A thesis entitled

THE ATOMISATION AND DETERMINATION OF VOLATILE METALS IN COAL

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Abstract

The analytical advantages of some novel approaches to atomisation using gaseous sample transport and slurry nebulization have been investigated and applied to the determination of trace metals in coal. A cold vapour atomic fluorescence spectroscopic method for the determination of mercury using a gas-sheathed atom cell and front surface illumination was developed. With a manual injection technique the detection limit was 0.01 ng. Replacement with a continuous flow system yielded a more rapid and precise method with a detection limit of 0.045 $ng.ml^{-1}$. Quantitative recoveries of mercury from a standard coal were obtained through liberation of the analyte using non-oxidative pyrolysis.

Continuous hydride generation methods for the determination of arsenic and selenium using atomic absorption and atomic fluorescence spectrometry were developed. The detection limits (0.34 $ng.ml^{-1}$ for arsenic and 0.13 $ng.ml^{-1}$ for selenium) were adequate for levels typically present in coal. Arsenic and selenium were determined in coal after digestion with perchloric acid and isolation from interferents by co-precipitation on lanthanum (III) hydroxide. Results for the determination of mercury, arsenic and selenium in standard coals are presented.

The analysis of aqueous whole coal slurries (up to 25% $^{m}/v$) using a Babington type nebuliser with an inductively coupled all-argon plasma is described. The effects on atomisation efficiency of particle size, slurry concentration and sample pumping rate were investigated. Comparisons are drawn between slurry and aqueous solution optimum operating conditions and a two-stage slurry atomisation process is postulated. Spectral and background interferences were alleviated by scanning the analytical lines used. Promising results are presented for a range of coals.

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1 INTRODUCTION

1.1 THE DEVELOPING ENERGY CRISIS AND COAL AS AN ENERGY SOURCE

The 1970's in particular was a decade in which the industrial world became painfully aware of the exhaustibility of fossil fuels, with the realisation that the era of cheap energy had passed. In contrast to the ephemeral nature of oil and gas reserves, coal represents a much longer term source of energy. The world's relative abundance of coal reserves and their more strategic distribution make coal an attractive alternative to oil as a feedstock for the chemical and fuel industries. Estimates of coal reserves in Britain range up to 200 x 10^9 tons, which can be compared to the present National Coal Board yearly output of 120 x 10^6 tons. Although only a small percentage of the former figure is recoverable by present day mining methods, it is evident that coal will be the dominant fossil fuel throughout the 21st century.

In recent years natural gas has been welcomed as a relatively clean and easily delivered energy source but eventually supplies of such gas will end. Attention must then be turned to producing substitutes from other available sources of fossil fuel and it seems likely that we shall return to gas supplies produced from coal. Although it might at first sight appear economically unattractive and thermally inefficient to gasify or liquefy the primary fuel, as opposed to using it direct, there are several major advantages arising from the former course of action.

The conventional usage of coal involves straightforward combustion, the evolved heat being used to generate steam to drive turbines which in turn generate electrical power. In recent years, coal combustion (along with other means of producing energy) has been identified as a potential source of pollution from volatile trace elements. Many elements have been identified in coal (1, 2) and it is a subject of intensive study as to which become airborne after combustion. Coal has been suspected because of the general knowledge that a variety of trace elements, some of which are toxic to animal and plant life in other chemical combinations, occur in coal (3).

The particulate emissions from coal fired steam plants, equipped with modern pollution control devices, consist primarily of sub-micron particles. Recent work (4,5) has shown that the smaller fly ash particles produced may be considerably enriched in several toxic trace elements. The most widely accepted mechanism (4) involves volatilisation of these elements during combustion followed by adsorption or condensation on the available matrix material, mainly non-volatile oxides of Al, Mg, Fe and Si. These smaller particles, enriched in potentially toxic trace metals, also have the highest atmospheric mobilities and are deposited predominantly in the lungs ($< 1\ \mu m$), while larger particles ($1-20\ \mu m$) are deposited primarily in the nasal and bronchial regions of the human respiratory system (4).

In addition to problems of toxic trace element discharges to the environment through particulate fly ash emissions, the disposal of fly and bottom ashes also requires careful planning. In a typical plant the larger, electrostatically precipitated fly ash particles and stack or bottom ashes are often disposed of as slurries (6). Such processes are fraught with a number of problems, particularly effluent leakages and in reclamation of ash covered land. Plants grown on ash amended soils have absorbed unusually high levels of As, B, Mo, P and Se (7, 8, 9, 10). Animals and aquatic organisms (11, 12) have accumulated selenium from fly ash effluents and this element causes particular concern.

The large tonnages of coal to be consumed could lead to relatively large amounts of toxic materials entering the environment. Some studies (13) on the fate of trace elements during coal combustion have revealed that the relatively volatile metals, As, Hg, Ni and Se, gave negative material balances. These studies indicated that up to 85%, 60% and 55% of the Hg, As and Se respectively, originally present in the coal, could not be accounted for in the waste streams analysed. More recent work (14), however, has shown that, through the application of superior analytical techniques to waste analysis, effective and quantitative material balances are obtainable. The authors conclude that almost all the arsenic and selenium present in the coal appear in the fly ashes and exhaust gases, large proportions of which elude the pollution control mechanisms.

Coal liquefaction and gasification, however, are necessarily carried out in pressurised vessels and by-product and waste offtake are more readily monitored. The Lurgi (15) gasification process was first demonstrated commercially in 1936 and it has been extensively developed since then. In this process individual lumps of fuel are progressively gasified as they slowly descend through the upward flow of gaseous products. This arrangement promotes heat transfer from gas to solid so that the heat released is used efficiently. Molten slag is continuously removed from the base of the reactor and collected in "quench" water, which will therefore contain a high proportion of the non-volatile metals present in the coal feedstock. Gas offtake temperatures are low, typically 200-600° C, resulting in many of the volatile constituents appearing in the condensable hydrocarbon byproducts. The high mobility of these metals may cause undesirably high levels to appear in the final product. Thus there is increased interest in determining these metals in coal and related materials, for example, so that trace metal balances in coal gasification plants may be constructed.

The toxicity and carcinogenicity of the metals of interest constitute potentially severe health hazards. For detailed discussions of specific subject areas the reader is referred to some of the specialised texts (16, 17, 18, 19) available. However, a review by Piperno (20) is both readable and informative and some salient points are worthy of immediate consideration.

1.2 TRACE ELEMENT EMISSIONS: ASPECTS OF ENVIRONMENTAL TOXICOLOGY

1.2.1 GENERAL TOXICOLOGY

Increased potential health risks are now associated with those elements which are highly volatilised (e.g. mercury, arsenic and selenium) and those discharged primarily as submicron particles (such as Cd, Pb, Ni and V; see section 1.1). Available pharmacological and toxicological data provide a basis for predicting the biological consequences of excessive trace element exposures. Whilst parameters and mechanisms of injury are known, in many instances, tolerable body burdens for each trace element must be defined.

1.2.2 BIOCHEMICAL TOXICOLOGY

The chemical and physical dissimilarities of trace elements account for their wide scope of toxicological effects. Many metals, however, share common properties which may serve as a basis for their toxicity. Hg, As, Se, Cd and Pb, for example, all inhibit a large number of enzymes having functional -SH groups. Binding to nucleic acids affects their conformations and disrupts pathways of oxidative phosphorylation. Heavy metals stimulate or inhibit a wide variety of enzyme systems, sometimes for protracted periods and these effects may be so sensitive as to precede overt toxicity. Heavy metal metabolic injury, in addition to producing primary toxicity, can adversely affect drug detoxification mechanisms, with possible secondary consequences. From a toxicological viewpoint the classification of trace elements into essential and non-essential may have been over-emphasised since both categories may produce toxicity. The factors affecting trace element toxicity include the physical and chemical characteristics of the substance, its dose or concentration, exposure time, absorption rate, metabolic rate and indigenous defence mechanisms. A further significant threat posed by heavy metals is their tendency towards long biological half-lives, for example, 10-25 years for cadmium. In addition to cadmium, other metals known to accumulate in man are As, Hg and Pb.

1.2.3 GENETIC AND NEONATAL TOXICITY

The ability of heavy metals readily to cross the placenta and disrupt nucleic acids, coupled with the high sensitivity of the foetus and neonate increases the potential dangers of congenital and neonatal toxicity.

Teratogenicity in experimental animals has been demonstrated with arsenic, cadmium, lead, inorganic and organic mercury. The organic forms of mercury cross the placenta more readily than inorganic forms.

Some elements, notably Cd, Hg, Se and Zn are likely to be isomorphous and may compete for the same enzyme binding sites. Thus, under certain conditions, either synergistic or antagonistic effects may be observed.

Some workers have reported the prevention of mercury poisoning by selenium and vice versa. Similar effects have been reported for other metal pairs.

