PLASMA ASHING FOR TRACE METALS ANALYSIS IN RESIDUAL OILS AND COAL

by

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TO MY PARENTS AND UNCLES

ABSTRACT

A method was developed for the determination of the trace metals V, Ni, Fe, Cu, Pb and Zn in residual oils and coal. In this method, in order to decompose organic materials prior to trace metals analysis, an apparatus for low temperature (100-200 °C) plasma ashing (L.T.P.) was constructed in the laboratory where a stream of oxygen was passed through a radiofrequency field (13·56 MHz) to produce reactive oxygen. The concentration of metals was determined by dissolving the ash in dilute HNO_3 and using Atomic Absorption Spectrophotometry.

A brief description of the occurrence, nature and significance of metals in oil and coal is discussed and their analysis by chemical and instrumental methods are reviewed. The importance and applicability of the various techniques used for trace metals analysis in petroleum and coal are discussed.

The history, theory and principles of plasmas and Atomic Absorption Spectrometry are described briefly and the construction and development of the plasma apparatus, the determination of plasma factors and their effect on the rate of oxidation are discussed in more detail.

The results of six trace metals analysis are calculated for both types of samples by using a calibration and a standard addition method for each metal. A separate study is carried out on the retention of trace metals after low temperature plasma ashing in aqueous standards (spiking method).

The effect of dilution in the analysis of metals along with the precision of the method is determined.

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CHAPTER 1

1. INTRODUCTION

Petroleum consists predominantly of hydrocarbons but most of them contain measurable quantities of many metals. Similarly the coal is an aggregate of heterogenous substances composed of organic and inorganic materials. A better understanding of the effect and significance of the non hydrocarbon constituents of petroleum on refining processes and product characteristics has led to trace analysis problems. Thus analytical methods of increased sensitivity have been developed in recent years following the awareness of the significance of the trace elements and the importance of detecting them accurately. The main problem in trace metals analysis is the determination of a small quantity in the presence of an overwhelming amount of organic substance. In recent years various analytical techniques have been used for the analysis of oil and coal. Many of these techniques require preconcentration of the metals, usually by ashing techniques and consequently involve the risk of loss of volatile metals or contamination by reagents.

To decompose organic materials prior to trace metals analysis a number of techniques had been used, eg, wet ashing with mineral acids, and dry ashing. Wet ashing is tedious and potentially hazardous. The anions which are introduced tend to interfere with subsequent analysis in wet ashing. Dry ashing requires heating of the sample at 400 °C to 900 °C, during which elements from the container and atmosphere may be introduced into the sample, biological materials tend to froth and char, volatile metals are lost from compounds which are decomposed easily, and hardly soluble compounds may be formed. In the dry and wet ashing methods thousands of grams of oil sample have been used for one metal analysis and the volatile metal loss has been prevented by sulphation. The time for analysis has also been too great.

In coal analysis, practically all the chemical methods depend on ashing as a first step before dissolution, but some attempts have been made to include reflux heating of coal with oxidising acid mixtures such as $HClO_4$ + HIO_4, and HNO_3 + H_2SO_4 or in the Par bomb

with aqua-regia + HF or with fuming HNO_3. These methods have disadvantages of either incomplete dissolution or losses of certain volatile elements due to highly vigorous dissolution conditions plus contamination from the acids used. In the coal analysis there are two alternative procedures, high temperature and low temperature ashing. Due to high temperature ashing a general loss in trace elements has been reported (400, 414, 415). The loss of many elements during dry ashing has been reported. Since some coals contain appreciable amounts of sulphates, this will help in retaining the trace elements during ashing. However, addition of large amounts of sulphates is not very desirable when the trace elements in the coal have to be determined in the end. The objections applied to Parr (286) and King (199) formulae is that they have to assume that the clay meneral.. in coals have a constant average water of decomposition, and they ignore the possible presence of quartz, which yields no water of decomposition on heating. The disadvantages in direct determination of mineral matter by digestion with hydrochloric and hydrofluoric acids are that pyrites is not extracted and the residue contains adsorbed hydrochloric acid, necessitating supplementary analysis to determine correction factors for the mineral matter content.

Due to practical disadvantages inherent in the conventional methods of ashing, an alternate method is described in this thesis. It employs a high frequency (13·56 MHz) electromagnetic field to produce a stream of reactive oxygen, which decomposes the organic substances at low temperature (60 °C). The apparatus for low temperature plasma ashing (LTA) was constructed in the laboratory. The ash of the residual oils and coal samples was completely soluble in 0·5% HNO_3, and determined by Atomic Absorption Spectrophotometry (Perkin Elmer 2280 and IL 455) as an end technique. The residual oils (F-80 and F-31) and coal samples (A and B-120 B.S. Mesh) were provided by British Petroleum and the National Coal Board respectively. The residual oil sample (0·4g) is weighed on four filter papers, whatman No. 1 (5·5 cm) in a Petri dish (6 cm in diameter) and ashed by oxygen plasma. An average rate of oil and filter paper oxidation (0·311 g/hr^{-1}) was obtained with conditions of 200 W, flow-rate 150 ccs/min and pressure 0·2 torr.

The coal sample (0·3 g) is ashed directly on a petri dish

and no filter paper is used. The aqueous standards are prepared for each metal determined in residual oils and coal samples. Both the calibration and the standard addition methods are used for each metal in both the samples. Filter paper blank is prepared by ashing four filter papers with oxygen plasma, dissolving in 0•5 % HNO_3 and then determining by AAS for oil samples. Double distilled water blanks are determined for both of the samples without ashing them. The determinations are carried out for each metal by ashing ten Petri dishes or more for the each metal depending upon the metal concentration in the sample and the sensitivity and limit of detection of the instrument. The average rate of coal oxidation was 0•038 g/hr^{-1} with conditions as follows:- power 200 W, flow rate 150 ccs/min and pressure 0•2 torr.

A separate study is carried out on the retaining of the metals in aqueous standards after low temperature plasma ashing. The ash of aqueous standards is dissolved in 0•5% HNO_3 and determined by AAS. Organic standards are not used because of their higher vapour pressure (during ashing) and their need for an organic phase as solvent (as compared to an aqueous phase for the salts usually employed.). The trace metals are also analysed by spiking aqueous standards with metal solutions. The rate of filter paper ashing ($1•7 \times 10^{-3}$ mg/min/ at flow rate of 250 ccs/min) at different power and flow rate levels is determined. The temperature is recorded by using a mercury thermometer.

This method of oxidation yields more reliable results than acid digestion (255). The mineral matter is in a suitable form for elemental analysis. In coal the mineral constituents, which are important in coal washing, coke making and blast furnace operation, may be studied. This activated oxygen method has been employed successfully in this laboratory in the ashing of residual oils and coal samples.

The low temperature plasma oxidation process typically prepares samples at room temperature to 250 °C. The reaction of an oxygen plasma directly in a cold trap at -196 °C has been reported (410). The low temperature ashing (L.T.A.) of organic materials is carried out with minimum loss of volatile elements. The oxidation rate and the sample temperature can be very carefully controlled in LTA. In the radio

frequency discharge method, electrical energy is transfered directly to a stream of low pressure gas producing highly excited states of oxygen. The reaction of these species with the elements in the samples is selective, carbon, hydrogen, nitrogen and Sulphur in organic materials form the respective oxides in LTA. The gases released by the oxidation process are themselves subject to excitation in the discharge. Pure oxygen produces a dull pink glow in the sample chamber. For samples containing carbon,(probably 90% of the sample) the evolved carbon oxides (CO, CO_2) produce a deep blue colour in the discharge. Thus as the oxidation commences the flow turns from pink to blue and when the sample is completely ashed the pink colour returns, thereby providing immediate visual indication that the sample is completely ashed.

The results of plasma experiments strongly depend upon parameters such as pressure, electrical field strength, gas velocity, and the tube diameter. To initiate a plasma a certain field strength is necessary. The magnitude of the plasma depends upon the pressure and the nature of the gas. After initiation the field strength drops to lower value. In a plasma the electric field accelerates the electrons and these electrons transfer their energy to molecules by collisions. The higher the field strength is, the more energy the electrons can pick up between collisions. An increase in the field strength thus raises the average electron energy. This leads to a greater number of inelastic collisions and thus increases the chemical yield.

Since the pressure, field strength, tube diameter and flow rate influence the average electron energy, the degree of ionization, the gas temperature, and the rate of convertion, it is not possible to give accurate values of optimal working conditions valid for a variety of reactions (18, 46, 247, 248, 244, 245, 261, 262, 361, 400, 414, 415).

Since no simple methods of plasma diagnostics are available at present, it is not possible to give values of electron densities and electron energy distributions necessary for a specific reaction. As a consequence for every reaction a series of optimizing experiments is necessary. Within the limits indicated above, the experimental

parameters are varied and the influence of this procedure on the yield is determined for the filter paper, oil and coal samples.

CHAPTER 2

2. FUNDAMENTAL PROCESSES IN PLASMA CHEMISTRY

2.1 Introduction

The plasma chemistry deals with the occurrence of chemical reactions in a partially ionized gas composed of ions, electrons and neutral species.

The first observation of gas discharges was made in the course of electrostatic investigations. In the seventeenth century it was found that the charged conductors gradually lost their charge. By the end of the eighteenth century it was confirmed that the loss was due to surrounding atmosphere. In the early nineteenth century electric arc by touching electrodes together connected to a battery was discovered. In the second half of the nineteenth century cathode rays in a discharge tube at low pressure was discovered and led to intensive research. Later on the progress was steady whereas the interest in thermonuclear reactions started a search for the high temperatures, and an intense gas discharges was a possible source for such temperature. The term plasma physics is now used to describe the general study of ionized gasses (401, 402). The general idea that atoms could be important agents in chemical reactions arose from the study of photochemistry (263) for the production of free radicals by reaction with organic substances (362). Meanwhile Wood (403, 404) described the production of hydrogen atoms by passing it through the discharge. In oxygen discharge the important active species produced are O atoms (157-159, 127).

The polymerization effect and the formation of new products (radicals) was studied by the breakdown of hydrocarbons (48, 248, 363, 364). During this early period recombination of atoms, detection and estimation of atoms and radicals was also made.

The discharge results when randomly occuring free electrons are accelerated by the electric field and transfer the energy to the gas molecules, leading to the formation of variety of new species including metastables, atoms, free radicals and ions (410, 411, 412). Electrons formed in this ionization are in turn accelerated and produce further ionization. This progressive effect causes extensive breakdown of the gas,

the current rises and the discharge is established. Very soon a steady state is reached in which there is an equilibrium between the rate of formation of ions and the rate of their recombination occuring mainly on the walls of the containing vessel at low pressures. This drift of electrons in the field is responsible for the electrical conductivity of plasma as it is electrons that carry the current.

In plasma the concentration of positive and negative charge carriers are approximately equal, and this is satisfied when the dimensions of the discharged gas volume Λ are significantly larger than the Debye length, which defines the distance over which charge imbalance can exist.

$$\lambda_D = \left(\frac{\varepsilon_o K T_e}{ne^2}\right)^{\frac{1}{2}} \qquad \text{2.1}$$

In equation 2.1 ε_o is the permittivity of free space, K is the Boltzmann constant, Te is the electron temperature, n is the electron density and e is the charge on the electron.

Two regions of great interest to plasma chemistry are glow discharges and arcs. The glow discharges are characterized by average electron energies 1-10 ev, and electron densities of 10^9-10^{12} cm^{-3}. The electron temperature is much higher than gas temperature (T_e/T_g = 10-10^2) in glow discharges, and this absence of thermal equilibrium makes the electrons more energetic to break the molecular bonds, and to cause chemical reactions in thermally sensitive materials.

The elastic collisions of electrons are of negligible importance for the chemistry in glow discharges since they transfer very little energy, but the inelastic collisions lead to various species. Electrons of low energy may add to the molecules and form negative ions, and they transfer part of their energy into the vibrational energy of the molecules in short time.

$$O_2 + e \longrightarrow O_2^- \quad , \quad O_2^- \longrightarrow O + O^-$$

When molecules collide with electrons of higher energy they may become excited or ionized, eg. the appearance potential for O_2^- ion formed is 4·53 ev, and at higher energies (17·28 ev) O^+ and O^- ions are formed. Electrons of higher energy than that required to produce a given species may produ with correspondingly higher kinetic energy. The atoms resulting from dissociative mechanism will also be excited by electron collision to higher states or may form metastable states which are comparatively long lived and decay only by further collisions which raise or lower their energy to values that permit radiation. In high frequency discharges the distribution of electron energy is closely Maxwellian.

Ion-molecule reaction is very fast, so a large fraction of gas molecules passing through the discharge could therefore be ionized in short time, (ions lose charge by charge transfer reaction). When an ion captures an electron then an energy of 10 ev is liberated, which is high enough to damage the molecule. Normally recombination occurs in three body collisions where third body can be a molecule, an electron or the wall.

At lowest electron energy, an addition of the electron by electron resonance capture occurs, giving a negative ion,

$$AB + e \longrightarrow AB^-$$

this ion may dissociate to give a neutral atom and a negative ion,

$$AB^- \longrightarrow A + B^- \text{ or } (A^- + B)$$

At higher energies the production of ions may occur,

$$AB + e \longrightarrow A^+ + B^- + e$$

and at still higher energies the positive molecular ion is formed,

$$AB + e \longrightarrow AB^+ + 2e$$

which may dissociate to give a positive ion together with a radical or atom,

$$A^+B \longrightarrow A^+ + B$$

When these various species (ions, free radicals, electrons),

generated by electron impact on gas molecules, are directed to the organic sample, then the sample may form the products through monomolecular processes by rearrangements or fragmentations or by interactions with neighbouring molecules. It is also conceivable that they are first transformed into reactive intermediates, which then lead to the final products through monomolecular or bimolecular processes, Fig. 2.1.

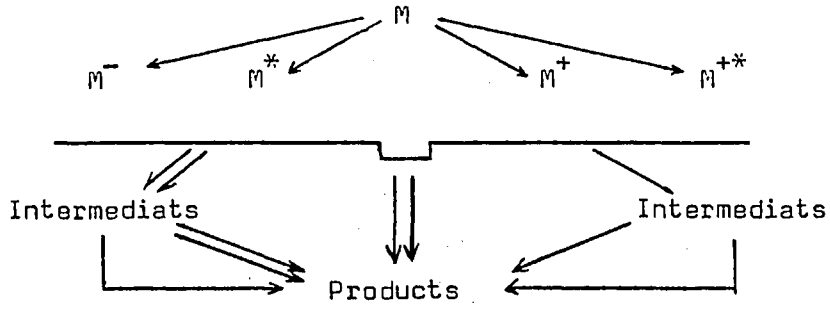


Fig. 2.1 Possible Elementary Process in Plasma Reactions

For organic molecules which tend to form negative ions or ion-molecule complexes, these recombination processes are important,

$$M^+ + M^- \longrightarrow M^* + M^* \quad \text{or} \quad M + M^*$$
$$MM^+ + e^- \longrightarrow M^* + M^* \quad \text{or} \quad M + M^*$$
$$MM^+ + M^- \longrightarrow 2M^* + M \quad \text{or} \quad 2M + M^*$$

Two body collision processes have much higher probability, and organic molecules due to numerous bonds can take up a lot of energy in the form of vibration and may therefore withstand such recombination processes in that dissociation.

The chemistry involved in mechanism of plasma reactions is complex and only in rare cases it is possible to obtain information on reaction intermediates. Among the experimental parameters only pressure, gas velocity, and power uptake can be measured easily. The degree of ionization, the average electron energy, the field strength, the concentration and the nature of the intermediates are normally not known and can only be determined by complicated measurements.

In this project a stream of oxygen at low pressure is passed through a radiofrequency discharge, producing highly excited states of oxygen which are used for decomposing organic matter prior to trace metals analysis.

2.2 Plasma Kinetic Theory

2.2.1 Electron Velocity Distribution Function

The plasma kinetic theory explains the factors controlling the electron velocity distribution and thus the average electron energy.

The electron velocity distribution defines the physical properties of plasma by explaining the electron energy distribution, the average electron energy, the electron transport properties, and the rate constants for the reactions involving electron-molecule collision. The shape of the distribution depends upon the magnitude of the applied electric field and the nature of elastic and inelastic interactions which the electrons undergo.

The electron velocity distribution function f represents the density of electrons in both position (vector r) and velocity (vector v), space.

$$f(r , v) \text{ , product } f\ dr\ dv$$

where $dr = dx\ dy\ dz$ and $dv = dv_x\ dv_y\ dv_z$

The product $f\ dr\ dv$ describes the number of electrons whose positions are located within the volume element dr and whose velocities lie within the volume element dv. If $f dr dv$ is divided by dr and integrated, then electron density at point r, is

$$n = \int_{-\infty}^{\infty} f\ dv \qquad \text{2.2}$$

Thus the average translational velocity $\langle v_x \rangle$ is given as,

$$\langle v_x \rangle = \frac{1}{n} \int_{-\infty}^{\infty} v_x\ f\ dv \qquad \text{2.3}$$

Similarly, average electron energy can be calculated. The velocity V can be expressed as the sum of the random velocity plus the translational velocity of the whole electron cloud $V = v + \langle v \rangle$. Since the positive and negative values of V are equally probable, the average value of v will be equal to zero. The total translational kinetic energy can be expressed as:

$$= \frac{1}{2} m (v_1^2) + \frac{1}{2} m (v_2)^2 \qquad \text{2.4}$$

where v_1 and v_2 are the magnitudes of the velocities V and $\langle V \rangle$, respectively.

The first term in the equation 2.4 represents the kinetic energy associated with random motion of electrons and the second term represents the kinetic energy associated with the translation of the electron cloud as a whole. In a system where velocity distribution is Maxwellian, the random kinetic energy can be related to the elctron temperature, by

$$\frac{1}{2} m (v_1^2) = \frac{3}{2} k Te \qquad \text{2.5}$$

The Boltzmann equation explains the velocity distribution function by the gain and the loss of electrons from an incremental volume in phase space defined by dr, dv and also the net rate at which the electrons are removed from the differential volume dv by binary collisions (410). Boltzmann's equation is expressed as,

$$\frac{\partial f}{\partial t} + V \cdot \nabla_r f + \frac{eE}{m} \cdot \nabla_v f = \left(\frac{\partial f}{\partial t}\right)_{coll} \qquad \text{2.6}$$

The first term on the left-hand side gives the local variation of the distribution function with time. The second term describes the variation in the distribution function resulting from electrons streaming in and out of a given volume element, related to the dispersion of diffusion. The third term is the variation of the distribution function resulting from an applied electric field E

acting on the electrons. The single term on the right-hand side of equation 2.6 accounts for the net transfer of electrons from the differential volume by the mechanism of the binary collisions between electrons and molecules, ions and other electrons. Different types of binary collisions in plasma are broken down into categories of elastic and inelastic collisions. The inelastic collisions differ from elastic collisions in that the target particle is left in an excited state after collision. The nature of these excitations ranges across the energy spectrum from rotational excitation (0•01-0•1 ev energy is absorbed) to ionization (more than 10 ev energy is absorbed) (19,85, 249, 410).

The solution to Boltzmann's equation describes the velocity distribution function, since it is very complicated so an approximate solution is sought.

The solution can be expressed as the sum of an isotropic portion plus a small anisotropic agitation. The basis of this observation is that in the absence of any field or gradients in electron concentration, the velocity distribution becomes completely isotropic. Thus the effect of spatial gradients and the external forces is assumed to produce an agitation onto the isotropic solution, so the distribution function f can be expressed as,

$$f = f^{o} + \phi(v) \qquad \text{2.7}$$

Where f^{o} is the isotropic distribution, and $\phi(v)$ anisotropic distribution. It may be further assumed that anisotropic contribution is largest when velocity v is in the direction of gradient or force causing the perturbation and smallest when it is perpendicular to it. So the anisotropic distribution is, as given below.

$$\phi(v) = \frac{v}{v_1} \cdot F' \qquad \text{2.8}$$

The factor F' points in the direction of electron drift as the result of the external field and spatial gradients. The total distribution

can be written as,

$$f = f^{o} + \frac{v}{v_1} F' \qquad \text{2.9}$$

V_1 = Speed of the electron

Substitution of the approximate solution of (2.9) into the Boltzmann equation leads to the identification of two differential equations which can be solved for f^{o} and F'. The procedure by which this is accomplished is quite complex and it is suggested to consult the discussion of this problem given by Allis (19) and Hollahan and Bell (410).

Dreicer (85) explained the solution of the Boltzmann equation for the electron velocity distribution in hydrogen plasma, taking into account an inelastic collision as well as random two body coulombic collisions. Elastic collisions between electrons and hydrogen molecules are neglected on the basis that they represent only a small energy loss term. In coulombic interactions only those occuring between two electrons are retained since it is shown that electron-ion encounter result in negligible energy losses from the electron. The numerical solutions obtained for E/p equal to 28·3 V/cm torr is illustrated (85). The electron-energy distribution function is related to the velocity distribution function by

$$f(\mathcal{E}) = \frac{4\pi}{m} v f^{o}(v) \qquad \text{2.10}$$

Where $\mathcal{E} = \frac{1}{2} mv^2$. For each value of E/p, the effects of the extent of ionization are identified by the value of n/N. At very low energies $f(\mathcal{E})$ decreases as the extent of ionization (n/N) increases. At the highest degree of ionization the distribution function is very nearly Maxwellian.

The effects of electrons interactions on the average energy are reported in (85). As the degree of ionization increases, the average energy at first rises and then falls. The rise depends upon the fact that the slow electrons produced in inelastic encounters exchange energy with other electrons, and are quickly redistributed over the body of the distribution. For a fixed value of E/p and N,

the rise in average energy is accomplished by the addition to the distribution of electrons whose average energy exceeds the average energy corresponding to $n/N = 0$. The subsequent fall in average energy as n/N increases even further reflects the fact that coloumb encounters have decreased the population in the neighbourhood of the first excitation potential and have redistributed these electrons primarily into lower energy regions. A small number of electrons are also redistributed into the very high energy tail of the distribution. Ultimately, when n/N becomes large enough so that the rate at which electrons exchange energy with each other greatly exceeds the rate at which they gain energy from the field, the distribution function becomes Maxwellian.

The electron velocity distribution can be used to evaluate the transport properties of electrons. The electron conductivity and diffusivity are used to determine the spatial distribution of charged particles in a plasma and the rate at which the energy is transferred from the sustaining electric field (410).

The transfer of energy to the plasma occurs principally through the action of electric field on the free electrons.

2.3 Chemical Reactions Occurring in Plasma

Since various chemical reactions occur in plasma, in this part a very brief description is given for reactions between electrons and oxygen molecules. Fig. 2.3 explains the potential energy diagram for O_2 (410). The ground state is given by spectroscopic symbol $x^3 \Sigma g$. Above this lie four higher states $a' \Delta g$, $b' \Sigma_g^+$, $c^3 \Delta u$, and $A^3 \Delta_u^+$, all of which dissociate into ground-state atoms. Oxygen in the metastable $a' \Delta g$ state is known as 'singlet' oxygen. This species is long lived and participates in a number of chemical reactions in oxygen discharges. The next highest state is the $B^3 \Sigma_u^-$ and vertical excitation to this state from the ground state leads to dissociate-ion producing, one ground-state atom and one singlet O-atom. Further excitation leads to the ionization of the molecule and the formation of O_2^+ in the $X^2 \Pi g$ state.

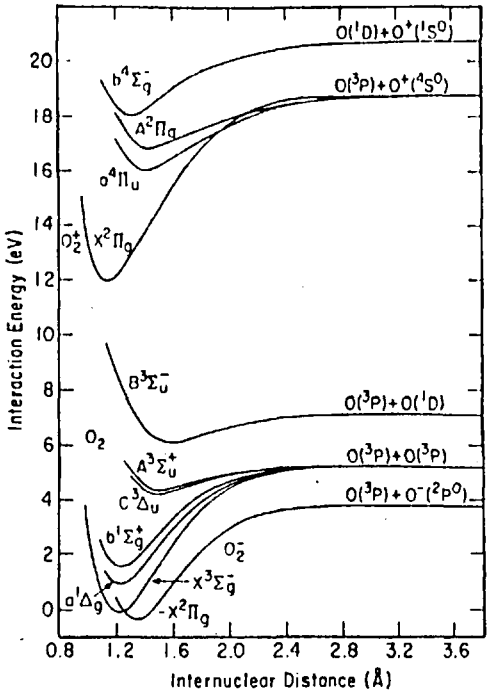


Fig. 2.3 Potential Energy Curves for some States of O_2^-, O_2 and O_2^+

Electrons colliding with molecules of oxygen undergo either elastic or inelastic collisions where at low energies, the principal inelastic processes are the excitation of rotational and vibrational levels of ground-state O_2 (128, 160). For electron energies above 1 ev it becomes possible to excite higher electronic levels and the cross section rises rapidly at threshold energy. Due to electronegative nature oxygen forms negative ions either by direct or dissociative attachment. At steady state the rate of energy gain from the field just balances the loss of energy due to electron molecule collision as well as other losses.

The fractional energy losses in oxygen plasma and the determination of effective ion temperature as a function of applied field are illustrated (410, 341).

The value of Ee/p in a plasma plays an important role in determining the properties of the plasma and the rates at which chemical processes, occurring in it, proceed. So a method is developed to predict Ee/p both at breakdown and steady state operating conditions

(342, 343, 410).

Production of atomic oxygen in a microwave discharge, the rate of oxygen dissociation and the loss of atomic oxygen due to homogeneous and heterogeneous processes in a discharge are illustrated (198, 215, 129, 250, 410).

2.4 Reactions of Atomic Oxygen with Hydrocarbons

There are three ways in which oxygen atoms can attack hydrocarbon compounds: (i) hydrogen abstraction (ii) by addition to double bond, sometimes followed by fragmentation of the addition complex (iii) by entry in C-H or C-C bonds (412).

2.4.1 Hydrogen Abstraction

Harteck and Kopch (159) found that CH_4 reacted to the extent of only about 1% at room temperature and 6% at 190°C, giving products H_2O and CO_2 in the ratio 2:1. Ethane reacted up to 5% only and n-butane also reacted very slowly, several hundred times slower than the butenes(70, 71). Benzene and toluene also reacted about one hundred times slower than olefines, during these reactions OH bonds are excited and it was calculated that the initial step could be,

$$O + CH_4 \longrightarrow OH + CH_3$$

followed by a very fast reaction between the radical and an oxygen atom.

2.4.2 Addition to a Double Bond

Geib (161) suggested a step-wise reaction of atomic oxygen during the additon to a double bond,

$$O + C_2H_2 \longrightarrow [C_2H_2O]$$
$$O + C_2H_2O \longrightarrow C_2H_2O_2$$

The main reaction for olefines is the addition of an oxygen atom to the double bond which produces epoxides and carbonyl

compounds. The addition occurs preferentially at the less substituted carbon atom in the double bond, and probably produces a biradical, the deactivation or rearrangement of which then results in the formation of main products observed.

Fragmentation following the formation of addition complex is likely to occur more readily for simple olefines such as ethylene or propylene where the energy rich intermediates have fewer degrees of freedom in which this energy can be distributed. Hence the extensive decompositions found in discharge experiments with such compunds at normal temperatures and the addition compounds which result from the condensation of the products at very low temperatures (412).

2.4.3 Reactions of Atomic Oxygen with Compounds of H, C and O

When HCHO was reacted with atomic oxygen (412, 70, 71), then 40% CO, 40% H_2, and 20% CO_2 was obtained; the mechanism of reaction is as given,

$$O + HCHO \longrightarrow CHO + OH$$
$$CHO \longrightarrow CO + H$$
$$H + HCHO \longrightarrow H_2 + CHO$$
$$O_2 + CO \longrightarrow CO_2 \text{ etc.}$$

CHAPTER 3

3. DESIGN AND DEVELOPMENT OF THE PLASMA APPARATUS

3.1 Description of the Reactor Design

A suitable design and scale up of plasma reactors have not yet been developed and are still a topic of active research. A brief summary of the physical elements to provide a quantitative description of reactor performance is given here.

The main factors which influence the reactor size and geometry are gas pressure, flow rate, discharge power and the source frequency. All of these factors vary at the discretion of the designer. On the other hand gas velocity (profile) and temperature within a reactor are also very important for the product yield. The size and the geometry of the reactor depends upon the choice of source frequency. Most plasma applications utilize an electrodeless discharge. Either a radio frequency (r.f. $1-10^2$ MHz) or a microwave (10^2-10^4 MHz) source of power may be chosen. The former offers a great deal of flexibility in the choice of reactor size and geometry since the external electrodes or coils used to supply energy can be made of any size or shape desired. The major disadvantage of r.f. discharges is their tendency to give a non uniform glow because the glow concentrates near the sustaining electrodes. This effect increases with the discharge gap size and the gas pressure. The velocity profile of gas when it flows through the reactor has a notice-able effect on the product yield. The rate of electron-molecule reactions in the region where the glow is concentrated is higher at the centre of gap, leading to a non-uniform rate of production of the active species. The portions of the gas nearer the walls travel more slowly and therefore would have a longer residence time than the portions of gas moving along the centre line. The combination of more intense rates of reactions and larger residence time in this region contribute to a higher yield of the active species.

The temperature profile also effects the rates of the reaction significantly and it is therefore a very important factor to be considered for a set of operating conditions. Since an accurate

measurement of the gas temperature in a glow discharge is not possible due to practical limitations therefore one should rely on the empirical observations. As it is necessary to know the fraction of the dissipated electrical power converted into molecular kinetic energy by the elastic electron-molecule collisions; self absorption of radiation released by plasma and exothermic reactions occuring both in the gas phase and at the container walls. The compensation for the above thermal energy is provided by the conduction of heat through the gas as well as by infra-red radiations. Bell and Kwong (44) described that the temperature remains fairly uniform throughout most of the discharge but decreases in the vicinity of cylindrical wall, and greater is the power the greater is the temperature.

It is however possible to examine the problem of the reactor design in terms of relatively simple model, if the effects of the spatial variations in the gas velocity and temperature could be excluded. Bell (410) has described a reactor modelling procedure by considering the overall kinetics for the formation of atomic oxygen. Generally a modelling procedure can be divided into three stages: (1) identification of the mechanism by which atomic oxygen is formed and lost and an evaluation for the rate constants for these primary reactions; (2) derivation of an expression for the net rate of atomic oxygen production and (3) estimation of the electron density and the average energy as a function of the chosen operating conditions. The rate of the dissociation of oxygen can be calculated by the methods described in the literature (44, 285, 410).

3.2 Description and Development of the Organic Asher

The schematic diagram of the organic asher is described in Fig. 3.1. A borosilicate glass plasma tube (A)is connected by PVC tubing to the oxygen supply at (B) and pressure gauge at (C). The pressure gauge (D) indicates the internal pressure of the plasma tube. The plasma tube is surrounded by a r.f coil (E), which produced an intense oscillating field. Oxygen is admitted via an air filter (H) and a flow meter (60-600 ccs/min) (L) to the plasma tube (A) through a capillary tube (B). The radio frequency coil (E) and oscillator (J) were cooled by cold water. An air pump (M) is also

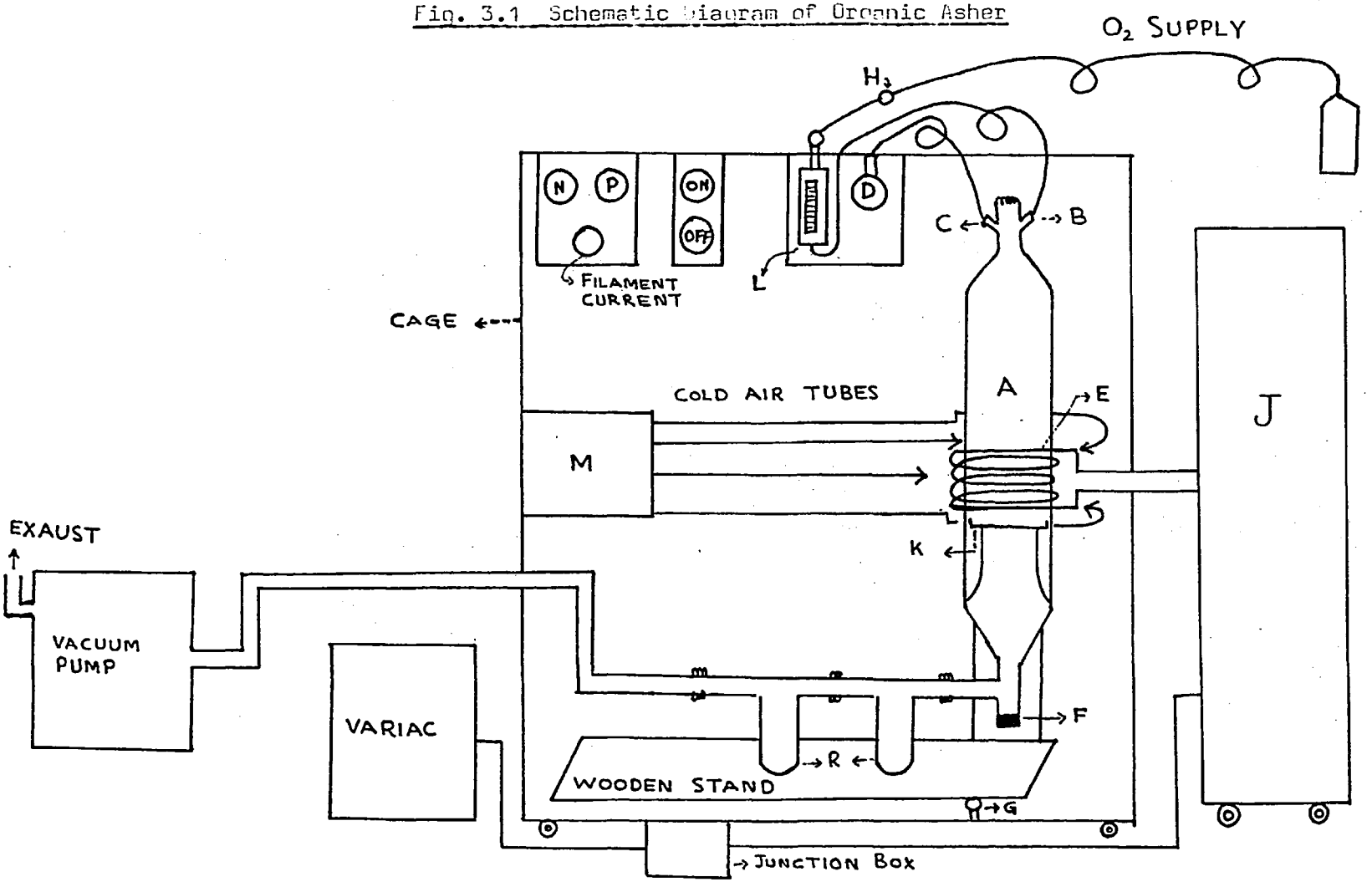
used to cool the r.f. coil and the reaction chamber below r.f. coil in the plasma tube.

