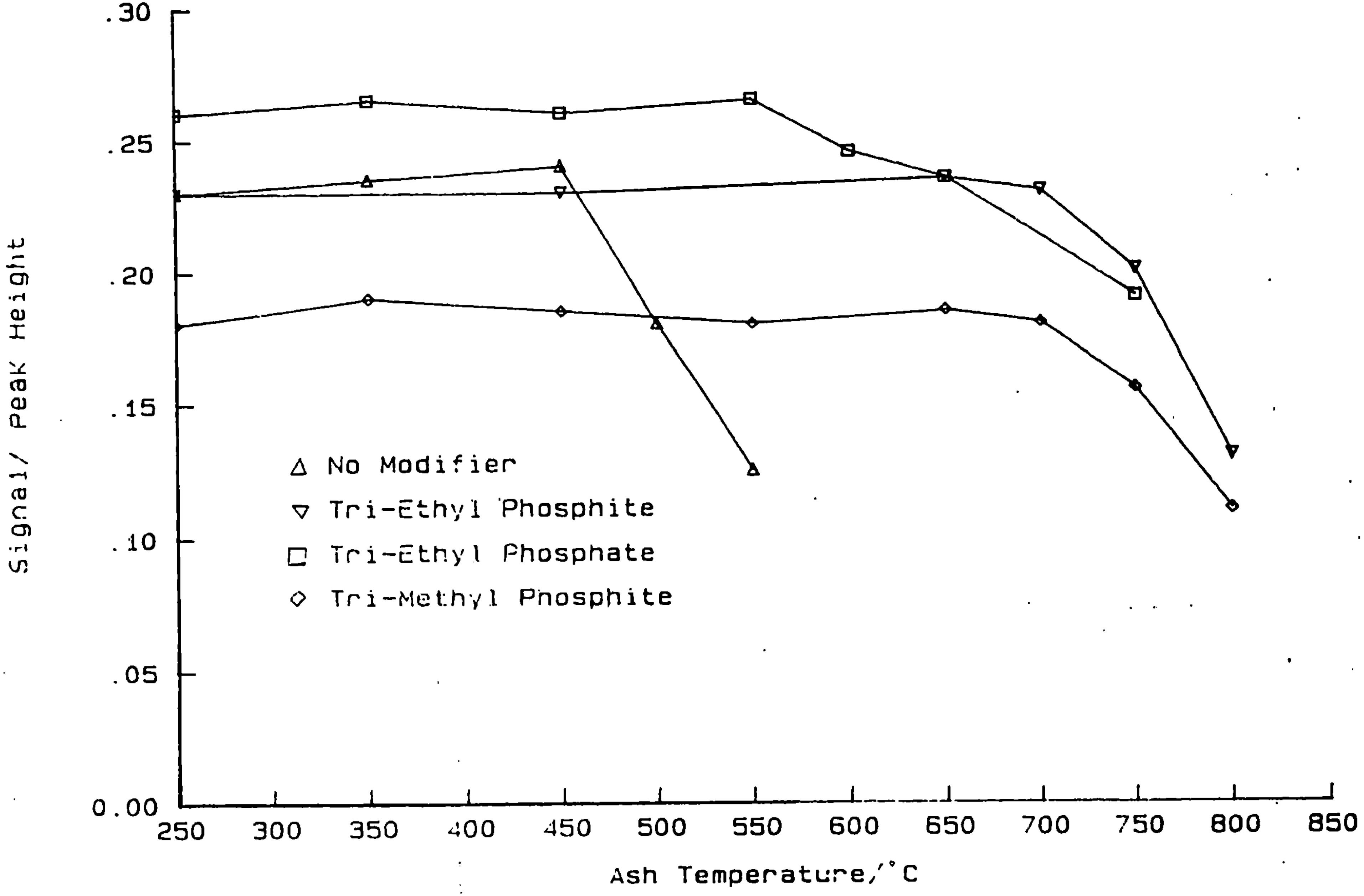
Stage	Temp/°C	Hold time/s	Ramp/°C s^{-1}
Dry	110	35	20
Ash	-	20	50
Atomise	1600	2.5	FP*
Clean	1800	3	FP*

* FP = Full Power

TABLE 5.2: ANALYTICAL OPERATING CONDITIONS FOR CADMIUM ANALYSES

Wavelength	228.8 nm
Lamp current	4 mA
Bandpass	0.5 nm
Injection volume	20 µl

Fig 5.1 Ash Plots Of Cadmium With Different Modifiers. No Platform.



Tri-methyl phosphite was used because it could be expected to have a higher vapour pressure than the ethyl derivative. It should therefore be more efficient in transporting modifying species to the furnace. Its powerful smell seemed to confirm that it does have a higher vapour pressure. The results obtained show that it was no more efficient at stabilising the cadmium than the ethyl derivative, indicating that either it may not be so readily hydrolysed or, the amount of tri-ethyl phosphite vapour reaching the tube is sufficient to induce the maximum modifying effect. In addition to that, the use of tri-methyl phosphite also resulted in a loss of sensitivity which could not be readily explained.

For all three modifiers there was found to be no increase in the blank signal, indicating that the vapour reaching the graphite tube was cadmium free.

5.4 The Use of Platform Atomisation

5.4.1 Introduction and Procedure

Since the use of a platform is one of the pre-requisites of the Stabilised Temperature Platform Furnace (STPF) concept, and that the majority of cadmium analyses are performed using one, it was necessary to repeat some of the work using platform atomisation. Since the tri-ethyl phosphite was found to be far superior to the tri-ethyl phosphate in its ability to stabilise cadmium, and was considerably less pungent and, unlike tri-methyl phosphite, did not lead to a loss of sensitivity, it was decided that tri-ethyl phosphite should be the only organic liquid to be used in these experiments.

Ash plots for 1 ng ml^{-1} cadmium with no modifier, with tri-ethyl phosphite and with ammonium phosphate 'wet chemical' modifier were constructed. The analytical operating conditions are given in Table 5.2. The furnace programme used for no modifier and the tri-ethyl phosphite are given in Table 5.3. The furnace programme for the ammonium phosphate plot is given in Table 5.4. The procedure during this plot was to inject the cadmium standard, dry it, allow the furnace to cool and inject 1% ammonium phosphate (AnalaR, BDH Chemicals Ltd) on top, during a cool stage.

5.4.2 Results and Discussion

The ash plots obtained are shown in Figure 5.2. As expected, the use of a platform enabled a higher ash temperature to be used with no modifier present (550°C cf 450°C from wall atomisation). The presence of either of the modifiers enabled the use of ash temperatures of 900-950°C, indicating that the gaseous modifier was as efficient as its 'wet chemical' counterpart. However, the use of ammonium phosphate lead to an increased cadmium signal in both a standard and a blank. The amount of cadmium originating from the standard was 0.02 ng, indicating that the amount added as a contaminant by the modifier was approximately 0.004 ng. Such an amount is obviously undesirable if

TABLE 5.3: FURNACE PROGRAMME FOR ASH PLOTS FOR CADMIUM USING PLATFORM ATOMISATION

Stage	Temp/°C	Hold time/s	Ramp/°C s^{-1}
Dry	180	35	30
Ash	-	20	50
Atomise	2000	3	FP*
Clean	2200	4	FP*

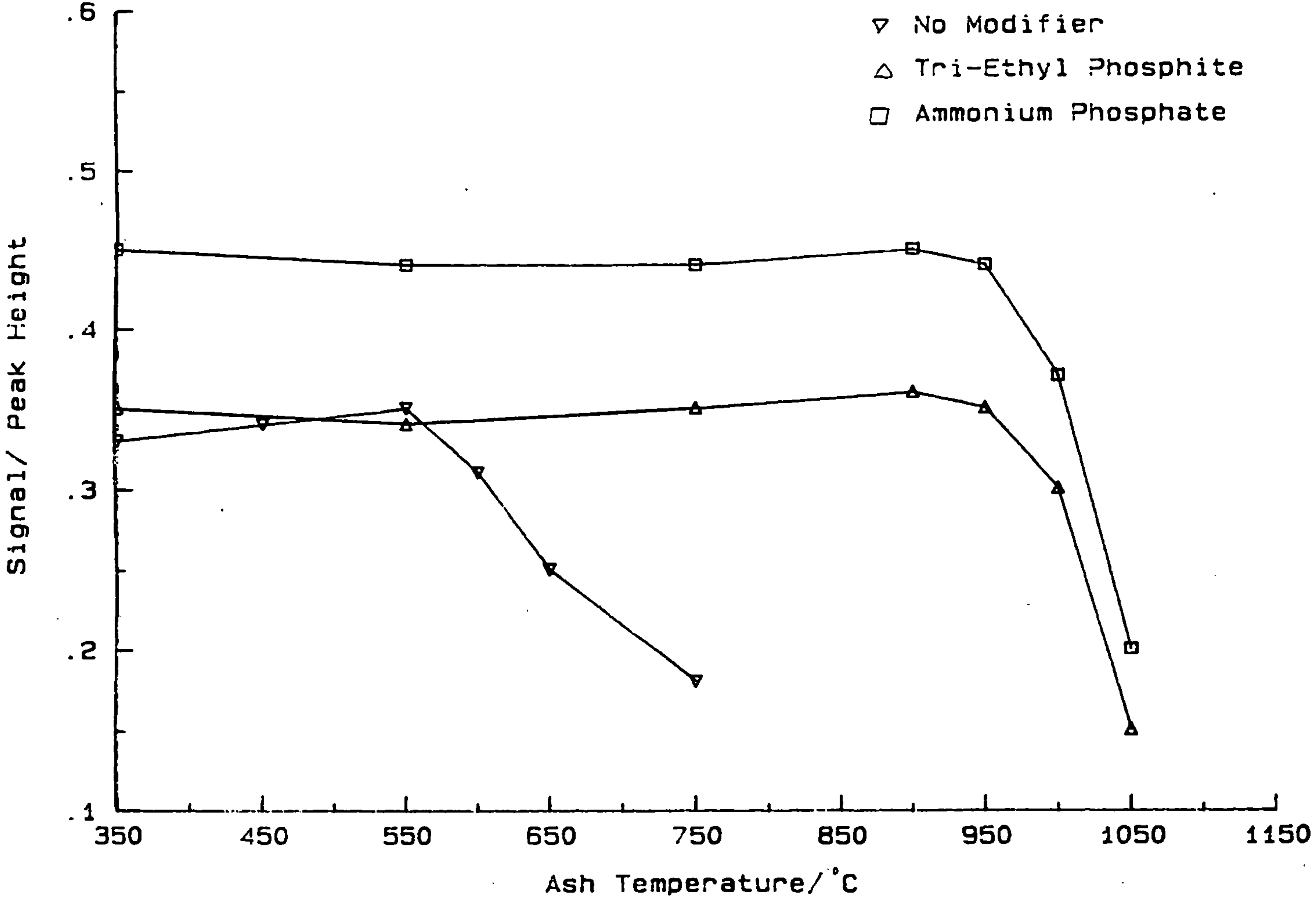
* FP = Full Power

TABLE 5.4: FURNACE PROGRAMME FOR ASH PLOTS FOR CADMIUM USING A PLATFORM AND AMMONIUM PHOSPHATE MODIFIER

Stage	Temp/°C	Hold time/s	Ramp/°C s^{-1}
Dry	180	35	30
Cool	20	20	-
Dry	180	35	30
Ash	-	20	50
Atomise	2000	3	FP*
Clean	2200	4	FP*

*FP = Full Power

Fig. 5.2 Ash Plots For Cadmium From a Platform.



analyses close to the detection limit are to be performed.

5.5 Evaluation of the Method

Having established that aqueous cadmium standards may be thermally stabilised by tri-ethyl phosphite vapour, it was necessary to evaluate the method with real samples. Certified reference materials NIES 5 hair and NIES 9 Sargasso (National Institute for Environmental Science, Yatabe-Machi, Tsukuba, Iberaki, Japan) were chosen to validate the method.

5.5.1 Preparation of CRM Digests

Material (approximately 0.2g) was weighed accurately into acid washed PTFE bomb receptacles. Nitric acid (2 ml, Aristar, BDH Chemicals Ltd) was then added, and the receptacles were fastened securely in the stainless steel bomb cases. These were then heated to 105°C in an oven for two hours. After cooling, perchloric acid (0.5 ml, AnalaR, BDH) was added to the receptacles which were then refastened in the cases, and replaced in the oven for a further hour. After cooling, the contents were transferred quantitatively into acid washed 25 ml volumetric flasks, and diluted to volume with de-ionised water. A blank was prepared in a similar fashion, but omitting the reference material.

Moisture contents were determined in the manner specified on the certificates (85°C for 4 hours).

5.5.2 Procedure

Ash plots of the digests from wall atomisation, were constructed to ensure that the tri-ethyl phosphate would thermally stabilise cadmium in real samples as well as aqueous standards. The analytical operating conditions and the furnace programme used are shown in Tables 5.2 and 5.1 respectively. The optimum ash temperature thus found was then used for the analysis of the samples.

5.5.3 Results and Discussion

The results obtained for the ash plots for the materials NIES 5 (hair) and NIES 9 (Sargasso) indicate that for both materials a maximum ash temperature of 700°C may be used in the presence of the modifiers, but only 600°C in its absence. The results for hair are shown in Figure 5.3. Since the maximum ash temperature for an aqueous standard in the absence of any modifier was only 450°C, it would appear that the matrix was exerting a stabilising effect on the cadmium. Presumably this was due to the presence of phosphate ions in the matrix. The results, based on peak area measurements, obtained from the analysis of the materials using ash temperatures of 700°C are shown in Table 5.5. Reasonable agreement with the certified values were obtained indicating that cadmium may be determined accurately in these samples using tri-ethyl phosphite vapour as a matrix modifier. Since accurate results were obtained from wall atomisation, it was unnecessary to use a platform, indicating that sufficient interfering species had been removed during the ash stage.

Fig. 5.3 Ash Plots For Certified Reference Material Hair.

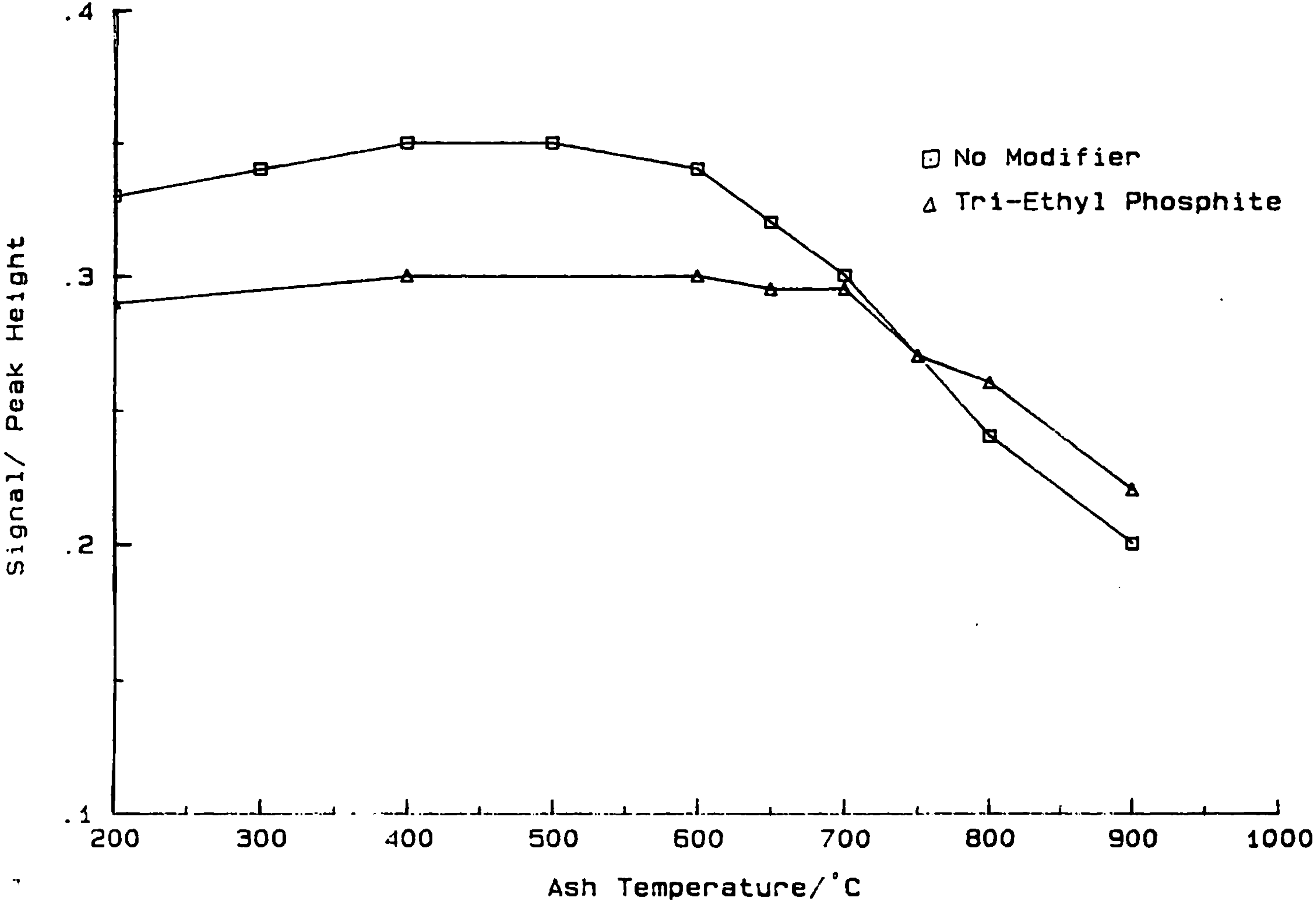


TABLE 5.5: RESULTS FOR THE ANALYSIS OF CERTIFIED REFERENCE MATERIALS

Material	Certified Value/$\mu g\ g^{-1}$	Value Obtained /$\mu g\ g^{-1}$
NIES 5 Hair	0.2 ± 0.03	0.2 ± 0.02
NIES 9 Sargasso	0.15 ± 0.02	0.122 ± 0.02

5.6 General Conclusions

Due to the extremely volatile nature of many of its compounds, matrix modification has become almost compulsory for cadmium determinations. The use of 'wet chemical' modifiers for cadmium are fraught with problems since they usually contain cadmium as a trace contaminant, which results in an erosion of detection limits. Tri-ethyl phosphite vapour has been used successfully to thermally stabilise cadmium to temperatures comparable with its 'wet chemical' counterparts, but without the concomitant problems of cadmium contamination. Other organic vapours have also been found to exert a stabilising effect on cadmium, but in some cases, eg. tri-ethyl phosphate to a lesser extent, and in others, eg. tri-ethyl phosphite, to the same extent, but result in a loss of sensitivity, and also because of their foul smell, were unpleasant to use.

