

DETERMINATION
ATOMIC ABSORPTION ~~ANALYSIS~~ OF METALS IN OILS

by

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To my parents

ABSTRACT

The application of the carbon filament atom reservoir to the determination of metals in oils at trace and additive levels is extended to include calcium, magnesium and barium.

Hydride generation followed by atomisation in a carbon furnace is used to determine antimony, tin and lead in aqueous and oil media.

The determination of sulphur in aqueous and oil media by chemiluminescent emission of the S_2 species in a hydrogen/inert gas diffusion flame following conversion to the hydride is described. In this chapter the emission due to CO in a carbon furnace is noted.

Throughout the work the emphasis is placed on organic solutions and the development of methods to deal with real samples.

ACKNOWLEDGEMENTS

The work presented in this thesis was carried out in the Chemistry Department of the Imperial College of Science and Technology between October 1973 and October 1975. It is entirely original, except where due reference is made, and no part has previously been submitted for any other degree.

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PART ONE

INTRODUCTION

Chapter 1

Introduction

1.1 Origins and Occurrence of Crude Oil

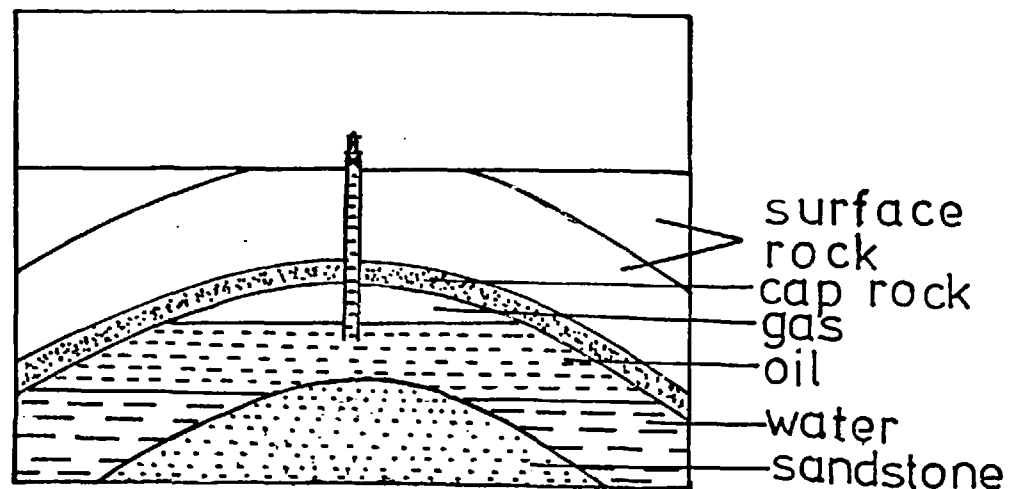
It is generally accepted that crude oil is formed by the anaerobic decomposition of organic material. The pre-cambrian seas were heavily populated with plankton which died and sank to the sea bed where they were decomposed by bacteria. In the course of time this organic material was compacted by sediment being deposited in the same location; the result was the formation of rocks rich in protopetroleum called source rocks, an example of which may be seen today in Canada as black shale. It is possible to extract oil from these shales but it has not until recently been an economic proposition and most of the world's oil is brought up from the earth in liquid form by drilling oil wells.

Clearly there is a considerable difference between shales where the oil is held with its connate water in the pores between rock particles and the classic picture of an underground reservoir of oil. Geologists tell us that the transformation from shale oil to the more convenient and economical reservoir oil starts during the compaction stage. The mud on the sea bed containing the incipient oil is compressed and the fluids associated with it are displaced into the adjacent sandstone which is a permeable rock and has a constant flow of water through it. The oil and the water move along, with the oil tending to move upwards as it is less dense than water. The movement of the oil ceases when it reaches a layer of impervious rock. A typical geological formation in which oil may be trapped is an anticline where the impervious rocks are arched in a dome-shaped structure as shown in Figure 1.1. If such a suitable structure does not present itself the oil will manifest itself as a surface seep. Gaseous hydrocarbons, often contaminated with nitrogen, carbon dioxide and hydrogen sulphide, may be present dissolved in the crude oil, or, as is more common, they occur in

sufficient quantities to saturate it under the physical conditions prevailing in the reservoir and form a gas cap on top of the layer of crude oil.. It may be recalled that in the early days of exploration for North Sea oil considerable quantities of natural gas were found; those discoveries preceded the striking of oil by several years. Finally it must be remembered that in the search for oil it is only possible to predict where oil might be found; the only certain way of knowing is to drill.

Figure 1.1

Oil reservoir



1.2 Analysis of Crude Oil

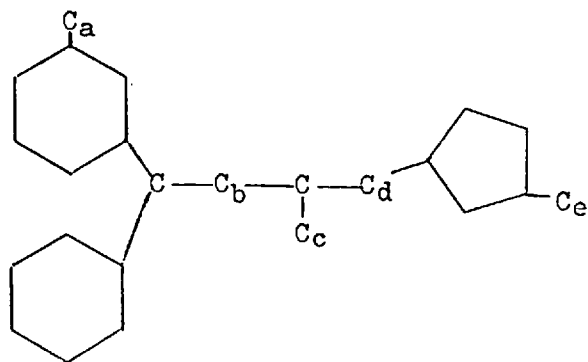
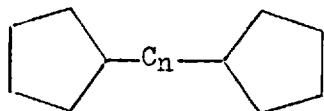
Before any decisions can be made about refining a crude oil it is necessary for the refiner to know the nature of the substance with which he is dealing. A typical crude oil analysis will give information on its physical properties from which it is possible to deduce the distribution of various fractions in a particular sample. These fractions consist mostly of mixtures of hydrocarbons such as linear and cyclic paraffins and various aromatics. Some examples of the more complex types present are shown in

Figure 1.2. The chemical analysis will give the non-hydrocarbon content. The ash content of a crude oil is typically $< 0.01\%$ whereas a good bituminous coal is ca 4% (1).

Methods referred to here are standard ASTM or IP procedures unless otherwise stated (2).

Figure 1.2 Hydrocarbons in Crude Oil
(carbon skeletons)

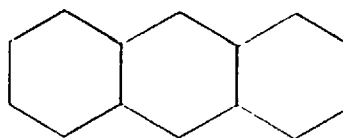
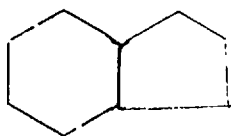
(a)



Naphthene rings joined by paraffin chains

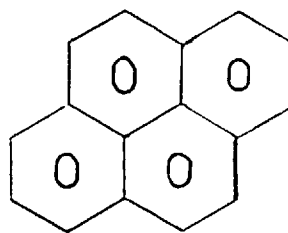
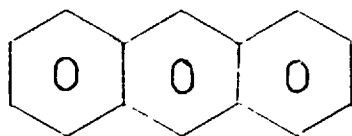
a - e are integers

(b)



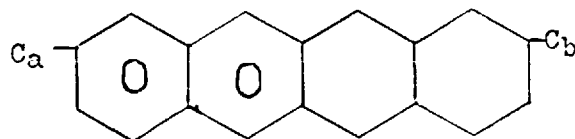
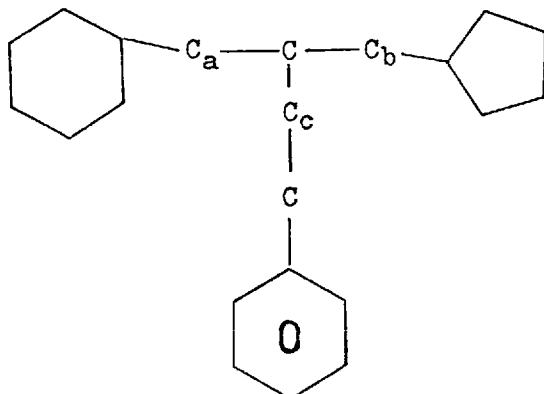
Fixed naphthene rings

(c)



Fused aromatics

(d)



Mixed aromatic and naphthenic rings with paraffin linkages/side chains

1.2.1 Sulphur

Sulphur is probably one of the most important non-hydrocarbons present in crude oil. Sulphur contents of different crudes vary from less than 0.1% up to 7%. Middle Eastern crudes tend to have a high sulphur content while North Sea oil is very low in this element. The analysis will give details of total sulphur, mercaptan sulphur and dissolved hydrogen sulphide. Sulphur largely occurs in comparatively unreactive forms where the element is bound in a ring structure, however thiols and dissolved hydrogen sulphide are not only corrosive but also a health hazard for refinery workers. Most refineries are made of sulphur resistant materials or are protected by the addition of basic substances to counteract the effects of these light sulphur compounds. The presence of heavier sulphur compounds presents problems to the refiner. Consider a molecule of molecular weight ca. 300 which contains one atom of sulphur: the sulphur content will be about 1%. If a refiner were to remove the sulphur-containing compound he would indeed have rid the crude of 1% sulphur but in addition would have also removed a large amount of otherwise useful hydrocarbon material; for example it is not uncommon that in the higher boiling ranges of a sulphurous crude 3 - 5% sulphur may represent half the total bulk of the fraction. It is thus most important for the refiner to know not only the total amount of sulphur present but also the manner of its combination. Methods for the analysis of sulphur will be discussed in Chapter 9.

1.2.2 Oxygen and Nitrogen

Oxygen compounds in crude oils are of three main types: naphthenic acids, phenols and naphthols, and oxyaromatics. In general the refiner is only interested in the acidic properties of these oxygen containing compounds and if the acidity of a crude is found to be too high it is treated with base before the refining process is commenced.

Nitrogen compounds are usually present in very low concentrations in the form of aromatic compounds which give rise to colour instability and interfere with hydrocracking processes. Their presence in these forms lends weight to the organic theories of the origin of oils.

1.2.3 Halogens

The most common halogen present in crude oils is chlorine, both in the anionic form and bound in organic compounds. A desalting process removes most of the halogens but catalytic procedures in refining are easily poisoned by them and so it is necessary to monitor trace quantities. Inorganic chlorides may be determined by precipitation with silver nitrate. Organic halides are decomposed by sodium biphenyl and the sodium chloride thus produced extracted into nitric acid and determined either potentiometrically or colorimetrically. Iron (III) and mercuric thiocyanate are added, mercuric chloride is precipitated and the ferric thiocyanate produced determined photometrically. X-ray fluorescence (XRF) has also been used.

1.2.4 Nickel and Vanadium

Nickel and vanadium both occur in crudes as organometallic compounds similar to chlorophylls and porphyrins. Both are notorious catalyst poisons and are therefore of considerable interest to the refiner. They also, however, have forensic significance in cases of marine pollution. Venezuelan crudes have high nickel and vanadium contents, Middle Eastern ones moderate levels of these elements and those from Africa and Australia are low in both substances. The ratio of the two elements within each group is relatively constant; thus in Venezuelan products there is always ten times more vanadium than nickel; in Middle Eastern crudes this drops to three and in the other group there is ten times more nickel than vanadium. Hence it is possible to fingerprint an oily pollutant and identify the offending vessel. Vanadium also has deleterious effects on boiler materials.

The concentrations of vanadium found can range from fractions of a ppm to over 1000 ppm. Nickel is present in more moderate quantities, 200 ppm being considered fairly high. It is necessary to be able to analyse both elements down to very low levels.

The ASTM method for the analysis of vanadium is by the colorimetric determination of the phosphotungstovanadic acid complex. Other colorimetric methods have been developed which employ other phosphate-tungstate complexes (3); the use of a catechol complex has also been reported (4). These methods are suitable for concentrations in the ppm range. Since vanadium is often sought along with other metals, spectrographic methods often commend themselves on grounds of convenience; however it is sometimes necessary to use a preconcentration step although methods such as the rotating disc have been shown to be quite feasible propositions (5). Atomic absorption spectrometry (AAS) has been widely applied to the determination of this element with a considerable degree of success, in spite of the fact that it forms a refractory oxide. The sample is usually dissolved in a solvent such as xylene or methyl isobutyl ketone (MIBK) and sprayed into a nitrous oxide-acetylene flame (6). Non-flame cells have also been applied to this problem, for example the HGA 70 furnace was used to determine vanadium in fuel oils at a level in excess of 20 ppm (7). One of the most interesting developments in the application of flameless AAS is the work of Everett et al. (104) who used a solvent extraction procedure as a preconcentration step to extend the normal range, 0.5 - 20 ppm, for the determination of vanadium in oils on the carbon filament to include the range 0.01 - 0.5 ppm. Gibbison and co-workers (9) used neutron activation analysis (NAA) to determine 0.02 ppm of vanadium in crudes and an order of magnitude less than this in light oils. X-ray emission techniques have been employed to determine levels of 0.1 ppm in oil matrices (10). Although electrochemical methods have been reported they tend to be involved and

subject to interferences from the matrix.

The atomic and nuclear techniques referred to above are also suitable for the determination of nickel in oils. Nickel may be routinely determined by emission spectrography at levels ranging from 30 - 1000 ppm (5). Flame AAS has been used to determine levels of nickel between 0.7 and 50 ppm (11, 12) while flameless procedures are capable of measuring quantities as low as tens of picograms (13, 14). Alder and West (15) obtained good agreement with spark emission spectrography when they determined nickel in crudes and residual fuel oils by carbon filament AAS.

The wet chemical methods for the determination of nickel are for the most part based on the complexation reaction with dimethylglyoxime (DMG). Usually the finish is gravimetric, but photometric techniques have been proposed and compare quite favourably with their gravimetric forebears (16), being useful down to tens of ppm.

1.2.5 Lead and Arsenic

Both these elements occur naturally in crudes as trace elements and both are very efficient catalyst poisons. It is thus necessary to determine these substances in very low concentrations. Methods for the analysis of lead will be discussed in Chapter 8.

There is a number of methods for analysing arsenic in naphtha feedstocks a typical example of which consists of extracting the arsenic from the organic matrix into an oxidising sulphuric acid medium followed by colorimetric determination with silver diethyl dithiocarbamate. It is possible to detect as little as 1 ppb with this technique. Techniques based on the generation of arsine may be applicable to the analysis of oils; they are currently in use in the paint industry for the detection of ppm levels of arsenic and do not appear to suffer from interferences (17).

1.2.6 Sodium and Potassium

Both these elements occur naturally in crudes and may be introduced by contamination, for example from sea water. In this context they are usually analysed by spark emission or flame photometry.

1.2.7 Copper and Iron

Although they both occur naturally in crudes in trace quantities, iron may be present in greater quantities due to contamination from pipelines and storage tanks. Copper chloride is used as a catalyst to convert thiols into disulphides before refining and thus may be present in more than trace concentration in unrefined oils. Both elements are catalyst poisons and exhibit oxidant activity.

There is a number of methods for the photometric determination of copper which are based on the complexes formed with either diethyldithiocarbamate (18) or neocuproine (2,9-dimethyl-1,10-phenanthroline) (19) either before or after some preliminary ashing step. Emission, XRF and AAS have been applied to the determination of copper in oils (3). Alder and West have described the direct determination of copper by flameless AAS with a detection limit of 190 pg (20).

Iron is usually analysed instrumentally, emission being a very well established technique for this (21). The nitrous oxide - acetylene flame has been applied to the atomic absorption analysis of iron in oils (3) and flameless methods bring the limit of detection down to picogram levels (13, 14). XRF has also been successfully used in this type of analysis (22).

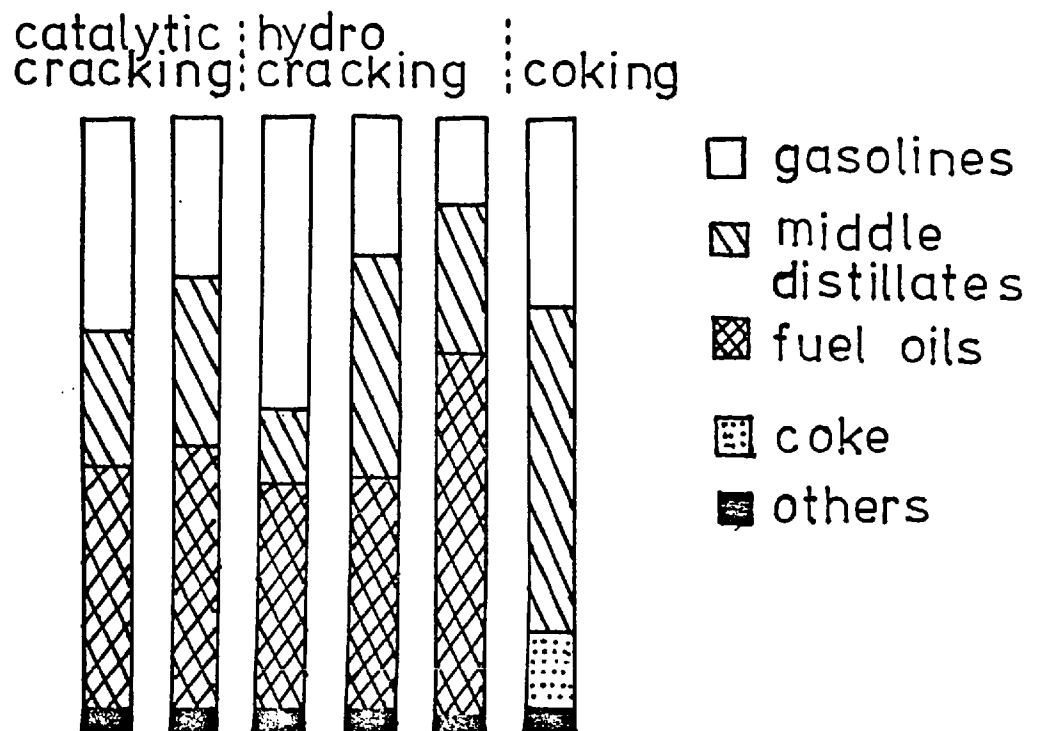
1.3 Oil Refining

In the modern world it is necessary to produce refined products tailored to specific markets.. No two countries will have the same patterns

of consumption; for example the dominance of the motor car in the U.S. requires that the refiner convert a large proportion of each barrel into motor spirit while in Japan the trend is toward more economical cars and this combined with the lack of any alternative supply of energy in quantity requires that there be less emphasis placed on motor spirit and so more fuel oil is produced. The proportions of the various fractions obtained does not depend solely on the crude itself; by choosing one refining process rather than another it is possible to maximise a particular cut at the expense of others; this illustrated in the bar chart, Figure 1.3.

Figure 1.3

Possible yields from a single crude



1.3.1 Sulphur

The treatment of thiols in fractions boiling up to ca 250°C has been described in section 1.2.7 although it is not uncommon for gasoline fractions to be subjected to extraction procedures in order to lower their total sulphur content and this is likely to become the rule in the near future with the increasing controls on automobile emissions. The problems relating to the removal of heavy sulphur containing molecules has been discussed in section 1.2.1; these problems are often overcome by the catalytic removal of the sulphur atoms.

1.3.2 Distillation

Fractional distillation is the major physical separation step in the refining of crude oil. Distillation under normal pressure is used to separate substances boiling at less than 350°C from the rest. The residue is distilled under vacuum to give waxy distillates. The residue from this process is bitumen which finds uses in road making and roofing materials. The waxy distillates are washed with liquid propane under pressure to extract high-- viscosity oils. The oil dissolves in the propane which is then removed from the solution by distillation and recycled. The wax residue is then purified and turned into candles. Figure 1.4 shows a typical range of products obtained on distillation.

1.3.3 Chemical Processes

These processes fall into four main groups: cracking, reforming, polymerisation and isomerisation. Cracking is the breakdown of large hydrocarbon molecules into smaller ones. It may be carried out either catalytically in which case the products will be olefins, or thermally in the presence of hydrogen when the products will be lower paraffins. Reforming which

Figure 1.4
Oil distillation cuts

Cut point °C	
gas	30
gasoline	90
benzene	130
naphtha	175
kerosene	200
light gas oil	300
heavy gas oil	350
fuel oil & residues	

again may be carried out by catalysis or thermally produces aromatic compounds from linear and cyclic aliphatic molecules. Catalytic polymerisation in this context is concerned with the formation of gasolines which will have higher octane numbers, for example by joining up two C_4 paraffins. Isomerisation is carried out using a platinum catalyst; the object of this reaction is also to improve the octane rating of gasoline fractions. Normal paraffins are converted to branched chain paraffins which burn more evenly in the reciprocating engine and so minimise pre-ignition or "knock".

1.4 Refined Products and Analysis of Non - hydrocarbons

In the modern practice of producing "tailor - made" petroleum products the use of a single fraction - or straight run - is the exception rather than the rule. Most products marketed today are blends which may contain sometimes as many as six different components (1). The fractions described below are, in general, best regarded as being components which are blended together to form a commercial product.

1.4.1 Gas and Liquified Petroleum Gas (LPG)

These are hydrocarbons which contain up to four carbon atoms. They find use as fuels in the refinery itself and are also useful as starting materials for many petrochemical derivatives. Butane, for example, is used to impart desirable volatility characteristics to motor spirit. The butanes are easily liquified under pressure at normal temperatures and are marketed in this state as bottled gas. It is very important that there is only a minimal quantity of oxygen contaminating these gases. Two official methods are described. One employs gas chromatography using a flame ionisation detector; the other consists of oxidising Mn^{2+} followed by iodometric titration with thiosulphate.

1.4.2 Motor Spirit (Gasoline)

The boiling range of this fraction is between 30°C and 90°C but a straight run from this fraction would cause severe knock in a modern automobile engine. Knock is reduced by increasing the proportion of branched chain paraffins and various chemical processes are available to do this (see section 1.3.3). An alternative method of decreasing knock (raising the "octane rating") produced by a gasoline is by the addition of lead tetraalkyls (notably lead tetramethyl and tetraethyl) to an extent of about 3 ml per Imperial Gallon (IG). This is a very effective and cheap procedure but with increasing concern for the environment and a certain trend towards lower compression engines its desirability has come under increasing scrutiny. The numbers of methods for the analysis of lead in gasolines are considerable and will be discussed later but suffice it to say here they include most techniques in the analyst's repertoire.

1.4.3 Aviation Fuel

Aviation fuel falls into two classes: those suitable for piston-engined aircraft and those suitable for combustion in gas turbines. Both types of fuel must come up to the very stringent specifications that must of necessity be applied to substances such as these. The fuel must have suitable knock characteristics so that the aircraft can take off under maximum power but then be able to cruise with maximum economy. It must remain pumpable at low temperatures but not cause vapour locks in fuel lines due to excessive volatility of any of its components and in this context it must be noted that the kinetic heating of an aircraft skin can easily give rise to temperatures in excess of 200°C so aviation turbine fuel is blended from fractions in the 150° - 200°C boiling range. Substances which form ashes or varnishes must be kept to a minimum. For further details of the specification for aviation gas turbine fuels the reader is referred to ASTM specification D 1644 (2).

1.4.4 Gas Turbine Fuels

The specification for these non - aviation gas turbine fuels is given in ASTM specification D 2880 (2). The official method for trace analysis is flame AAS, the elements analysed being calcium, lead, magnesium, sodium, potassium and vanadium. Vanadium is a highly corrosive element which forms low melting compounds such as vanadium pentoxide (m.p. 691°C) that cause severe damage to high temperature alloys used for making gas turbine blades. Sodium and potassium can also combine with vanadium and form low melting eutectic materials (m.p. 556°C) which can cause severe corrosion as well. Calcium acts as an inhibitor to the deleterious effect of vanadium but can lead to hard deposits which are not easily removed. Magnesium is added to gas turbine fuels when vanadium is present in quantities greater than 2 ppm. The levels of magnesium added are such that the Mg/V ratio lies between 3 and 3.5.

1.4.5 Diesel Fuel

The Diesel engine most familiar in everyday life is the high - speed Diesel engine in buses and lorries. The fuel is known commonly in this country as DERV or gas oil. The fuels are blends from the range 150° - 400°C which overlaps to some extent with kerosene. Ships are also powered by Diesel engines but they operate at much lower speeds and use fuels from higher boiling ranges such as residual fuel oils. These fuels tend to be high in sulphur content (see section 1.2.1) and it is important to monitor the concentration of this element in order to avoid corrosion of machinery.

1.4.6 Lubricating Oils and Greases

These terms cover a wide range of products designed to assist the

smooth operation of machinery. The viscosity of such substances can vary from the low viscosity oils for lubricating delicate instruments such as wrist watches to the highly viscous greases which lubricate heavy machinery.

Lubricating oils are produced from vacuum distillates as described in section 1.3.2. The properties of raw lubricants generally leave something to be desired and as a result many additions are made to improve this situation. These are discussed in some detail below.

1.4.6.1 Oxidation Inhibitors

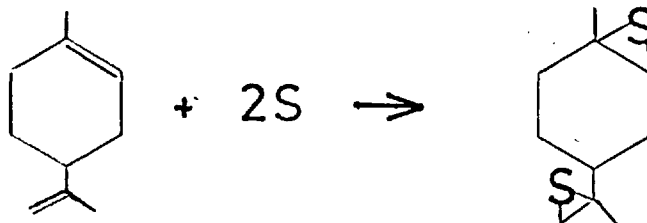
Hydrocarbon oils react with oxygen when exposed to air at normal temperatures; they react rather more rapidly in the oxidizing conditions prevailing in the crankcase of a typical reciprocating engine. The oil is agitated in the presence of air at comparatively high temperatures for hundreds of hours, in addition, metals which may catalyse oxidation are present in the form of additives and the very fabric of the engine itself. The products of oxidation come into three main classes (a) varnishes and sludges from unstable aromatic compounds which have not been removed during the refining process, (b) oil soluble products in the molecular weight range 500 - 3000 which lead to marked increases in oil viscosity and (c) organic acids, those of low molecular weight being particularly corrosive to metals especially of the copper and lead type bearing materials. It is clear that such oxidation is undesirable and inhibitors are added to counteract this effect. The mechanisms by which these additives function have not yet been fully elucidated but it is thought that they decompose organic peroxides which would otherwise give rise to the above mentioned undesirable materials. It is also probable that they reduce the catalytic activity of metals, after the fashion of a catalyst poison.

Four main groups of compounds are employed as oxidation inhibitors:

(a) Sulphur Compounds

Sulphurised sperm oil was one of the first antioxidants used. The trend

now is to have the sulphur chemically combined for example in sulphurised terpenes:



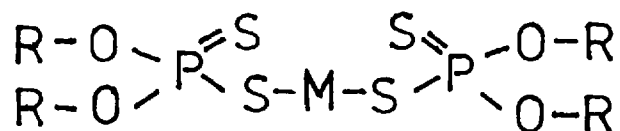
The sulphur, being combined is less corrosive than a solution of elemental sulphur in oil. Aromatic and non - aromatic sulphur compounds such as dibutyl phenol sulphide and t-dibutyl disulphide are also very effective oxidation inhibitors.

(b) Phosphorus Compounds.

Solutions of elemental phosphorus in oil exhibit oxidation inhibiting properties, however, as in the case of sulphur the elemental phosphorus is corrosive to non-ferrous metals; thus oil-soluble organo-phosphorus such as tributyl or triphenyl phosphite are employed. The official method of analysis commences with the oxidation of the sample to phosphate with sulphuric acid, nitric acid and hydrogen peroxide. The phosphate thus produced is then estimated photometrically as the molybdovanadophosphoric acid if the phosphorus content is below 2% or above this level the finish is gravimetric, the phosphate being precipitated as the magnesium ammonium phosphate which is then ignited and weighed as magnesium pyrophosphate.

(c) Sulphur/Phosphorus Compounds.

As both sulphur and phosphorus exhibit anti-oxidant properties, oil-soluble compounds containing both elements have shown themselves to be very effective indeed in this rôle. The most popular substances of this type are the zinc or tin dialkyl or diaryl thiophosphates:



R = alkyl or aryl group M = Zn or Sn

In addition to their anti-oxidant effects they also impart valuable anti-wear characteristics to the lubricant.

(d) Amine and Phenolic Compounds

Compounds such as phenyl naphthylamines or 2,6-ditertbutyl methyl phenol are used in oils and greases where the temperatures encountered are moderate. Calcium salts of such compounds are also used. Under more severe operating conditions these compounds are inadequate and are employed in conjunction with compounds of the types described above.

1.4.6.2 Detergents and Dispersants

These additives keep particulate matter such as fuel soots, resins and oil oxidation products in suspension. If these materials are not kept in suspension they may settle out on metal surfaces as varnishes or in the sump as a sludge. Detergents are used under high temperature/heavy duty operating conditions whereas dispersants are preferred for oils which are employed under less severe conditions. Engines which are to be used under mixed conditions must be lubricated with oils containing an appropriate mixture of both types of additives. The presence of a metal ion in most detergent/dispersant additives causes them to exhibit some oxidant activity.

Detergent Additives

Most detergent additives consist of three parts:

- (a) a group 2 or group 3 metal (group of the periodic table)
- (b) an organic anionic component which is the true detergent section
- (c) an organic lyophillic component which imparts organic solubility to the compound as a whole.

(a) The most commonly used metals are the alkaline earths and aluminium. These have the property of neutralising acidic materials which may be present in a lubricating oil as a result of its oxidation or blow-by contamination. Since this basicity is a desirable property in a lubricating oil efforts have been made to increase it without adding more of the organic constituents and without affecting the lubricant's other properties. As

a result of these endeavours the overbased oil is now firmly established. These oils are manufactured by heating the oil-soluble anionic portion of the incipient additive with a high proportion of metallic base in the presence of a suitable catalyst; the resulting substance may contain up to ten times the stoichiometric amount of metal. Clearly it is most important to be able to monitor the concentrations of metals in these additives at all stages of production and the first part of this thesis describes methods of analysis for calcium, magnesium and barium.

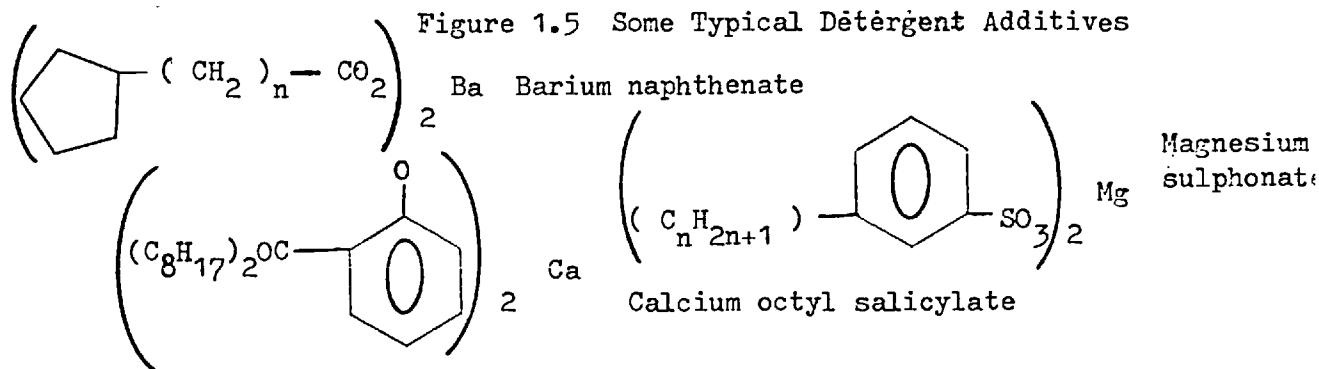
Metal - free (or ashless) detergents have been developed; an example of this is a copolymer of lauryl methacrylate and diethyl amino ethyl methacrylate (23).

(b) The organic ion is generally in the form of a carboxylate, phenate, alcoholate or sulphonate radical. Sulphur present in the form of sulphonate does not exhibit anti-oxidant properties.

(c) The lyophilic part of the molecule presents a great deal of variety. These sections of the additive have 'molecular' weights of 200+; they may be in the form of straight or branched chain aliphatics, saturated or unsaturated, or aromatics substituted with the above aliphatics.

Some types of detergent contain elements other than those already mentioned such as chlorine in the form of calcium dichlorostearate or alkaline earth alkyl phenol sulphides such as barium amylphenol sulphide, which is also an oxidation inhibitor.

Some typical examples of additives are shown below:



The analysis of calcium, magnesium and barium will be discussed in chapters 3, 4 and 5 respectively. The two other main metals used in this context are aluminium and zinc. Aluminium 8-hydroxyquinolate is precipitated and treated in one of two ways: it is either dried and weighed as the oxyquinolate complex or dissolved and determined iodometrically. Zinc is precipitated as zinc sulphide and then ignited to the oxide. A polarographic method, following ignition and acid digestion, for the determination of zinc at levels below 2% is also described. Complexometric methods have been described for both elements (24, 25). Zinc has been determined rapidly by XRF when present in quantities up to 2% (26). Both elements have been determined by emission spectrography (27, 28) and ppm quantities can easily be measured using AAS (29, 30). Jackson (31) compared AAS and atomic emission spectroscopy (AES) for the analysis of lubricants and found that although both gave approximately the same sensitivity, AAS gave more precise results.

Dispersant Additives

These compounds are specifically designed to disperse cold sludges which are produced from oil and fuel combustion products. The most widely used dispersants are the ashless surface active compounds characterised as polypolar polymers. Typically these molecules consist of two parts: a nitrogen containing monomer which contributes the surface activity and acts as a point of attraction for the polar sludge producing compounds and a lower polarity lyophilic monomer which contributes organic solubility to the whole polymer.

1.4.6.3 Extreme Pressure (EP) Additives

When a gear is used under light loadings it is not necessary to add any special anti-weld additive, however with increasing gear loadings the high local temperatures and pressures encountered become significant.

EP additives are thought to act by forming a solid layer of sulphide, chloride or phosphide on the mating metal surfaces. The compounds thus formed have lower shear strength and coefficients of friction than the metal surfaces on which they are formed. In the absence of such additives gear teeth weld together on contact and are then wrenched apart causing severe damage. Probably the most well known additive is lead naphthenate which is usually combined with a sulphur compound and is used in, for example, leaded gear oils. Mild EP additives are based on fatty oils or acids. Chlorinated hydrocarbons and non-corrosive sulphur compounds have also been used.

1.4.6.4 Corrosion Inhibitors

Corrosion inhibitors can be divided into two classes: those giving temporary storage protection and those acting on a long term basis; these two classes can be further subdivided into those which form thick films and those which form thin films. The additives of greatest interest in this context are those which form thin films and afford temporary protection. Overbased detergents have already been mentioned. Alkaline earth sulphonates of molecular weight more than ca,500 are adsorbed as monolayers onto metal surfaces in addition to forming emulsions with water thus isolating it from metal surfaces.

1.4.6.5 Thickening Agents

These are substances which will act as gelling agents in liquids, while remaining suspended therein and exerting inter-particle forces to keep the whole system in relative equilibrium. The nature of these forces will be dependent on the type of gelling agent. Gelling agents can be divided into two classes: soaps and non-soaps. Metal soaps with the exception of aluminium soaps form three-dimensional crystalline

networks. Non-soaps do not form these types of network and their mode of action is not fully understood.

The use of soaps for lubrication is very ancient indeed; it is known that the ancient Egyptians used calcium based soaps to lubricate the wheels of their chariots. Modern soap making dates from the middle of the last century. Soaps are the salts of fatty acids; those which are of the greatest interest here are those in which the carbon chain is at least twelve atoms in length. The cation used imparts many of its interesting properties to the grease. Calcium imparts extreme pressure properties to a grease while both calcium and magnesium greases have the capacity to fix large quantities of water - for example calcium greases can absorb up to 60% by volume water to form a water in grease emulsion and then under pressure express this water. Lead is used in greases which are subject to high pressures in use. Several different properties may be incorporated into a single grease by adding different cations in various proportions.

1.4.6.6 Other Additives

Viscosity Index (VI) Improvers

The viscosity of an engine oil is essentially a compromise between minimising friction at low temperatures when the engine is being started and maximising lubricant adhesion and film strength during normal operation. Thus it is clear that it is desirable for viscosity to remain effectively constant over quite a wide range of temperatures. To this end VI improvers such as polymethacrylates or polyisobutylenes are added to oils where they exist as colloidal suspensions.

Pour Point Depressants

At low temperatures oils do not flow freely; at low enough temperatures wax will crystallise out and as the temperature decreases still further

the wax crystals interlock and form a gel so that the oil can no longer be poured. This temperature is called the pour point. Polyalkyl-naphthalenes, polyalkylphenol esters or polyalkylmethacrylates are added to oils to modify the wax structure and thus depress the pour point. Very small quantities of these agents are effective and the usual concentrations in a lubricant are 0.01% to 0.3%.

Antifoaming agents

Ppm quantities of polymethyl siloxanes are added to lubricants to control foaming. This undesirable phenomenon becomes more important as the viscosity of the lubricant increases.

1.5 Engine Wear and Wear Metals in Used Oils

Wear is a feature of all operating mechanical systems. The precise rate of wear and its type will depend on the conditions prevailing during operation. The main causes of wear are discussed below.

1.5.1 Corrosive Wear

The chief cause of engine wear is generally accepted as being due to chemical attack by a combination of moisture and acids which have their origin as by-products of the combustion process. At high operating temperatures these substances are generally in the vapour state and do not linger in the engine, being blown out via the exhaust system. At lower operating temperatures these corrosive compounds remain in the engine and lead to severe damage. An example of this type of wear is that caused to bearings; bearing materials are typically lead or tin based with additions of antimony and/or copper. Initially antimony will be leached out from the bearing surface causing pitting; an increase in antimony concentration in the lubricant will be observed. As the surface of the bearing becomes more irregular the film of lubricant breaks down and erosive wear takes

place and all the bearing constituents appear in the lubricating oil. These changes in the lubricant are detectable before serious mechanical faults manifest themselves and hence may be used to predict the failure of an engine.

1.5.2 Abrasive Wear

This is caused usually by an inefficient air filter. Its symptoms will be the appearance in the crankcase oil of piston ring constituents. Worn piston rings will also cause the consumption of oil to rise.