The gas flow rate is controlled and measured by an anode voltage meter (N) and anode current meter (P) mounted on the cage. The temperature of the reaction chamber was measured by a thermometer (the hole at the base of the reaction chamber) inserted from the part F. The plasma tube has a ground glass joint with the reaction chamber. The samples were placed on the Petri dish (K) for oxidation in the reaction chamber. The exaust gases were passed through the traps (R) and pumped out to the main ——— system (S). The height of trap tubes (R) and reaction chamber (K) can be controlled by a screw (G). The samples were placed at 6•5 cm from the lower end of the r.f. coil. A 13•56 MHz frequency was supplied by a conventional radio frequency oscillator (J). The gas pressure in the plasma tube was lowered to 0•5–2 torr, in order to establish the discharge. To find optimum conditions of oxidation a number of experiments were performed at different power, flow rates, and distance of petri dish from the r.f. coil.

3.3 Electronics in Radio-Frequency Equipment

A suitable apparatus for electrodeless discharge of oxygen has been described by several authors (125, 126, 410). The discharge was sustained by high frequency electric field produced by radio frequency power supply, and the energy of the field was introduced to the gas by means of a coil surrounding the plasma tube. The efficiency and flexibility of converting energy to the gas depends upon the design of the reactor. In the earlier designs a direct connection between the radio frequency power amplifier and a resonant LC tank has been employed (125, 126), where the plate impedence was several hundred ohms. In these designs the LC tank and the associated gaseous discharge approximated a several hundred ohm termination, therefore only a small fraction of the generated power could be delivered to the load. The impedence mismatch resulted into over heating the power amplifier. Similarly other methods like link coupling and the use of polygonal inductors have also been employed (125, 126).

Fig. 3.1 Schematic Diagram of Organic Asher



In the present work the radio frequency system which has been employed, consisted of a high frequency generator which produced 13·56 MHz, an impedence matching net-work which transforms the impedence of the generator to that of the load, a device for applying radio frequency field to the reactor, a reactor, and a device for measuring r.f. power supplied to the discharge.

Fig. 3.2 illustrates the circuit diagram of the supply and inter connections in the radio frequency system. Three phase electrical supply was supplied to the circuit breaker (A) (15A 500V), the fuse box (B) (20A 500V), junction box (C) and to the r.f. generator (D). From the r.f. generator (D), the three phase supply was passed through the junction box (C) to the variac (0-415V) (E) and then back to r.f. generator (D). A one phase supply was provided to the vacuum pump (F) and an airpump (G).

High voltage discharges generally require less equipment therefore offers greater flexibility and ease of operation and probably more suitable for laboratory as well as for large scale use. A frequency range from about 2-60 MHz has been found to be the most convenient because the dimensions of the r.f. coupling elements allow easy handling (410).

3.4 Specifications

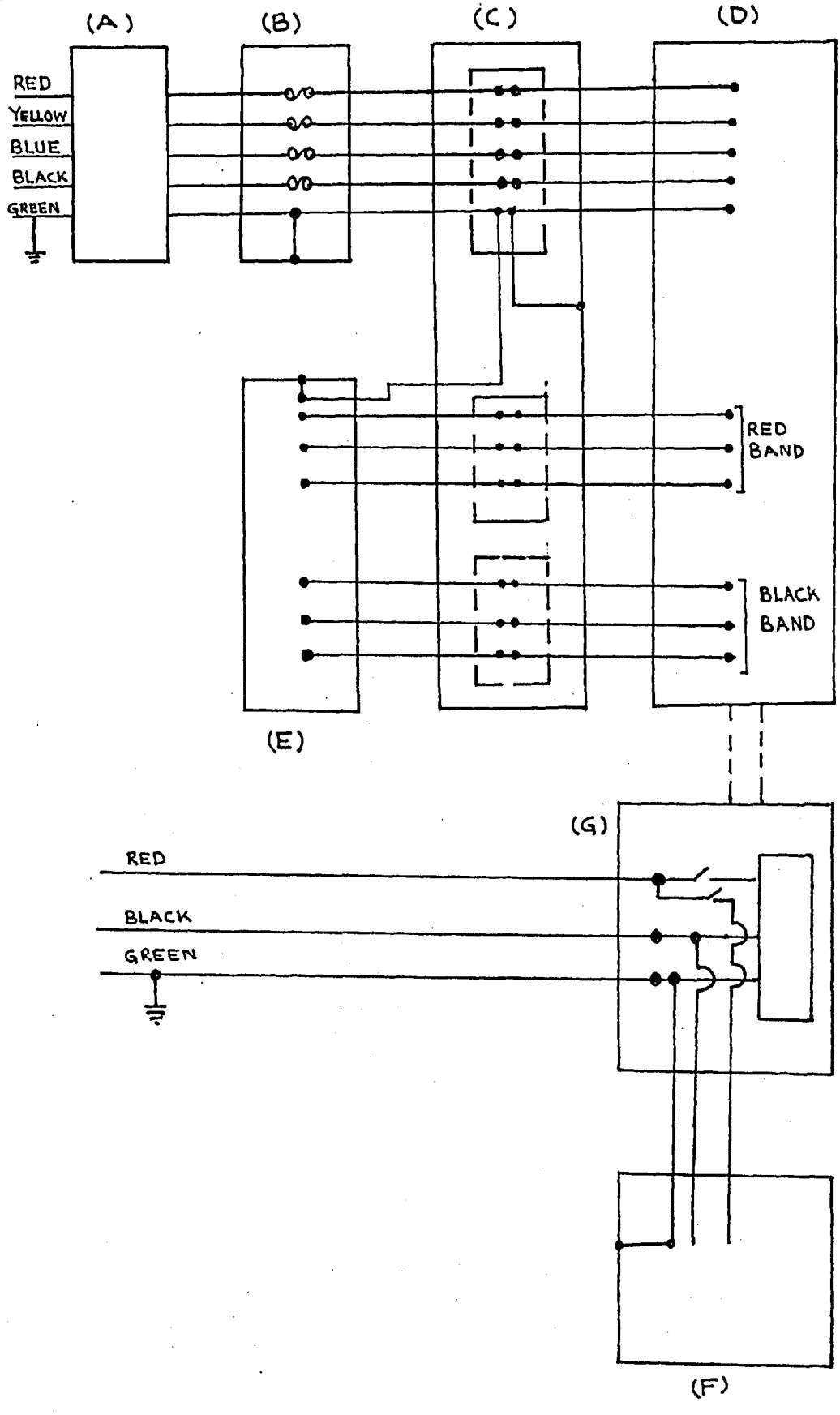
The specifications of the organic asher used in this project, are as follows:

operating frequency	=	13·56 MHz
ON FULL LOAD (PLASMA ON)		
Maximum k.v.	=	6·0-6·5 kv
Maximum Anode current	=	2A
Grid current	=	450-500 mA
Grid current unloaded	=	650-700 mA

3.5 Development of the Sample Holder

A round bottom flask with a ground glass joint and two outlets

Fig. 3.2 Electrical Supply and Inter-Connections of Organic Asher



(Fig. 3.3a) was designed to hold the sample boat. The ground glass joint (B) was clamped to the plasma tube (A) in Fig. 3.3b. The sample inside the round bottom flask was kept in a long stem, high edged Petridish (O.D. 5 cm) so that it could reach well inside the plasma tube (A) (6·9 cm i.d.). The Petridish could be taken out for loading and unloading by opening the ground glass joint. The distance between the Petridisn (P.d.) and r.f. coil was 7 cm. More than fifty observations for the optimum rate of oxidation was carried out by using this type of sample holder at constant power and flow rate.

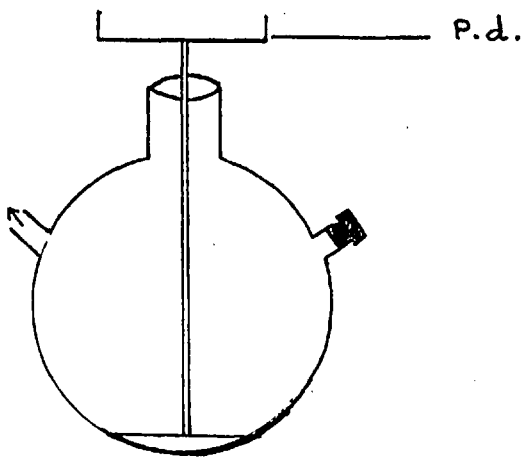


Fig. 3.3a Round Bottom Flask

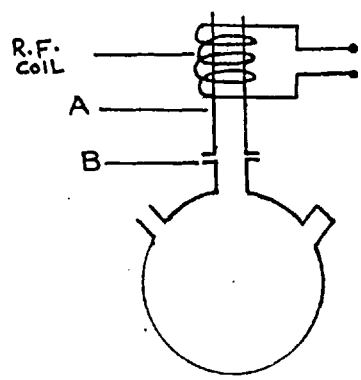


Fig. 3.3b

It was suspected that the observed rates of oxidation might have been lower due to the flow of plasma through the gap between the P.d. (5 cm) and plasma tube (6 cm), therefore glass wool was spread onto the Petridish and the sample (Whatman Filter Paper No. 1) was placed over it. A higher rate of oxidation (0·015 g . min^{-1}) was observed as compared to (0·0077 g . min^{-1}) in the previous case. The average weight of the sample was 0·211 g. The observed higher rate of oxidation in the later experiment was evidently due to: (1) even flow of plasma and that (2) the edges of Petridish were covered. It was concluded that the Petridish should have a diameter nearly equal to the internal dia of the plasma tube, and that the sample surface should be paralell to the edge of the Petridish.

A Petridish with 16 holes (3 mm) was designed and the sample was oxidised on it. The rate of oxidation was found to be 0·0075 g .min^{-1}.

This rate of oxidation (0•0075 g . min^{-1}) was lower than the previous (0•015 g . min^{-1}) because after a part of the sample had been oxidised the plasma had probably an easy passage through the holes in that part and therefore did not effect the rest of the sample. Later on it was concluded to use a sample boat with small pores of equal sizes so that the plasma could penetrate easily and the sample boat should fit into the plasma tube (6•5 cm).

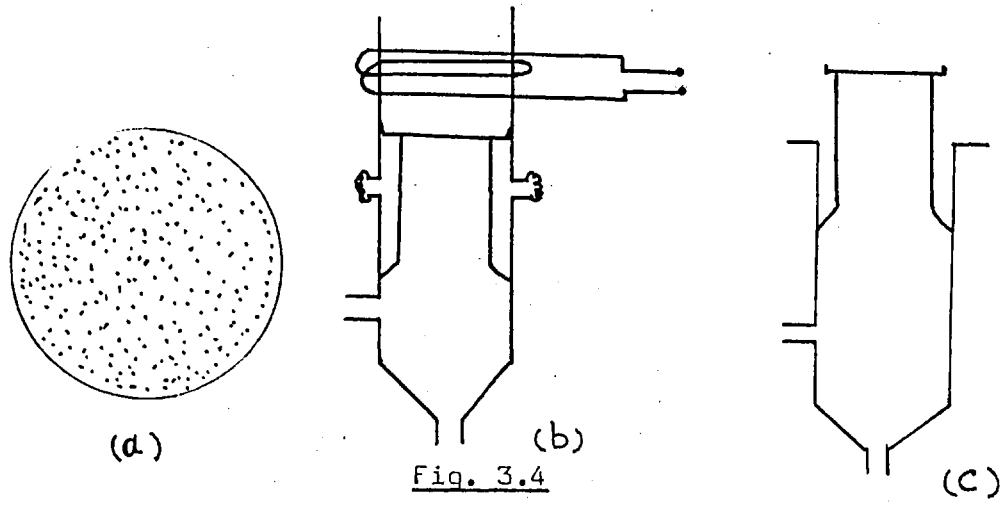


Fig. 3.4

A porous glass slab 3.4a(3 Porosity) was chosen to put the sample on it. A higher rate of oxidation (0•014 g . min^{-1}) than the previous (0•0075 g . min^{-1}) was obtained by this method but it had limitations of loading and removing the ash of the sample after complete oxidation. The rate of oxidation increased due to even holes in the glass slab.

Keeping these factors in view a sample holder given in Fig. 3.4c was finally designed. A Petridish of 6cm diameter having 116 even holes (1-3mm) allowing a uniform passage of the plasma through it was selected. The sides of the glass wall were joined at point A to prevent the plasma to pass through the gap. A higher rate of oxidation (0•015 g . min^{-1}) was obtained. This sample holder was adopted for oil as well as for coal samples. The samples were put on a petridish which was placed on top of the sample holder. The lower part B of the sample holder was made in such a way that a thermometer or thermocouple could be inserted through for measuring the temperature of the surroundings of the Petridish.

3.6 Measurement of the Temperature

The increase in the ashing temperature is related to the loss of the volatile material during the ashing of oil or coal samples. The ashing temperature varies with the power as well as the pressure inside the plasma tube. As a result of increasing the ashing temperature the rate of oxidation and the percentage recovery of the volatile elements decreases. The surface temperature of the sample is quite different from the bulk temperature (126). Gleit (125) found that the surface temperature of the wall of the discharge flow tube can effect the plasma oxidation rate for carbonaceous compounds. As the temperature increases the oxidation rate decreases.

Infra red radiation pyrometers and pigments for the measurement of the temperature have been used (125). Thermo-couples have been recomended by Bell and Kwong (44) and Hollahem and Bell (410) but they might be affected by radio frequency field.

A thermometer was used through an air tight hole at the base of the sample holder tube. The thermometer was held to touch the base of the petridish and therefore the temperature of base was monitored and it was assumed that the temperature was the most probable temperature of the sample surface. The temperature was recorded by varying the power at a constant flow rate (Fig. 3.5). It was noted that the temperature increased with an increase in the power. The rate of oxidation also increased with the increase in power. It was difficult to sustain the plasma at and above 500 W for a flow rate of 250 ccs/min and for the reactor in use. The temperature of the sample increased as the oxygen flow rate was increased due to an increase in the rate of recombination of oxygen atoms. For a given power level there is an optimum rate of oxygen flow to achieve higher rate of oxidation.

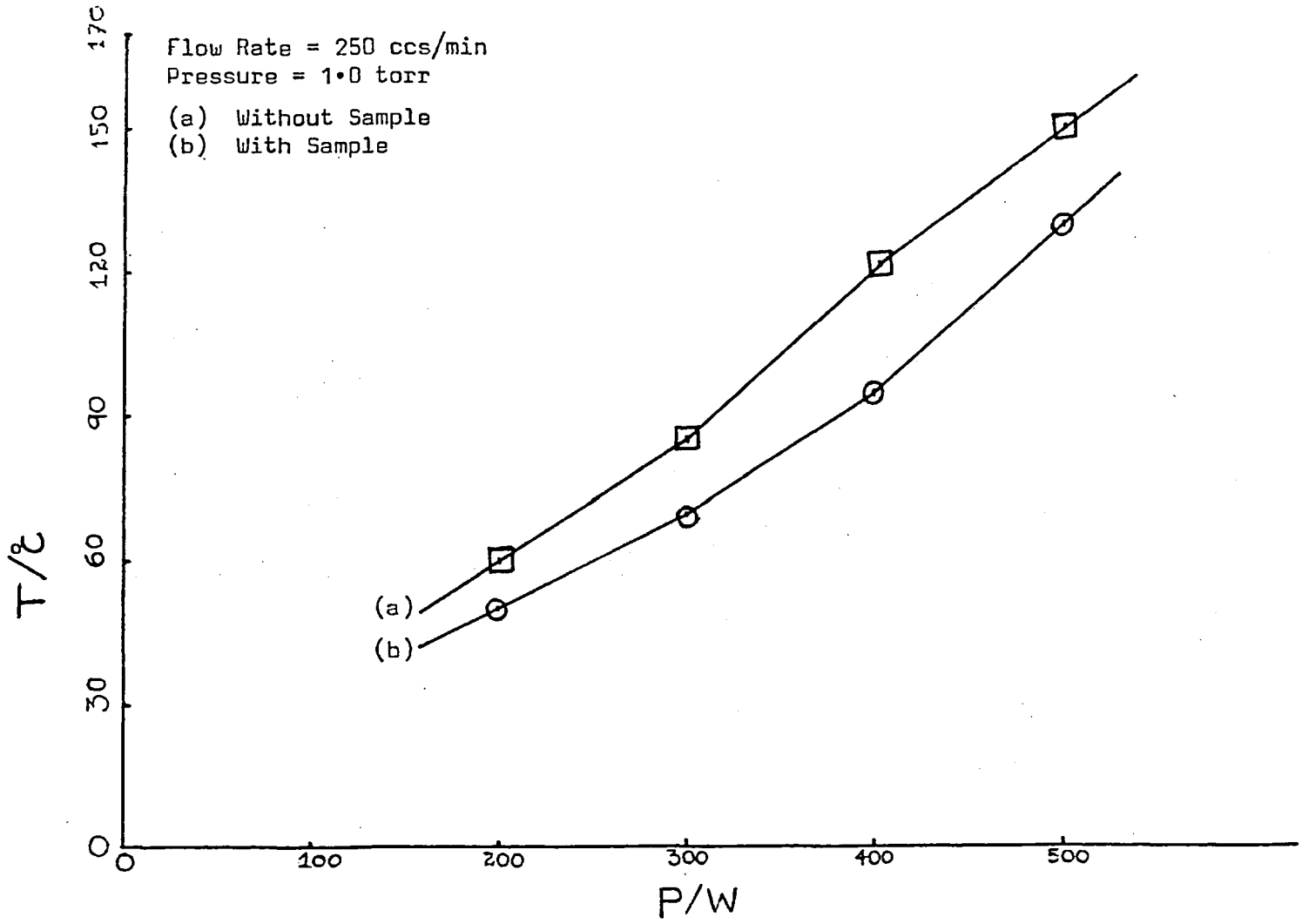


Fig. 3.5 Temperature (T) as a Function of Power (P)

Table 3.1

Measurement of Temperature at Different Power and Flow Rate = 250 ccs/min, Pressure = 1·0 torr

NO.	Power W	Temp. with Sample °C	Temp. Without Sample °C
1	200	50	60
2	300	70	85
3	400	95	121
4	500	130	150

3.7 Rate of Oxidation as a Function of Power and Flow Rate

Fig. 3.6 shows the rate of oxidation of filter paper (0·211 g) measured by varying the power (100–500 W) at constant flow rate (250 ccs/min) and pressure. The ashing of filter paper was recorded as a function of time. The rate of oxidation increased rapidly from 100 W to 400 W but after that it levelled off. The filter paper sample started charring above the power level of 400 W. When the power was increased from 100 W to 200 W a 25% increase in the rate of oxidation was observed. From the power level of 200 to 500 W the rate of oxidation was found to be $1{\cdot}7 \times 10^{-3}$ mg/min/ . As the power was increased the rate of oxidation and the temperature increased.

Fig. 3.7 shows the dependence of the rate of oxidation for Whatman filter paper No. 1 on the flow rate of oxygen in the plasma tube. The pressure was not controlled independently, so when the oxygen flow increased the system pressure also increased. The rate of oxidation at two power levels (a) 250 W and (b) 500 W was measured. Two different rates of oxidation were obtained at (a) and (b) in Fig. 3.7 for the same flow rate, (e.g. at oxygen flow rate of 200 ccs/min) the rate of oxidation observed for 250 W was 10·3 mg . min^{-1} and for 500 W was 20·6 mg . min^{-1}. The plasma was very intense below flow rate of 200 ccs/min at power 500 W, (the paper catches fire) so this range was not selected. In (a) Fig. 3.7 the rate of oxidation increased from the oxygen flow rate of 100 ccs/min to 200 ccs/min, and in (b) the rate of oxidation increased linearly from flow rate of 300 ccs/min to 450 ccs/min. After that the rate of oxidation rapidly decreased.

Fig. 3.6 Rate of Oxidation (Ra) as a Function of Power (P)

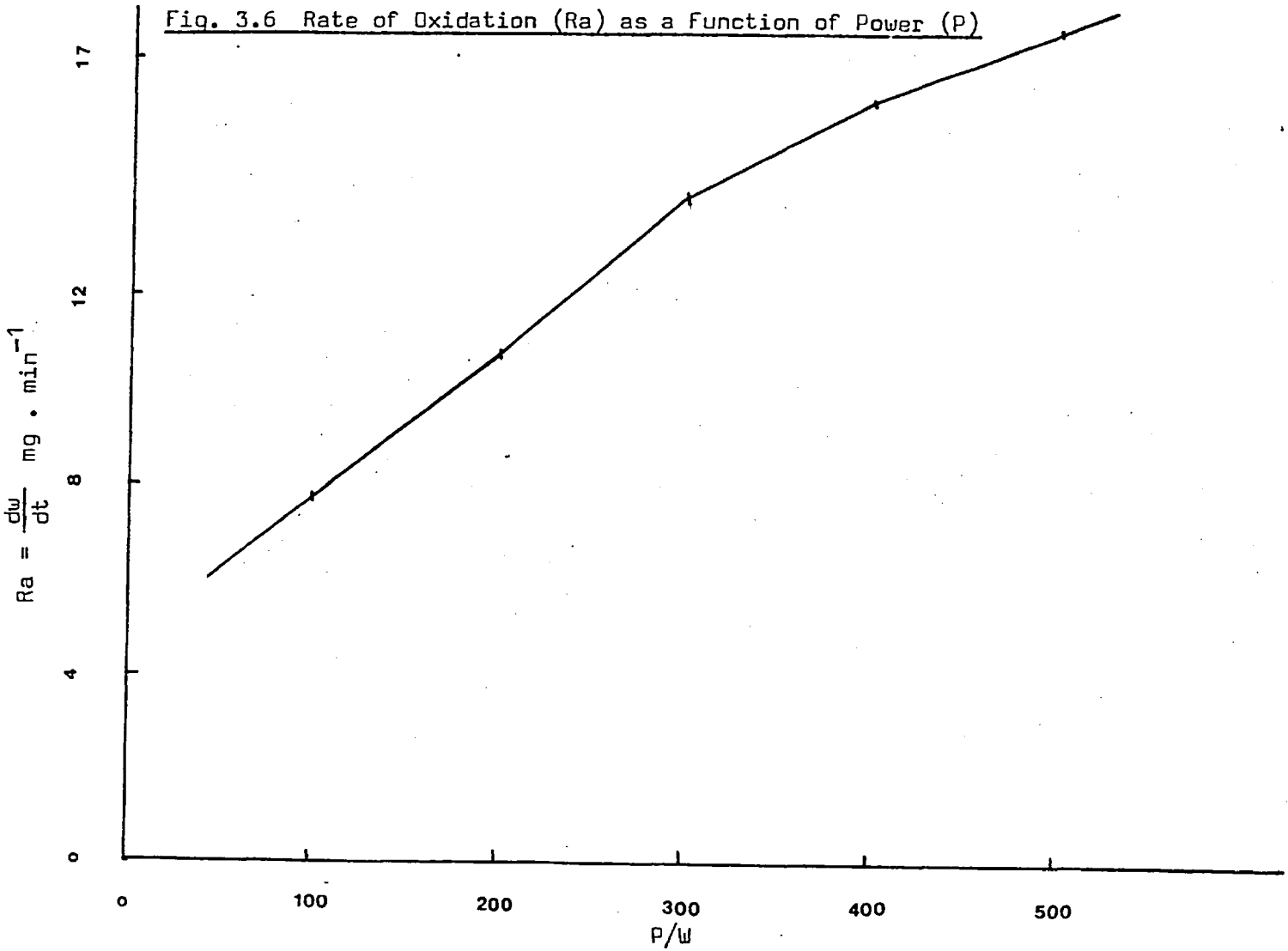
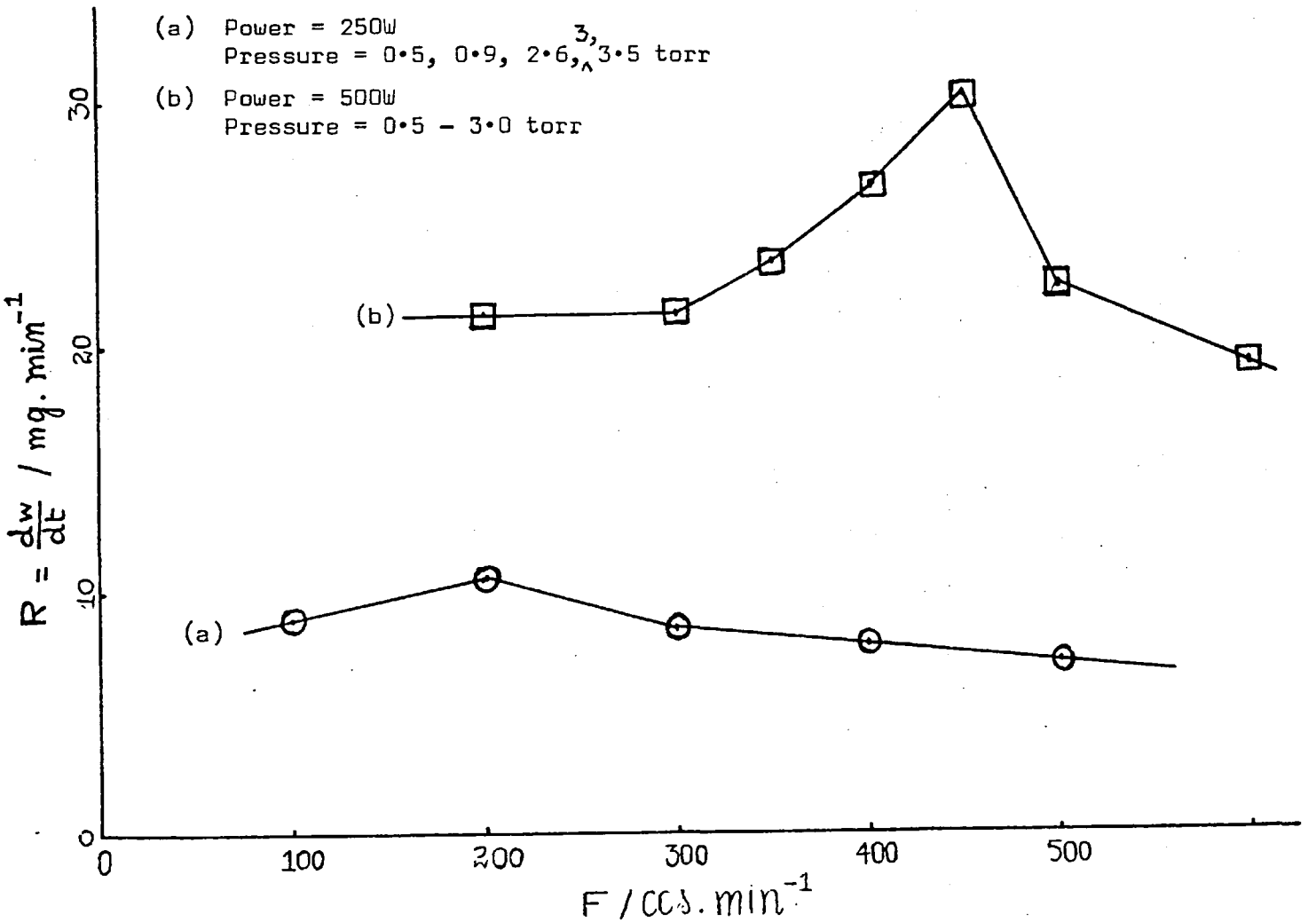


Fig. 3·7 Rate of Oxidation (R) as a Function of Flow Rate (F)



It was found that oxidation rate was a function of exposed sample surface to the plasma, and decreased markedly as the surface became covered with a mineral residue. The oxidation rate was highest in the coil region where the electric field was greatest and it fell quite rapidly as the sample surface was moved few centimetres away from the coil.

3.8 Discussion

The radio frequency discharge technique offers a convenient method of decomposing a wide range of organic substances. The higher rates of oxidation (R.O.) were obtained at high power and low pressure ——————— (Fig. 3.6). The response of R.O. to variations in the experimental variables was different, the best R.O. is obtained at intermediate powers and low pressures (Fig. 3.6 and 3.7). The slow increase in the rate of oxidation with power 300 W to 500 W (Fig. 3.6) suggests that the arrangement employed does not fully utilize the excited oxygen species. When the rate of oxidation does not increase with the increase in the power then the further increase in the power serves only to heat the sample additionally and at that point an incipient thermal oxidation starts. By using a minimum power the needless heating of the sample can be avoided. Thus in order to retain the trace metals in oil and coal samples and to achieve a satisfactory rate of oxidation the power chosen was between 200-250 W.

The gas temperature in a stagnant discharge has been found to rise rapidly with power (Fig. 3.5 and 7.1). Increase in pressure produced a slight increase in the temperature as did increase in the flow rate. The later effect was attributed to the gas composition which at high flow rates contains more molecular oxygen and hence has a lower thermal conductivity. The results in Fig. 3.5 and 3.7 indicate that the elevation in the gas temperature might have reduced the gas density thereby the dissociation rate was lowered or it has increased the surface recombination ratio (261, 262, 410). The temperature was decreased when the flow rate was decreased (Fig. 7.1). because at lower flow rates the extent of dissociation was increased, leading to a gas containing more atomic oxygen (261, 410). The thermal conductivity of atomic oxygen is greater than that of molecular oxygen therefore a greater loss of heat by conduction will take place by the

presence of large fraction of atoms. As a result the gas composition present at a lower flow rates (Fig. 7.1) should cool more rapidly and attain a lower temperature than the gas present at high flow rates.

The optimum rates of oxidation require a balance of radio-frequency input power, gas flow through the system and the gas pressure within the system. Fig. 3.7 indicates that the rate of oxidation increased with the increase of flow rate until more oxygen (500ccs/min) is present than the energy density (power) to cause excitation. Thus a further increase in the oxygen flow rate does not significantly promote the rate of oxidation, because at higher discharge pressure or gas flow rate atomic oxygen recombination occurs at greater extent which lowers the rate of oxidation (410). In Fig. 3.7a the oxidation rate decreased when the flow rate and the pressure was increased at and above 200 ccs/min. The power was kept constant. The variation in the rates of oxidation of filter paper with increasing pressure at constant power will also be dependent upon the geometry and the efficiency of the reactor Since the later determines, to some extent, the production and utilization of atoms. An increase in the pressure reduces the average mean free path of the electrons. As a consequence they pick up less energy between collisions. An increase in pressure (>2·5 torr) thus shifts the electron energy distribution to lower values and reduces the rate constants for inelastic collisions. At lower pressures (0·1–2 torr) most of the energy imparted to the gas is carried away as the kinetic energy of the free electrons. At higher pressures (> 3 torr) greater portion of the energy is transferred to the atomic species and at still higher pressures the recombination and the de-excitation reactions between species are more frequent (261, 262, 410, 414). Thus in order to achieve a higher rate of oxidation and to retain the trace metals after ashing an oxygen flow rate of 150–170 ccs/min for a power level of 200–250 W was selected.

The foregoing determination of the rate of oxidation as a function of plasma conditions is a qualitative measurement since accurate statement of the power, pressure and flow rate values is related to and characteristic of the specific design of the plasma system used in the experiment and to the nature of the sample material. Since the energy of the electrons depend on the dimensions of the reactor, a decrease in the plasma tube diameter would increase the average energy of the electrons.

CHAPTER 4

4. ATOMIC ABSORPTION SPECTROMETRY

4.1. History

Spectroscopy has its beginnings in 1663 when Sir Issac Newton discovered that white light could be resolved into its constituent colours by the use of a prism. In 1802 Wollaston (419) reported the presence of dark bands in the continuum emission spectrum of the sun. Later on it was studied in detail by Fraunhofer (99). In 1860 Bunsen and Kirchhoff (182, 183) developed a spectroscope of high sensitivity, with which they domonstrated that the visible lines were due to the atomic emission of various elements which resulted in the discovery of Cs, Rb, Tl, In and Ga. By 1955 a wide range of elements could be determined by Atomic Emission Spectroscopy. Later Walsh (370) published his highly significant paper on the possibility of highly selective method of quantitative trace analysis by Atomic Absorption (AA). Alkemade and Miltz (2) postulated the feasibility of an Absorptic Flame Photometer for the analysis. Walsh and his co-workers (290) determined 15 elements by using AA which therefore was established as an analytical technique.

Since 1957 there have been many publications on the application and improvement of Atomic Absorption and Atomic Fluorescence (3, 89, 202, 222, 291, 204, 314, 371, 372). Reviews on the comparison of AA and AF with other analytical techniques have been published by West, Winefordner and Manfield (376, 377, 378).