1.2.4 PHYTOTOXICITY AND RELATED PROBLEMS

Plants represent man's single most important source of trace elements. When industrial contamination of soil occurs, pollutants may be incorporated into surrounding food crops. Heavy metal toxicity in plants is infrequent. In many cases, metal concentrations in plants show poor correlation with soil concentrations of the elements. Plants tend to exclude certain elements and readily accept or concentrate others. Natural plant:soil concentration ratios of 0:05 or less have been reported for As, Be, Cr, Ga, Hg, Ni and V. Human blood levels of selenium are reported to correlate somewhat with soil concentrations of the element.

Of the elements cited, Hg, As and Se are of particular interest in coal and a study of volatile toxic trace metals is timely. If applied to the analysis of coal, tars, effluents and other related materials, such studies would enable the construction of environmentally significant trace metal balances within a coal gasification plant. Initial attention has been directed to coal samples since this matrix poses the most severe analytical problems.

The approaches to and problems of sample pretreatment are discussed in the next section, along with an appraisal of the scope and limitations of the analytical techniques commonly used in the determination of trace metals in coal.

1.3 JUSTIFICATION FOR THE RESEARCH AND CURRENT METHODOLOGIES

Although the metals of particular concern, Hg, As and Se are present in coal in only trace amounts, the large tonnages of coal to be gasified could lead to relatively large amounts of these metals entering the environment. It is therefore becoming necessary to accumulate data on the levels of these metals in coal and their fate during combustion, gasification and liquefaction. Thus, analytical techniques applicable to both coal and related products (i.e. various ashes, gases, tars, slags and liquors) are required. The problem of sample treatment is intensified because of the highly intractable nature of the coal matrix and a variety of approaches have been used to obtain solutions suitable for analysis. The optimum requirements for such a method are: destruction of the matrix to avoid interference problems; avoidance of elevated temperatures, thereby minimising losses of volatile elements; prevention of undue dilution of the sample or contamination from reagents used.

It has been proposed (21) that spark source mass spectrometry offers a technique whereby trace metals may be determined in coal without sample dissolution, but this has not been widely confirmed. While coal may be irradiated in order to determine trace metals by neutron activation analysis it may be necessary to combust (22) or digest (23) the coal later in order to concentrate the metals prior to counting to obtain the necessary sensitivity.

Most alternative analytical methods for coal entail prior destruction of the matrix. Recently, low temperature ashing (150°C) using radio frequency excited oxygen at low pressure has been used to prepare coal samples for analysis. This method, however, requires specialist instrumentation and while the majority of metals are retained, some of the more volatile may still be lost (22, 23). The longer established methods of high temperature ashing (450-500°C) and fusion or wet digestion still attract considerable interest.

Flame atomic absorption spectroscopy is a simple, rapid and relatively inexpensive method of determining trace metal levels and has the advantage of being reasonably free from interferences. Conventionally the working range of the technique is around 0.1 to 10 $\mu g.ml^{-1}$ in solution. Replacement of aspiration of aqueous samples into the flame, a major source of inefficiency, by gaseous sample transport has significantly lowered this working range for several elements. Mercury displays an appreciable vapour pressure even at room temperature and thus, after reduction of Hg^{2+} to metallic mercury it may be aerated from solution and the vapours transported to a non-flame atom cell. Several metals, notably As, Bi, Ge, Sb, Se and Te, form gaseous covalent hydrides which may be swept into a flame or electrically heated atom cell where they are decomposed and atomised. A major advantage of these techniques is that complete matrix removal may no longer be necessary, although precautions may need to be taken to prevent interferences by concomitant elements in the generation of the hydrides. Several workers determining Hg (24), As (25) and Se (25) have reported systems in which discrete aliquots of sample are used for vapour generation. Other reports (26, 27, 28), however, describe the use of semi and fully automated systems providing constant vapour generation. Although relatively complex and expensive the feasibility of such systems is apparent and the advantages of such systems include: steady state signals, leading to greater convenience and accuracy; elimination of discrete variables, leading to improved precision; greater freedom from interferences (29), leading to a potentially wider range of applications. If improved sensitivity is still required it has been shown that atomic fluorescence spectrometry is often more sensitive and reproducible than corresponding atomic absorption methods.

The metals of interest have their principal resonance lines below 350 nm and therefore should be more amenable to analysis using atomic absorption or atomic fluorescence methods (see section 1.5, p. 24) rather than conventional atomic emission methods (e.g. flame and spectrographic methods). The very much hotter atom cell of the inductively coupled plasma (ca 7000 K) can, by increasing the population of excited analyte atoms, offer sensitivities approaching or exceeding those of atomic absorption and atomic fluorescence at wavelengths in the spectral region of interest.

Methods combining matrix destruction and sample atomisation into one step will inevitably attract interest and the analysis of finely powdered coal as an aqueous slurry is one such method. The high temperature atom cell and, under certain conditions, long residence times offered by the inductively coupled plasma should assist rapid and complete matrix destruction and analyte atomisation. Hence it may be possible to achieve equivalent sensitivities for slurry and aqueous concentrations.

Before suitable analytical methods can be selected certain practical limitations must be considered and these are subsequently discussed in section 1.5. First a brief account of the theory of analytical atomic spectroscopy will be given to enable a critical understanding of these limitations.

1.4 THEORY OF ATOMIC SPECTROSCOPIC TECHNIQUES

1.4.1 HISTORICAL DEVELOPMENT

Around the middle of the last century the experiments of Bunsen and Kirchoff established the basic principles of atomic spectroscopy, the emission and absorption of radiation by discrete atoms. Numerous examples of alkaline metal determinations using flame derived spectra were reported (30, 31). The first applications of atomic spectroscopy were in the fields of astrophysics and astrochemistry, and later in more fundamental spectroscopic and atomic studies. The publication of a series of papers (32) by Lundegardh in 1928, in which an air-acetylene flame and a pneumatic nebuliser were used for atomic emission spectroscopy, revived interest in analytical atomic spectroscopy. In the mid 1940's instruments became available mostly for the determination of the alkali metals, exploiting their easily excited resonance lines. More recently atomic emission spectroscopy has been used to determine a range of elements which encompasses most of the periodic table. In 1955 Alkemade and Milatz(33), and Walsh (34) independently published papers on the analytical usefulness of atomic absorption spectroscopy, although Walsh had previously demonstrated a complete laboratory system in a patent specification in 1953 (35). The first of many experimental developments of the technique were reported (36) by Walsh and co-workers in 1957.

Atomic fluorescence spectrometry, the measurement of radiation from discrete atoms which have been excited by absorption of radiation from a source not seen by the detector, was first reported by Wood (37) in 1905 when he succeeded in exciting fluorescence of the D lines of sodium vapour. The analytical applications were first pointed out by Alkemade (38) in 1962, who used the atomic fluorescence of sodium in flames to study the excitation and deactivation of atoms. The theoretical basis of an analytical method was outlined by Winefordner and Vickers (39) who in 1964 published the first of many papers reporting experimental results.

Since the theory and methodology of these three techniques are comprehensively described in the literature (34, 40-45), the following section will attempt only to summarise some of the more relevant points.

1.4.2 THEORY AND METHODOLOGY

The absorption and emission of radiation are associated with and characteristic of transitions of atoms from one steady state to another. For two steady states, i and j, of energies E_i and E_j, where $E_j > E_i$, then the absorption of light accompanies the transition $i \rightarrow j$, and the emission of light accompanies the transition $j \rightarrow i$. The characteristic frequency ν_{ji} is given by:

$$\nu_{ji} = \frac{E_j - E_i}{h} \qquad \ldots. \qquad 1.1$$

where h is Planck's constant.

Einstein's quantum theory of radiation defines three types of transition between levels i and j:

1. emission ($j \rightarrow i$), spontaneous transitions from an excited state into a lower energy state;
2. absorption transitions ($i \rightarrow j$), in response to the action of external radiation of frequency ν_{ji};

3. emission transitions ($j \rightarrow i$) stimulated by external radiation of frequency ν_{ji}.

The three techniques of atomic spectroscopy are based on the first two types of transition and thus are closely related. In atomic absorption and atomic fluorescence spectroscopy the atoms are excited ($i \rightarrow j$) by means of external light sources emitting radiation characteristic of the analyte atoms, ν_{ji}. In atomic absorption the fraction of radiation absorbed by the analyte atoms is monitored, whereas in atomic fluorescence a portion of the radiation produced by radiational deactivation is monitored. In atomic emission spectroscopy the analyte atoms are excited through collisions with flame gas molecules. A portion of the radiation emitted when a fraction of the excited atoms undergo radiational deactivation is measured.