1.5.3 Erosive Wear

Erosive wear is caused by metal to metal contact which may result in some cases from corrosive wear. For the average motor car erosive wear takes place when the engine is being started: the oil is cold and not circulating efficiently, the petrol mixture is very rich because the choke is out and this tends to wash from the walls of the cylinders what little lubricant there is. Erosive wear is not a major problem of steady operation in a properly lubricated engine.

1.5.4 Analysis of Wear Metals

The predictive capacity of wear metal analysis has been mentioned in section 1.5.1. In the past twenty years with the advent of ultra-micro techniques of analysis many of the world's armed forces have monitored the composition of used lubricants as a means of predicting engine failure.

The major methods for performing these analyses are emission spectrography using the traditional types of atom source (28, 5) or more recently McElfresh and Parsons (32) employed a plasma jet and obtained calibration curves which were linear up to 50 ppm. XRF has been applied to the analysis of used jet-engine oils; chromium, iron, nickel, tin and lead were

determined with good reproducibility at the 5 ppm level and were detectable at the 1 ppm level (22). Winefordner and fellow workers have done a great deal of valuable work on the analysis of used jet engine oils. Their earlier work was on atomic emission and fluorescence using flames as atom sources (33, 34) but they did not in general commend these procedures for use on a routine basis. It should be mentioned at this point that the sample is not homogenous and in the case of work with flames especially, particulate material is not going to be nebulised, which will lead to certain inaccuracies. As early as 1966 Slavin and Slavin (35) described a fully automated atomic absorption analysis of used aircraft lubricants but there was wide disagreement with the analyses obtained by emission spectrography. In spite of these difficulties AAS is a widely used technique for this type of analysis (31, 36, 37).

The advent of flameless AAS has meant that the difficulties in sampling can to a great extent be overcome as the sample can be warmed and thoroughly shaken and the aliquot taken before particulates have settled out. Varian Techtron described the determination of nanogram quantities of aluminium using a Model 61 Mini - Massmann furnace (38). The most common wear metals which have been determined using a carbon filament atom reservoir (CFAR) are silver, copper, iron, nickel, lead, tin, chromium, magnesium, cadmium and sodium (8, 13, 15, 20, 39, 40, 41). An interesting application of the CFAR technique is the sequential determination of copper and silver (42). The monochromator is adjusted such that resonance lines from both elements enter it and the elements are sequentially volatilised from the CFAR. Everett and West (148) vaporised tin from a carbon filament into an air - hydrogen diffusion flame to measure successfully 0.3 ppm of the element in oils.

Flameless AAS is now a well established technique and with the development of instruments capable of handling up to twelve samples simultaneously,

coupled to direct readout devices which have been constructed (43) it is likely that this method of analysis will probably come much more to the fore in the field of oil analysis in the near future.

A brief review of the theory and application of flameless AAS is given below.

1.6 Background to AAS

The history of atomic spectroscopy has recently been reviewed by Thorburn Burns (44). Emission spectroscopy was well established as a routine technique by the end of the last century. Since the publication of Walsh's classic paper in 1955 (45) AAS has become a widely used procedure.

Many works have been published on the theory of AAS (46 - 52) and only a brief outline will be given here. The fundamental equation of atomic transitions is

$$E_n - E_m = h\nu \quad \text{.....} \quad 1.1$$

where ν is the frequency of radiation associated with the transition from energy level E_m to E_n and h is Planck's constant. When employing the technique of AAS a population of ground state atoms is illuminated with resonant radiation, intensity I_0 , the radiation which has passed through the atom cloud is then isolated and its intensity, I , recorded. I_0 and I are related by the Beer - Lambert law, expressed in equation 1.2, where a is a constant, N_m the number of atoms in the ground state and l is the path length.

$$I = I_0 \exp(-aN_m l) \quad \text{.....} \quad 1.2$$

Absorbance, A , is defined as $\log(I_0/I)$ and equation 1.2 may be rewritten

$$A = cN_m l \quad \text{.....} \quad 1.3$$

where c is a constant. Thus absorbance is linearly related to the number of absorbing atoms. This relationship, however, only holds at low optical

density; at higher optical densities the relationship breaks down and the analytical curve bends towards the concentration axis. One of the reasons for this derives from the assumption inherent in the Beer-Lambert law that the radiation is monochromatic whereas the lines involved have a finite width. For a fuller discussion the reader is referred to G. F. Kirkbright's Silver Medal Address to the Chemical Society (53).

AAS is a highly selective technique due to the "lock and key" mechanism of its operation. Spectral interferences such as those found in atomic emission (AES) are much fewer in number. In the case of AAS it is possible to make use of such interferences for the determination of relatively large quantities of analyte as described in section 3.3.

AAS is a very flexible technique; for example the absorbance signal may be varied by altering the path length along which absorption takes place. This type of flexibility is applied in the determination of calcium in cement, of which it is a major constituent; the burner is turned through 90° and so a short path is presented to the resonant radiation (72).

1.6.1 Atom Cells

The purpose of an atom cell is to produce and maintain a population of ground state atoms from a matrix containing those atoms. Ideally an atom cell should be stable, have a low background noise level, not exhibit memory effects and be safe to use. Flames fulfil these conditions and are the standard cell supplied with most commercial instruments. A number of flames is in common use and by making the correct choice a

wide variety of elements can be determined with ease on a routine basis; the scope of flame AAS was considerably increased with the introduction of the nitrous oxide - acetylene flame which permits the determination of the more refractory elements (147).

The other group of atom cells which are currently commercially available can be broadly classified as non-flame cells. These include plasmas (54), stainless steel tubes (55), the silica tube employed by Thompson and Thomerson (56) which will receive further comment later and also the novel work of Tyson and West (91) on liquid phase AAS which utilises electrolytic reduction to produce a population of ground state atoms. The non-flame cells of most interest in this context are those of the graphite furnace and filament type.

Winefordner (57) has set up models for comparing atomic concentrations in flames and graphite furnaces and concludes that in an unpurged graphite furnace the atomic concentration will be at least sixty times as high as in a flame. The two main reasons for the higher atomic concentration in the furnace are the efficiency of the transfer of the sample to the atom cell (a discrete sample is placed directly inside the furnace whereas samples reach a flame via a nebuliser) and the absence of diluting expanding gases which are present in flames.

A direct result of the higher atomic concentration obtained in a graphite furnace is the ability to use smaller samples 1 μ l as opposed to 1 - 2 ml. The major advantage of these cells is their low background, notably the absence of any noise analagous to flame flicker, and hence they have been used to determine nanogram quantities of sulphur and iodine by AAS (58).

The most significant disadvantage of non-flame cells is in the analysis of samples which do not require dilution. In this case it is usually quicker to use a flame technique by which it is possible to obtain a signal in 30 seconds, whereas for a non-flame cell each determination may take ca. 30

seconds and more than one is needed for statistical significance.

Flame and non-flame techniques should not be regarded as competitive but as complementary. In general one system will commend itself to a particular situation on grounds of sensitivity, precision, accuracy, speed and cost.

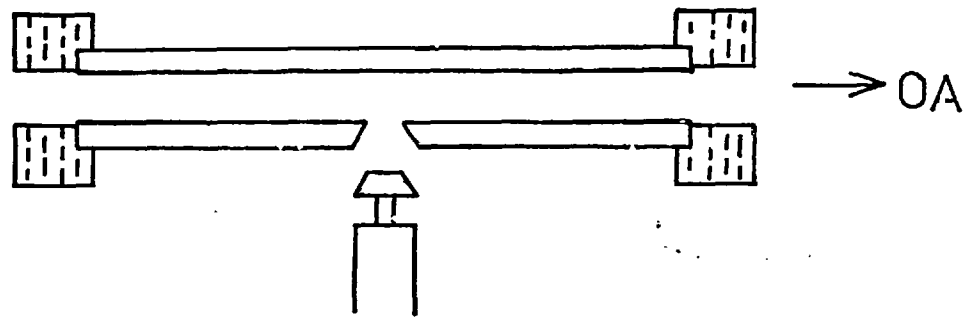
1.6.1.1 Furnaces

The earliest of the present generation of graphite furnaces was described by L'Vov in 1961 (59), Figure 1.6 (a). It consists of an electrically heated graphite tube 30 - 50 mm in length with an opening in the wall ca 4 mm in diameter; the sample is introduced into this opening on an auxiliary electrode and the assembly purged with an inert gas. The electrode is heated independently from the tube and the sample vaporised by the application of an electric pulse to the electrode. The system has been automated by having several auxiliary electrodes ready on a turntable below the furnace; in this way a sample can be vaporised every 20 - 30 seconds. Very high sensitivities - for example 3 pg magnesium - have been reported by L'Vov using this method (60).

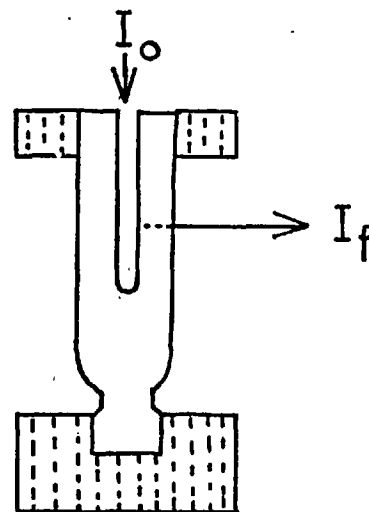
A simpler type of graphite cuvette was developed by Massmann (61). In the absorption mode a tube 55 mm x 6.5 mm with a 2 mm hole to permit introduction of the sample, Figure 1.6 (c), is employed; a cup shaped cuvette is used for work in the fluorescence mode, the radiation being viewed through a slit in the side of the cup, Figure 1.4 (b). These types of furnace are used in several commercially available instruments. The tube supplied by Perkin Elmer for the HGA 70 was of similar dimensions to that described by Massmann but in their current model, the HGA 74, the length has been halved. The sensitivities obtainable with these types of furnaces are approximately the same as those for the L'Vov furnace (61).

Figure 1.6

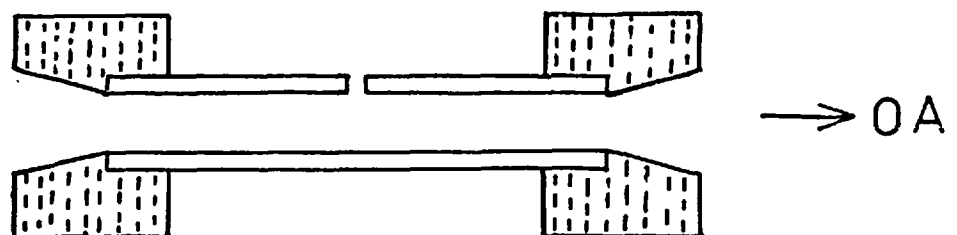
Graphite furnaces



(a) L'Vov cuvette



(b) Massmann cuvette (AF)



(c) Massmann furnace (AA)

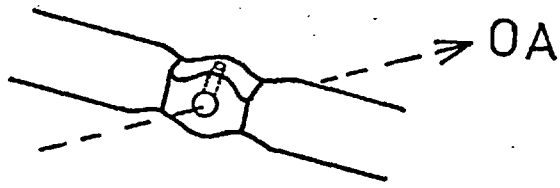
Varian Techtron have produced two types of very small Massmann - type furnaces; the former, the now obsolete mini - Massmann used with the Model 61 graphite atomiser, consisted of a 5 mm diameter carbon filament with a 1.5 mm diameter hole drilled transversely through the centre and a smaller opening drilled perpendicularly to this to admit the sample, Figure 1.6 (d). Brodie and Matousek (62) detected 10^{-10} g magnesium in petroleum products using this system. The Model 61 has been superseded by the Model 63 in which a tube ca 6 mm long is used, Figure 1.6 (e). The sensitivity is similar to that of the mini - Massmann (8). Due to their small size these furnaces are subject to interference from carbon particle scatter and background radiation reaching the monochromator. Furnace atomisers are not completely free from chemical interferences; recently Robinson (63) has proposed a hollow T - shaped carbon atomiser in which atomisation takes place in the stem and the atoms are then drawn slowly during a period of several seconds into the crosspiece where the absorption measurements are made; in this way complete destruction of the matrix is effected and interferences minimised; this method has been successfully applied to the determination of both vaporised and particulate atmospheric lead. A modified version of this type of atomiser has been coupled to a gas chromatograph and used for the determination of lead alkyls in gasolines (64).

The furnaces described above are all resistively heated. Headridge and Smith have described inductively heated devices (65, 66); they are shown in Figures 1.6 (f) and (g).

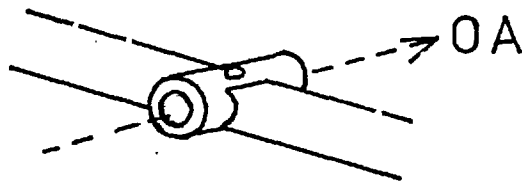
1.6.1.2 Filaments and Open Cells

In 1969 West and Williams (67) introduced the carbon filament atom reservoir (CFAR), Figure 1.7 (a); since then it has developed into a powerful tool in AAS and AFS. The original filament consisted of a piece

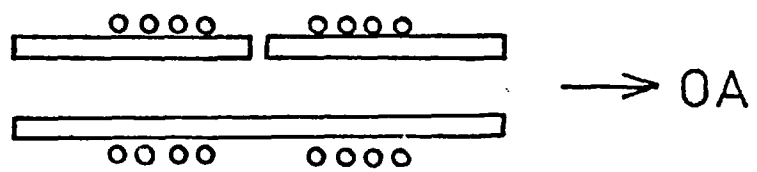
Figure 1.6



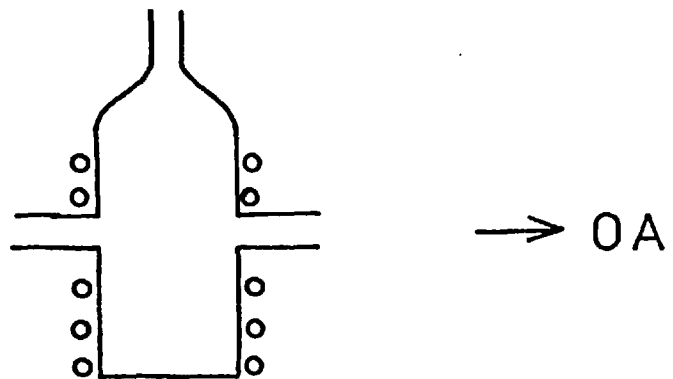
(d) Model 61 mini-Massmann



(e) Model 63 tube mode



(f) Inductively heated tube



(g) Inductively heated well

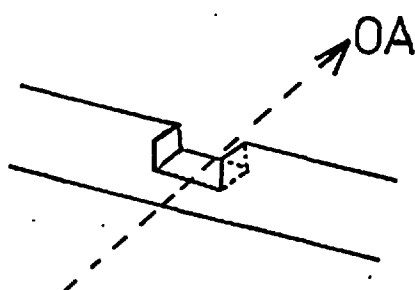
of graphite 2 mm in diameter and 20 mm in length which was heated resistively to 2500°C within 5 seconds. The filament is suitable for use with small (up to ca 5 μ l) liquid samples. Sensitivities obtained with this type of atom cell are in the order of pg. Interference from carbon particle scatter is almost absent from the West - type filament but in general due to the absence of additional energy above the filament interferences due to condensation of the atomic vapour are more frequent than in furnace techniques; efforts to overcome these interferences by viewing close to the filament or surrounding it with a hydrogen diffusion flame have shown that it is possible to use aqueous standards for work on oil samples (40); this modification may be applied with some success to those elements which form refractory oxides.

Variations on the carbon filament have consisted largely of using differing lengths and diameters of graphite from the 10 mm x 1 mm rod employed by Everett (8) to the 60 mm x 4 mm Ringsdorff filament described in chapter 5. One exception to this generalisation is the Varian Techtron Model 63 graphite atomiser used in the "cup" mode, Figure 1.7 (b). This versatile atom cell has been used as a filter for gases prior to the determination of trace metals therein; it can also accomodate solids and this has found application in the routine determination of lead and cadmium in blood at B.P. Laboratories; a drop of blood is spotted onto filter paper, dried, the discs punched from the papers put in the cup and atomised in the normal way. Liquid samples up to ca 20 μ l in volume can be used with the "cup" atomiser.

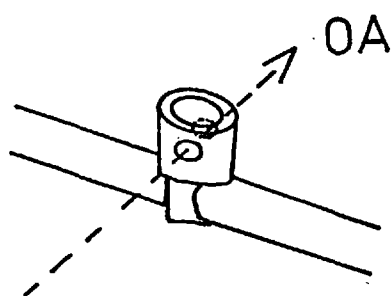
Cantle and West (68) used 2 mm diameter tungsten rods as atom reservoirs; they found enhanced sensitivity and reduced interferences in comparison to the CFAR, but some metals could not be atomised possibly due to the absence of the reducing action of the carbon.

Figure 1.7

Graphite filaments



(a) West filament



(b) Model 63 "Cup" mode

1.6.1.3 Conclusions

The most commercially successful non-flame cells have been graphite furnaces. Their success has been due to their sensitivity, versatility and simplicity. Ng to pg quantities may easily be determined with these devices and where the sensitivity for a particular analysis is too low it is possible apparently to increase this by the use of several aliquots, evaporating the solvent from each in turn. Elements as different as iodine (69) and iron (70) have been determined in graphite cells in matrices ranging from oils (8) to oysters (71). For a detailed review of the vast number of applications for these techniques the reader is referred to the work of Kirkbright and Sargent (52) and ARAAS published by the Chemical Society (London).

Chapter 2

Apparatus

All the atomic absorption work presented in this thesis, except that on barium, was carried out using the apparatus described in this chapter. The apparatus developed for the analysis of sulphur is described in chapter 9.2

2.1 Description of Apparatus

A Hilger and Watts d.c. supply, capable of providing up to ca 30 mA at 800 V, was used to power hollow cathode lamps that were used as spectral line sources.

The atom reservoir employed for this work was designed by J. F. Alder and H. G. Cobley in this department and is shown in Figures 2.1 and 2.2. Previous designs of CFAR (8, 20) have suffered from inefficient cooling at the ends of the filament which led to the melting of the electrode - filament connections and subsequent poor contact. These assemblies also suffered from relatively protracted cooling times, typically 30 seconds but up to two minutes when determining the more refractory elements. The CFAR used here embodies several major improvements which have successfully eliminated these problems. The electrical contact with the filament is made by a graphite block, Figure 2.1 (2), which makes contact with the steel electrode, Figure 2.2 (5), over an area of ca 200 sq. mm.; it is over this comparatively large area that thermal contact is also maintained. The cooling is so efficient that it is possible to fire the filament at full power and perform a replicate determination in under one minute. In addition the electrodes are mounted on a bed, Figure 2.1 (7), and are free to move against a spring, Figure 2.2 (2); this permits expansion of the filament while maintaining good electro-thermal contact. The filament may be replaced easily by withdrawing one of the electrodes along the bed by means of the

Figure 2.1

CFAR - elevation
(tube mode)

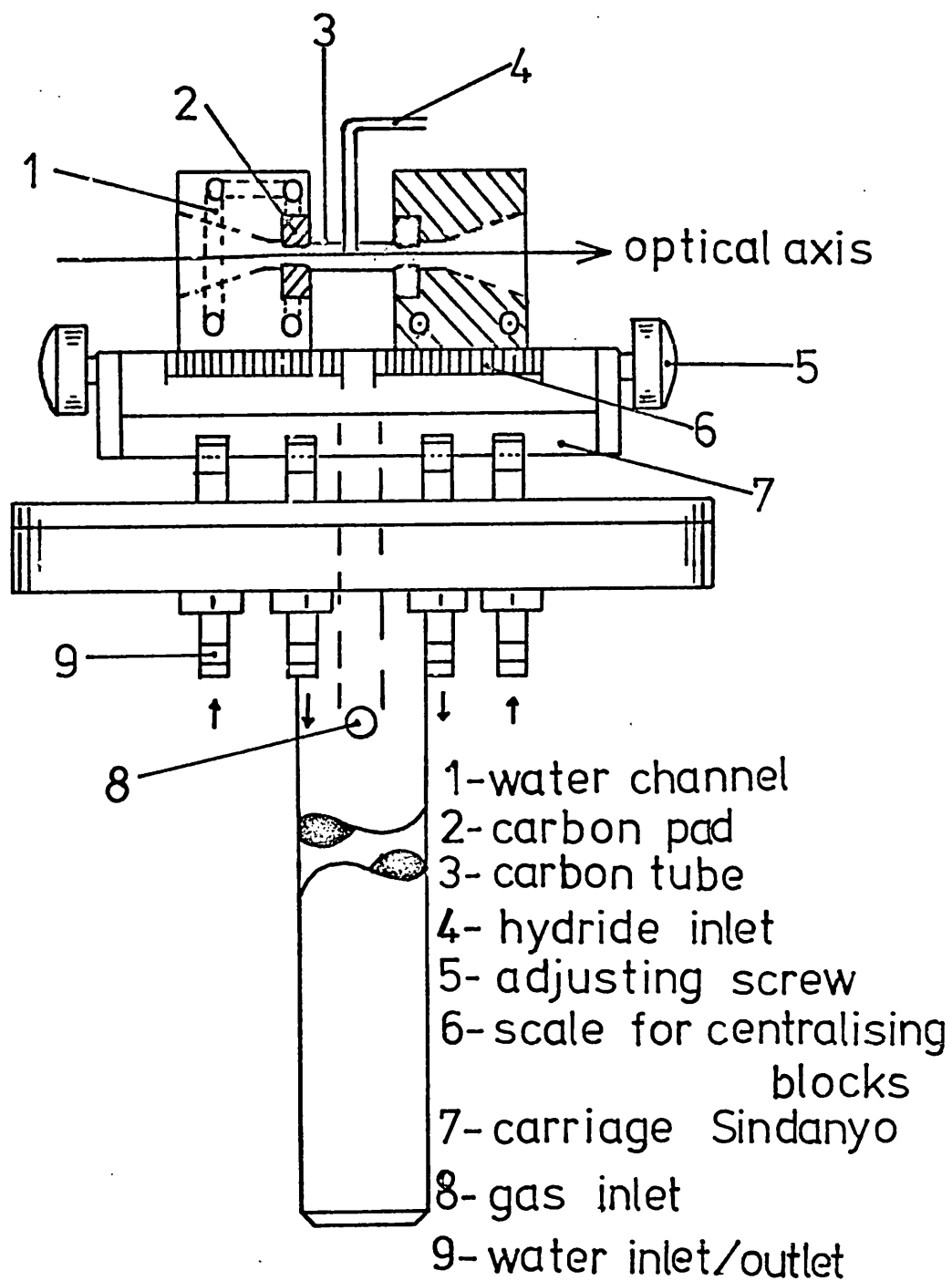
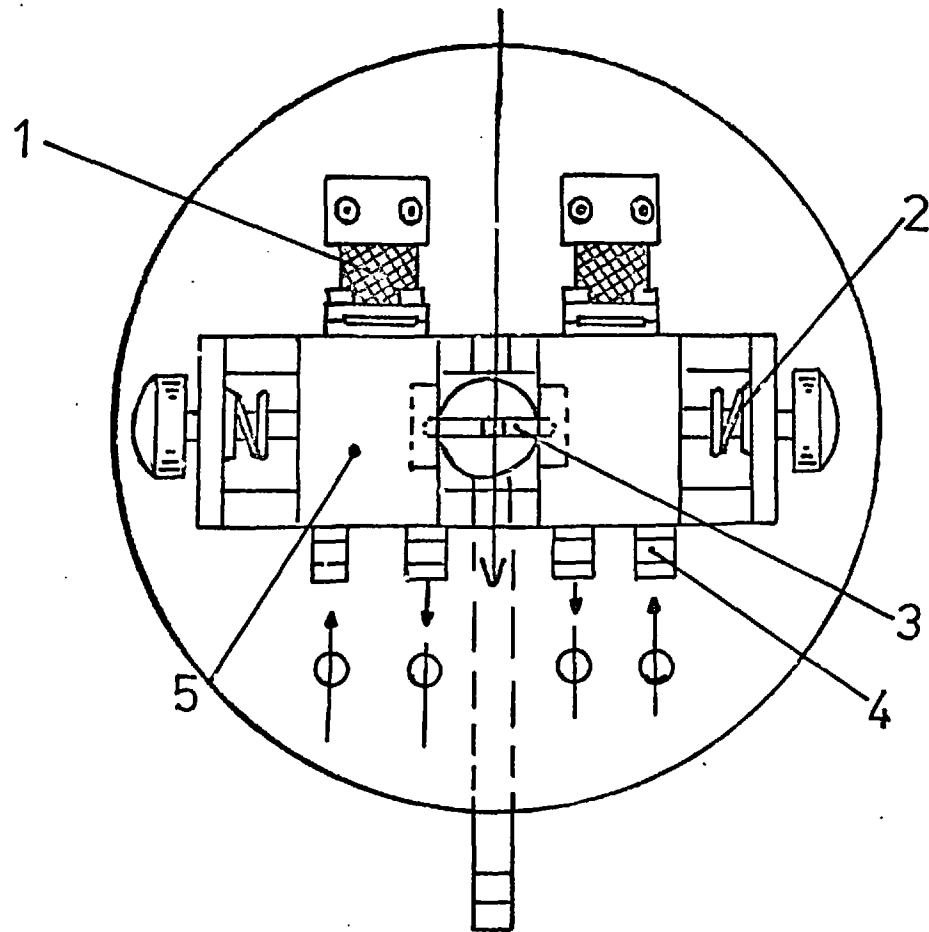


Figure 2.2

CFAR - plan
(filament mode)

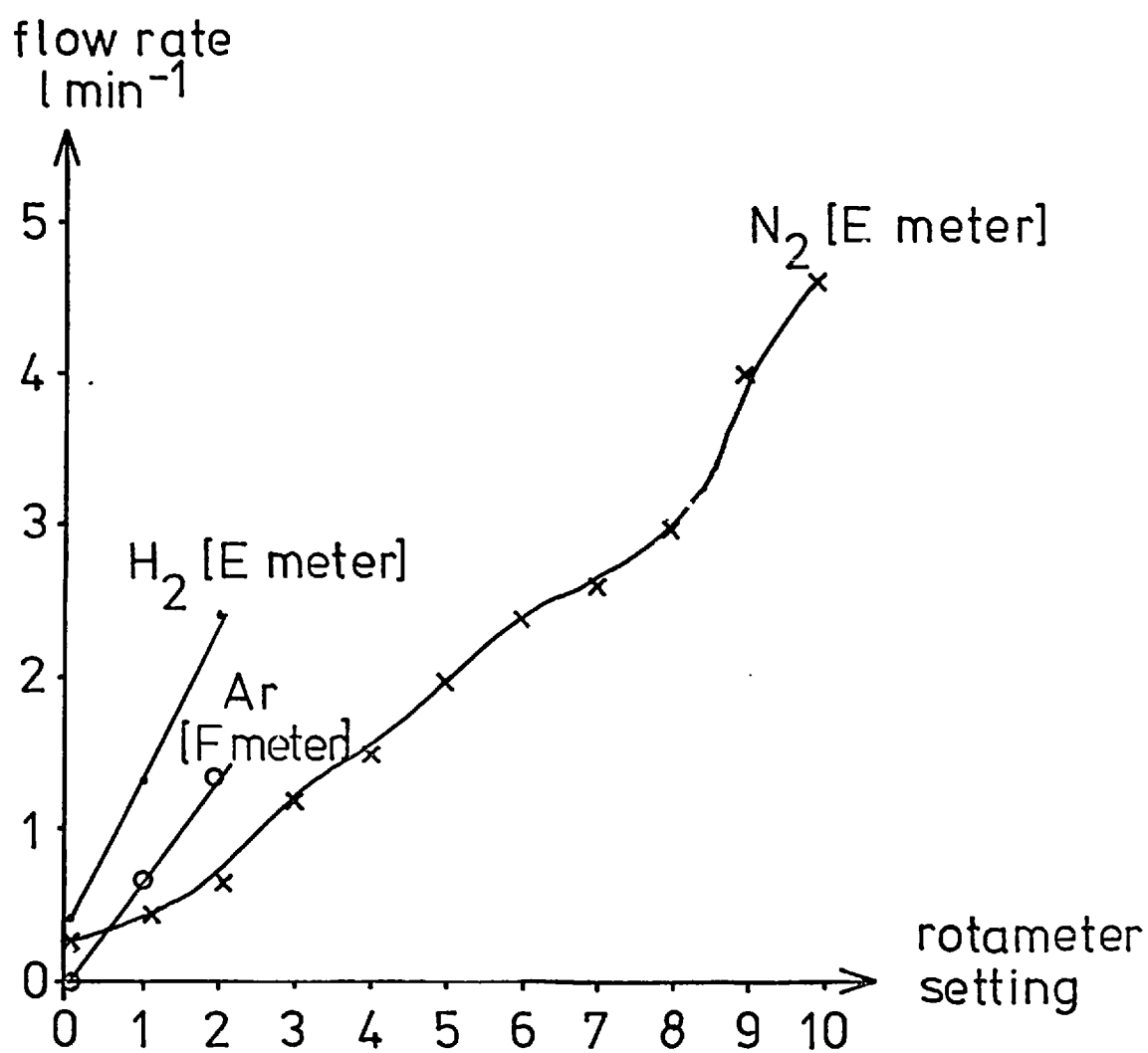
optical axis



- 1- terminal braids
- 2- springs for expansion
- 3- carbon filament
- 4- water inlet/outlet
- 5- stainless steel terminal block

Figure 2.3

Gas flow rates



screw, Figure 2.1 (5). Nitrogen sheathing gas (B.O.C. Ltd) surrounded the rod from a drilled asbestos base, giving adequate protection from the atmosphere without using a glass dome. Calibration curves for the rotameters and gases used are shown in Figure 2.3.

The filaments themselves were made from 3 mm diameter Specpure graphite rod (Johnson Matthey Chemicals). 10 - 15 mm sections were cut from these rods and the ends turned to a suitable point to make contact with the aperture in the carbon block with a device like a pencil sharpener. A notch was filed in the centre of the prepared rod with a jeweller's file. The cell may also be used as a tube furnace, as shown in Figure 2.1. When adapted to this mode drilled out end caps are employed in conjunction with Perkin - Elmer HGA 74 tube furnaces.

The reservoir was heated resistively by power drawn from a 1.2 kW step - down welding transformer connected to the mains via a 'Variac' transformer. This enabled the power supplied to the reservoir to be varied continuously from 0 - 12 V. The circuit diagram is shown in Figure 2.4.

Figure 2.4

CFAR power supply

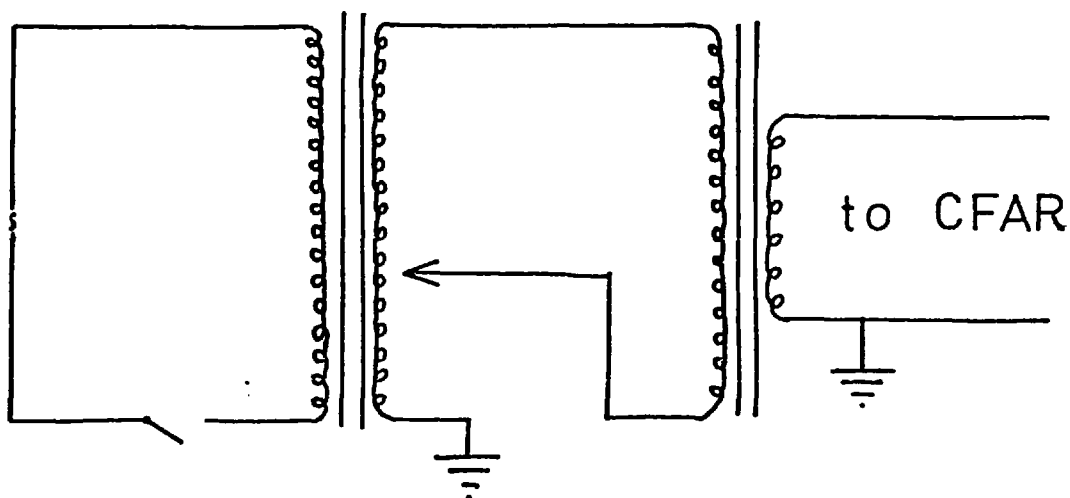


Figure 2.5

Calibration of carbon filament

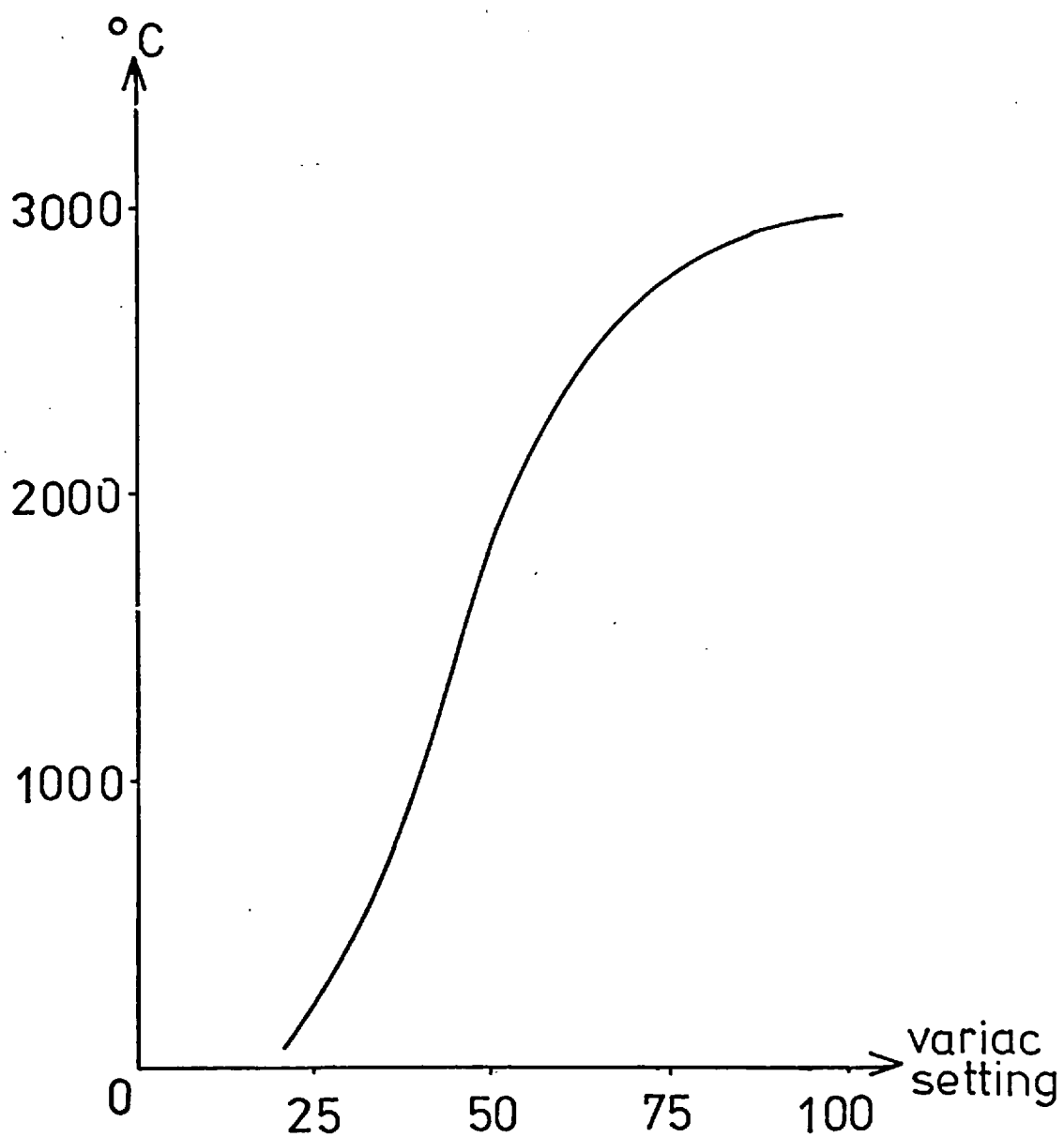


Figure 2.6

Calibration of carbon tube

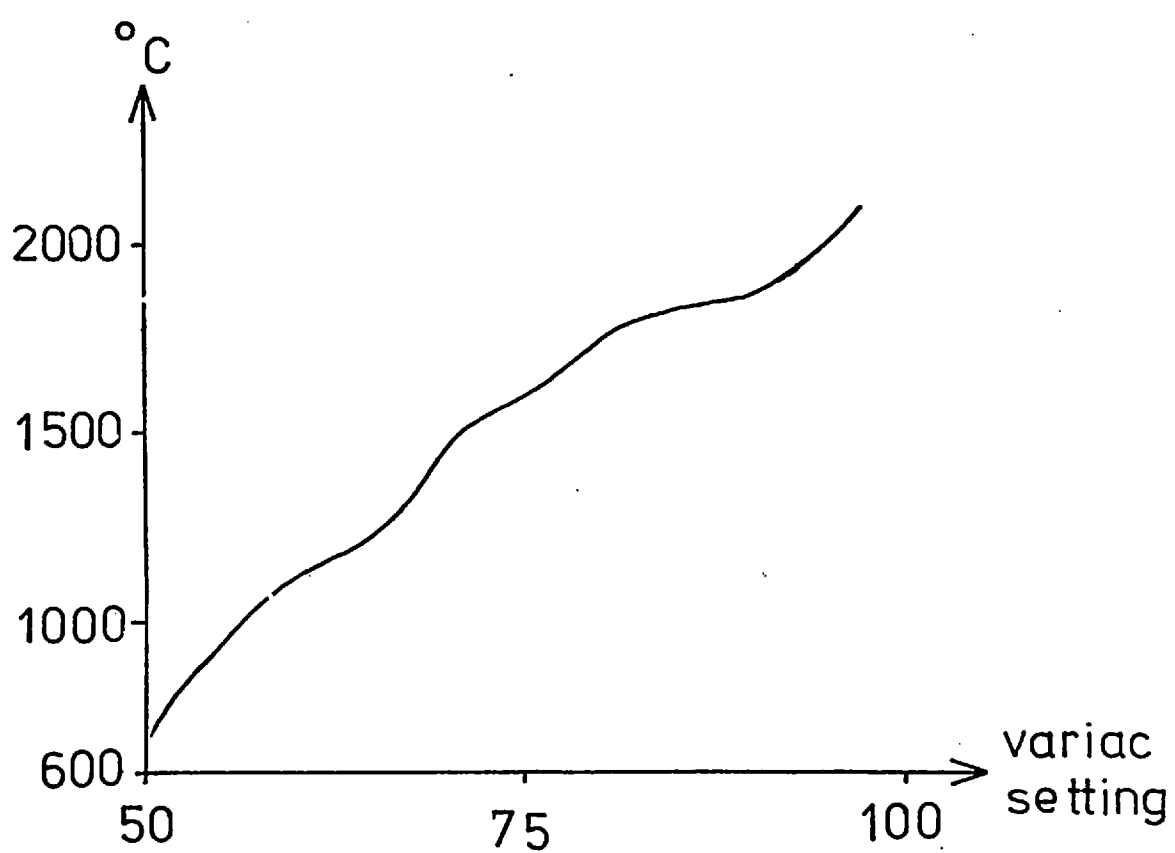
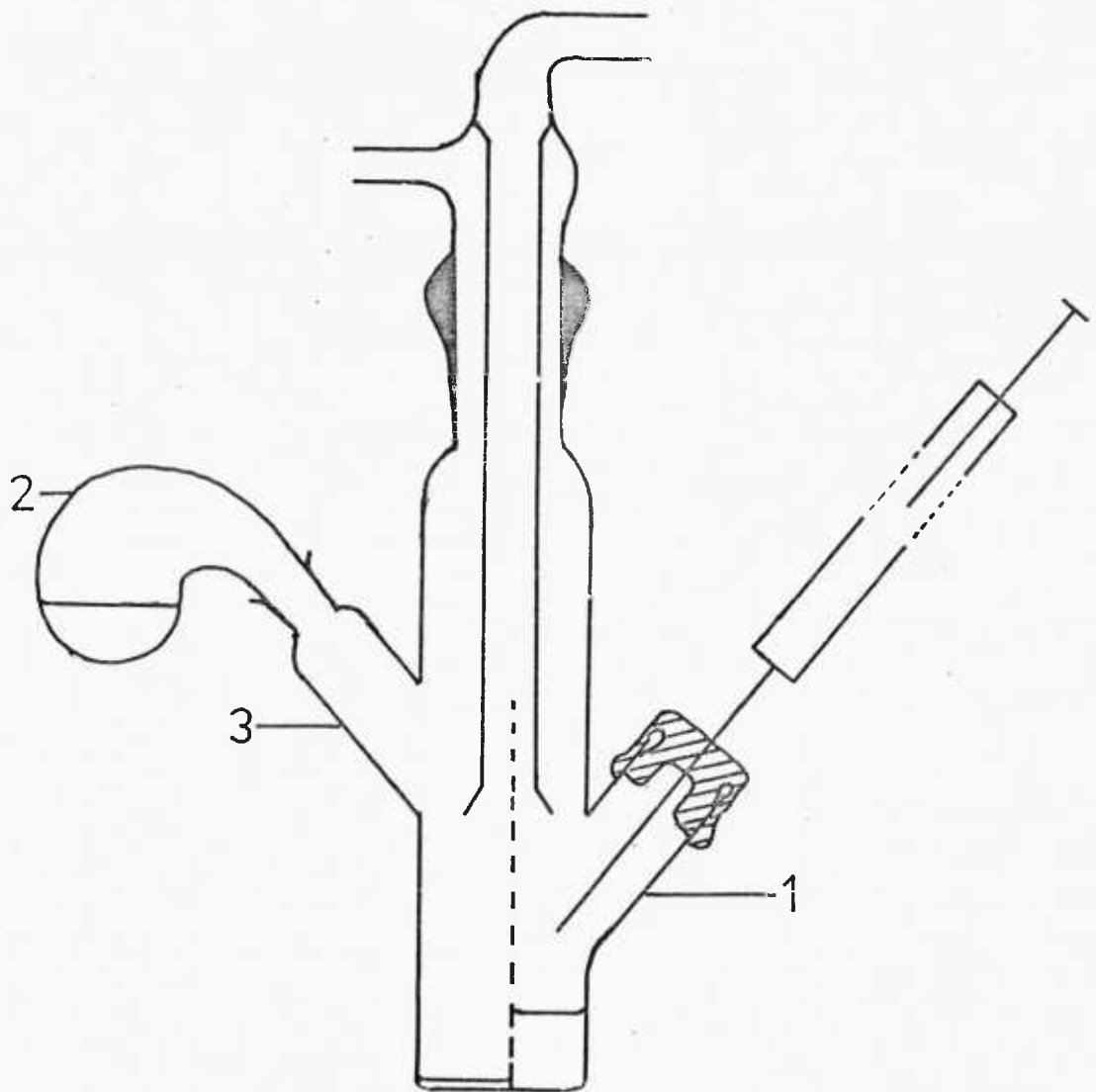