4.2. Theory

In view of the large number of books and literature available (184, 202, 272, 313) on the subject only a brief theoretical outline of Atomic Absorption will be given in this thesis.

When electromagnetic radiation characteristic of electronic transitions in the outer orbitals of atoms of a particular element is passed through an atomic vapour of that element, the radiation at certain frequencies is attenuated. The absorbed radiation excites electrons from the ground state to various higher energy levels

(excited states) and the degree of absorption is a quantitative measure of the concentration of ground state atoms in the vapour.

Consider two steady states designated i and j (corresponding to energies E_i and E_j, where $E_j > E_i$) the transition between these states will result in the absorption or emission of radiation with a characteristic frequency,

$$E_j - E_i = h\nu_{ji}$$

$$\nu = \frac{E_j - E_i}{h}$$

where h is the Plank's Constant.

The degree of absorption depends upon the length of the path traversed and the lower energy state population and it can be described by an analogue of Beer and Lambert's Law,

$$I = I_o \exp(-K_c l)$$

$$A = -\log 10 \frac{I}{I_o} = 0{\cdot}434\ K_c l$$

where I = intensity of the transmitted light

I_o = intensity of the incident light

l = absorption path length

K_c = absorption co-efficient at frequency ν

A = absorbance

The absorption ———— may then be linearly related to the concentration of analyte present.

The relative population of energy levels, that is the proportion of analyte species occupying them, has a direct bearing on line intensities and is determined by the spacings of the levels and the thermodynamic temperature. The relationship is expressed in the Maxwell-Boltzmann equation,

$$\frac{n_j}{n_o} = \frac{g_j}{g_o} \times \frac{e^{-(E_j / KT)}}{e^{-(E_o / KT)}}$$

where n_j is the number of atoms in the upper energy state (energy E_j), n_o is the number of atoms in the lower energy state (energy E_o), T is the absolute temperature, K is the BOltzmann constant, and g_j and g_o are the statistical weights of the excited state and ground state respectively.

4.3. The Shapes of Spectral Lines

The absorption is observed not at a discrete frequency, but over a small range, i.e. the absorption has a finite width. If K (degree of absorption) is plotted against V, a typical result would be that shown in Fig. 4.1.

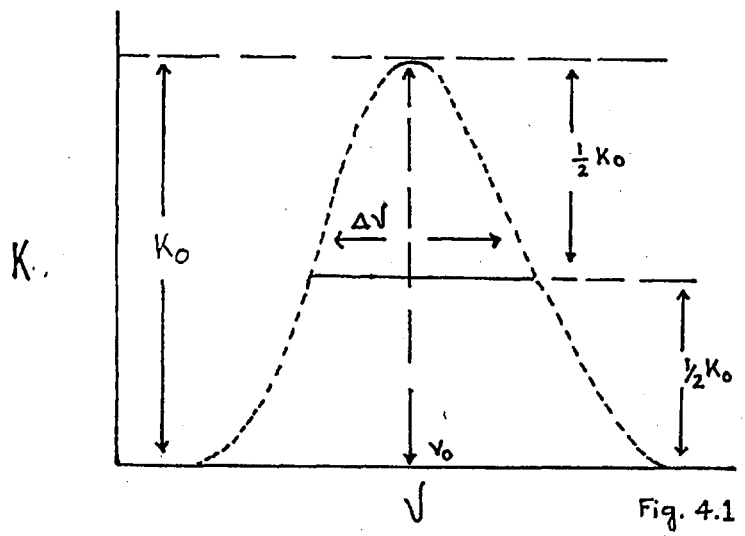


Fig. 4.1

K_o is the maximum value of K

ν_o is the value of ν at the peak

is called the half width of the line, and is the width at half the height of the line.

$\Delta\nu$ is called half width of the line.

The finite thickness of the absorption line can be attributed to the following main causes (373).

(a) Natural Width (10^{-5}nm)

This arises because the atom in the excited state has a finite

life time . It is given by

$$\Delta\nu_n = \frac{1}{2\pi T}$$

(b) Doppler Broadening (10^{-1} - 10^{-3} nm)

This is due to the random thermal motion of the atom relative to the observer. If an atom has velocity V_x relative to the observer, then the observed frequency of absorption is displaced from original line centre V_o by $\Delta\nu$, where

$$\Delta\nu = \frac{V_x}{c} \cdot V_o$$

c = velocity of the light.

The simplified half width of the line due to Doppler broadening ΔV_D is determined by,

$$\Delta V_D = \frac{2V_o}{c}\sqrt{\frac{2\ln 2RT}{M}}$$

where M = atomic weight, R = gas constant and T is the absolute temperature.

(c) Lorentz Broadening

Lorentz broadening (or collision or pressure broadening) is due to the collision of foreign gas molecules with the analyte atoms and increases with increasing pressure of foreign molecules, associated with the shift of line centre (205, 379).

Other forms of broadening encountered include resonance broadening caused by the collisions with the atoms of the same kind. The Stark and Zeeman broadening are caused by the splitting of the atomic line by the effect of electric and magnetic fields on the energy levels.

4.4 Instrumentation

A diagram of an Atomic Absorption Spectrometer is shown in Fig. 4.2. It consists of a sharp line radiation source (Hollow Cathode Lamp) characteristic of the element of interest, a means of producing an atomic vapour of the sample, e.g. a solution nebulizer and a burner, and a monochromator, a photomultiplier and recording system. The purpose of monochromator is to isolate a particular emission line from a number of characteristic lines emitted by the hollow cathode lamp. The components are aligned so as to allow radiation from the lamp to pass through the flame and then via the monochromator to the detector. The measurement of the absorption is made by comparing the intensities of radiation reaching the detector with and without the sample solution being aspirated into the flame.

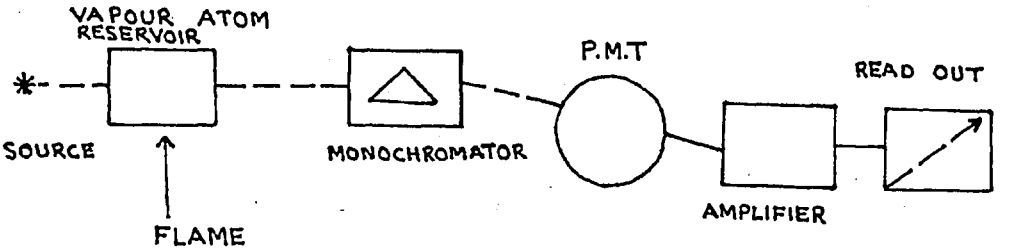


Fig. 4.2 Schematic Diagram of
Atomic Absorption Spectrophotometer

Most scientific publications in AAS have been devoted to the source and the means of converting the sample to an atomic vapour.

4.4.1 Sharp-Line Sources

In AA ——— spectroscopy the design of spectral source is of great importance because the emission line should have a half width less than that of the corresponding absorption line. The most suitable and widely used source which fulfills the requirements is hollow cathode lamp (HCL) (145, 352). In 1959 Walsh (300) reported that the atomic vapour produced in HCL extends beyond the cathode. Later on he (114) described that metal sample was machined to a hollow cylinder. After filling with argon the sample became a hollow cathode and a current of 60 mA was passed. Fresh filler gas was

admitted, the discharge repeated and absorption measurement was made (114). Mass-mann(232) determined volatile metals in iron by a similar device. Aluminium (115) and Graphite (166) hollow cathode lamps were described by two workers. Mass-mann(230) developed a hollow cathode sputtering device which could be used at high temperature to reduce the chemical interferences for metal samples.

The cathode is fabricated with the element to be determined. By reducing the pressure inside the envelope and passing current at an applied potential, a low pressure glow discharge confined to the inside of the cathode and characteristic of the cathode material is produced. The action of the gas used to fill the system is to bombard the cathode thereby vaporizing atoms from the surface, a process known as 'sputtering'. The resulting emission spectrum contains lines from both the cathode material and the filling gas. The choice of the gases is restricted to those whose emission lines do not coincide with lines from the cathode itself and which will not ionize sputtered atoms , (e.g. Neon or Argon).

Electrodeless discharge tubes are also used as sources in AAS where radiation is derived from a sealed quartz tube containing a few milligrams of an element or a volatile compound and neon or argon at low pressure. The discharge is produced by a microwave source via a waveguide cavity and the emission spectrum of the element concerned contains only the most prominent resonance lines and with intensities up to one hundred times those derived from a hollow cathode lamp (78, 233).

Mossotti et al (231) used a pulsed laser microprobe into the light path of an atomic absorption spectrometer to atomise the surface of a solid sample.

4.4.2 Flames as Atom Cells

The flame is still the most popular medium for atomization, because, due to wide choice of fuels and oxidants, a satisfactory flame may be made to determine most elements. The solvent in the flame evaporates to form clotlets, which are converted to gaseous

state by fusion and evaporation, resulting in molecular dissociation to give a gaseous dispersion of mostly ground state atoms.

The flames should have adequate temperature to form active species and should be stable with suitable geometry. The molecular species are dissociated to atoms depending upon the dissociation energy, partial pressure of the species present, flame temperature and the residence time of the molecule in the flame. In the literature advantages (185), disadvantages(140) and the modification (141, 165, 186, 316, 294, 368, 380, 381) have been reported. The most generally useful flame is air-acetylene, with a moderate burning velocity and a temperature of about 2700 K. Hot nitrous-oxide acetylene flame (382) has been used to overcome incomplete atomisation (383) and stable oxides ——— formation. The elements like alkali and alkaline earth metals are easily ionized in flames and it may be necessary to add more readily ionized metal than the analyte to reduce this effect (4).

The disadvantage due to background emission arising from excited molecules and radicals in the flame gases are controlled by different workers (102, 187, 186).

4.4.3 The Use of Non-Flame Cells as Atom Reservoirs

Various non-flame cells have been designed to overcome the disadvantages of the flames and among these cells the graphite cell is probably the most succesful among all.

A fixed volume of the analyte is used in non-flame cells in order to overcome the low efficiency of solution transfer to the atom cells by flame cells. Winefordner (384) has calculated theoretically the efficiency of atomization by using a graphite cell (202).

The principle advantages of the non-flame cells are as follows,

(i) Smaller volume of analyte (0·5 - 1 µl) is required and the sensitivity and detection limit is expressed in absolute terms.

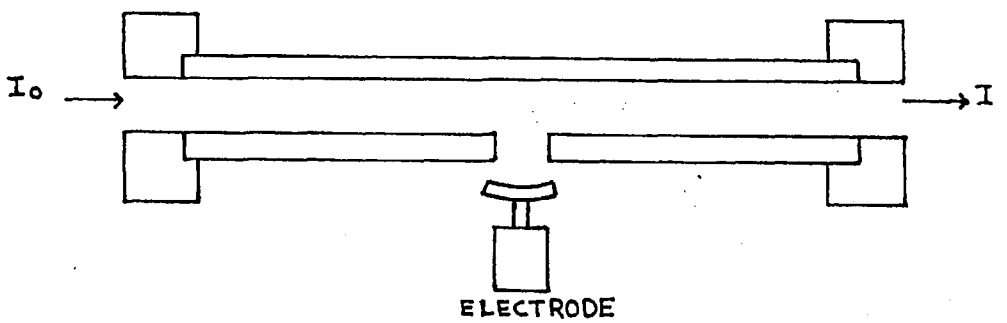
(ii) Solid samples can be used, and much lower concentration of the elements can be detected.

(iii) By selective volatilization matrix elements which might interfere can be easily removed from the surface of the cell if the vapour pressures of the analyte and the species differ sufficiently.

There are few disadvantages of non-flame cells too, where the dilution is unnecessary it is much faster to use a flame method. A good signal is obtained from flame in 10 seconds but non-flame cells would normally take about 30 seconds or sometimes even more (185, 385).

(a) Furnaces

The graphite tube furnace is one of the most popular non-flame cells for A.A. studies. The first furnace as atom cell used for analytical measurements was that of L'vov Cuvette, Fig. 4.3 (electro thermal) in which very high sensitivity was obtained (10^{-12}g for 1% absorption) (206-210).



I_o = Incident Radiation

I = Transmitted Radiation

Fig. 4.3 L'vov Furnace

In both flameless atom cells (furnace and filament) the temperature is raised rapidly to about 2500 K by the passage of a heavy current for a period of 1 to 2 minutes. Tube furnaces, which are usually 5 or 10 cm x 3 mm, may be flushed through with argon before vaporizing the sample so as to prevent the formation of refractory oxides. The axis of the furnace is aligned along the

optical path of the radiation from the lamp and as the vaporized sample is contained within this region, maximum sensitivity can be obtained.

Massmann(223) used a resistively heated graphite tube for both AA and AF, and obtained good sensitivity for aqueous solutions and later on high temperature for refractory metals (224, 266). He obtained detection limit of 1 ng for arsenic at low wave length (225), and later on a similar furnace (Perkin Elmer HGA-70) was used for the determination of copper and strontium in natural water (103), sea water (317), polyester fibres (211), vanadium and nickel in mineral oils (266) and air (267). There are more applications given in the literature (61, 104, 75, 105, 172, 257, 295).

Pickford and Rossi (273) used the furnace for multi-element analysis. Headridge and Smith (142) inductively heated the furnace by R.F. coils and determined trace metals in powder (226). A sealed tube type furnace (274), and Pt furnace nebuliser system (25) are used for metal analysis.

(b) Filaments

Filaments (electrically heated rods, metal strips or boats) release the atomic vapour which passes through an unconfined volume in the absorption or fluorescent light path and transient analytical signals are obtained. In filaments no further energy is available to prevent the condensation of atomic vapour.

A filament atom reservoir was first introduced by West and Williams (386) for the trace analysis. The cell consists of two stainless steel electrodes mounted vertically 22 mm apart, and the carbon filament was clamped between the upper ends of the electrodes. Kirkbright (185) applied "West Type" filament and determined Ni, V and Cr in TiO_2 (171), Fe in carbon fibers (1), Pb in blood and food-stuffs (58) and Co in soils (188, 227, 268). The major development in carbon filament atomization have been in the design (227, 349) and a filament model 61 Mini-Massmann CRA is used to determine metals in biological fluids (5, 26, 228), petroleum products (296)

and geological samples (27).

Later on Au (349) and Cu and Ag in gold (275, 297) were determined with good sensitivity..

Metal filaments (28) are also used for the determination of different elements (62) in AA. Platinum loops have been used with a microwave plasma to determine S, I, P and Hg by Atomic Emission Spectroscopy (219) and other elements in AF (229). Williams and Piepmeier (387) obtained 1% absorption sensitivity in the range of 3.10^{-10}g - 3.10^{-12}g for Mn, Fe, Mg, Cu, Cr, and Ca by using a filament of ordinary light bulb. Tantalum is the most popular metal for filaments making (76). Hwang et al (143) determined lead in blood with good sensitivity with a similar device. The advantage of tantalum over carbon is that it can be cooled easily and the speed of the analysis is high.

(c) Miscellaneous Non-Flame Cells

Walsh and co-workers (173) reported cathodic sputtering during the manufacturing of hollow cathode light source. Later on it was used as non-flame atom reservoirs (114, 388) for the determination of metals, i.e. silver in copper, and silicon and aluminium in steel. Massmann (230) determined solids by AA using hot cathode assembly, and in another technique sample is evaporated on to a graphite or alumina electrode (116).

A.C. arc in A.A. has been examined by Kautor and Erdy (189) where as Robinson (298) suggested a discharging spark into which a sample solution containing aluminium was sprayed.

Many workers have used radio frequency (RF) or microwave plasmas as atom cells in AA (29, 117, 106, 350, 389, 390). By this technique temperature can be controlled accurately, thus matrix effects can be minimised, and it also facilitates the determination of those metals which form refractory oxides. The efficiency of atomisation can be such that PO_4^{3-} does not interfere with calcium absorption.

Other methods of non-flame atomisation are laser excitation (231), electron bombardment (299), the a.c. arc (189), and ignition of pellets prepared from powdered sample and solid propellant powder (351).

The Delves cup has been developed for clinical analysis and is succesfully used for the determination of both lead (77) and cadmium (91) in small blood samples.

4.5 Interferences

Interferences in absorption measurements can arise from both chemical and physical sources. Spectral interference is rare because of the simplicity of the absorption spectra. Chemical effects include stable compound formation and ionization, both of which decrease the population of free atoms in the sample vapour and thereby lower the measured absorbance, e.g. reactions between alkaline earth metals and oxy anions (aluminates, silicates, etc.). Stable oxides can be dissociated by using a divided or hotter flame or incorporating complexing agents in the sample solution. Ionization of sample atoms can be suppressed by adding an ionization buffer (Li, Na & K)

Physical interferences include volatilization due to the formation of solid solutions of one element in another, e.g. chromium in iron and variation in the rate of sample aspiration into a flame caused by changes in viscosity and surface tension with solution composition. The former can usually be obviated by using a releasing agent and the latter by careful matching of samples and standards, i.e. with regard to acidity, total salt concentration and other major constituents.

The relative precision of atomic absorption measurements is good, 0·5 to 2%.

Calibration curves invariably show curvature towards the concentration axis when absorbances exceed one. This non-linearity is caused by unabsorbed radiation reaching the detector or when the half width of the emission line from the lamp approaches or exceeds

that of absorption line. In practice, $\Delta\lambda$ could be achieved with a continum source only if expensive intrumentation of extremely high resolving power were used. An alternative arrangement is to measure K_c (absorption co-efficient) at the centre of the absorption line, where it reaches a maximum value, using a sharp line radiation source characteristic of the element of interest. Assuming that Doppler broadening is the only significant line broadening effect, then maximum value of K_v is given by,

$$K_c = \frac{2\lambda^2}{\Delta\lambda}\left(\frac{\ln 2}{\pi}\right)^{\frac{1}{2}} \frac{\pi e^2}{mc^2} N_v f$$

and f is the oscillator strength

where $\Delta\lambda$ is the Doppler line-width at wavelength λ_λ.

Thus K_c is directly proportional to N_v, the sample concentration. The profiles of an absorption line, an emission line from a sharp line source and a band pass of a monochromator are shown in Fig. 4.4, where the radiation from the sharp line source is absorbed at the centre of the absorption line and that the amount absorbed represents a substantial portion of the total radiated intensity.

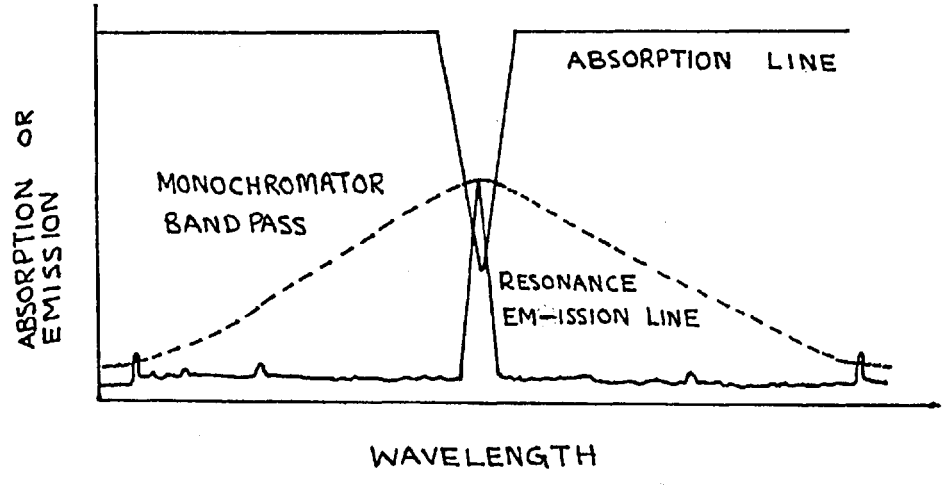


Fig. 4.4 Profiles of an Absorption line, an Emission Line from a Sharp Line Source and a Bandpass of a Monochromator

CHAPTER 5

5. GENERAL CONSIDERATIONS ON TRACE METALS IN PETROLEUM

5.1 Introduction

Due to the increase in the sensitivity of the analytical methods, the trace metal analysis has become an important part of analytical chemistry. Instrumental methods are generally used for trace analysis because they are fast and require a small amount of samples. The trace elements in petroleum or in its products, occur in particulate matter or sediment, in solution, or in both phases (138, 174, 258, 320, 321).

Theories explaining origin of the petroleum are divided into the following two groups, (i) the inorganic theories explain the formation of petroleum as a geochemical reaction between carbon dioxide, water and various inorganic substances such as carbides and carbonates of some commonly occuring metals; (ii) the organic theories explain the formation of petroleum from the decomposition products of vegetable or animal organisms living in the sea water in old geological periods. These decomposition products remain in the form of sediments along ocean shores and on the continental shelves (30, 90, 139, 347, 391).

5.2 Occurence and Effect of Metals

Crude oils contain water soluble salts and oil soluble organometallic compounds either as complexes, metallic soaps or in the form of colloidal suspensions. Table 5.1 shows the number of oils containing various levels of concentration of each of the 28 elements indicated by number inserted on the bars. Most of the oils contain vanadium and nickel as more abundant metals. The levels of metals in the oil are given as weight per cent (30).

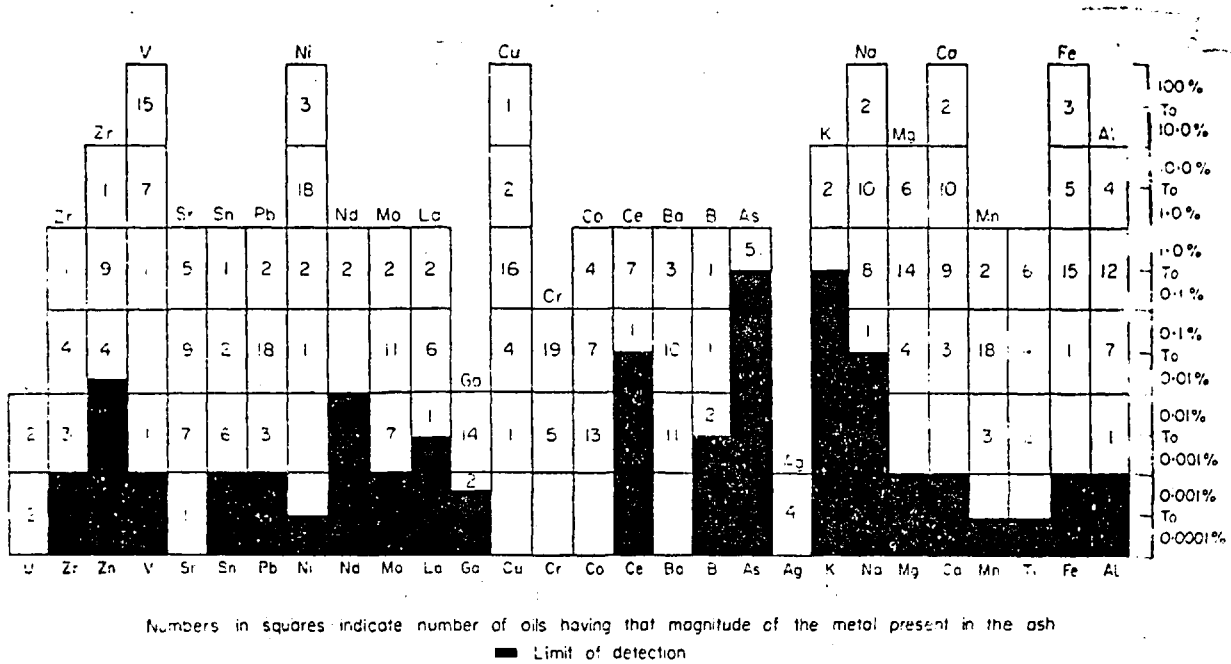
The spectrographic determination of the 23 crude oils in America has revealed that the 28 elements, occur in ash (30), the more abundant oil soluble metals are V and Ni. V and Ni increase with the asphaltic content of petroleum (353). Currently the metallic components occuring naturally in petroleum are classified as metalloporphyrin chelates and transition metal complexes of tetradentate mixed ligands

such as V, Ni, Fe, Cu, Co and Cr.

The principal central ions of the complexes are V, Ni, Fe, Co, Cu and Cr and they are classified as porphyrins and non-porphyrin metals. These complexes are held tightly in the organic matrix and thus exert strong influence on the properties of petroleum samples (64, 79, 321, 353) (refining problems). Table 5.2 shows the number of oils containing various levels (wt. %) of concentration of each of 28 elements indicated by the numbers inserted on the bars (30).

Table 5.1

Distribution of Trace Metals in Ashes of 24 Crude Oils (30)



Numbers in squares indicate number of oils having that magnitude of the metal present in the ash

Limit of detection

Some metallic components, known as additives are also added to the petroleum products to achieve the desirable properties. Tetra ethyl lead (T.E.L.) and tetra methyl lead (T.M.L.) are added to produce high octane number (276). Some used lubricating oils may contain wear metals in addition to the metals added deliberately (277). An analysis for metallic and non-metallic elements in Petroleum according to their frequency of occurence in certain products has been reported (375).

Metals concentration in petroleum varies from less than 1 µg/g to more than 100 µg/g (145, 301, 327), and this concentration

represents the maturation (146) and the depth and the age of oil (31, 190, 324, 259). In the investigation for the biogenic origin of petroleum, the origin of nickel and vanadium have been studied extensively in crude oils and it states that significant amount of nickel and vanadium in crude oils cannot be accounted for the free metalloporphyrins (323, 392, 393).

The ash content resulting from petroleum varies from about 0·001 to about 0·05 per cent, and since it is non-volatile it becomes concentrated in heavy fuel oil. Small amounts of metallic elements have a considerable effect on the performance and processing of petroleum and petroleum products. The corrosive effect of vanadium on turbine blades and destructive effect on fire clay brick make the removal of vanadium very necessary (92, 324). The presence of Ni, V, Fe and Cu are known for contaminating the catalyst for petroleum processing (80, 118, 235, 236). Trace elements also cause various refinenary problems (235), such as, by enhancing the rate of unwanted chemical reactions, or by concentrating into the crank case oil which can effectively poison the catalysts (81, 174, 191, 212). Lang and co-workers (418) determined trace metals in crude oils before and after centrifuging and filtering.

5.3 Sample Preparation For Trace Metals Analysis

The determination of trace elements in petroleum can be studied in three ways: (1) by decomposition techniques (ashing, wet oxidation, extractive decompositon and oxygen flask method) (2) by separation procedures and (3) by direct measurement methods.

5.3.1 Decomposition Techniques

In order to analyse inorganic components the organic matter is decomposed by the following various techniques.

(a) Ashing

The usual method of preparing samples of petroleum derivatives for the determination of metals, involve ashing, and the amount of sample can be varied for the final test. Thousands of grams of sample are used to proceed. The simplest and direct ashing technique is the burning of oil and igniting of the residue until only an inorganic ash

remains (65, 237). The ash is generally prepared by dry ashing, sulphated ashing or wet ashing. In dry ashing procedures, the weighed sample of oil is burned in a tared dish, and the residue ignited in a furnace until the carbonaceous material is oxidised. In sulphated ashing the sample is burned as usual and the residue is drenched with sulphuric acid. Then the residue is fumed off on a hot plate, and ignited at about 550 °C until most of the carbon is oxidised. It is then cooled, re-treated with sulphuric acid and finally ignited for a few minutes at 775 °C (6, 118). The final acid treatment is adopted to convert any sulphide formed to sulphate. The volatilization or entrainment in dry ashing often causes the loss of metals (235), which can be prevented by the sulphation of the oil during the combustion step (7, 191, 354). Morgan and Turner (238) showed that if the combustion and the final ignition temperature are carefully controlled then the loss of metals like Fe, Ca and Na is very small. Shultz and his co-workers (341) proposed that the ashing can be completed in a fraction of the usual time by burning the sample in the presence of benzene sulphonic acid.

(b) Wet Oxidation

Possible losses associated with ignition procedure can be avoided by the decomposition of the material by an oxidative digestion (239, 325). The best technique is to char the sample by heating with sulphuric acid and adding concentrated nitric acid in 1 or 2 ml increments. Strong hydrogen peroxide solution is then added dropwise, directly on to the digestion mixture. A Kjeldahl flask is a suitable apparatus for this analysis, since the long neck prevents mechanical losses.

The rate of decomposition can depend upon the vanadium concentration because the V acts as a catalyst for some oxidation processes (32). Fredrick (107) in his work on the wet ashing of the organic matter employing hot concentrated perchloric acid, referred to the liquid fire reaction. In wet oxidation, a large acid to sample ratio is needed and only a limited amounts of sample can be decomposed, and this is the great disadvantage of this technique.

(c) Extractive Decomposition

Difficulties associated with the ashing and wet oxidation procedures are avoided by this technique, where the element of interest is extracted before decomposition. Hot hydrochloric

acid is the extractant most widely used, for the determination of metals (9, 302). Hacket (147) proposed suitable extractants for the determination of some specific elements and compounds. The soluble copper was extracted from mineral oil with alcoholic hydrochloric acid (147). Griggings and his co-workers (119) developed two methods for the determination of lead in gasoline and naphthol. Snyder (326) described that both the methods are the modification of dithizone colorimetric method (119, 142). Barney and Haight (33) have compared a number of ashing and extraction procedures for the determination of Cu, Fe, Pb, Ni and V in fuel stock. The additive metals in lubricating oils have been extracted with trifluoro-acetic acid followed by water (326, 33) and with dilute hydrochloric-acetic acid mixture (33, 34). A lubricating oil has been analysed for additive metals by a similar approach involving a reaction with an aqueous solution of (ethylene dinitrilo) tetra acetic acid (EDTA) in the presence of acetone (120, 121, 394).

(d) Oxygen Flask Method

In 1892, Hampel used oxygen flask technique for the macro determination of sulphur in coal and organic materials, by putting the sample in a platinum gauze basket, and suspending it from a stopper of a 10 litre flask. The flask was filled with oxygen and the sample was ignited by means of an electric current. The combustion products were absorbed in a reagent solution in the flask and determined by classical analytical methods. Schöniger (327) developed the technique for micro analysis in 1955 and accurate results were obtained. Belcher and MacDonald (35, 240) have practiced this method for the decomposition of a wide range of organic compounds on micro, semi-micro and ultra-micro scale. Zinc, Cadmium and Magnesium can be determined on the micro-scale by absorbing the products of combustion in IN hydrochloric acid and then titrating against EDTA (206, 207).

The oxygen flask method is simple but is restricted in the size of the sample for safety reasons. In the trace analysis its application is limited to the elements having highly sensitive detecting system.

5.3.2 Separation Procedures

The interferences vary the degree of selectivity, thus in order to get a good selectivity and meaningful measurement, isolation and separation become a necessary step. In the trace analysis, the separation of minor constituents in the presence of major components in the sample, often creates problems. Supersaturation may delay the formation of precipitates, and the coagulation of the small amounts of colloidally dispersed substances is often difficult. In order to minimise losses during transfer and filteration, a chemical collector can be introduced, which serves to carry the desired minor constituents out of the sample. Sandell (109, and also 315) involved extraction, precipitation, electrolysis and distillation for separation procedure.

Ion exchange, chromatography and chelation or other masking devices have extensively been employed for the separation of copper, lead, iron and alkali metals (36, 328). Copper compounds have been quantitatively removed by adsorption on the cation exchange resins (36). In several fundamental studies gas chromatography is used to separate metals in the form of their volatile acetyl-acetonates (37, 93, 109, 149, 175). Coulson (66) recently applied a micro-colorimetric titration to the determination of sulphur in the effluent from the gas chromatographic gas-oline and noted the utility of this approach in elemental trace analysis. West and Cooke (395) also used complex formation methods for the separation.

5.3.3 Direct Determination

The direct methods such as Emission, Atomic Absorption, Atomic Fluorescence Spectroscopy have been applied for the determination of trace metals in oils (10, 11, 38, 82, 221, 330, 329). The methods are rapid, accurate and involve less loss of volatile complexes. The details of these methods are given in section 5.5 in this thesis.

5.4 Effect of Determined Metals On Petroleum

Nickel and Vanadium effectively poison the cracking catalysts by forming higher percentage of coke and various undesirable

gases at the expense of more desirable liquid products. Deposition of vanadium during the burning of vanadium bearing oils may result in slagging and corrosion of furnace walls. The origin and age of an oil can be determined by the presence or absence of vanadium as a trace metal (39, 194, 221).

Copper and iron effects both the catalysts as well as the stability of the refined petroleum products (221). Normally copper is present in low concentrations in crude oil, however significant amounts of Cu in the petroleum products can be sometimes added to the petroleum as antiknock agents. The determination of lead and arsenic is particularly important in connection with platinum reforming and environmental problems. Lead in trace quantities may also result from carry over of sodium plumbite treating agent. Arsenic acts as a permanent poison for the dehydrogenation and isomerization activity of the catalyst and therefore the recommended arsenic level in the reforming feed - stocks must be held at 15 ppb (163, 408). Thus the analysis of lead and arsenic in petroleum is of great practical importance and therefore require the need for the development of more efficient method of their analysis.

5.5 Analytical Methods Used For The Determination of Trace Metals in Petroleum

5.5.1 Spectrographic Methods

Spectrographic methods have been widely used in petroleum analysis since they can provide simultaneous determination of many metals. Trace metals can be directly determined by employing a carbon electrode impregnated with oil samples (65) or by using a jet injection device for sample introduction (203). In order to concentrate the metals some workers (54, 83, 122, 150, 155, 305, 355) used an ashing procedure followed by addition of buffer and an internal standard before excitation. Buncak (40) determined vanadium by decomposition of oil samples on silica containing a cobalt salt. Vigler and Conard (360) developed a direct method for the determination of iron in Petroleum coke, and later iron was determinated in lubricating oils by Hensen and his co-workers (154). Some workers (42, 110) used a direct current arc (to increase the sensitivity) followed by a buffer and the electro-chemical titrations (304, 335) to determine trace metals in oil. Alumina is used as

spectrographic a-id for analysing iron in oils (397). Blackwell and his co-workers (41) and others (303) extracted the trace metals as complexes and determined them photometrically, and spectrographically respectively.