The method of modification by tri-ethyl phosphite has been validated by the analysis of two certified reference materials using ash temperatures higher than normal. The results obtained were in reasonable agreement with the certified values.

CHAPTER 6: THE USE OF HALOGENATED MATRIX MODIFIERS

6.1 Introduction

Halogenated compounds have been used by Kirkbright et al. (119, 120) to assist in the vaporisation of refractory elements from graphite rods into an inductively coupled plasma (ICP). The formation of the volatile analyte halide species resulted in increased sensitivity of up to two orders of magnitude for many analytes, and a linear working range of four orders of magnitude. The mechanism by which the enhanced sensitivity was obtained was postulated to be a reduction in the amount of stable carbide formation on the graphite rod caused by the preferential formation of the halide species. These were then volatilised more efficiently into the plasma.

In electrothermal atomic absorption Spectroscopy (ETAAS), the use of halogenated modifiers has not received much attention. Ericson et al. (121) and Bermejo-Barrera et al. (44) have both used barium difluoride as a matrix modifier for molybdenum determinations, with the result of decreased appearance temperature, increased sensitivity and decreased matrix interference effects. In addition, the decreased appearance temperature enabled extended tube life-time.

Silicon is another analyte that has been modified by halogenated compounds. Nater and Burau (45) used alkali metal fluorides to react with silicon producing metal-hexafluorosilicates which subsequently dissociated rapidly in the gas phase. Kantor and Alvarez-Prieto (122) determined trace amounts of silicon by the addition of either trichlorotrifluoroethane, ($C_2Cl_3F_3$) or copper hydroxyfluoride (CuOHF) into a furnace, followed by atomisation of the evolved silicon tetrafluoride in a nitrous-oxide - acetylene flame. Copper hydroxyfluoride has also been used for boron determinations (123). Hydrogen fluoride, caesium fluoride and copper fluoride have also been used to increase the sensitivity and decrease the appearance temperature of aluminium (124).

Halogenated compounds have also been used to separate the matrix from analytes thereby facilitating their determination (125). By passing hydrogen chloride gas over gallium at 120-165°C, the matrix could be removed as gallium trichloride, and the impurities in gallium could be determined by ETAAS. Separation of the matrix from trace impurities by volatilisation has also been accomplished by Bachmann (126).

Halogens and halogenated gases have been used by manufacturers to purify graphite tubes (127). By heating the tubes in the presence of freon, the refractory impurities may be removed as their volatile fluorides. However, it has been reported (128) that halogens become intercalated, _ie_. they move between the planes of the graphite lattice and become tightly bound in large quantities. This has been proposed as an explanation of why some batches of new tubes initially exhibit poor sensitivity. The intercalated halogen is released in subsequent firings.

Freon 23 (Tri-fluoromethane) has been used as an alternative gas in ETAAS by Welz and Schlemmer (129). However, they found that although the fluorides were readily formed, the analytical signal was found to decrease markedly, indicating failure of the analyte fluoride to dissociate. There would therefore appear to be some disagreement over the analytical usefulness of halogenated compounds as matrix modifiers for ETAAS.

6.2 Experimental

6.2.1 Reagents and Standards

Matrix modifiers such as dichloromethane (AnalaR), chloroform (AnalaR) and iodine (Laboratory Reagent), were obtained from BDH, (BDH Ltd., Poole, UK.). Carbon tetrachloride (Technical grade) was obtained from M and B (May and Baker Ltd, Dagenham, UK), and a 2% v/v mix of Freon 23 in argon was obtained from BOC (BOC Special Gases, London, UK). Stock standards (1000 $\mu g\ ml^{-1}$) were obtained from BDH (Spectrosol, BDH Ltd., Poole, UK).

6.2.2 Instrumentation

All work was performed on either an atomic absorption spectrometer (SP9, Philips Scientific) fitted with a video furnace programmer (PU 9095, Philips) and a furnace atomiser (SP9 Philips), or an atomic absorption spectrometer (PU

9100X, Philips Scientific) fitted with an electrothermal atomiser (PU 9390X, Philips) and a data station (PU 9178X, Philips). Pyrolytically coated tubes were used throughout. Samples were introduced to the furnace manually by hand held micropipette (Gilson).

6.3 Preliminary Experiments

6.3.1 Procedure

Following the reported success of barium difluoride and alkali metal fluorides as matrix modifiers for molybdenum (121, 44) and silicon (45) respectively, it was thought possible that other refractory analytes should also form volatile fluorides. A gaseous modifier such as freon 23 was found not to work for titanium (129), but this was still used as a matrix modifier during the construction of ash/atomise curves for aluminium. The furnace programme and operating conditions used are detailed in Tables 6.1 and 6.2 respectively.

6.3.2 Results and Discussion

The results obtained for the ash/atomise curves for aluminium with and without 2% freon 23 introduced during the ash or atomise stages are illustrated in Fig. 6.1. It can be seen that a considerable loss of sensitivity resulted. Introduction of freon during the ash stage resulted in analyte loss at considerably lower temperatures than normal, indicating that aluminium fluorides were being formed, and were vaporising away. Closer inspection of the atomise

TABLE 6.1: FURNACE PROGRAMME USED FOR THE CONSTRUCTION OF ASH/ATOMISE CURVES FOR ALUMINIUM WITH AND WITHOUT FREON 23

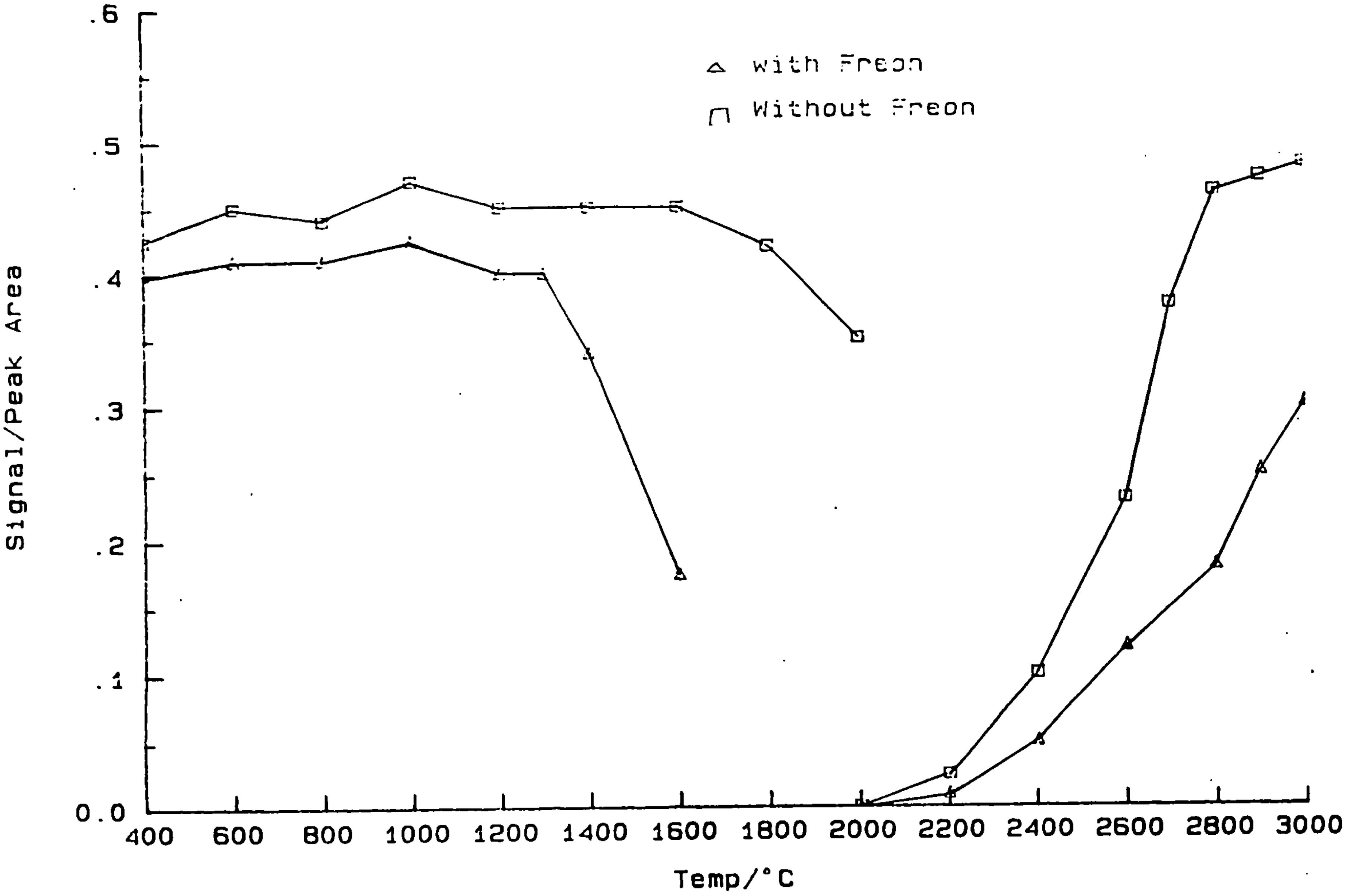
Phase	Temp/°C	hold time/s	Ramp/°C s^{-1}
dry	110	30	20
ash	400 or varied	15	50
atomise	2800 or varied	4	FP*
clean	2900	3	FP*

* FP = Full Power

TABLE 6.2: OPERATING CONDITIONS USED FOR ASH/ATOMISE PLOTS FOR ALUMINIUM

Wavelength/nm	309.3
bandpass/nm	0.5
lamp current/mA	10
injection volume/µl	20

Fig. 6.1 Ash/Atomise Curves for Aluminium With And Without 2% Freon 23.



curve in which freon was present reveals that the signal was still increasing as the temperature was increasing. Even at 3000°C, complete atomisation was not achieved. Inspection of the bond energies of the species of interest provides an explanation of the results. The energy for Al-F is 663.6 kj mol^{-1} and for Al-O it is 500 kj mol^{-1} (103). This implies that the aluminium fluoride molecule is likely to be considerably more stable than aluminium oxide. This would appear to be at odds with the results of Nater _et_ _al_. (124) who claimed that aluminium fluoride molecule dissociated rapidly and more readily than aluminium oxide. A reason for this discrepancy is not readily available. Although the bond energy for Al-C could not be found, it was reported to sublime at 1400°C and to decompose at temperatures in excess of 2200°C (103), and as such should not detract too much from the sensitivity at the atomise temperatures used. It was therefore concluded that although the analyte fluoride was formed, it failed to dissociate again. Very similar results were obtained for vanadium. It would therefore appear that aluminium and vanadium behave in a similar fashion to titanium (129).

The use of other halogenated materials such as carbon tetrachloride, chloroform or dichloromethane was then attempted. It has been reported (119) that carbon tetrachloride thermally decomposes to CCl_3 and Cl at temperatures of between 300-500°C, and readily transfers the liberated chloride to various analytes. The bond strength for Al-Cl is considerably less than for Al-F (494 kj mol^{-1}

cf 664 kj mol^{-1}) (103). The aluminium chloride formed during the decomposition of the chlorocarbon could therefore be expected to be more readily dissociated than the fluoride analogue.

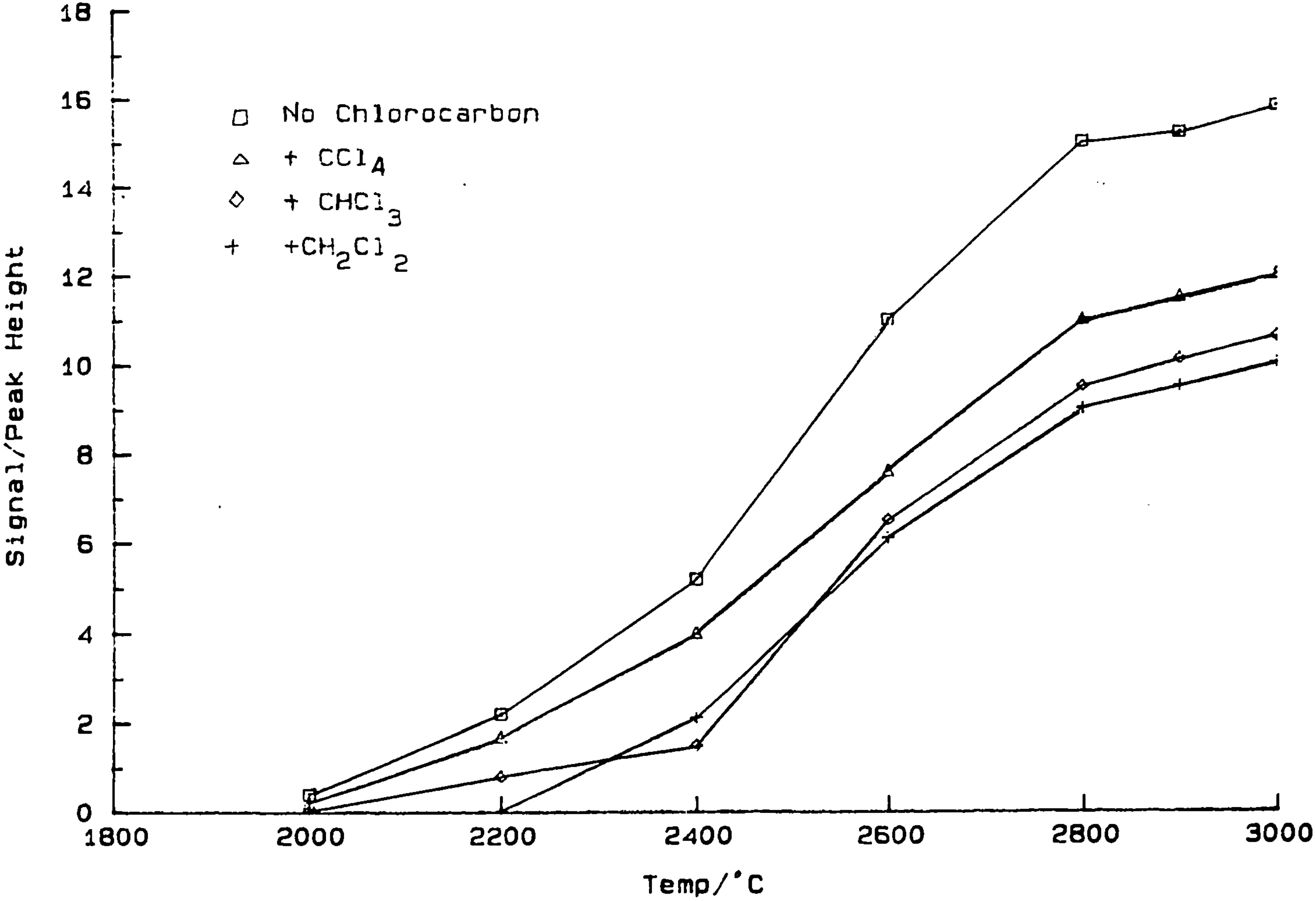
The chlorocarbon was placed in a Dreschel flask placed in the gas line, as described in Section 5.2.1. In initial experiments using these compounds, the quartz windows in the SP9 furnace head became misted, and needed to be cleaned every 8-10 firings. This was obviously undesirable, and to prevent the problem from recurring, the windows were removed. Atomise plots for 10 ng ml^{-1} aluminium were constructed in the presence of each chlorocarbon using the furnace programme detailed in Table 6.3. Measurement was at the aluminium 309.3 nm line using a lamp current of 10mA, and a spectral bandpass of 0.5 nm. The results obtained are shown in Fig. 6.2. To some extent, the use of chlorocarbons all led to a loss of sensitivity. Again, it can be seen that the atomise curves in which the chlorocarbon modifiers were used did not plateau, ie. they never reached a temperature at which atomisation was optimal. It can also be seen that the magnitude of the loss of sensitivity differed between each chlorocarbon. This may be a function of the differing vapour pressures of the chlorocarbons. It has been found (103) that the vapour pressure of dichloromethane is greater than that of chloroform, which in turn is greater than that of carbon tetrachloride. However, in all cases, the chloride ions released from the

TABLE 6.3: FURNACE PROGRAMME USED FOR THE CONSTRUCTION OF AN ATOMISE PLOT FOR ALUMINIUM WITH AND WITHOUT CHLOROCARBONS

Phase	Temperature/°C	hold time/s	Ramp/°C s^{-1}
dry	110	30	20
ash	500	15	50
atomise	variable	4	FP*
clean	2900	3	FP*

*FP = Full Power

Fig. 6.2 Atomise Curves for Aluminium with Different Chlorocarbons.



chlorocarbons combined with the analyte, and then behaved in a similar way as the fluoride analogues, ie. once formed, it failed to dissociate again. The bond energy for Al-Cl is virtually identical to that of Al-O (494 kj mol and 500 kj mol^{-1} respectively). Since it was found that in the presence of the chloride, the sensitivity was markedly decreased, it may be concluded that bond energy was not the only factor affecting the rate of atomisation. It is possible that the graphite may assist in the reduction of the Al-O species at greatly elevated temperatures, but since chlorides are not reduced by carbon (107) the same effect would not be observed in the presence of the halocarbons.