An admirable discussion of spectroscopic theory and notation has been given by Mavrodineanu and Boiteux (45). In addition, a number of texts concerning the rules governing the transitions which give rise to observed atomic spectra are available. A detailed study of these area is outside the scope of this work, but the reader is referred to the work of White (46) in particular.

1.4.3 THEORY OF QUANTITATIVE ATOMIC SPECTROMETRY

1.4.3.1 ATOMIC EMISSION

The probability of transitions from given levels with a fixed atomic population was expressed by Einstein in the form of three coefficients. These so-called transition probabilities are written A_{ji}, B_{ij} and B_{ji}, which refer to spontaneous emission, absorption, and stimulated emission respectively. They represent the ratio of the number of atoms undergoing a transition to the number in the initial level. The intensity of a spontaneous emission line is related to A_{ji} by the equation:

$$Iem = A_{ji} . h\nu_{ji} . N_j \qquad \ldots\ldots \qquad 1.2$$

For a system in dynamic equilibrium the number of atoms in the excited state, N_j, is given by the Boltzmann Distribution Law;

$$N_j = N_o \frac{g_j}{g_o} \exp - (E_j/kT) \qquad \ldots\ldots \qquad 1.3$$

where N_o is the number of atoms in the ground state, with energy $E_o = 0$ and g_j and g_o are the statistical weights of the jth and ground states respectively.

Thus:

$$\frac{N_j}{N_o} = \frac{g_j}{g_o} \frac{\exp(- E_j/kT)}{\exp(- E_o/kT)} \qquad \ldots\ldots \qquad 1.4$$

If the total number of atoms present, N, is expressed as the sum of the population of all levels, i.e.

$$N = \sum_j N_j$$

$$\frac{N_j}{N} = \frac{g_j}{\sum_j g_j} \quad \frac{\exp(-E_j/kT)}{\exp(-E_j/kT)}$$

$$= g_j \frac{\exp(-E_j/kT)}{F(T)} \qquad \ldots. \qquad 1.5$$

where F (T) is known as the partition function.

For a system in thermodynamic equilibrium and neglecting self absorption:

$$Iem = A_{ji}.h\nu_{ji}.N \frac{g_j \exp(-E/kT)}{F(T)} \qquad \ldots. \qquad 1.6$$

Thus the intensity of atomic emission is critically dependent on temperature. Moreover at low analyte concentrations (i.e. for negligible self absorption) a plot of emission intensity against sample concentration is a straight line.

1.4.3.2 ATOMIC ABSORPTION

As with Lambert's law in molecular spectroscopy, atomic absorption exhibits an exponential relationship between intensity of transmitted light, I, and the absorption path length, ℓ:

$$I = I_o \exp(-k_\nu \ell) \qquad \ldots. \qquad 1.7$$

where I_o is the incident light beam intensity and k is the absorption coefficient at the frequency ν. In quantitative spectroscopy absorbance, A, is defined as:

$$A = \log (I_o/I) \qquad \ldots\ldots \qquad 1.8$$

thus from equation 1.7 a linear relationship is obtained:

$$A = k_\nu \ell \log e$$
$$= 0.4343\ k_\nu \ell \qquad \ldots\ldots \qquad 1.9$$

Atomic absorption corresponds to transitions from lower to higher energy levels and therefore the degree of absorption depends on the lower level population, which, for a system in thermodynamic equilibrium is governed by Boltzmann's law (1.3 above). Since the excited level populations are usually small relative to the ground state population (i.e. the lowest energy state peculiar to the atom) absorption is greatest in lines resulting from transitions from the ground state. Such lines are termed resonance lines.

In theoretical studies three methods of measuring absorption have been extensively used, based on the measurement of:

1. the integrated absorption coefficient of a resonance line;
2. the total energy absorbed from the continuous spectrum by a resonance line;
3. the relative absorption of light from a source with a line spectrum.

Techniques based on the third method involving measurement of the absorption coefficient directly at the line centre were first proposed by Walsh (34). Hollow cathode lamps with narrow emission line profiles were proposed as spectral sources and flames, where the absorption lines are broadened by Lorentz and Doppler effects as the atom cell. Using a monochromator the emission line is isolated and the intensity measured photoelectrically with and without absorbing analyte atoms in the optical path. The absorbance, A, is related to the concentration of analyte atoms in the volume of the atom cell examined. The advantage of this method is that only a moderate monochromator is required whereas integrated absorption coefficient measurements require an instrument with high resolving power.

1.4.3.3 ATOMIC FLUORESCENCE

Atomic fluorescence radiance is dependent (47, 48, 49) on the radiance of the exciting source (I_s), the dimensions of the absorption cell (ℓ_1,ℓ_2 and ℓ_3), the solid angle of excitation (Ω), the concentration of absorbing ground state atoms (N_o), the efficiency of the absorption and fluorescence processes, the transition probability and the extent of line broadening. Winefordner (47) derived the following expression, which relates at low analyte concentrations, these parameters to the fluorescence intensity (I_f) emitted at right angles to the source:

$$I_f = k_o{}^D \; N_o \; x_\ell f \delta_{ij} I_s{}^{Y'} \left(\frac{\Omega}{4\pi}\right)\left(\frac{\ell_1 \; \ell_2 \; \ell_3}{A_R}\right) \quad \ldots . \qquad 1.10$$

where x_ℓ is the fraction of N_o undergoing transition, f is the absorption oscillator strength, δ_{ij} is a factor to account for the finite half-width of the source compared to the absorption line, Y' is the fluorescence power yield and A_R is the total surface area of the irradiated atom cell.

At low concentrations I_f is proportional to N_o (for practical purposes the analyte concentration) and at high concentrations I_f is related to $N_o^{-\frac{1}{2}}$. Growth curves of log I_f versus log N display this behaviour. It should be noted also that I_f is directly related to I_s and intense, stable, sharp line sources are desirable, though lasers, which are capable of providing large amounts of energy over a small spectral range have proved suitable for use in atomic fluorescence spectrometry.

It is not proposed here to review thoroughly the various flame and non flame atom cells used in atomic emission, absorption and fluorescence techniques. Instead a short account of the particular merits of the atom cells adopted will be given in the appropriate chapters. However, in view of the particular advantages of the inductively coupled plasma as an atom reservoir and its proposed application to the analysis of solid samples, a brief account of the development and analytical advantages of this source is given below.

1.4.4 PLASMAS

Several different types of plasma have been used as atomic emission sources and the applications and limitations are well documented. In recent years the inductively coupled plasma has attracted the greatest attention though recent review articles have appeared on the d.c. arc plasma (50), the capacitatively coupled plasma (51), and the microwave induced plasma (51, 52).

1.4.4.1 THE INDUCTIVELY COUPLED PLASMA

The inductively coupled plasma (ICP) developed in the 1960's has gained much popularity in recent years. The source utilises a high frequency (7-50 MHz) magnetic field applied to a coil, at powers of about 0.5-15 kW, to induce a discharge in an argon or argon/nitrogen gas flow.

Since this work uses the ICP a summary of the development, spectroscopic analytical properties and advantages of this source will follow.

1.4.4.2 HISTORY AND DEVELOPMENT OF THE INDUCTIVELY COUPLED PLASMA

In the early 1940's Babat (53, 54) observed an ICP discharge in air, using power levels up to 100 kW. This work was concerned with static plasmas and it was not until 1961, with the work of Reed (55, 56) that flowing plasmas were reported. Reed used both argon and argon/nitrogen plasmas in order to grow refractory crystals and although the potential for producing emission spectra was recognised the plasma was not used for analytical purposes. The torch described has formed the basic design for ICP torches used today, which have changed little from the Reed design.

In 1963 the ICP was first employed as a spectroscopic source by Greenfield and co-workers (57) who also introduced the next important modification of the plasma by using an annular shaped discharge. The torch is described in detail by Greenfield (57, 58) et al and has proved popular though several other torches have recently been reported (59, 60, 61). This design of torch uses a central 'injector tube' to introduce the sample aerosol which punches a hole in the flattened base of the plasma. There was disagreement initially about the desirability of an axial channel through the plasma. In 1965 Wendt and Fassel (62) used a laminar flow torch which produced a 'solid' ellipsoidal plasma, (similar to that of Reed)(55, 56) claiming an advantage of less turbulence over the vortex flow arrangement. Veillon and Margoshes (63) used a similar system but excluding the injector tube and reported serious solute vaporisation interferences, resulting presumably from inefficient heating of the analyte as it passed around instead of through the discharge.

In 1969 Dickinson and Fassel (64) achieved improved powers of detection using a three-tube torch similar to that of Greenfield and an ultrasonic nebuliser for sample introduction. In the period 1976-1980 the inductively coupled plasma has been reviewed by a number of authors. Greenfield et al.have reviewed plasma jets, microwave and capacitatively coupled sources and the ICP in a three part article (51, 58, 65). Barnes (66) has produced an extensive review of the literature, while Sharp's (52) review contains some theoretical considerations of emission spectrometry. The wide range of applications papers that has appeared shows that ICP atomic emission spectrometry has been widely accepted.