5.5.2 Ashing Methods

Milner (221) extracted Cu directly from petroleum with hydrochloric acid and determined it photometrically. Lower results were observed than when the sample was ashed and the ash dissolved in hydrochloric acid. Later on the method was recomended and improved by many workers (33, 67, 68, 153, 333).

5.5.3 Atomic Absorption Spectroscopy (AAS)

AAS is widely used in the petroleum industry where mostly xylene or methyl isobutyl ketone are used as solvents and the organic metal complexes as standards. A.A. analysis of Ni and V in MIBK are reported by standard addition method (145).

Everett and his co-workers (95) developed an AAS method for the determination of vanadium in petroleum by the use of a carbon filament. A sensitivity at 1% absorbance of $1{\cdot}3 \times 10^{-10}$ g$_{\lambda}$ was reported. The reproducibility for 15 replicate analyses at 10 µg level was ± 4·0% by using vanadium electrode discharge lamp (14, 176, 357). Sebor and his co-workers determined trace metals in petroleum by using xylene solutions and N_2O-acetylene flame (332). Later on a carbon porous filament (for atomization) (13), and air-acetylene flame (145) were used for metals analysis in AAS (65).

Some workers have used a direct method to determine lead in gas-oline (312) and iron in standard samples (196). Kahn and his co-workers (197) added HCl to the MIBK solution to get good results of iron (372 nm) in oil. Alder and West (11) determined copper and silver in used and clean lubricating oils by using a carbon filament reservoir without any sample pretreatment. Milner and his co-workers (242) determined trace metals in jet engine oils by using a combined apparatus of flame atomic fluorescence - atomic emission d.c. spectrophotometer. Reeves and his co-workers (296) used a graphite rod atomiser for the determination of iron by AAS. The results were in

comparison to those obtained by N_2O - acetylene flame method. Golden (124) determined iron in used gas turbine lubricating oil samples by different methods (AAS, AES and X-ray).

Molnar and his co-workers (297) used graphite rod AAS for the determination of copper in oils at 327·4 nm. Johnson and his co-workers determined trace metals in petroleum by using argon separated air-acetylene flame (179). A method is developed (180) for the spiked oil samples and the used lubricating oils diluted to 1:4 (W/v) with isobutyl methyl ketone. By some other workers copper is determined by using spectral (a.c. arc) method (336), electrothermal excitation in AAS (284) and air-acetylene flame in AAS.

Pasculesco and his co-workers (279) determined vanadium and nickel by ultra violet emission spectrography, where standard deviation for 2·5 ppm of vanadium (±0.20 ppm) and 3.1 ppm of Ni (±0.35 ppm) was reported. Ivanov and his co-workers (169) heated the oil sample with carbon powder, mixed with NaF and introduced the mixture into a cavity in a carbon electrode. They vaporized sample in 18-A a.c. arc and absorption was measured at 310·4 nm. The sensitivity for 1% absorption is 10 pg of V.

5.5.4 Electrochemical Methods

Parks and Agazzi (280) suggested an amperometric method for the rapid determination of vanadium. The sample is treated chemically and determined by measuring the anodic wave formed on oxidation by polarography (213). A polarographic method (358) was applied to petroleum residues where a cathodic wave was used for trace metals analysis. Samuel and Brunhick (334) preferred a polarographic method for copper because of its rapidity as compared to the colorimetric method.

5.5.5 X-Ray Methods

Trace metals in petroleum are determined by x-ray fluorescence (84, 82, 81) using an accurate internal standard, and later on by pouring the sample directly into the sample cell (373, 398). Hale and King (151) determined less than 0·1 ppm of nickel in petroleum with confidence limit (95%) of ± 0·07 ppm of nickel. Yousaf and his co-workers (399) determined vanadium in crude oil by using x-ray

fluorescence. A standard addition method was used and sensitivity of 2 ppm for V was obtained.

5.5.6 Neutron Activation Analysis (NAA)

Gibson and his co-workers (123) and others (15,241,281, 239) favoured the determination of vanadium by NAA over alternative methods. The L.O.D. of light oil and crude oil was reported as 0·002 ppm and 0·02 ppm respectively. Recently other trace metals have been determined by NAA where the samples of crude oils were irradiated at 10^{12}n cm^{-2} s^{-1} for 2 to 240 minutes and γ-ray spectra was recorded (47). Block and Daus (164) determined arsenic by NAA where the samples were contained in polyethylene phials, irradiated for 5 minutes and counting was done with Ge (Li) detector. Shaw and his co-workers (337) determined twenty elements in shale oil products by NAA. The L.O.D. reported was $<$ 1 ppm except for Fe (10 ppm).

5.5.7 Colorimetric Methods

Sandell (315) defines colorimetric sensitivity as the number of micrograms of an element, converted to coloured complex which, in a column of solution of cross section 1 cm^2, has an absorbance of 0·001. Thus on this basis vanadium hematoxylin complex has a sensitivity of 0·0025 $\mu g/cm^2$. The reagent used was 3-pyridyl-fluorone (0·0004 $\mu g/cm^2$).

Bodevsky and Johnovac (43) determined vanadium colorimetrically by igniting, ashing and then oxidising the sample and thus converting the vanadium to pentavalent form. Vanadium can also be determined (333) as yellow phosphotungstovanadic acid by the colorimetric method. Smith and Co-worker (359) stated that ammonium ion causes precipitation of phosphotungstate and therefore the method oxidation of vanadium salts with ammonium per-sulphate has been replaced by other methods.

The ASTM method for phosphotungstovanadic acid, gives repeatability of 0·3 ppm to 0·2 ppm and reproducibility of 50% for the vanadium content over the range of 0-6 ppm (16,17).

Wise and Brandt (396) used benzohydroxamic acid as a reagent for the colorimetric determination of vanadium in oil.

Patterson (282) has briefly reviewed the colorimetric methods for the determination of vanadium. Vanadium was assayed in a mineral oil ash by Piazzi (283) employing a colour formation reaction with acetone. Janousek (177, 178) leached the vanadium from fuel oil ash, with acid. The interference of ions was removed by the use of a cation exchange resin and the determination of the elements was carried out spectrophotometrically after reaction with xylenol orange. Milner (221) has listed some other organic compounds that may form complexes with vanadium or alternative may be oxidised by the vanadate to form coloured reaction products.

A number of approaches have been taken to the analysis of liquid stocks for arsenic content. As has usually been extracted in an oxidising sulfuric acid solution (265) or collected on an adsorbent (221). The isolated arsenic has often been determined by a modification method (221) in which arsine is evolved to be measured by the colour of its reaction product with mercuric bromide test paper. The less sensitive molybdenum blue colour method has been used and an adequate sensitivity was achieved by a specifically designed spectrophotometer cell. The colour reaction between arsine and silver diethyldithio carbamate in pyridine has been used to estimate the arsenic. The method is rapid and accurate within a range of 1 to 100 ppb (221).

A method for the determination of lead (221) based on the formation of lead sulphide was applied to the traces of tetra ethyl lead in jet and motor fuels. The colour of the suspension is matched visually with that of standards; precision over the range of 0 to 20 ppm was estimated to be 1ppm.

The ASTM colorimetric method (22) is based on decomposing lead compounds with bromine and extracting lead with nitric acid, buffered at pH 9·5–11 and treated with chloroform solution of dithizone, the resulting absorbance being measured and related to lead content. Snyder (326) used a method to determine lead involving extraction from a solution buffered at pH 11·5. In order to determine lead at the ppb level, the dithizone procedure (13) is often used to achieve a better sensitivity than the already described methods (22, 326).

5.5.0 Miscellaneous Methods

I'Lysov (168) used electron paramagnetic resonance spectroscopy as a rapid and precise method for the determination of vanadium in petroleum. Nikishenko and his co-workers (260) determined quadrivalent vanadium (0·5 to 20 μg or 10 to 150 ppm) in distillation residues from various petroleum samples by electron spin resonance spectroscopy.

Livingstone and Lawson (214) described a rapid photometric method for the quantitative determination of copper by extraction in gas-oline. The accuracy of the method has been reported to be 10%. The extracted copper has also been determined spectrographically (334) as well as polarographically (33). Buchwald and Wood (36) reported that copper can be removed quantitatively from mineral oils by absorption on cation exchange resin. They reported that ion exchange method is rapid and gives accurate and repeatable results as compared to dry and wet ashing. Zall and his co-workers (394) described a direct method for the determination of copper in petroleum products by treating oi with neocuproine in a chloroform solution for the development of a copper neocuproine complex. The solution is diluted with chloroform and the maximum absorbance was measured at 450 nm.

Sebestyen (344) determined traces of lead in gas-oline by an inverse voltametric method where the relative error is ± 6%, and a L.O.D. of 1 ppb of Pb has been reported.

Hulanicki and Karwowska (155) developed a spectrophotometric method for the determination of lead in petrochemicals. The sample was ashed with conc. H_2SO_4 and the ash was dissolved in 5 M HCl. Lead was determined at 520 nm with dithizone up to L.O.D. of 5 ppb.

B.S.I. developed a method for the determination of total lead in gas-oline by iodine monochloride method. Berenguer and his co-workers (55) determined lead in petrol by Atomic Absorption Spectrometry where a gel was made which on dilution with water was determined at 283·2 nm. The calibration graph was rectilinear for 0 to 20 ppm of Pb.

Grinkman and his co-workers (56) determined trace metals in petroleum by using Atomic Fluorescence Emission Spectrometry where a 300 W Xenon arc lamp was used as a source.

CHAPTER 6

6. AN INTRODUCTION TO COAL ANALYSIS

6.1 Introduction

Coal is a solid fossil fuel formed through biochemical and geochemical processes by the action of temperature and pressure on plant debris. The differences in the plant material and the extent of its decomposition during the first stage of its development largely determines the different petrographic types. A series of substances such as peat, lignite, bituminous coal, and anthracite are developed during this process generally known as 'coalification'. The various amounts of moisture and minerals are associated with organic part of the coal (339). The degree of coalification or rank of the coal increases progressively from lignite through low-rank coal to high-rank coal to anthracite. The carbon content increases and the oxygen and hydrogen contents decrease throughout the series, while the reactivity decreases.

The main chemical components ofcoal are C, H , O , N , S, H_2O and various inorganic minerals and trace of metallic and non-metallic elements. The classification (417) of coal is based on the contents of volatile matter (339). The mineral matter in coal is a result of its parent vegetation, contribution from the diagenatic stage, transportation, deposition from the percolating mineral water, and by various ion exchange processes (251). Trace elements cover a wider range but are grouped according to their tendency to associate with minerals of single class as given in Table 6.1. However 95% of the mineral matter is comprised of clay minerals, carbonates, sulphides and silica, and hence over 95% of the ash consists of alumina, calcium oxide, iron oxide, magnesia and silica (416). Most of the remainder is accounted for by oxides, chlorides, sulphates and phosphates of various elements, e.g. K, Na and Ti (130, 131, 306, 405).

There is a need to understand the nature and behaviour of mineral matter in coal utilization. The quality of coke is related

Table 6.1

Minor and Trace constituents of Mineral Matter (339)

"Rare" elements in coal ash (PPM)

Arsenic(8000;500)	Germanium(11,000;500)	Platinum(0•7;-)
Beryllium(1000;300)	Gold(0•1;-)	Silver(10;2)
Bismuth(200;20)	Indium(2;-)	Thallium(5;-)
Boron(3000;600)	Lead(1000;100)	Tin(500;200)
Cadmium(50;5)	Lithium(500;-)	Yttrium(800;100)
Cobalt(1500;300)	Molybdenum(500;200)	Zinc(10,000;200)
Gallium(400;100)	Nickel(8000;700)	Zirconium(5000;-)

Maximum concentrations of minor elements in ash of western US coals (PPM)

Location	1•0–0•1	0•1–0•01	0•01–0•001	0•001–0•0001
(1)	As, B, Ba, Be, Co, Mn, Mo, Ni, Pb, Sr, Ti, U, Zn, Zr	Cu, Cr, Ga, Ge, La, Li, Sc, V, Y	Sn	Ag, Yb
(2)	B, Ba, Mo, P, Sr, Ti, U, Zr	Co, Cr, Cu, Ga, Ge, La, Mn, Ni, Pb, V, Zn	Sc, Sn, Y	Ag, Be, Yb
(3)	B, Ba, Mn, Mo, Sr, Ti, Y	Co, Cr, Cu, Ni, Pb, V, Zr	Be, Ga, Ge, La, Sc, Sn, U	
(4)	B, Ba, Mn, Ni, Sn, Sr, Ti	Co, Cr, Cu, Pb, V, Y, Zn, Zr	Be, Ga, Ge, Mo, Sc, Yb	

to its ash and sulphur content which are both dependent on the mineral composition of the feed coal. The inorganic constituents of coaking coals can have a marked effect on yields of carbonization products, structure, strength and reactivity of the resulting coke. When coal is burned in a combustion unit, mineral matter undergoes major changes which lead to problems of clinker formation, fly ash, slagging, boiler tube corrosion and environmental consideration (253). The renewed interest in coal gasification and liquefaction has also produced a need for a better understanding of the behaviour of the mineral matters in these processes.

The mineral wastes from the coal preparation and the mine development constitute a major environmental problem. The disease pneumaconiosis needs a complete chemical analysis of coal dust. The development of the necessary control technologies for human and environmental protection requires quantitative evaluation of the extent and severity of the problem because the emission of pollutants in the air are dependent both on the quantity of the material combusted or processed and on the concentration of pollutants in the material. A large number of environmentally sensitive elements ($>30\ \mu g/g$) are reported in the coal (400).

6.2 Ashing of Coal

With reference to coal and coke, ash is defined as the residue remaining after complete combustion under strictly controlled conditions. The determined ash may not, however, be considered as synonymous with mineral matter.

During the course of combustion, carbon dioxide is lost from mineral carbonates, water of hydration from hydrated silicates ($600\ ^{o}C$) and pyrite is converted to ferric oxide resulting in the loss of sulphur. Ash having high contents of calcium tends to combine with sulphur from pyrite to form calcium sulphate. The ratio of the determined ash to the original matter depends upon the composition of the mineral matter (339, 360).

Various authors (360, 367) have developed formulae to calculate the mineral matter in coal based on the ash and sulphur, forms of sulphur, chlorine and carbon dioxide contents. In ASTM D3174 the sample is placed on a cold muffle furnace and heated to 500 °C for one hour and at 750 °C for two hours until constant weight of the ash is achieved. The ISO 1171 method of ashing specifies a maximum temperature of 815 ± 10 °C for all coals regardless of rank and coke.

6.3 Determination of Mineral Matter

Several methods for the calculation of mineral matter in coal have been proposed.

The two most commonly used are those given by Parr (286) and King et al (199). Millot (254) and Given et al (134) have described modification in Parr (286) and King et al (199) formulae respectively. In ISO 602 method mineral matter is determined by treatment with hydrochloric and hydrofluoric acids.

If chemical analysis of a mineral mixture is known then it is possible to estimate the amount of each mineral present by normative or rational method (268, 406).

Generally the most reliable means of obtaining the mineral matter contents of a coal, in literature, is by acid demineralization procedure due originally to Radmacher (307) and later modified by Bishop (50).

Gluskoter (132) found low temperature ashing (LTA) method to be suitable for the liberation of coal minerals in a comparatively unaltered form. Since then the method has been widely used for quantitative analysis of minerals associated with coals (131, 267, 267a, 267b, 268, 366, 407). Frazer and Belcher (112) studied the applicability of LTA as a method of determining mineral matter in Australian coals. Miller (255) has made an extensive study of the changes in the minerological composition which occur during LTA and found that

specified conditions of ashing must be adhered to include the radio frequency power level (256, 252).

6.4 Analytical Methods for the Determination of Mineral Matter

Generally it is regarded that no single method will yield a complete analysis of mineral matter in coal, it is often desirable to employ a combination of various methods. The samples should be stored in dry and inert atmosphere.

6.4.1 X-Ray Diffraction

X-ray diffraction is considered to be the best method for mineral identification. However, its application can be limited because of the orientation effects. Thus it is necessary to use a reliable method of sample preparation. LTA is preferred. Rao and Gluskoter (366) investigated several methods of sample preparation for semiquantitative and quantitative analysis. They found that water smears and alcohol-water smears can produce chemical reactions and orientation effect. They suggested a cavity mount technique to be used in all the x-ray analysis.

Novak et al (264) described the application of x-ray photo-electron spectrocopy (XPS) to determine lead, chemical states of sulphur and nitrogen in smong particles. Avaktingi et al (20) have made an analysis of air-borne particulate samples by XPS. They concluded that lead exists in at least two forms (halide and oxide) in approximately equal amounts.

Schultz and Nelson (341) found that Pb_3O_4, PbO, PbO_2, NiS, NiO, As_2O_3 and As_2O_5 were observed in coal samples. Many other elements (Al, Br, Na, O, Fe, Cl, C and Ca) have been studied by Carter (72) and Avaktingi et al (20, and also 73). Bensen (53) determined the major and trace elements in raw coals by Wave Length Dispersion X-Ray Spectrometer. Optimum excitation conditions for each element (Ni, Cu, Pb, As and others were achieved by using various secondary targets.

6.4.2 Neutron Activation Analysis

Neutron Activation Analysis (NAA) has developed from an analytical technique requiring elaborate chemical separations to detect separate isotopes to a multi-element technique. Tamura (369) used neutron activation (non-destructive) for the analysis of trace elements in coal. Lehmden (217) used inorganic ion exchangers for NAA of arsenic in coal ash. Nadkarni (262) determined mineral matter in coal by drying sample over P_2O_5 for one week and weighing in a suitable phial for irradiation using NAA.

Ondov et al (270) determined elemental concentrations in coal and fly ash standards using NAA. Stainnes and Rowe (343) used thermal and epithermal neutrons and short-lived nuclides for instrumental activation analysis. Optimum conditions are reported for determining 40 elements in coal by instrumental NAA by the use of Ge (Li) detector and multi-element solution (309). Rowe and Stainnes (310) determined thirty elements in coal and fly ash by thermal and epithermal neutron activation analysis. Ryan and co-workers (311) analysed fly ash for 78 elements by NAA with a SLOW POKE REACTOR. The fluxes were stable, homogeneous and reproducible. Germani et al (135) has analysed bituminous and sub-bituminous coal of standard reference materials (NBS) by NAA and Neutron Capture Prompt γ-Ray Activation Analysis. The results of the two methods agree with each other. Recently Boeck et al (52) determined trace elements of coal, coal ashes and fly ashes by activation analysis with short-lived nuclides.

6.4.3 Atomic Absorption Spectrophotometry

Atomic Absorption Spectrophotometry (AAS) is recomended for majority of elements due to its good accuracy and precision. There are some elements that cannot be determined or are insensitive using this technique. Thus special methods are recomended in such cases, e.g. As, Sn, bismith, germanium, tellurium and tin are determined by hydride evolution technique, where volatile hydride are generated and analysed with a conventional AAS system (19).

Spielholtz and co-worker (342) used AAS for the determination

of As in coal and insecticides after ashing the sample with $HClO_4$ and HIO_4 . Argon plasma emission excitation source is used for coal ash analysis (162). Hartstein and his co-workers (162) heated coal sample with fuming HNO_3 at 150°C for 2·5 hours in a Parr bomb lined with PTFE, then with HF at 150°C for 15 minutes. Block (51) determined mineral matters in coal by decomposing the sample with 14M HNO_3 - 30M HF in a PTFE lined bomb at 230 °C for 6 hours. Owens and Gladney (268b) used lithium metaborate fusion for the determination of trace elements in fly ash by flameless AAS. A coal sample was decomposed with a mixture of HNO_3, H_2SO_4 and $HClO_4$ and then with ascorbic acid and NaI to determine As, Sb, Se by extraction and using AAS. O'Reilley and Hale (269) determined trace metals in coal slurries by AAS and Atomic Emission Spectrophotometry. Nadkarni (261) determined 20 trace elements in coal and fly ash by using Low Temperature Oxygen Plasma for ashing and Inductively Coupled Plasma Emission Spectrometry for end analysis. Epstein et al (96, 97) determined iron in fly ash b, using laser excited Atomic Fluorescence Spectrometry (LOD 0·6 $\mu g\ ml^{-1}$ and 0·2 $\mu g/ml^{-1}$). Ibrara and co-workers (170) determined Na, K, Mn, Ca, Mg, Fe and Al in coal ash by AAS. Langmyhr and Aadalen (216) reported that matrix did not interfere during the direct determination of Cu, Ni and V in coal and petroleum coke by AAS.

6.4.4 Mass Spectrometry

Guidoboni (136) determined Zn, Mn, Ni, Cu, Cr, and V in coal ash by Spark Source Mass Spectrometry. CO-efficient of variation ranged from 6 to 15% and L.O.D. is reported to be 1 to 2 ppm with respect to whole coal but might be improved to 0·03 to 0·1 ppm. Donohue and co-workers (86) determined As and Co in coal standards (NBS) by using Spark Source Mass Spectrometry. The results showed good precision and accuracy at levels of <1PPM of As.

6.4.5 Miscellaneous Methods

Bishop and Ward (50) directly determined mineral matter in coal. Brown et al (57) determined inorganic matter in coal by low temperature oxidation (non-destructive) and acid digestion method (destructive). Both of these methods gave closely comparable results.

Later on both of these methods (50, 57) were combined together to overcome the disadvantage of both. Seventeen trace elements have been determined directly (271) in coal by making slurry of the powdered sample. Egorov and co-workers (98) reported that the trace elements in the combustion of brown and bituminous coal are lost at temperature range of 500 °C to 800 °C. They recommended a combustion temperature of 500 °C to determine Cr, Be, Cu, and Co in coal and a direct determination without loss is recommended for volatile elements like Pb, V, B and Mn in coal.

Parasad (289) determined mineral matter in coal by decomposing the sample with $HClO_4$ solution and using EDTA titrations, colorimetry and Flame Photometry for different elements.

CHAPTER 7

7. ASHING PROCEDURE AND THE RESULTS

7.1 Development of the Method for Oil and Coal Ashing

Different methods have been tried for plasma ashing of residual oil and coal samples. The coal samples were directly ashed on a Petridish whereas for ashing of the oil samples a different method was adopted. The residual oil sample could not be completely ashed on the Petridish glass surface due to the sticking of the oil onto the glass surface. A hard layer was developed on the oil sample, due to the metals in it. The plasma could not penetrate this hard layer and thus the oxidation was stopped. In order to overcome this problem the sample (0•2 g) was placed over a filter paper (Whattman No. 1) but when the sample was ashed with plasma the oil penetrated through the filter paper and stuck to the glass surface. The filter paper was oxidised in 32 minutes at power of 240 W, flow rate of 70 ccs/min, and pressure of 1•2 torr, but the whole of the sample was not ashed even in five hours. 3 and 4 filter papers were used separately and it was found that 0•2 g oil was completely ashed at above given conditions with four filter papers. Different weights (0•2–0•5 g) of oil were tried with different numbers of filter papers. The ideal combination for the residual oil oxidation in this plasma apparatus was found to be 0•4 g of residual oil on four filter papers at power 200 W and flow rate 150 ccs/min (pressure 0•3 torr). Four filter papers were ashed without oil for the blank determination of each metal in filter papers.

At a later stage different kinds of filter papers were also tried, eg. Whatman No. 41, 42, 541 and 542; but Whatman No. 1 (5•5 cm) was found to be suitable for the complete sample ashing. In hardened filter papers the oil could not penetrate through and thus formed a hard surface for plasma to attack. The oil evaporated and stuck to the petridish edges when hard filter paper was used, and 0•2 g of oil took 12 hours for the partial oxidation. In order to disperse the sample in these filter papers I.R. lamp was used.

The oil sample was treated with dilute mineral acids but

the rate of oxidation (R.O.) was not appreciably increased. In another experiment the oil sample (0•2 g) was kept for 72 hours in a desiccator before ashing, so that the oil should be completely spread inside the filter papers. A high rate of oxidation (0•0087 g/min^{-1} at 200 W and 150 ccs/min) was achieved but the time to keep the sample in the desiccator was too long so this method was not adopted.

An oil sample (0•2 g) was heated with IR lamp (at 10 cm distance) for 3-5 minutes. A loss of weight was recorded possibly due to evaporation of the water vapours from the sample as well as from the filter papers. The water by the filter papers was however regained when the sample was removed from the lamp. A loss of the weight due to the heat (IR lamp) was recorded on four filter papers only (without oil) and they also regained the original weight when removed from the IR lamp. Eight residual oil samples (0•2 g each) on four What-man No. 1 filter papers were taken. Four samples were heated with an IR lamp just after weighing and then ashed. The time taken was four hours for complete ashing (rate of oxidation was 0•0044 g/min^{-1}). The other four samples were ashed directly just after weighing without IR treatment. The time taken was eight hours for complete ashing (rate of oxidation 0•00217 g/min^{-1}). The conditions selected were power 200 W, and flow rate 150 ccs/min (pressure 0•3 torr). Due to the treatment by IR lamp, the sample was evenly spread, providing more area for oxidation and the whole of the oil was absorbed inside the filter papers. Thus the rate of oxidation was high due to the IR lamp treatment of the sample. In this case there was no 'swollen oil' when the sample was placed at low pressure in the plasma. There was however one major disadvantage of this method that when the sample was heated by IR lamp, charring and agitation in the sample surface was observed which may result in the loss of the volatile substances. A few black spots of oil were also observed at the surface of the Petridish which could not be ashed even after a long time of oxidation. Therefore IR lamp treatment was avoided.

In order to spread the sample evenly, to increase the surface area for plasma attack, to avoid the swollen sample (under low pressure) and the sticking of the oil to the Petridish surface, the sample was

warmed on a hot-plate. A residual oil sample (0·4 g) on four What-man No. 1 filter papers was ashed in 4 hours at a power of 200 W, flow rate of 150 ccs/min and pressure of 0·3 torr (rate of oxidation was 0·00518 g/min^{-1}). The average weight of the ash obtained was 0·0018 g. The temperature was measured at different power levels during oxidation of the oil sample as shown in Fig. 7.1. At 200 W power and flow rate of 150 ccs/min, the temperature recorded was 65 °C.

Coal samples were obtained from NCB (-120 BS Mesh). Different weights of the coal sample (0·3-1·0 g) were taken and ashed directly on a Petridish in the plasma at the power level of 200 W and the flow rate of 150 ccs/min, until a constant weight of the ash was obtained. The sample was stirred after every two hours during ashing. Coal samples (0·3 g) were ashed in 8 hours (rate of oxidation 0·00062 g/min^{-1}). The sample stirring provided a fresh surface for plasma to attack. The samples were ashed either to a constant weight or to a difference of 0·0002 g in sample weight after two hours ashing. In most cases 77% of the sample was ashable. In order to cause further oxidation the first two samples were kept for another period of 8 hours in plasma but no considerable loss in weight was observed. Coal samples were kept in plasma at low power (60W) and flow rate (60 ccs/min) for one hour to evaporate the moisture.

7.2 Preparation of Aqueous Standards

A standard solution (1000 µg/ml) for each metal was prepared and stored in a polyethylene bottle.

7.2.1 V Standard

2·2964 of NH_4VO_3 was dissolved in 100 ml of deionized distilled water (DDH_2O), 10 ml of concentrated HNO_3 was added and made up the volume to 1000 ml by DDH_2O.

7.2.2 Ni Standard

1·00 g of nickel metal was dissolved in 10 ml of hot concentrated HNO_3 and diluted by DDH_2O upto 1 litre.

Table 7.1

Determination of Aqueous Standards After Ashing by Plasma

Weight of the Standard Ashed = 0·5 g (0·5 ml)

METAL	Standard Actual Conc. PPM	Dilution	Graph Reading (ppm)	Result PPM ± σ
V	50	5	4·89	48·9 ± 1·5
	100	10	4·89	97·78 ± 1·8
	150	10	7·33	146·67 ± 1·6
Ni	50	10	2·44	48·8 ± 0·9
	100	10	4·76	95·27 ± 1·5
	150	20	3·66	146·39 ± 1·9
Cu	50	20	1·20	47·97 ± 0·9
	100	25	1·86	92·89 ± 1·5
	150	50	1·47	146·75 ± 1·8
As	5	100	20 ppb	4 ± 1·4
	10	50	16·67 ppb	8·33 ± 0·8
	20	250	36·67 ppb	18·33 ± 1·8

7.2.3 Pb Standard

1·5980 g of lead nitrate was dissolved in 1% (v/v) HNO_3 and diluted to 1 litre by 1% v/v HNO_3.

7.2.4 Fe Standard

1·0000 g of iron wire was dissolved in 50 ml of (1+1) HNO_3 and diluted to 1000 ml by DDH_2O.

7.2.5 Cu Standard

1·0000 g of copper metal was dissolved in 50 ml of (1+1) HNO_3 and diluted to 1 litre by 1% (v/v) HNO_3.

7.2.6 As Standard

1·3203 g of As_2O_3 was dissolved in 3 ml of 8 M HCl and diluted to 1 litre by DDH_2O water.

The ashed samples were dissolved in aqueous phase therefore the aqueous standards of oil and coal were chosen. The oil standards could not be used because of their organic phase and the solvent in the oil standards have more chances of evaporation during ashing. The retaining of metals after plasma ashing was observed (Table 7.1). For this purpose aqueous standards of four metal (V, Ni, Cu, As) were chosen and ashed by plasma. The ash was dissolved by 0·5% HNO_3 and determined by Atomic Absorption Spectrphotometer (AAS) at the conditions described in section 7.4 for individual metal. The concentration of individual metal standard was calculated by using the calibration plots of V (Fig. 7.2), Ni (Fig. 7.8), Cu (Fig. 7.13), and As (Fig. 7.17). A mean of three signal readings for each metal standard concentration (50, 100, 150 ppm) is given in Table 7.1.

Measurements were also made, for stray radiations at a wavelength near the original λ but no response was obtained.

7.3 Spiking of Samples and Standards

A spiking method was used to check the method of analysis for Ni and V in residual oil and coal (A) samples by using AAS (Perkin Elmer 2280). The samples and sample plus standards were ashed at constant conditions of plasma (Power 200 W, Flow Rate 150 ccs/min, Pressure 0·3 torr). Four filter papers were ashed separately for the blank determination. The ash was dissolved in 10 ml of 0·5% HNO_3 and determined by AAS at the conditions described for individual metals in Table 7.2.

The total sample taken in oil and coal was 1 g. Thus three samples 0·4 g, 0·4 g and 0·2g(total 1 g) were taken in three separate Petridishes to which 0·1 ml or 0·2 ml of aqueous standards of each metal was added as given in Table 7.2. This procedure was repeated for three times for each concentration of metal and metal plus standards. The results have shown that metals and the standards were retained after ashing. The results obtained were reproducible.

The temperature is recorded for an oil sample at different power and flow rate, (Table 7.3 and Fig. 7.1).At the power level of 200 W and flow rate of 150 ccs/min the recorded temperature was 65 °C.