A similar experiment in which iodine crystals were placed in the Dreschel flask yielded similar results. It was therefore concluded that gaseous halogen containing modifiers, or halogenated materials with high vapour pressure were of no use in the analysis of refractory analytes, in as much as they failed to decrease the appearance temperatures.

6.4 The use of Freon 23 as a Purification Agent

6.4.1 Introduction and Procedure

It has been reported (127) that fluorine, introduced as freon, has been used by tube manufacturers to rid tubes of refractory impurities before they are sold. The use of freon during the clean stage of a furnace cycle may therefore exert the same affects, and decrease the memory effects that occur for many analytes.

An aqueous standard of vanadium (10 μg ml^{-1}) was prepared, and its absorbance at 318.5 nm was measured using the furnace programme shown in Table 6.3 and an atomise temperature of 2400°C. Since, at this wavelength, the standard was two orders of magnitude above the linear working range, considerable memory effects could be expected to result. By measuring the subsequent tube blank firings it was possible to determine the rate at which the memory effects were removed.

6.4.2 Results and Discussion

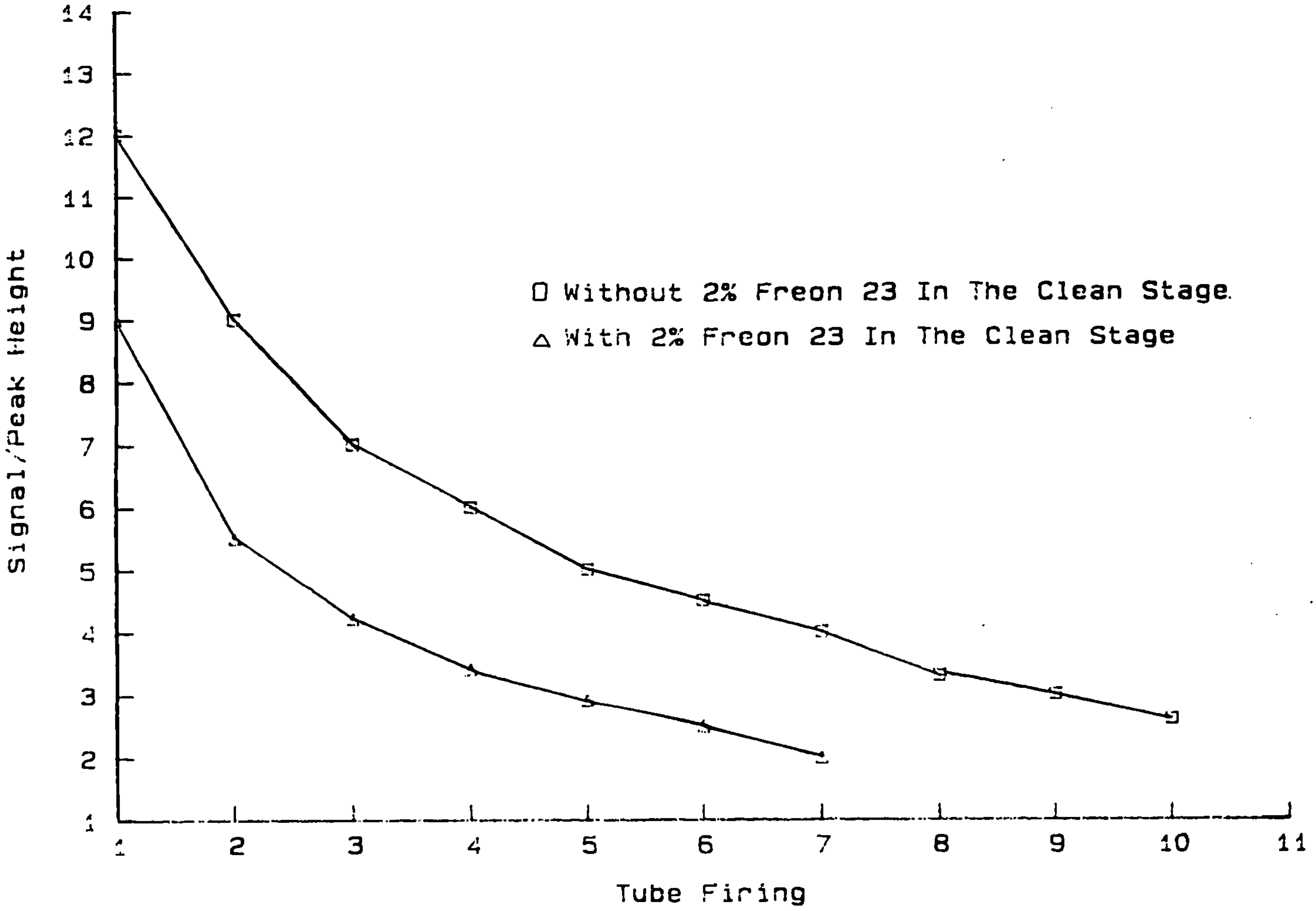
The results obtained are shown in Fig. 6.3. The results indicate that the presence of freon in the clean stage greatly accelerates the rate at which memory effects are removed. Since most freons thermally decompose at temperatures of 500-600°C the volatile fluorides may be removed from the tube at considerably lower temperatures. The use of high temperature clean out stages would therefore become unnecessary, thereby increasing the useful lifetime of the graphite tubes. The results obtained also support the theory that once formed, the fluoride species fail to dissociate again, but are volatilised away as a molecule.

6.5 The use of Freon 23 as a Stabilising Agent

6.5.1 Introduction

Cadmium fluoride has a melting point of 1100°C (103). Provided it is not reduced by the active sites on the tube

Fig. 6.3 The Affects Of 2% Freon 23 On Memory Effects.



surface, the cadmium fluoride could be expected to be thermally stable up to at least 1100°C. Ediger (23) reported that the addition of ammonium fluoride allowed ash temperatures of up to 900°C before the onset of analyte loss. This enables ash temperatures approximately 500°C higher than in the absence of any modifier.

6.5.2 Procedure

An aqueous standard (2 ng ml^{-1}) of cadmium was prepared by serial dilution of 1000 μg ml^{-1} stock standard (Spectrosol, BDH). Ash plots for this standard were constructed using the furnace programme and operating conditions detailed in Tables 6.4 and 6.5 respectively. The procedure was repeated twice, once using a 0.1% ammonium fluoride (AnalaR, BDH) solution and then with 2% freon 23 as matrix modifiers. Conventional wall atomisation from electrographite tubes was used. Sample introduction was by manual injection using a micropipette (Gilson).

6.5.3 Results and Discussion

The results obtained are shown in Fig. 6.4. As expected, the use of ammonium fluoride extended the available ash temperatures. The curve obtained for the freon modifier showed a peculiar but highly repeatable trait when peak area measurements were used. The same trait was evident, but considerably less pronounced when peak height measurements were plotted. The sudden increase in signal obtained at ash temperatures of 500-550°C could possibly be attributed to a gas phase interference. If the cadmium atomised into the

TABLE 6.4: FURNACE PROGRAMME USED FOR THE ASH PLOTS OF CADMIUM WITH AND WITHOUT FREON 23

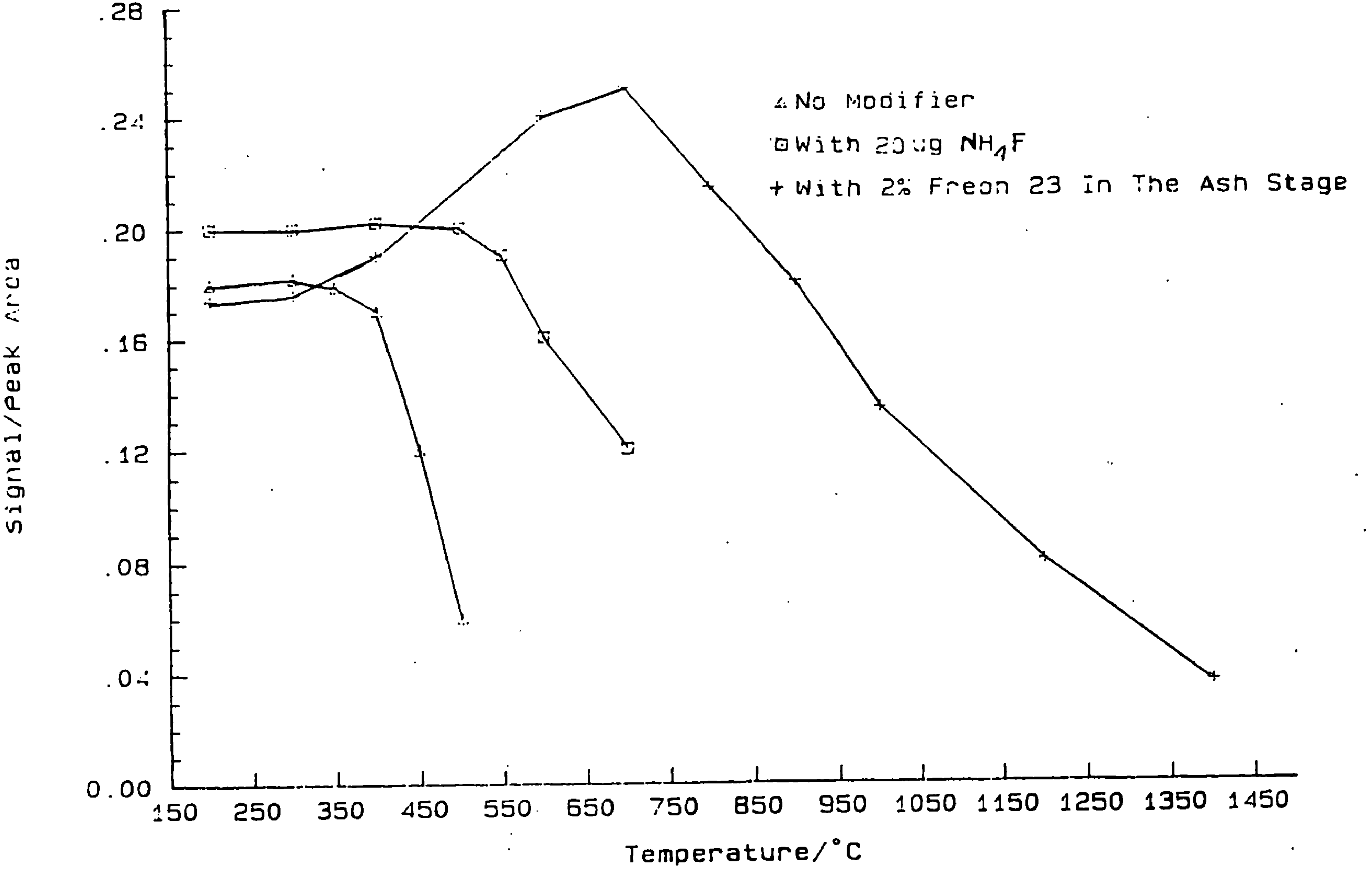
Phase	Temperature/°C	hold time/s	Ramp/°C s^{-1}
dry	110	30	20
ash	variable	20	50
atomise	1700	2	FP*
clean	2100	3	FP*

*FP = Full Power

TABLE 6.5: OPERATING CONDITIONS FOR THE ASH PLOTS OF CADMIUM

Wavelength/nm	228.8
bandpass/nm	0.5
Lamp current/mA	5
injection volume/µl	20

Fig. 6.4 Ash Plots For Cadmium With Different Modifiers And Wall Atomisation



light beam and then reacted with residual fluoride radicals, it would re-condense back onto the tube wall, where it would re-atomise. This would explain why the peak area measurements began to increase, but peak height measurements remained virtually the same. It is unclear why the same effects were not observed with the aqueous modifier. It is possible that it could be due to the concentration of the aqueous modifier being twenty times less than the gaseous one, and hence the vapour phase interference being twenty times less.

6.6 The use of a Platform to Overcome Vapour Phase Interferences

6.6.1 Introduction

If the explanation of the results obtained in 6.5.3 is correct, then the use of a platform should overcome the interference effects because of the more isothermal atmosphere obtained during atomisation. By delaying the atomisation of the cadmium until the gas phase is equally hot, the problem of re-condensation should be substantially decreased.

6.6.2 Procedure, Results and Discussion

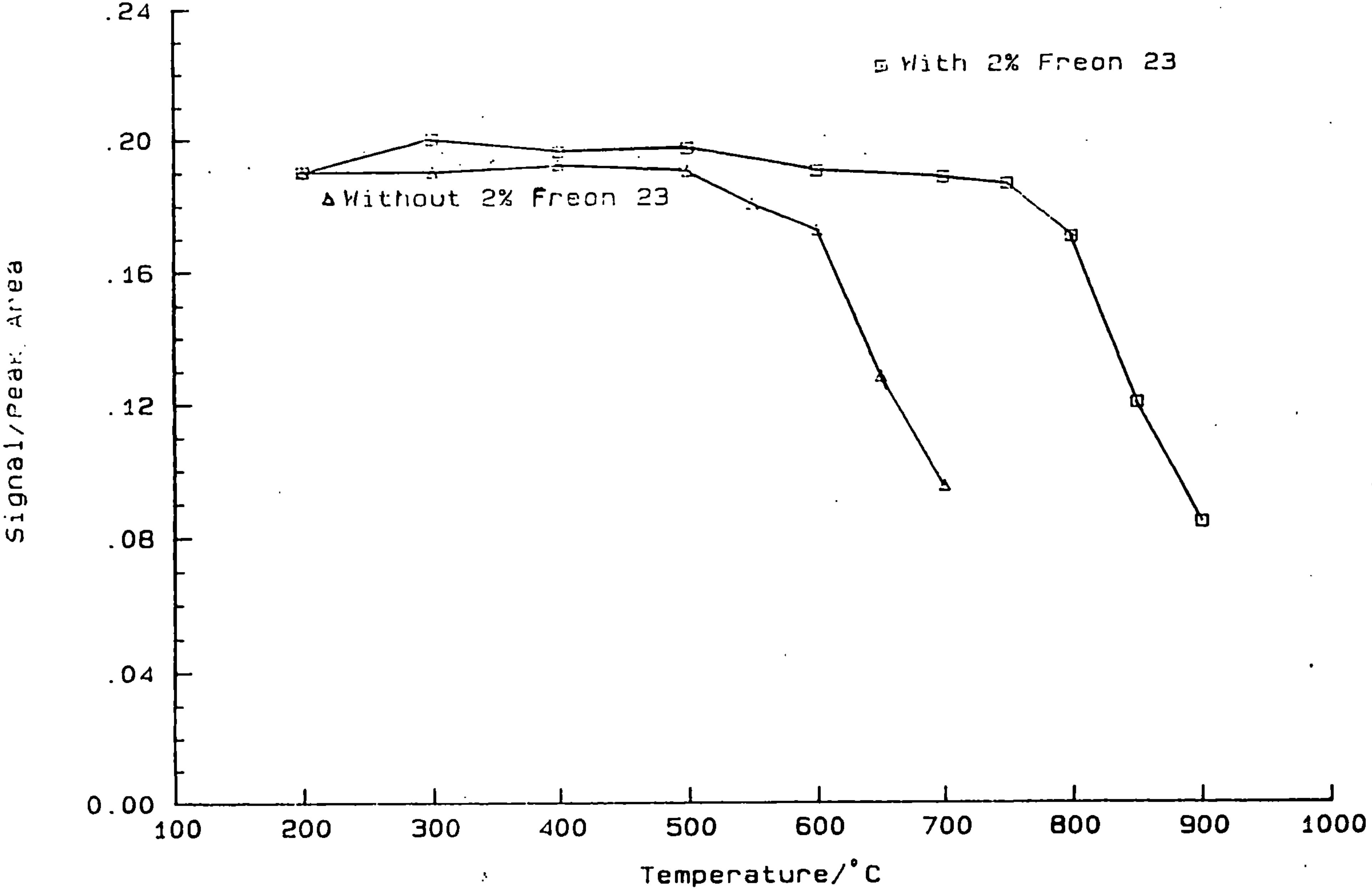
A similar experimental protocol was performed, but with an electrographite platform fitted in the tube. The temperature programme used was a modified version of the one used for tube wall atomisation, and is shown in Table 6.6. The results obtained are shown in Fig. 6.5. It can

TABLE 6.6: FURNACE PROGRAMME USED FOR CADMIUM ASH PLOTS FROM PLATFORM ATOMISATION WITH AND WITHOUT FREON

Phase	Temperature/°C	hold time/s	Ramp/°C s^{-1}
dry	170	40	20
ash	variable	20	50
atomise	1800	3	FP*
clean	2100	3	FP*

*FP = Full Power

Fig. 6.5 Cd Ash Plots From Platform Atomisation With And Without 2% Freon.



immediately be seen that the ash plot in the presence of the freon no longer exhibited the peculiar shape obtained with wall atomisation, and reverted to the shape of a 'typical' ash plot. This indicated that tube wall atomisation did suffer from a strange vapour phase interference, which could be removed by platform atomisation.