Potentially one of the most important assets of the ICP is that it may allow the direct analysis of solid or slurried samples. This was recognised as early as 1964 by Greenfield (57) and several papers have appeared reporting the analysis of: beryllium and boron in aluminium and magnesium oxides (69) and trace metals in standard orchard leaves and coal (70). The successful determination of several metals in mineralogical samples using slurry atomisation has recently been reported (71).

1.4.4.3 ADVANTAGES OF THE ICP AS AN EMISSION SOURCE

Summarising the properties of the ICP there are five main advantages of the source which are attractive to analytical spectroscopists:

1. low detection limits, due to the high temperatures experienced by the analyte passing through

the plasma (6-7000 K) and the inherently low background of the source;

2. the source is optically 'thin' and linear calibration ranges of 4-5 orders of magnitude are widely reported;
3. relative freedom from chemical interferences compared with other techniques, particularly arc and spark sources and possibly atomic absorption spectrometry;
4. the potential to deal with liquid, slurried, solid and gaseous samples;
5. simultaneous or rapid-scanning multi-element capability.

Before suitable analytical methods can be selected certain practical limitations must be considered and these are discussed below.

1.5 PRACTICAL LIMITATIONS AND POSSIBLE METHODOLOGIES

Flame atomic absorption and atomic fluorescence generally offer better sensitivity than flame atomic emission for elements having their principal resonance lines below approximately 350 nm. This is principally due to the inability of even the hottest flames to produce significant populations of excited atoms to undergo high energy, short wavelength transitions. Furthermore other studies (47, 72, 73) have shown that if an atomic resonance line is measured by all three techniques, flame atomic emission should produce lower detection limits than atomic absorption or atomic fluorescence for resonance lines above approximately 400 nm, between 300 and 400 nm all three methods should give similar limits, but below 300 nm atomic absorption and atomic fluorescence should provide lower detection limits. Systematic errors arising from monochromator drift and small variations in detector response during analysis are absent in atomic absorption methods since the ratio of the absorbed and unabsorbed signals is measured. This is both an advantage and a disadvantage since it is difficult experimentally to measure a vanishingly small difference in two large quantities and thus a limit is placed on the sensitivity of atomic absorption techniques. The sensitivities of atomic emission and atomic fluorescence are not limited in this way and may be increased by using higher temperatures (emission) and brighter sources (fluorescence). Moreover, the use of a high temperature atom cell, such as the inductively coupled plasma, very largely eliminates the limitations of atomic emission at wavelengths below 400 nm. Published results for the inductively coupled plasma tend to confirm this.

Sample pretreatment methods also require careful attention if analytical methods suitable for routine use are to be realised. Unless elevated temperatures, pressures or highly oxidising acids are used, coal is extremely resistant to conventional acid digestion techniques. This naturally causes problems in attempts to digest coal while quantitatively retaining volatile trace metals. Moreover, typical sample solution concentrations are unlikely to exceed about 5% m/v. In some American coals an average mercury concentration of 0.24 μg.g^{-1} has been estimated (22), which for a 5% m/v sample solution represents a solution containing 1.2 ng.ml^{-1} of mercury. This concentration is too low to be determined by atomic absorption techniques using pneumatic nebulisation and air/acetylene flames. For mercury, however, a specific approach is possible, using cold vapour reduction-aeration techniques. The working range of atomic absorption measurements is then significantly lowered. The atom cells used in cold vapour atomic absorption determinations are frequently of the closed system type which use quartz tubes to contain the mercury in the optical path. This type of cell is unsuitable when the use of atomic fluorescence spectrometry is desired, for example, when extra sensitivity is required for low mercury coals. Thus a suitable atom cell is required if atomic fluorescence spectrometry is to be used to determine very low levels of mercury.

An entirely analogous situation exists for arsenic and selenium. Although typical concentrations of these metals in coal are generally higher than that of mercury, problems of poor sensitivity and precision are again encountered using pneumatic nebulisation and air/acetylene flames. The poor signal to background ratios observed at the principal resonance lines of arsenic and selenium (193.7 and 196.0 nm respectively) are mainly attributable to the high absorption at these wavelengths of flame gas species. This may largely be overcome by using the more transparent hydrogen-based entrained air diffusion flames, using either argon or nitrogen as support gas. These cooler flames, however, are prone to interferences caused by incomplete salt dissociation and molecular absorption when solutions are aspirated directly. Nebulisation and atomisation efficiency can be improved by generation and aspiration of gaseous hydrides directly into the atom cell. The flame and electrically heated quartz tube atomisers used in atomic absorption determinations are incompatible with atomic fluorescence methods. An atom cell comprising of a suitably designed burner and a hydrogen based/ entrained air diffusion flame should offer several advantages when used with atomic fluorescence spectrometry. Argon is to be preferred to nitrogen as the flame support gas since the latter seriously quenches fluorescence.

Prior destruction of the coal matrix may be avoided if a reliable method for the analysis of whole coal samples can be developed. The direct introduction of aqueous whole coal slurries into an inductively coupled plasma may be suitable, but efficient and rapid matrix destruction and analyte atomisation are essential if sufficient sensitivity and precision are to be obtained. The hot atom cell and, under certain circumstances, long residence times available with the inductively coupled plasma may satisfy these conditions.

When sensitivity is not critical it is generally easier to use atomic absorption rather than atomic fluorescence spectrometry. However, the typical levels of these metals in coal, coupled with the limitations of conventional wet chemical digestion procedures, means that atomic absorption is unlikely to provide sufficient sensitivity for their routine determination in coal.

1.6 OBJECTIVES AND SCOPE OF THIS WORK

For coal, as with oil and gas, it is essential to use its energy content efficiently, not only to conserve reserves, but also to minimise process plant size, feedstock requirements and thus final product cost. Coal gasification and liquefaction offer not only routes for the production of fuels and chemicals at high thermal efficiencies, but also a means of producing them with significantly reduced pollution hazards relative to those associated with coal combustion. Furthermore, dependence on increasingly costly and uncertain supplies of petroleum feedstock is reduced.

We have seen from the preceding discussions that the increased use of coal may lead to significant amounts of several volatile trace metals entering the environment. The toxic and carcinogenic properties of these metals causes particular concern and it is becoming increasingly necessary to accumulate data on their dispersion and fate in and around coal-utilising power plants. Before the construction of environmentally significant mass balances is possible, reliable analytical methods suitable for the routine determination of these volatile metals in coal are necessary. We have also discussed some of the limitations of conventional sample preparation and analytical techniques commonly used in the determination of low levels of trace metals. The work presented in this thesis is directed towards the attainment of a number of goals, which are summarised as the development of:

a. reliable and quantitative methods for the extraction and collection of volatile metals from coal samples;

b. methods for the generation and transport of gaseous analytes from the solutions produced in a. above;

c. atom reservoirs suitable for the determination of mercury, arsenic and selenium using atomic fluorescence spectrometry;

d. methods for the determination of trace metals in whole coal through the direct introduction of aqueous whole coal slurries into an inductively coupled plasma.

Of the elements cited, mercury, arsenic and selenium are of particular interest in coal and would conveniently illustrate the problems and potentialities of these approaches to atomisation. Gaseous sample transport and slurry injection offer several analytical advantages and an opportunity to study these novel approaches to atomisation.

Chapter 2. DETERMINATION OF MERCURY USING COLD VAPOUR ATOMIC FLUORESCENCE SPECTROMETRY AND A GAS-SHEATHED ATOM CELL.

2.1 INTRODUCTION

Accompanying the awareness of the dangers of pollution by mercury is the need for more accurate and reliable methods applicable to the wide range of materials which may contain traces of mercury present in both organic and inorganic combination. Although many methods for the determination of low levels of mercury have been published in the last 50 years, most date from less than 15 years ago. Each method has its characteristic advantages and limitations which are discussed briefly below. For a fuller discussion the reader is referred to the review by Chilov (74).