Figure 2.7

Hydride generation cell



The temperatures reached by the filament and furnace at various 'Variac' settings are shown in Figures 2.5 and 2.6. Temperatures up to 900°C were measured with a thermocouple (The Industrial Pyrometer Co. Ltd, Birmingham) and those between 900 and $2,800^{\circ}\text{C}$ with an optical pyrometer (Leeds and Northrup and Co., U.S.A.). At full power the filament will reach temperatures in excess of $2,800^{\circ}\text{C}$.

The hydride generation cell, shown in Figure 2.7, used for the generation of antimony, tin and lead hydrides was substantially the same as that used by Thompson and Thomerson (56); this is shown on the left hand side of the diagram. This arrangement was not satisfactory for the generation of hydrogen sulphide and for this purpose the neck, 1, was added in the position shown.

Radiation from the CFAR was passed to a Unicam SP 900A monochromator. The dispersing element is a silica prism which gives good resolution in the u.v. region but is less good in the visible; this is illustrated in Figure 2.8. The radiation was then passed to an E.M.I. 9601B eleven stage photomultiplier which is sensitive in the range 200 - 700 nm. All measurements were made in this region. The p.m.t. was powered by a Brandenburg EHT unit set at -1100 V (8). In order to measure the transient signals obtained effectively, the output from the p.m.t. was fed to a type K amplifier incorporated into a Telequipment type D535 storage oscilloscope. Everett (3) found that although the use of a $0.068\ \mu\text{F}$ condenser increased the rise time from 70 ms to 300 ms the increase in reproducibility compensated for the loss in sensitivity.

2.2 Instrumental Arrangements

Figure 2.9 shows the instrumental arrangement used for filament work.

Figure 2.8

Resolution of the monochromator

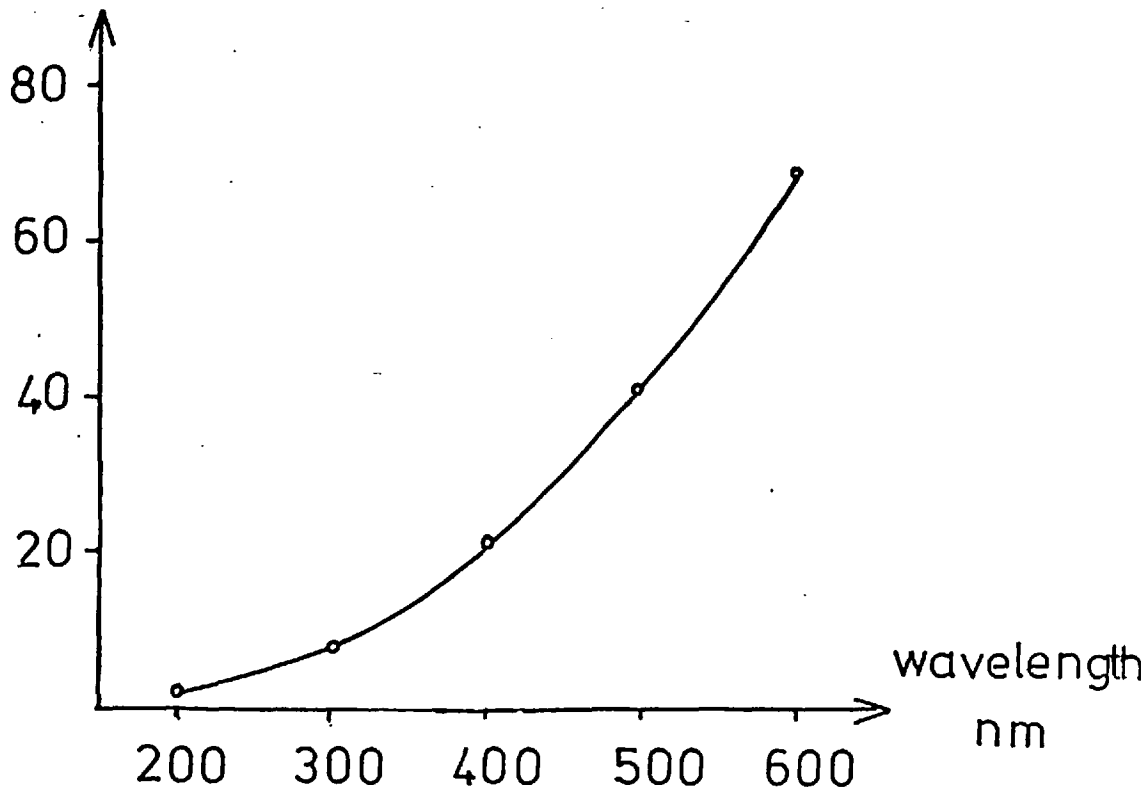
band pass
nm/mm

Figure 2.9

Instrumental arrangement:

filament

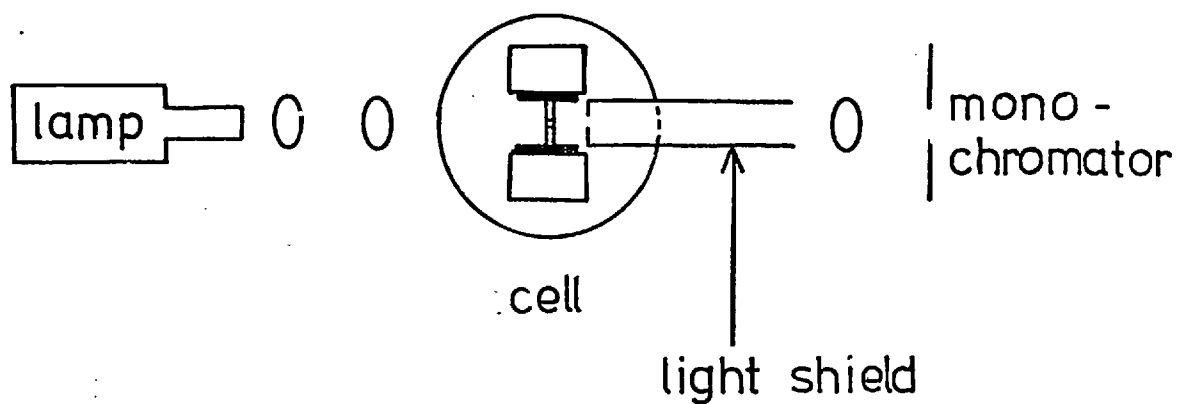
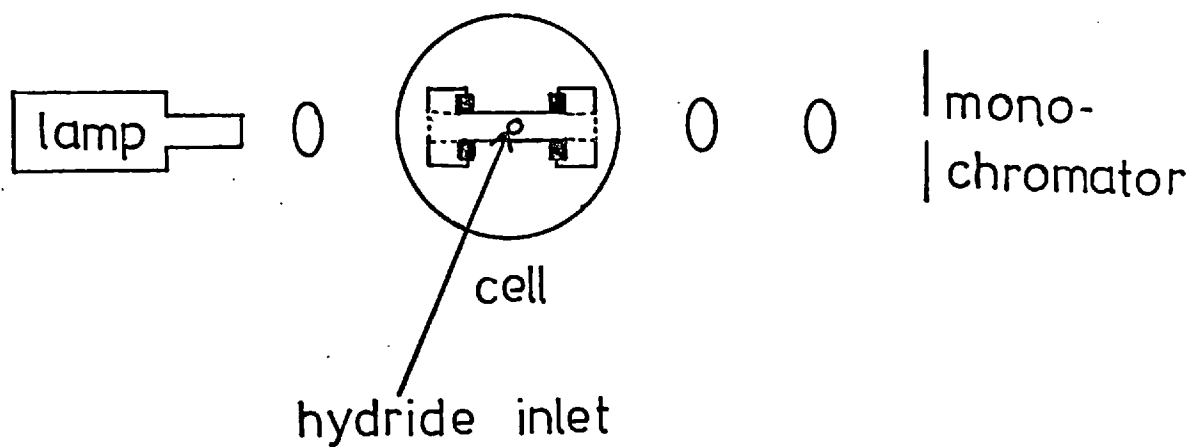


Figure 2.10

Instrumental arrangement:

tube



Radiation from the hollow cathode lamp was focussed onto an area ca 0.02 mm above the notch in the rod. The temperatures required to atomise calcium and magnesium were such that the filament glowed white and this radiation swamped the absorption signal. To overcome this difficulty a light shield was placed immediately behind the filament. The shield consisted of a copper disc ca 1 cm in diameter with a 1 mm diameter hole in the centre. This aperture was aligned with the light from the hollow cathode lamp. From there the light was refocussed onto the monochromator entrance slit.

For use with a furnace, the cell was turned through 90° as shown in Figure 2.10. The light from the spectral source was focussed such that it gave the maximum signal. The temperatures needed in these studies were comparatively low and radiation emitted by the tube was not a problem and the light shield was not used. The radiation emerging from the tube was focused onto the monochromator entrance slit.

2.3 Handling of Solutions

Organic standard solutions were prepared by dissolution of the concentrates supplied by BP in either petroleum ether (100/120°C boiling range) or SAE 10 metal-free base oil (density 0.866 g ml^{-1} at 20°C) and subsequent dilution. Aqueous standards were prepared by dissolving a suitable salt (AnalaR grade) in distilled water. The micropipettes used to handle these solutions were treated with 'Repelcote' silicone water repellent (Hopkin and Williams). The petroleum ether solutions were handled in the same way as the aqueous ones with the exception of the use of 'Repelcote'. The oil solutions however required special handling techniques. For the preparation of standards three pipettes were calibrated for use in a specific manner: the pipette was filled to the mark and the outside wiped clean; the oil was blown out and the pipette allowed to drain in a vertical position for 45 seconds

(55 seconds for the 1 ml pipette) and blown out again. The 1 ml pipette was allowed to drain for a further minute and blown out again. The results obtained are shown in Table 2.1.

Table 2.1 Calibration of Pipettes

Nominal volume	Weight of oil delivered
1 μ l	$58.2 \pm 4.9 \times 10^{-5}$ g
1 ml	0.824 ± 0.005 g
2 ml	1.621 ± 0.010 g
5 ml	4.183 ± 0.006 g

Sample introduction onto the filament was effected by use of a Drummond 1 μ l pipette (Drummond Scientific Co., Berks.). The solution was sucked into the pipette and the outside wiped clean with a tissue. The sample was then cautiously expelled to form a drop which was touched onto the filament. Calibration of these pipettes for use with SAE 10 oil is given in Table 2.1. The pipettes were recalibrated for use with oils of other viscosities.

Sample introduction into the hydride cell was effected using a Finn adjustable 0 - 50 μ l pipette (Jobling Ltd). This was recalibrated each time a new volume was selected. The sample was introduced into the pipette, the outside wiped clean with a tissue, the tip of the pipette was then touched onto the bottom of the cell and the plunger depressed; the pipette was lifted slightly and the oil delivered to the cell.

PART TWO

FILAMENT TECHNIQUES

Chapter 3

The Determination of Calcium

3.1 Introduction

Calcium is added to lubricants to serve as a detergent and to neutralise acid combustion gases; it also exhibits rust preventing properties. The determination of calcium is of interest at both the level of additives to the oils and at trace levels to check for contamination.

Two official methods are described for the determination of calcium in oils. The first procedure requires the sample to be ashed and calcium oxalate precipitated. The precipitate is then either thermally decomposed to the oxide and weighed or the precipitate is dissolved in sulphuric acid and the oxalate determined by redox titration with potassium permanganate. The second method prescribes the use of an air - acetylene flame for the AAS determination of trace quantities of calcium in gas turbine fuels.

Several workers (24, 73, 74) have applied complexometric titration to the determination of calcium in oils and additives in the concentration range 0.02 - 3.0 %. These procedures take ca. 3 hours as compared to 24 - 30 hours when using classical methods (73). Milligram quantities have been determined photometrically (75, 76), Beer's Law being applicable in the range 0.1 - 1.0 mg.

XRF has been used to determine up to 1% calcium in lubricants and additives (26) and NAA to determine up to 400 ppm in residual fuel oil (RFO) and up to 20 ppm in gasolines (77). Spectrography (27) and AES using an air - methane flame (78) have also been employed for the analysis of calcium in lubricating oils as has mass spectrometry (77).

Numerous workers (11, 79 - 86) have described the use of AAS for the rapid determination of calcium in petroleum products. Tago et al. treated the ashed oil with hydrochloric acid and diluted the resulting solution such that the concentration of calcium reaching the flame was in the range

0 - 10 ppm. The relative error in these determinations was 5%. Peterson and Kahn (85) diluted lubricating oils and additives with xylene to bring the concentration of calcium into the range 2 - 20 ppm and added potassium cyclohexylbutyrate as an ionisation suppressant; strontium has also been used as a releasing agent (85). Hopp (81) used water as a diluent and sprayed an emulsion into a flame.

3.2 Experimental

The atom reservoir was used in the filament mode as described in section 2.1. Aqueous solutions were made up from calcium nitrate; organic standards were made by suitable dilution of 4% calcium naphthenate. 1 μ l aliquots were used and five replicate determinations performed in each case. The optimum operating conditions are displayed in Table 3.1 below; curves illustrating the dependence of absorbance on some of these parameters are shown in Figures 3.1 - 3.5. The heating cycles used are shown in Table 3.2. A high atomisation temperature was required in order to break down the refractory carbide formed.

Table 3.1 Experimental Parameters - Calcium

Wavelength	422.7 nm
*Filament height	0.18 cm
Monochromator slit-width	0.15 mm
Lamp current	18.0 mA
Atomisation temperature	ca. 3000 °C
Nitrogen flow rate	2.2 l min ⁻¹
Damping	0.068 μ F

*distance of filament below collimator slit

Figure 3.1

Optimisation of filament height

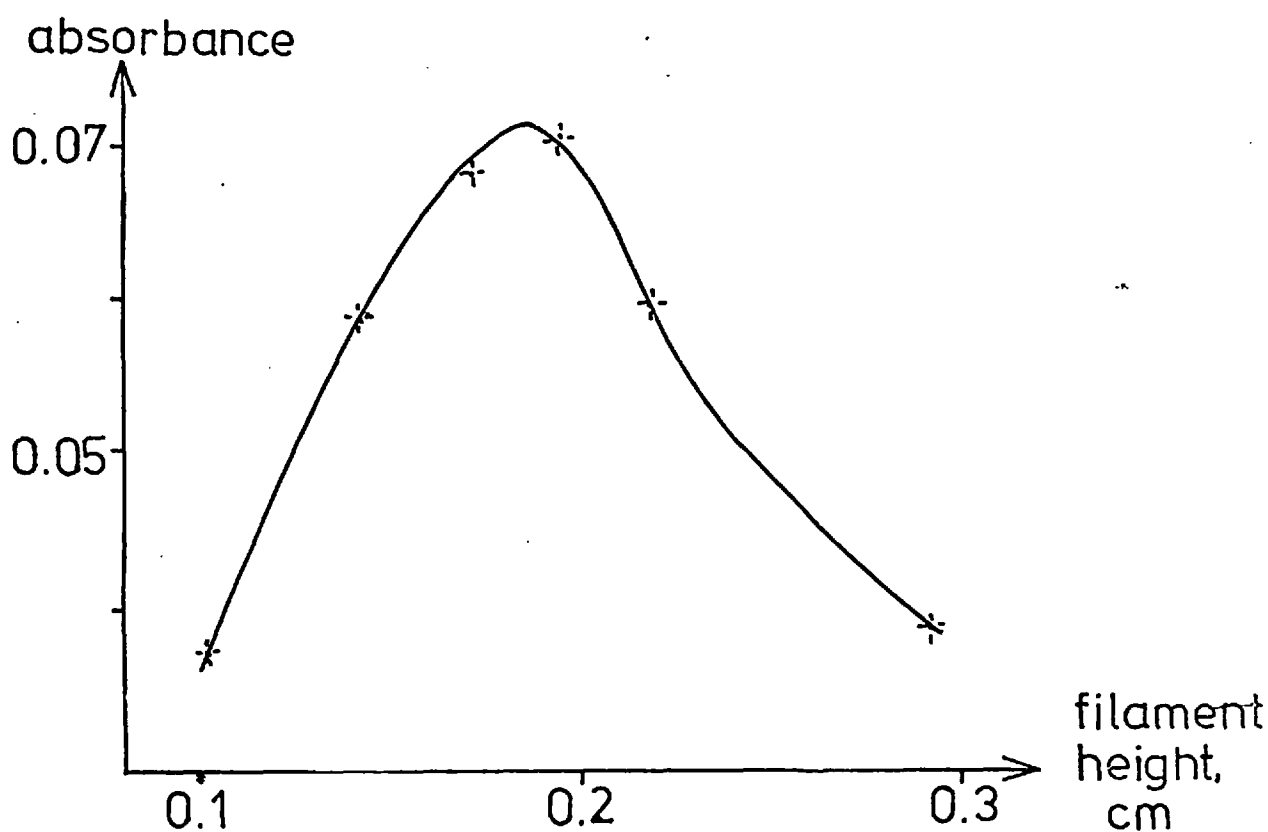


Figure 3.2

Optimisation of slit-width

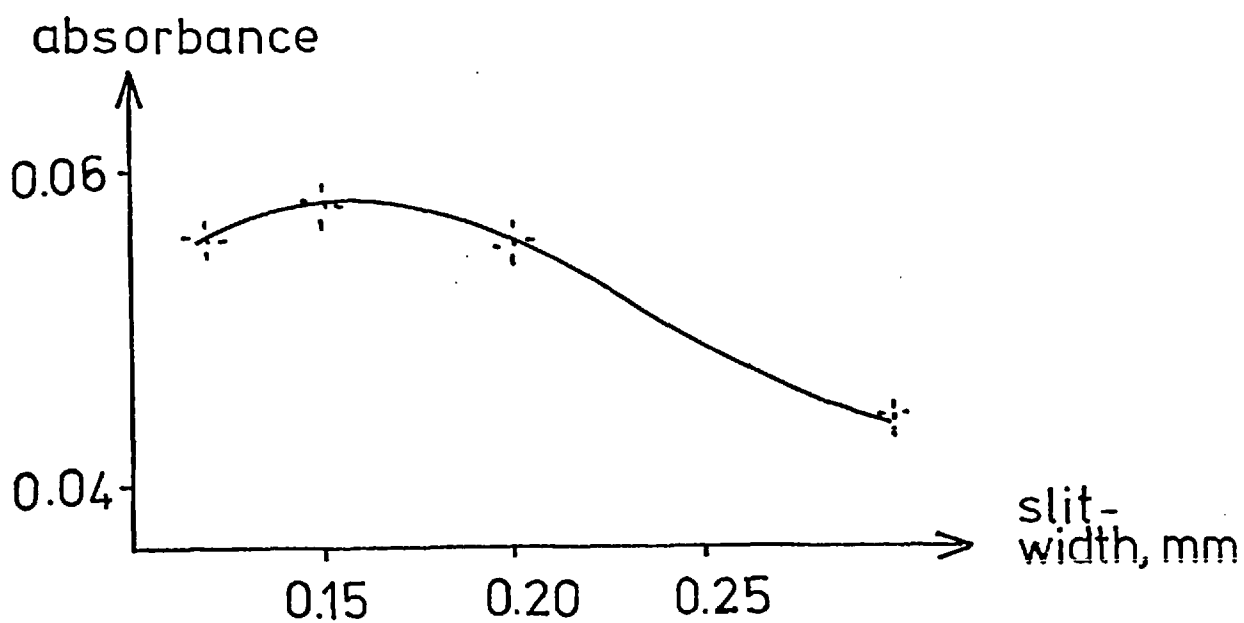


Figure 3.3
Optimisation of lamp current

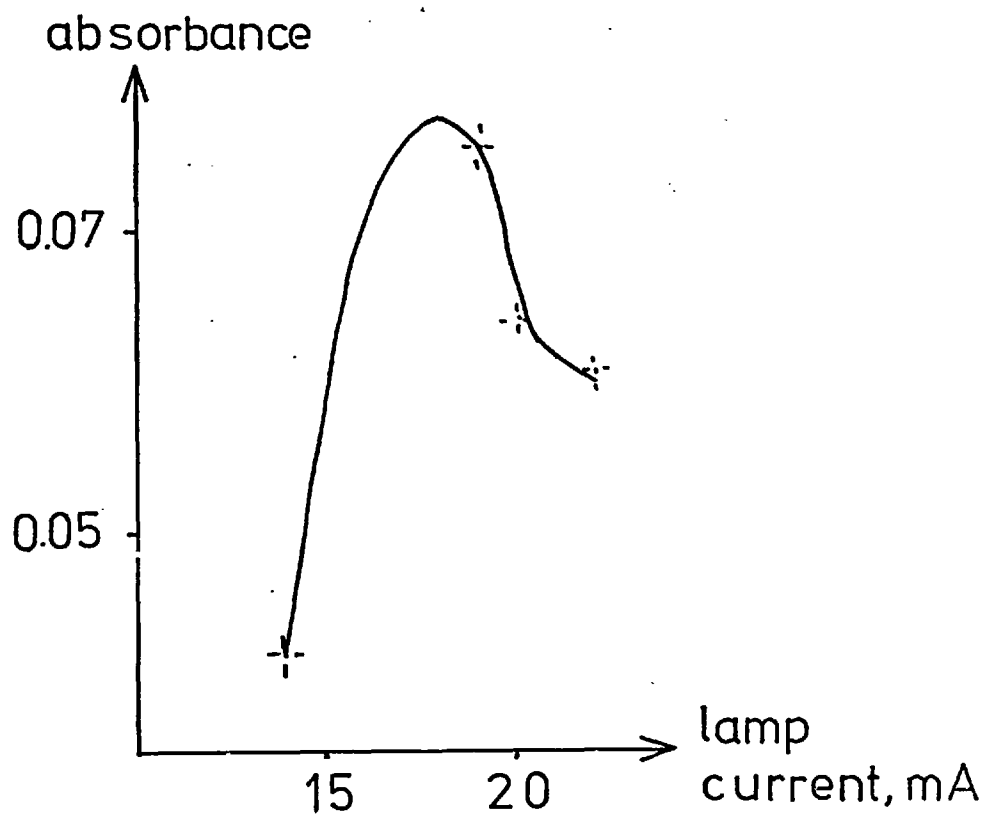


Figure 3.4
Optimisation of atomisation temperature

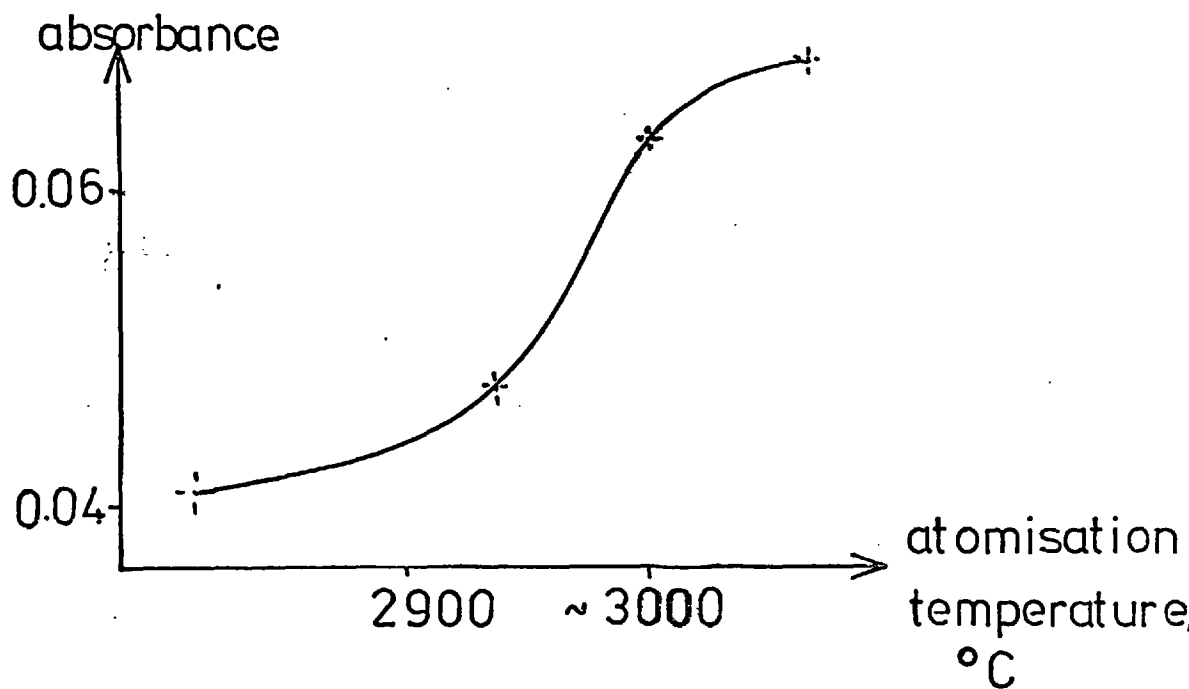


Figure 3.5

Optimisation of N₂ flow rate

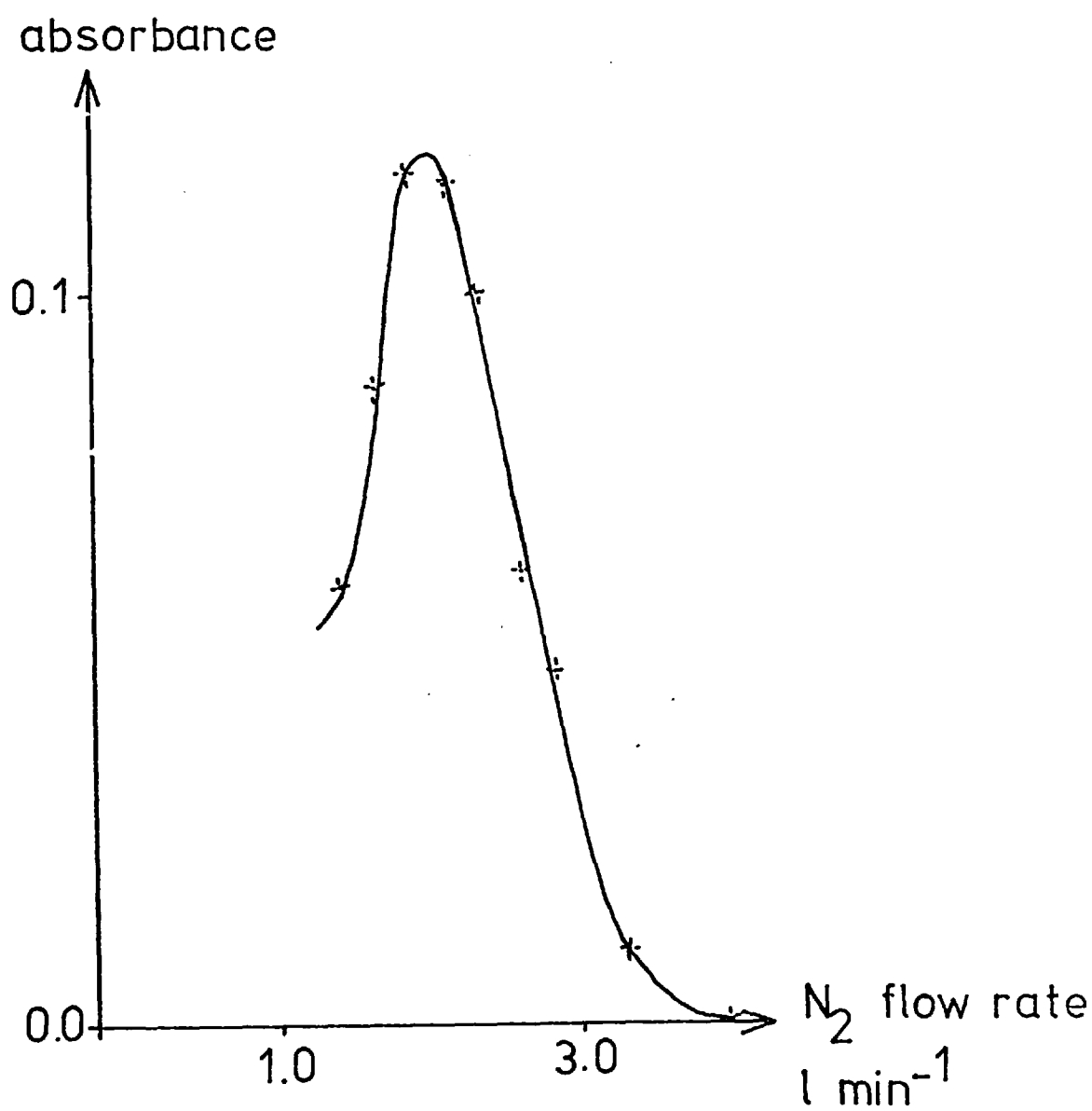


Table 3.2 Heating Cycles - Calcium

Matrix	Water	Oil	Pet. Ether
Dry	2 secs : 120°	5 secs : 240°	2 secs : 120°
Ash	-	8 secs : 1230°	8 secs : 1230°
Atomise	<u>ca</u> 3000°	<u>ca</u> 3000°	<u>ca</u> 3000°

Analysis of Real Samples

The sample was warmed in an oven at 80°C for ca one hour, shaken thoroughly and then, if necessary suitably diluted in petroleum ether. The analyte concentration was determined by the method of standard additions, Figure 3.7, and/or interpolation onto the appropriate calibration curve.

3.3 Results and Discussion

Calibration curves were constructed for aqueous, oil and petroleum ether media, Figure 3.6. Limits of detection and sensitivities (obtained by extrapolation since they are lower than the limits of detection) are shown in Table 3.3.