Table 7.2

Determination of V and Ni in Residual Oil F-80 and Coal (A) Samples After Spiking with their Standards

V-Ni Blank = 0

O = Oil
C = Coal

(A) = Ashed
(N) = Not Ashed
S = Standard

Dilution = 10 and 20 times

NO	STD+ SAMP PPM	Wt.gm SAM	Wt.gm STD	STANDARD CONC. (A)		Calc. Conc. PPM	Approx. Actual Conc. PPM SAM+STD	Difference PPM
1	4(N)	-	-	-	FOR CALIBRATION	-	-	-
2	8(N)	-	-	-		-	-	-
3	16(N)	-	-	-		-	-	-
4	O+S(A)	1	0•1	100 PPM		60•65	62•61	1•96
5	O+S(A)	1	0•2	200 PPM		72•22	72•50	0•28
6	O+S(A)	1	0•2	300 PPM		111•11	112•50	1•39
7	O (A)	1•6	-	-		52•78	-	-
8	C+S(A)	1	0•1	100 PPM		82•83	84•07	1•24
9	C+S(A)	1	0•2	200 PPM		112•96	114•07	1•11
10	C+S(A)	1	0•1	300 PPM		101•09	104•07	3•06
11	C(A)	1•2	-	-		74•07	-	-
1	1(N)	-	-	-	FOR CALIBRATION	-	-	-
2	4(N)	-	-	-		-	-	-
3	8(N)	-	-	-		-	-	-
4	O+S(A)	1	0•1	100 PPM		26•94	27•44	0•50
5	O+S(A)	1	0•2	200 PPM		56•57	57•44	2•13
6	O+S(A)	1	0•1	300 PPM		45•62	47•44	1•82
7	O (A)	1•6	-	-		17•44	-	-
8	C+S(A)	1	0•1	100 PPM		34•20	34•69	0•49
9	C+S(A)	1	0•2	200 PPM		60•80	64•49	3•89
10	C+S(A)	1	0•1	300 PPM		54•45	54•69	0•24
11	C(A)	1•2	-	-		24•69	-	-

Table 7.3

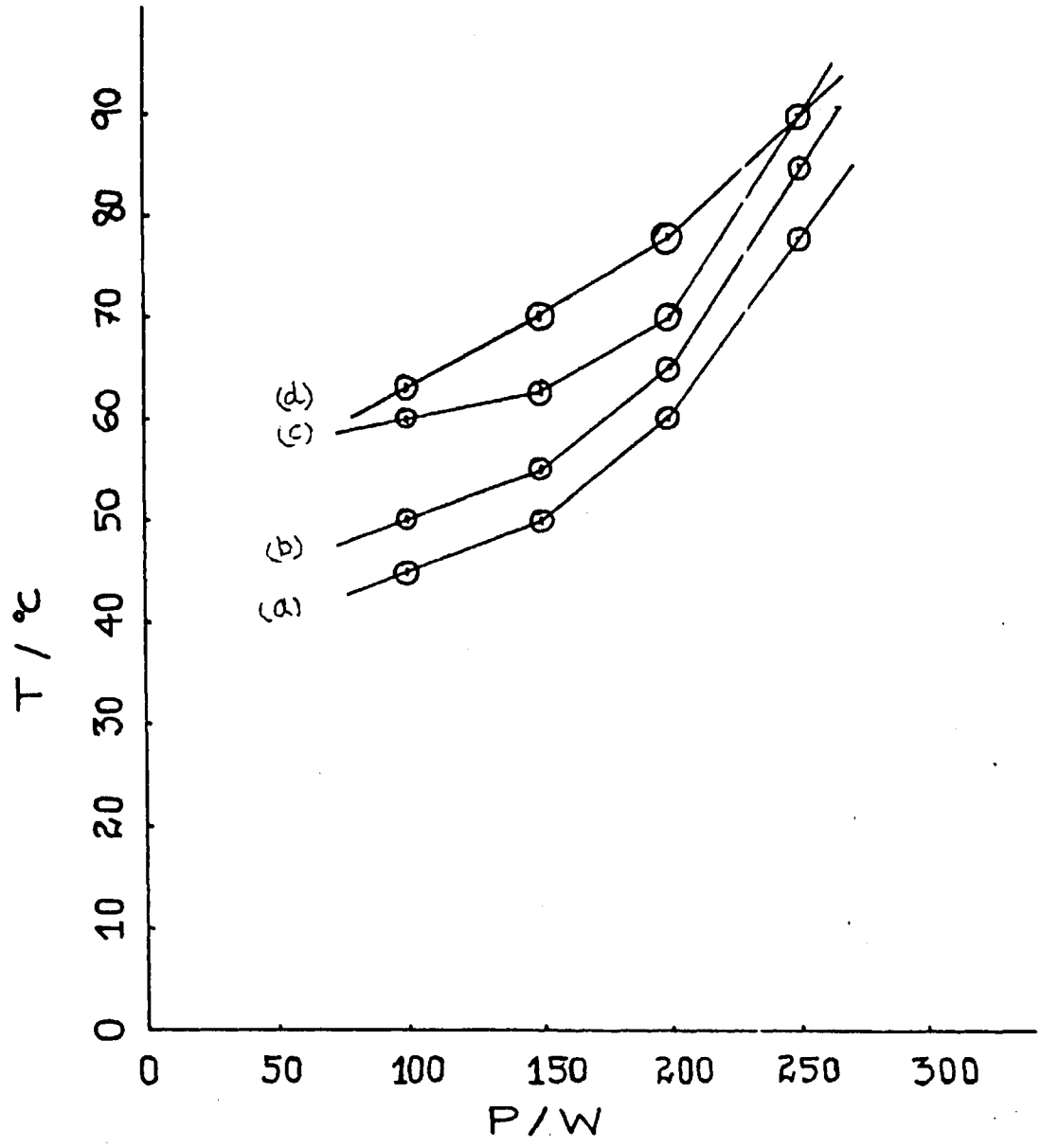
Determination of Temperature by Varying Power and Flow Rate Using a Mercury Thermometer

No	Power W	Flow Rate 100 ccs/min			Flow Rate 150 ccs/min			Flow Rate 200 ccs/min			Flow Rate 250 ccs/min		
		P Torr	T °C 15 min (a)	T °C 30 min	P Torr	T °C 15 min (b)	T °C 30 min	P Torr	T °C 15 min (c)	T °C 30 min	P Torr	T °C 15 min (d)	T °C 30 min
1	100	0•3	30	45	0•8	45	50	1•2	60	60	1•5	60	63
2	150	0•3	50	50	0•8	55	55	1•2	60	65	1•5	70	70
3	200	0•08	60	60	0•3	65	65	0•9	68	70	1•1	78	78
4	250	0•08	78	78	0•1	85	85	0•7	90	90	1•1	90	90

P = Pressure

Fig. 7.1 Determination of Temperature (T) as a Function of Power (P) at a different Flow Rate (a-d)

(a) = 100 ccs/min
(b) = 150 ccs/min
(c) = 200 ccs/min
(d) = 250 ccs/min



7.4 Procedure For The Determination Of Trace Metals

The concentration of trace metals (V, Ni, Cu, Pb, Fe and As) in residual oils (B.P. F-80 and F-31) and coal samples (NCB - A and B) was determined by Flame Atomic Absorption spectrophotometer (Perkin Elmer 2280) for V, Ni, Cu, Fe and Pb, and an electrothermal (flameless) Atomic Absorption Spectrophotometer (IL 455) for As and Pb. Perkin Elmer 2280 was programmed to take an average of three readings per second for each sample solution. The standard deviations for each set of three readings were recorded by the instrument. A sample of 20 µl was injected in IL 455.

The samples (0•4 g oil and 0•3 g coal) were ashed in oxygen plasma with power of 200 W and flow rate of 150 ccs/min. In the oil samples the ash of one Petridish was dissolved in 2 ml of 0•5% HNO_3, heated and diluted to 5-100 ml. The further dilution was done with 0•5% HNO_3. The oil ash was completely soluble in 0•5% HNO_3. In coal samples the ash was dissolved in 0•5% HNO_3, heated and filtered.

The range of aqueous standards chosen for V, Ni, Cu, Fe and Pb is between 0•5 to 20 ppm and for As 5 to 40 ppb.

The dilution and the weight taken for the determination of each metal in the samples is given in their individual table. Both the samples (oil and coal) are determined by calibration and standard addition methods. The concentration of metals in blanks (DDH_2O and filter papers) was determined and excluded.

7.4.1 Determination of Vanadium in Residual Oil and Coal Samples

(a) Residual Oil Samples

0•4 g of residual oil sample F-80 was taken in a Petridish (P.d.) and ashed. The ash was dissolved in 0•5% HNO_3. The solution of 4 P.ds. was mixed together and volume was made up to 10 ml with 1 ml of 1% Al solution. A similar procedure is adopted for coal sample B. The data and the graphs for oil samples are given in tables 7.4a, 7.4b and 7.5, and in figures 7.2 and 7.3 respectively.

(b) Coal Samples

0•3 g of coal sample A was taken in a P.d. and ashed by LTA. The ash was dissolved in 0•5% HNO_3 by heating on a hot plate. The solution of 4 P.ds. (1•2 g) was mixed together and volume was made up to 10 ml with 1 ml of 1% Al solution. A similar procedure is adopted for coal sample B. The data and the graphs for coal samples are given in tables 7.6, 7.7 and 7.8, and in figures 7.4 and 7.5 respectively.

The aqueous standards chosen were between 4 to 20 ppm for oil and coal analysis containing 1 ml of 1% Aluminium solution.

The sensitivity of the instrument (AAS) 1•7 µg/ml V for 1% absorption was reported. The conditions selected are as follows:

Wave Length	=	318•8 nm
Slit Width	=	0•7 mm
Flame	=	Nitrous Oxide-Acetylene
Source	=	Hollow Cathode Lamp

7.4.2 Determination of Nickel in Residual Oil and Coal Samples

(a) Residual Oil Samples

The ash of 4 P.ds. was dissolved in 10 ml of 0•5% HNO_3 solution and determined by AAS for both residual oil samples (F-80 and F-31) separately. The data and the graphs are given in the tables 7.9, 7.10 and 7.13, and the figures 7.6 and 7.7 respectively.

(b) Coal Samples

The ash of 4 P.ds. was dissolved in 10 ml of 0•5% HNO_3 solution. The solution was filtered and the metal was determined by AAS in both coal samples A and B separately. The data and the graphs are given in the tables 7.11, 7.12 and 7.14, and the figures 7.8 and 7.9 respectively.

The aqueous standards chosen were between 1 to 6 ppm for oil and coal samples.

The instrument (AAS) sensitivity, reported, was 0•15 µg/ml Ni

for 1% absorption. The conditions selected were as follows:

Wave length	=	231•1 nm.
Slit Width	=	0•2 nm
Flame	=	Air-Acetylene
Source	=	Hollow Cathode Lamp

7.4.3 Determination of Iron in Residual Oil and Coal Samples

(a) Residual Oil Samples

The ash of 2 P.ds. was dissolved in 10 ml of 0•5% HNO_3 solution for each sample (F-80 and F-31) and determined by AAS. The data and the graphs are given in tables 7.15, 7.16 and 7.19, and in figures 7.10 and 7.11 respectively.

(b) Coal Samples

The ash of 1 P.d. was dissolved in 10 ml of 0•5% HNO_3 solution for each sample A and B. The solution was filtered and determined by AAS. The data and the graphs are given in the tables 7.17, 7.18 and 7.20, and the figures 7.11 and 7.10 respectively.

The aqueous standards chosen were 1 to 4 ppm for both oil and coal samples.

The instrument (AAS) sensitivity, reported, was 0•12 µg/ml Fe for 1% absorption. The conditions selected were as follows:

Wave length	=	240•8 nm
Slit Width	=	0•2 nm
Flame	=	Air-Acetylene
Source	=	Hollow Cathode Lamp

7.4.4 Determination of Copper in Residual Oil and Coal

(a) Residual Oil Samples

The ash of 8 P.ds. was dissolved in 10 ml of 0•5% HNO_3 solution for each sample (F-80 and F-31), and determined by AAS. The data and the graphs are given in the tables 7.21, 7.22 and 7.25, and the figures 7.13 and 7.12 respectively.

(b) Coal Samples

The ash of 1 P.d. was dissolved in 10 ml of 0•5% HNO_3 solution for each sample A and B. The solution was filtered and determined by AAS. The data and the graphs are given in the tables 7.23, 7.24 and 7.26, and the figures 7.13 and 7.12 respectively.

The aqueous standards chosen were between 0•5 to 2•0 ppm for both oil and coal samples.

The linear working range of the instrument at the standard conditions is 5 µg/ml. The conditions selected are as follows:

Wave length	=	324•8 nm
Slit Width	=	0•2 nm
Flame	=	Air-Acetylene
Source	=	Hollow Cathode Lamp

7.4.5 Determination of Lead in Residual Oil and Coal

(a) Residual Oil Samples

The ash of 1 P.d. was dissolved in 10 ml of 0•5% HNO_3 solution for each sample F-80 and F-31. The metal was determined by electrothermal AAS (IL 455). The sensitivity of the instrument reported was 5×10^{-12} g. The conditions selected were as follows:

Wave Length	=	283•3 nm
Slit Width	=	320 nm
Source	=	Hollow Cathode Lamp
Lamp Current	=	6 mA
Carrier Gas	=	Argon 15 SCFH

Indicated Temperature	-	75	225	475	600	2700	2700
Time (Sec) x 4	-	4	4	3	3	0	0

The aqueous standards chosen were 5 to 40 ppb. The data and the graphs are given in the tables 7.27, 7.28 and 7.37, and the figures 7.15 and 7.14 respectively.

(b) Coal Samples

The ash of 6 P.ds. was dissolved in 10 ml of 0•5% HNO_3 for each sample A and B. The solution was filtered and determined by AAS (Perkin Elmer 2280). The data and the graphs are given in tables 7.29, 7.30 and 7.32, and the figures 7.15 and 7.14 respectively.

The aqueous standards chosen were between 2 to 8 ppm. The sensitivity of the instrument given was 0•5 µg/ml Pb for 1% absorption, and linear working range was 20 µg/ml in aqueous solutions. The conditions selected are as follows:

Wave Length	=	283•3 nm
Slit Width	=	0•7 nm
Flame	=	Air-Acetylene
Source	=	Hollow Cathode Lamp

7.4.6 Determination of Arsenic in Residual Oil and Coal Samples

(a) Residual Oil Samples

The ash of 1 P.d. was dissolved in 25 ml of 0•5% HNO_3 with 2•5 ml of 0•5% Ni $(NO_3)_2$ solution for each sample F-80 and F-31, and determined by electrothermal AAS (IL 455). The data and the graphs are given in tables 7.33, 7.34 and 7.37, and in figures 7.17 and 7.16 respectively.

(b) Coal Samples

Coal samples A (0•5 g) and B (0•3 g) were ashed and diluted to 200 ml and 250 ml respectively with 0•5% HNO_3. The final solution (200 ml and 250 ml) contained 10% of 0•5% Ni $(NO_3)_2$. The sample solutions were filtered and determined by electrothermal AAS (IL 455). The data and the graphs are given in the tables 7.35, 7.36 and 7.38 and the figures 7.17 and 7.16 respectively.

The aqueous standards chosen were between 5 to 40 ppb for both the oil and coal samples. The reported sensitivity of the instrument was 12×10^{-12} g for the 1% absorption. The conditions selected for the analysis were as follows:

Wave Length	=	193•7 nm
Slit Width	=	320 mm
Gas	=	Argon 20 SCFH
Source	=	Hollow Cathode Lamp
Lamp Current	=	20 A
Analysis Mode	=	SB/A-B
Integration Time	=	1/16 sec

Indicated Temperature	-	75	225	375	500	2700	2700
Time (Sec) X 4	-	4	4	3	3	0	2

Table 7.4a

Determination of Vanadium in Residual Oil F-80 by Calibration Method

Dilution = 10 Times

Wt. of the Sample = 1•6 g

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppm)	RESULT (ppm)
1	0•038	8•4	52•50
2	0•037	8•2	51•25
3	0•038	8•4	52•50
4	0•039	8•7	54•38
5	0•038	8•4	52•50
6	0•038	8•4	52•50
7	0•038	8•4	52•50
8	0•038	8•4	52•50
9	0•039	8•7	54•38
10	0•038	8•4	52•50

$\bar{X}$ = 52•8 ppm

σ = $\pm$ 0•9 ppm

$\sigma/\bar{X}$ = 0•01

$100\ \sigma/\bar{X}$ = 1•8 %

$\sigma/\sqrt{n}$ = 0•3 ppm

Table 7.4b

Determination of Vanadium in

Residual Oil F-31 by Calibration Method

Dilution = 10 times

Wt. of Sample = 1•6 g

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppm)	RESULT (ppm)
1	0•040	8•89	55•56
2	0•043	9•56	59•75
3	0•041	9•11	56•94
4	0•040	8•89	55•56
5	0•042	9•33	58•31
6	0•043	9•56	59•75
7	0•044	9•78	61•11
8	0•042	9•33	58•31
9	0•043	9•56	59•75
10	0•042	9•33	58•31

$\bar{X}$ = 58•3 ppm

σ = $\pm$ 1•8 ppm

$\sigma/\bar{X}$ = 0•03

100 $\sigma/\bar{X}$ = 3•2 %

$\sigma/\sqrt{n}$ = 0•6 ppm

Table 7.5

Determination of Vanadium in Residual Oils by Standard Addition Method

Dilution = 10 Times Wt. of Sample = 1·60 g

F-80				F-31			
NO	SAMPLE	ABSORBANCE	RESULT (ppm)	NO	SAMPLE	ABSORBANCE	RESULT (ppm)
1	SAMPLE + HNO_3	0·032		1	SAMPLE + HNO_3	0·036	
2	SAMPLE + 8 ppm	0·057		2	SAMPLE + 8 ppm	0·059	
			56 ± 3σ				64·4 ± 5σ
3	SAMPLE + 12 ppm	0·070		3	SAMPLE + 12 ppm	0·070	
4	SAMPLE + 16 ppm	0·087		4	SAMPLE + 16 ppm	0·091	

Table 7.6

Determination of Vanadium in

Coal Sample A by Calibration Method

Dilution = 10 times

Wt. of Sample = 1·2 g

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppm)	RESULT (ppm)
1	0·039	8·37	69·75
2	0·040	8·59	71·58
3	0·038	8·15	67·92
4	0·040	8·59	71·58
5	0·038	8·15	67·92
6	0·041	8·80	73·30
7	0·042	9·02	75·18
8	0·041	8·59	73·30
9	0·041	8·59	73·30
10	0·039	8·37	69·75

$\bar{X}$ = 71·3 ppm

σ = $\pm$ 2·5 ppm

$\sigma/\bar{X}$ = 0·03

100 $\sigma/\bar{X}$ = 3·4 %

$\sigma/\sqrt{n}$ = 0·8 ppm

Table 7.7

Determination of Vanadium in

Coal Sample B by Calibration Method

Dilution = 10 Times

Wt. of Sample = 1•2 g

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppm)	RESULT (ppm)
1	0•042	9•02	75•17
2	0•0 45	9•67	80•58
3	0•0 41	8•80	73•33
4	0•0 44	9•46	78•83
5	0•0 42	9•02	75•17
6	0•0 43	9•24	76•99
7	0•0 45	9•67	80•58
8	0•0 43	9•24	76•99
9	0•0 43	9•24	76•99
10	0•0 42	9•02	75•17

$\bar{X}$ = 76•98 ppm

σ = $\pm$ 2•4 ppm

$\sigma/\bar{X}$ = 0•03

100 $\sigma/\bar{X}$ = 3•1 %

$\sigma/\sqrt{n}$ = 0•7 ppm

Table 7.8

Determination of Vanadium in Coal Sample A and B by Standard Addition Method

Dilution = 10 Times Wt. of Sample = 1·6 g

SAMPLE A				SAMPLE B			
NO	SAMPLE	ABSORBANCE	RESULT (ppm)	NO	SAMPLE	ABSORBANCE	RESULT (ppm)
1	SAMPLE + HNO_3	0·037		1	SAMPLE + HNO_3	0·038	
2	SAMPLE + 8 ppm	0·070		2	SAMPLE + 8 ppm	0·060	
			78·7 ± 4σ				85 ± 3σ
3	SAMPLE + 12 ppm	0·087		3	SAMPLE + 12 ppm	0·075	
4	SAMPLE + 16 ppm	0·100		4	SAMPLE + 16 ppm	0·095	

Fig. 7.2 Calibration Graph for the Determination of Vanadium in Ashed Aqueous Standards and in Residual Oil Samples

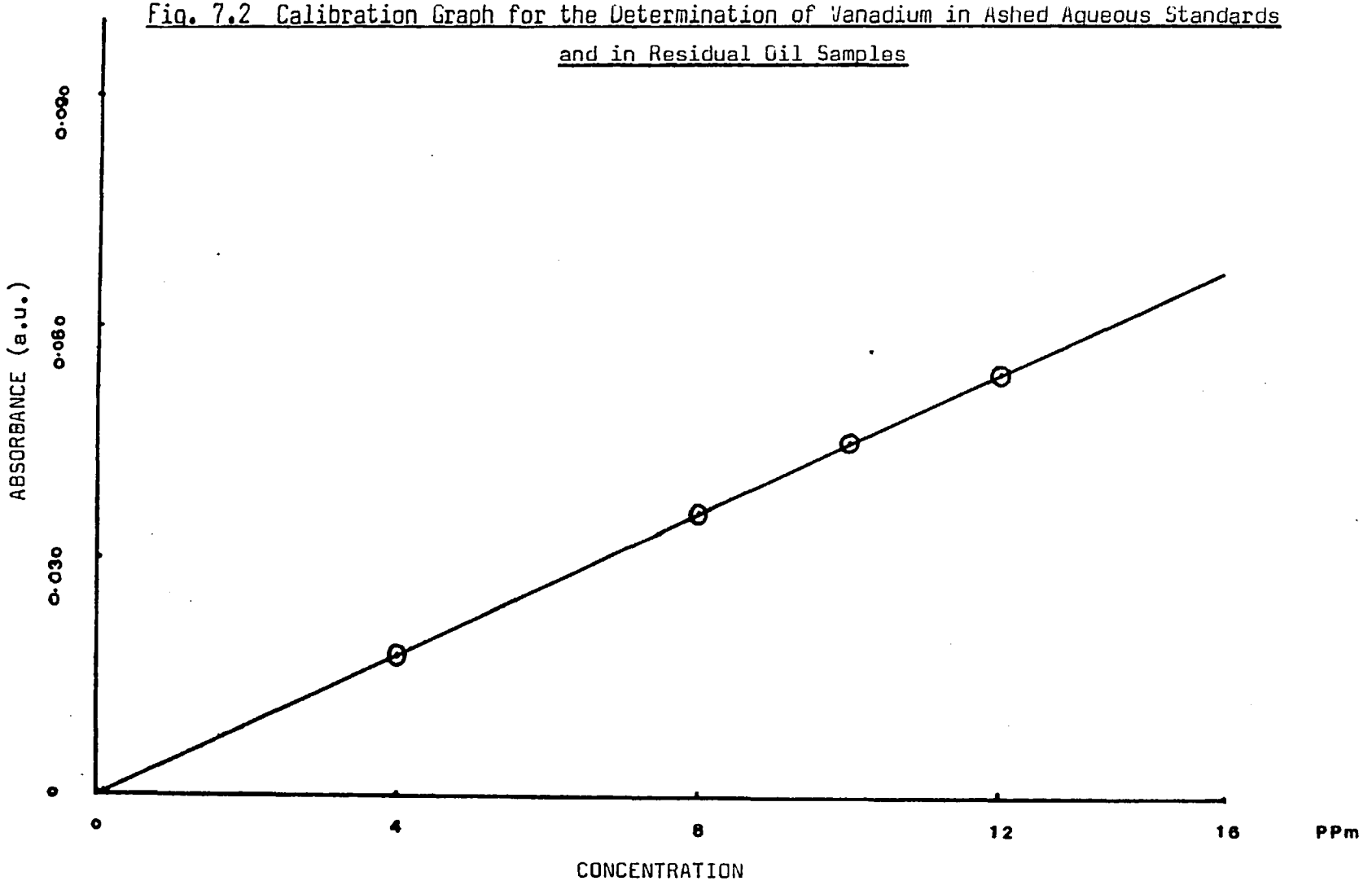


Fig. 7.3 Extrapolated graphs for the Determination of Vanadium in Residual Oil Samples by Standard Addition Method

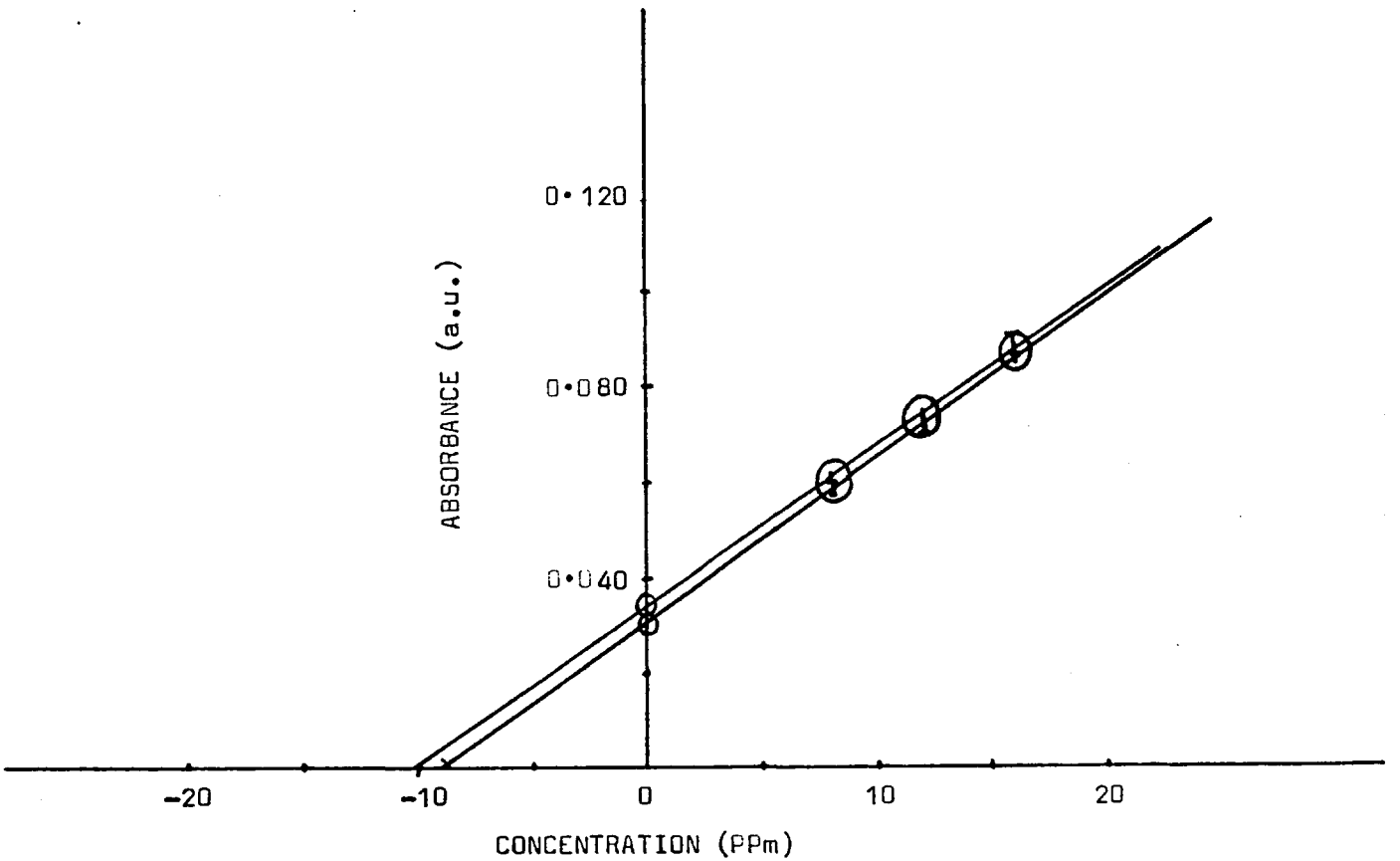
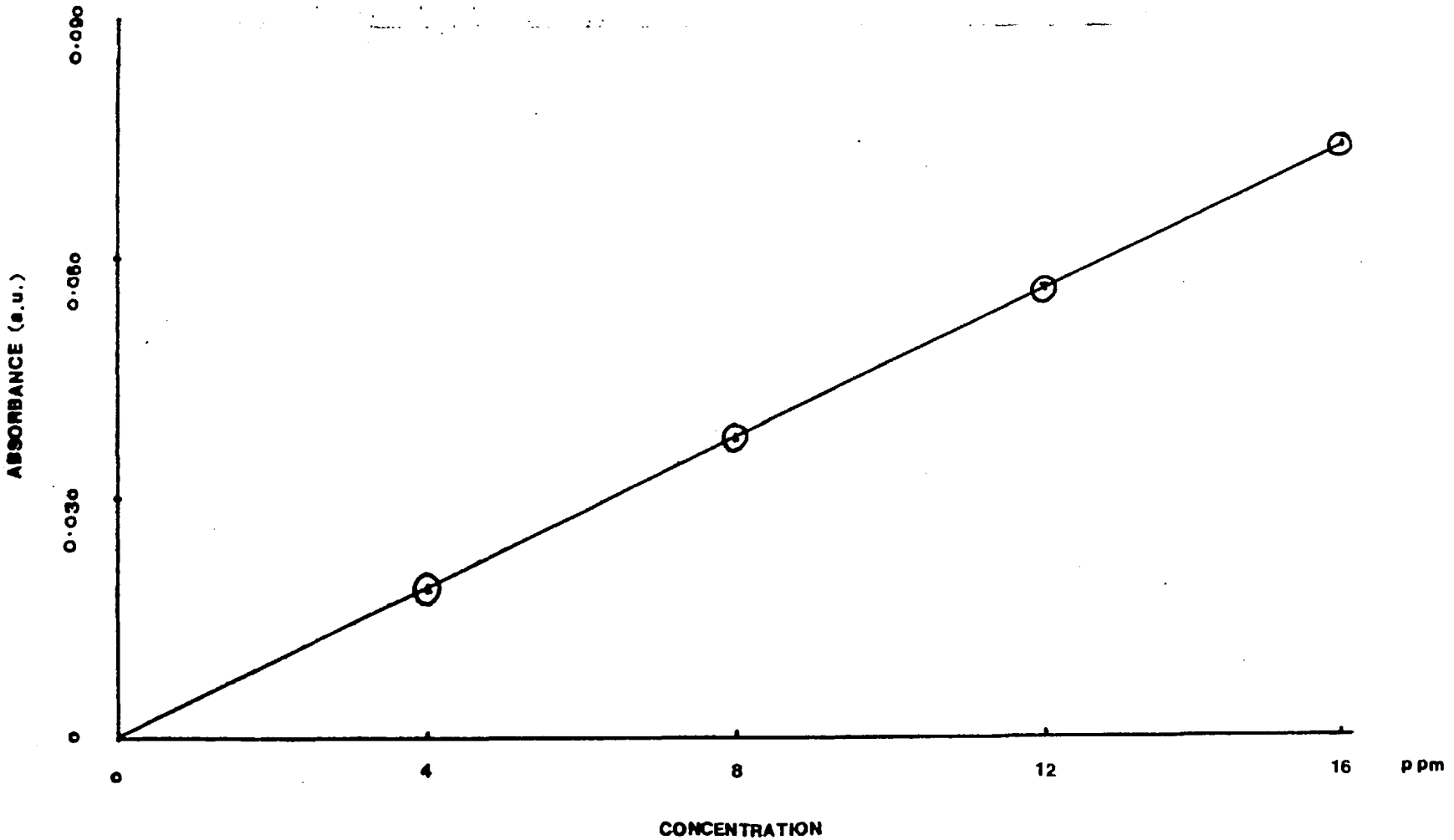


Fig. 7.4 Calibration Graph for the Determination of Vanadium in Coal Samples



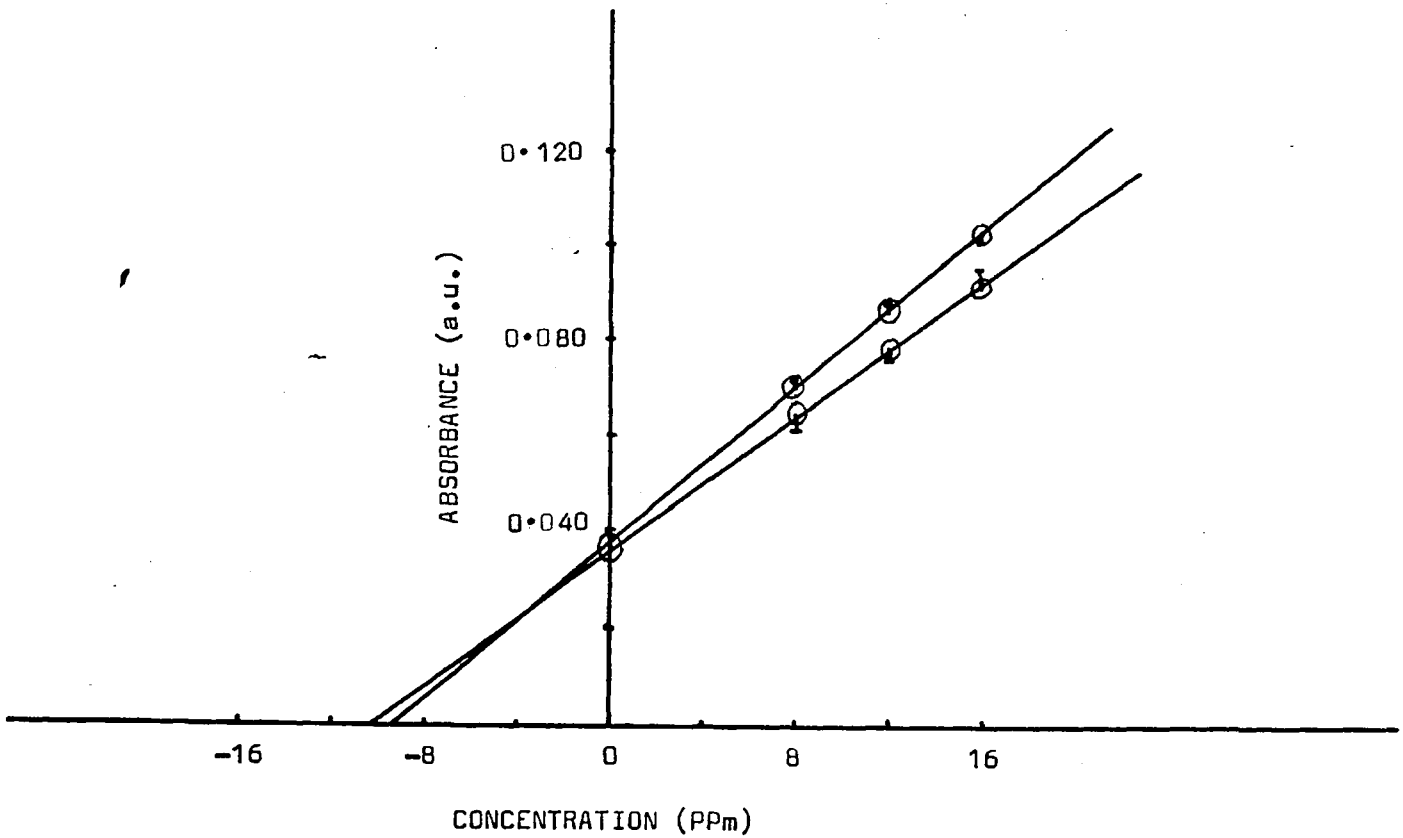


Fig. 7.5 Extrapolated Graphs for the Determination of Vanadium in Coal Samples by Standard Addition Method

Table 7.9

Determination of Nickel in

Residual Oil F-80 by Calibration Method

Dilution = 10 Times

Wt. of Sample = 1·6 g

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppm)	RESULT (ppm)
1	0·056	3·14	19·60
2	0·050	2·80	17·48
3	0·052	2·91	18·19
4	0·054	3·02	18·89
5	0·048	2·68	16·72
6	0·046	2·57	16·06
7	0·045	2·51	15·70
8	0·057	3·19	19·96
9	0·040	2·23	13·93
10	0·058	3·25	20·31