Under ideal conditions colorimetric procedures may be very sensitive (capable of detecting approximately 0.1 $\mu g.\ ml^{-1}$ of mercury), but the susceptibility to interferences and the tedious methods required to minimise such interferences may make them unsuitable for coal analysis. Volumetric procedures tend to lack sensitivity while methods based on catalysis or enzyme inhibition by mercury (II) ions are prone to interferences. Although applicable to samples containing as little as 0.1 $ng.g^{-1}$ neutron activation analysis is not widely used. Specialised equipment and instrumentation are required and considerable sample manipulation is often necessary. Nevertheless, where the amount of sample is small neutron activation provides a suitable means of non-destructive analysis. The difficulty in obtaining suitable activation sources and radio-tracers limits the usefulness of radiochemical methods. Such methods are, however, sensitive and require less sample manipulation and activation than neutron activation methods. In addition radioisotope dilution methods are readily automated. Poor precision and sensitivity may result from the severe matrix effects frequently encountered in X-ray fluorescence methods. Corrections for these interferences may require involved calculations, while methods for reducing interferences by separation of the mercury from the matrix may be tedious. Emission spectrographic methods exhibit poor sensitivity and preconcentration of the mercury may be necessary, while d. c. arc plasma methods suffer from poor precision, due to the irreproducible way in which the sample enters the plasma and also from matrix interference effects. Of the instrumental techniques discussed neutron activation analysis is proving the most popular in the analysis of coal and related materials.

The popularity of atomic absorption and atomic fluorescence spectrometric methods for the determination of low levels of mercury is well reflected in the number of reports which have been published in the last 12-15 years. The review articles by Ure (75), in particular, and Chilov (74), both give fuller accounts of the determination of mercury by atomic absorption and atomic fluorescence spectrometry using both flame and flameless atom cells. The next section is devoted to a brief examination of the analytical merits of these techniques.

2.2 DETERMINATION OF MERCURY USING ATOMIC ABSORPTION AND ATOMIC FLUORESCENCE SPECTROMETRY.

Elemental mercury exhibits an appreciable vapour pressure at room temperature; the vapour is monatomic and it is therefore unnecessary to employ a flame or furnace for atomisation. In 1939

Woodson (76) determined mercury using atomic absorption spectrometry after collecting the metal on a cadmium sulphide pad prior to volatilisation into a silica absorption cell. Atomic absorption was measured at the 253.7 nm resonance line and molecular absorption was compensated for using a continuum background source. A landmark in the development of cold vapour techniques was the paper by Hatch and Ott (77), which has formed the basis for most subsequent work. In this method the solution obtained by digestion of rocks with sulphuric acid was oxidised with hydrogen peroxide and potassium permanganate. Treatment of this solution with a mixture of sodium chloride and hydroxyammonium sulphate was followed by reduction with tin (II) sulphate solution. Air was bubbled through the solution and passed through a magnesium perchlorate drier, transporting the mercury into the absorption cell. Hence the term "cold vapour reduction/aeration technique".

In flames, typical detection limits are 0.5μg.ml^{-1} for atomic absorption (78) and 0.1 μg.ml^{-1} for atomic fluorescence (79). When cold vapour reduction/aeration techniques are used the reported detection limits are much lower, typically 0.6 ng for atomic absorption (80) using 5 ml samples and 0.02 ng for atomic fluorescence (81) using 1 ml samples. In the flameless technique there is less dilution of the mercury vapour in the optical path at any given moment and enhanced sensitivity results.

Two methods are commonly used to generate mercury vapour for subsequent delivery into the optical path of an atomic spectrometer. The first involves amalgamation of the mercury electrolytically onto copper wire (82), or directly from solution onto silver screens or coils (83, 84), or from the vapour onto gold wool (85) followed by desorption of the mercury vapour upon heating. Such methods have the advantage of introducing both a preconcentration step and a selective separation step, whereby potential interferences may be rejected, but they can be quite complex. The second method, the cold vapour reduction/aeration technique is generally to be preferred due to its simplicity, cheapness and robust nature. Cold vapour atomic absorption methods, however, suffer from several disadvantages which may be overcome by using atomic fluorescence spectrometry. With cold vapour atomic absorption spectrometry, fogging of the cell walls by moisture necessitates drying the vapours prior to their entry to the atom cell, and the desiccant can be both a source of contamination or mercury loss (86); when a windowless cell is used in atomic fluorescence spectrometry, such problems are avoided. Molecular absorption interferes with cold vapour atomic absorption spectrometry and background correction is highly desirable; in atomic fluorescence spectrometry molecular absorption poses a smaller problem. Advantages of improved sensitivity and greater linear working range are also available with atomic fluorescence spectrometry.

The design of the atom cell is of critical importance if the full advantages of atomic fluorescence over atomic absorption spectrometry are to be achieved. Thompson and Reynolds (87) recognised this when they used a cell without windows, later modified by using a simple sheathing unit constructed from acetyl resin (81). Full details of the construction of the sheath, which was designed to produce a laminar shield of argon around the atom cell were not given, but an improvement in the signal of a factor of two, attributed to decreased quenching by entrained air, was reported.

Cavalli and Rossi (88) reported a "gas-shielded mercury vapour sprayer" for atomic fluorescence spectrometry. This was manufactured from perspex and the central mercury vapour channel was protected by a laminar flow of argon issuing from a 1 mm annulus. An improvement in the intensity of the fluorescence signal of 28-fold was obtained, but this device appears to require careful engineering.

A large number of previous reports have described manual injection techniques using discrete samples. Such methods are relatively time consuming and a fully-automated system using the reduction/aeration atomic absorption,procedure has been described (26). Although relatively expensive and complex this report indicated the feasibility of developing a continuous flow procedure. The advantages of such a procedure may be summarised as: steady state signals are achieved, leading to greater convenience and improved accuracy; injection and other discrete variables are eliminated, yielding improved precision; the control over experimental conditions is increased; the baseline establishes the background level unambiguously and this remains essentially constant.

In this work the use of a simple,improved argon-sheathed atom cell, used as the basis of the detection system for the determination of mercury by cold-vapour atomic fluorescence spectrometry is described. Both discrete manual injection and continuous flow systems were used to generate mercury vapour. The reduction cell was purged with argon and the evolved mercury vapours were swept to the windowless, argon-sheathed atomic fluorescence cell.

The performance of the optimised system was evaluated by determining the mercury content of a barley seed sample and N.B.S. Orchard Leaves, SRM 1571.