The extent to which the freon stabilised the cadmium was disappointing. In the presence of the freon, the cadmium could be ashed at 100°C higher than in its absence, but the maximum temperature of 750°C, was considerably less than the 1100°C expected from the melting point data. This indicated that cadmium fluoride formation was incomplete and that the unstabilised cadmium was lost at elevated temperatures. The performance of the freon modifier was therefore less adept than other established modifiers for cadmium. In addition, it is also considerably more costly.

6.7 General Conclusions

The use of halogenated compounds to decrease the appearance temperatures of some extremely refractory analytes was attempted. The results indicated that fluorinated and chlorinated hydrocarbons thermally decomposed and readily formed the volatile analyte halide, but this was then too stable to dissociate at temperatures obtainable by the atomiser. The result was a considerable loss of sensitivity. The use of iodine vapour was also tested. This provided very similar results to the other halogens. It was noticeable though that as the stability of the halide decreased, the decrease in sensitivity diminished.

The introduction of freon to the clean stage at the end of the furnace cycle resulted in a decrease in memory effects. This could save tube life by rendering extended clean out stages at high temperatures unnecessary.

An attempt was also made to use freon 23 as a stabilising agent for cadmium. Although the use of freon in conjunction with a platform proved partially successful in that it stabilised cadmium to 100°C higher than normal, it was considered to be too expensive to be used routinely since only a marginal increase in stability was achieved.

CHAPTER 7: THE USE OF BI-NUCLEAR GASEOUS MATRIX MODIFIERS

7.1 Introduction

The gases used in this chapter were nitrous oxide (N_2O), carbon monoxide (CO) and hydrogen sulphide (H_2S). The amount of work performed using these gases did not warrant a chapter each, and therefore it was decided to present these studies in one chapter. Since all the gases contain two different atoms they were given the title of bi-nuclear gases.

7.2 Instrumentation

All work was performed on an atomic absorption spectrometer (PU 9100X, Philips Scientific) fitted with an electrothermal atomiser (PU 9390X, Philips Scientific) and a data station (PU 9178X, Philips Scientific). Samples were introduced to the atomiser by manual injection using a high precision micropipette (Gilson).

7.3 The Introduction of Nitrous-Oxide to the Ash Stage

7.3.1 Introduction and Procedure

It has been reported (130) that nitrous oxide dissociates to nitrogen and oxygen at elevated temperatures. It could therefore be expected to exhibit similar effects as air or oxygen. It was therefore decided to construct ash plots for lead (15 ng ml^{-1}) with and without nitrous oxide (99.5% Air Products). The temperature programme and general operating conditions used are detailed in Tables 7.1 and 7.2 respectively.

TABLE 7.1: FURNACE PROGRAMME USED FOR LEAD WITH AND WITHOUT NITROUS OXIDE

Phase	Temperature /°C	Hold time /s	Ramp /°C s^{-1}	Internal Gas
dry	110	35	30	Ar
ash	varied	20	50	Ar/N_2O
ash	varied	10	-	Ar
atomise	1800	3	FP*	GS**
clean	2000	3	FP*	Ar

*FP = Full Power **GS = Gas Stop

TABLE 7.2: GENERAL OPERATING CONDITIONS USED FOR LEAD WITH AND WITHOUT NITROUS OXIDE

Wavelength/nm	283.3
Bandwidth/nm	0.5
Lamp current/mA	5
Injection volume/μl	20

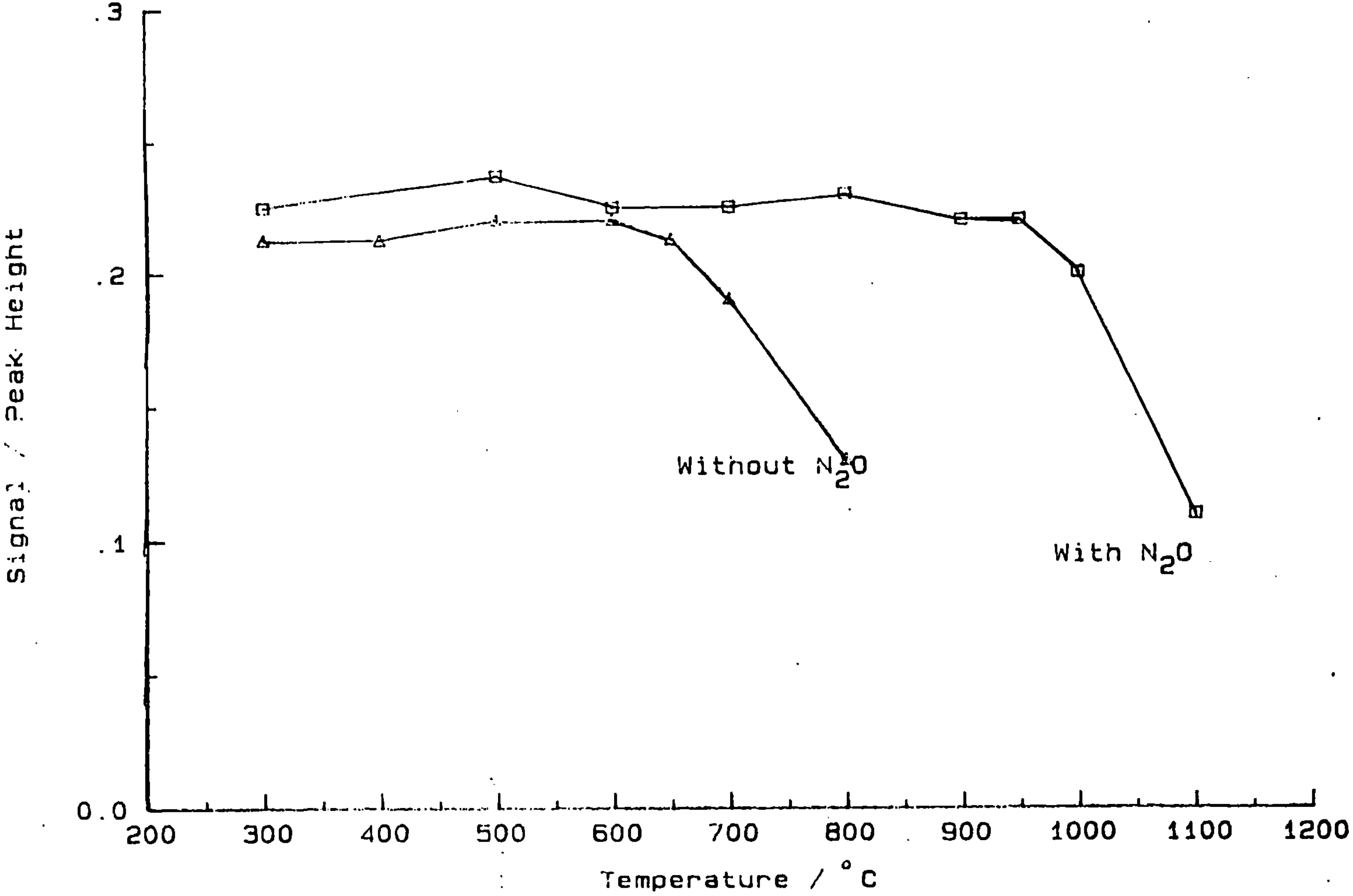
7.3.2 Results and Discussion

Initially the temperature programme used did not include the second ash stage to remove the residual reactive gas from the furnace. As a result, tube life-time was reduced to about five firings. In addition, the presence of residual nitrous-oxide in the atomise phase resulted in a crackling sound, which may have been a succession of minor explosions. Consequently the second ash phase was inserted to flush the reactive gas from the atomiser. The results obtained using the modified temperature programme, with and without nitrous oxide in the ash phase, are displayed in Fig. 7.1. By comparison with Fig. 2.1 it can be seen that the nitrous-oxide affects the thermal stability of lead in a similar fashion to air. The mechanism by which this occurs is presumably the same as that for air, which was described in detail in Section 2.3.2.

7.3.3 Conclusions

Although the introduction of nitrous-oxide during the ash stage of the furnace cycle proved successful in that it managed to thermally stabilise lead to temperatures of up to 950°C, and would presumably act as an ashing aid for samples with a carbonaceous matrix; its routine use as a matrix modifier would be limited due to its cost and more hazardous nature with respect to air.

Fig 7.1 Ash Plot For Lead With And Without Nitrous Oxide



7.4 The use of Carbon Monoxide as a Gaseous Modifier

7.4.1 Introduction

Carbon monoxide has been used in atomic spectroscopy as a means of greatly improving the sensitivity of nickel determinations. Lee (131) determined nickel in sea-water by first reducing nickel ions to nickel metal, and then bubbling carbon monoxide through the sample. The nickel and carbon monoxide then combined, forming the readily volatile nickel carbonyl ($Ni(CO)_4$), which was collected in a cryogenic trap before being flushed to the atom cell. Several modifications to the method have been made by several authors (132-135). Detection limits have been reported to be typically in the low pg ml^{-1} range. Determination by carbonyl generation therefore enables matrix separation and pre-concentration of the nickel.

Carbon monoxide has found other uses in ETAAS. Ascorbic acid has been used by some workers as a matrix modifier for lead (136). At elevated temperatures the ascorbic acid thermally decomposes to carbon monoxide and hydrogen. The result was that the appearance temperature for lead was decreased. The same effect has been observed for lead, bismuth and chromium, but not for copper, when carbon monoxide was added to the argon purge gas (137). Peile *et al*. (138) have used carbon monoxide to decrease the interference of iron on selenium determinations. The proposed mechanism was that the carbon monoxide scavenged residual oxygen thereby preventing the formation of iron oxide, which they believed, caused a spectral interference.

However, this paper has since been criticised since it is believed that the effects these authors observed was due to the presence of platinum and not to the carbon monoxide.

Carbon monoxide has therefore acquired several roles in atomic spectroscopy, although as yet its use has not become routine.

7.4.2 The Affects of Carbon Monoxide on the Atomic Signal for Lead

As was described in 7.4.1, ascorbic acid has been used as a matrix modifier for lead (136), which resulted in a decrease in appearance temperature. The affects of carbon monoxide (99.5%, BDH, Poole) on a lead standard (15 ng ml^{-1}) prepared by serial dilution of a stock standard (1000 mg l^{-1}, Spectrosol, BDH) were therefore determined. Aliquots (20 μl) of the lead standard were analysed using the furnace programme shown in Table 7.3.

7.4.3 Results and Discussion

The peak profiles obtained for lead without and with carbon monoxide introduced during the ash stage are shown in Figs. 7.2 and 7.3 respectively. It is clear that the presence of the carbon monoxide significantly decreased the appearance temperature of the lead, and is therefore in agreement with the observations of other workers (137). This may be due to the carbon monoxide scavenging any oxygen present, and hence allowing more active sites on the graphite surface to reduce

TABLE 7.3: THE FURNACE PROGRAMME USED TO DETERMINE THE AFFECTS OF CARBON MONOXIDE ON LEAD

Phase	Temperature/°C	Hold time/s	Ramp/°C s^{-1}
dry	110	35	20
ash	500	20	100
atomise	1800	2	FP*
clean	1900	3	FP*

*FP = Full Power

Fig. 7.2: Peak profile for lead without carbon monoxide in the ash stage.

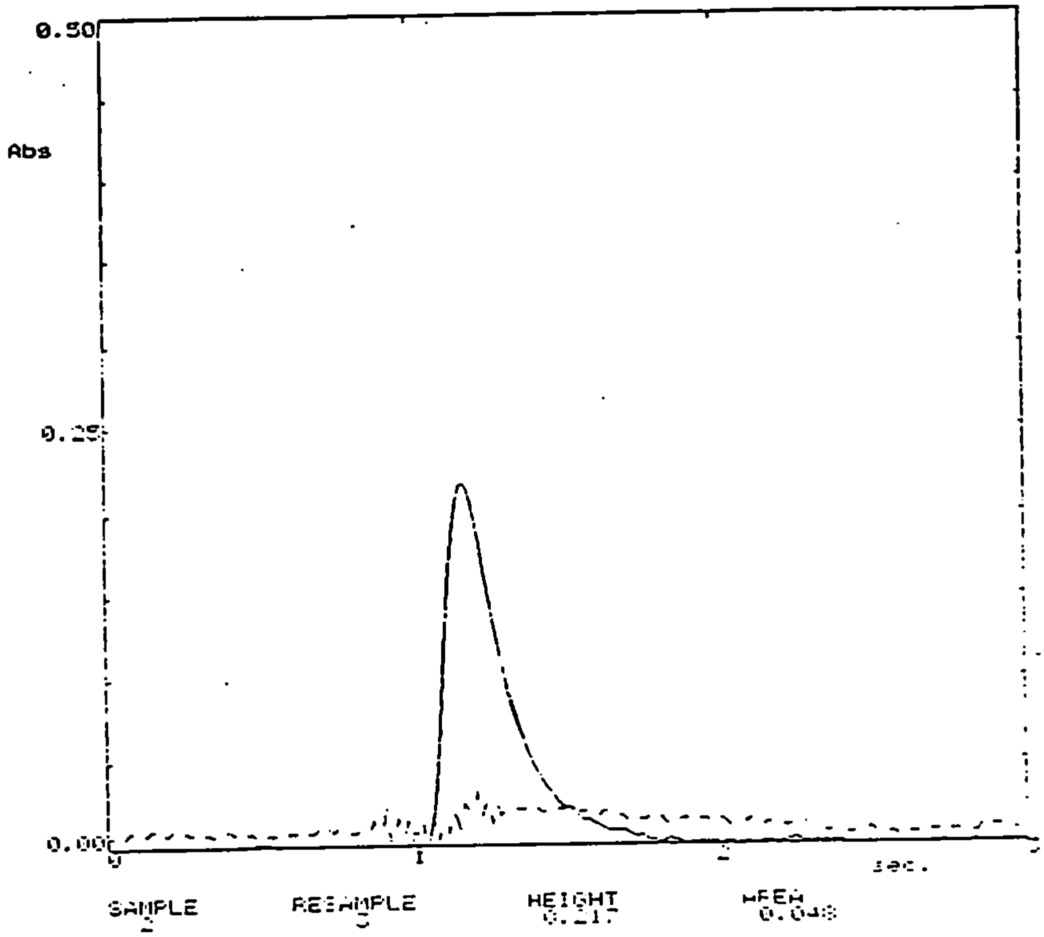
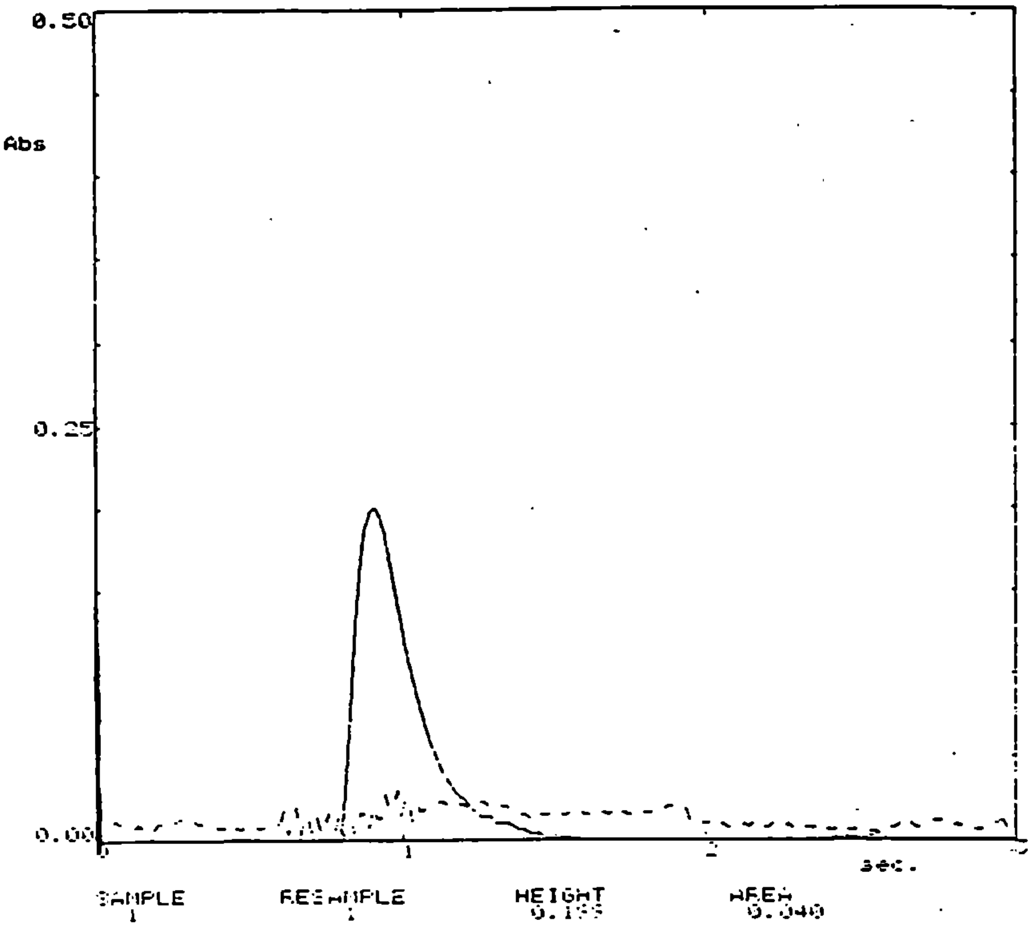


Fig. 7.3: Peak profile for lead with carbon monoxide in the ash stage.



the lead oxide species or, the carbon monoxide assisting in the reduction of lead oxide. Inspection of an Ellingham diagram for oxides (107) shows that carbon monoxide does not reduce lead oxide via the reaction $PbO + CO \rightarrow Pb + CO_2$ until temperatures of approximately 1800°C. It would therefore seem unlikely that this reaction would occur in the atomiser at the ash temperature used, and hence the more likely explanation for the decreased appearance temperature is the scavenging of residual oxygen. If more active sites are available, then more efficient reduction of the lead oxide would occur.