Table 3.3 Sensitivity Data - Calcium

Matrix	Limit of Detection	Sensitivity
Water	$1.0 \times 10^{-11} \text{ g}$	$4.0 \times 10^{-12} \text{ g}$
Oil	$1.8 \times 10^{-11} \text{ g}$	$7.0 \times 10^{-12} \text{ g}$
Pet. Ether	$1.5 \times 10^{-11} \text{ g}$	$5.0 \times 10^{-12} \text{ g}$

The origins of all signals were confirmed as being due to calcium by measuring the signal obtained using the neon line at 423.3 nm; no

Calibration curves

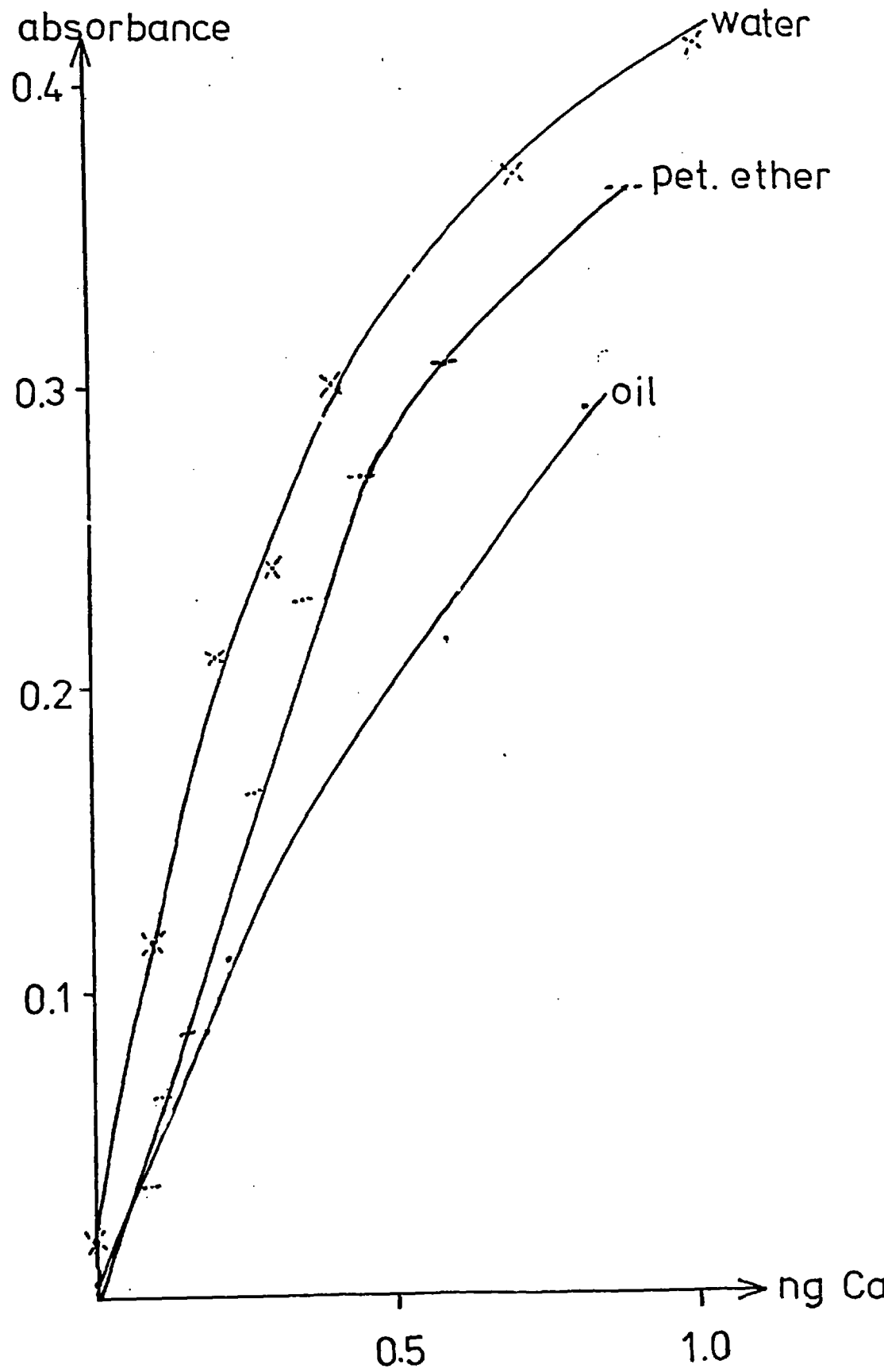
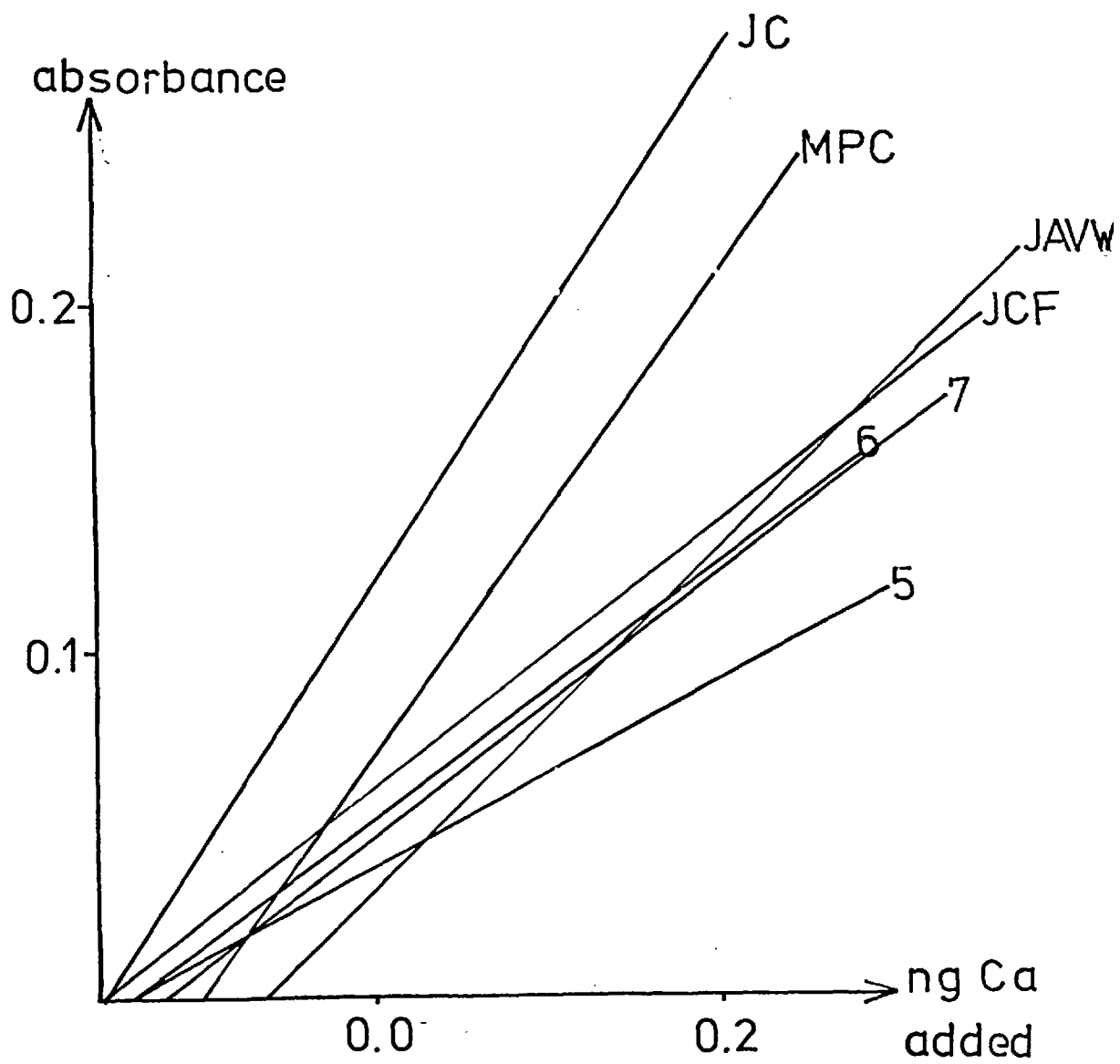


Figure 3.7

Standard addition curves



signal was obtained.

Superficial inspection of the sensitivities and detection limits obtained suggests that the analyte is atomised to an equal extent in each matrix. However, a clear trend is exhibited by the calibration curves shown in Figure 3.6. The differences between the curves are most probably due to the formation of refractory carbides. In the case of aqueous solutions carbides may be formed by reaction of the analyte at the surface of the carbon filament, but in the case of the organic solutions, especially those made up in oil, the analyte is intimately mixed with carbon from the matrix; as a result refractory carbides may be formed with considerably greater ease.

The real samples analysed fell into three groups: three solutions containing known concentrations of calcium made up by weight (1-3); four new lubricants analysed at B.P. Laboratories by flame AAS (4-7) and four used car lubricants also analysed at B.P. Laboratories. Clearly there are matrix effects but adequate results were obtained and these are shown in Table 3.4.

Table 3.4 Results - Calcium

Designation/Type	ppm Ca given	ppm Ca found	
		standard addition	interpolation
1 known sol ⁿ	0.120	-	0.160 $\pm$ 0.016
2 " "	0.150	-	0.180 $\pm$ 0.013
3 " "	0.240	-	0.245 $\pm$ 0.042
4 new oil	< 1.0	-	0.670 $\pm$ 0.240
5 " "	1200	1450 $\pm$ 340	1390 $\pm$ 150
6 " "	550	676 $\pm$ 97	725 $\pm$ 73
7 " "	25	27.9 $\pm$ 5.5	26.1 $\pm$ 3.2
JAVW used oil	490	500 $\pm$ 47	520 $\pm$ 47
JC " "	1550	1930 $\pm$ 460	1890 $\pm$ 230
MPC " "	1850	1835 $\pm$ 290	1835 $\pm$ 183
JCF " "	2500	3300 $\pm$ 330	3100 $\pm$ 300

The results in general agreed with those obtained by B.P. to within ca 20%. The relative standard deviations on most of the results lay in the range 10 - 15%. The use of a hydrogen diffusion flame around the filament, after Molnar et al. (14), did not make a significant difference to the results and was not used.

The calcium resonance line employed in these studies is centred at 422.673 nm. There exists in the germanium atomic spectrum a non-resonance line centred at 422.657 nm. This line overlaps sufficiently for its radiation to be absorbed by ground state calcium atoms; the application of this to the AAS of calcium was demonstrated by Thompson in 1970 (87). The sensitivities he found in the air - acetylene and nitrous oxide - acetylene flames were 8.3 and 6.8 ppm respectively and the corresponding useful ranges of the analytical curves extended to 1500 and 1000 ppm. Attempts were made to apply this technique to the determination of high levels of calcium in oils but no signal was obtained.

In conclusion it may be stated that the CFAR affords a rapid method for the determination of calcium in oils with a minimum of sample preparation. No significant interferences were found.

Chapter 4

The Determination of Magnesium

4.1 Introduction

Magnesium additives to lubricants fulfil a similar role to calcium. Magnesium acts as an inhibitor to the deleterious effects of vanadium especially in gas turbine fuels (section 1.4.4); it is used in preference to calcium in this case as it does not form hard, water-insoluble ash nodules. It is necessary to determine magnesium at both additive levels to lubricants and at trace levels to monitor contamination.

The official methods for the determination of magnesium in oils are either by weighing of the pyrophosphate or by AAS with an air-acetylene flame at trace levels in gas turbine fuels.

A number of instrumental methods has been applied to the analysis of magnesium in oils. NAA has been used to determine up to 100 ppm in gasolines while AES may be employed for the analysis of as little as 0.01 ppm in the same matrix (77). 2 ppm of magnesium in RFO has been measured by mass spectrometry. Winefordner and co-workers (33, 34, 88) have applied AES and AFS to this problem; they determined 0.03 ppm in used jet-engine oils diluted with MIBK by AFS with a continuum source. The diluted oil was burned in an air - hydrogen flame using a total consumption burner (33).

Flame AAS is a well established method for the determination of this element in both new and used lubricants. Slavin and Slavin (35) measured 0.01 ppm with a precision of 10 % or greater in used aircraft oils. Hopp (81) employed the technique of spraying an aqueous emulsion into a flame for the analysis of magnesium as well as for calcium. A number of workers (30, 37) has used flame AAS including Barnett et. al.(29) and Jackson et al. (89) who determined magnesium as part of multielement analyses of oils.

Figure 4.1

Optimisation of filament height

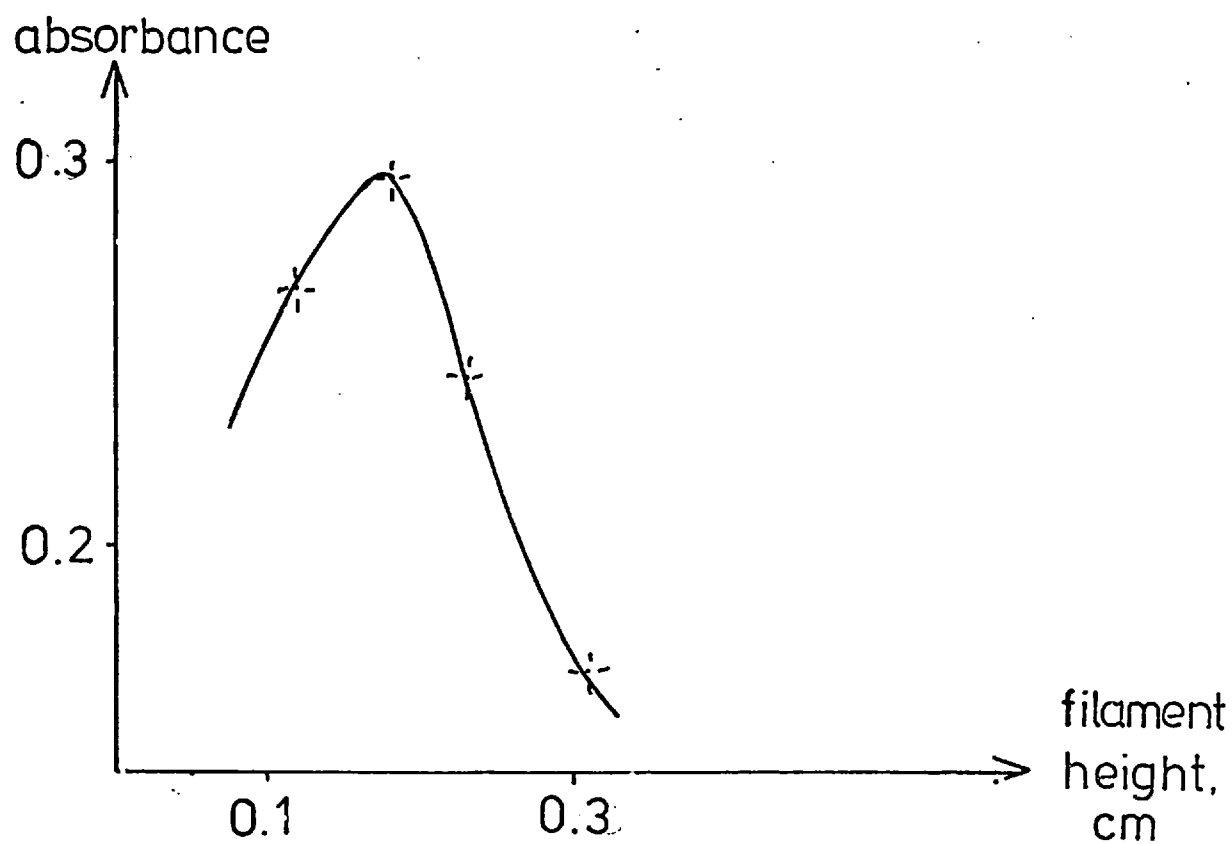


Figure 4.2

Optimisation of slit-width

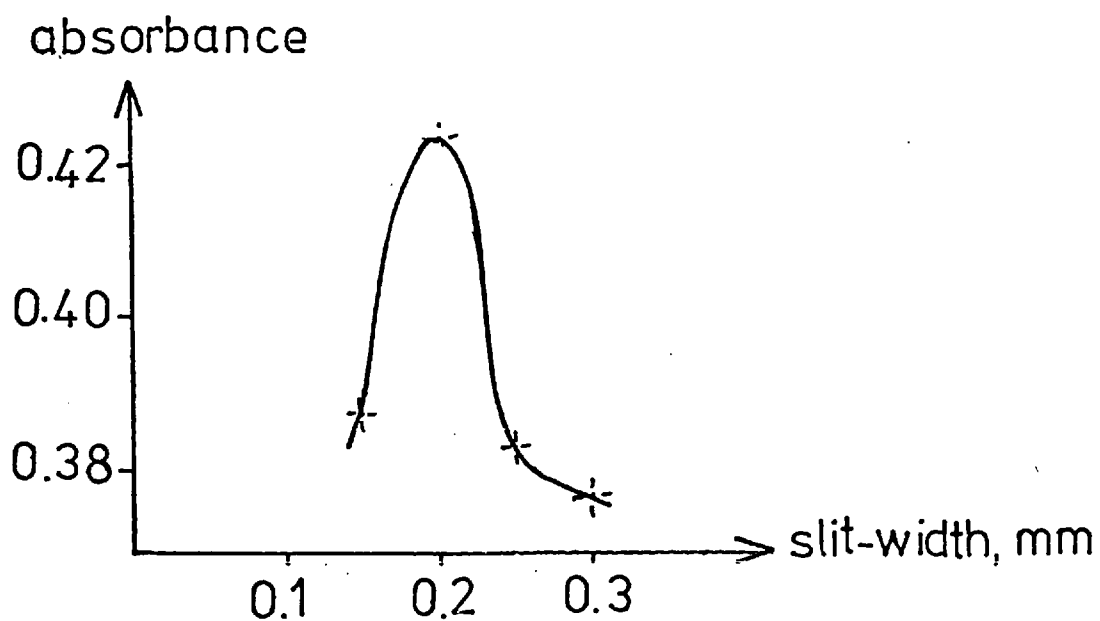


Figure 4.3

Optimisation of lamp current

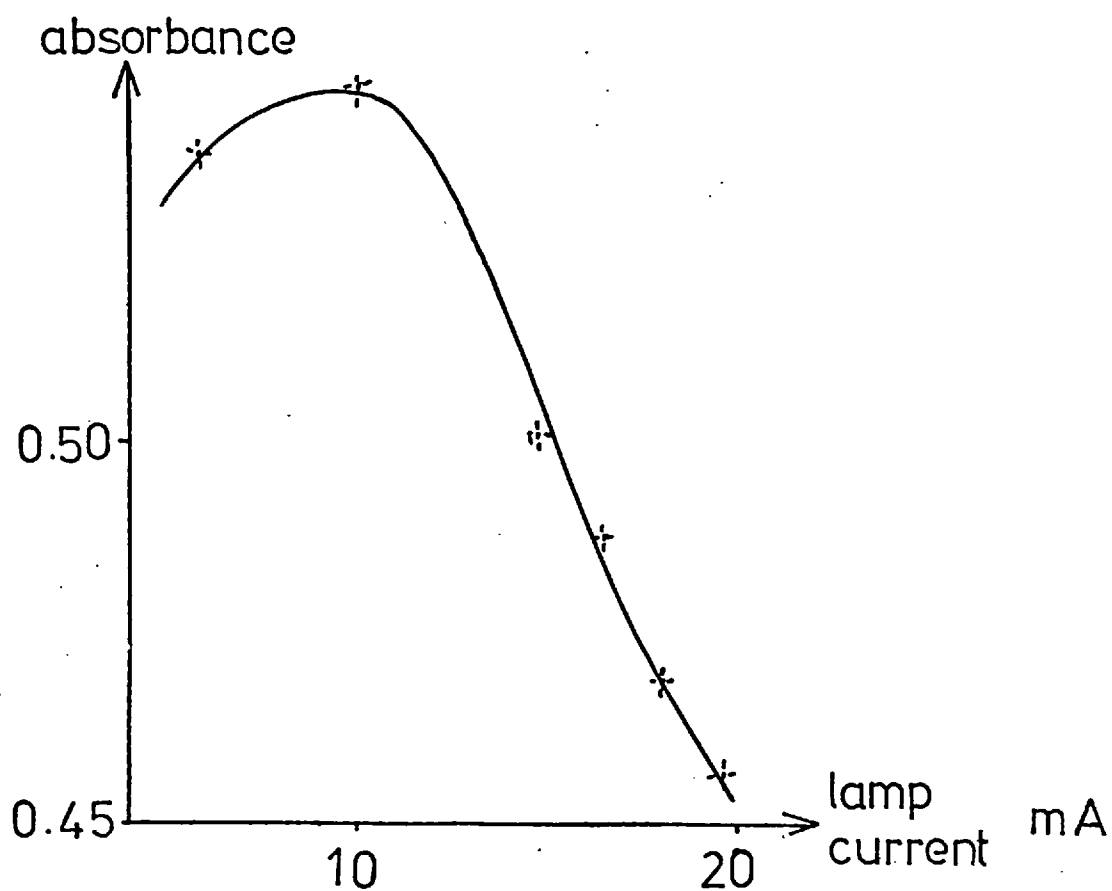


Figure 4.4

Optimisation of atomisation temperature

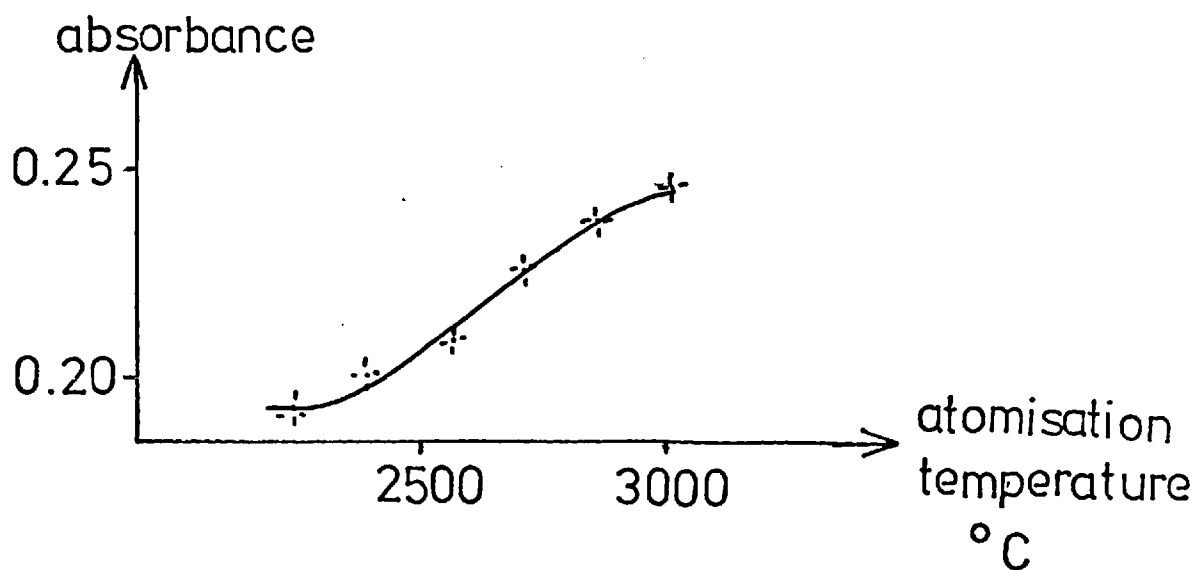
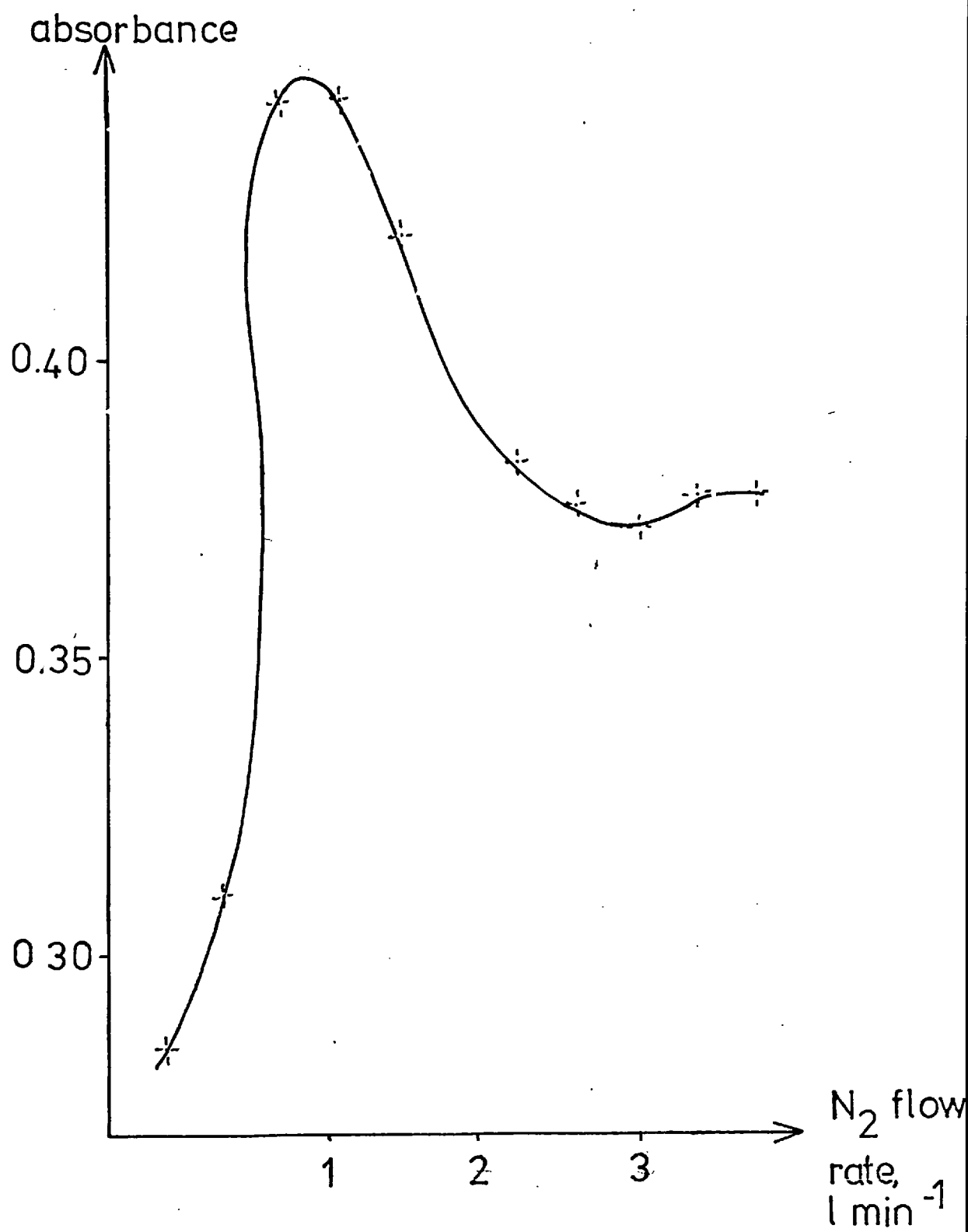


Figure 4.5
Optimisation of N_2 flow rate



The CFAR has been used for the determination of magnesium in petroleum products prior to the work presented below. Molnar et al. (14) and Chuang et al. (90) atomised samples from a carbon filament into an argon - hydrogen diffusion flame obtaining detection limits of 1 pg. Brodie and Matousek (62) drilled a hole in the filament, turning it into a furnace and measured 0.1 ng magnesium in oils, using aqueous standards. Chuang and Winefordner (40) also used aqueous standards in their work on jet engine oils.

Since the work described below was completed Araktingi et al. (39) published the results they obtained in similar fashion.

4.2 Experimental

The experimental arrangements and procedures were substantially the same as those employed for the work on calcium as described in section 3.2. Aqueous standards were made up from magnesium chloride and organic standards from 7.12 % magnesium sulphonate (Bryton Hybase). Optimum operating conditions are shown in Table 4.1; graphs relating to those conditions are shown in Figures 4.1 - 4.5.

Table 4.1 Experimental Parameters - Magnesium

Wavelength	285.2 nm or 202.5 nm
Filament height	0.19 cm
Monochromator slit-width	0.20 mm
Lamp current	9.0 mA
Atomisation temperature	<u>ca.</u> 3000 °C
Nitrogen flow rate	0.9 l min ⁻¹
Damping	0.068 μ F

The heating cycles used are shown in Table 4.2; the remarks about the atomisation of calcium apply also to magnesium.

Table 4.2 Heating Cycles - Magnesium

Matrix	Water	Oil	Pet. Ether
Dry	10 secs : 120°	5 secs : 260°	3 secs : 260°
Ash	-	8 secs : 1230°	5 secs : 1230°
Atomise	<u>ca</u> 3000°	<u>ca</u> 3000°	<u>ca</u> 3000°

4.3 Results and Discussion

Calibration curves for magnesium in water, oil and petroleum ether were constructed for the 285.2 nm line and for petroleum ether at the 202.5 nm line, Figures 4.6 and 4.7. Sensitivity data is shown in Table 4.3.

Table 4.3 Sensitivity Data - Magnesium

Matrix	Limit of Detection	Sensitivity	Wavelength
Water	$9.0 \times 10^{-12} \text{ g}$	$8.0 \times 10^{-13} \text{ g}$	285.2 nm
Oil	$1.5 \times 10^{-11} \text{ g}$	$6.0 \times 10^{-12} \text{ g}$	285.2 nm
Pet. Ether	$5.3 \times 10^{-12} \text{ g}$	$2.0 \times 10^{-12} \text{ g}$	285.2 nm
Pet. Ether	$6.5 \times 10^{-10} \text{ g}$	$7.0 \times 10^{-11} \text{ g}$	202.5 nm

A similar trend in sensitivities to that found for calcium is observed for magnesium and similar conclusions may be drawn. Very low levels of calcium and magnesium may be detected; both elements are extremely ubiquitous and present in comparatively large quantities on the skin, hence great care must be taken with regard to cleanliness in working.

Figure 4.6

Calibration curves

wavelength- 285.2 nm

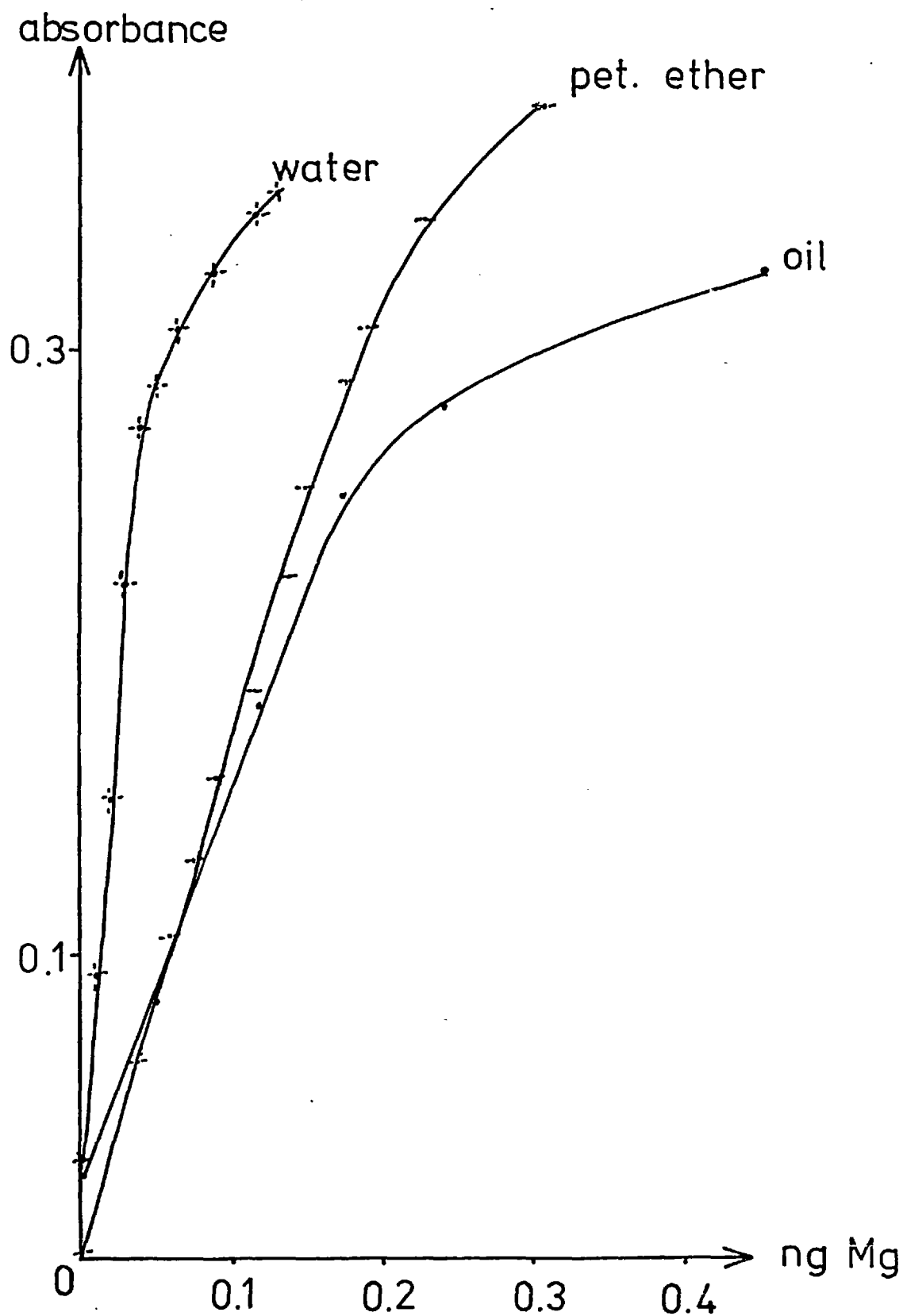
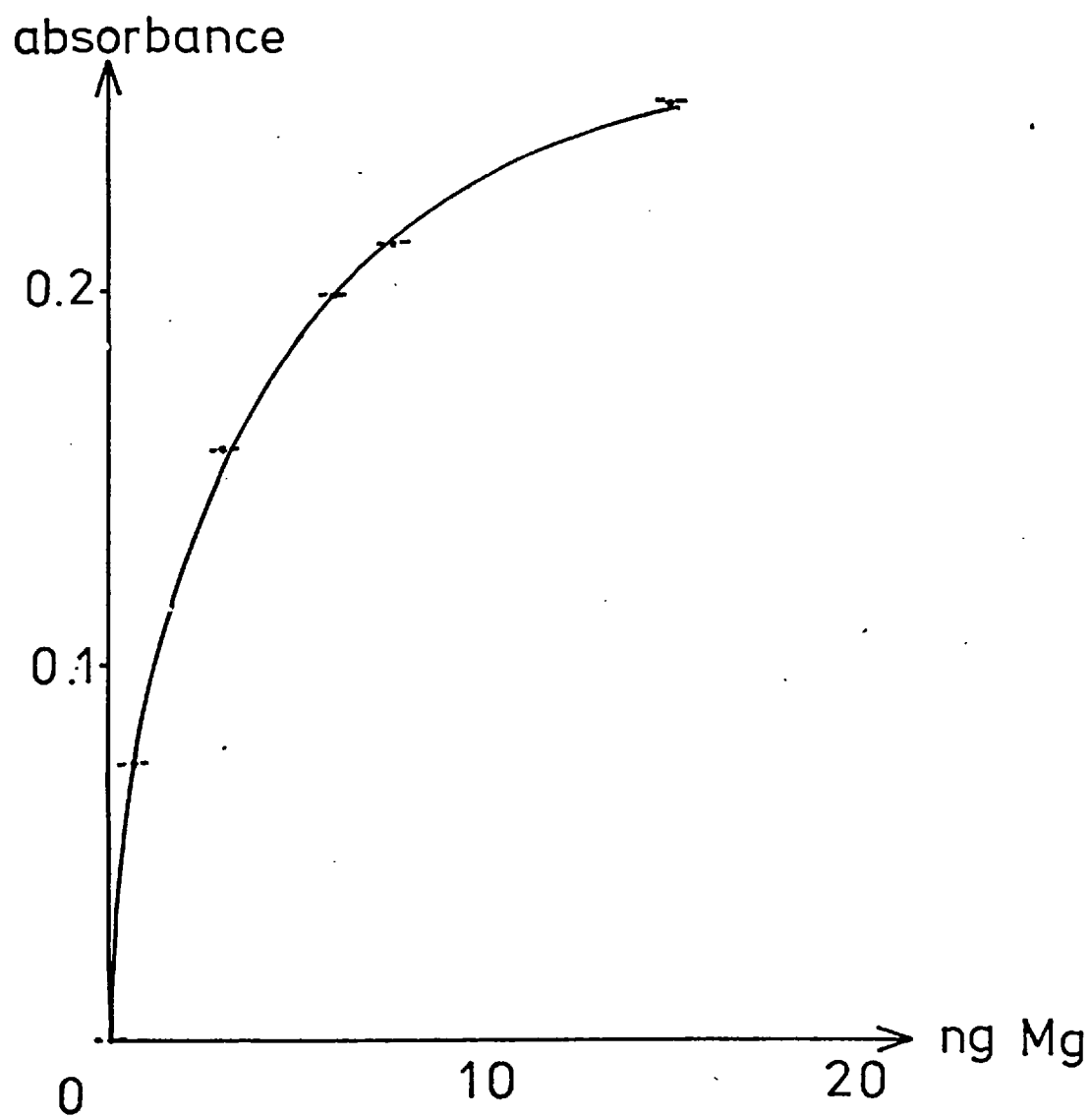


Figure 4.7

Calibration curve

wavelength - 202.5 nm



For corresponding matrices the limit of detection using the 202.5 nm line is two orders of magnitude higher than at 285.2 nm. This reduced sensitivity allows the determination of magnesium in the tens of ppm range which, as may be noted from Table 4.4 was convenient for some samples. The origins of the signals were checked using the antimony resonance line at 287 nm; all the signals were due to the atomic absorption of magnesium.

Table 4.4 Results - Magnesium : wavelength 202.5 nm

Designation	ppm Mg given	ppm Mg found by interpolation
JC	26	26.4 $\pm$ 2.6
JCF	50	56.0 $\pm$ 8.0
JAVW (oil wet)	66	31.2 $\pm$ 2.6
MPC	12	15.1 $\pm$ 1.5

Results obtained for 14 samples using the 285.2 nm line are shown in Table 4.5. The samples analysed fell into three groups: 1 - 6 were new lubricants containing less than 0.5 ppm which were analysed with an accuracy and precision of ca 10%; 7 - 9 were also new lubricants containing between 100 and 700 ppm; the accuracy of these analyses lay between 3% and 10% although the precision varied from ca 10% to as much as 30% in some cases; the final group were used crankcase oils containing 10 - 70 ppm; these analyses were performed with a precision of greater than 12% but again the accuracy was rather variable in that it lay between 2 and 30%. The results are compared to those figures given by B.P. which were obtained by flame AAS.