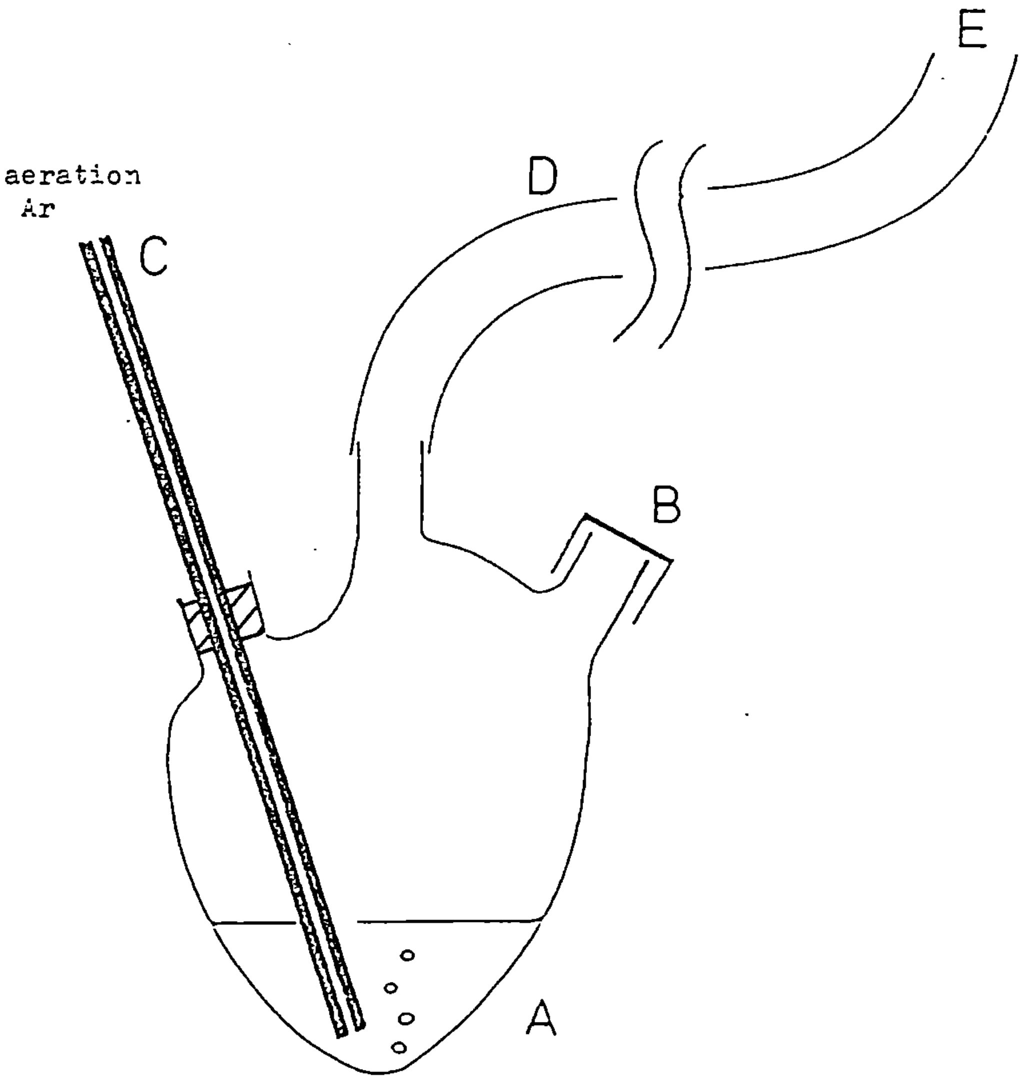
2.3 EXPERIMENTAL

2.3.1 EQUIPMENT

Mercury vapours were generated using both discrete injection and continuous flow systems. In the former the reduction cell was a three-necked, pear-shaped flask of 25 ml capacity and a syringe was used to inject sample aliquots via a rubber septum into tin (II) chloride solution (fig. 1). Continuous generation of mercury vapour was achieved by using two small peristaltic pumps to deliver tin (II) chloride and sample solutions simultaneously to the reduction cell. To accomodate this arrangement a new reduction cell was designed and constructed which included a constant head drainage tube (fig. 2). In each case mercury was removed by a small flow of argon and swept to the atom cell which was constructed as follows. Approximately 150 capillary tubes (60 mm long, 0.7 mm i.d.), of the type commercially available as melting point tubes, were glued around the outside of a pyrex glass tube (6 mm i.d.). This arrangement was secured inside a shortened Hirsch filter tube (22 mm i.d.), using the side arm as gas inlet (fig. 3). The bottom of the outer tube was sealed with a rubber bung and the glassware painted matt black on the outside, Mercury vapours entering the fluorescence cell through the central channel were constrained in the optical path by a second flow of argon which passed through the surrounding capillary tubes to produce a laminar stream of argon around the central flow. Fluorescence was excited and measured in the volume 0-25 mm above the laminar flow device.

The cell was mounted vertically in an atomic absorption spectrometer in place of the burner/nebuliser assembly, and at the focal point of the spectrometer lens. The spectral source, a mercury electrodeless discharge lamp, was positioned so that the volume immediately above the cell was irradiated and fluorescence radiation passed through the spectrometer focussing lens to the monochromator. The geometry of this arrangement is shown in fig. 4. The distances were: light source to cell, 65 mm; cell to lens, 78 mm; an angle of 45° was subtended. The mercury lamp was air-cooled by directing the air stream from the spectrometer compressor down through the top of the microwave cavity. The spectrometer was operated in the "emission" mode and fluorescence was detected at 253.7 nm with a spectral bandpass of 2.0 nm. Using the manual injection technique fluorescence peaks were obtained on a strip chart recorder and an integrator provided peak area measurements. The steady state signals obtained with the continuous flow system were sampled using the spectrometer integrator. Instrumentation and operating conditions are given in Table 1.

Fig. 1 Reduction vessel for generation of mercury vapour using the manual injection technique



A Reduction cell plus tin (II) chloride solution

B Rubber septum

C Capillary tubing inlet for aeration argon

D Polypropylene tubing

E Mercury vapours to atom cell

Fig. 2 Continuous flow system for the generation of mercury vapour

A. Peristaltic pump, tin (II) chloride solution, 2.5 ml.min^{-1}

B. Peristaltic pump, sample/standard solution 7 ml.min^{-1}

C. Reduction cell

D. Drain, to waste

E. Carrier gas inlet, 0.4 l.min^{-1} argon

F. Mercury vapours to atom cell

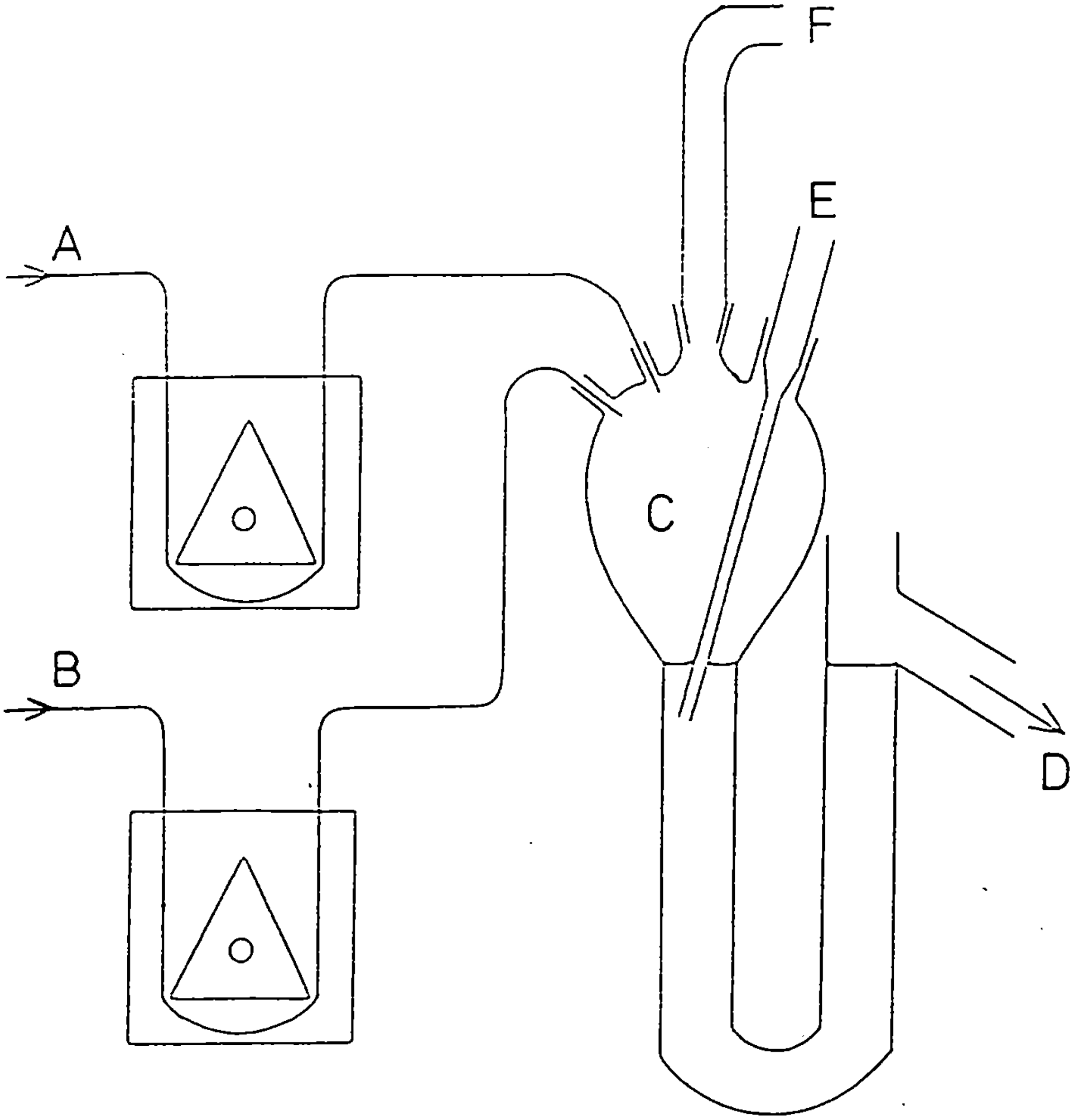
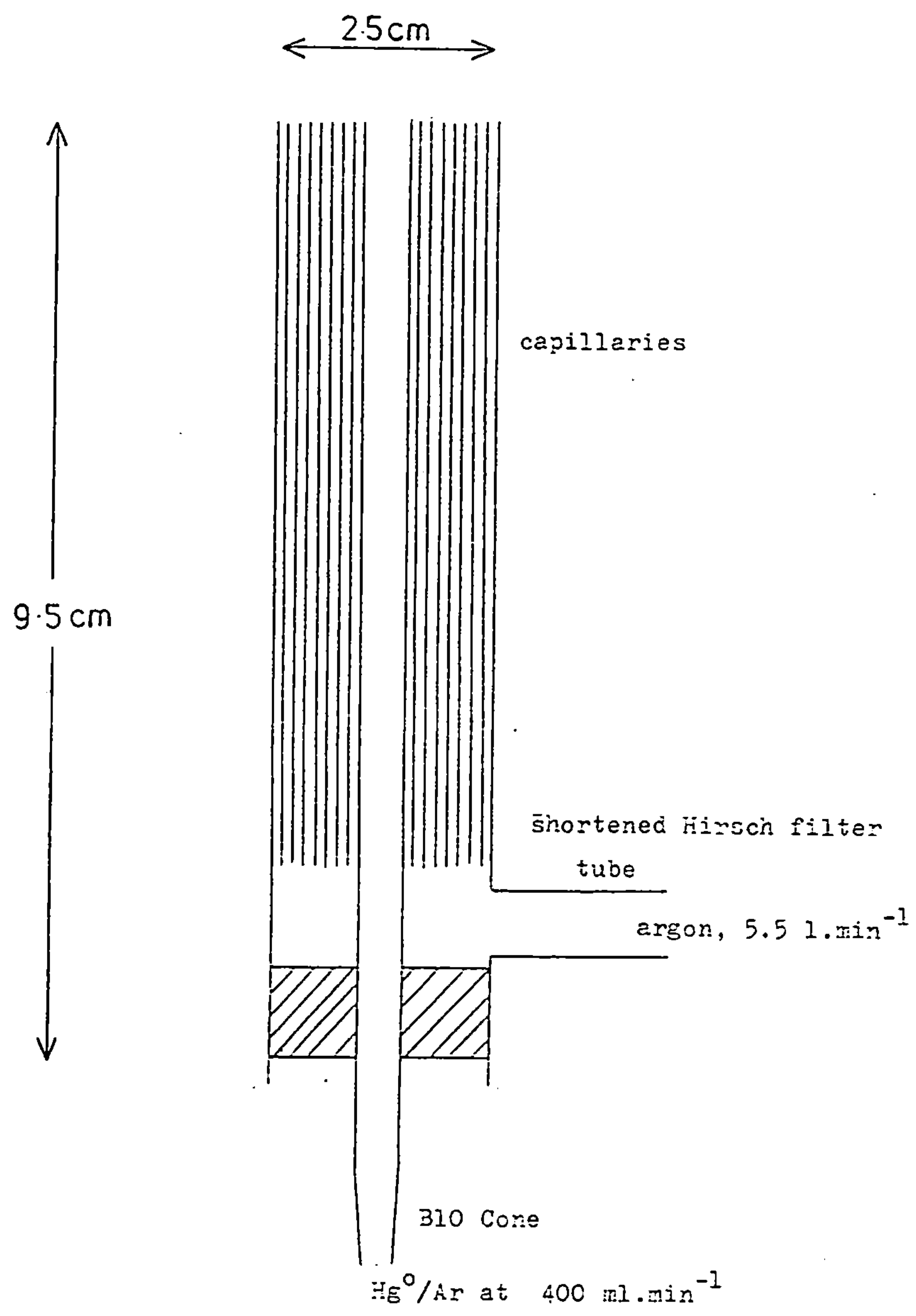