7.4.4 The Affects of Carbon Monoxide on the Atomic Signal for Nickel

Since many nickel species are known to be toxic (135), nickel determinations are fairly common. However, nickel is an extremely common matrix modifier for volatile analytes such as selenium, arsenic or bismuth. Since very large quantities of nickel are required to stabilise these analytes, it accumulates in the graphite tube, and hence renders the tube unusable for nickel determinations. However, if the nickel contamination could be removed from the tube at low temperatures; the tube may still have a useful lifetime. Nickel carbonyl formation has been reported to occur at room temperature, and its thermal decomposition to begin at 60°C (103). If nickel contamination could be removed without having to resort to extended high temperature clean cycles, tube lifetime could be preserved.

An experiment was therefore performed to determine whether or not carbon monoxide could be used to volatilise away nickel as its carbonyl. The temperature programme and the operating conditions used are detailed in Table 7.4. A 1000 mg l^{-1} nickel standard (0.4953 g of nickel nitrate dissolved in water (100 ml)) was injected into the furnace, and dried. After that,the furnace was allowed to cool to ambient temperature, and carbon monoxide introduced. A stage in which the residual carbon monoxide was flushed from the system by argon followed, and finally the signal obtained during atomisation was measured. As a comparison, the same experiment was performed but in the absence of the carbon monoxide.

7.4.5 Results and Discussion

The nickel signal produced in the presence of carbon monoxide was similar in magnitude to that produced in its absence. Although this was discouraging, since to be useful analytically, the carbon monoxide must be capable of removing nickel concentrations such as this, it was decided to repeat the experiment but using a less concentrated standard. A nickel standard of 100 ng ml^{-1} was therefore prepared by serial dilution of the stock standard. This time a large increase in signal was produced when carbon monoxide was introduced. This implied that the carbon monoxide was attacking some nickel component, possibly present as stainless steel, in the gas line, and was

TABLE 7.4: FURNACE PROGRAMME USED TO DETERMINE THE AFFECTS OF CARBON MONOXIDE ON NICKEL

Phase	Temperature/°C	Hold Time/s	Ramp/°C s^{-1}
dry	110	35	30
ash	50	60	-
ash	50	10	-
atomise	2500	3	FP*
clean	2600	3	FP*

*FP = Full Power

depositing the nickel within the graphite tube. Since continued use of carbon monoxide may result in severe degradation of the instrumentation, it was decided to discontinue its use.

7.4.6 Conclusions

The use of carbon monoxide has been shown to decrease the appearance temperature of lead. This is in agreement with the observations of other workers (137). However, the extended use of carbon monoxide in the Philips PU 9390X electrothermal atomiser is not to be recommended, since the gas extracts nickel from the gas line. Although this may be of use analytically in that it may stabilise analytes such as selenium or arsenic, it may well curtail the life of the atomiser.

7.5 The use of Hydrogen Sulphide to Thermally Stabilise Mercury

7.5.1 Introduction

Mercury is a notoriously difficult element to analyse by ETAAS because of its extreme volatility. Losses of mercury can readily occur at temperatures as low as those used to dry the sample. As a result mercury analyses are more often performed by cold vapour AAS. However, some workers have used ETAAS in conjunction with matrix modifiers to determine mercury levels. Modifiers that have been used include tetramethylene dithiocarbamate and tetraethylthiuram (140), potassium dichromate (27), ammonium sulphide (141), complexing agents with thiol groups (142) and amalgamating agents such as palladium (37). It is noticeable that many of these modifiers contain sulphur. By using x-ray diffraction (Grgic et al. (140) have shown the formation of the thermally stable mercury sulphide (HgS), before atomisation. It was therefore proposed that gaseous hydrogen sulphide introduced during or prior to the dry stage may also lead to the formation of HgS.

7.5.2 Procedure

Ash plots of a 200 ng ml^{-1} mercury standard in 2% v/v nitric acid were performed using both wall and platform atomisation with and without hydrogen sulphide (10% v/v in argon, Air Products Special Gases), introduced prior to and during the dry stage. NB. Due to the offensive and hazardous nature of hydrogen sulphide good fume extraction is required. The furnace programme used for wall and platform atomisation are detailed in Tables 7.5 and 7.6 respectively; and the operating conditions are described in Table 7.7.

7.5.3 Results and Discussion

The results of the ash plots for mercury with wall atomisation and with platform atomisation both with and without H_2S are shown in Figs. 7.4 and 7.5 respectively. From the results, it is obvious that the presence of H_2S causes a large increase in the mercury signal for both wall and platform atomisation. By running a blank with H_2S it was possible to show that this increase in signal was due to an enhancement in sensitivity rather than the introduction

TABLE 7.5: FURNACE PROGRAMME USED FOR MERCURY ASH PLOTS WALL ATOMISATION

Stage	Temperature /°C	Time /s	Ramp /°C s^{-1}	Internal Gas Type
dry	70	20	35	10% H_2S
dry	110	30	20	10% H_2S
ash	varied	20	50	Ar
atomise	1200	3	FP*	GS‡
clean	1600	3	FP*	Ar

*FP = Full Power ‡GS = Gas Stop

TABLE 7.6: FURNACE PROGRAMME USED FOR MERCURY ASH PLOTS FROM PLATFORM ATOMISATION

Stage	Temperature /°C	Time /s	Ramp /°C s^{-1}	Internal Gas Type
dry	70	20	35	10% H_2S
dry	140	30	20	10% H_2S
ash	varied	20	50	Ar
atomise	1400	3	FP*	GS‡
clean	1800	3	FP*	Ar

*FP = Full Power ‡GS = Gas Stop

TABLE 7.7: OPERATING CONDITIONS FOR MERCURY ASH PLOTS

Wavelength/nm	253.7
lamp current/mA	5
bandpass/nm	0.5
injection volume/µl	20

Fig. 7.4 Ash Plots of Mercury, With and Without H_2S, Wall Atomisation.

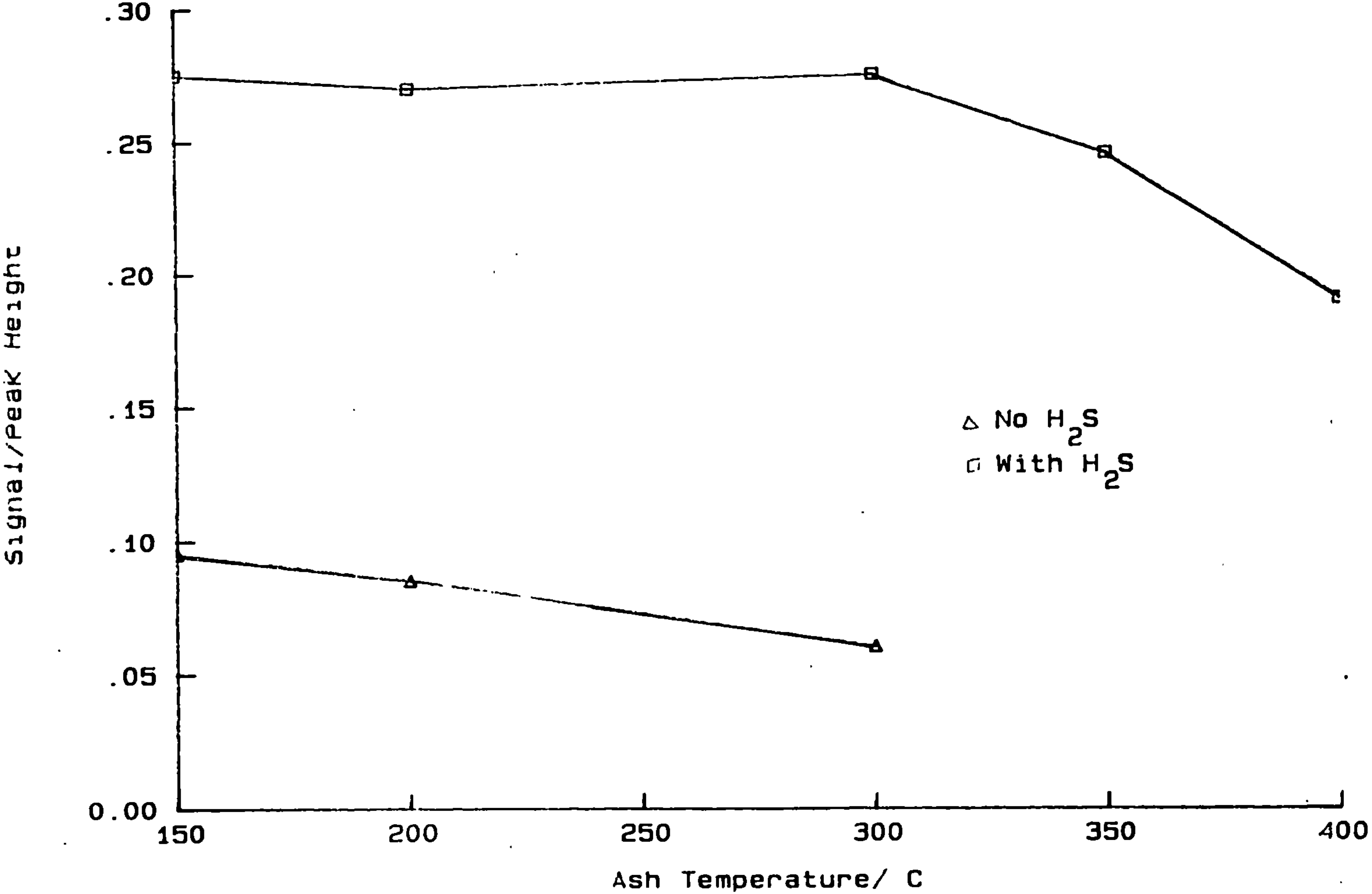
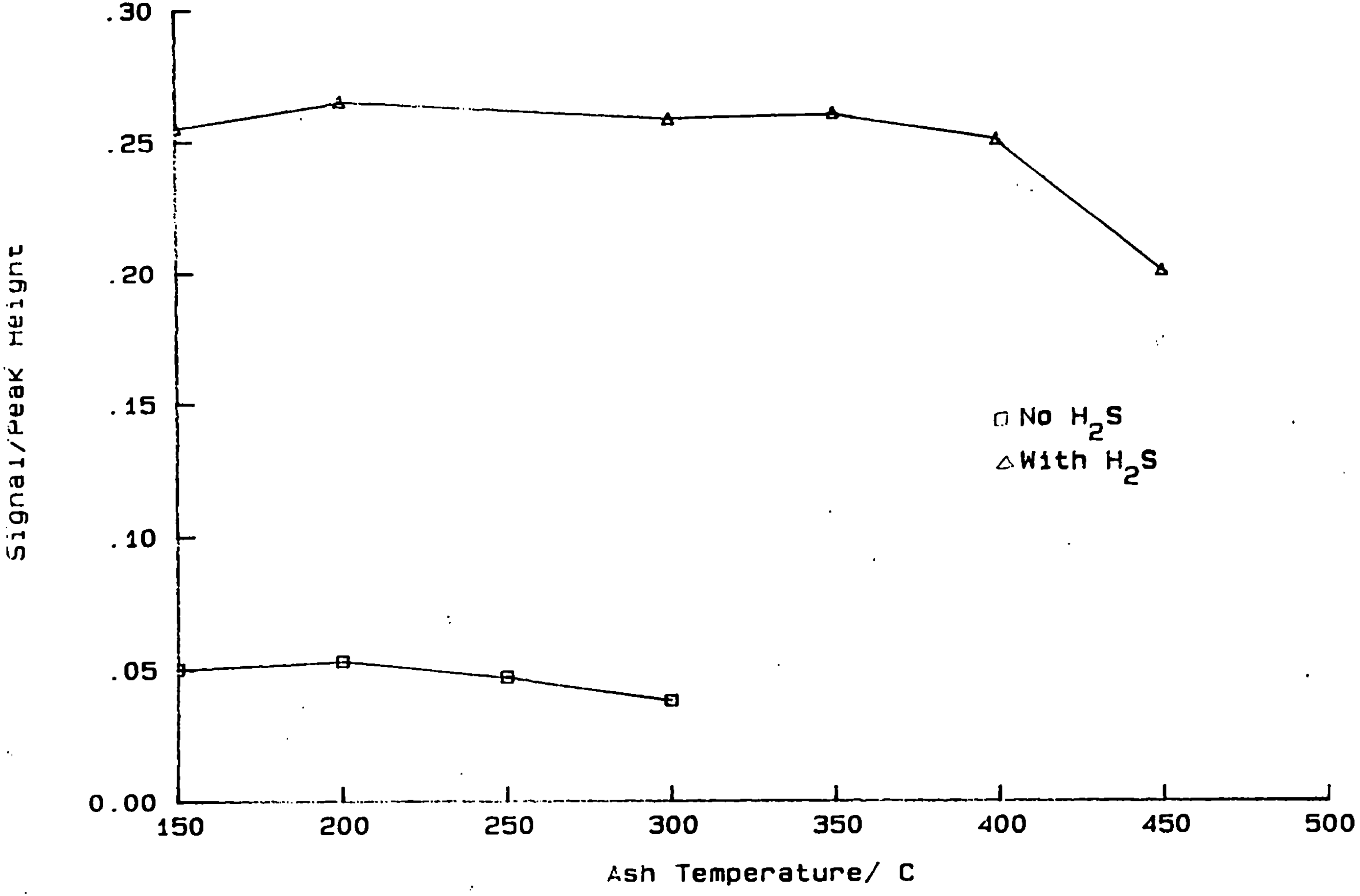


Fig. 7.5 Ash Plots of Mercury, With and Without H_2S, Platform Atomisation.

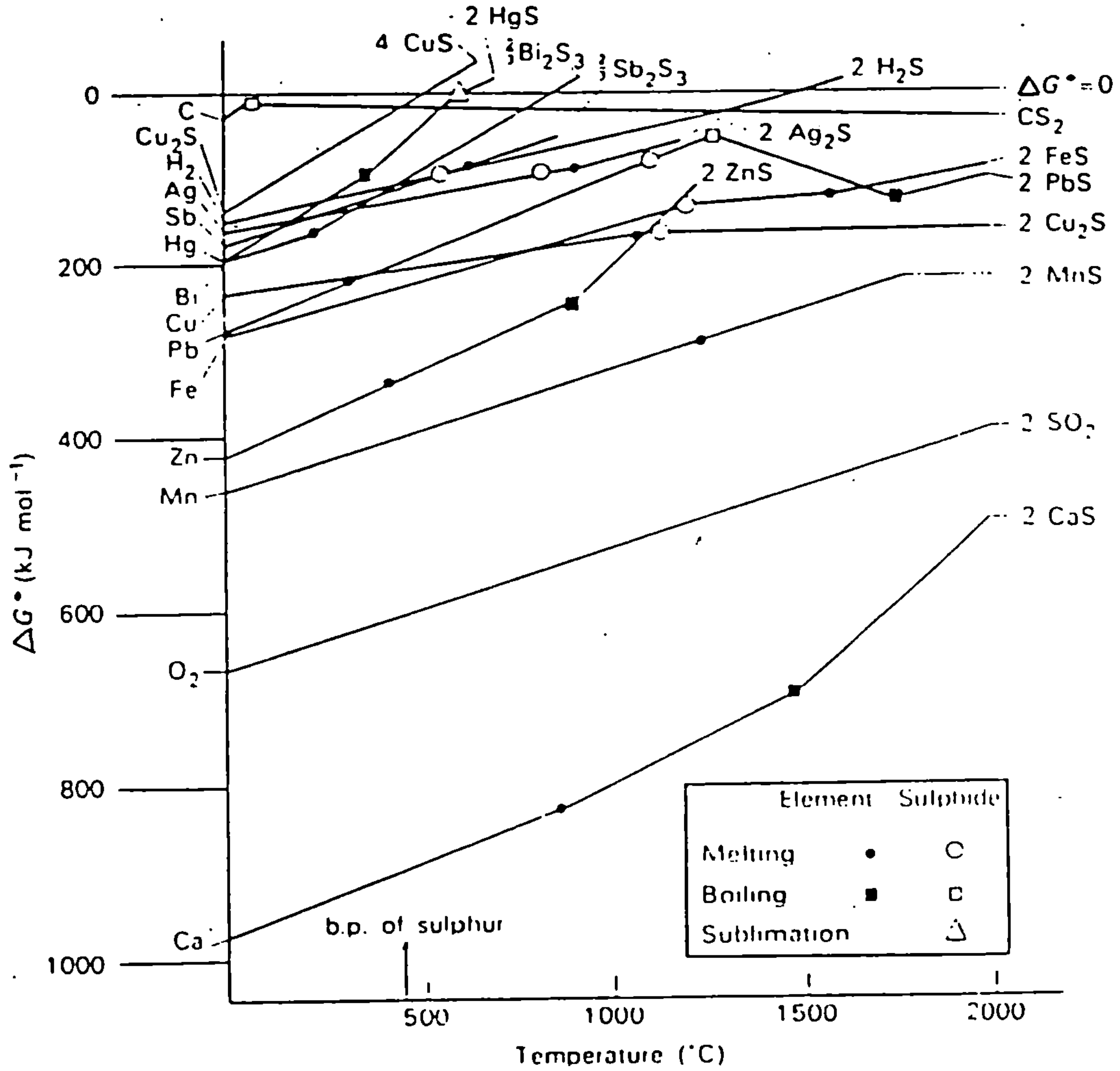


of mercury vapour as a contaminant from the gas. The presence of hydrogen sulphide in the early stages of the furnace cycle allowed ashing at 300°C for wall and 350°C for platform atomisation. In the absence of hydrogen sulphide no stable signal was obtainable for wall atomisation, ie. any increase in ash temperature above the drying temperature resulted in a decrease in signal. For platform atomisation the mercury signal appeared to be stable until approximately 200°C before analyte loss was observed.