In general the results obtained compare favourably with those obtained by other workers (section 4.1). The system is quick and easy to use and the use of the less sensitive line at 202.5 nm affords a

Figure 4.8

Standard addition curves

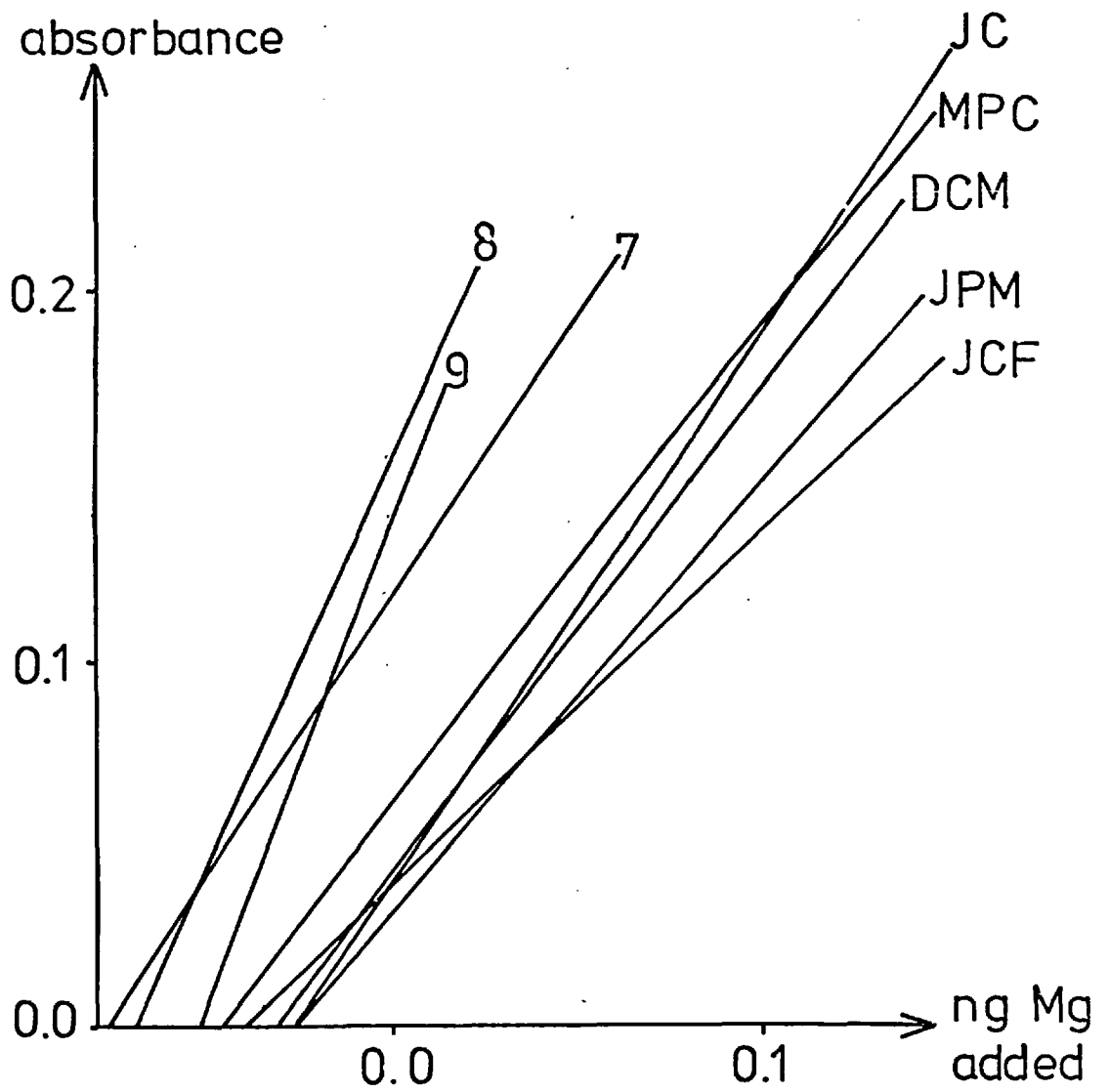


Table 4.5 Results - Magnesium : wavelength 285.2 nm

Designation/Type	ppm Mg given	ppm Mg found	
		standard addition	interpolation
1 SAE 10	0.1	-	0.066 $\pm$ 0.005
2 SAE 50	0.1	-	0.039 $\pm$ 0.002
3 SAE 50	0.1	-	0.074 $\pm$ 0.002
4 SAE 10/30	0.3	-	0.31 $\pm$ 0.03
5 SAE 10/50	0.2	-	0.18 $\pm$ 0.02
6 SAE 20/50	0.4	-	0.43 $\pm$ 0.03
7 SAE 20/50	100	160 $\pm$ 10	130 $\pm$ 10
8 SAE 20/50	160	136 $\pm$ 9	210 $\pm$ 6
9 SAE 20/50	700	550 $\pm$ 40	850 $\pm$ 40
10 JC used oil	26	36 $\pm$ 12	40 $\pm$ 12
11 JCF " "	52	51 $\pm$ 1	56 $\pm$ 3
12 DCH " "	41	45 $\pm$ 6	30 $\pm$ 4
13 JPM " "	44	49 $\pm$ 6	46 $\pm$ 3
14 MPC " "	15	19 $\pm$ 6	18 $\pm$ 2

most convenient procedure for the analysis of more concentrated solutions.

Chapter 5

The Determination of Barium

5.1 Introduction

Organic salts of barium combine detergency with rust prevention when present in lubricating oils (section 1.4.6.4). Barium is the preferred cation to be combined with wax - substituted phenol detergents for addition to motor oils. Barium compounds are also used as anti-smoking additives in Diesel fuels; in addition oxides of sulphur formed in the combustion of these high sulphur fuels (section 1.4.5) are precipitated as barium sulphate. It is necessary to determine barium at the level of additives and at trace levels to check for contamination. B.P. have recently begun to monitor changes in the barium concentration of sea water in the vicinity of their North Sea drilling platforms (92); the prevailing concentration at present is ca 30 ppb; the work presented below will show that flameless AAS lends itself to this application.

In the ASTM procedure (2) barium is determined gravimetrically as its sulphate following removal of the organic material. Complexometric titration has also been proposed (24, 74) for concentrations between 0.04 and 3.0% in lubricating oils and up to 30% in additive concentrates. Instrumental methods are well established techniques for the analysis of this element in petroleum products. Landolt and Struckmeyer (93) determined 10 mg in Diesel fuel by NAA with a precision of 8%. The use of XRF has been reported (26) in the range 0 - 0.68%; the time for each sample is about 40 minutes and the precision ca 2%, however the results must be corrected for interferences from sulphur.

Flame photometry has been used to analysis of barium in lubricating oils (75) and greases (78) but Anand et al. (75) noted the interfering effect of the presence of large amounts of lead while Pop et al. (78) reported general interferences in their determinations. Spectrographic methods, however,

have been more successfully employed (27, 28, 94). Typical analyses take 5 minutes, the relative errors reported were 20 - 30% in the concentration range up to 10 ppm and 10 - 20% in the 10 - 200 ppm range (94).

A considerable body of work has been published on the flame AAS determination of barium in oils (77, 79 - 83); the concentration ranges reported were from 0.014 ppm (83) to more than 20 ppm (85), although Peterson and Kahn found the optimum range to be 2 - 20 ppm (85). Several workers have reported interferences (83, 85, 86); the use of a nitrous oxide - acetylene flame, employed to ensure atomisation and overcome such interferences, itself leads to ionisation of the analyte though the addition of potassium cyclohexylbutyrate is reported to be effective in suppressing this (85). Holding and Rowson (83) observed an interference from calcium but they found that it could be overcome by sufficient dilution of the solution sprayed. Sastri et al. (86), who investigated these interference phenomena, concluded that they were due to the formation of involatile mixed oxides of the analyte and the interferent.

5.2 Experimental

A Varian AA5 atomic absorption spectrophotometer (Varian Associates Ltd) was employed for this work in conjunction with the Varian Model 63 CRA carbon filament attachment. The tube used was as supplied by Varian and the carbon rod was Ringsdorff RW 1235, 4 mm diameter. A Varian barium hollow cathode lamp served as spectral source and the lamp and detector were modulated at 285 Hz. The carbon furnace was sheathed in a stream of argon with a small addition of propane. The propane pyrolyses on the hot graphite depositing a layer of carbon on the surface and in this way greatly increases the furnace lifetime (95). A collimating device consisting of a metal shield and a 1.5 mm i.d. x 6 mm tube was put just after the filament/

furnace to cut down the thermal radiation from the filament/furnace reaching the monochromator entrance slit. The light from the hollow cathode lamp was focussed on the opening of the tube situated close to the carbon furnace and passed through into the monochromator. In this way the signal: background noise ratio was improved considerably.

Aqueous standards were prepared from barium nitrate and organic standards from a 5000 ppm Conostan barium sulphonate standard (Continental Oil Co. U.S.A.) made up in filtered white spirit or SAE 10 metal - free oil.

Samples of new and used oils were treated substantially as described in section 3.2, being diluted where necessary with filtered white spirit. 5 μ l aliquots were introduced into the atom reservoir using a 5 μ l Eppendorf pipette (supplied by Varian Associates Ltd) and five replicate determinations performed in each case. Calculation of the barium concentration in the samples were made either by interpolation or by standard additions.

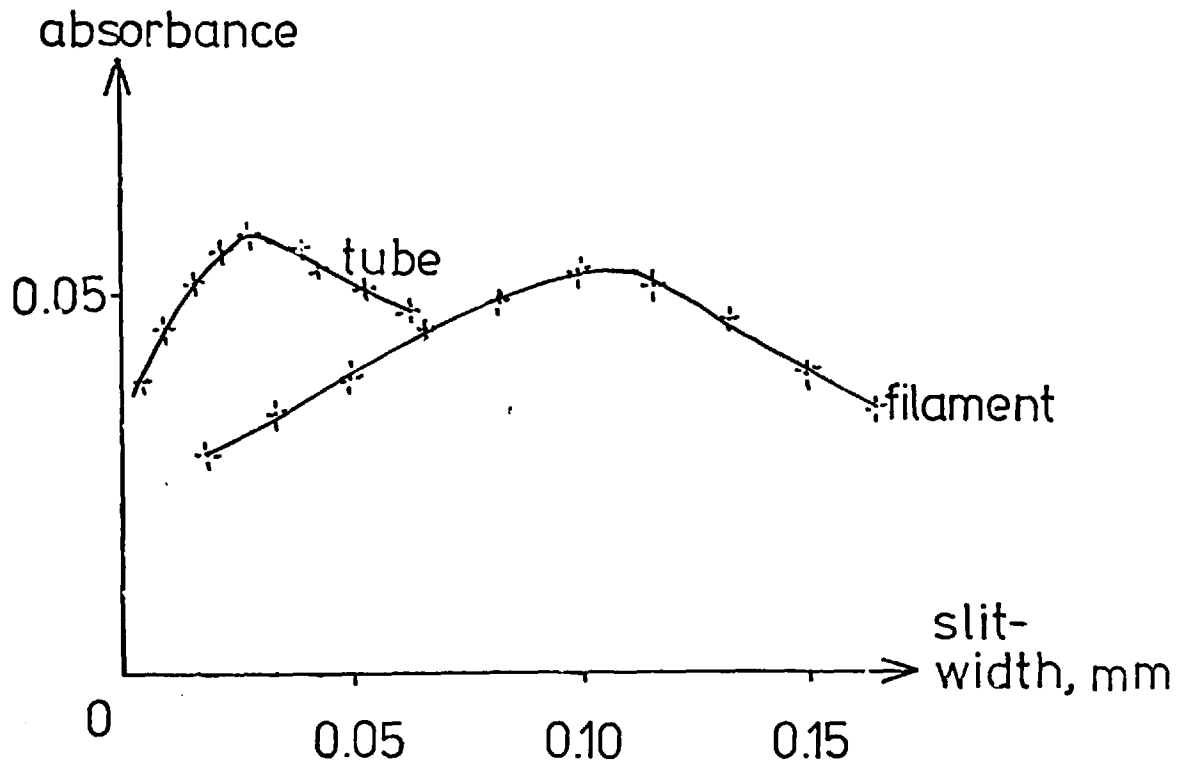
The optimum operating conditions are given in Table 5.1. Curves relating to some of these parameters are shown in Figures 5.1 - 5.3. The heating cycles used are shown in Table 5.2; the remarks referring to the atomisation of calcium (section 3.2) apply equally to barium.

Table 5.1 Experimental Parameters - Barium

Parameter	Carbon Tube	Carbon Filament
Wavelength	553.5 nm	553.5 nm
Monochromator slit-width	0.025 mm	0.100 mm
" band pass	0.1 nm	0.4 nm
Lamp current	15.0 mA	15.0 mA
Atomisation temperature	>2500 °C	> 2500 °C
Argon flow rate	3.0 l min ⁻¹	2.5 l min ⁻¹
Propane flow rate	0.1 l min ⁻¹	0.1 l min ⁻¹

Figure 5.1

Optimisation of slit-width

Table 5.2 Heating Cycles - Barium

Matrix	Water	Oil	White Spirit
Dry	10 secs : 130°	10 secs : 370°	10 secs : 150°
Ash	-	5 secs : 1600°	5 secs : 1600°
Atomise	> 2500°	> 2500°	> 2500°
Cool	60 secs	60 secs	60 secs

Figure 5.2

Optimisation of Ar flow rate

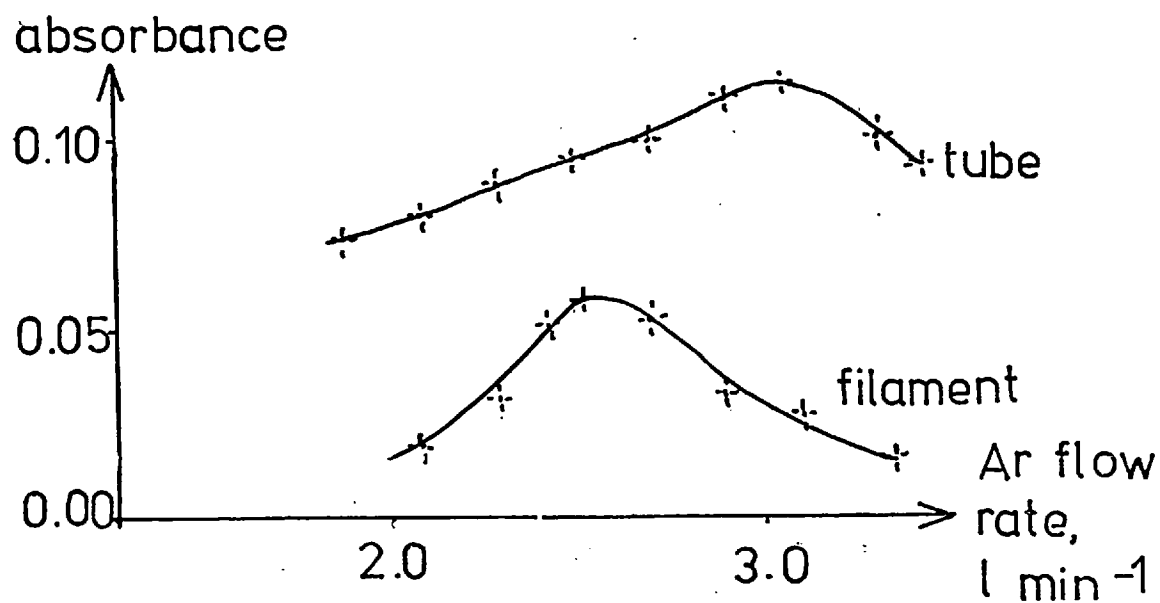
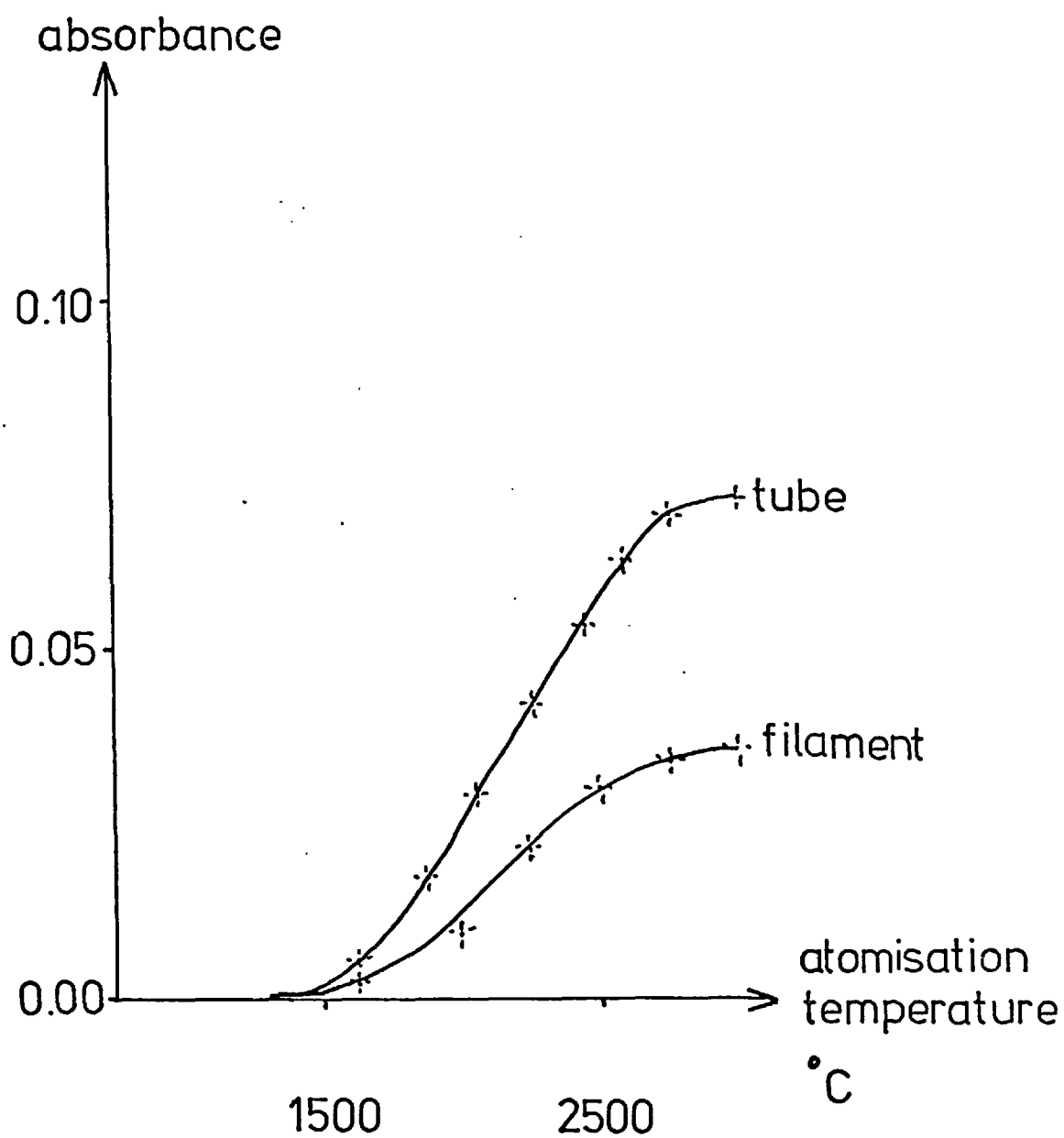


Table 5.3 Sensitivity Data - Barium

Matrix	Limit of Detection		Sensitivity	
	Filament	Tube	Filament	Tube
Water	$6.6 \times 10^{-10} \text{ g}$	$1.4 \times 10^{-10} \text{ g}$	$1.4 \times 10^{-9} \text{ g}$	$2.6 \times 10^{-10} \text{ g}$
Oil	$3.9 \times 10^{-10} \text{ g}$	-	$1.0 \times 10^{-9} \text{ g}$	-
White Spirit	$2.9 \times 10^{-10} \text{ g}$	$9.2 \times 10^{-11} \text{ g}$	$1.2 \times 10^{-9} \text{ g}$	$2.0 \times 10^{-10} \text{ g}$

Figure 5.3

Optimisation of atomisation temperature



5.3 Results and Discussion

Calibration curves were constructed for aqueous, white spirit and oil matrices using both the tube and West - type reservoirs, Figures 5.4 and 5.5. Non-atomic absorption was checked using the neon line at 585.2nm and found never to be more than 1%. Limits of detection and sensitivities are shown in Table 5.3. For each atom reservoir the sensitivities and limits of detection are of the same order for each matrix which indicates that the analyte is fully atomised in each case. The sensitivities of the tube furnace were significantly higher than that of the filament as would be expected from consideration of path lengths and residence times involved. The sensitivities obtained for the tube mode indicate that 30 ppb may be determined easily using a 5 μ l aliquot.

The results obtained on five new and three used oils are displayed in Table 5.4. In most cases the results agreed to within 10% of those obtained by flame AAS at B.P.'s laboratories. The precision was also, in general, of a similar order although it too fell to ca 20% in some instances. These levels of accuracy and precision compare favourably with flame AAS.

Each determination took nearly two minutes; over half of this period was the cooling time needed for the filament to return to a sufficiently low temperature for the next sample to be introduced. The Model 63 CRA has a number of undesirable characteristics which result from poor design. It is awkward to set up, takes large amounts of power, heats up relatively slowly and is cooled extremely inefficiently. The use of the CFAR described in section 2.1 would reduce the time for each determination to less than a minute as in the cases of calcium and magnesium and enhance the desirability of this procedure.

Table 5.4 Results - Barium

Designation/Type	ppm Ba given	ppm Ba found			
		filament		tube	
		addition	interpol. ⁿ	addition	interpol. ⁿ
MPC used oil	78	53 $\pm$ 5	67 $\pm$ 6	75 $\pm$ 7	73 $\pm$ 5
JC " "	325	316 $\pm$ 40	316 $\pm$ 16	387 $\pm$ 35	356 $\pm$ 18
JCF " "	2535	2460 $\pm$ 120	2170 $\pm$ 120	-	-
D78 new oil	2100	1740 $\pm$ 370	1600 $\pm$ 90		
L1 " "	8		8.9 $\pm$ 1.5		
L2 " "	42		42.5 $\pm$ 1.0		
L3 " "	8		9.8 $\pm$ 1.0		
T1 " "	43		0.4 $\pm$ 0.05		

Figure 5.4

Calibration curves-tube

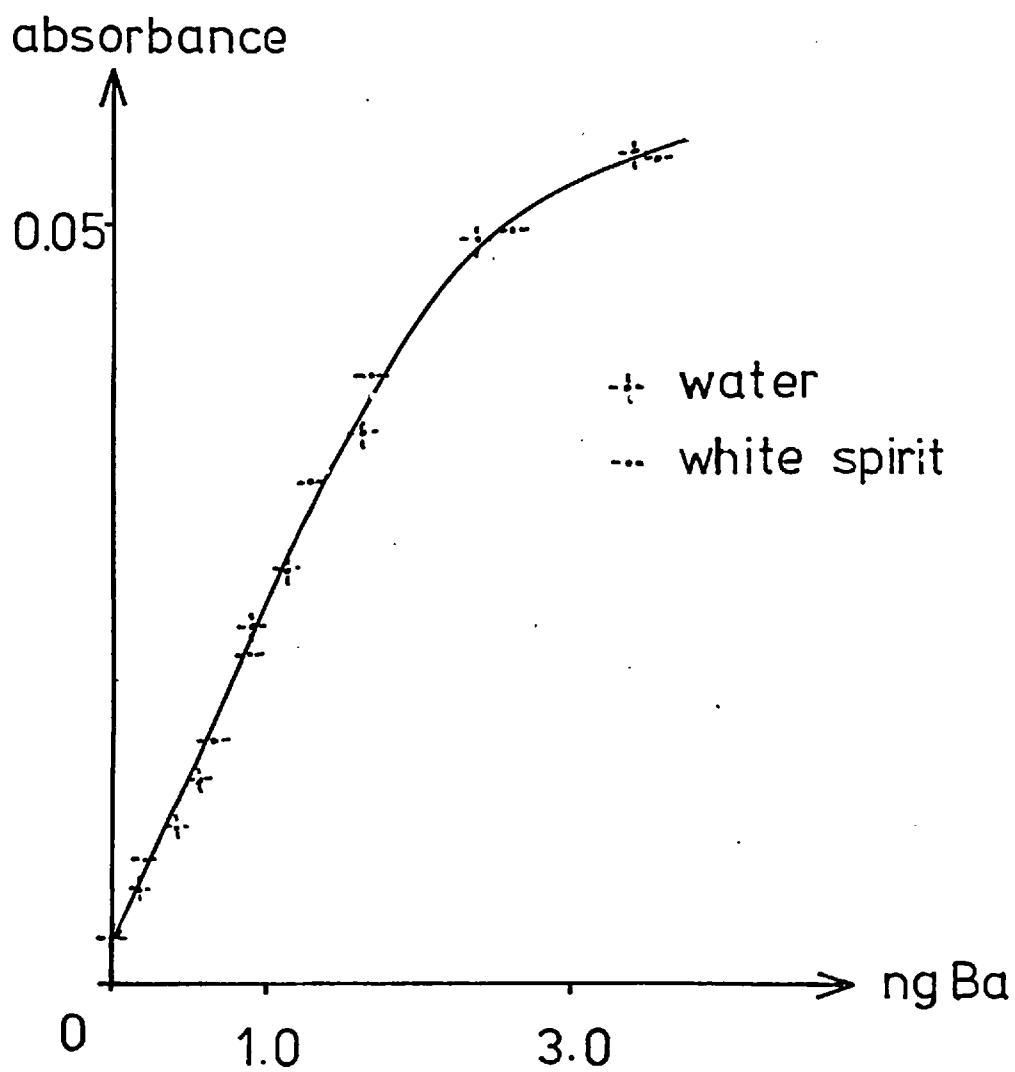


Figure 5.5
Calibration curves - filament

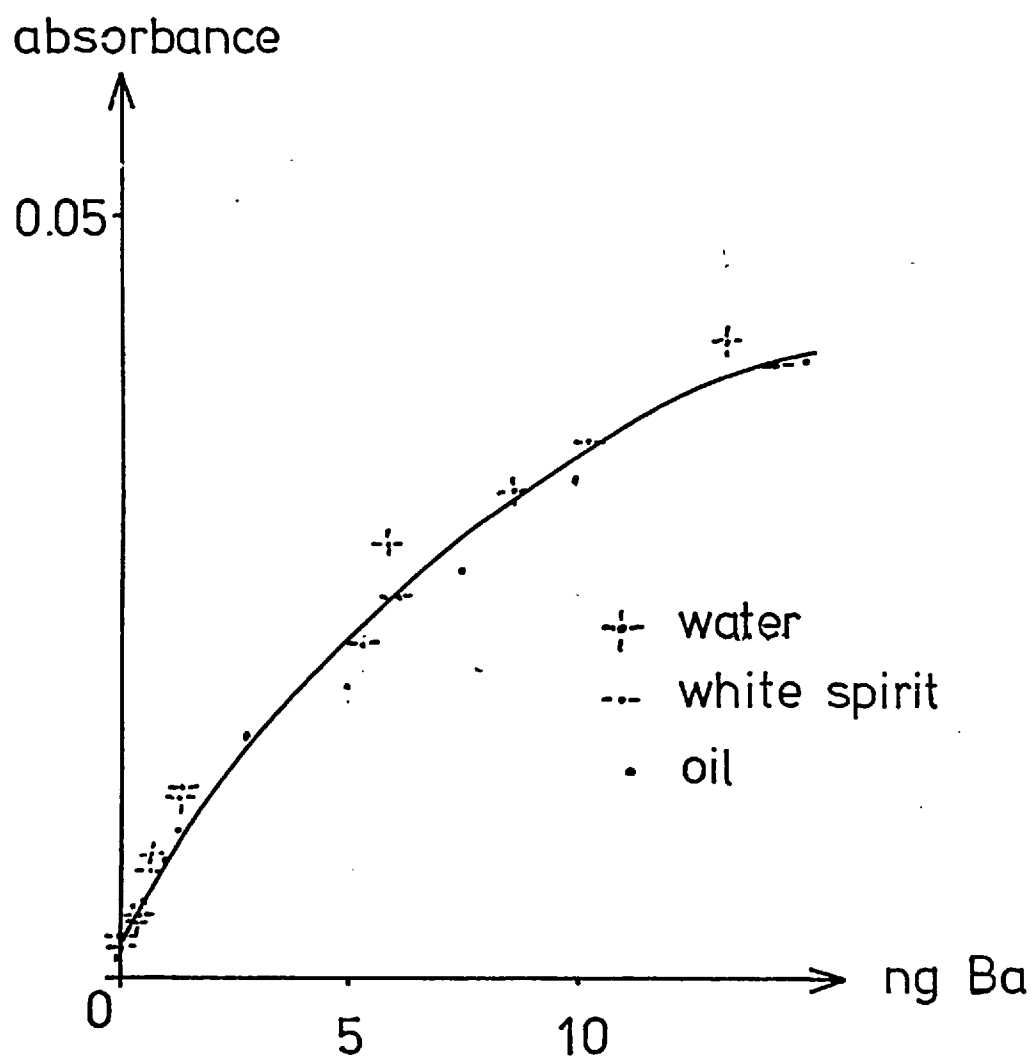
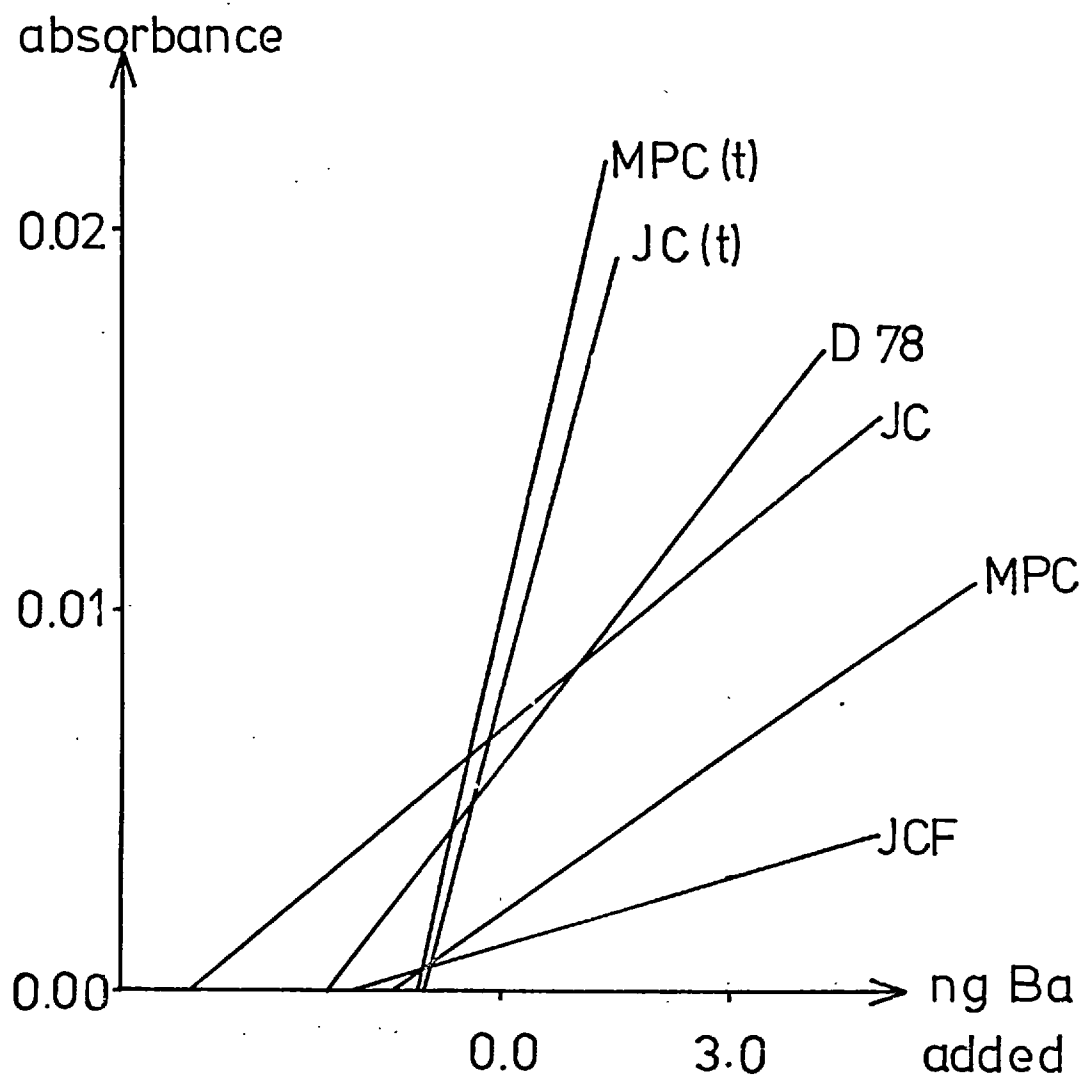


Figure 5.6

Standard addition curves



(t) = tube reservoir

Conclusions - Filament Work

The work presented in Chapters 3, 4 and 5 shows that the CFAR is suitable for the determination of calcium, magnesium and barium at trace and, after suitable dilution, additive levels. These determinations are rapid, with the exception of barium for the reasons stated in section 5.3, simple and of a precision and accuracy comparable with other techniques currently in favour. Although matrix effects were noted these were not of the serious type found in flames (83,85,86) which are caused by the formation of refractory mixed oxides. The reducing nature of the carbon present in this technique effectively breaks down any such oxides formed.

In conclusion the technique can be said to be successful and is to be recommended for this type of analysis. It would be desirable for the CFAR to be used more routinely in industry as a complement to flame procedures.

PART THREE

HYDRIDE TECHNIQUES

Hydride Techniques: Introduction

A major problem in the flameless AAS determination of antimony, tin and lead is the loss of analyte during ashing. Generation of the volatile hydrides, stibine, stannane and plumbane followed by AAS on these compounds obviates the need for an ashing step.

The Gutzeit test for the determination of arsenic has been an established method for many years. Initial AAS work using hydride techniques employed a zinc metal reduction followed by collection of the gas evolved prior to atomisation in a hydrogen - argon diffusion flame (96 - 101). Pollock and West (102, 103) employed titanous chloride as a reductant and Fernandez successfully employed sodium borohydride for the reduction process (100). Among the disadvantages of these techniques are the relatively long collection times required for the gases and subsequent dilution of the analyte by the flame gases. Thompson and Thomerson (56) have overcome these disadvantages using acid to catalyse the reduction thus removing the necessity for collection vessels and atomising the hydrides in a 17 cm x 0.8 cm silica tube heated in an air acetylene flame. The work presented in the following three chapters describes the determination of antimony, tin and lead in lubricating oils by hydride generation followed by atomisation in a carbon tube furnace.

Chapter 6

The Determination of Antimony

6.1 Introduction

Antimony is added to oils and greases as its dialkyldithiocarbamate or dialkylphosphorodithioate in which forms it exhibits anti-wear and extreme pressure properties at levels of 1 - 3%. In addition at these and lower levels they function as antioxidants. Antimony also occurs as a wear metal, having its origin in the white metal (lead - antimony - tin) bearings.

The currently used wet method for the determination of antimony in oils consists of sulphuric acid digestion followed by potassium permanganate titration (105) but it is tedious and time-consuming. Supp (106) has reported the use of flame AAS as a practical alternative to the wet method; the sample containing between 1.4 and 11% of the analyte was sprayed after appropriate dilution in MIBK in the presence of 2-ethylhexanoic acid which acted as a solubilizing agent. Curvature of the analytical curve above 60 ppm was reported. The determination of antimony on the carbon furnace has been reported (107); metallurgical samples were dissolved and extracted into MIBK. These samples were free of extraneous material requiring ashing prior to atomisation. In order to determine antimony (b.pt. 1330°C) in oils using the techniques described in Chapters 3 - 5 it would be necessary to subject the sample to an ashing step at ca 1200°C . This would result in significant loss of analyte. The recent work of Thompson and Thomerson (56) indicated the feasibility of using hydride generation as a means of separating the analyte from its matrix. They used sodium borohydride to generate a number of covalent hydrides, including stibine, from acidic solutions of the corresponding chlorides followed by atomisation in a silica tube. The sensitivity found for antimony was 0.5 ng (1 ml sample).

6.2 Experimental

The atom reservoir used was the CFAR described in section 2.1 in the tube mode (Figure 2.1). The Perkin-Elmer HGA 74 furnace was modified by having the sample inlet aperture enlarged with a jewellers' file to a sufficient size to accomodate a piece of silica tubing ca 3 mm in diameter (1.5 mm i.d.). This tube, ca 3 mm in length, was attached to the hydride generation vessel with PTFE tubing.

The hydride generation vessel employed was substantially the same as that of Thompson and Thomerson (56), having a capacity of ca 20 ml. The left-hand side of Figure 2.7 shows the vessel and its associated bulb (2) for dispensing the requisite amount of sodium borohydride solution. The hydride produced was swept into the CFAR with a stream of nitrogen.

Work on aqueous solutions was carried out in a manner similar to that of Thompson and Thomerson (56). A 1 ml aliquot of antimony trichloride solution which was 1M with respect to hydrochloric acid was introduced into the cell and the bulb containing 2 ml 1% sodium borohydride put into position. The variac was switched on and the oscilloscope triggered; when a steady base line was obtained, the light path was interrupted to give the 100% absorption reading and then the bulb was inverted delivering the borohydride into the vessel. A transient peak was recorded.

Interferences due to iron, copper and lead as their nitrates and phosphate, nitrate and sulphate as their acids were studied.

Curves relating to the optimisation of analytical conditions are shown in Figures 6.1 - 6.3 and the operating parameters are shown in Table 6.1.

Table 6.1 Experimental Parameters - Antimony

Absorbing wavelength	231.0 nm
Non-absorbing wavelength	242.6 nm
Monochromator slit-width	0.10 mm
Nitrogen flow rate	5.0 l min ⁻¹
Damping	0.068 μ F
Atomisation temperature	950 °C

In order to determine antimony in oils it was necessary to modify the above procedure and initial attempts to use 1 ml aliquots of oil dissolved in the water-miscible solvent THF was impractical due to the volatility of this solvent; significant quantities of it were carried over by the purge gas into the CFAR and gave a signal equivalent to 90 % absorption. The use of smaller aliquots was unsuccessful since as little as 50 μ l would give rise to a signal of almost the same magnitude as larger ones.

It was clearly necessary to convert the analyte in the oil sample into a water - soluble/miscible form without complex oxidation/extraction techniques. Concentrated (ca 70 %) nitric acid commended itself as a suitable reagent on two grounds: its well known oxidizing effect on organic materials and the solubility of the nitrates formed. This reagent proved to be highly successful for this purpose and the experimental procedure is described below.