Fig. 3 Laminar flow device



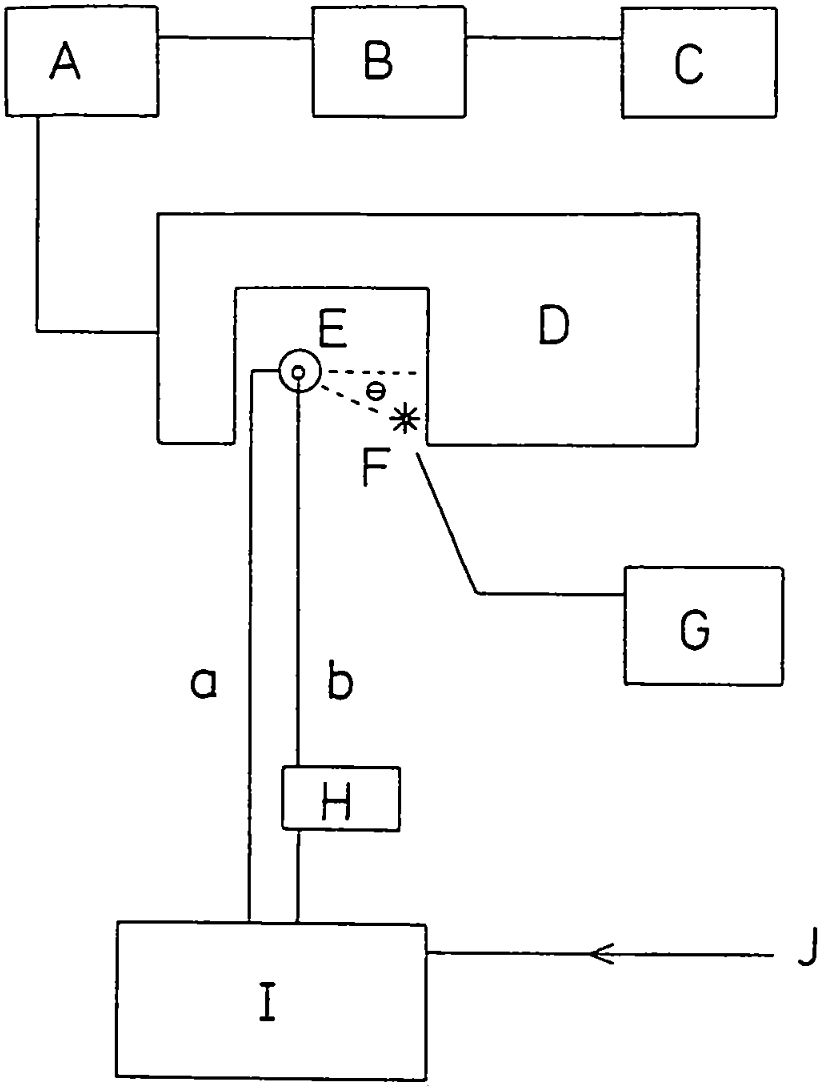


Fig. 4 Block Diagram of Instrumentation

A	Linear amplifier
B	Precision integrator
C	Chart recorder
D	Atomic spectrometer
E	Laminar flow device
F	Electrodeless discharge lamp in microwave cavity
G	Microwave generator
H	Reduction cell
I	Gas pressure and flow controller
J	Argon supply
a	Argon for laminar flow
b	Argon for aeration of Hg to atom cell
θ	Angle subtended by source, atom cell and slit, 45°

TABLE 1

Instrumentation and Optimum Operating Conditions

Component	Model	Supplier	Operating Conditions
Spectrometer	1L151	Instrumentation Laboratories Inc. Lexington, Massachusetts, U.S.A.	Flame Emission damping factor 1s; scale expansion X5; PMT voltage 700; wavelength 253.7 nm; spectral band pass 2.0 nm.
Excitation source	Mercury EDL	EDT Research Ltd., London NW10	36W incident power cooled by a flow of ∿ 3ℓ min^{-1} air.
Microwave cavity	Broida ¼ wave cavity, 210 L powered by a Microtron 200 Mark III microwave generator	Electromedical Supplies Wantage, Oxon.	
Gas flow rate controller	Pye Panchromatogram	Pye Unicam, Cambridge.	Using reference outlet for aeration flow and column 1 outlet for laminar flow. Column 2 outlet closed.
Chart recorder	Elecktronic 194	Honeywell, Brentford, Middlesex.	Typically 5 min inch^{-1} and 10 mV full-scale deflection.
Integrator feeding linear amplifier	5530000	Honeywell	10 mV span.
G.C. Integrator	TP503	Honeywell	Typically 1% threshold level, 1s response time.
Syringe	1 mℓ disposable syringe (plastic)	Gillette Brentford, Middlesex.	
Reduction cell		Laboratory constructed	
Peristaltic Pumps	Mark III -	Schuco Scientific	10 rpm delivering 2.5 mℓ.min^{-1}.
	Mark IV -	Halliwick Court Place Woodhouse Road, London	60 rpm delivering 7 mℓ.min^{-1}.

2.3.2 REAGENTS

Unless otherwise stated the reagents used were of analytical grade.

Tin (II) chloride solutions.

Prepared by dissolving 400 g and 100 g of tin (II) **chloride** dihydrate in hydrochloric acid (1 litre, 1 M) for the manual injection and continuous flow systems respectively. In practice suspensions were formed but shaking before use yielded suitably homogeneous mixtures. A few granules of tin were added to prevent aerial oxidation and the solutions were purged with argon for about 5 minutes each day before use to expel any absorbed mercury.

Potassium dichromate solution.

Prepared by dissolving potassium dichromate (0.3 g) in dilute nitric acid (1 litre, 1.6 M).

Mercury (II) nitrate solution.

Prepared by dissolving mercury (II) nitrate hemihydrate (1.6630 g) in potassium dichromate solution (1 litre). Calibration standards were prepared by appropriate dilutions.

Phenylmercury (II) acetate solution.

Phenylmercury (II) acetate was prepared as described by Makarova and Nesmeyanov (89) and twice recrystallised from ethanol. A stock solution of 0.4197 g in potassium dichromate solution (1 litre) was prepared.