Inspection of an Ellingham diagram for sulphide (Fig. 7.6) shows that the mercury sulphide is stable to approximately 550°C before it is reduced by carbon, or 600°C before it spontaneously dissociates to mercury and sulphur (ie. $\Delta G = 0$). The sublimation point of mercury sulphide is 583.5°C or 446°C depending on the crystal structure (140). The ashing temperature of up to 350°C achieved in the presence of hydrogen sulphide is therefore in reasonable agreement with the maximum theoretical ash temperatures of 450-500°C. It is also in reasonable agreement with the observations of other workers (140) who claimed that maximum ashing temperatures of 300-350°C could be used in the presence of sulphide forming compounds.

Inspection of an Ellingham diagram shows that H_2S does not dissociate until approximately 1500°C. It must therefore be concluded that the hydrogen sulphide must dissolve in the aqueous matrix of the sample, and precipitate the mercury as its sulphide onto the atomiser.

Fig. 7.6: An Ellingham diagram for sulphides.



When the introduction of hydrogen sulphide was continued into the ash stage, excessively large background signals were obtained (compare Figs. 7.7 and 7.8) which resulted in an extremely noisy and unreliable atomic signal. The extended use of hydrogen sulphide is therefore not recommended.

When the duration of the stage prior to drying was increased, the atomic signal for mercury increases but so too did the background signal. After 90 seconds the atomic signal reached a maximum, but the background signal continued to increase with increasing time. After 120 seconds the excessive background signal caused the deuterium background correction device to over-correct, resulting in a depression of the atomic signal. This would appear to add support to the theory that the hydrogen sulphide dissolves in the aqueous matrix and combines with the mercury.

Validation of the method by the analysis of certified reference materials (CRMs) proved to be extremely difficult. No suitable CRM could be found. Although materials such as sewage sludge contains considerable amounts of mercury, the matrix proved to be too refractory for efficient ashing, and hence no reliable data could be obtained. Other materials with more simple matrices contained amounts of mercury that were below the limit of detection of the method.

Fig. 7.7: Peak profile obtained for mercury without hydrogen sulphide introduced during the ash stage.

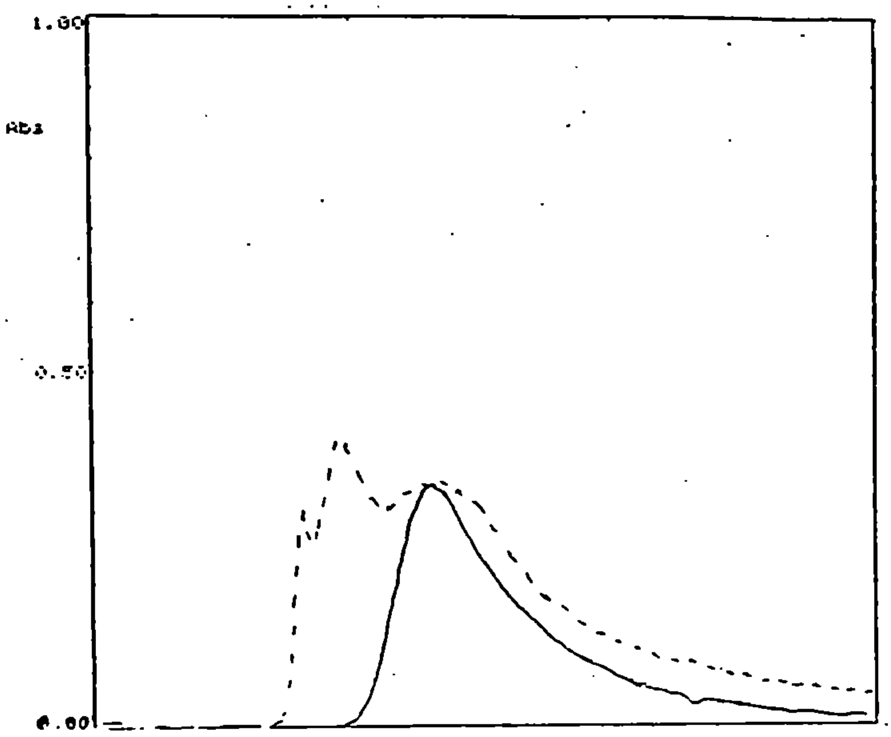
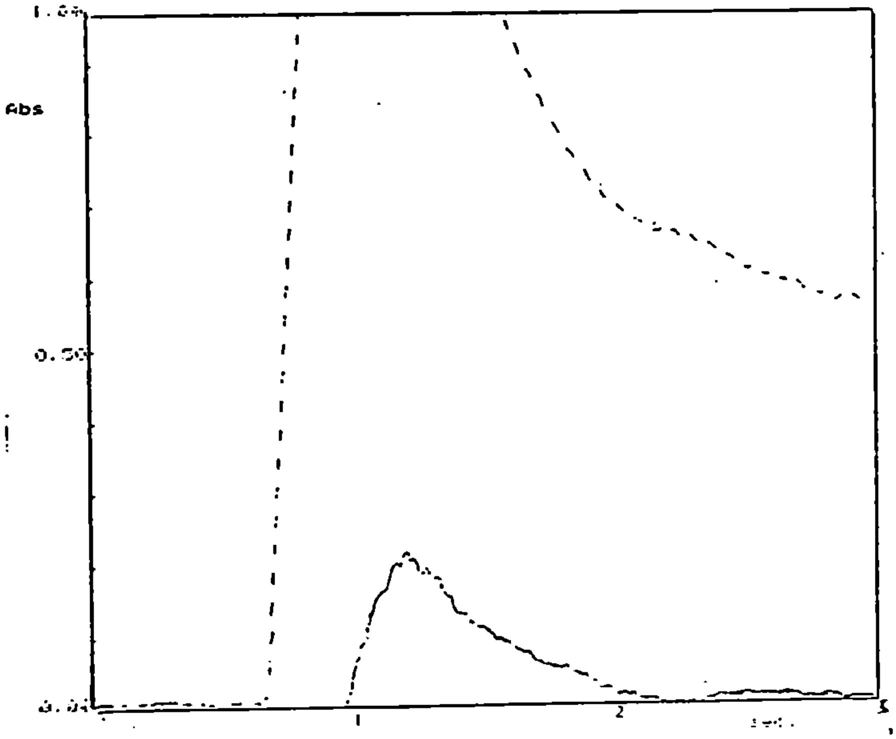


Fig. 7.8: Peak profile obtained for mercury with hydrogen sulphide introduced during the ash stage.



7.5.4 Conclusions

The use of 10% v/v hydrogen sulphide in argon, when introduced prior to or during the ash stage, was found to increase the sensitivity of mercury analyses (up to 8 fold enhancement); and thermally stabilised mercury to temperatures of up to 350°C. This may facilitate mercury analyses in simple matrices such as water, but it is still insufficient for more complex matrices where higher ash temperatures are required.

CHAPTER 8: CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

8.1 Conclusions

The use of a variety of gaseous matrix modifiers has been demonstrated. Oxidising gases such as air and nitrous oxide that contain or thermally decompose to produce oxygen have been found to thermally stabilise analytes, such as lead, that rely on the active sites on the graphite surface to reduce their oxide to the atomic metal. The mechanism has been described as a blocking of the active sites by oxygen and hence prevention of the analyte oxides from binding and becoming reduced. In addition, the oxygen present also acted as a powerful pyrolysing agent, and therefore samples with carbonaceous matrices were more rigorously ashed, resulting in atomisation more free from matrix interferences. Tube degeneration did not occur unless temperatures in excess of 950°C were used in the presence of oxygen. Interference by other species eg. magnesium chloride was also found to decrease, presumably because of the formation of less volatile lead species.

Reducing gases have also been used as matrix modifiers. If introduced during the ash stage, methane was found to enhance the sensitivity for many refractory analytes. This was found to be partially due to the hydrogen liberated during the thermal decomposition of the methane, but more significantly to the reducing carbon or hydrocarbon radicals produced by the same process. In addition, the carbon also formed a robust, inert and dense layer of pyrolytic carbon on the graphite surface. This had the affect of reducing sample soaking and sample interaction with the graphite, and resulted in less sample spreading, improved precision and decreased memory effects. Other hydrocarbon gases, ie. ethane and propane were also used. They exhibited the same advantages proferred by methane, but had the disadvantage of producing loose sooty deposits when used at more than 1% v/v in argon.

When introduced during the ash stage, hydrogen was found to marginally enhance the sensitivity of some refractory analytes and also for lead. The main advantage offered by hydrogen, however, was that it efficiently removed the non-specific absorbance interference and light scatter caused by carbonaceous matrices. The mechanism was hypothesised to be by the formation of hydrocarbons, which absorb or scatter less light than carbon particles. In addition, hydrogen was found to decrease both the vapour and appearance temperatures of many analytes. Hydrogen proved to be unsuccessful in the removal of the interference effects of 0.5% w/v sodium chloride on lead determinations.

The use of organophosphorus vapours such as tri-ethyl phosphite during the dry stage, resulted in the stabilisation of cadmium to temperatures comparable with 'wet chemical' modifiers but without the concomitant contamination problems. The proposed mechanism was that the organophosphorus vapour hydrolysed in the moist atmosphere, and deposited the phosphorus on the tube wall, where it could interact with the cadmium forming a much less volatile species.

Other gases that have been investigated in this study include a variety of halogenated compounds and the vapour of iodine. This was an attempt to increase the volatility of extremely refractory analytes such as aluminium and vanadium, and hence save on tube life-time, and possibly enhance the sensitivity by decreasing stable carbide formation. The experiments were partially successful in that the analyte-halide bonds did form, however, the halogenated species were too thermally stable to dissociate at temperatures obtainable in a graphite furnace. As a result, a large drop in sensitivity was obtained. The halogenated compounds could however be used in the clean stage to decrease memory effects. A 2% v/v mix of freon 23 in argon was found to stabilise cadmium to a temperature of 750°C. However, platform atomisation had to be used since wall atomisation suffered heavily from condensation effects.

Carbon monoxide was used in an attempt to remove nickel contamination from the atomiser as volatile nickel carbonyl. However, the nickel signal was found to increase in the presence of carbon monoxide, indicating that the gas was leaching nickel from the gas lines. The use of carbon monoxide was therefore curtailed to prevent excessive damage to the instrumentation.

Hydrogen sulphide (10% v/v in argon) was used in an attempt to thermally stabilise mercury via the formation of mercury sulphide. The experiments were successful in that ash temperatures of up to 350°C could be utilised before the onset of analyte loss, whereas without hydrogen sulphide, mercury was lost at temperatures below 200°C.

8.2 Further Work

Many of the mechanisms by which the various gases work have been hypothesised by observation and deduction. There has been no experimental work to provide additional support. Electron microscopy has been used by other workers to study the graphite tubes surface (139), and it could be used here, for example, to determine whether or not the organophosphorus vapours did deposit phosphorus, or what affects the hydrogen has on very finely divided carbon. Another technique that could be used to elucidate mechanistic aspects of the various processes is evolved gas analysis. Techniques such as these should enable a much clearer understanding of the mechanisms by which the gaseous modifiers work.

In addition to taking a much more theoretical approach, the affects of other gases could also be determined. Chlorinated gases eg. HCl (125) have been used to volatilise away the matrix while leaving the analyte unaffected, and hence facilitating atomisation more free from matrix interferences. The use of freons, halocarbons or iodine vapour may have the same affect, while possessing less hazardous or irritant properties. The use of halocarbons or halogens could also be extended to other refractory analytes. It has been reported (130) that boron tri-chloride or tri-bromide is readily reduced to elemental boron by the application of heat and hydrogen. A mixture of a halogen and hydrogen introduced during the atomise phase may therefore drastically decrease the appearance temperature for boron and could increase sensitivity by reducing the amount of carbide formation.

A gaseous modifier that could be used to increase the thermal stability of volatile analytes such as arsenic, the other metalloids and possibly mercury, is nickel carbonyl. This is known to thermally decompose at elevated temperatures to nickel and carbon monoxide. It could therefore be used as a convenient way to deposit nickel within the graphite tube. Its extremely toxic nature could however preclude its routine use unless exceptionally efficient fume extraction systems were available.

The use of organophosphorus vapours to thermally stabilise cadmium has already been demonstrated, however, their use for other analytes such as lead and zinc that are also known to be stabilised by phosphate, has not. Extending the use of these vapours to other analytes would be useful analytically, in that matrix modifiers should affect as many analytes as possible.

All of the experiments performed so far have been in a graphite atomiser. Although hydrogen has been used in metal atomisers (84-91), many of the other gases have not. By extending the use of the gases into other atomisers, eg. metallic or glassy carbon, the possibility of their ubiquitous use as matrix modifiers may be examined.

REFERENCES

1. King, A.S., Astrophys. J., 21, 236, 1905.

2. King, A.S., Astrophys. J., 27, 353, 1908.

3. L'Vov, B.V., Spectrochim. Acta, 17, 761, 1961.

4. Massmann, H., Spectrochim. Acta, Part B, 23, 215, 1968.

5. West, T.S., and Williams, X. K., Anal. Chim. Acta, 45, 27, 1969.

6. Ebdon, L., "An Introduction to Atomic Absorption Spectroscopy, a Self Teaching Approach", Heydon and Son Ltd., London, 1982.

7. Fuller, C.W., "Electrothermal Atomisation for Atomic Absorption Spectrometry", Analytical Sciences Monograph number 4. The Chemical Society, 1977.