Two burettes were set up, one containing 1 % aqueous sodium borohydride made up fresh daily, the other containing concentrated nitric acid. The samples of oil were warmed as described in section 3.2 and diluted where necessary with SAE 10 metal - free oil. 5 μ l aliquots were introduced carefully to the cell using a Finn microlitre adjustable

Figure 6.1

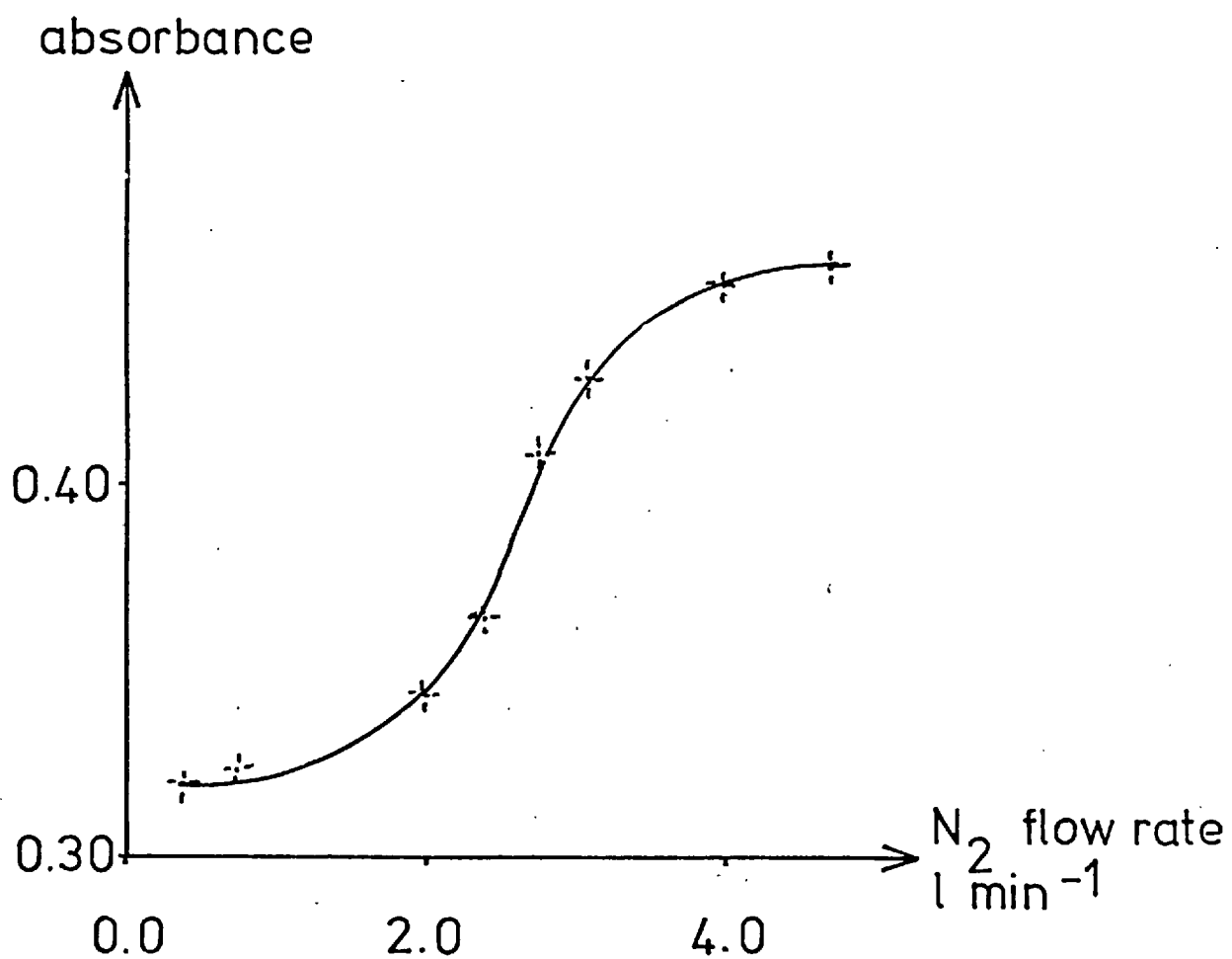
Optimisation of N_2 flow rate

Figure 6.2
Optimisation of slit-width

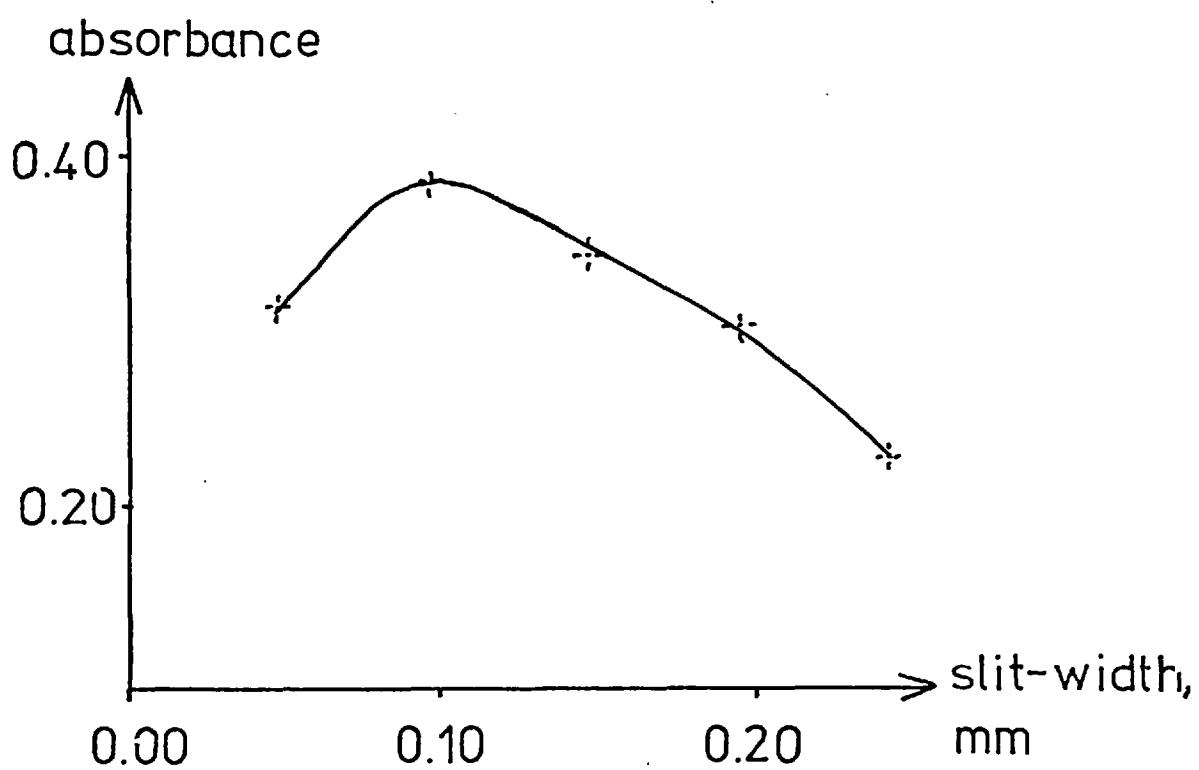
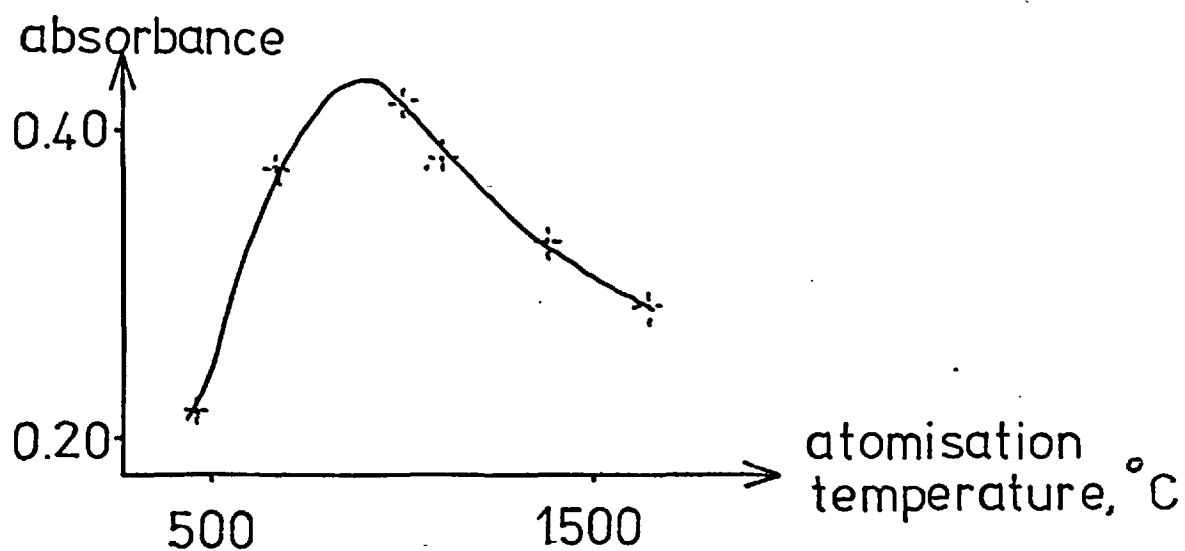


Figure 6.3
Optimisation of atomisation temperature



pipette and 0.2 ml concentrated nitric acid added to decompose the oil. The procedure described for aqueous solution was then followed. After the reaction had taken place the cell was washed with water, tetrahydrofuran and finally distilled water. The cycle could be repeated in ca 2 minutes. In order to analyse oils containing lower concentrations of analyte it is possible to employ aliquots of up to 50 μ l.

Interferences due to tin, copper, lead and iron as their naphthenates and sulphur, phosphorus and chlorine as their acids were investigated.

Non - atomic absorption was investigated; none was found.

6.3 Results and Discussion

Calibration curves were constructed for aqueous and oil matrices, Figures 6.4 and 6.5. Limits of detection, sensitivities (obtained by extrapolation) and linear ranges found are shown in Table 6.2.

Table 6.2 Sensitivity Data - Antimony

Matrix	Limit of Detection	Sensitivity	Linear Range
Water	$9.0 \times 10^{-9} \text{g}$	$2.0 \times 10^{-9} \text{g}$	$9 - 60 \times 10^{-9} \text{g}$
Oil	$30.0 \times 10^{-9} \text{g}$	$8.0 \times 10^{-9} \text{g}$	$30 - 800 \times 10^{-9} \text{g}$

The differences in the values obtained for aqueous and oil matrices may indicate that the reaction is more complete in aqueous media or that the hydride formed is partly decomposed by the nitric acid. Increasing the concentration of acid or borohydride had no effect on the signal obtained.

Interference studies revealed no significant interferences from any of the elements investigated except tin and copper, the former

Figure 6.4

Calibration curve - water

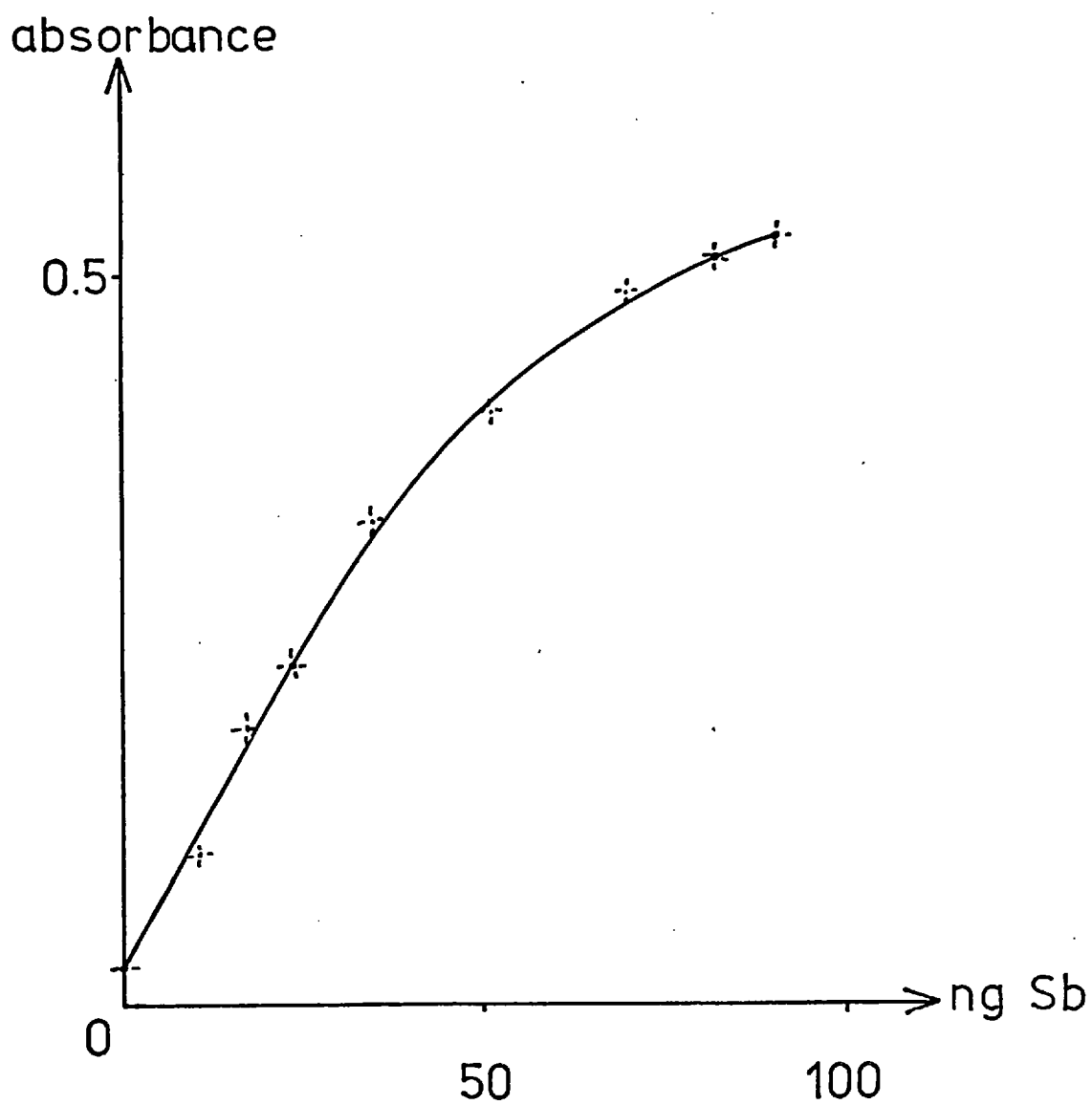
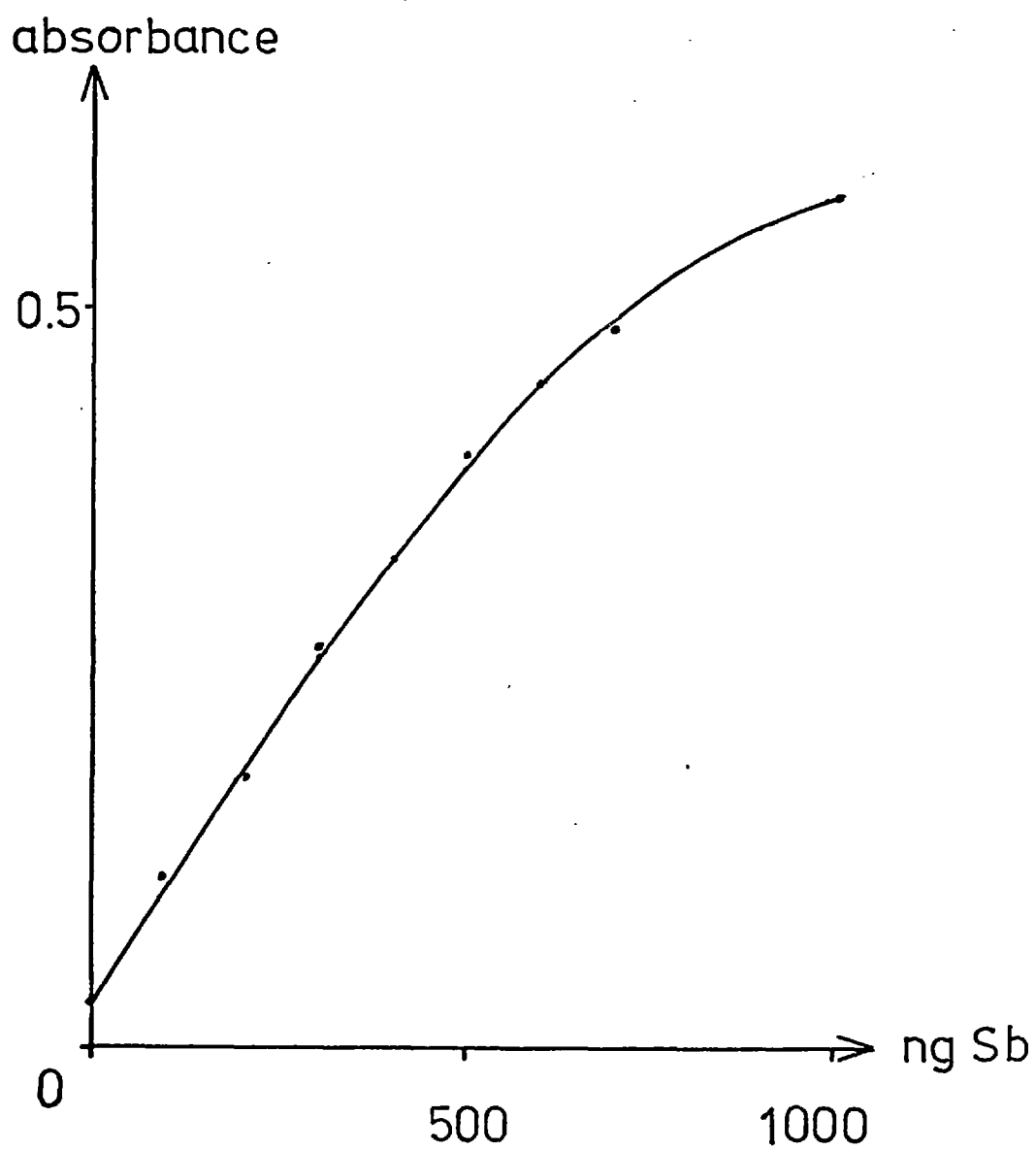


Figure 6.5
Calibration curve-oil



causing a depression of ca 2 % when present in a concentration of 1000 ppm. The latter however causes a 50 % suppression when as little as 50 ppm is present; when the reduction is performed in the presence of copper a black precipitate is formed. Stibine is a very strong reducing agent, reducing not only the usual oxidizing agents such as potassium permanganate and dichromate but also the salts of heavy metals depositing the metal (110); the black precipitate observed is probably finely divided copper. Increasing the concentration of either acid or reductant has no effect. Belcher et al. (108) have reported the successful elimination of these interferences by making the sample 0.01M with respect to EDTA.

Three real samples were analysed by this technique; one was an unused lubricating oil (analysed by spark source emission spectrometry at BP laboratories); the other two were used motor car lubricants spiked with known quantities of analyte. No significant interferences were found despite the rather 'dirty' matrix; this effect has also been noted in the analysis of geological samples (109). The accuracy and precision are within ca 10 - 20 %. The results are shown in Table 6.3.

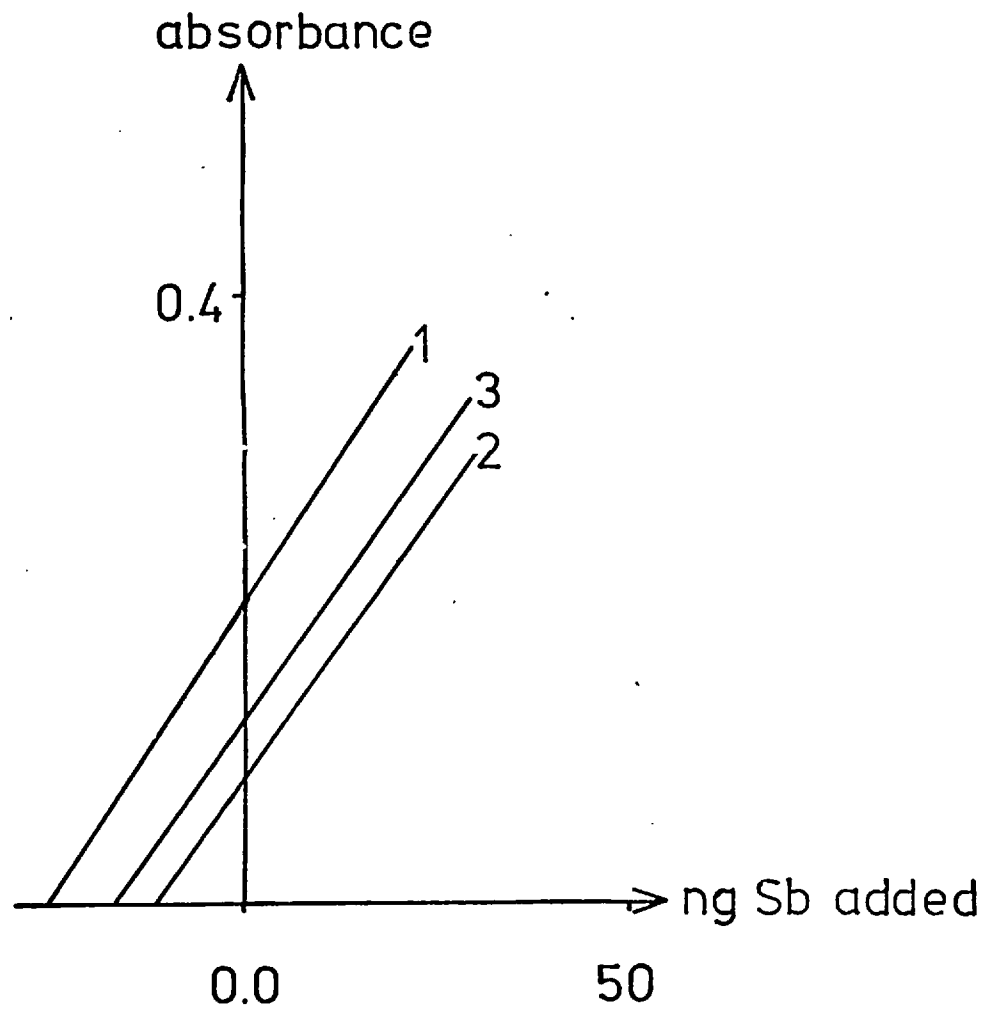
Table 6.3 Results - Antimony

Matrix	ppm Sb given	ppm Sb found	
		standard addition	interpolation
1 unused lubricant	700	715 $\pm$ 72	650 $\pm$ 80
2 used spiked lubricant	960	1230 $\pm$ 190	1160 $\pm$ 200
3 "	3380	3000 $\pm$ 310	3570 $\pm$ 400

The method shows itself to be successful for this type of analysis.

Figure 6.6

Standard addition curves



Chapter 7

The Determination of Tin

7.1 Introduction

Tin rarely occurs in crude oils in any quantities. Stannous oleate, naphthenate and ricinoleate are efficient anti-oxidant and anti-smoking agents in lubricating oils when present at levels of ca 0.25 %. Stannous phenyl stearate has been developed as an agent which lessens sludge and disperses carbon leading to the formation of softer rather than harder carbon deposits. It is added in the concentration range 0.5 - 2.5 %.

Tin may be present in used lubricants due to bearing wear; the concentration of tin from this source would be in the order of ppm.

The ASTM method for the determination of tin is by precipitation of tin dioxide after ashing and subsequent gravimetric determination by loss of tin as its iodide. A number of instrumental methods has been applied to the analysis of tin in oils. Marangoni et al. (22) used XRF and achieved good reproducibility at the 5 ppm level in work on used aircraft lubricants. Kyuregyan and Marenova (5) examined wear products in oil filters of internal combustion engines by emission spectrography. They determined 1 - 1000 ppm tin with a precision of 7% at the 300 ppm level.

Several workers have determined tin in oils by flame AAS with some success (30,35,37); Shallis and Kahn (111) obtained a sensitivity of 3 ppm at 286.3 nm in a nitrous oxide-acetylene flame. The major problem in the analysis of tin is due to the formation of the refractory oxide, SnO. The use of a fuel rich hydrogen flame gives considerable increases in sensitivity for example to a level of 0.3 ppm (112). This enhancement is probably due to the formation of SnH which is easily

decomposed thermally to atomic tin.

Reeves et al. (41) used a graphite rod atomiser to determine tin in used engine oils, while Chuang and Winefordner analysed jet-engine oils using aqueous standards and a graphite filament atomiser (40).

Everett et al. (148) obtained a sensitivity of 0.1 ng with a carbon filament surrounded by a hydrogen diffusion flame. They noted some loss of tin, notably as SnCl , during the ashing step.

The use of the hydride generation technique brings the analyte in a comparatively 'clean' form to the atom reservoir.

7.2 Experimental

The experimental procedure was substantially the same as that employed for antimony (section 6.2). The operating parameters are shown in Table 7.1; curves relating to the optimisation of these parameters are shown in Figures 7.1 - 7.3.

Table 7.1 Experimental Parameters - Tin

Absorbing wavelength	286.3 nm
Non-absorbing wavelength	264.0 nm
Monochromator slit-width	0.10 mm
Nitrogen flow rate	5.0 l min ⁻¹
Damping	0.068 μF
Atomising temperature	1450 °C

Aqueous tin chloride was made 1M with respect to hydrochloric acid. Organic standards were made from tin oleate (27.7 %, Nuodex) dissolved in metal-free SAE 10 base oil.

A large blank (equivalent to 100 ng tin/1 ml 1 % sodium borohydride) was obtained from the reagent supplied by BDH. The Alfa Inorganics

Figure 7.1

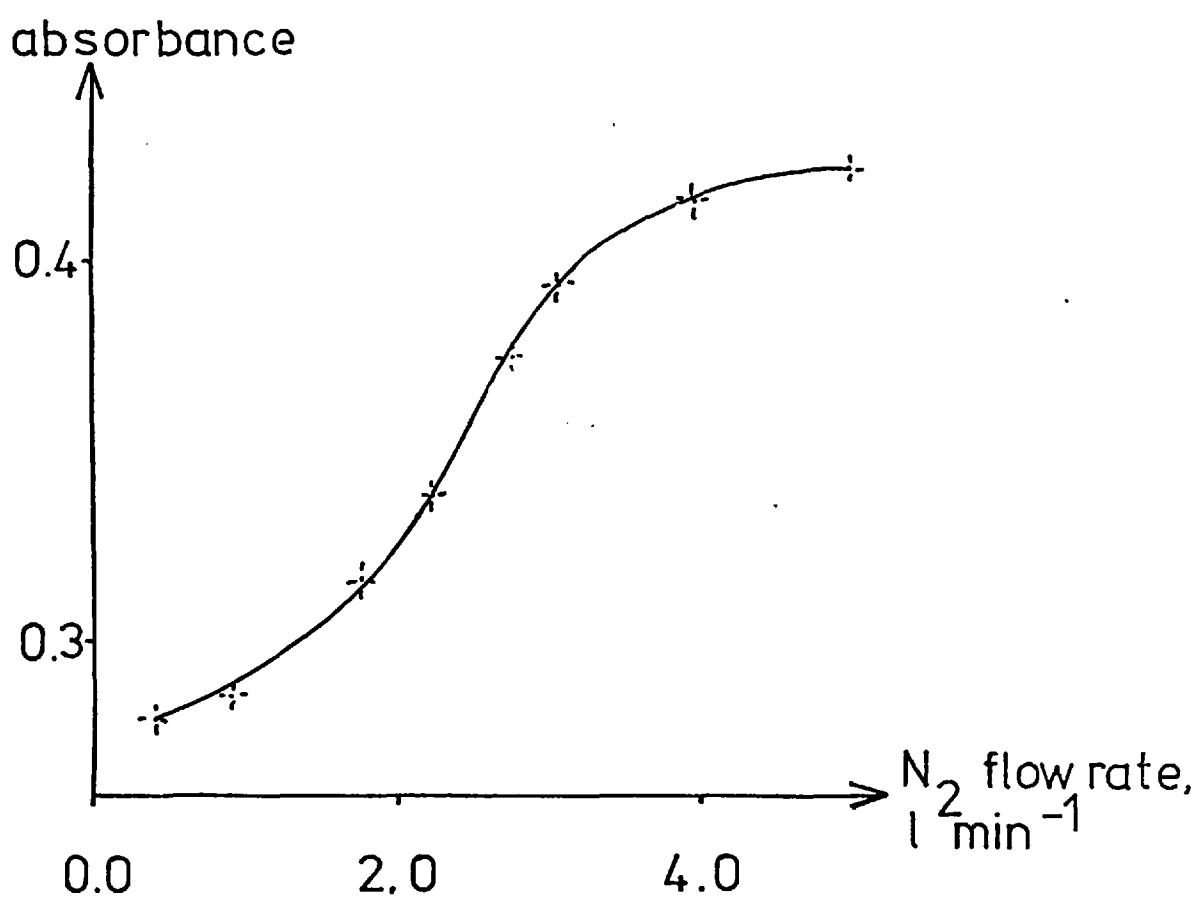
Optimisation of N_2 flow rate

Figure 7.2

Optimisation of slit-width

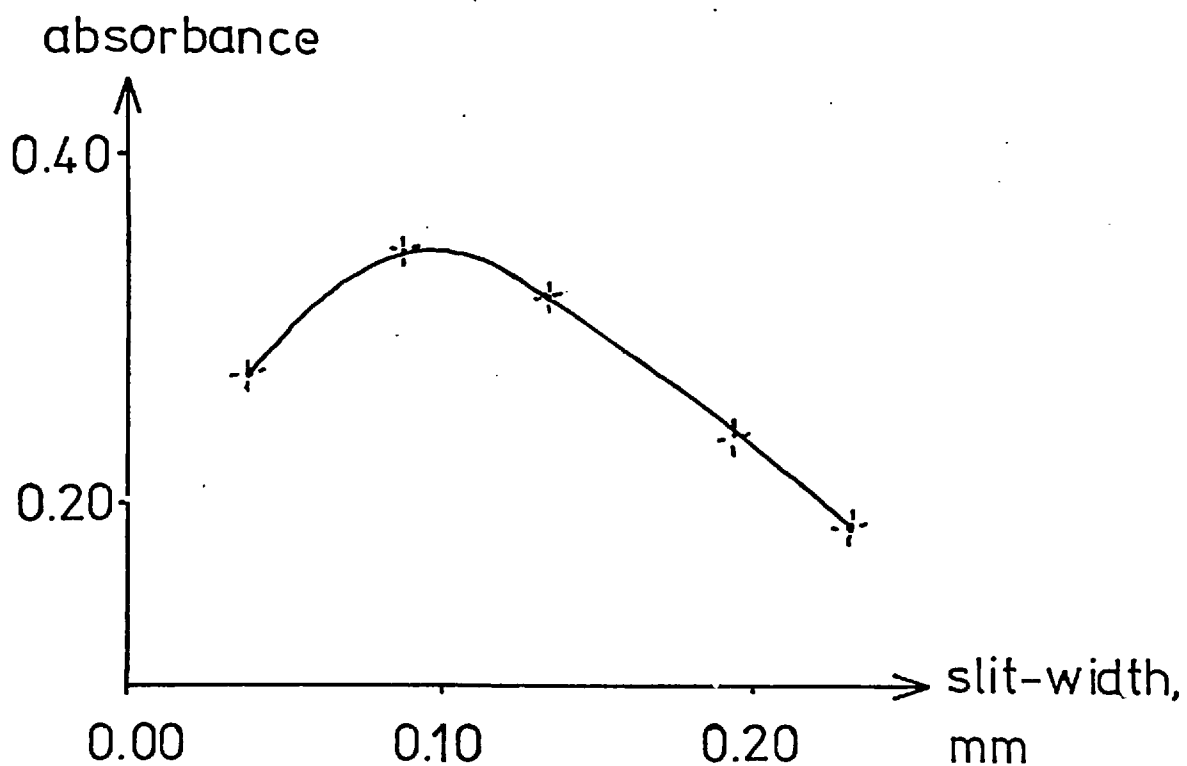
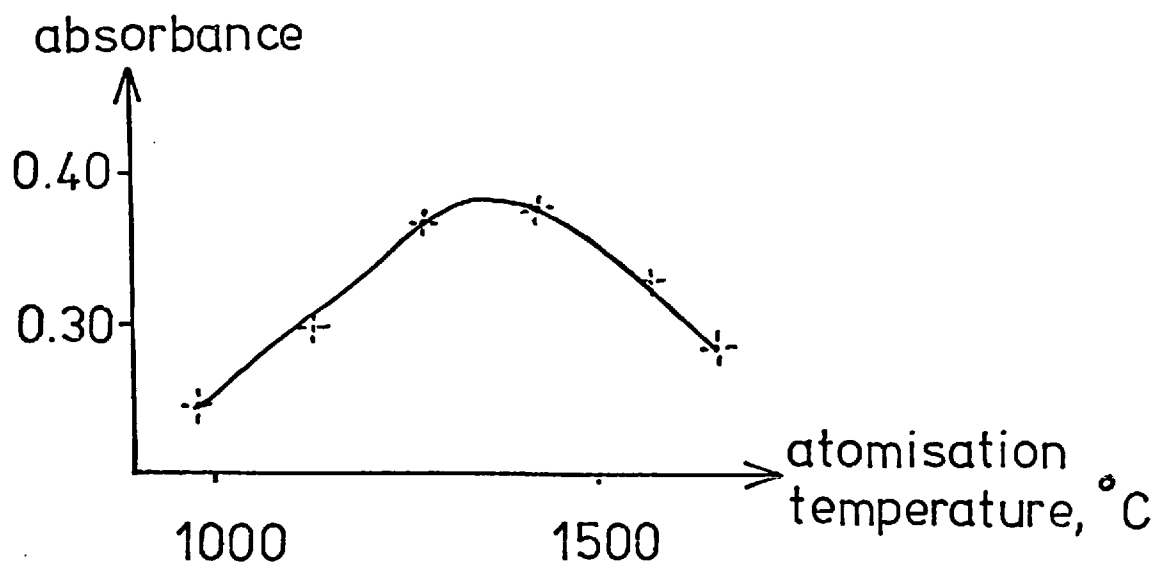


Figure 7.3

Optimisation of atomisation temperature



product was purer and by reducing the volume of borohydride used an acceptable blank level (25 ng tin) was obtained.

Interferences due to up to 2000 ppm of copper, iron, lead, vanadium, chlorine, phosphorus and sulphur on tin in oil were studied.

7.3 Results and Discussion

The calibration curves constructed for oil and aqueous media are shown in Figures 7.4 and 7.5. As in the case of antimony, the sensitivity in the oil medium was considerably lower than in the aqueous solution. Sensitivity data are shown in Table 7.2.

Table 7.2 Sensitivity Data - Tin

Matrix	Limit of Detection	Sensitivity	Linear Range
Water	$9.0 \times 10^{-9} \text{ g}$	$2.0 \times 10^{-9} \text{ g}$	$9 - 200 \times 10^{-9} \text{ g}$
Oil	$93.0 \times 10^{-9} \text{ g}$	$40.0 \times 10^{-9} \text{ g}$	$93 - 2600 \times 10^{-9} \text{ g}$

Copper was the only element investigated which gave rise to severe interference effects. 15 ppm copper caused a 30% suppression in the signal on reduction of a 60 ppm tin solution. This rose to a maximum of 50% when the copper concentration reached 40 ppm.

Three new lubricants (supplied by B.P. and analysed by spark emission) and two spiked used crankcase lubricants were analysed. The new lubricants contained a variety of metals as did the used lubricants; the interferences caused by these substances are evident from the results displayed in Table 7.3.