$\bar{X}$ = 17·7 ppm

σ = $\pm$ 2·05 ppm

$\sigma/\bar{X}$ = 0·12

100 $\sigma/\bar{X}$ = 11·6 %

$\sigma/\sqrt{n}$ = 0·6 ppm

Table 7.10

Determination of Nickel in Residual Oil F-31 by Calibration Method

Dilution = 10 Times

Wt. of Sample = 1·6 g

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppm)	RESULT (ppm)
1	0·052	2·90	18·12
2	0·054	3·02	18·87
3	0·056	3·14	19·62
4	0·057	3·19	19·94
5	0·058	3·25	20·31
6	0·057	3·19	19·94
7	0·053	2·97	18·56
8	0·056	3·14	19·62
9	0·054	3·02	18·87
10	0·053	2·97	18·56

$\bar{X}$ = 19·2 ppm

σ = $\pm$ 0·7 ppm

$\sigma/\bar{X}$ = 0·03

100 $\sigma/\bar{X}$ = 3·8%

$\sigma/\sqrt{n}$ = 0·2 ppm

Table 7.11

Determination of Nickel in

Coal Sample A by Calibration Method

Dilution = 10 Times

Wt. of Sample = 1•2 g

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppm)	RESULT (ppm)
1	0•050	2•79	23•25
2	0•052	2•91	24•23
3	0•048	2•68	22•33
4	0•047	2•62	21•80
5	0•053	2•97	24•70
6	0•051	2•85	23•75
7	0•050	2•79	23•25
8	0•056	3•14	26•13
9	0•049	2•74	22•80
10	0•044	2•45	20•42

$\bar{X}$ = 23•3 ppm

σ = $\pm$ 1•6 ppm

$\sigma/\bar{X}$ = 0•06

100 $\sigma/\bar{X}$ = 6•8 %

$\sigma/\sqrt{n}$ = 0•5 ppm

Table 7.12

Determination of Nickel in

Coal Sample B by Calibration Method

Dilution = 10 Times

Wt. of Sample = 1·2 g

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppm)	RESULT (ppm)
1	0·063	3·54	29·45
2	0·060	3·36	28·03
3	0·065	3·65	30·41
4	0·062	3·48	28·98
5	0·060	3·36	28·03
6	0·068	3·82	31·83
7	0·064	3·59	29·93
8	0·062	3·48	28·98
9	0·056	3·14	26·13
10	0·062	3·48	28·98

$\bar{X}$ = 29·07 ppm

σ = $\pm$ 1·5 ppm

$\sigma/\bar{X}$ = 0·05

100 $\sigma/\bar{X}$ = 5·3 %

$\sigma/\sqrt{n}$ = 0·5 ppm

Table 7.13

Determination of Nickel in Residual Oil Sample by Standard Addition Method

Dilution = 10 Times Wt. of Sample = 1·6 g

F-80				F-31			
NO	SAMPLE	ABSORBANCE	RESULT (ppm)	NO	SAMPLE	ABSORBANCE	RESULT (ppm)
1	SAMPLE + HNO_3	0·046		1	SAMPLE + HNO_3	0·049	
2	SAMPLE + 2 ppm	0·070	16·8 ± 2·2σ	2	SAMPLE + 2 ppm	0·079	20·5 ± 2·0σ
3	SAMPLE + 4 ppm	0·107		3	SAMPLE + 4 ppm	0·108	
4	SAMPLE + 6 ppm	0·140		4	SAMPLE + 6 ppm	0·136	

Table 7.14

Determination of Nickel in Coal Sample A and B by Standard Addition Method

Dilution = 10 Times Wt. of Sample = 1•2 g

SAMPLE A				SAMPLE B			
NO	SAMPLE	ABSORBANCE	RESULT (ppm)	NO	SAMPLE	ABSORBANCE	RESULT (ppm)
1	SAMPLE + HNO_3	0•053		1	SAMPLE + HNO_3	0•064	
2	SAMPLE + 2 ppm	0•075	25•3 ± 1•2 σ	2	SAMPLE + 2 ppm	0•088	33•2 ± 3 σ
3	SAMPLE + 4 ppm	0•113		3	SAMPLE + 4 ppm	0•121	
4	SAMPLE + 6 ppm	0•146		4	SAMPLE + 6 ppm	0•151	

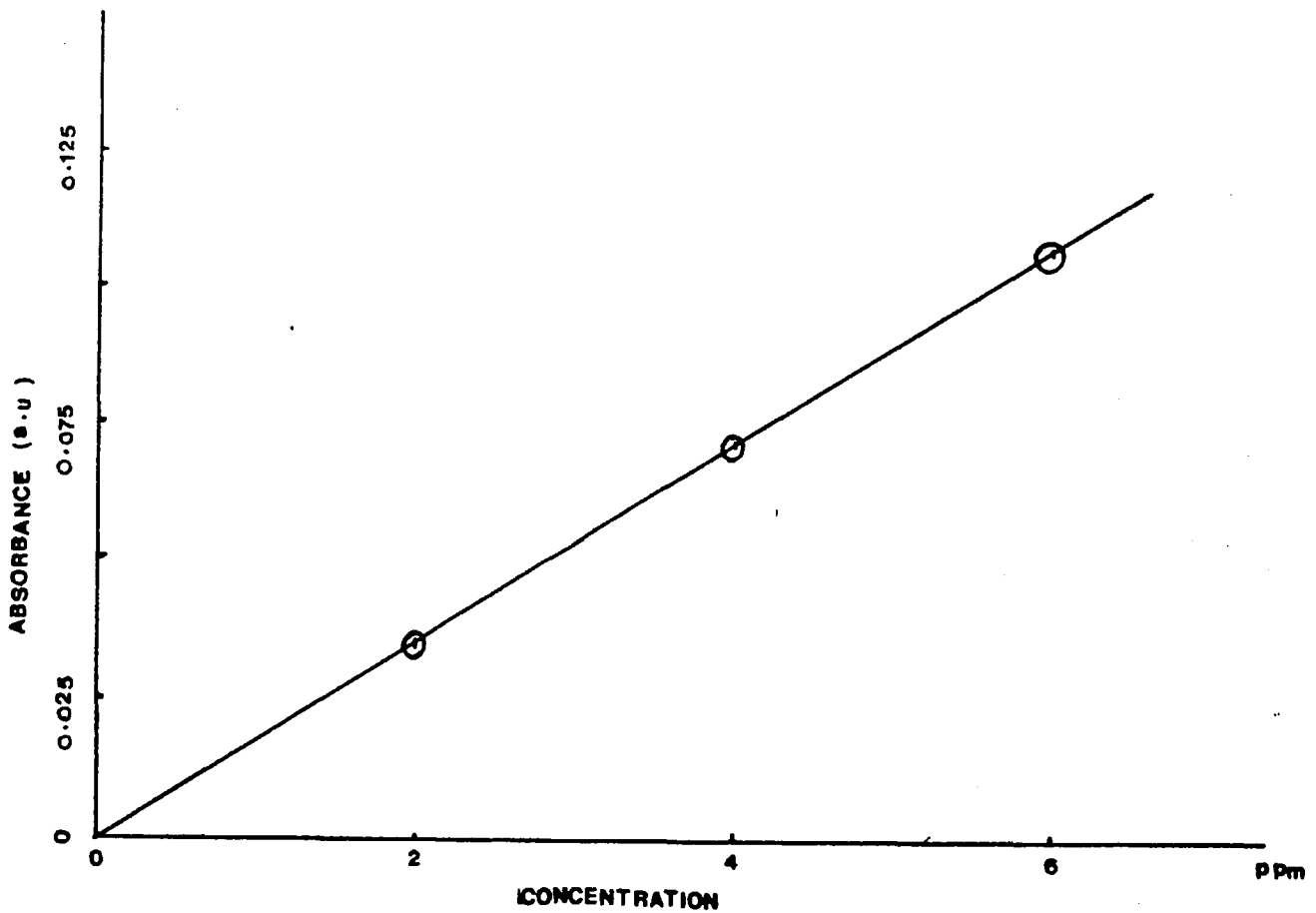


Fig. 7.6 Calibration Graph for the Determination of Nickel in Residual Oil Samples

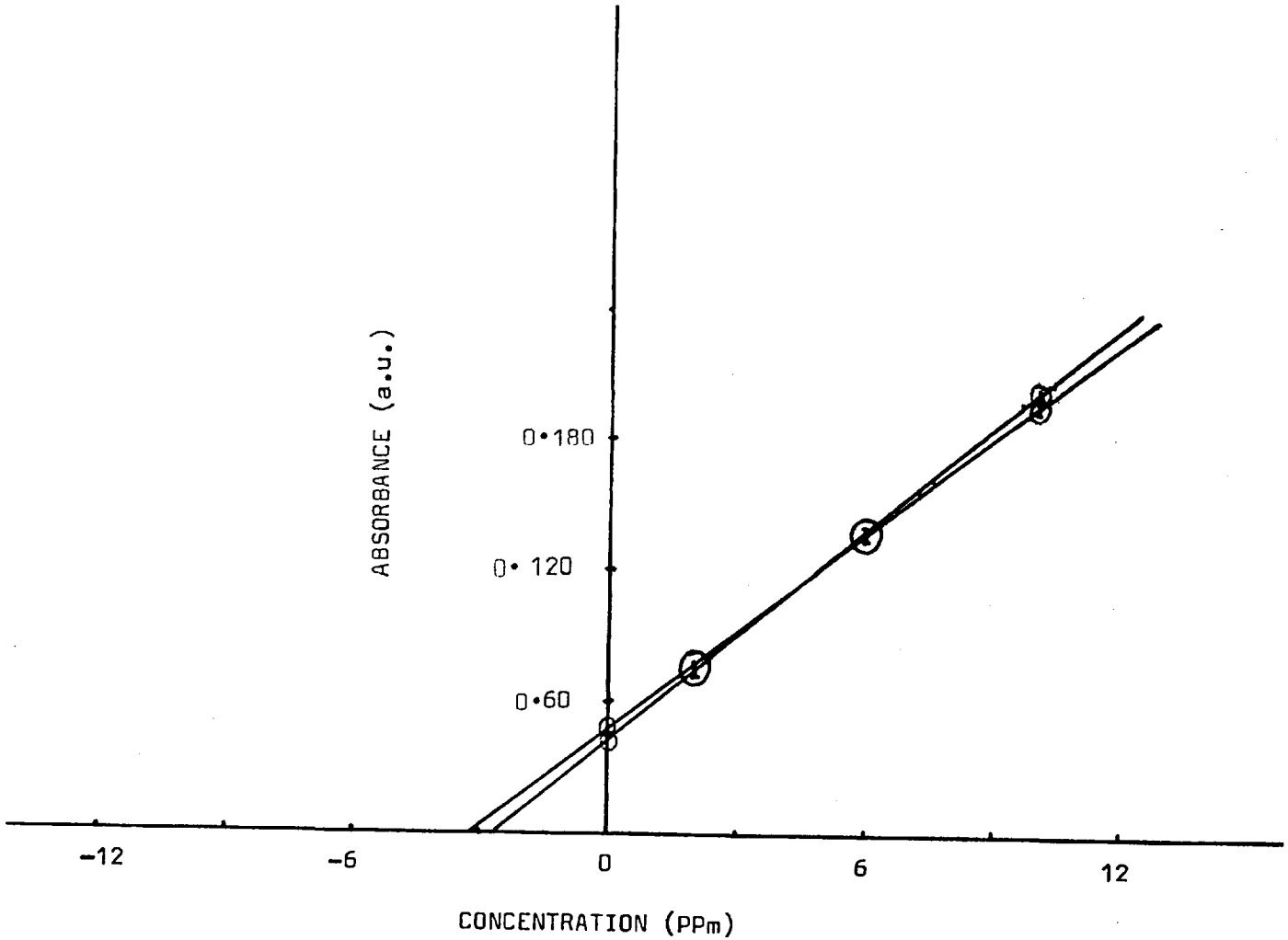


Fig. 7.7 Extrapolated Graphs for the Determination of Nickel in Residual Oil Samples by Standard Addition Method

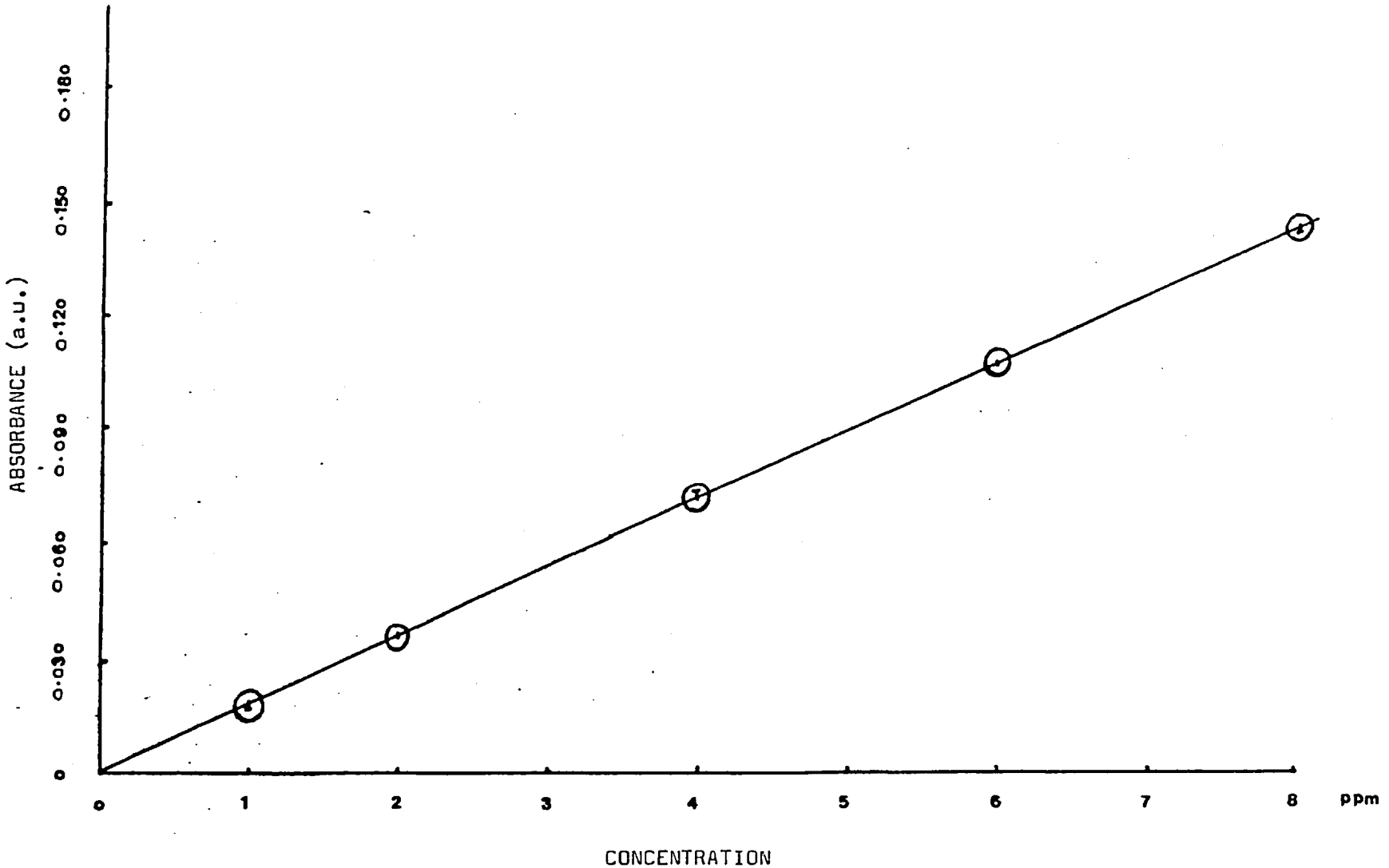


Fig. 7.8 Calibration Graph for the Determination of Nickel in Coal Samples

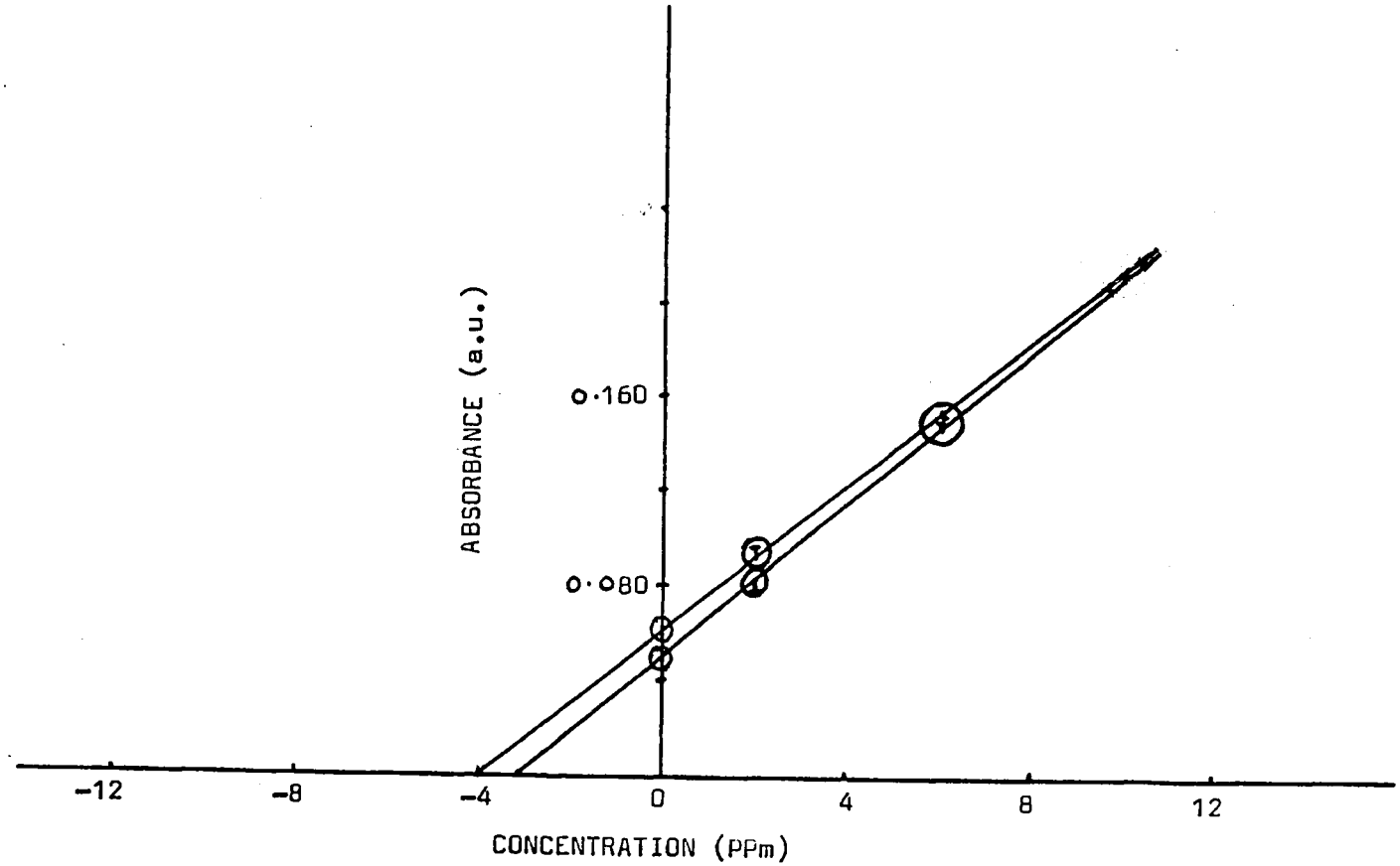


Fig. 7.9 Extrapolated Graphs for the Determination of Nickel in Coal Samples by Standard Addition Method

Table 7.15

Determination of Iron in

Residual Oil Sample F-80 by Calibration Method

Dilution = 10 Times

Wt. of Sample = 0·8 g

Blank Reading = 3·665

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppm)	RESULT (ppm)
1	0·054	2·43	26·71
2	0·054	2·43	26·71
3	0·052	2·34	25·59
4	0·052	2·34	25·59
5	0·052	2·34	25·59
6	0·048	2·16	23·39
7	0·050	2·25	24·47
8	0·048	2·16	23·39
9	0·050	2·25	24·47
10	0·050	2·25	24·47

$\bar{X}$ = 25·03 ppm

σ = $\pm$ 1·2 ppm

$\sigma/\bar{X}$ = 1·3

100 $\sigma/\bar{X}$ = 4·8 %

$\sigma/\sqrt{n}$ = 0·4 ppm

Table 7.16

Determination of Iron in Residual Oil F-31 by Calibration Method

Dilution = 10 Times

Wt. of Sample = 0•8 g

Blank Concentration = 3•61 ppm

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppm)	RESULT (ppm)
1	0•043	1•93	20•51
2	0•044	1•98	21•14
3	0•041	1•84	19•39
4	0•042	1•89	20•01
5	0•045	2•02	21•64
6	0•042	1•89	20•01
7	0•043	1•93	20•56
8	0•045	2•02	21•64
9	0•041	1•84	19•39
10	0•044	1•98	21•14

$\bar{X}$ = 20•5 ppm

σ = $\pm$ 0•8 ppm

$\sigma/\bar{X}$ = 0•04

100 $\sigma/\bar{X}$ = 4•1 %

$\sigma/\sqrt{n}$ = 0•3 ppm

Table 7.17

Determination of Iron in Coal Sample A by Calibration Method

Dilution = 2000 Times

Wt. of Sample = 0·3 g

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppm)	RESULT
1	0·047	2·19	1·46%
2	0·050	2·32	1·55%
3	0·052	2·41	1·61%
4	0·051	2·37	1·58%
5	0·052	2·41	1·61%
6	0·055	2·54	1·69%
7	0·048	2·24	1·49%
8	0·045	2·11	1·41%
9	0·050	2·32	1·55%
10	0·050	2·32	1·55%

$\bar{X}$ = 1·55%

σ = $\pm$ 0·1%

$\sigma/\bar{X}$ = 0·05

100 $\sigma/\bar{X}$ = 5·2%

$\sigma/\sqrt{n}$ = 0·02%

Table 7.18

Determination of Iron in

Coal Sample B by Calibration Method

Dilution = 2000 Times

Wt. of Sample = 0•3 g

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppm)	RESULT
1	0•042	1•97	1•32%
2	0•042	1•97	1•32%
3	0•041	1•93	1•29%
4	0•043	2•02	1•35%
5	0•040	1•89	1•26%
6	0•041	1•93	1•29%
7	0•043	2•02	1•35%
8	0•039	1•84	1•23%
9	0•042	1•97	1•32%
10	0•042	1•97	1•32%

$\bar{X}$ = 1•3%

σ = $\pm$ 0•03%

$\sigma/\bar{X}$ = 0•02

100 $\sigma/\bar{X}$ = 2•9%

$\sigma/\sqrt{n}$ = 0•01%

Table 7.19

Determination of Iron in Residual Oil F-80 and F-31 by Standard Addition Method

Dilution = 20 Times Wt. of Sample = 0·8 g

F-80				F-31			
NO	SAMPLE	ABSORBANCE	RESULT (ppm)	NO	SAMPLE	ABSORBANCE	RESULT (ppm)
1	SAMPLE + HNO_3	0·025		1	SAMPLE + HNO_3	0·023	
2	SAMPLE + 1 ppm	0·036		2	SAMPLE + 1 ppm	0·033	
			30·3 ± 5σ				25 ± 5σ
3	SAMPLE + 2 ppm	0·065		3	SAMPLE + 2 ppm	0·063	
4	SAMPLE + 3 ppm	0·078		4	SAMPLE + 3 ppm	0·079	

Table 7.20

Determination of Iron in Coal Sample A and B by Standard Addition Method

Dilution = 4×10^3 Times Wt. of Sample = 0·3 g.

SAMPLE A				SAMPLE B			
NO	SAMPLE	ABSORBANCE	RESULT	NO	SAMPLE	ABSORBANCE	RESULT
1	SAMPLE + HNO_3	0·025		1	SAMPLE + HNO_3	0·021	
2	SAMPLE + 1 ppm	0·037	1·65 % ± 0·1σ%	2	SAMPLE + 1 ppm	0·034	1·37 % ± 0·12σ%
3	SAMPLE + 2 ppm	0·065		3	SAMPLE + 2 ppm	0·060	
4	SAMPLE + 4 ppm	0·079		4	SAMPLE + 4 ppm	0·075	

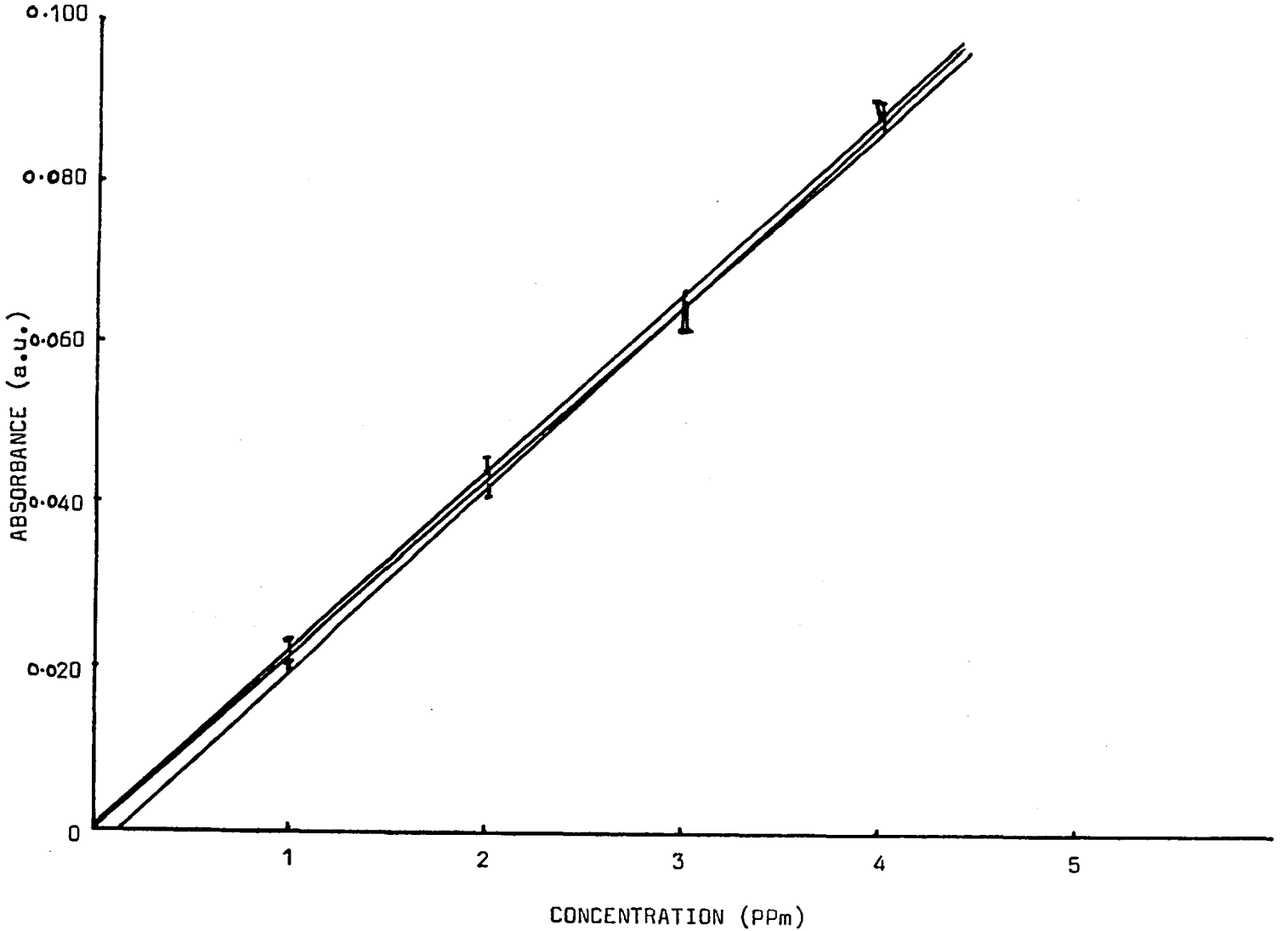


Fig. 7.10 Calibration Graphs for the Determination of Iron in Residual Oil and in Coal Samples

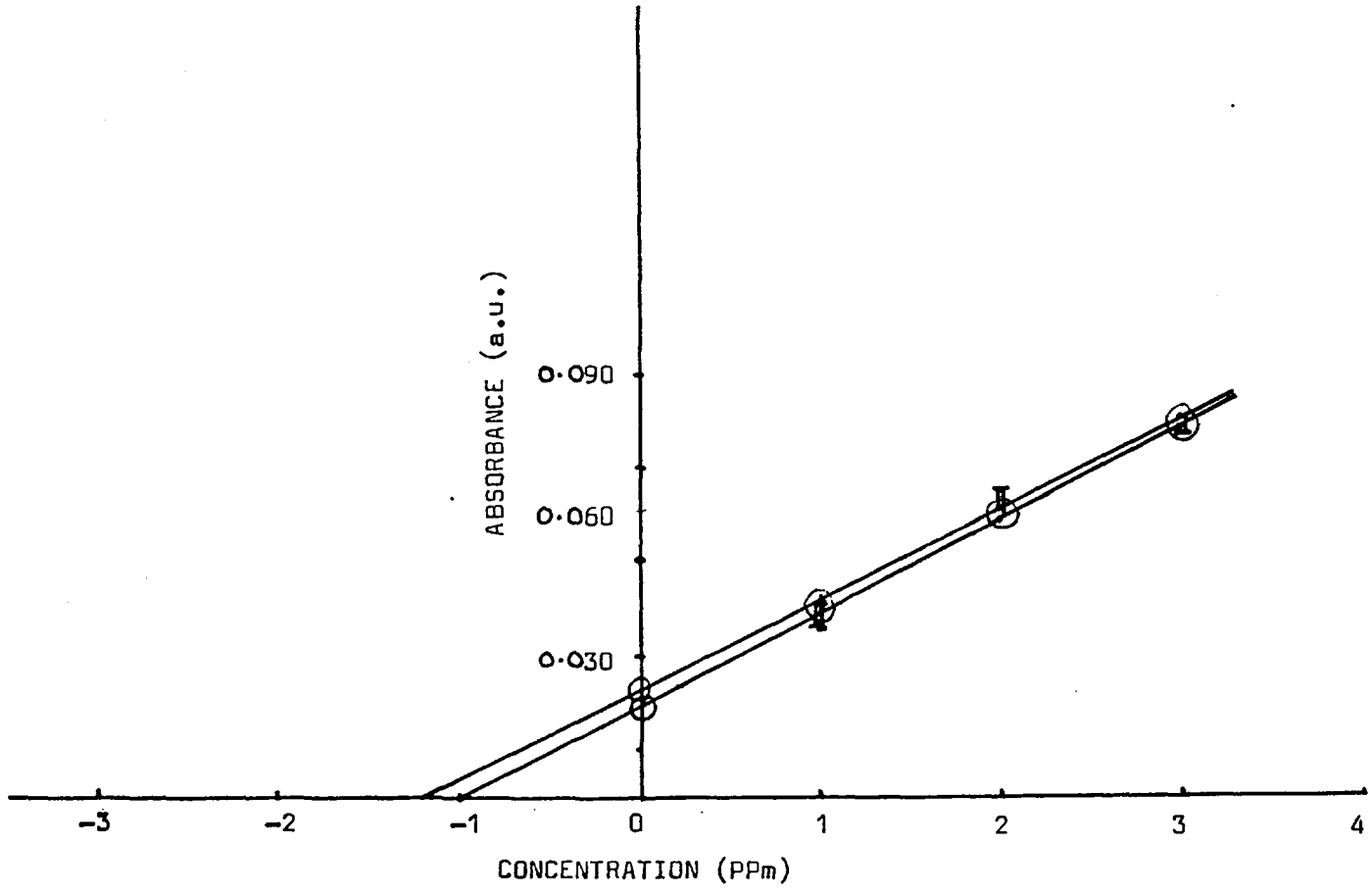


Fig. 7.11 Extrapolated Graphs for the Determination of Iron in Residual Oil and in Coal Samples by Standard Addition Method

Table 7.21

Determination of Copper in Residual Oil F-80 by Calibration Method

Dilution = 10 Times

Wt. of Sample = 3•2 g

Blank = 0•005 (signal)

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppm)	RESULT (ppm)
1	0•036	0•78	2•44
2	0•038	0•83	2•59
3	0•035	0•73	2•34
4	0•041	0•90	2•81
5	0•039	0•85	2•66
6	0•033	0•70	2•19
7	0•037	0•80	2•50
8	0•037	0•80	2•50
9	0•038	0•83	2•59
10	0•036	0•78	2•44

$\bar{X}$ = 2•50 ppm

σ = $\pm$ 0•2 ppm

$\sigma/\bar{X}$ = 0•1

$100\ \sigma/\bar{X}$ = 6•9%

$\sigma/\sqrt{n}$ = 0•05 ppm

Table 7.22

Determination of Copper in Residual Oil F-31 by Calibration Method

Dilution = 10 Times

Wt. of Sample = 3•2 g

Blank = 0•005 (signal)

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppm)	RESULT (ppm)
1	0•034	0•73	2•28
2	0•037	0•80	2•50
3	0•040	0•87	2•72
4	0•038	0•83	2•59
5	0•034	0•73	2•28
6	0•036	0•78	2•44
7	0•036	0•78	2•44
8	0•035	0•75	2•34
9	0•034	0•73	2•28
10	0•036	0•78	2•44