8. Dymott, T.C., "Atomic Absorption with Electrothermal Atomisation", 3rd edition. Pye Unicam Ltd., Cambridge, 1985.

9. Donega, H.M., and Burgess, T.E., Anal. Chem., 42, 1521, 1970.

10. L'Vov, B.V., and Pelieva, L.A., Can. J. Spectrosc., 23, 1, 1978.

11. Cresser, M.S., and Mullins, C.E., Anal. Chim. Acta, 68, 377, 1974.

12. Slavin, W., Manning, D.C., and Carnrick, G.R., Spectrochim. Acta, 44B, 1237, 1989.

13. Bradshaw, D., and Slavin, W., Spectrochim. Acta, 44B, 1245, 1989.

14. Slavin, W., and Manning, D.C., Prog. Anal. At. Spectrosc., 5, 243, 1982.

15. Matousek, J.P., Prog. Anal. At. Spectrosc., 4, 247, 1981.

16. Lawson, S.R., Dewalt, F.G., and Woodriff, R., Prog. Anal. At. Spectrosc., 6, 1, 1983.

17. Frech, W., Lundberg, E., and Cedergren, A., Prog. Anal. At. Spectrosc., 8, 257, 1985.

18. Siemer, D.D., Lundberg, E., and Frech, W., Appl. Spectrosc., 38, 389, 1984.

19. L'Vov, B.V., Spectrochim. Acta, 33B, 153, 1978.

20. Littlejohn, D., Cook, S., Durie, D., and Ottaway, J.M., Spectrochim. Acta, 38B, 295, 1984.

21. Brown, A.A., J. Anal. At. Spectrom., 3, 67, 1988.

22. Frech, W., Baxter, D.C., and Hutsch, B., Anal. Chem., 58, 1973, 1986.

23. Ediger, R.D., At. Absorpt. Newsl., 14, 127, 1975.

24. Maessen, F.J.M.J., Balke, J., and Massee, R., Spectrochim. Acta, 33B, 311, 1978.

25. Gladney, E.S., At. Absorpt. Newsl., 16, 114, 1977.

26. Guevremont, R., Anal. Chem., 52, 1574, 1980.

27. Kirkbright, G.F., Hsiao-Chuan, S., and Snook, R.D., At. Spectrosc., 1, 85, 1980.

28. Shan Xiao-quan, Luan Shen, and Ni Zhe-Ming, J. Anal. At. Spectrom., 3, 99, 1988.

29. Machata, G., and Binder, R.Z., Zeitschrift fur Rechtsmedizin, 73, 29, 1973.

30. Geetha, R., Thiruvengadasami, A., and Mahalingham, T.R., J. Anal. At. Spectrom., 4, 447, 1989.

31. Slavin, W., Carnrick, G.R., and Manning, D.C., Anal. Chem., 54, 621, 1982.

32. Vanhoe, H., Vandecasteele, C., Desmet, B., and Dams, R., J. Anal. At. Spectrom. 3, 703, 1988.

33. Henn, E.L., Anal. Chem., 47, 428, 1975.

34. Alderman, F.R., and Gitelman, H.J., Clin. Chem., 26, 258, 1980.

35. Fuller, C.W., At. Absorpt. Newsl., 16, 106, 1977.

36. Czobik, F.J., and Matousek, J.P., Talanta, 24, 573, 1977.

37. The Analytical Report, Perkin Elmer, Beaconsfield, Feb. 1988.

38. Lechotycki, A., J. Anal. At. Spectrom., 5, 25, 1990.

39. Bauslaugh, J., Radziuk, B., Saeed, K., and Thomassen, Y., Anal. Chim. Acta, 165, 149, 1984.

40. Szydlowski, F.J., At. Absorpt. Newsl., 16, 60, 1977.

41. Sefzik, E., Vom Wasser, 50, 285, 1978.

42. Slavin, W., Carnrick, G.R., and Manning, D.C., Anal. Chim. Acta, 138, 103, 1982.

43. Voellkopf, U., Grobenski, Z., and Welz, B., GIT Fachz. Lab., 26, 444, 1982.

44. Bermejo-Barrera, P., Pita-Calvo, C., and Cocho De Juan, J.A., Anal. Chim. Acta, 231, 321, 1990.

45. Nater, E.A., and Burau, R.G., Anal. Chim. Acta, 220, 83, 1989.

46. Subramanian, K.S., J. Anal. At. Spectrom., 3, 111, 1988.

47. Hinds, M.W., Katyal, M., and Jackson, K.W., J. Anal. At. Spectrom., 3, 83, 1988.

48. Knowles, M.B., and Brodie, K.G., J. Anal. At. Spectrom., 3, 511, 1988.

49. Slavin, W., Carnrick, G.R., Manning, D.C., and Pruszkowska, E., At. Spectrosc., 4, 69, 1983.

50. Shan, X-Q., and Wang, D.X., Anal. Chim. Acta, 173, 315, 1985.

51. Bass, D.A., and Holcombe, J.A., Anal. Chem., 59, 974, 1987.

52. Carnrick, G.R., and Slavin, W., J. Anal. At. Spectrom., 3, 1023, 1988.

53. L'Vov, B.V., Nikolaev, V.G., Norman, E.A., Polzik, L.K., and Mojica, M., Spectrochim. Acta, 41B, 1043, 1986.

54. Slavin, W., Manning, D.C., and Carnrick, G.R., At. Spectrosc., 2, 137, 1981.

55. De Benzo, Z.A., Fraile, R., Carrion, N., and Loreto, D., J. Anal. At. Spectrom., 4, 397, 1989.

56. Foote, J.W., and Delves, H.T., Analyst, 113, 911, 1988.

57. Delves, H.T., and Woodward, J., At. Spectrosc., 2, 65, 1981.

58. Beaty, M., Barnett, W., and Grobenski, Z., At. Spectrosc., 1, 72, 1980.

59. Carrion, N., Benzo, Z., Moreno, B., Fernandez, A., Eljuri, E., and Flores, D., J. Anal. At. Spectrom., 3, 479, 1988.

60. Hinds, M.W., and Jackson, K.W., J. Anal. At. Spectrom., 3, 997, 1988.

61. Stephen, S.C., Littlejohn, D., and Ottaway, J.M., Analyst, 110, 1147, 1985.

62. Ebdon, L. and Parry, H.G.M., J. Anal. At. Spectrom., 3, 131, 1988.

63. Kundu, M.K., and Prevot, A., Anal. Chem., 46, 1591, 1974.

64. Salmon, S.G., and Holcombe, J.A., Anal. Chem., 54, 630, 1982.

65. Bass, D.A., and Holcombe, J.A., Anal. Chem., 60, 578, 1988.

66. Katskov, D.A., Burtseva, I.E., and Grinshtein, I.C., Zh. Prikl. Spektrosk., 31, 573, 1979.

67. Hodges, D.J., Analyst, 102, 66, 1977.

68. Sturgeon, R.E., and Chakrabarti, C.L., Anal. Chem., 49, 90, 1977.

69. Manning, D.C., and Ediger, R.D., At, Absorpt. Newsl. 15, 42, 1976.

70. Allen, P.D., Hampson, N.A., Moore, D.C.A., and Willars, M.J., Anal. Chim. Acta., 101, 401, 1978.

71. Chamsaz, M., Sharp, B.L., and West, T.S., Talanta, 27, 867, 1980.

72. Clyburn, S.A., Kantor, T., and Veillon, C., Anal. Chem., 46, 2213, 1974.

73. Clyburn, S.A., Bartschmid, B.R., and Veillon, C., Anal. Chem., 46, 2201, 1974.

74. Morrow, R.W., and McElhaney, At. Absorpt. Newsl., 13, 45, 1974.

75. Thompson, K.C., Godden, R.G., and Thomerson, D.R., Anal. Chim. Acta, 74, 289, 1975.

76. Sperling, K.R., Fresenius Z. Anal. Chem., 283, 30, 1977.

77. Wall, C.D., At. Absorpt. Newsl., 17, 61, 1978.

78. Steiner, J.W., and Kramer, H.L., Analyst, 108, 1051, 1983.

79. Welz, B., and Schlemmer, G., At. Spectrosc., 9, 76,

1988.

80. Thomerson, D.R., and Thompson, K.C., Amer. Lab., 6, 53, 1974.

81. Walish, W., and Jaenicke, O., Talanta, 22, 167, 1975.

82. Schlemmer, G., and Welz, B., Fresenius Z. Anal. Chem., 323, 703, 1986.

83. Amos, M.D., Bennett, P.A., Brodie, K.G., Lung, P.W.Y., and Matousek, J.P., Anal. Chem., 43, 211, 1971.

84. Ohta, K., and Suzuki, M., Anal. Chim. Acta, 96, 77, 1978.

85. Ohta, K., and Suzuki, M., Anal. Chim. Acta, 104, 293, 1979.

86. Ohta, K., and Suzuki, M., Anal. Chim. Acta, 107, 245, 1979.

87. Suzuki, M., and Ohta, K., Fresenius Z. Anal. Chem., 322, 480, 1985.

88. Ohta, K., and Mizuno, T., Microchem. J., 37, 203, 1988.

89. Ohta, K., Aoki, W., and Mizuno, T., J. Anal. At. Spectrom., 3, 1027, 1988.

90. Ohta, K. and Mizuno, T., Anal. Chim. Acta, 217, 377, 1989.

91. Ohta, K., Sugiyama, T., and Mizuno, T., Analyst, 115, 279, 1990.

92. Routh, M.W., Anal. Chem., 52, 182, 1980.

93. Frech, W., and Cedergren, A., Anal. Chim. Acta, 82, 83, 1976.

94. Ottaway, J.M., and Hutton, R.C., Analyst, 102, 785, 1977.

95. Zhe-Ming Ni, Heng-bin Han, and Xiao-chun Le, J. Anal. At. Spectrom., 1, 131, 1986.

96. Frech, W., and Cedergren, A., Anal. Chim. Acta, 82, 93, 1976.

97. Thompson, K.C., Wagstaff, K., and Wheatstone, K.C., Analyst, 102, 310, 1977.

98. Frech, W., and Cedergren, A., Anal. Chim. Acta, 88, 57, 1977.

99. Chakrabarti, C.L., Wu, S., and Bertels, P.C., 29th

Conf. Spectrosc. Soc. Canada. Sept. 1982.

100. Chakrabarti, C.L., Wu, S., Karwowska, R., Rogers, J.T., Haley, L., Bertels, P.C., and Dick, R., Spectrochim. Acta, 39B, 415, 1984.

101. Siemer, D., and Frech, W., Spectrochim. Acta, 39B, 261, 1984.

102. Littlejohn, D., and Ottaway, J.M., Analyst, 103, 595, 1978.

103. Weast, R.C., 'CRC Handbook of Chemistry and Physics', 65th edition, CRC Press, 1984.

104. Johnson, D.J., West, T.S., and Dagnall, R.M., Anal. Chim. Acta, 66, 171, 1973.

105. Welz, B., "Atomic Absorption Spectroscopy" 2nd Edition, VCH Verlagsgesellschaft mbH, FRG, 1985.

106. 'Atomic Absorption Data Book', 5th Edition, Philips Scientific, Cambridge, 1988.

107. Kneen, W.R., Rogers, M.J.W., and Simpson, P., 'Chemistry, Facts, Patterns and Principles', Addison Wesley Publishers Ltd., London, 1985.

108. Alvarado, J., and Petrola, A., J. Anal. At. Spectrom. 4, 411, 1989.

109. Calapaj, R., Chiricosta, S., Saija, G., and Bruno, E., At. Spectrosc., 9, 107, 1988.

110. Knowles, M.B., J. Anal. At. Spectrom., 4, 257, 1989.

111. Bettinelli, M., Baroni, U., and Pastorelli, N., J. Anal. At. Spectrom., 3, 1005, 1988.

112. Hunt, D.T.E., and Winnard, D.A., Analyst, 111, 785, 1986.

113. Majidi, V., and Holcombe, J.A., J. Anal. At. Spectrom., 4, 439, 1989.

114. Bulska, E., Grobenski, Z., and Schlemmer, G., J. Anal. At. Spectrom., 5, 203, 1990.

115. Welz, B., Schlemmer, G., and Mudakavi, J.R., J. Anal. At. Spectrom., 3, 695, 1988.

116. Smeyers-Verbeke, J., Yang, Q., Penninckx, W., and Vandervoort, F., J. Anal. At. Spectrom., 5, 393, 1990.

117. "Analytical Methods for Furnace Atomic Absorption Spectrometry". Perkin-Elmer, Norwalk, Ct. 1984.

118. BDH, Hazard Data Sheets, BDH Chemicals Ltd., Poole, 1989

119. Kirkbright, G.F., and Snook, R.D., Anal. Chem., 51, 1938, 1979.

120. Kirkbright, G.F., and Zhang Li-Xing, Analyst, 107, 617, 1982.

121. Ericson, S.P., McHalsky, M.L., and Jaselskis, B., At. Spectrosc., 8, 101, 1987.

122. Kantor, T., and Alvarez-Prieto, M., J. Anal. At. Spectrom., 3, 53, 1988.

123. Chapman, J.F., and Dale, L.S., Anal. Chim. Acta, 89, 363, 1977.

124. Nater, E.A., Burau, R.G., and Akeson, M., Anal. Chim. Acta, 225, 233, 1989.

125. Hu, W.-D., Vandecasteele, C., Wauters, G., and Dams, R., Anal. Chim. Acta, 226, 193, 1989.

126. Bachmann, K., Talanta, 29, 1, 1982.

127. Slavin, W., Manning, D.C., and Carnrick, G.R., Anal. Chem., 53, 1504, 1981.

128. Chung, D.D.L., Rev. Sci. Instrum., 51, 932, 1980.

129. Welz, B., and Schlemmer, G., At. Spectrosc., 9, 81, 1988.

130. Cotton, F.A., and Wilkinson, G., "Advanced Inorganic Chemistry, A Comprehensive Text", fourth edition, John Wiley and Sons, Chichester, 1980.

131. Lee, D.S., Anal. Chem., 54, 1182, 1982.

132. Vijan, P.N., At. Spectrosc., 1, 143, 1980.

133. Alary, I., Vandaele, J., Escruit, C., and Haran, R., Talanta, 33, 748, 1986.

134. Sturgeon, R., Willie, S.N., and Berman, S.S., J. Anal. At. Spectrom., 4, 443, 1989.

135. Drews, W., Weber, G., and Tolg, G., Fresenius Z., Anal. Chem., 332, 862, 1989.

136. McClaren, J.W., and Wheeler, R.C., Analyst, 102, 542, 1977.

137. Frech, W., Lindberg, A.O., Lundberg, E., and Cedergren, A., Fresenius Z. Anal. Chem., 323, 716, 1986.

138. Peile, R., Grey, R., and Starek, R., J. Anal. At. Spectrom., 4, 407, 1989.

139. Welz, B., Schlemmer, G., Ortner, H.M., and Birzer, W., Spectrochim. Acta, 44B, 1125, 1989.

140. Grgic, I., Hudnik, V., Gomiscek, S., Anal. Chim. Acta, 226, 203, 1989.

141. Issag, H.J., and Zielinski, W.L., Anal. Chem., 46, 1436, 1974.

142. Slovak, Z., and Docekalova, H., Anal. Chim. Acta, 115, 111, 1980.

LECTURES AND ASSOCIATED STUDIES

i. Plymouth Polytechnic Chemistry Society, 6th November 1987, Plymouth Polytechnic, Dr S Haswell, "Gas Sensors".

ii. RSC Lecture, 13th November 1987, Plymouth Polytechnic, Dr A Howard, "Speciation".

iii. RSC Lecture, 29th January 1988, Plymouth Polytechnic, Prof. A Townshend, "Flow Injection Analysis - The First Decade".

iv. AGM of the Peninsula Section of the RSC, 13th May 1988, Plymouth Polytechnic, Dr C Fisher, "Heavy Metals in Food - Is there a Problem?"

v. Research Visit, 18th October 1988, ICI Brixham.

vi. RSC Lecture, 17th January 1989, Plymouth Polytechnic, Dr P Worsfold, "Flow Injection Analysis - Hands Off Analysis".

vii. RSC Lecture, 17th February 1989, Polytechnic South West, Prof. M Barber, "Modern Mass Spectrometry".

viii. RSC Lecture, 21st November 1989, Polytechnic South West, Dr S K Scott, "Clocks, oscillations and chaos in chemistry".

ix. RSC Lecture, 26th January 1990, Polytechnic South West, Dr J P Leahey, "Studies in the environmental fate of a new insecticide".

x. Combined Chromatography and Spectrometry in Analysis. 16th October 1990. Open Day Swansea University.

xi. RSC Lecture, 17th January 1991, Polytechnic South West, Dr R J Perriman. "Chemical manufacturing and the Environment".

xii. Weekly Departmental Research seminars 1987-1991 Plymouth Polytechnic/Polytechnic South West.

MEETINGS ATTENDED

i. North East Region Atomic Spectroscopy and Molecular Spectroscopy Groups jointly with the U.V. Spectrometry Group and Atomic Spectrometry Updates of the RSC, 19th and 20th March 1988, Hull.

ii. Atomic Spectroscopy Group of the RSC jointly with the Spectroscopy Group of the Institute of Physics, "Fourth Biennial National Atomic Spectroscopy Symposium". 29th June-1st July 1988, York.

iii. Analytical Division of the RSC Research and Development Topics in Analytical Chemistry, 18th and 19th July 1988, Plymouth.

iv. Atomic Spectroscopy Group and Atomic Spectrometry Updates of the RSC, 30th March 1989, Glasgow.

v. Atomic Spectroscopy Group and Atomic Spectrometry Updates of the RSC, 30th March 1990, Guildford.

vi. Analytical Division of the RSC meeting on Research and Development Topics in Analytical Chemistry 16th and 17th July 1990, Runcorn.

vii. Atomic Spectroscopy Group of the RSC jointly with the Spectroscopy Group of the Institute of Physics, "Fifth Biennial National Atomic Spectroscopy Symposium", 18th-19th July 1990, Loughborough.

PRESENTATIONS AND PUBLICATIONS

Posters

i. "Utilising an Air Ashing Phase in the Analysis of Slurries by Electrothermal Atomisation Atomic Absorption Spectrometry" A S Fisher, L Ebdon, and H G M Parry, 28th June-1st July 1988, York.

ii. "Reactive Gases in Electrothermal Atomisation Atomic Absorption Spectrometry", A Fisher, L Ebdon and H G M Parry, 18th and 19th July 1988, Plymouth.

iii. "Matrix Modification by a Reactive Gas for ETAAS", A Fisher, L Ebdon and S Hill, 16th and 17th July 1990, Runcorn.

iv. "The Affects of Reducing Gases on Analytical Signals in ETAAS", A Fisher, L Ebdon and S Hill. 17th-19th July 1990.

Papers

i. "Direct Atomic Spectrometric Analysis by Slurry Atomisation. Part 10. Use of an Air-Ashing Stage in Electrothermal Atomic Absorption Spectrometry". L Ebdon, A S Fisher, H G M Parry and A A Brown. J. Anal. At. Spectrom., 5, 321, 1990.

ii. "Determination of Grease Additives Using Direct Current Plasma-Atomic Emission Spectrometry". J A Armstrong, L Ebdon and A Fisher. Submitted to J. Anal. At. Spectrom.

Direct Atomic Spectrometric Analysis by Slurry Atomisation

Part 10.* Use of an Air-ashing Stage in Electrothermal Atomic Absorption Spectrometry

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The use of an air-ashing stage in electrothermal atomic absorption spectrometry for slurry atomisation is described. Air-ashing was shown to reduce significantly interferences from non-specific absorption and allow a wider range of ashing temperatures without sample loss. A significant decrease in the interference of magnesium chloride on lead determinations was also observed. Chromium, cobalt, lead and manganese were successfully determined in slurries of five biological certified reference materials (tomato leaves, human hair, mussel, *Chlorella* and sewage sludge) and good agreement was obtained with certified values.

Keywords: *Electrothermal atomisation; atomic absorption spectrometry; air ashing; slurry atomisation; solid samples*

Electrothermal atomic absorption spectrometry (ETAAS) has become one of the most commonly used analytical techniques for ultra-trace analysis. It has several advantages over flame AAS, including increased sensitivity and the capacity to cope with solid samples. The problems of interferences have, in recent years, been partially overcome by the use of better designed furnaces, improved spectrometers and chemical modification.

Recently, there has been growing interest in the use of slurries as a means of introducing solids into a graphite furnace (*e.g.*, references 1–6), because slurries are relatively simple to prepare, they require no aggressive chemical pre-treatment and are thus less susceptible to contamination. The viability of calibration using aqueous standards is a major advantage. A problem with slurries, solids or liquids that have an organic matrix is incomplete ashing of the matrix. Several workers have therefore used air or oxygen as an ashing aid.[4,6–8] This converts the normal charring stage into an oxidative decomposition process. Without the air or oxygen, carbonaceous residue would be left in the tube after atomisation. After several analyses, this residue increases to the extent that it begins to obstruct the light beam, and hence causes an increase in background absorption.

There have been several reports of studies of the mechanism by which oxygen interacts with the graphite and the analyte.[9,10] These reports have indicated that analytes such as lead may be ashed using much higher temperatures than usual, without the problem of analyte loss. This was found to be due to the formation of less volatile lead species that do not enter the vapour phase until much higher temperatures are reached. As a consequence, more effective removal of the matrix can be achieved.

In this paper, the use and advantages of an air-ashing stage in the analysis of slurries is described. Sample pre-treatment was kept to a minimum, and no "wet" chemical modification was used. Ash plots with and without air are shown for different elements in a slurry, demonstrating the use of air in the ashing stage. The method was calibrated using aqueous standards, and was validated using various certified reference materials with Pb, Co, Cr and Mn as the analytes.