It is clear that the hydride generation procedure does not always give reliable results when applied to a lubricant containing other metals; accordingly its use cannot be recommended for the analysis

Figure 7.4

Calibration curve - water

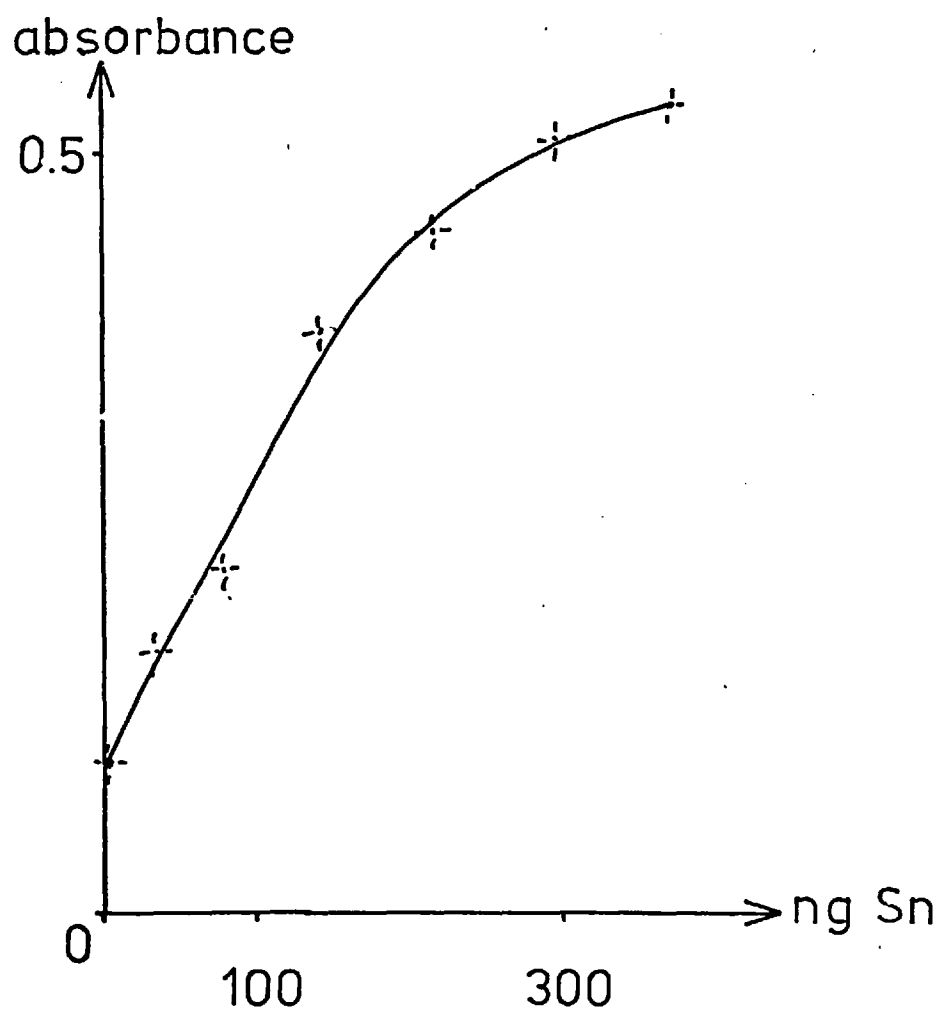


Figure 7.5

Calibration curve - oil

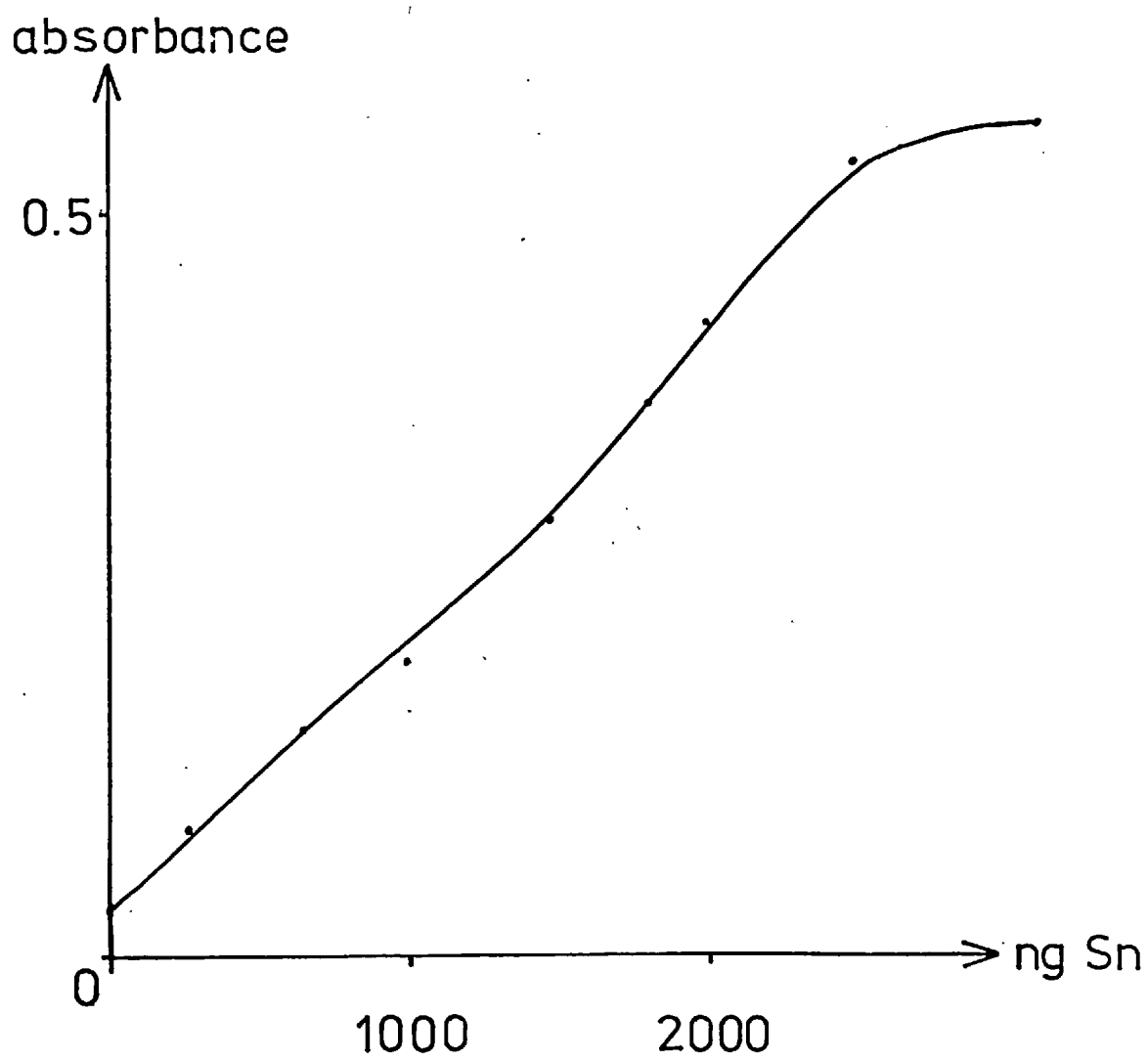


Table 7.3 Results - Tin

Matrix	ppm Sn given	ppm Sn found	
		standard addition	interpolation
used spiked lubricant	927	-	515 ± 70
"	35	37 ± 7	56 ± 8
unused lubricant	8	-	10 ± 1
"	7	-	26 ± 3
"	7	-	11 ± 2

of this type of lubricant.

Chapter 8

The Determination of Lead

8.1 Introduction

Lead naphthenates and oleates are added in per cent quantities to lubricating oils and greases endowing them with the capacity to be used under conditions of extreme pressure, for example in hypoid gears and retracting landing equipment. They are often used in conjunction with sulphur compounds that break down under pressure releasing the element which forms a layer of lead sulphide on the gear teeth. The nature of the films formed when lead soaps are used alone is not fully understood (113). Lead soaps are also known to exhibit rust preventing (113) and water-proofing properties.

Elemental lead may be found in used engine lubricants, having its origin in the white metal bearing alloys.

There is a number of methods approved by the ASTM for the analysis of lead in lubricants and fuels. Precipitation as the chromate following wet oxidation is recommended for levels down to 50 ppm in gasolines. Spectrophotometric determination of the dithizone complex is effective down to 0.2 ppm in fuels. New and used greases are ashed with nitric/sulphuric acid/hydrogen peroxide and the precipitate thus obtained boiled with ammonia solution. Following acidification with nitric acid lead is determined electrolytically as its peroxide. An atomic absorption method using an air - acetylene flame is also described for the determination of lead in gas turbine fuels; samples are diluted such that the solution finally sprayed is in the concentration range 0 - 30 ppm. Two other instrumental methods are officially approved of, they are XRF for down to 20 ppm in gasoline and the polarographic determination of lead tetraalkyls following their extraction into hydrochloric acid.

In recent years a large body of work on the analysis of lead in petroleum products has been published, much of it concentrating on the tetraalkyls in gasoline. Holding and Hooks (25) describe a complexometric procedure for lead in gasoline while Campbell and Moss (114) report the use of colorimetry to determine trace quantities in crudes and products. 100 - 1250 ppm lead as its tetraethyl has been analysed by potentiometric titration with EDTA (115). Inverse polarography has been employed for the range 1 - 100 ppb (116) but the sample must be chemically digested first.

Although the lower limit recommended by the ASTM for the use of XRF is 20 ppm, Larson et al. (117) report its successful use down to 0.5 ppm. Other workers (22, 118) describe its application to lubricants.

Kyuregan and Marenova (5) in their emission spectrographic work on wear metals in oil filters determined lead in the range 0.003 - 1.05 %, however the relative standard deviation at 0.1% Pb was 17%.

Flame atomic absorption is a well established method for the determination of lead in oils (119). Slavin and Slavin (35) found wide disagreement with emission spectrography which they attributed to more complete vaporisation of the analyte in the flame. Tago et al. (11) burned gasolines containing 0 - 20 ppm lead to an ash which they then treated with hydrochloric acid prior to dilution. McCorriston and Richie (120) used a total consumption burner for the analysis of 5 ppm lead in gasolines with an accuracy of 2%. A novel application of gas chromatography combined with AAS has been the determination of individual and total lead alkyls in gasolines (121); the detection limit was 0.2 ppm lead for each alkyl and each sample was analysed in five minutes.

A large number of workers have applied the CFAR to the problem of the determination of lead in oils (13, 14, 40, 41, 122, 123).

Some of the first work was that of Molnar et al. (14) who used an

electrically heated filament surrounded by an argon - hydrogen flame. The limit of detection they found was 75 pg. Bratzel and Chakrabarti (122) improved on this by using a dry ashing process first, thus avoiding losses of analyte during the ashing step. Their limit of detection was 10 pg. Hall et al. (13) obtained similar results with a mini-Massmann furnace for the analysis of crudes and used lubricants. More recently, Chuang and Winefordner (40) have reported the successful use of aqueous standards in the analysis of jet engine oils.

As in the cases of antimony and tin some losses of analyte occur during the ashing step. The hydride generation technique leaves the unwanted organic component in the reduction cell, obviating the need for an ashing step.

8.2 Experimental

A similar experimental procedure to that employed for antimony was used for lead. Experimental parameters are shown in Table 8.1; curves relating to the optimisation of these parameters are shown in Figures 8.1 - 8.3.

Table 8.1 Experimental Parameters - Lead

Absorbing wavelength	283.0 nm
Non-absorbing wavelength	287.0 nm
Monochromator slit-width	0.20 mm
Nitrogen flow rate	5.0 l min ⁻¹
Damping	0.068 μ F
Atomising temperature	1480 °C

Aqueous lead nitrate standards were made 1M with respect to nitric

Figure 8.1

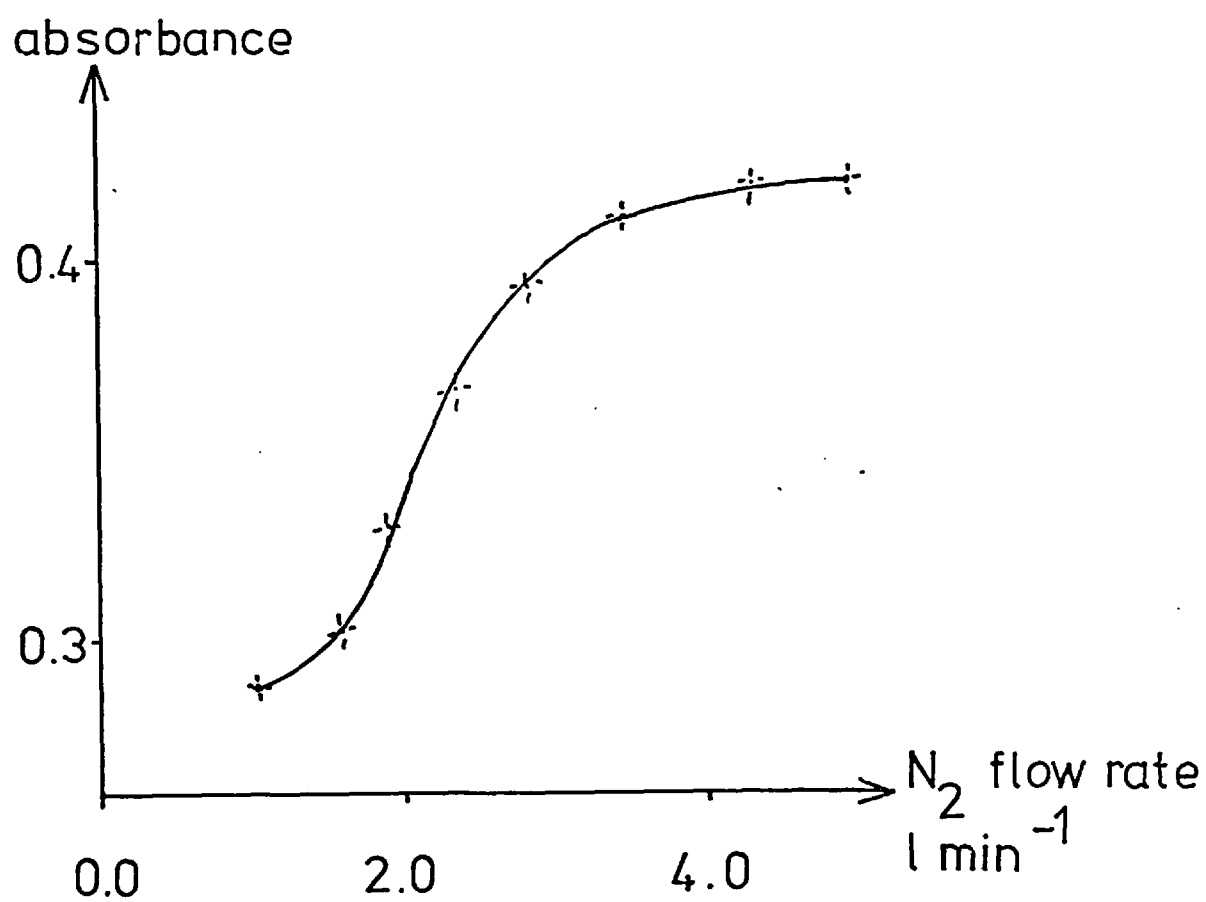
Optimisation of N_2 flow rate

Figure 8.2
Optimisation of slit-width

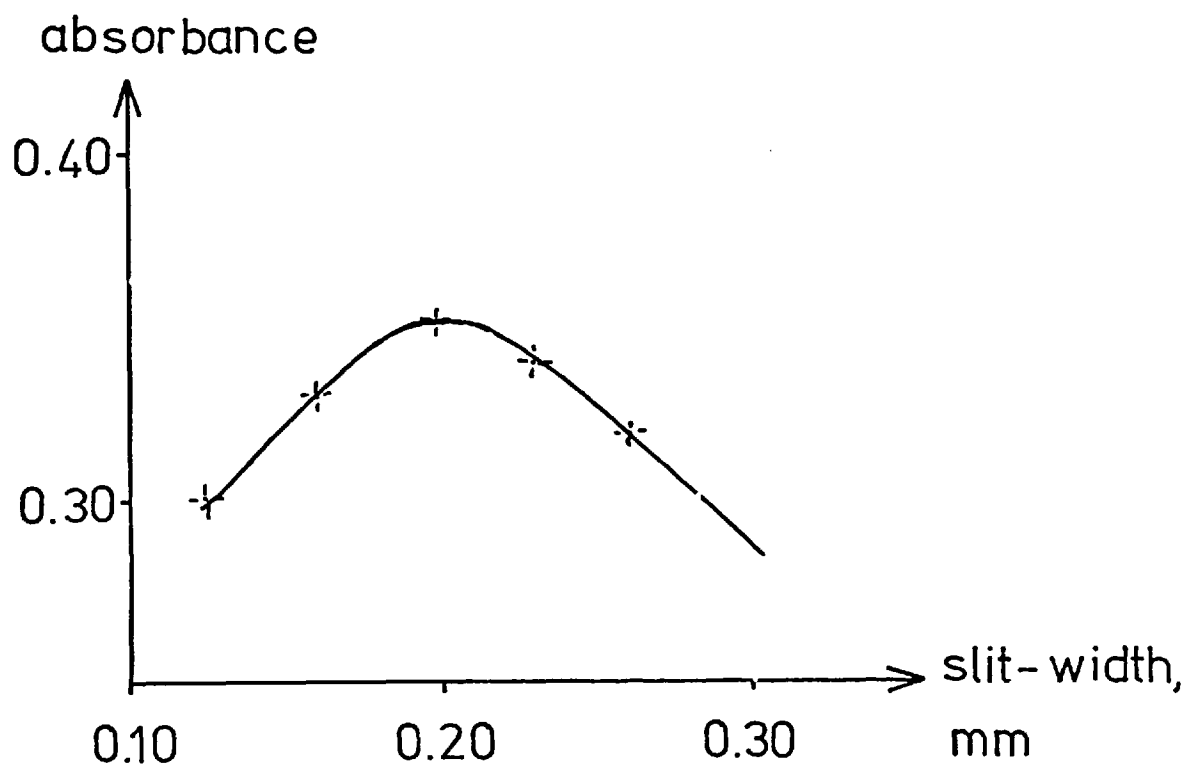
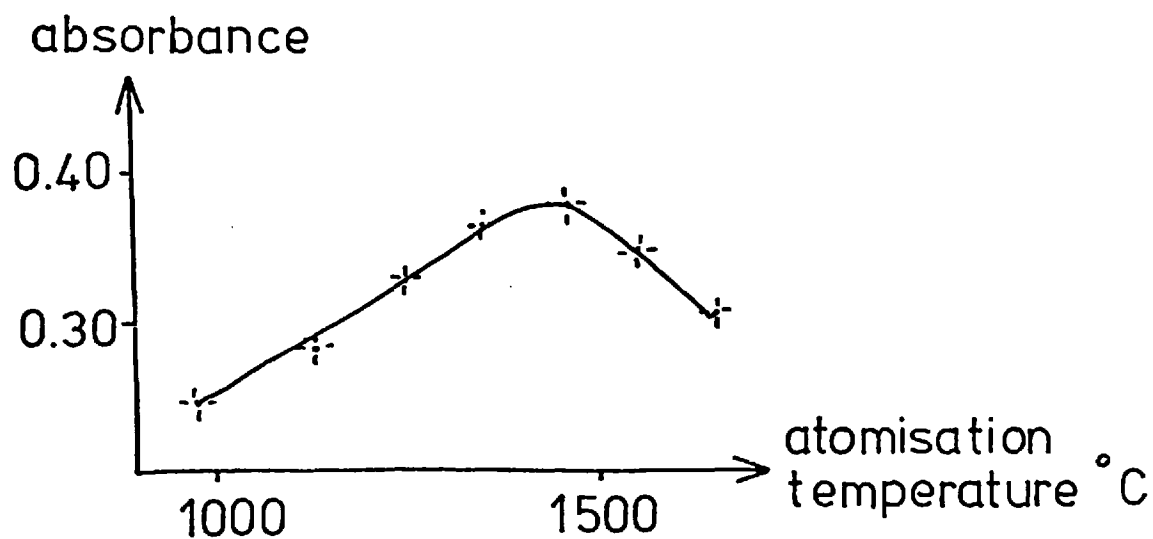


Figure 8.3
Optimisation of atomisation temperature



acid. Organic standards were 2.4 % lead naphthenate diluted in metal-free SAE 10 oil. An attempt was made to determine lead in gasoline, but this was unsuccessful due to the high background signal obtained from the more volatile components of the fraction (cf. section 6.2).

8.3 Results and Discussion

Sensitivities, limits of detection and linear ranges obtained for oil and water matrices are shown in Table 8.2; calibration curves are shown in Figures 8.4 and 8.5.

Table 8.2 Sensitivity Data - Lead

Matrix	Limit of Detection	Sensitivity	Linear Range
Water	$11.0 \times 10^{-6} \text{ g}$	$2.5 \times 10^{-6} \text{ g}$	$11 - 500 \times 10^{-6} \text{ g}$
Oil	$4.0 \times 10^{-6} \text{ g}$	$1.5 \times 10^{-6} \text{ g}$	$4 - 140 \times 10^{-6} \text{ g}$

The sensitivity of this element is three orders of magnitude less than either tin or antimony, which might be explained by the instability of plumbane; it is highly likely that much of the plumbane formed decomposes in the cell and does not reach the CFAR. The reaction is also somewhat slower than that for antimony and tin as indicated by the rounding of the absorption peaks. Thompson and Thomerson (56) noted that the generation of plumbane was very sensitive to pH, etc. This type of matrix effect possibly also explains the reversal of the trend in limits of detection etc. noted here compared to antimony and tin.

Results obtained for the analysis of real samples were disappointing. One satisfactory result was obtained by standard addition, $0.76 \pm 0.7 \%$ (but that obtained by interpolation was $0.91 \pm 0.3 \%$) on the analysis of leaded gear oil known to contain 0.72 % lead and 0.49 % sulphur.

Figure 8.4

Calibration curve - water

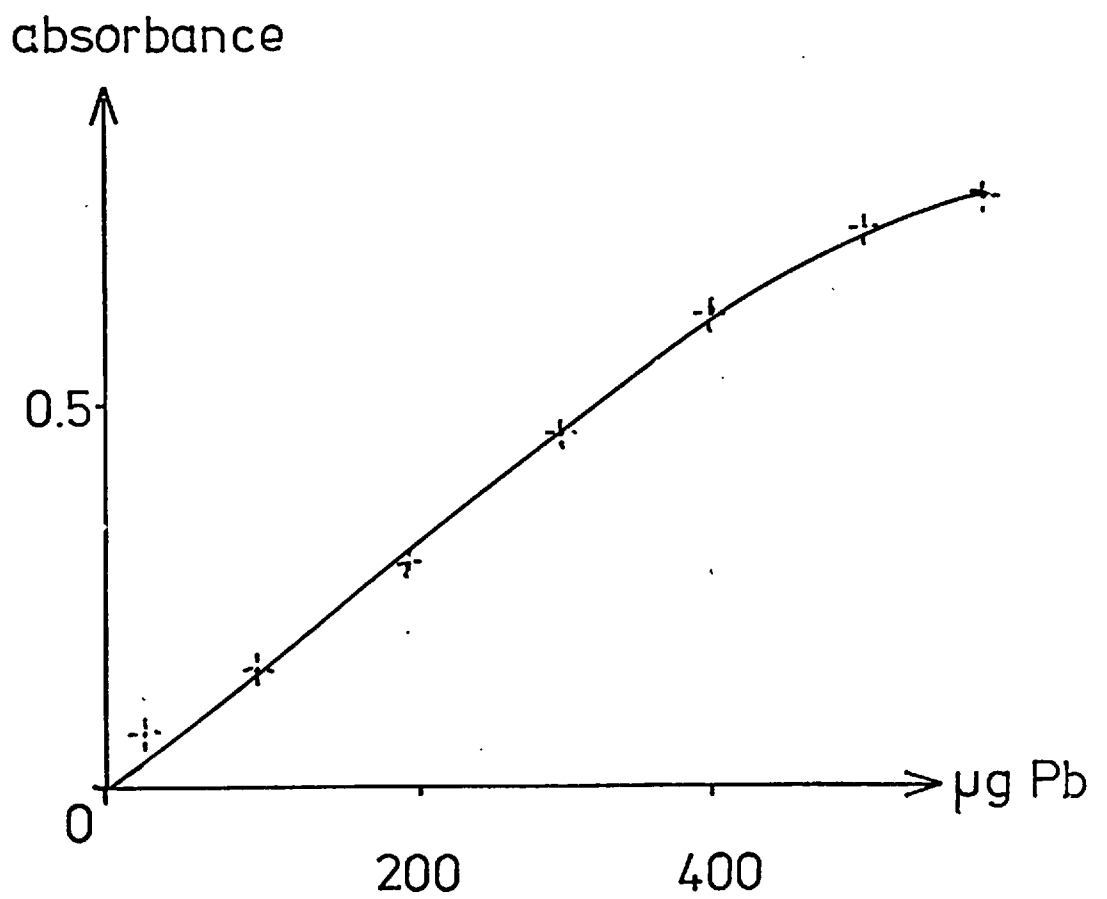
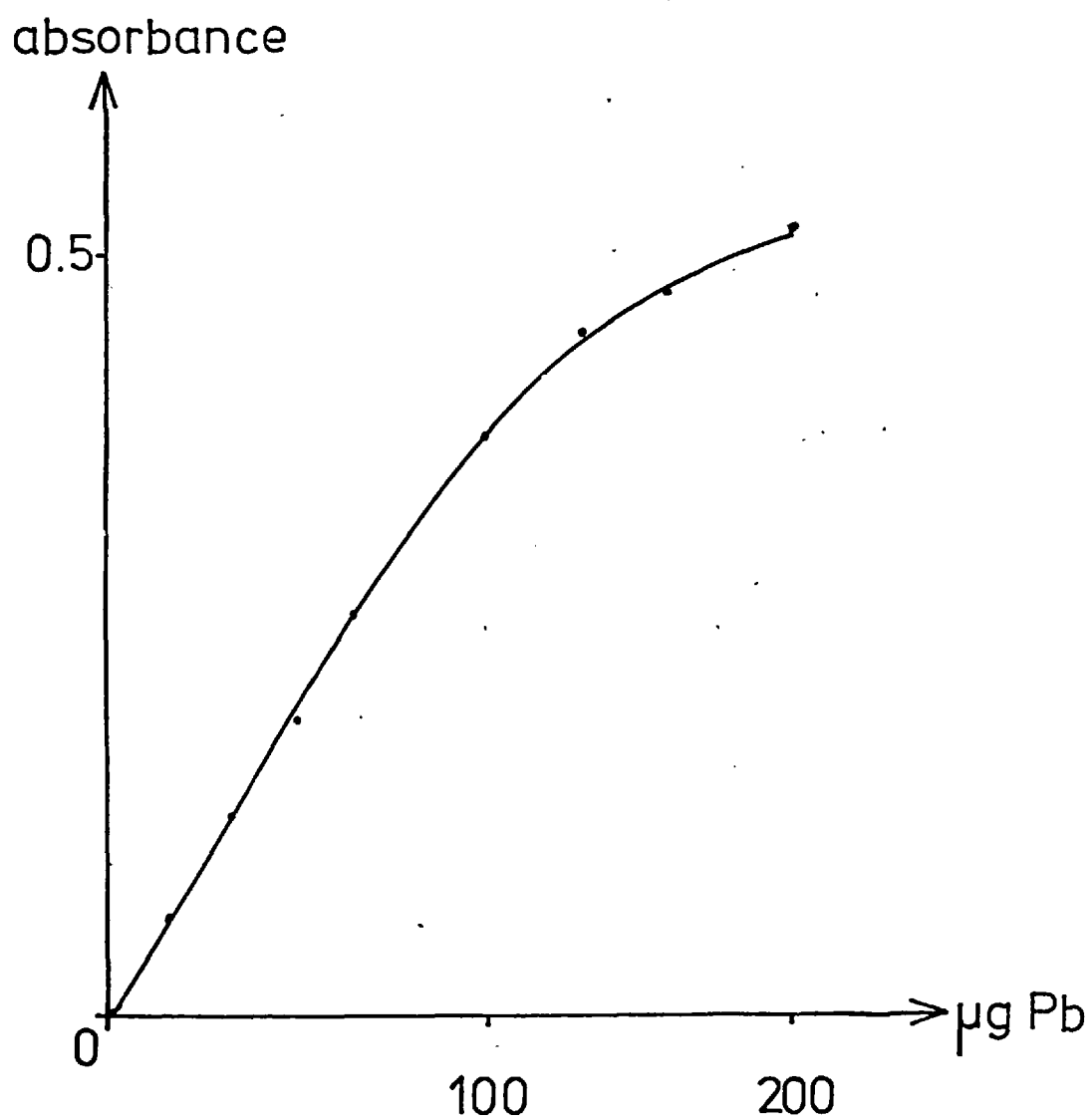


Figure 8.5

Calibration curve - oil



Analyses of oils containing quantities of other elements were found to give absorbances enhanced by up to one order of magnitude; accordingly the method proposed here is not recommended for these matrices.

Conclusions

The work described in this section shows that it is very simple to modify the CFAR for use in conjunction with the hydride generation technique.

Sensitivities found using the modified CFAR were typically 5 to 10 times less than those obtained by Thompson and Thomerson (56) ; however the path lengths involved were 2.5 cm and 17.0 cm respectively. The lowered sensitivities for antimony and tin in the oil matrix may be attributed to incomplete mixing of the reductant and analyte trapped in oily globules remaining in the acid. Accordingly, this lowered sensitivity leads to an apparent increase in linear range. In the case of lead, the conversion to the hydride is very inefficient, ca 5 % (56); in addition plumbane is very easily decomposed so, clearly, marked matrix effects are to be expected.

Antimony was the only element sufficiently unaffected by the matrix to be determinable in a used oil matrix. All three elements, however, could be determined in fairly clean lubricating oils and directly in the additive concentrates. For the latter this method is ideally suited since the linear ranges extend through two or three orders of magnitude into thousands of ppm permitting analysis without prior dilution. thus reducing the time for each determination.

Future work on hydride generation techniques might include the determination of bismuth and selenium in oils and also the examination of other organic matrices. The use of solvent extraction both as a means of separating the analyte from interfering ions and as a preconcentration step would probably prove to be effective. It would be interesting to develop hydride generation techniques for the detection of boron, silicon, sulphur and phosphorus. A method for sulphur is presented in Chapter 9.

Chapter 9

The Determination of Sulphur

9.1 Introduction

The importance of sulphur in crude and refined products is described in sections 1.2.1, 1.3.1, 1.4.6.1 and 1.4.6.3.

There is a large number of methods for the determination of sulphur recommended by the ASTM. Total sulphur determinations cover the concentration range 2 ppm to 5 %. Several of these commence with the combustion of the sample; the sulphur dioxide produced is absorbed usually in hydrogen peroxide and the sulphate produced determined gravimetrically or, if the sulphur content of the sample is less than 20 ppm, turbidimetrically; titrimetric finishes using sodium hydroxide or barium perchlorate are also described. Sulphur dioxide may also be absorbed in acidic potassium iodide, standard potassium iodate is then added in the presence of starch indicator. The disadvantages of these oxidation methods are that they are time-consuming, 2 - 4 hours for each determination (138), and require a skilled technician to perform the analyses. XRF is also recommended for total sulphur in liquid samples containing more than 10 ppm sulphur.

Mercaptans give rise to unpleasant odours and cause corrosion, this is especially so in the case of aviation turbine fuels. Two methods are described for this determination. The sample is shaken with acidic cadmium sulphate solution to remove hydrogen sulphide; the resulting solution is then either titrated with silver nitrate with a potentiometric or amperometric finish or excess silver nitrate is added and back titrated with ammonium thiocyanate with ferric alum indicator.

Hydrogen sulphide is determined either iodometrically or colorimetrically by the conversion of lead acetate to lead sulphide; the

colour produced varies from yellow to black according to the amount of hydrogen sulphide present.

The importance of the sulphur problem in the petroleum industry is reflected by the number of publications on its analysis, some of which are reviewed below.

The methods of analysis fall into three main groups:

- (a) Combustion methods. In these methods (124 - 128) the sulphur is converted to sulphur dioxide - Hoshino (127) used a high - frequency furnace - and followed by a gravimetric (124), coulometric (125 - 127) or gas-sensing electrode (128) finish. This last was used to determine 0.1 - 0.4 % sulphur while the coulometric finishes have been used for levels of sulphur ranging from 0.01 % (125) to 2.5 % (127). Carter (125) reported the determination of 0.01 % in two minutes although variations in recoveries for different sulphur compounds were noted.
- (b) Instrumental methods. A number of instrumental methods is described in recent literature. Several workers have reported the use of XRF or emission (26, 129, 130) spectroscopy; the limits of detection were typically 20 ppm with precisions in the range 3 - 6 %. Neutron activation (132, 133) and neutron capture γ -ray spectroscopy (131) have been used down to 0.5% sulphur in oils. Kirkbright et al. (134) have demonstrated the feasibility of determining sulphur in oils by AAS; they analysed oils containing 0.49 - 2.73 % sulphur in an inert gas shielded nitrous oxide - acetylene flame. The oils were diluted in MIBK and sprayed into the flame. The results they obtained had errors relative to the standard of - 13.9 % to 2.0 %.
- (c) Reduction methods. This group includes those methods in which the analyte is converted into hydrogen sulphide and those in which the analyte is burned in a hydrogen flame. Kimbell (135) described the

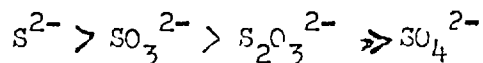
conversion of the hydrocarbon oil to its hydrides, any sulphur present being converted to hydrogen sulphide which was then analysed as such. Fensom et al. (137) described the determination of low levels of sulphur in light petroleum by the reduction of the analyte to hydrogen sulphide with Raney nickel. The hydrogen sulphide so produced was collected and determined titrimetrically. Honarkhah (138) has described the use of Raney nickel to reduce sulphur contained in hydrocarbon oils (containing less than 2 % olefinic compounds) to hydrogen sulphide, which was then absorbed into borax solution and determined titrimetrically with iodine/thiosulphate. By varying the mass of sample used between 500 g and 10 g he was able to determine total sulphur between 0.01 and 100 ppm with an accuracy greater than 3 %; each determination took ca 1.5 hours.

Molecular emission methods for the determination of sulphur fall into two categories: those based on the CS band emission which predominates at temperatures $>1000^{\circ}\text{C}$ and those based on the S_2 emission which predominates at temperatures below this. The conditions for producing this intense blue emission were first described by Salet (136) in 1869. The mechanism of excitation is not fully understood (8) but the presence of a cool surface or a diluent gas is essential for this emission to be observed. The hydrogen - nitrogen/argon diffusion flame provides a suitable thermal environment with low background radiation for the production of the S_2 emission at 384 nm.

Veillon and Park (139) applied the Salet effect to the determination of sulphur in a variety of inorganic compounds and also in petroleum fractions, nebulising solutions directly into a hydrogen diffusion flame. They found that the S_2 emission signal obtained in organic solvents was considerably lower than that obtained in aqueous solvents.

This they attributed to the increase in flame temperature caused by the combustion of the organic compounds or by the presence of organic radicals quenching the emission; they did however obtain satisfactory results on three oils, the lowest containing 45 ppm. Everett (146) used a CFAR as a microsampling device; the oil was vaporised from the filament into a hydrogen diffusion flame and although results were obtained for six fuel oils containing per cent quantities of sulphur quenching effects were noted.

Many workers (8, 138, 140) have noted the differences in S_2 emission obtained with different compounds, Shiffman and Frank (140) observing that the S_2 emissivity of thioacetamide was twice that of thiourea. Dagnall et al. (141) reported the order of emissive response for sulphur - containing groups to be:

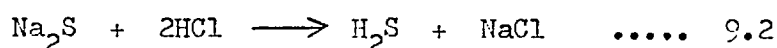
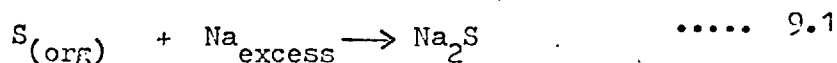


In order to analyse sulphur - containing mixtures reliably it is desirable to convert all the sulphur present to a common form. Hydrogen sulphide is the obvious choice for such an intermediate since it has a high S_2 emissivity and is a gas at room temperature enabling it to be separated easily from the matrix.

Fernandez (142) attempted, unsuccessfully, to generate the hydride of sulphur using sodium borohydride as the reductant in a similar fashion to that described in Chapters 6 - 8. The work of Honarkhah using Raney nickel is described above, however the presence of more than 2% olefinic compounds introduces appreciable errors (143). Shiffman and Frank (140) decomposed sulphur - containing organic compounds in the presence of finely divided magnesium producing magnesium sulphide. The decomposition process took ca one hour. The decomposition products were then acidified, releasing hydrogen sulphide which was collected and subsequently

burned in a hydrogen - nitrogen diffusion flame. The samples analysed contained ca 3 mg sulphur; the mean deviation of replicate samples was in the range $\pm 10\%$ although variations up to 25% were noted.

In the work presented below conversion of sulphur in oils to hydrogen sulphide is effected via a sodium fusion procedure followed by acidification, the relevant reactions being

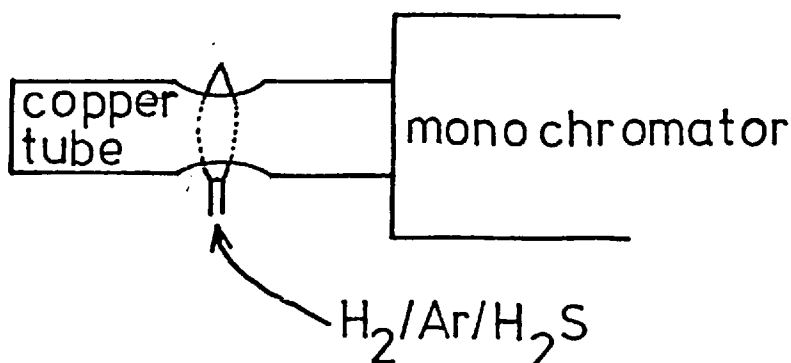


9.2 Experimental

Initial experiments were performed to investigate the feasibility of using the CFAR as a source of sulphur molecular emission. A mixture containing 1% hydrogen sulphide in air was passed into a CFAR at ca 800° ; a blue emission was seen in the tube and a signal obtained on the oscilloscope. On replacing the hydrogen sulphide/air mixture with pure sulphur dioxide a signal was again obtained, but on passing pure H_2S into the CFAR no signal was obtained nor was the blue emission seen. It was concluded that the signal was due to CO emission. The further work carried out on this is described in the Appendix.

The CFAR was replaced with a piece of silica tubing which acted as a burner port for a hydrogen - nitrogen diffusion flame. A silica

Figure 9.1



disc ca 2 mm thick and 2 cm in diameter was taped over the monochromator entrance to prevent the entry of corrosive gases. Some extraneous light was cut out by the use of a copper tube (after Everett (146)) as shown in Figure 9.1.