$\bar{X}$ = 2•43 ppm

σ = $\pm$ 0•1 ppm

$\sigma/\bar{X}$ = 0•05

100 $\sigma/\bar{X}$ = 5•9%

$\sigma/\sqrt{n}$ = 0•04 ppm

Table 7.23

Determination of Copper in

Coal Sample A by Calibration Method

Dilution = 10 Times

Wt. of Sample = 0•3 g

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppm)	RESULT (ppm)
1	0•041	1•02	34•00
2	0•042	1•05	35•00
3	0•043	1•07	35•67
4	0•045	1•12	37•33
5	0•040	1•00	33•33
6	0•043	1•07	35•67
7	0•044	1•10	36•67
8	0•042	1•05	35•00
9	0•043	1•07	35•67
10	0•039	0•97	32•43

$\bar{X}$ = 35•0 ppm

σ = $\pm$ 1•5 ppm

$\sigma/\bar{X}$ = 0•04

100 $\sigma/\bar{X}$ = 4•3%

$\sigma/\sqrt{n}$ = 0•3 ppm

Table 7.24

Determination of Copper in

Coal Sample B by Calibration Method

Dilution = 10 Times

Wt. of Sample = 0·3 g

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppm)	RESULT (ppm)
1	0·060	1·49	49·67
2	0·050	1·24	41·46
3	0·054	1·34	44·67
4	0·056	1·39	46·39
5	0·058	1·44	48·03
6	0·051	1·27	42·28
7	0·054	1·34	44·67
8	0·056	1·39	46·39
9	0·053	1·32	43·92
10	0·059	1·47	48·85

$\bar{X}$ = 45·6 ppm

σ = $\pm$ 2·7 ppm

$\sigma/\bar{X}$ = 0·05

100 $\sigma/\bar{X}$ = 5·9%

$\sigma/\sqrt{n}$ = 0·8 ppm

Table 7.25

Determination of Copper in Residual Oil F-80 and F-31 By Standard Addition Method

Dilution = 10 Times Wt. of Sample = 3·2 g Blank = 0·56 ppm

F-80				F-31			
NO	SAMPLE	ABSORBANCE	RESULT (ppm)	NO	SAMPLE	ABSORBANCE	RESULT (ppm)
1	SAMPLE + HNO_3	0·036		1	SAMPLE + HNO_3	0·035	
2	SAMPLE + 0·5 ppm	0·045	3·6 ± 0·64 σ	2	SAMPLE + 0·5 ppm	0·044	3·4 ± 0·4 σ
3	SAMPLE + 1 ppm	0·060		3	SAMPLE + 1 ppm	0·060	
4	SAMPLE + 1·5 ppm	0·074		4	SAMPLE + 1·5 ppm	0·073	

Table 7.26

Determination of Copper in Coal Sample A and B by Standard Addition Method

Dilution = 20 Times Wt. of Sample = 0·3 g

SAMPLE A				SAMPLE B			
NO	SAMPLE	ABSORBANCE	RESULT (ppm)	NO	SAMPLE	ABSORBANCE	RESULT (ppm)
1	SAMPLE + HNO_3	0·021		1	SAMPLE + HNO_3	0·026	
2	SAMPLE + 0·5 ppm	0·035	38·0 ± 2σ	2	SAMPLE + 0·5 ppm	0·039	53·6 ± 2·5σ
3	SAMPLE + 1 ppm	0·055		3	SAMPLE + 1 ppm	0·057	
4	SAMPLE + 1·5 ppm	0·072		4	SAMPLE + 1·5 ppm	0·072	

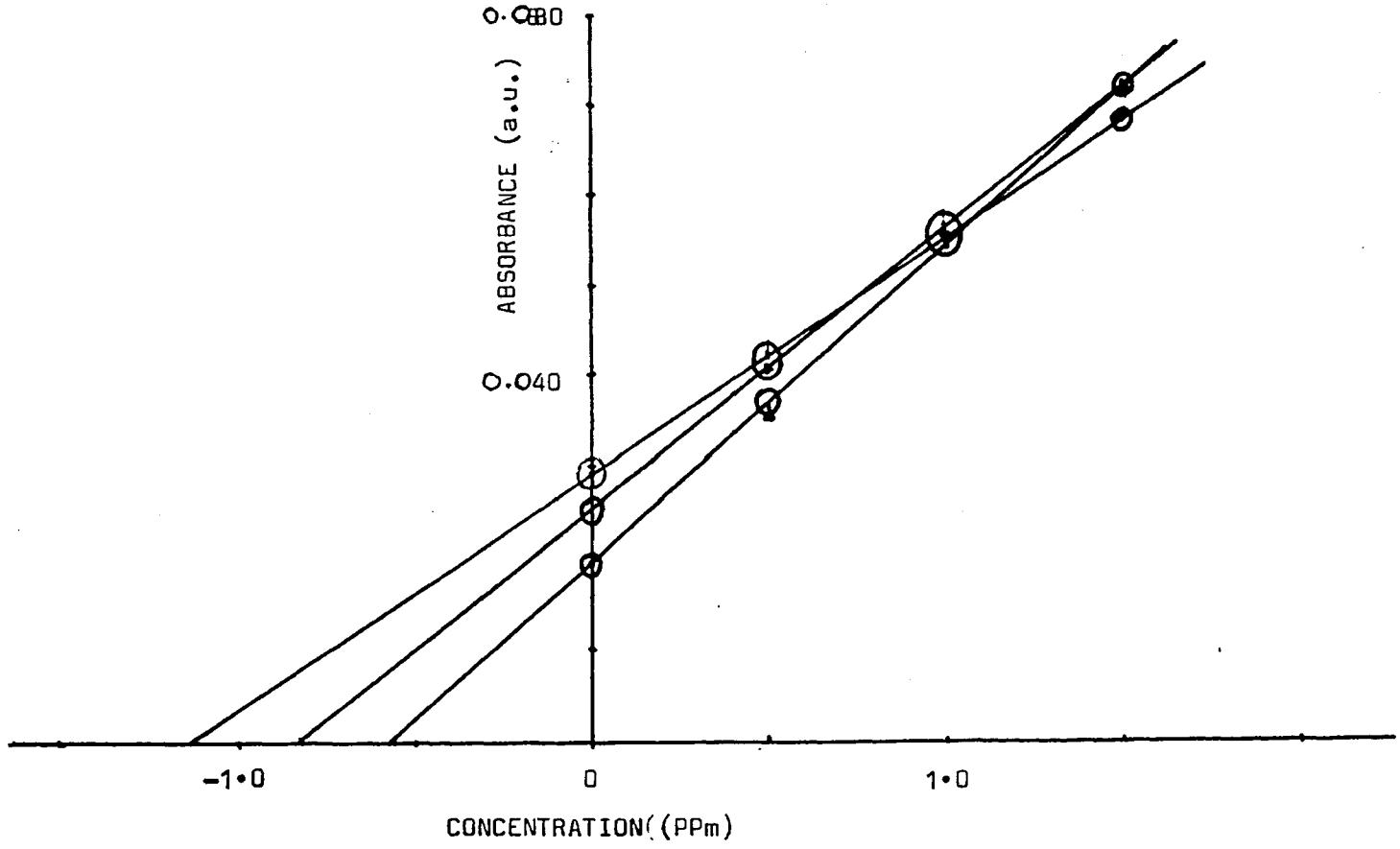


Fig. 7.12 Extrapolated Graphs for the Determination of Copper in Residual Oil and in Coal Samples by Standard Addition Method

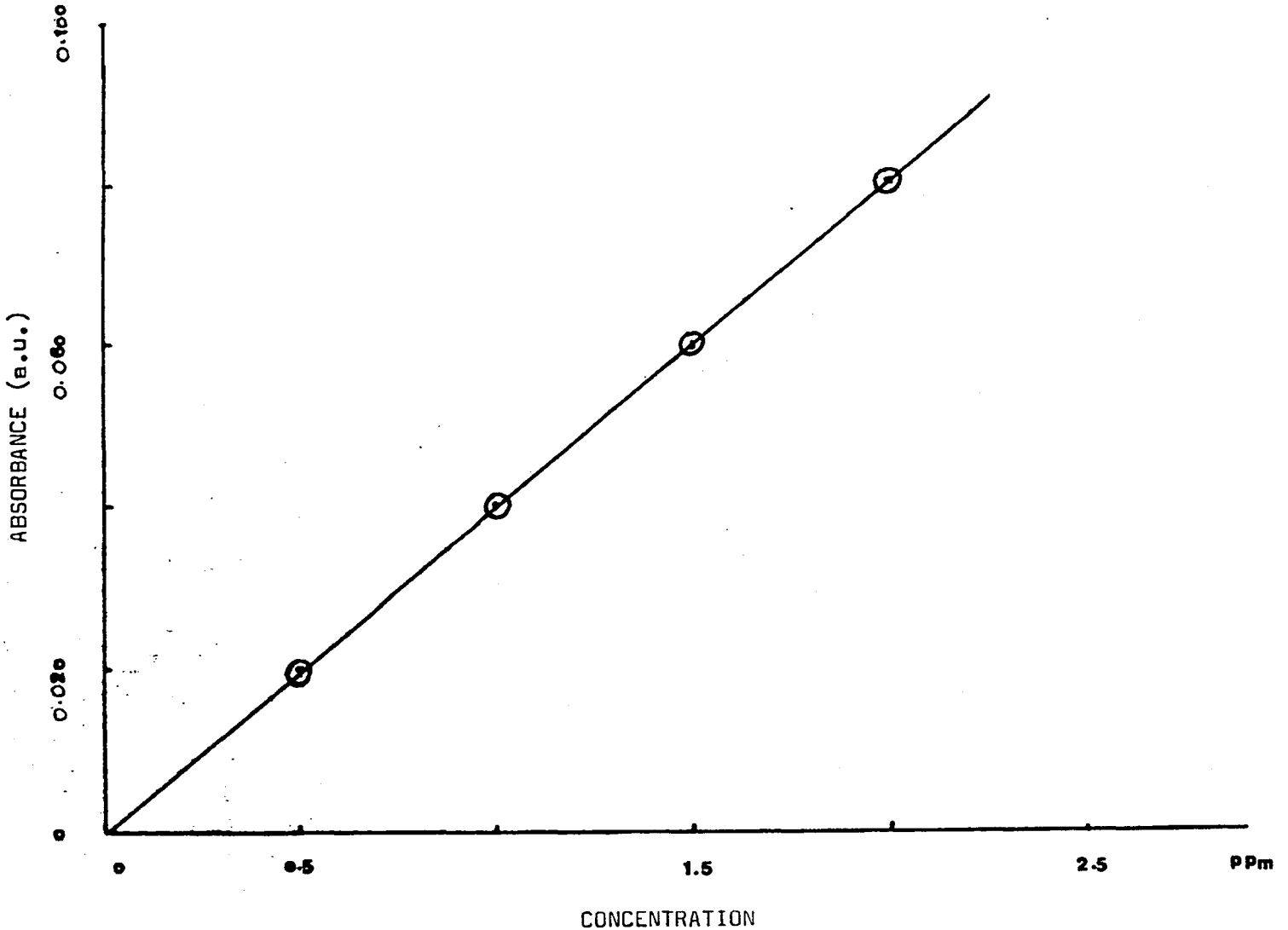


Fig. 7.13 Calibration Graphs for the Determination of Copper in Residual Oil and in Coal Samples

Table 7·27

Determination of Lead in

Residual Oil F-80 by Calibration Method

Dilution = 10 Times

Wt. of Sample = 0·4 g

Filter Paper Blank = 0·12 PPb (signal 0·009)

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppb)	RESULT (ppm)
1	0·037	26·40	0·54
2	0·037	26·40	0·54
3	0·035	24·90	0·50
4	0·034	24·16	0·48
5	0·038	27·15	0·56
6	0·035	24·90	0·50
7	0·036	25·65	0·52
8	0·037	26·40	0·54
9	0·035	24·90	0·50
10	0·037	26·40	0·54

$\bar{X}$ = 0·52 ppm

σ = $\pm$ 0·03 ppm

$\sigma/\bar{X}$ = 0·05

100 $\sigma/\bar{X}$ = 4·9%

$\sigma/\sqrt{n}$ = 0·008

Table 7.28

Determination of Lead in

Residual Oil F-31 by Calibration Method

Dilution = 10 Times

Wt. of Sample = 0·4 g

Filter Paper Blank = 0·12 ppb (signal 0·009)

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppb)	RESULT (ppm)
1	0·040	24·72	0·50
2	0·045	27·93	0·58
3	0·044	27·29	0·56
4	0·046	28·58	0·59
5	0·044	27·29	0·56
6	0·042	26·00	0·53
7	0·041	25·36	0·51
8	0·039	24·07	0·48
9	0·040	24·72	0·50
10	0·039	24·07	0·48

$\bar{X}$ = 0·53 ppm

σ = $\pm$ 0·04 ppm

$\sigma/\bar{X}$ = 0·07

100 $\sigma/\bar{X}$ = 7·7%

$\sigma/\sqrt{n}$ = 0·01 ppm

Table 7.29

Determination of Lead in

Coal Sample A by Calibration Method

Dilution = 10 Times

Wt. of Sample = 1·8 g

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppm)	RESULT (ppm)
1	0·024	4·00	22·22
2	0·028	4·67	25·93
3	0·024	4·00	22·22
4	0·025	4·17	23·15
5	0·023	3·83	21·30
6	0·024	4·00	22·22
7	0·026	4·33	24·07
8	0·024	4·00	22·22
9	0·022	3·67	20·37
10	0·025	4·17	23·15

$\bar{X}$ = 22·69 ppm

σ = $\pm$ 1·5 ppm

$\sigma/\bar{X}$ = 0·06

100 $\sigma/\bar{X}$ = 6·7%

$\sigma/\sqrt{n}$ = 0·5 ppm

Table 7.30

Determination of Lead in

Coal Sample B by Calibration Method

Dilution = 10 Times

Wt. of Sample = 1·8 g

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppm)	RESULT (ppm)
1	0·028	4·67	25·93
2	0·026	4·33	24·07
3	0·025	4·17	23·15
4	0·027	4·50	25·00
5	0·029	4·83	26·85
6	0·024	4·00	22·22
7	0·028	4·67	25·93
8	0·029	4·83	26·85
9	0·027	4·50	25·00
10	0·027	4·50	25·00

$\bar{X}$ = 25·0 ppm

σ = $\pm$ 1·5 ppm

$\sigma/\bar{X}$ = 0·06

100 $\sigma/\bar{X}$ = 6·0 %

$\sigma/\sqrt{n}$ = 0·5 ppm

Table 7.31

Determination of Lead in Residual Oil F-80 and F-31 by Standard Addition Method

Dilution = 20 Times Wt. of Sample = 0·4 g

F-80				F-31			
NO	SAMPLE	ABSORBANCE	RESULT (ppm)	NO	SAMPLE	ABSORBANCE	RESULT (ppm)
1	SAMPLE + HNO_3	0·011		1	SAMPLE + HNO_3	0·011	
2	SAMPLE + 10 ppb	0·014	0·99 ± 0·2 σ	2	SAMPLE + 10 ppb	0·014	0·94 ± 0·18 σ
3	SAMPLE + 20 ppb	0·020		3	SAMPLE + 20 ppb	0·021	
4	SAMPLE + 30 ppb	0·026		4	SAMPLE + 30 ppb	0·027	

Table 7.32

Determination of Lead in Coal Sample A and B by Standard Addition Method

Dilution = 20 Times Wt. of Sample = 1·8 g

SAMPLE A				SAMPLE B			
NO	SAMPLE	ABSORBANCE	RESULT (ppm)	NO	SAMPLE	ABSORBANCE	RESULT (ppm)
1	SAMPLE + HNO_3	0·012		1	SAMPLE + HNO_3	0·012	
2	SAMPLE + 2 ppm	0·018	24·0 ± 3·0 σ	2	SAMPLE + 2 ppm	0·017	25·0 ± 3·0 σ
3	SAMPLE + 6 ppm	0·040		3	SAMPLE + 6 ppm	0·041	
4	SAMPLE + 10 ppm	0·059		4	SAMPLE + 10 ppm	0·057	

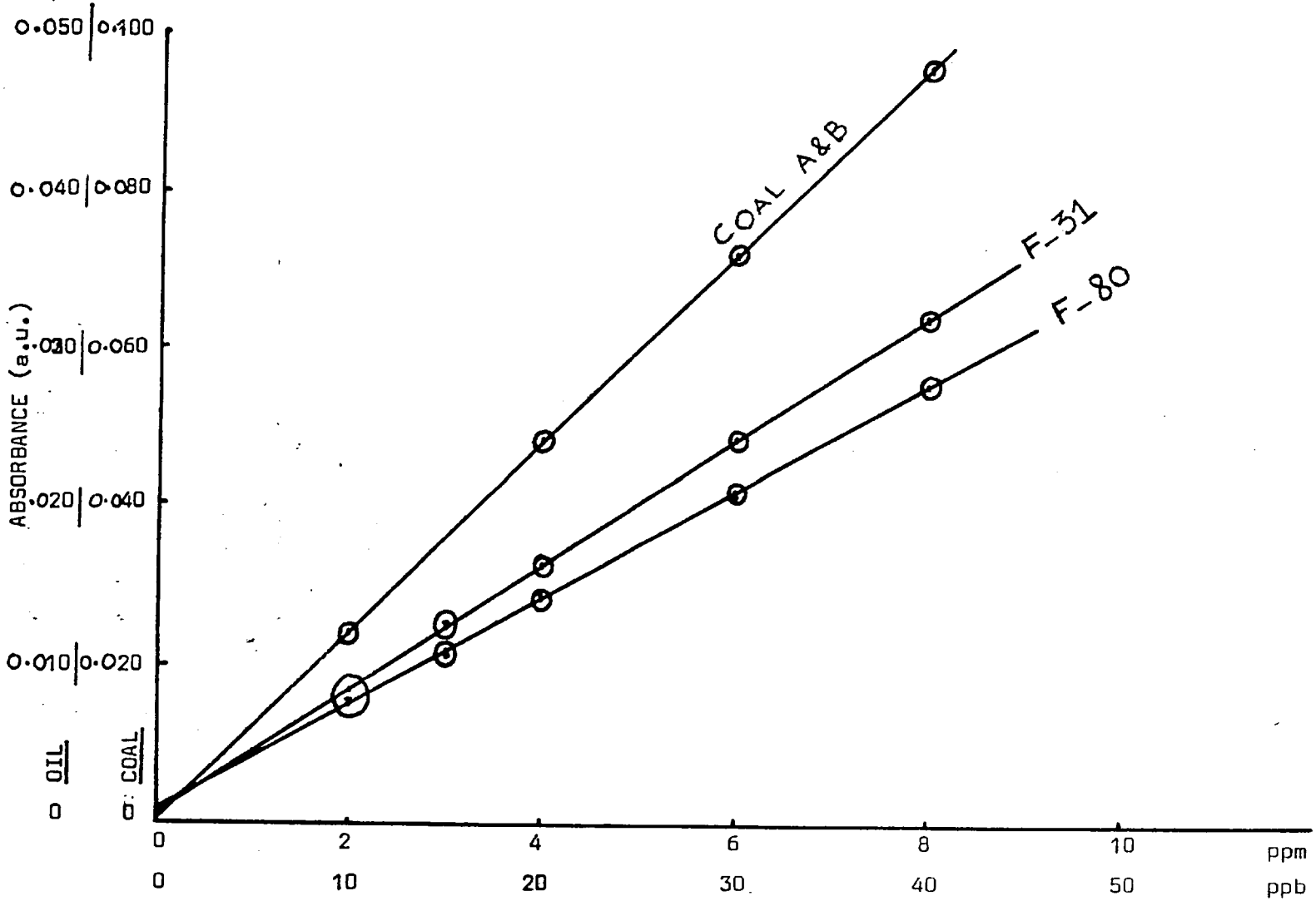


Fig. 7.14 Calibration Graphs for the Determination of Lead in Residual Oil and in Coal Samples

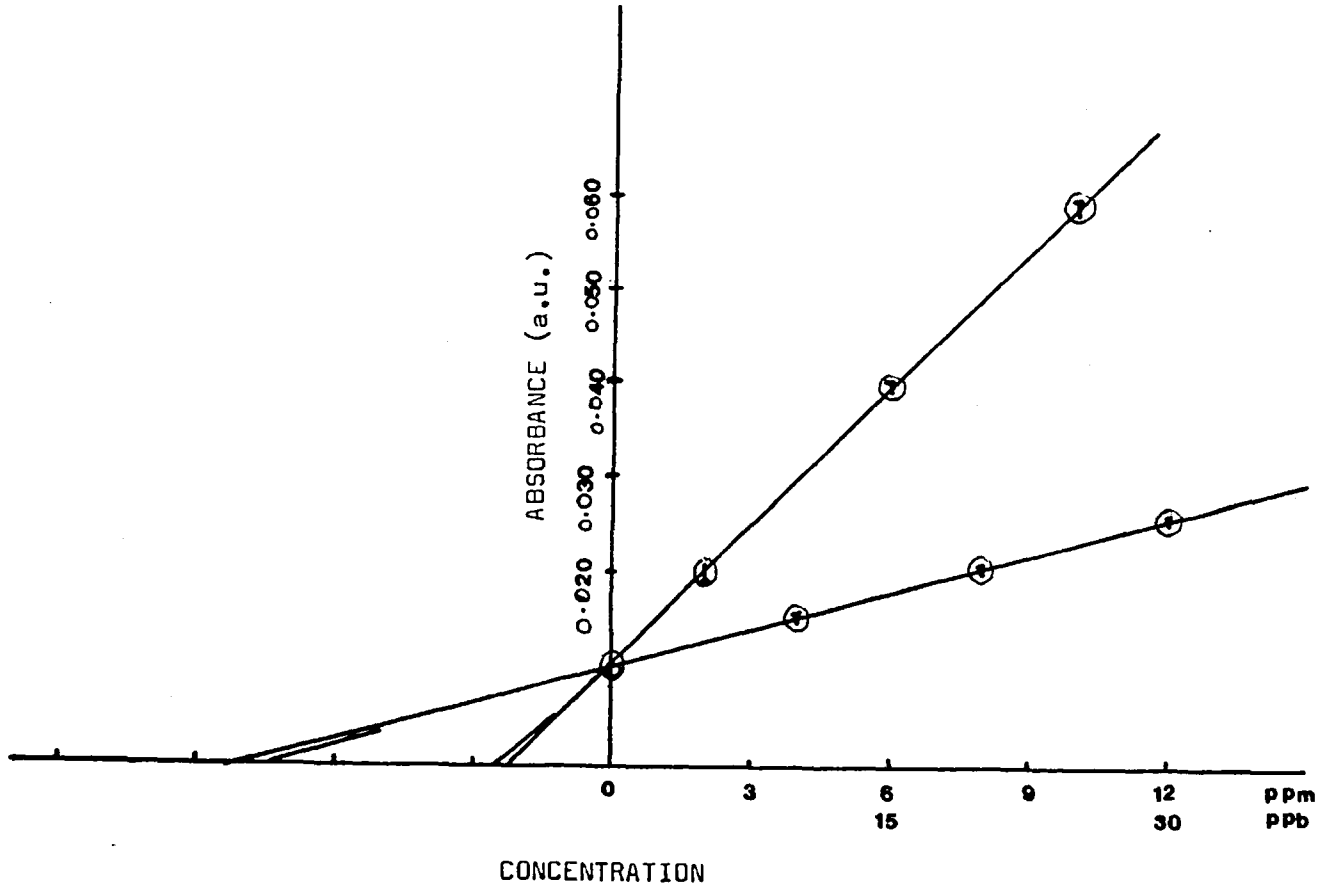


Fig. 7.15 Extrapolated Graphs for the Determination of Lead in Residual Oil and in Coal Samples by Standard Addition Method

Table 7.33

Determination of Arsenic in

Residual Oil F-80 by Calibration Method

Dilution = 25 Times

Wt. of Sample = 0·4 g

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppb)	RESULT (ppm)
1	0·030	33·71	2·11
2	0·032	35·96	2·25
3	0·034	38·21	2·39
4	0·031	34·84	2·18
5	0·029	32·59	2·04
6	0·028	31·46	1·97
7	0·033	37·09	2·32
8	0·026	29·21	1·83
9	0·030	33·71	2·11
10	0·028	31·46	1·97

$\bar{X}$ = 2·1 ppm

σ = $\pm$ 0·2 ppm

$\sigma/\bar{X}$ = 0·1

100 $\sigma/\bar{X}$ = 8·2%

$\sigma/\sqrt{n}$ = 0·05 ppm

Table 7.34

Determination of Arsenic in

Residual Oil Sample F-31 by Calibration Method

Dilution = 5 Times

Wt. of Sample = 0·4 g

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppb)	RESULT (ppm)
1	0·014	17·30	0·22
2	0·020	25·09	0·31
3	0·020	25·09	0·31
4	0·020	25·09	0·31
5	0·018	22·49	0·28
6	0·016	19·89	0·25
7	0·018	22·49	0·28
8	0·016	19·89	0·25
9	0·018	22·49	0·28
10	0·018	22·49	0·28

$\bar{X}$ = 0·28 ppm

σ = $\pm$ 0·03 ppm

$\sigma/\bar{X}$ = 0·1

100 $\sigma/\bar{X}$ = 10·6%

$\sigma/\sqrt{n}$ = 0·01 ppm

Table 7.35

Determination of Arsenic in Coal Sample A by Calibration Method

Dilution = 200 Times

Wt. of Sample = 0·4 g

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppb)	RESULT (ppm)
1	0·022	25·47	12·74
2	0·021	23·76	11·88
3	0·020	22·62	11·31
4	0·023	26·61	13·31
5	0·020	23·19	11·60
6	0·019	22·05	11·03
7	0·022	24·90	12·45
8	0·023	26·04	13·02
9	0·021	24·33	12·17
10	0·022	25·47	12·74
11	0·021	24·33	12·17

$\bar{X}$ = 12·2 ppm

σ = $\pm$ 0·7 ppm

$\sigma/\bar{X}$ = 0·05

100 $\sigma/\bar{X}$ = 5·9%

$\sigma/\sqrt{n}$ = 0·2 ppm

Table 7.36

Determination of Arsenic in Coal Sample B by Calibration Method

Dilution of = 250 Times

Wt. of Sample = 0·3 g

SAMPLE NUMBER	ABSORBANCE	CONC. FROM GRAPH (ppb)	RESULT (ppm)
1	0·025	33·11	27·59
2	0·026	34·44	28·70
3	0·027	35·76	29·80
4	0·024	31·79	26·49
5	0·027	35·76	29·80
6	0·025	33·11	27·59
7	0·027	35·76	29·80
8	0·027	35·76	29·80
9	0·025	33·11	27·59
10	0·025	33·11	27·59
11	0·025	33·11	27·59

$\bar{X}$ = 28·4 ppm

σ = $\pm$ 1·2 ppm

$\sigma/\bar{X}$ = 0·04

$100\ \sigma/\bar{X}$ = 4·3%

$\sigma/\sqrt{n}$ = 0·04 ppm

Table 7.37

Determination of Arsenic in Residual Oil Sample F-80 and F-31 by Standard Addition Method

Dilution of Sample F-80 = 50 Wt. of Sample F-80 = 0•4 g

Dilution of Sample F-31 = 5 Wt. of Sample F-31 = 0•4 g

F-80				F-31			
NO	SAMPLE	ABSORBANCE	RESULT(ppm)	NO	SAMPLE	ABSORBANCE	RESULT(ppm)
1	SAMPLE + HNO_3	0•015		1	SAMPLE + HNO_3	0•015	
2	SAMPLE + 20 ppb	0•027	2•7 ± 0•3 σ	2	SAMPLE + 20 ppb	0•025	0•31 ± 0•07 σ
3	SAMPLE + 30 ppb	0•035		3	SAMPLE + 30 ppb	0•032	
4	SAMPLE + 40 ppb	0•042		4	SAMPLE + 40 ppb	0•038	

Table 7.38

Determination of Arsenic in Coal Sample A and B by Standard Addition Method

Dilution of Sample A = 300 Wt. of Sample A = 0·3 g

Dilution of Sample B = 400 Wt. of Sample B = 0·3 g

SAMPLE A				SAMPLE B			
NO	SAMPLE	ABSORBANCE	RESULT(ppm)	NO	SAMPLE	ABSORBANCE	RESULT(ppm)
1	SAMPLE + HNO_3	0·009		1	SAMPLE + HNO_3	0·008	
2	SAMPLE + 10 ppb	0·014	12·6 ± 2·5 σ	2	SAMPLE + 10 ppb	0·014	31·1 ± 3·0 σ
3	SAMPLE + 20 ppb	0·017		3	SAMPLE + 20 ppb	0·017	
4	SAMPLE + 30 ppb	0·028		4	SAMPLE + 30 ppb	0·019	

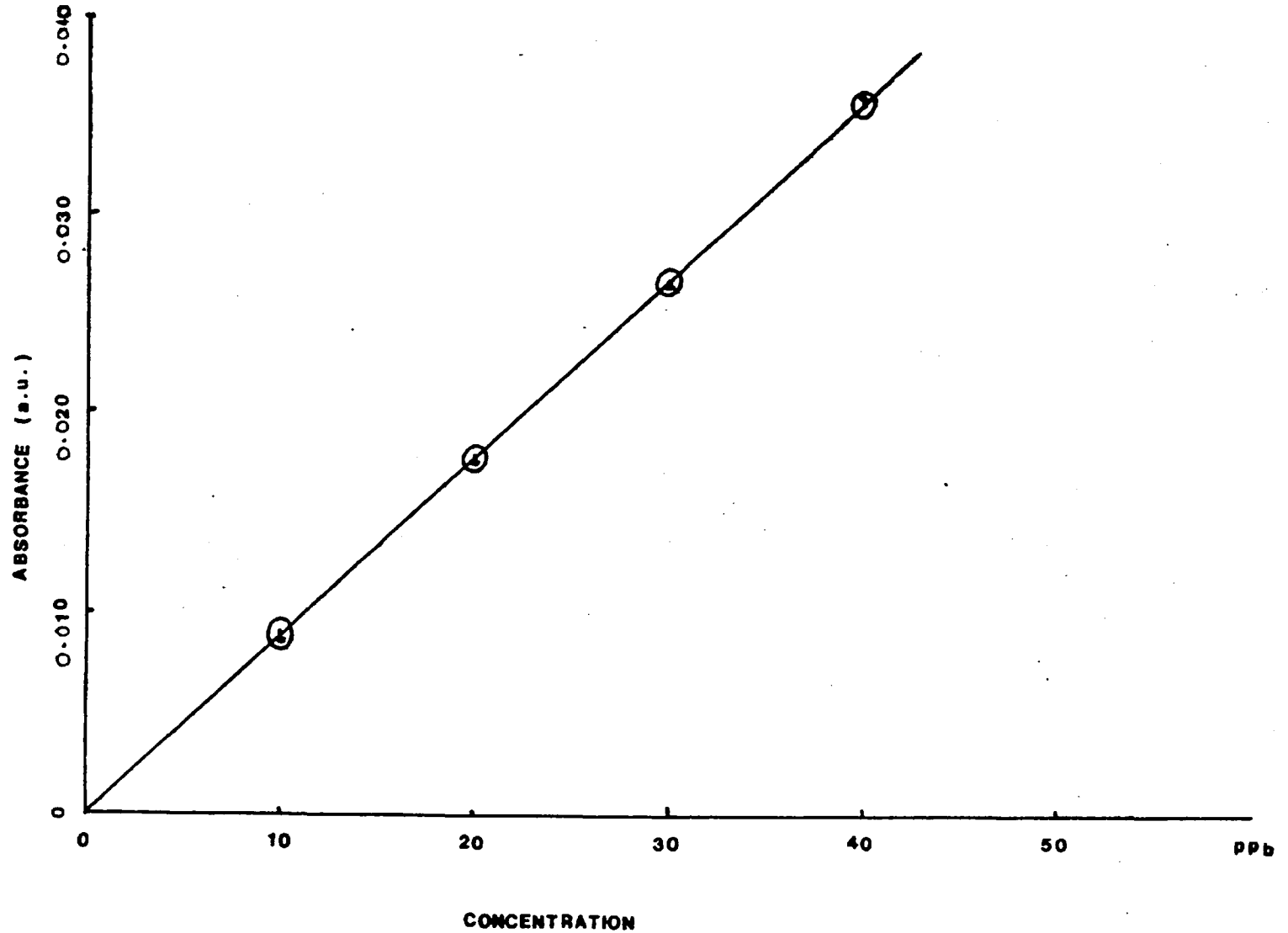


Fig. 7.16 Calibration Graphs for the Determination of Arsenic in Residual Oil and in Coal Samples