Experimental

Reagents and Standards

High-purity water was obtained by using reverse osmosis (Milli-RO4; Millipore, Harrow, Middlesex, UK) followed by adsorption, de-ionisation and ultrafiltration (Millipore Milli-Q system).

Nitric acid (sp.gr. 1.42) of Pronalysar grade (May and Baker, Dagenham, UK) and hydrochloric acid (sp.gr. 1.18) of AnalaR grade (BDH, Poole, Dorset, UK) were used.

Stock standard solutions of Co, Cr, Mn and Pb (1000 mg l^{-1}) were prepared in the following manner. Cobalt metal powder (0.100 g) (BDH) was dissolved in the minimum volume of aqua regia and diluted to 100 ml with water. Potassium dichromate (0.2829 g) (BDH) was dissolved in water and made up to 100 ml. Manganese metal (0.100 g) (BDH) was dissolved in hydrochloric acid and diluted to 100 ml with water. Lead nitrate (0.1598 g) (BDH) was dissolved in water and diluted to 100 ml. All stock standard solutions were stored in acid-washed polyethylene bottles.

Working standard solutions were prepared daily by serial dilution of the stock standard solutions.

Sample Preparation

Approximately 1% m/v slurries of the certified reference materials (except hair) were made by weighing about 0.200 g of the material into a 30-ml polypropylene bottle. Zirconia beads (10 g) (2 mm diameter; Glen Creston, Stanmore, Middlesex, UK) and 3 ml of water were placed in the bottle and the bottles shaken, on a mechanical flask shaker, for 1–4 h. The slurries were then diluted to volume (20 ml) by the addition of water. A blank was made in exactly the same way but omitting the sample. No significant blank levels were seen for any of the elements studied. A 1% m/v slurry of hair was made by weighing *ca.* 0.250 g of material into a clean, pre-weighed platinum dish, which was placed in a muffle furnace at 300 °C for 3 h. The platinum dish was removed, placed in a desiccator and allowed to cool. The dish was re-weighed to determine the mass of the residual ash. The majority of this ash was then weighed into a polypropylene bottle and slurried as before. The final volume of the hair slurry was 20 ml.

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* For Part 9 of this series, see *J. Anal. At. Spectrom.*, 1990, 5, 67.

Table 1. Furnace conditions used for the ashing plots of bovine liver slurry

Phase	Temperature/°C	Hold time/s	Ramp/ °C s⁻¹	Gas	Gas flow-rate/ l min⁻¹
Dry	110	40	10	N_2	3.5
Ash 1	Varied	20	50	N_2 + air	3.5
Ash 2	Varied	20	0	N_2	3.5
Atomise	2200	3	>2000	Gas stop	0
Clean	2500	4	>2000	N_2	3.5

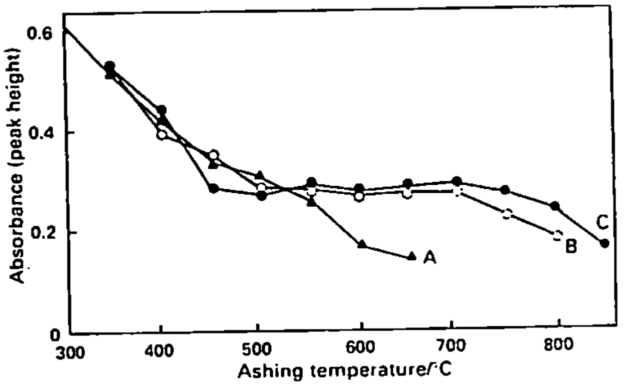

Fig. 1. Ashing plots for lead in bovine liver slurry using various amounts of air: A, 0; B, 1; and C, 2.5 l min⁻¹

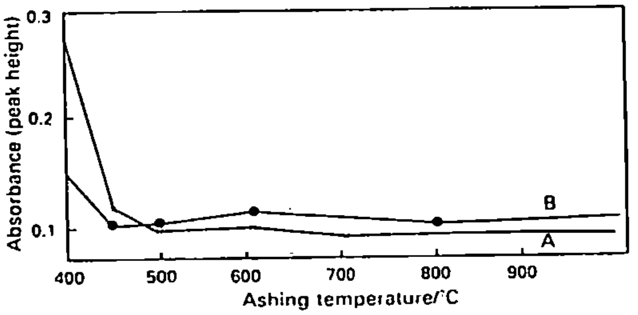

Fig. 2. Ashing plots for iron in bovine liver slurry: (A) without air and (B) with 2.5 l min⁻¹ air

Ashing in a muffle furnace prior to grinding overcame problems arising from the fibrous nature of hair. The value of carbonisation in overcoming such problems has been reported elsewhere.[11]

Instrumentation

An SP9 atomic absorption spectrometer (Philips Scientific, Cambridge, UK) fitted with a video furnace programmer (PU 9095, Philips Scientific) was used. Additionally, an alternative atomic absorption spectrometer (PU9400, Philips Scientific) fitted with an electrothermal atomiser (PU9390, Philips Scientific) was also used for repeat analyses of some certified reference material slurries. The two furnaces differ in that the gas flow in the SP9 - PU9095 system fills the entire furnace head and only enters the graphite tube by diffusion, whereas in the PU9390 the gas flows directly down the inside of the tube and out of the centre. Both spectrometers have deuterium continuum source background correction systems.

Pyrolytic graphite coated graphite tubes were used throughout. Both standards and slurries were introduced manually into the graphite furnace by micropipette (Gilson Medical Electronics, Villiers-le-Bel, France). In all the work reported conventional wall atomisation and the gas-stop mode were used. The slurries were agitated manually before pipetting. Air was introduced to the furnace via a switching valve between the air and nitrogen cylinders.

Results and Discussion

Initial experiments were performed on the SP9 to investigate the advantages of incorporating an air-ashing stage in the furnace cycle. Using the furnace parameters shown in Table 1, and lead as the analyte, ashing curves for bovine liver were constructed (Fig. 1).

A second ashing stage is required in which an inert gas is used to remove trace amounts of oxygen from the atmosphere and from the active sites on the graphite surface. When atomisation immediately followed the air-ashing stage, the tube degenerated rapidly.

As the amount of air bled into the inert gas flow increased, it was found that both higher and lower ashing temperatures could be used. Higher temperatures could be utilised presumably because of the formation of less volatile lead oxide species, rather than lead halides (boiling points: lead, 1751 °C; $PbCl_2$, 950 °C; and PbO, 1472 °C). The mechanism of this process and the subsequent reduction of PbO by carbon have been reported previously.[8,9] Lower ashing temperatures were practicable because pyrolysis became much more efficient and hence the organic matrix was removed more rapidly.

The ashing curve in which no air was used showed no plateau region, and hence it was impossible to select a temperature at which non-specific absorbance interference (smoke) had ceased but analyte loss had not begun. The large absorbance signals obtained when ash temperatures less than 500 °C were used were due to excessive smoke interference causing the continuum source background correction system to under-correct. This was shown by using the lead non-absorbing line at 280.1 nm. This gave signals at temperatures up to of 500 °C, indicating that the increased signal below 500 °C was due to smoke.

Similarly shaped ashing plots were obtained with and without air when the bovine liver slurry was analysed for cadmium. Again, even with the use of lower ashing temperatures, owing to more efficient pyrolysis organic samples could be analysed accurately. The use of higher ashing temperatures could, however, be used owing to the formation of less volatile species and are preferable for more refractory matrices. Similar results were obtained for Pb and Cd in a milk powder slurry.

Ashing plots were also constructed for some less volatile elements. Cobalt exhibited the same increase in the efficiency of pyrolysis, *i.e.*, lower background absorbance, but higher ashing temperatures were not advisable when air was used. The boiling points of the species of interest are Co = 2870 °C, $CoCl_2$ = 1049 °C and CoO = 1795 °C, which indicates that the maximum ashing temperature that should be used is 900–1000 °C. As air ashing at such temperatures would quickly result in degeneration of the graphite tube, it was decided that there was no point in extending the ashing plot beyond this temperature. Similar results were obtained for iron (Fig. 2), where the results below 500 °C are influenced by large, only partially corrected background absorbances.

An air-ashing stage also led to a decrease in the interference on lead determinations by magnesium chloride. It has been found[11] that magnesium chloride interacts with lead in the

Table 2. Furnace parameters for the analysis of slurries. All analyses incorporated a drying stage at 110 °C for 40 s. A tube-cleaning stage at 2800 °C for 3 s was also used for all analyses except lead, which had a cleaning stage at 2400 °C for 3 s. This table refers to both furnaces used. The SP9 had a gas flow-rate of 3.5 l min^{-1}, except during the atomise stage (gas stop). The PU9390 had an internal gas flow-rate of 200 ml min^{-1} during all stages except atomise

Element	Wavelength/ nm	Matrix	Slit-width/ nm	Lamp current/ mA	Ashing phase		Atomise phase/ °C
					Temperature/°C	Time/s	
Mn	403.1	*Chlorella*, mussel, hair	0.5	8	550	20	2400
	321.7	Tomato leaves, sewage sludge	0.1	8	550	20	2400
Cr	357.9	Tomato leaves, hair, mussel	0.5	8	550	20	2400
	520.5	Sewage sludge	0.1	8	550	20	2400
Co	240.7	Mussel, tomato leaves, *Chlorella*	0.5	8	550	20	2400
	304.4	Sewage sludge	0.5	8	550	20	2400
Pb	283.3	*Chlorella*, mussel, hair, tomato leaves	0.5	5	550	20	2200
	368.3	Sewage sludge	0.5	5	550	20	2200

Table 3. Results for slurry atomisation of various certified reference materials. In all instances $n = 6$; results are for repetitive analyses of a single slurry, and results are quoted ±1 SD. Values in parentheses are indicative only

Sample	Element	Certified value/ µg g^{-1}	Result obtained/µg g^{-1}	
			SP9	PU9400
Tomato leaves (NIST SRM 1573)	Mn	238 ± 7	260 ± 17	216 ± 22
	Cr	4.5 ± 0.5	4.24 ± 0.35	4.4 ± 0.25
	Co	(0.6)	0.57 ± 0.03	0.56 ± 0.05
	Pb	6.3 ± 0.3	6.1 ± 0.7	5.3 ± 0.6
Human hair (NIES 5)	Mn	5.2 ± 0.3	4.9 ± 0.6	5.6 ± 0.1
	Cr	1.4 ± 0.2	1.3 ± 0.1	1.4 ± 0.16
	Co	(0.1)	0.08 ± 0.03	—
	Pb	(6.0)	5.8 ± 0.9	6.6 ± 0.6
Mussel (NIES 6)	Mn	16.3 ± 1.2	16.5 ± 5.9	17.3 ± 0.4
	Cr	0.63 ± 0.07	0.56 ± 0.05	0.59 ± 0.03
	Co	(0.37)	0.35 ± 0.01	0.35 ± 0.02
	Pb	0.91 ± 0.04	1.03 ± 0.14	0.96 ± 0.05
Chlorella (NIES 3)	Mn	69 ± 5	65 ± 21	61 ± 3
	Cr	—	—	—
	Co	0.87 ± 0.05	0.91 ± 0.06	0.74 ± 0.03
	Pb	(0.6)	1.2 ± 0.12	—
Sewage sludge (BCR 145)	Mn	241 ± 12	244 ± 15	229 ± 25
	Cr	(105)	94.3 ± 6.3	120.9 ± 7.8
	Co	8.38 ± 0.71	8.63 ± 0.62	—
	Pb	349 ± 15	365 ± 22	330 ± 9

vapour phase, causing severe losses of the latter through volatilisation as the chloride. It has been reported[12] that as little as 40 mg l^{-1} of magnesium chloride totally suppressed the lead signal. The use of an air-ashing phase decreased the interference, which was attributed to the formation of lead oxide and the blocking of active sites on the graphite surface. It has previously been found that the use of $NH_4H_2PO_4$ or pre-treatment of the tube with 1% ammonium molybdate followed by the use of phosphoric acid as a chemical modifier[13] also decreased the interference by magnesium chloride. However, the use of an air-ashing system may be quicker, is less prone to contamination than the use of "wet" chemical modifiers and is more readily automated. Probe atomisation[14] can also be used to decrease this interference. Platform atomisation is a long-established method of decreasing interferences, owing to the isothermal atmosphere formed within the furnace.

The use of an air-ashing stage was found not to have any significant adverse affect on the precision of the technique. An experiment was performed in which the lead signal from a bovine liver slurry was measured and the relative standard deviation (RSD) calculated after every five firings. This continued over a period of 50 firings. The RSD was found to be below 4% in all instances. The experiment was repeated using a normal ashing period in place of the air-ashing period. The RSD was again found to be less than 4% in all instances.

The lifetime of the graphite tube was not significantly shorter when air was used, provided that the ashing temperature did not exceed 600–650 °C. Above this temperature the graphite became steadily more porous as its surface was oxidised.

Evaluation of the Method

Five certified reference materials were slurried as described previously. The levels of Pb, Co, Mn and Cr in the slurries were determined using the furnace parameters given in Table 2. The analyses were conducted on both an SP9 atomic absorption system and on a PU9400 fitted with a PU9390 electrothermal atomiser. As Fig. 1 shows, the more air is present, the more efficient is the ashing. Therefore, for all these analyses, 3.5 l min^{-1} of air were used. The results from the two furnace systems are given in Table 3.

In general, the results obtained were in good agreement with the certified values. The precision of some analyses on the SP9 was poor. This corresponded to situations in which the high concentration of the analyte elements in the samples necessitated the use of lines of relatively poor sensitivity. Unfortunately, these lines often showed poor signal to background ratios and noisy signals. The particular continuum source background corrector used in the older SP9 design did not function well above 350 nm. Using the newer PU9400, the alternative lines were easier to locate using the computerised peak-search routine and it was not necessary, when using the improved furnace design, to employ background correction above 350 nm. Thus for the Mn determination of the 403.1-nm line and the Pb analyses at the 368.35-nm line, the background corrector was switched off. The signals obtained therefore might include any background absorption. As Fig. 3 shows, the analyte peak precedes a large non-specific absorption peak. Therefore, by decreasing the read time to 1 s and by using peak-height measurements, the analyte was accurately determined. It was found that the PU9390 system was far more efficient at ashing the matrix, and therefore an ashing temperature of 450 °C could be used. This was probably due to the air being flushed through the tube, rather than just allowing it to diffuse through, as in the older system.

Conclusion

The use of an air-ashing stage in the analysis of slurries leads to more efficient pyrolysis. This has two advantages. Firstly, it decreases the amount of carbonaceous residue left in the tube after an analysis, and secondly, it facilitates atomisation free from interference caused by non-specific absorption after ashing at much lower temperatures. Interference from other species such as magnesium chloride was also found to decrease. This was presumably due to less volatile lead species being formed and, hence, reduced interaction with chloride ions in the vapour phase. Air-ashing was found to have no deleterious effect on either the tube lifetime, provided that ashing temperatures below 600 °C were used, or on the analytical precision. The use of an air-ashing stage in the analysis of Co, Cr, Mn and Pb in some slurries of certified reference materials gave results that were in good agreement with the certified values.

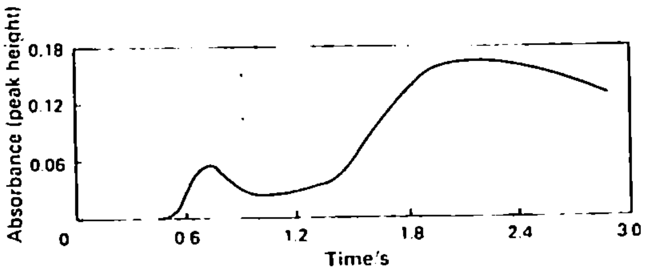

Fig. 3. Signal obtained for a slurry at the lead 368.35-nm line without background correction

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References

1. Carrión, N., de Benzo, Z. A., Moreno, B., Fernandez, A., Eljuri, E. J., and Flores, D., *J. Anal. At. Spectrom.*, 1988, 3, 479.
2. Hinds, M. W., and Jackson, K. W., *J. Anal. At. Spectrom.*, 1988, 3, 997.
3. de Benzo, Z., Fernandez, R., Carrion, N., and Eljuri, E., *At. Spectrosc.*, 1988, 9, 87.
4. Stephen, S. C., Littlejohn, D., and Ottaway, J. M., *Analyst*, 1985, 110, 1147
5. Ebdon, L., and Parry, H. G. M., *J. Anal. At. Spectrom.*, 1987, 2, 131.
6. Ebdon, L., and Parry, H. G. M., *J. Anal. At. Spectrom.*, 1988, 3, 131.
7. Shuttler, I. L., and Delves, H. T., *Analyst*, 1986, 111, 651.
8. Beaty, M., Barnett, W., and Grobenski, Z., *At. Spectrosc.*, 1980, 1, 72.
9. Bass, D. A., and Holcombe, J. A., *Anal. Chem.*, 1987, 59, 974.
10. Salmon, S. G., and Holcombe, J. A., *Anal. Chem.*, 1982, 54, 630.
11. Armstrong, J. A., Ebdon, L., and Sparkes, S. T., *J. Anal. At. Spectrom.*, in the press.
12. Slavin, W., and Manning, D. C., *Prog. Anal. At. Spectrosc.*, 1982, 5, 243.
13. Hodges, D. J., *Analyst*, 1977, 102, 66.
14. Brown, A. A., *J. Anal. At. Spectrom.*, 1988, 3, 67.

Note—References 5 and 6 are to parts 2 and 4 and of this series, respectively.

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