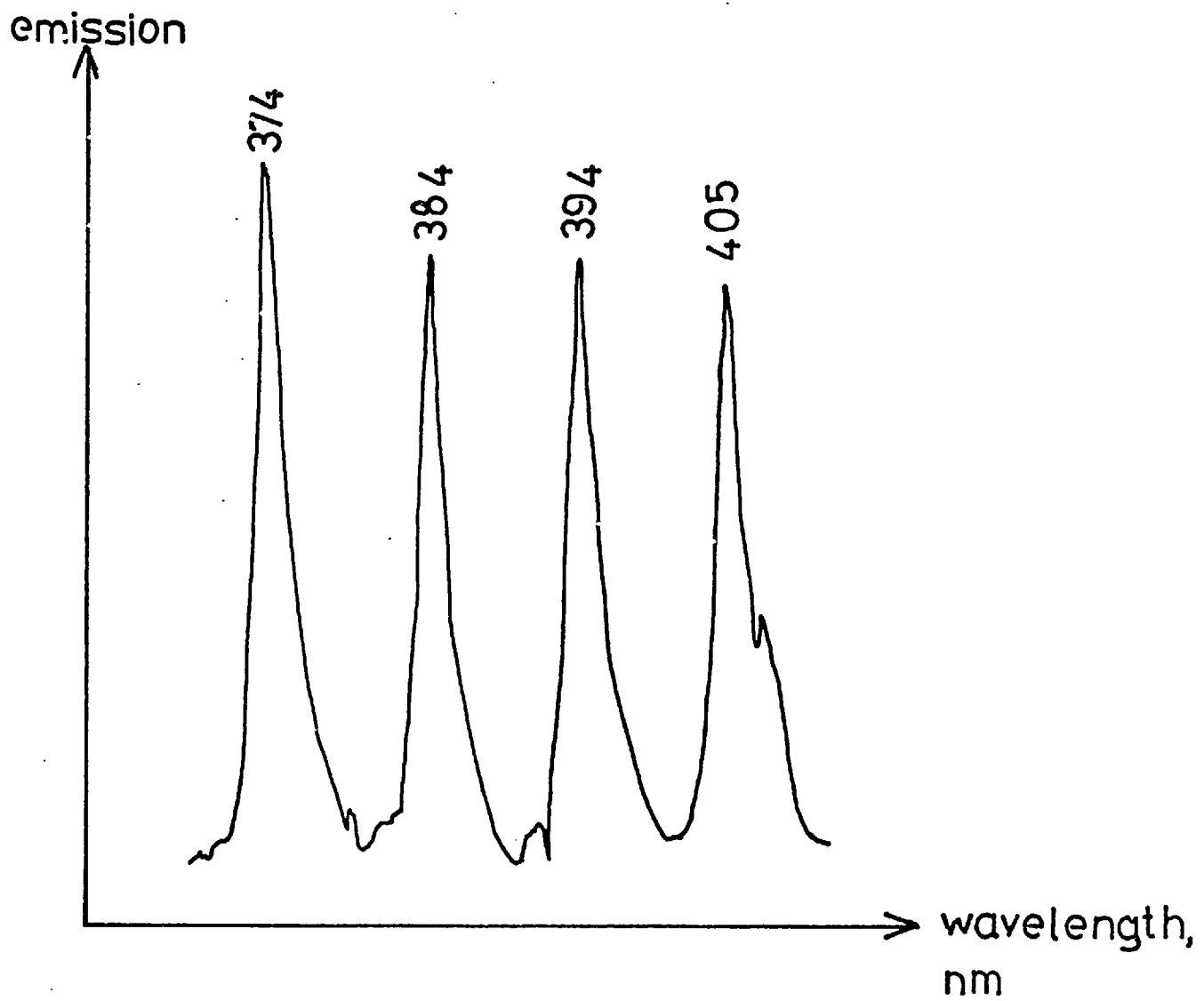
Although a signal was obtained the sensitivity was not satisfactory due to the high intensity of background light reaching the detector. In order to overcome these difficulties the copper burner assembly shown in Figure 9.2 was constructed. Once the flame was ignited the ferrule was turned round to exclude stray light. The mirror placed on the end of the horizontal tube increased the emission signal by 50% and covering its edges with black tape decreased the now lowered background by ca 30%. The original form of burner assembly employed a copper tube as the burner port, however after some use an increase in background and random flickering was noted. This was due to CuH emission; hydrogen chloride carried over from the hydride generation vessel reacted with the copper burner port to form copper chloride which formed the emitting species in the flame. This difficulty was overcome by glueing a silica tube (3 cm x 2 mm i.d.) inside the copper tube.

Hydrogen sulphide was generated, initially, in the hydride generation vessel as shown in the left hand side of Figure 2.7 but with the bulb replaced with a size B10 Subaseal (Gallenkamp, London). The vessel was swept with the mixture of hydrogen and inert gas which was ignited at the burner port.

Operating conditions were optimised using a continuous steady stream of hydrogen sulphide generated by a small crystal of sodium sulphide decomposing in dilute hydrochloric acid. The spectrum of sulphur in a hydrogen - nitrogen flame was recorded on a chart recorder and is shown

Figure 9.3

Spectrum of sulphur in a H_2/N_2 flame



in Figure 9.3. The origin of the signals was checked by setting the monochromator at 300 nm. No signal was obtained.

The least noisy flame was obtained with the hydrogen flow rate at its minimum. Nitrogen and argon flow rates were optimised accordingly, Figure 9.4. An inert gas flow rate greater than 2 l min^{-1} caused the flame to be extinguished.

The variation of monochromator slit width with log (response) is shown in Figure 9.5. As is to be expected from an emission method sensitivity increases with increasing slit width, however it reaches a maximum at ca 1.0 mm. Probably this indicates that the limits of response of the photomultiplier had been reached. Operating conditions are shown in Table 9.1.

Table 9.1 Experimental Parameters - Sulphur

Emission wavelength	384.0 nm
Non-emission wavelength	300.0 nm
Monochromator slit-width	1.0 mm
Hydrogen flow rate	0.4 l min^{-1}
Argon flow rate	1.6 l min^{-1}

Development of the hydride generation technique was carried out using aqueous solutions of AnalaR sodium sulphide. Initially 1 ml aliquots of the sulphide solution were pipetted into the cell and 2M hydrochloric acid (1 ml) added from the bulb. This was not very satisfactory; the reaction was not as violent as the borohydride technique so the self-agitating effect of the effervescence of the latter was absent and the use of a stirrer in so confined a space was not practical.

Figure 9.4

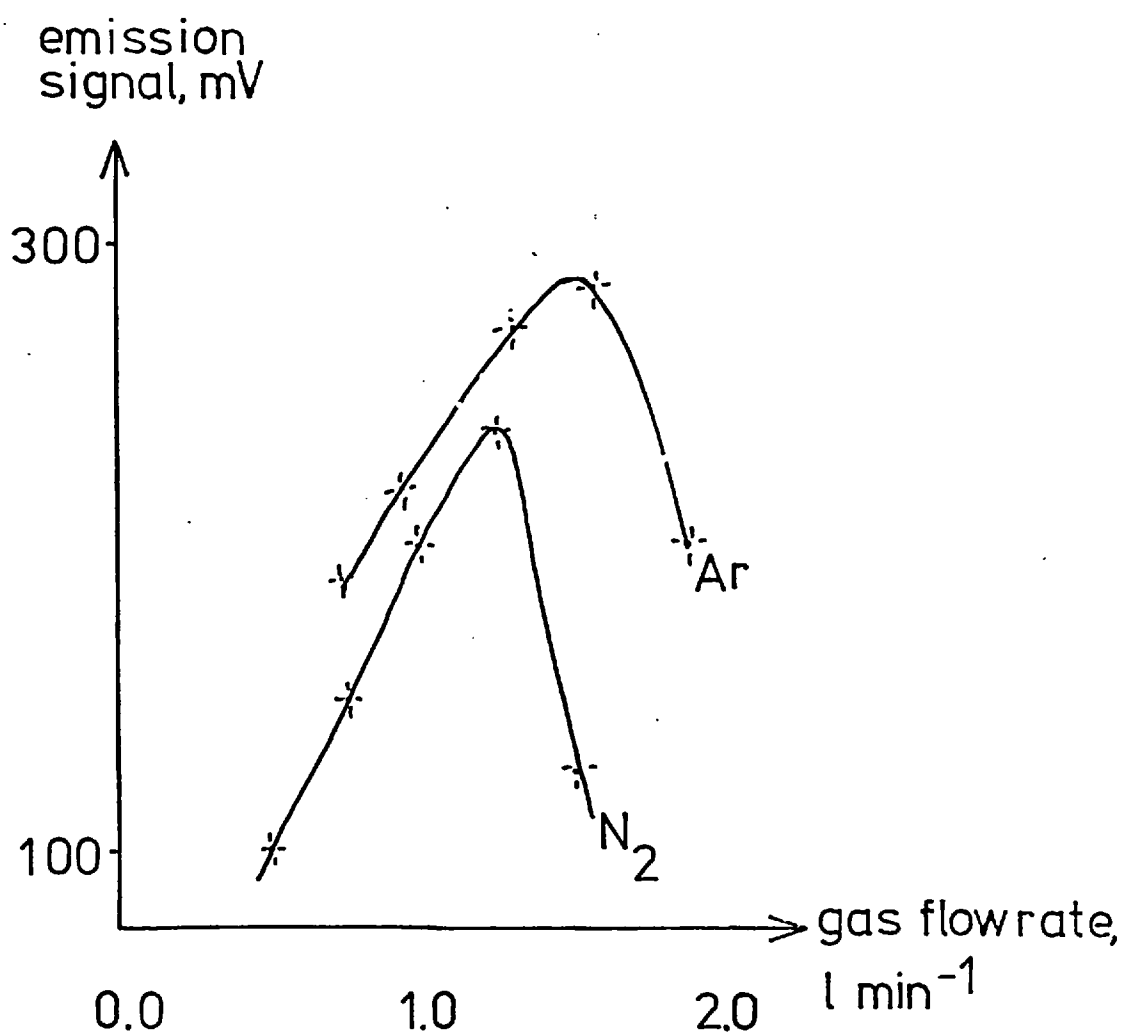
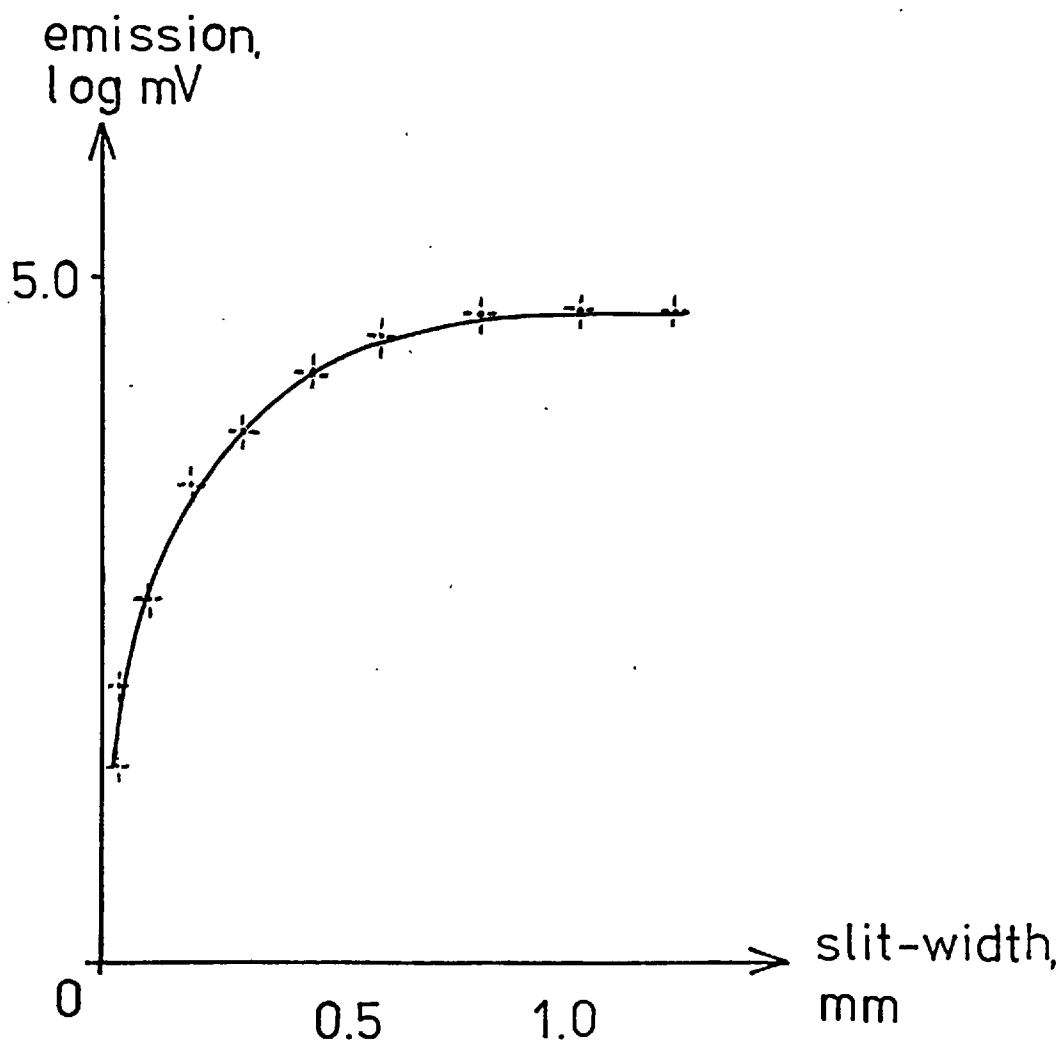
Optimisation of Ar/N₂ flow rate

Figure 9.5

Optimisation of slit-width



The bulb was replaced by a Subaseal and a 2 ml hypodermic syringe was used to deliver the acid; this was equally unsuccessful. Both of these techniques suffered from the disadvantage that after each reading the flame had to be extinguished for the cell to be cleaned out and re-filled. Accordingly 1 ml concentrated hydrochloric acid was put in the cell and aliquots of sodium sulphide solution injected through the Subaseal using a Hamilton 50 μ l syringe. Entirely satisfactory results were still not obtained due to the geometry of the cell - the injected solution often dripped onto the sweep gas inlet. To circumvent this, the neck (1) was added opposite to and 1 cm below the neck 3. 50 μ l aliquots of sodium sulphide solution were injected ca each fifteen seconds. 1 ml of concentrated hydrochloric acid was sufficient for at least 100 aliquots.

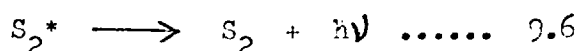
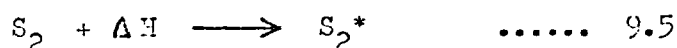
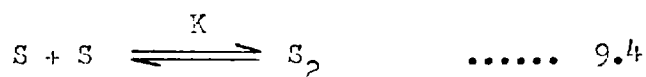
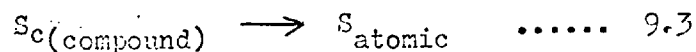
Conversion of sulphur in oil samples to sodium sulphide was carried out as follows. A 10 - 100 mg sample was weighed into an ignition tube (75 mm x 12.5 mm) and a freshly cut 2 mm cube of sodium added. The mouth of the tube was then plugged with glass wool. No significant differences in results between plugged and unplugged tubes were noted but the plug tended to confine smoke and some of the acrid fumes produced. The bottom of the tube was then warmed gently in a Bunsen flame until the sodium just melted (97°C). As the reaction proceeded the tube was heated to a dull red and then plunged into a measured quantity (5 - 25 ml) of distilled water. The larger pieces of the ignition tube were removed and the solution stirred. 50 μ l aliquots were taken from this solution. It was found unnecessary to boil the solution or to filter it.

Standards were made up from t - butyl disulphide (provided by B.P. Research) diluted in AnalaR liquid paraffin since the metal - free

SAE 10 base oil contained ca 200 ppm sulphur.

9.3 Results and Discussion

Calibration curves, plotting $\log I$ vs $\log S$, where I is the emission intensity and S the mass of sulphur, were constructed for aqueous sodium sulphide solutions using both nitrogen and argon as diluent, Figures 9.6 and 9.7. At the 30 ng of sulphur level the signal obtained from the flame diluted with argon was three times that from the flame diluted with nitrogen; the nitrogen molecule contains a very stable triple bond which despite its lower mass makes it considerably more effective as a quenching agent than the somewhat heavier but more compact argon atom. The slope of each curve was ca 2: this lends support to the concept that the chemiluminescent emission occurs in the four basic steps in equations 9.3 - 9.6.



The equilibrium constant K may be described:

$$K = \frac{[S_2]}{[S]^2} \quad \dots\dots 9.7$$

assuming $[S_2^*] \propto [S_2]$ and $[S] \propto [S_c]$ equation 9.7 may be rewritten

$$K' = \frac{[S_2^*]}{[S_c]} \quad \dots\dots 9.8$$

The intensity of emission, I , is proportional to the concentration of the emitting species, $[S_2^*]$, thus the intensity of emission is given by

$$I = K' S_c^2 \quad \dots\dots 9.9$$

Figure 9.6

Calibration curve - water
[N₂ diluent gas]

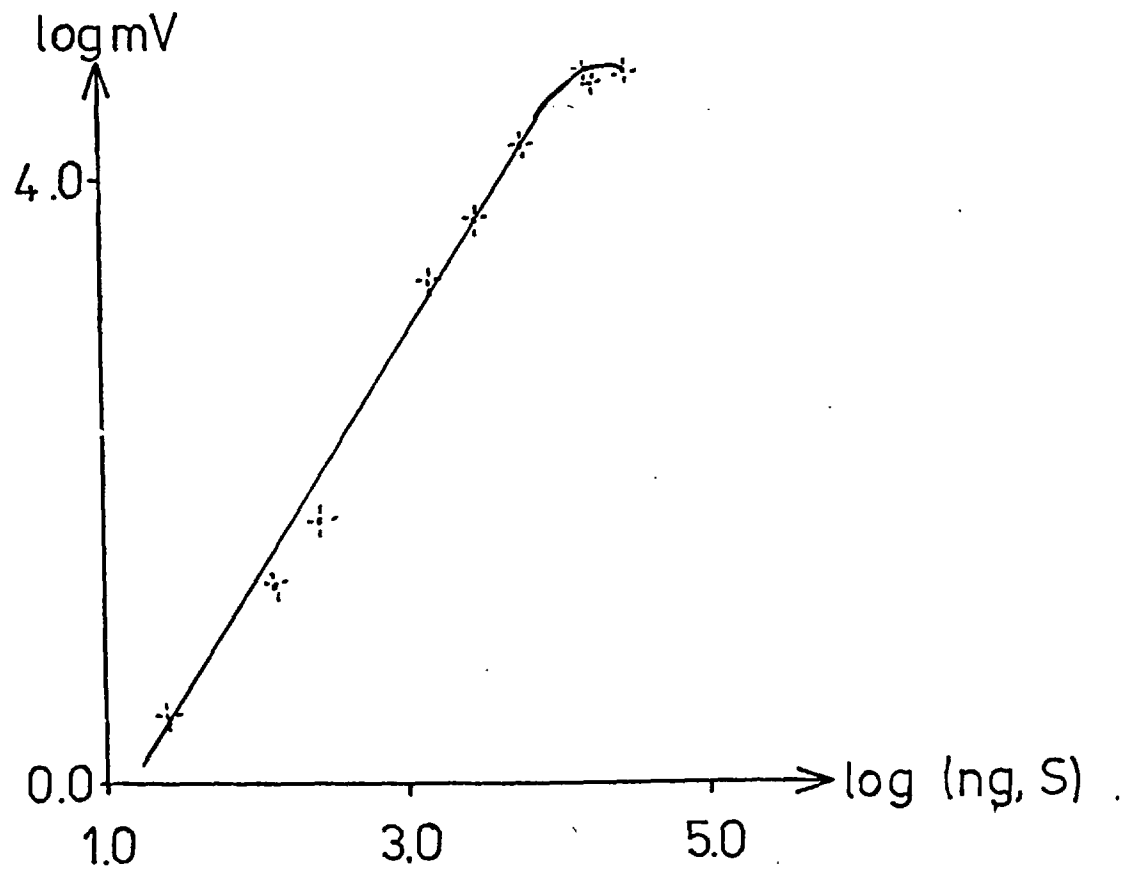
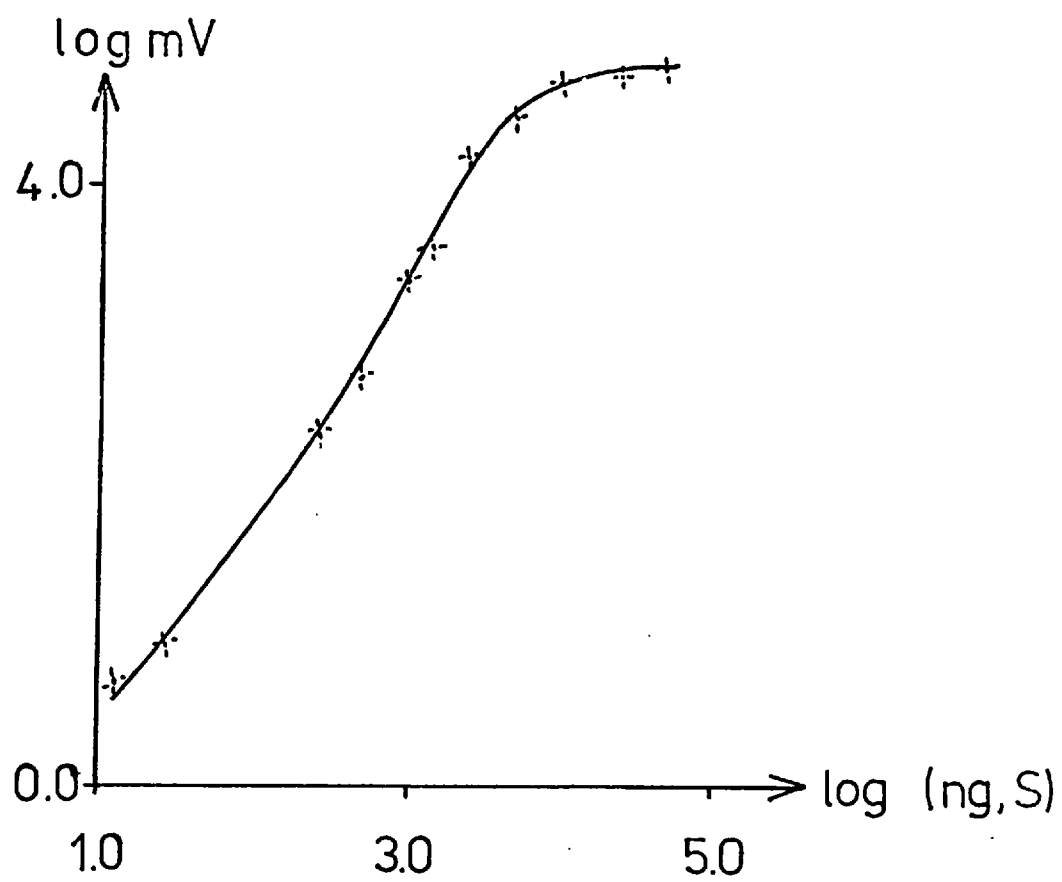


Figure 9.7

Calibration curve - water
[Ar diluent gas]



$$\text{or} \quad \log I = \log K' + 2\log [S_0] \quad \dots\dots 9.10$$

Both graphs curve off in the region of ca 10 μg S, this is probably due to self - absorption. Greer and Bydalek (144) have proposed a mathematical correction for this curvature which was applied with some success by Everett (3).

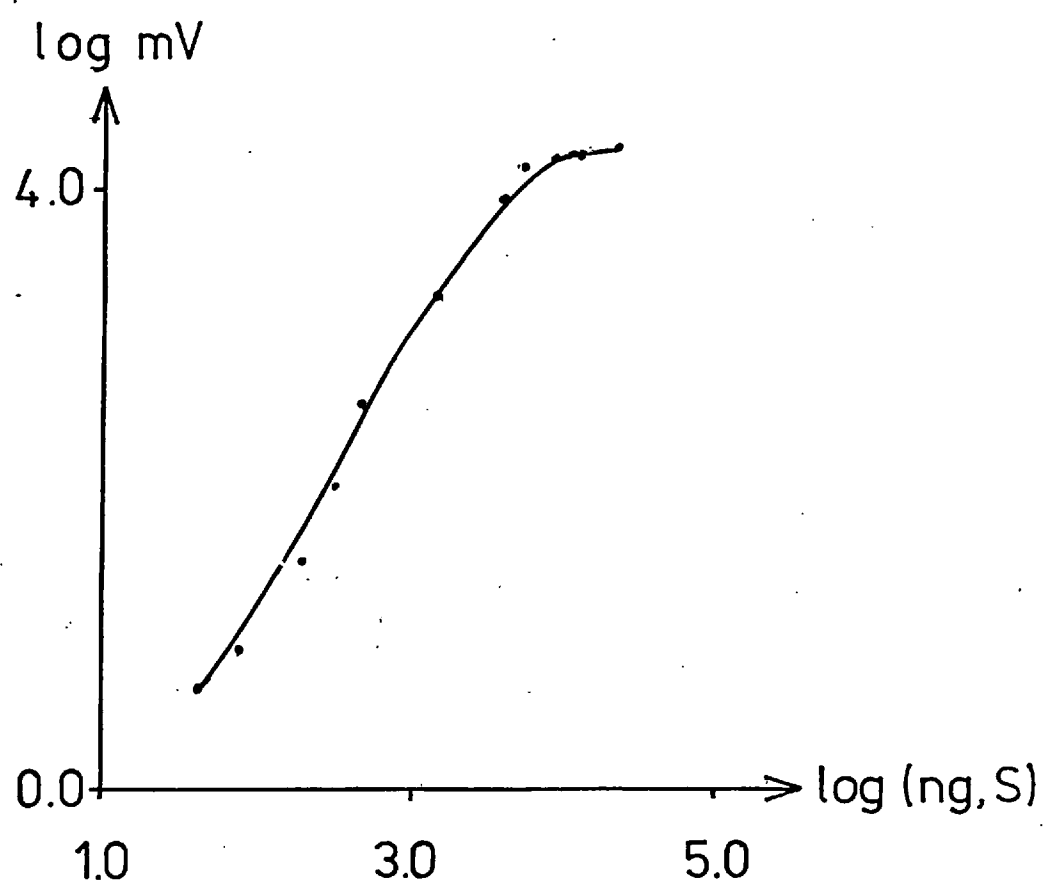
A satisfactory calibration curve was constructed for sulphur in oils, Figure 9.2. The signal obtained for a given mass of sulphur was ca one third that of the corresponding aqueous solution. The minimum detectable amount was approximately the same as for aqueous solutions analysed with a nitrogen diluted flame, being in the region of 30 ng; that for aqueous solutions analysed in an argon diluted flame was ca 10 ng. Since the sodium fusion solution was analysed in argon diluted flames this difference cannot be attributed to differences in quenching; it is possible that the sulphide is not generated as rapidly or efficiently due to the presence of foreign ions in the fusion mixture.

A number of real samples was analysed by this procedure. The results are shown in Table 9.2. Each analysis took under four minutes.

The majority of the results agree to within 15 % with those obtained by XRF at B.P.. The precisions were for many of the results within 10 %. The precision could be improved by controlling the speed of injection, for example by the use of spring loaded plunger pipettes of unique volume. Low results were possibly due to fusion of sulphide into the ignition tubes (145) or its occlusion onto the resulting charred carbon as well as by evaporation of sample.

An additional modification might be made by using a sealed tube such as employed by Campbell et al. (145). This would enable a lower concentration of sulphur to be determined, by use of a larger sample

Figure 9.8
Calibration curve - oil
[Ar diluent gas]



than is really practical when the fusion is performed in an ignition tube. However the use of such a system would be relatively time - consuming and would thus detract from the main advantage of this procedure.

Table 9.2 Results - Sulphur

Type	Number	Sulphur content given	Sulphur content found
Kerosene	K1	160 ppm	120 ± 12 ppm
"	K2	1090 ppm	1303 ± 150 ppm
"	K3	260 ppm	224 ± 14 ppm
Gas oil	G01	55 ppm	61 ± 8 ppm
"	G02	2800 ppm	1860 ± 143 ppm
"	G03	6190 ppm	5236 ± 570 ppm
Fuel oil	F01	2.70 %	2.25 ± 0.18 %
"	F02	2.45 %	2.73 ± 0.25 %
"	F03	0.62 %	0.54 ± 0.03 %
"	F04	2.17 %	2.47 ± 0.45 %
"	F05	1.99 %	1.52 ± 0.44 %
"	F06	1.01 %	0.77 ± 0.20 %
Leaded gear oil	GEO1	4900 ppm	5500 ± 1000 ppm

It may be concluded that this method is extremely effective for the very rapid analysis of total sulphur in oils. Future work could be carried out on other organic matrices and possibly with some modification on geological samples.

Phosphorus gives rise to a green emission (due to HPO) under similar conditions to those described for S_2 emission. It is possible to generate phosphine from inorganic phosphides in the presence of

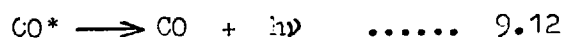
acid and indeed a green emission was observed when sodium sulphide was replaced with tin phosphide. However, sodium phosphide formed in the course of a fusion is largely hydrolysed by water, but if a non-aqueous medium were substituted there may be some potential for successful application of such a procedure.

9.4 Appendix

In section 9.2 it is noted that when hydrogen sulphide in air was passed into a carbon tube at ca 800°C a blue emission was seen. Further work suggested that this emission was due to CO, the maximum emission being obtained at ca 390 nm.

A stream of nitrogen was passed into the tube and quantities of air were injected into this stream using an ordinary hypodermic syringe. The nitrogen flow rate was optimised and it was found necessary to use a slit-width of 1mm, Figures 9.9 and 9.10.

Figure 9.11 shows that a straight line is obtained when emission intensity (I) is plotted against ml of air injected. The reactions involved are



By making similar assumptions to those in section 9.3 it may be deduced that

$$I = k CO^{\frac{1}{2}} \quad \dots\dots 9.13$$

Although this relation was not followed the curve obtained and the detection limit of 15 µg of oxygen indicated that the method might have some limited potential.

Interference effects from a number of gases were studied and although none was found from hydrogen sulphide, sulphur dioxide or nitrogen, significant effects were noticed for both carbon monoxide and carbon dioxide. These severely limit any application of this method.

Figure 9.9

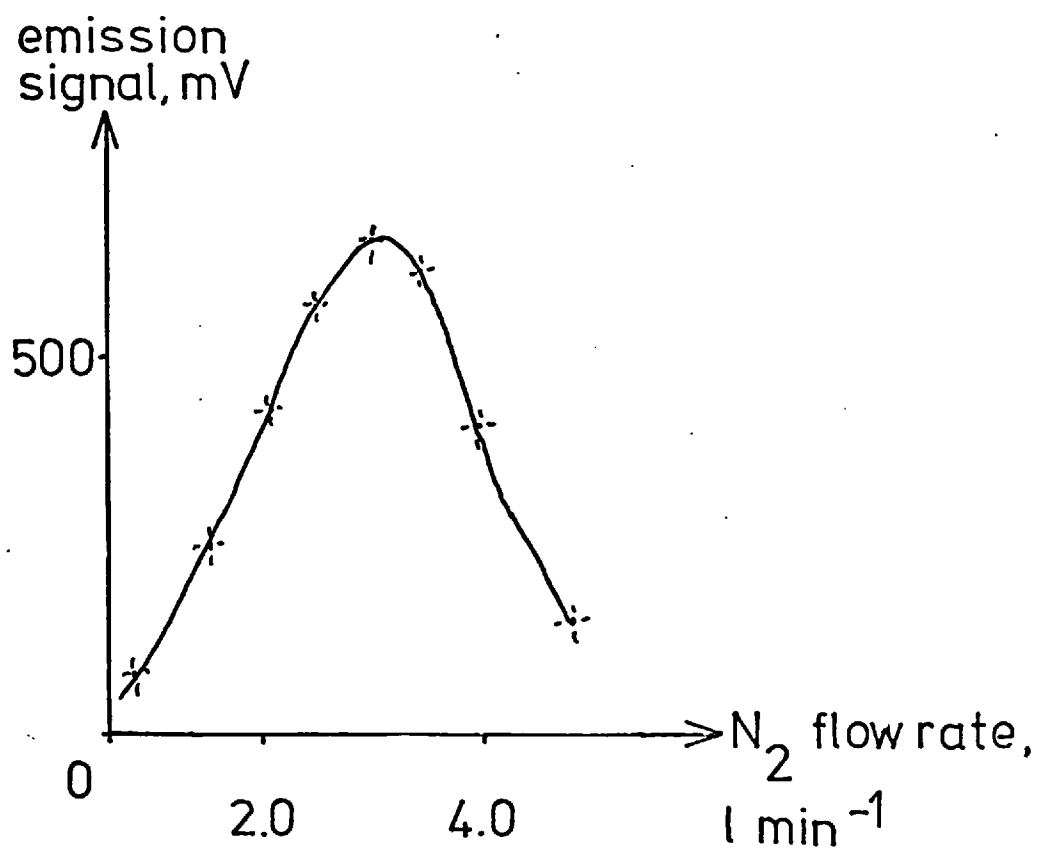
Optimisation of N_2 flow rate

Figure 9.10

Optimisation of slit-width

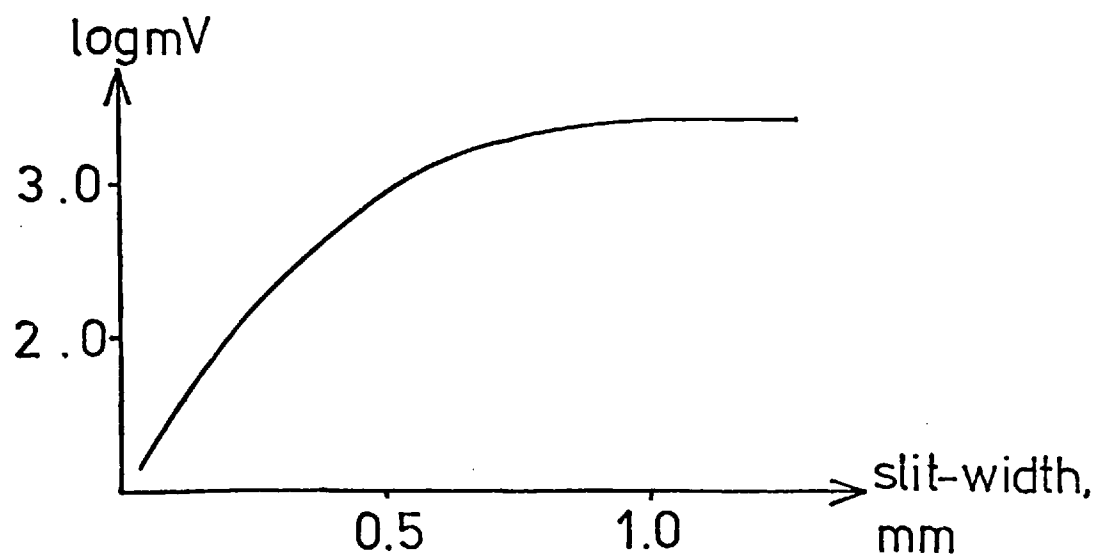
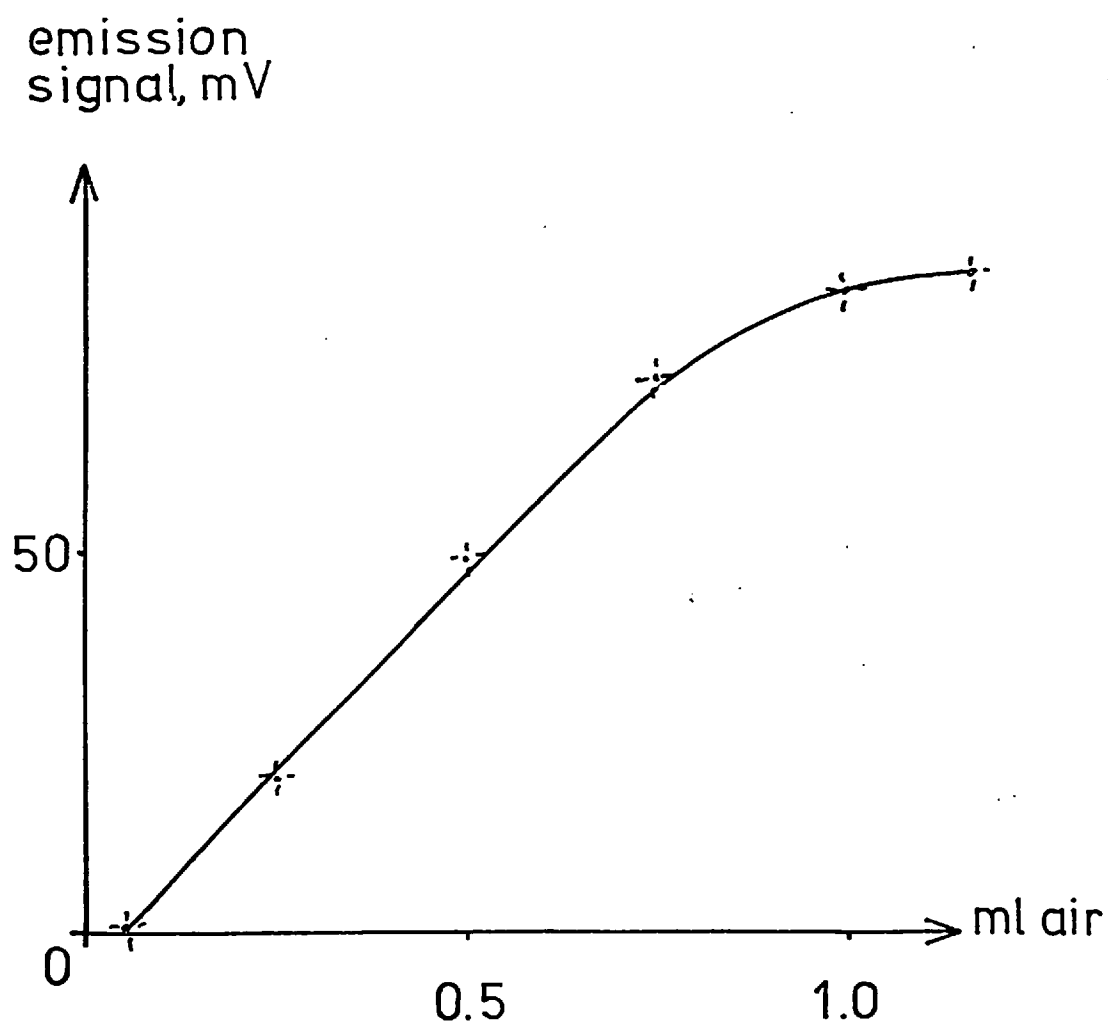


Figure 9.11

Calibration curve



General Conclusions

In the course of this study successful new microprocedures based on atomic absorption and molecular emission spectroscopy have been evolved for the determination of the following elements in petroleum products such as lubricating oils:

Calcium

Magnesium

Barium

Antimony

Tin

Lead

Sulphur.

There are serious limitations to the method for tin and lead connected with extraneous problems due to the effect of foreign metals on the hydride generation procedure.

As a result of this work quick reliable procedures have been made available and persuance of research along similar lines could extend the coverage to the determination of other elements present in or deliberately added to oils for various technological means.

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