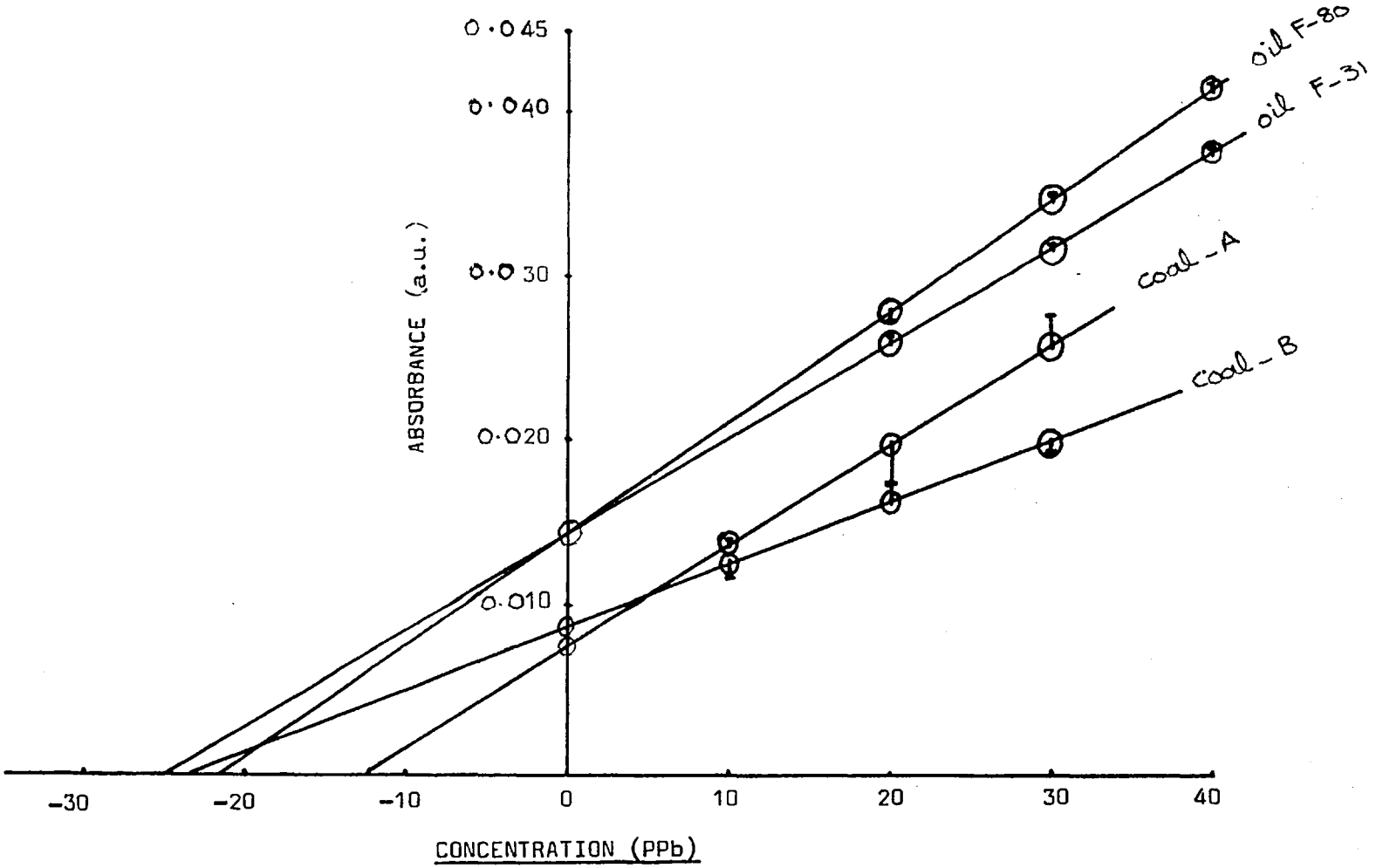


Fig. 7.17 Extrapolated Graphs for the Determination of Arsenic in Residual Oil and Coal Samples by Standard Addition Method

7.5 Statistical Analysis Of Experimental Results

In Figures 7.2 to 7.18 the data points shown were scattered and the linear regression provided the best estimated straight line through the points. After that some tests were carried out to assess the validity of the straight line approximation. The gradient and the correlation coefficient of the straight line were calculated. Table 7.39 summarises the statistical results. The mean ($\bar{X}$) standard deviation (σ), relative standard deviation (R.S.D. 100 $\sigma/\bar{X}$), variance (V), relative ($\sigma/\bar{X}$) and standard error ($\sigma/\sqrt{n}$) are given in Table 7.39. A 95% confidence limit ($\bar{X} \pm 2\sigma$) was calculated for all the samples (Table 7.39) and it is valid to reject some of the values from a set of data if the values lie out side the range of $\bar{X} \pm 2\sigma$. The correlation coefficient (c.c.) for each metal calibration (Table 7.39) varies between 0·99 to 1 indicating that it is 99% certain that the straight line approximation is valid. Precision (R.S.D.) is used to describe the reproducibility of the results. Stability and precision are discussed together because of their close inter-relationship (Table 7.39). Lack of precision can arise from uncertainty or variability in preparation and introduction of samples, and in the measurement of the analytical signal. An unstable excitation source will usually lead to poor measurement precision. The precision (R.S.D.) varies between 1·8% for V in residual oil (F-80) and 11·0% for Ni in residual oil (F-80) as given in Table 7.39. The data shows that most of the results are reproducible and have good precision. The standard error (Table 7.39) varies between 0·01% for Fe ($\bar{X}$ = 1·30%) to 0·86 ppm for Cu ($\bar{X}$ = 46 ppm) in coal sample B and 0·01 ppm for Pb ($\bar{X}$ = 0·52 ppm) to 0·7 ppm for Ni ($\bar{X}$ = 18 ppm) in oil sample F-80. The relative error (Table 7.39) varies between 0·02 for V ($\bar{X}$ = 53ppm) to 0·11 for Ni ($\bar{X}$ = 18 ppm) in residual oil sample F-80 and 0·03 for As ($\bar{X}$ = 29 ppm) to 0·06 for Pb ($\bar{X}$ = 25 ppm) in coal sample B. This indicates that the errors are not significant and the results are reproducible. A good standard deviation and confidence limit for each sample (Table 7.39) are achieved. Most of the results for each metal in residual oil and coal samples lie with in the 95% confidence limit. Thus the data in Table 7.39 indicates that the results are reproducible and have good precision.

In another experiment the precision of the four metals (V, Ni, Cu, As) was established by ashing standard metal solutions and then analysing them by flame and electrothermal AAS (Table 7.40).

Table 7.39 Statistical Analysis of Experimental Results

C = Calibration Method Y = Intersept C.C. = Coefficient of Correlation S = Standard Addition Method

Metal	Sample	S ppm	C $\bar{X}$ ppm	σ ppm	V	$\frac{\sigma}{\bar{X}}$	$\frac{\sigma}{\sqrt{n}}$ ppm	R.S.D. $\frac{100\ \sigma}{\bar{X}}$%	C.L. 95% (±)	Y	Slope	c.c.
V	F-80	56±3	53	0·9	0·8	0·02	0·3	1·8	1·9	0	4·5	1·0
V	F-31	64±3	58	1·9	3·1	0·03	0·6	3·2	3·7	0	4·5	1·0
V	Coal A	79±4	71	2·5	5·5	0·04	0·8	3·5	4·9	0·4	4·6	1·0
V	Coal B	85±3	77	2·4	5·3	0·03	0·8	3·1	4·8	0·4	4·6	1·0
Ni	F-80	17±2	18	2·0	3·8	0·11	0·7	11·0	4·0	0·7	17·6	1·0
Ni	F-31	21±2	19	0·7	0·5	0·04	0·2	3·9	1·4	0·7	17·6	1·0
Ni	Coal A	25±1	23	1·6	2·3	0·07	0·5	6·3	3·1	1·0	17·5	1·0
Ni	Coal B	33±3	29	1·5	2·1	0·05	0·5	5·3	3·0	1·0	17·5	1·0
Fe	F-80	30±5	25	1·2	1·3	0·05	0·4	4·8	2·4	−0·2	22·36	0·99
Fe	F-31	25±5	21	0·8	0·6	0·04	0·3	4·0	1·7	−0·2	22·36	0·99
Fe	Coal A	1·65% ±0·1	1·55%	0·08%	0·006	0·05	0·03%	5·2	0·2	−3·0	22·80	0·99
Fe	Coal B	1·37% ±0·12	1·30%	0·04%	0·002	0·03	0·01%	2·9	0·08	−3·0	22·80	0·99

Table 7.39 Statistical Analysis of Experimental Results (continued...)

C = Calibration Method Y = Intersept C.C. = Coefficient of Correlation S = Standard Addition Method

Metal	Sample	S ppm	C $\bar{x}$ ppm	σ ppm	V	$\frac{\sigma}{\bar{x}}$	$\frac{\sigma}{\sqrt{n}}$ ppm	R.S.D. $\frac{100\ \sigma}{\bar{x}}$ %	C.L. 95% ($\pm$)	Y	Slope	c.c.
Cu	F-80	3·6 ±0·6	2·60	0·2	0·03	0·07	0·06	5·7	0·4	-0·5	40·6	1·0
Cu	F-31	3·4±0·4	2·43	0·2	0·02	0·06	0·05	4·8	0·3	-0·5	40·6	1·0
Cu	Coal A	38±2·0	35	1·5	2·0	0·04	0·47	4·3	2·93	-0·5	40·6	1·0
Cu	Coal B	54±2·5	46	2·7	6·7	0·06	0·86	5·9	5·36	-0·5	40·6	1·0
Pb	F-80	0·99±0·2	0·52	0·04	0·002	0·08	0·01	9·2	0·08	0	6·0	1·0
Pb	F-31	0·94±0·2	0·53	0·03	0·001	0·05	0·01	4·9	0·05	0	6·0	1·0
Pb	Coal A	24±3·0	23	1·5	2·1	0·07	0·48	6·7	3·0	1·7	1·3	0·99
Pb	Coal B	25±3·0	25	1·5	2·0	0·06	0·48	6·0	2·97	1·6	1·6	1·0
As	F-80	3±0·3	2	0·17	0·03	0·08	0·05	8·1	0·34	0·03	0·9	0·99
As	F-31	0·31 ±0·1	0·3	0·03	0·001	0·11	0·01	10·6	0·06	0·7	0·8	0·99
As	Coal A	13±2·5	12	0·71	0·47	0·06	0·22	5·9	1·41	-0·34	0·9	1·0
As	Coal B	31±3·0	29	1·22	1·49	0·03	0·04	4·3	2·39	0·5	0·7	0·99

The standard deviation (σ), the relative standard deviation (R.S.D.) and percentage difference between actual and observed concentration is given in Table 7.40. In Table 7.40 most of the actual results lie within the 95% confidence limit. The R.S.D. varies from 1•1% for vanadium (146•7 ppm) to 36•3% for As (5 ppm). The difference between the observed and actual concentration of metals varies from -2•13% for Cu (146•8 ppm) to -20% for As (4 ppm). Thus the data in Table 7.40 indicates that the aqueous standard solutions of metals (V, Ni, Cu, As) showed a good recovery (80 to 98%) after ashing by LTA. The low recovery for arsenic is caused by the volatility of the arsenic compound. The overall precision and reproducibility of metals analysis are good. In this analysis no sample pretreatment was necessary except dilution after ashing with plasma. Thus for LTA ashing conditions, very little loss of metals (V, Ni, Cu) was observed for aqueous standards.

The observed concentration of two metals in the spiking method is compared with the actual concentration in Table 7.41. The percentage difference varies between 0•37% for 54•5 ppm of Ni to 11•32% for 101 ppm of V. The recovery of V is 97% and Ni 99%. This indicates that the recoveries of metals are good, and no or very little interference occurs. The metals are not lost during ashing and determination. The results are good, and acceptable except for 101 ppm of V where the percentage difference between observed and actual concentration is 11•32%. Generally the interferences from matrix and other metals are present in both oil and coal samples but they are not significant in this method of analysis.

In order to find out that the sample dilutions are not introducing errors, two different dilutions of the same ashed sample were selected and each diluted sample was determined three times. The results of two dilutions agreed completely which indicated no interference or error due to dilution.

To establish an optimum time for analysis (ashing and determination) with good precision, recovery and reproducibility, 0•4 g of residual oil F-80 was taken for vanadium and arsenic and determined. Table 7.42 shows $\bar{X}_A$ the mean of the observed readings, $\bar{X}_B$ the mean of

Table 7.40

Statistical Analysis of Aqueous Standards After Ashing By Plasma

Metal	Actual Conc. (ppm)	Observed Conc. ($\bar{X}$) (ppm)	$\pm \sigma$ (PPM)	R.S.D.%	Diff. %	Recovery %
V	50	48•9	1•6	3•2	−2•2	97•8
	100	97•8	1•9	1•9	−2•2	97•8
	150	146•7	1•7	1•1	−2•2	97•8
Ni	50	48•8	1•0	1•9	−2•4	97•6
	100	95•3	1•5	1•6	−4•7	95•3
	150	146•4	1•9	1•3	−2•4	97•6
Cu	50	48•0	1•0	2•0	−4•0	96•0
	100	92•9	1•5	1•6	−7•1	92•9
	150	146•8	1•9	1•3	−2•13	97•87
As	5	4•0	1•5	36•3	−20	80
	10	8•4	0•9	10•3	−16	84
	20	18•4	1•9	10•1	−8	92

Table 7.41

To Find the Percentage Difference in Metals Analysed by Spiking Method

No.	Metal	Actual Conc. (ppm)	Observed Conc. (ppm)	Difference %	Recovery %
1	V	62•6	60•6	−3•19	96•81
2	V	72•5	72•2	−0•41	99•59
3	V	112•5	111•1	−1•24	98•76
4	V	84•0	82•8	−1•43	98•57
5	V	114•0	112•9	−0•96	99•04
6	V	104•0	101•1	−2•79	97•21
7	Ni	27•4	26•5	−3•28	96•72
8	Ni	57•4	56•6	−2•92	97•08
9	Ni	47•4	45•6	−3•80	96•20
10	Ni	34•7	34•2	−1•44	98•56
11	Ni	64•5	60•8	−5•74	94•26
12	Ni	54•7	54•5	−0•37	99•63

metals (V and As) calculated previously (sec. 7.4), standard deviation, relative standard deviation and the percentage difference of the two means of the metals. The results $\bar{X}_A$ obtained in Table 7.42 for V and As are in good agreement with the results $\bar{X}_B$. The results $\bar{X}_A$ obtained in Table 7.42 are reproducible and have good precision. The percentage difference is +1·88 and −12·5 for 53 ppm of V and 2·1 ppm of As respectively. The standard deviation obtained is ±1·3 ppm (52·0 ± 1·3 ppm) and ± 0·2 ppm (2·4 ± 0·2 ppm) for Vanadium and Arsenic respectively. This indicates that the results are in good agreement and no significant difference is obtained. This shows that good results can be obtained from the samples just after two hours of high power and flow rate (300 W, 200 ccs/min) ashing, in comparison to long hours (4 to 24) of ashing used previously in section 7.4. If the analyses are performed on the electrothermal AAS then 6 metals can be determined in 0·2 g of ashed oil, because the sample injected is only 20 µl. Thus this technique offers considerable advantages in speed of analysis, ability to handle a minute quantity of sample with good agreement and reproducibility. The costs of analysis are low. In this method the overall precision of the method (volume measurement, weighing, etc.) is also improved because less weight and dilutions are required.

Table 7.42

The Determination of V and As

Employing Lower Weights of Samples

Metal	$\bar{X}_A$ (ppm)	σ (ppm)	R.S.D. %	$\bar{X}_B$ (ppm)	Difference %
V	52	1·3	2·5	53	+1·9
As	2·4	0·2	8·3	2·1	−12·5

Precision for the complete method was estimated by carrying out replicate analyses on one of the oil (F-80) and Coal A sample. Four separate Petri dishes were ashed and their solution was made for the determination of Vanadium in both of the samples. Four replicate analyses were then made on each of these four solutions for both of the samples. This procedure was used in order that the precision value obtained would include any contribution incurred due to ashing in preparing sample solutions, and due to the determination. The relative standard deviation for, in the results of, the 16 analyses for each sample were calculated, these are given in Table 7.43.

Table 7.43

Determination of the Precision of the Method

Sample	$\bar{X}$ (ppm)	σ $\pm$ (ppm)	R.S.D. %
F-80	53	0•82	1•54
Coal A	72	0•90	1•25

The R.S.D. calculated in this Table (7.43) is low, which shows that the results are in good agreement. The method is reproducible and has good precision.

7.5 Interference Effects

Interferences can occur at any stage of an analytical technique, from sampling the material to be analysed to registration of analytical signal. In order to avoid and find out the interferences affecting the analysis of coal and oil samples a standard addition method was used together with a calibration method. A comparison of the results obtained from the two methods (Table 7.44) shows the percentage difference from 0 to 47%. Both greater and smaller values are obtained by calibration curves indicating that the interfering substances were indeed present in some of the samples and either enhancement or

Table 7.44

Comparison of Concentration of Metals Determined by Standard Addition and Calibration Methods

S = Significant at 99•9% NS = Not Significant at 99•9%

Sample	Metal	Calibration Method (ppm)	Standard Addition Method (ppm)	Difference %	t-test
F-80	V	52•6	56	+5•7	S
F-31	V	58•3	64•4	+9•5	S
Coal A	V	71•30	78•7	+9•4	S
Coal B	V	76•98	85	+9•4	S
F-80	Ni	17•7	16•5	-7•3	NS
F-31	Ni	19•24	20•5	+6•1	S
Coal A	Ni	23•3	25•3	+7•9	NS
Coal B	Ni	29•07	33•2	+12•4	S
F-80	Fe	20•5	30•3	+32•3	S
F-31	Fe	20•5	25•2	+18•0	S
Coal A	Fe	1•55%	1•65%	+6•1	NS
Coal B	Fe	1•30%	1•37%	+5•1	NS
F-80	Cu	2•50	3•6	+30•6	S
F-31	Cu	2•43	3•4	+28•5	S
Coal A	Cu	35•08	38•0	+7•7	S
Coal B	Cu	45•6	53•6	+14•9	S
F-80	Pb	0•52	0•99	+47	S
F-31	Pb	0•53	0•94	+43	S
Coal A	Pb	22•69	24•0	+5•4	S
Coal B	Pb	25•0	25•0	0	NS
F-80	As	2•12	2•7	+21•5	S
F-31	As	0•28	0•31	+9•7	NS
Coal A	As	12•2	12•6	+3•2	NS
Coal B	As	28•4	31•1	+8•7	S

suppression of the results were possible. The highest (47%) and lowest (0%) percentage difference is obtained in the determination of lead in oil and coal samples respectively. By calibration and standard addition methods the lead in oil F-80 sample was obtained to be 0·52 (± 0·04ppm) and 0·99 ppm (± 0·2ppm) respectively. The difference is 0·47 ppm (or 47%). The concentration of Pb in oil is very low (< 1 ppm) thus a minute change can produce a difference of higher percentage. Since the full composition of the sample is not known, the effect of different metals on Pb could be immense. On the other hand the lead in coal sample was in higher concentration and the results totally agreed in that sample for the calibration and standard addition methods. The other metals (V, Ni, Fe, Cu, As) showed a little difference in the determined metal concentration by either method. The interferences are not serious, bearing in mind the lower concentrations of the metals in the samples.

In order to compare the mean results derived from two methods (Calibration and Standard Addition) the t-test in one of the forms used is:

$$t = \left[(\bar{X} - \mu)/\sigma\right] N^{\frac{1}{2}} \qquad \text{.....7.1}$$

The factor is calculated from an experimental set of results and compared with a table of critical values (313). If t_{exp} exceeds the critical value for the appropriate number of degrees of freedom, the difference between means is said to be significant.

$\bar{X}$ = mean experimental set

μ = assumed true value

σ = experimental standard deviation by calibration method.

N = number of results

In Table 7.44 most of the results show that the results are significant and a null hypothesis is rejected. Thus it is assumed that the interferences could be possible in the analysis.

The optimisation of this technique (LTA and AAS) depends upon the importance to be attached to each of the criterion of analytical performance (i.e. detection limits, interference effects, precision, linear range, and retaining of trace metals after ashing). The technique is kept very simple and of low cost by not adding any other chemical to remove the interferences. Strictly speaking, an optimisation performed on this basis is valid only for a particular determination as the requirements for the detection limits interference affects, etc. may vary with different applications.

CHAPTER 8

8 DISCUSSION AND CONCLUSION

8.1 Discussion

Analyses of oil and coal samples were completed to demonstrate the applicability of the method. The major difficulty of separating inorganic constituents is succesfully resolved. A better recovery of volatile inorganic materials has been achieved (As in oil and coal) with good reproducibility in comparison to N.C.B. and B.P. results.

Milner et al (242) has reported a better precision for the determination of mineral matter in coal by LTA upon acid demineralization and the Parr formula (286). Nadkarni (261) reported that LTA retains the elements in coal better than the High Temperature Ashing (HTA) procedure. Frazer and Belcher (111, 35) has reported repeatability tests for a coal sample containing 20% mineral matter and showed a standard deviation of 0•10% for both RF and air oxidation methods, whereas the ISO method had 0•14% for the repeatability test at the 20% ash level. They reported that comparison of the percentage mineral matter by the two methods shows that the RF oxidation analysis and that the respective combined water contents $(H_2O)^+$ are 0•03 to 0•3% higher. Pollack (287) reported that NAA and LTA values are almost identical while the Parr formula gave an average that is 7% lower. The Parr and KMC formulae ignore the possible presence of quartz which yields no water of decomposition on heating, in their formulae (32, 256). Gluskoter (132) oxidised bituminous coals by LTA from the U.S.A. and found that mineral matter residues weighed significantly more than those obtained from the Parr formula for ash to mineral matter.

A comparison between the results obtained in the present work and the results reported by N.C.B. and B.P., is given in the Table 8.1. The accuracy and percentage difference between both the calibration and standard addition methods with the reported results (N.C.B. & B.P.) has been calculated. The standard deviation and precision (R.S.D.) of obtained results are reported from Table 7.39. For the calibration method the accuracy ranges from −8 ppm for 46 ppm of Cu in Coal B to +4 ppm for 53 ppm V in oil. The percentage difference varies

Table 8.1 Comparison of Reported (B.P. & N.C.B.) and Obtained Results

S = Sample M = Metal O.R. = Obtained Results P = Precision (R.S.D.) D = Difference S.A. = Standard Add.

S	M	O.R. (ppm)	σ (PPM)	P	N.C.B., B.P. (ppm)	D (ppm)	D %	S.A. (ppm)	D %
F-80	V	53	0·9	1·8	49	+4	+8·2	56±3	+14·3
F-80	Ni	18	2·0	11·6	16	+2	+12·5	17±2	+6·3
F-80	As	2	0·17	8·2	<1	+1	+100	3±0·3	+200
Coal A	V	71	2·5	3·5	75	−4	−5·3	79±4	+5·3
Coal A	Ni	23	2·0	6·3	23	0	0	25±1	+8·7
Coal A	Fe	1·55%	0·08%	5·2	1·32%	+0·23	+17·4	1·65%±0·1σ	+25
Coal A	Cu	35	1·5	4·3	37	−2	−5·4	38±2	+2·7
Coal A	Pb	23	1·5	6·7	20	+3	+15·0	24±3	+20·0
Coal A	As	12	0·71	5·9	11	+1	+9·0	13±2·5	+18·0
Coal B	V	77	2·4	3·1	80	−3	−3·8	85±3	+6·3
Coal B	Ni	29	1·5	5·3	33	−4	−12·1	33±1	0
Coal B	Fe	1·30%	0·04%	2·9	1·53%	−0·23	−15·0	1·37%±0·1σ	−10·4
Coal B	Cu	46	2·7	5·9	54	−8	−14·8	54±2·5	0
Coal B	Pb	25	1·5	6·0	24	+1	+4·1	25±3	+4·2
Coal B	As	29	1·22	4·3	27	+2	+7·4	31±3	+14·3

between −15% for 1•30% of Fe in Coal B to +100% for 2 ppm As in oil. The better percentage recovery of arsenic in both oil and coal indicates that the LTA has retained the volatile metal better than the adopted laboratory methods. In the standard addition method a better accuracy and a positive percentage difference is obtained in comparison to NCB and BP results. This indicates that if the possible interferences are removed then higher results could be obtained. Thus LTA has been proved a good method of trace metals analysis.

In Tables 8.2 and 8.3 the percentage recovery of trace metals is obtained in comparison with the results reported by N.C.B. and B.P. (assumed as correct results μ). The percentage is calculated for both calibration (Table 8.2) and standard addition methods (Table 8.3). The percentage difference varies between 85% for 1•30% Fe in Coal B to 200% for 2 ppm As in residual oil F-80; and for the standard addition method between 89% for 1•37% Fe in Coal B to 300% for 3 ppm As in residual oil F-80. The average calculated recovery for calibration and the standard addition method is 108% and 121% (without arsenic 101% and 108%) respectively. The level of recovery shown is quite acceptable for oil and coal analysis at these concentrations. The recovery reported indicates that there is no significant difference detected in analysis of the six elements (Tables 8.1, 8.2 & 8.3).

The obtained results in Tables 8.1, 8.2 and 8.3 are higher than the reported results (N.C.B. & B.P.) for some elements, but on this data no true estimate of accuracies can be made on the reported concentrations since the absolute or true concentrations of elements in each sample are not known. The data represent the percent relative standard deviation of about 1•8 to 11•6% (Table 8.1) suggesting an error of approximately 1•8 to 11•6% can be due to the sample preparation (loss during extraction, digestion or ashing process, interferences peculiar to the analytical method or operator error).

In Table 8.2 the t-test (equation 7.1) is used where a comparison of the mean results derived from the two sets has been made. The factor is calculated from the experimental set of results and compared with a t-table of the critical values at 99•9% confidence

Table 8.2

Percentage Recovery of Metals by Using Calibration Method

S = Significant NS = Not Significant

Sample	Metal	Obtained Result (ppm)	N.C.B., B.P., Result (ppm)	Recovery %	t-test
F-80	V	53	49	108	S
F-80	Ni	18	16	112	NS
F-80	As	2	<1	200	S
Coal A	V	71	75	95	S
Coal A	Ni	23	23	100	NS
Coal A	Fe	1·55%	1·32%	117	S
Coal A	Cu	35	37	95	NS
Coal A	Pb	23	20	115	S
Coal A	As	12	11	109	NS
Coal B	V	77	80	96	NS
Coal B	Ni	29	33	88	S
Coal B	Fe	1·30%	1·53%	85	S
Coal B	Cu	46	54	85	S
Coal B	Pb	25	24	104	NS
Coal B	As	29	27	107	NS

Table 3.3

Percentage Recovery of Metals by Using Standard Addition Method

Sample	Metal	Obtained Result (ppm)	N.C.B., B.P. Result (ppm)	Recovery %
F-80	V	56	49	114
F-80	Ni	17	16	106
F-80	As	3	<1	300
Coal A	V	79	75	105
Coal A	Ni	25	23	109
Coal A	Fe	1·65%	1·32%	125
Coal A	Cu	38	37	103
Coal A	Pb	24	20	120
Coal A	As	13	11	118
Coal B	V	85	80	106
Coal B	Ni	33	33	100
Coal B	Fe	1·37%	1·53%	89
Coal B	Cu	54	54	100
Coal B	Pb	25	24	104
Coal B	As	31	27	114

Table 8.4

Calculation of the Confidence Interval (90%)

About the Experimental Mean

Sample	Metal	$\bar{X}$ (ppm)	σ (PPM)	C.L.(90%) (±)
F-80	V	52•80	0•94	0•55
F-31	V	58•30	1•85	1•07
Coal A	V	71•30	2•46	1•43
Coal B	V	76•98	2•42	1•40
F-80	Ni	17•70	2•05	1•19
F-31	Ni	19•24	0•73	0•42
Coal A	Ni	32•3	1•58	0•92
Coal B	Ni	29•07	1•53	0•88
F-80	Fe	20•50	0•83	0•48
F-31	Fe	20•50	0•83	0•48
Coal A	Fe	1•55%	0•08%	0•05
Coal B	Fe	1•30%	0•03%	0•02
F-80	Cu	2•50	0•17	0•09
F-31	Cu	2•43	0•14	0•08
Coal A	Cu	35•08	1•49	0•86
Coal B	Cu	45•60	2•72	1•58
F-80	Pb	0•52	0•02	0•01
F-31	Pb	0•53	0•04	0•02
Coal A	Pb	22•69	1•52	0•88
Coal B	Pb	25•00	1•51	0•87
F-80	As	2•12	0•17	0•10
F-31	As	0•28	0•02	0•01
Coal A	As	12•20	0•71	0•42
Coal B	As	28•40	1•22	0•70

level. In this t-test 40% of the results are not significant which indicate that the metal concentration obtained by LTA - AAS is not significantly different in these cases to that of metal concentration obtained by an accepted method.

In Table 8.4 a t-factor is used to calculate a confidence interval about the experimental mean, within which there is known (90%) confidence of finding the true mean. The limits of this confidence interval are given by the following equation.

$$\bar{X} \pm ts/N^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 8.1$$

where $\bar{X}$ is the experimental (exp) mean, t is the statistical factor derived from the normal error curve, S is the estimated standard deviation and N is the number of results. The data in Table 8.4 indicates that the obtained mean is a reasonable estimate of the true mean.

8.2 CONCLUSIONS

A method has been described for the routine determination of trace metals (V, Ni, Fe, Cu, Pb, As) in residual oils and coal samples. Handling of the sample and chemical procedures are simple and are applicable to a large number of samples. Analysis time can be short and capital investment is moderate and no special data processing is required. Good reproducibility for all the elements is obtained, with no significant interference from other metals contamination. LTA was originally developed for ashing of organic materials but here it has been extended to oil analysis. The distinct advantage of LTA over the other ashing methods is the retaining of volatile metals after ashing. The As and other metals have been determined with better recovery as compared to already used methods. The amount of oil ashed (0•2 g - 0•4 g) is very small as compared to the other ashing methods. The time of analysis is less and the usage of expensive chemicals is avoided. Most of the metals can be determined from a single oil or coal (0•2 g) ashed sample. The standard addition method has shown a little interference due to the other metals. Thus no separation is needed to prepare the sample for AAS analysis. The sample did not have matrix affecting

problems after ashing and thus the use of expensive complexing agents has been avoided. Dilute HNO_3 has been used for dissolving the ash. The dilution by HNO_3 does not produce any error or contamination. Reproducible results with good standard deviation and precision is obtained by LTA. The percentage recovery of metals in aqueous standards and aqueous standards added to oil and coal samples was good. This indicates no significant amount of sample is lost due to ashing. Reproducible results with good precision are obtained with 0•4 g of oil and 0•2 g of coal, and all the six metals could be detected. The study of interferences by a standard addition method explains that the results are not very different from those obtained by the calibration method. The highest percentage difference is obtained in the lowest concentration of the Pb present in oil, while the percentage difference for lead in coal is negligible. In comparison to the reported results (N.C.B. & B.P.) a good agreement is achieved, which indicates that the recovery and determination of metals by LTA and AAS is quite acceptable without major interference. The true mean is calculated and it has been found that the calculated mean is a reasonable estimate of the true mean.

The LTA oxidises the organic material without appreciably altering the bulk of the mineral matter in samples. Thus LTA opens many avenues of investigation into mineral matter in oil and coal. Previously the major difficulty was in separating the inorganic constituents. It is possible to retain the volatile inorganic elements in the Low temperature ashing that are lost in the high temperature ashing. In as much as the system is closed, it is possible to trap the gases produced by the oxidation of coal and oil, which can be analysed. The LTA method retains all the inherent advantages of the air-oxidation method and eliminates the disadvantages of applying correction factors based on extra analytical determinations in oil and coal. The reproducibility for trace metals is good in oil and coal. The shorter RF oxidation time (2 to 6 hrs) is advantageous in allowing a total analysis to be completed with less total elapsed time than other oxidation methods (air & wet). Elimination of carbon dioxide in the analysis of mineral matter in the RF oxidation method could result in a reduction of labour costs as compared with the air-oxidation method. The RF oxidation method quantitatively oxidises annthracite and coals with high pyrite contents

and hence has application to a wider range of coals than the air - oxidation method.

LTA has the following important advantages over other techniques:

(1) Very little, if any, reagents need to be added to the sample.

(2) The flow of oxygen required for LTA is very low so that a cylinder containing 270 cu ft of oxygen lasts for over 100 hrs ashing time.

(3) LTA is less hazardous and easier to perform than the wet ashing procedure in that the handling of large amounts of hot, concentrated HNO_3 and $HClO_4$ is eliminated, and the ashing once started requires little further attention until the process is completed.

(4) Using the special LTA quartz ashing chambers, sample handling and glassware contamination are minimized.

(5) Since temperatures of 100-125 ^{o}C or less are maintained throughout the LTA procedure, thus the loss by voltilization is not significant for the metals measured in this investigation. Although few elements were reported to be lost in LTA ashing, the losses are much less pronounced than with dry ashing.

The LTA provides a complete control of pressure, flow rate and input power. If the relationship between these parameters and the behaviour of the sample is understood then optimum operating conditions can be selected. It is only necessary to establish that there is a combination of these parameters which produces a result compatible with the requirements. The ashing rate in plasma depends on the sample area under attack by the plasma. Thus the ashing rate can be increased by enlarging the sample area. When the sample area is increased then more power can be supplied which will help to increase the rate of oxidation while the temperature will remain low. If a large Petri dish is used then a large amount of sample could be ashed, which will decrease the cumulative error caused by the mixing of various Petri dishes of low weight. Low temperature ashing rates are highly dependent on the kind and porosity of the sample and surface area exposed to the activated gas stream. Porous substances are readily ashed while non-porous samples proved difficult to ash completely because of the formation of an insulating layer of ash on the sample surface.

The main advantage of LTA method over other oxidation methods is that isolation of the unaltered mineral matter permits a more accurate expression of the sample analysis on a dry mineral matter free basis. Higher rates of oxidation can be achieved without increase in power by a more complex electrical generator and reaction chamber. Because the organic sample does not appreciably load the plate circuit, retuning the capacitor during ashing is not required and unaltered operation is feasible.

In addition to the metals discussed in this report, many others occur in oil and coal which are quite important from the analytical aspect. The increasing awareness of the important role of very small amounts of elements in chemical systems has greatly stimulated the requirement and extension of analysis at these levels. The analytical requirements imposed by minute quantities and typical complex systems involved, have led to development of methodology and instrumentation so specialized as to warrant consideration as a distinct field of analytical chemistry - trace analysis. The modern approach to trace analysis is by means of physical methods. It is emphasized that there are no universal methods, each one exhibits its own advantages and disadvantages.

The proposed method (LTA - AAS) offers considerable advantages in speed of analysis, in ability to handle minute quantities of materials at low detection limits, good precision and better recovery.

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