2.3.3 PROCEDURES

2.2.3.1 PRESERVATION OF STANDARDS AND SAMPLE DIGESTS.

These were stabilised by dilution with the solution of potassium dichromate in dilute nitric acid as recommended by Feldman (90). When the solutions were stored in borosilicate glassware this diluent prevented losses of mercury for several days at levels of 1 ng.ml^{-1} and lower, and for several weeks at concentrations of 20 ng.ml^{-1} and higher. Sample digests remained stable for at least 1 working day.

2.3.3.2 DIGESTION OF SEEDS AND ORCHARD LEAVES

Barley seeds (0.5 g) were shaken with concentrated nitric acid (10 ml) and refluxed on a water bath at 80°C for 30 minutes. Orchard leaves (2.0 g) were shaken with concentrated nitric acid (20 ml) and allowed to stand overnight before refluxing. The resulting solutions were transferred to volumetric flasks and made up to volume (100 ml for the seeds, 50 ml for the leaves) with the potassium dichromate diluent.

2.3.3.3 DETERMINATION OF MERCURY

(i) Manual injection technique

After switching on both argon flows, aliquots (0.5 ml) of the standard and sample solutions were injected into the tin (II) chloride solution (3 ml) contained in the reduction cell. The evolved mercury was swept into the atom cell and the peak area of the fluorescence signal recorded. Each solution was injected at least 5 times and the mean peak area calculated. Elution time varied as a function of the mass of mercury injected, but was typically complete in 30-100s.

(ii) Continuous flow system

After switching on both argon flows tin (II) chloride and sample solutions (2.0 ml and 7.5 ml respectively) were pumped simultaneously to the reduction cell. After equilibration the steady state signal was sampled using the spectrometer integrator (4 x 4s).

2.4 RESULTS AND DISCUSSION

2.4.1 OPTIMISATION OF THE MANUAL INJECTION TECHNIQUE

2.4.1.1 INSTRUMENTAL PARAMETERS

At the beginning of the work the operating conditions used were somewhat arbitrary. These conditions were:

incident microwave power	30 W
laminar flow rate	3 $l.min^{-1}$ argon
carrier flow rate	3 $l.min^{-1}$ argon
injection volume	1.0 ml 100 $ng.ml^{-1}$ mercury solution
tin (II) chloride solution	3 ml of 170 $g.l^{-1}$ Sn^{2+}

Fluorescence was measured at 90° but a disproportionately high level of background and scatter was observed. This was reduced, however, after a simple cardboard light trap was located around the EDL output aperture. A variety of parameters including slit width, photomultiplier voltage and scale expansion were examined until the best signal to noise ratio was obtained. In a number of satisfactory combinations of these parameters a rough limit of detection was found to be the same, approximately 12 $ng.ml^{-1}$. It was felt that a better detection limit would be realised if the level of background could be substantially reduced, permitting the use of higher PMT voltages. Consequently "front-face illumination" was examined. An immediate improvement in the characteristics of the baseline noise level was observed and background was virtually eliminated. This allowed much greater freedom in the choice of operating conditions. Again various combinations of these conditions were examined and the best combination (700 v; scale expansion x5; 2.0 nm slit width) gave a detection limit of 2 $ng.ml^{-1}$ and 5 $ng.ml^{-1}$ could routinely be determined.

The new geometry used to accomodate the front face illumination meant that the laminar flow device had to be moved from its position adjacent to, but just below the spectrometer lens to a position some 80 mm from the lens. Some degradation of performance had been anticipated since fluorescence intensity is inversely proportional to the square of the atom cell/slit distance and also the solid angle of fluorescence. In the new position the atom cell was located at approximately the focal length of the lens which may have contributed to the overall observed increase in intensity. In order to determine whether this increase was due to the use of 45° illumination or through more efficient collection of the atomic fluorescence, the atom cell was retained some 80 mm from the lens and 90° illumination used. The approximate detection limit was 6 $ng.ml^{-1}$. Thus the 6 fold improvement in detection limit (12 → 2 $ng.ml^{-1}$) was due to both effects, a 2 fold increase ($12 \rightarrow 6$ ng.ml^{-1}) resulting from the positioning of the atom cell at the focal length of the entrance slit lens, and a 3 fold increase ($6 \rightarrow 2$ ng.ml^{-1}) from the use of 45^{o} illumination.

At this stage relatively poor precision was obtained and this was thought to be due to fluctuations in the EDL output intensity. Since the EDL was not wholly contained in the cavity a temperature gradient was developing along the length of the EDL. This caused a cycling of the mercury vapour in the tube and resulted in extreme variations in output intensity. Consequently, the air line from the IL 151 compressor was directed down the central hollow of the microwave cavity. The flow rate used was 3 l.min^{-1} and this produced a steady baseline without markedly affecting overall output intensity. The optimum forward microwave power was then determined by measuring the fluorescence signal at different powers using 1 ml injections of 100 ngml^{-1}of mercury. The results are given in Table 2.

The value chosen for subsequent work was 38 W which gave the best compromise between reproducibility and signal to noise ratio.

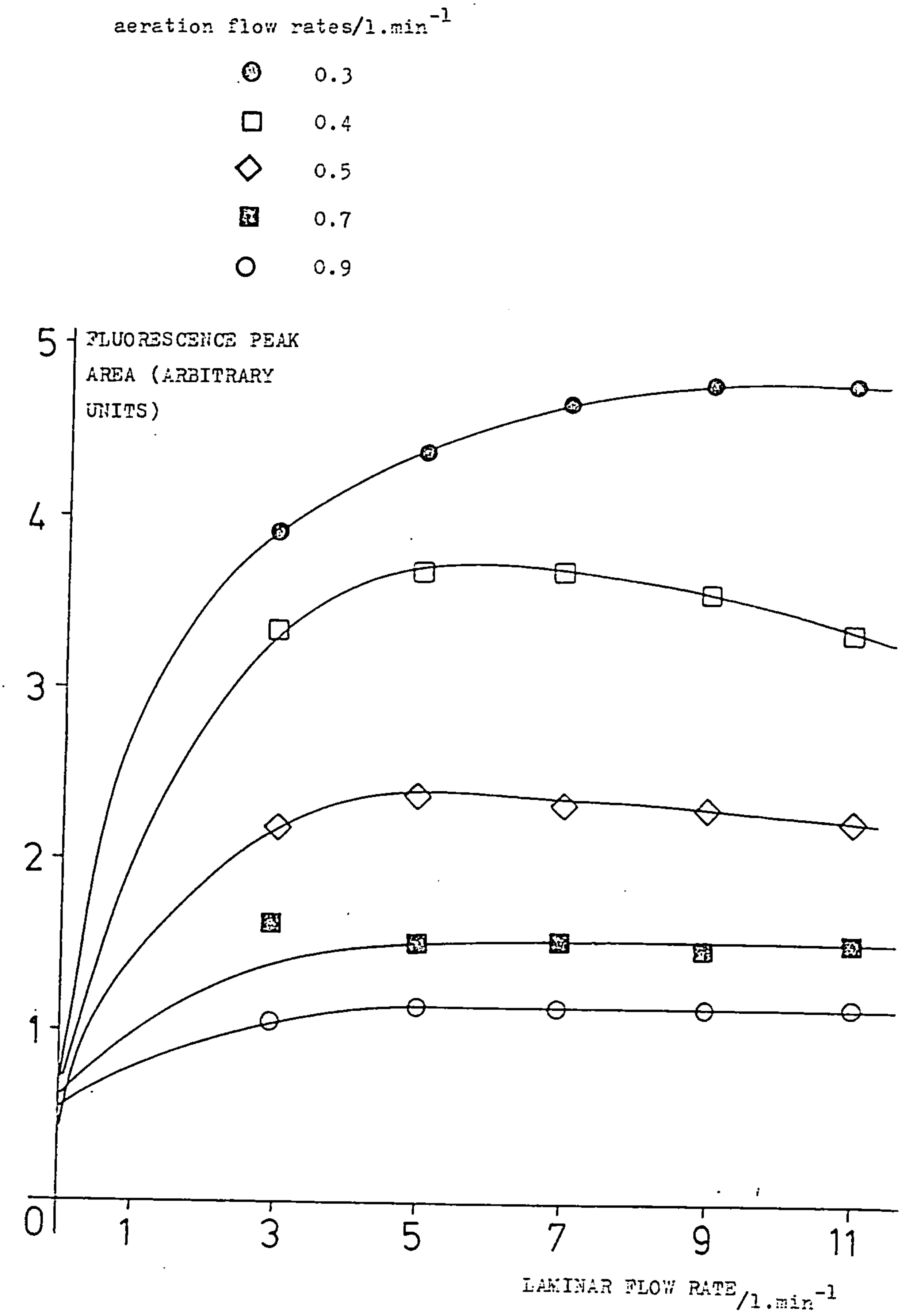
2.4.1.2 GAS FLOW RATES

Argon was chosen as the carrier gas and laminar flow gas because of its low cross section of quenching of fluorescence relative to air and nitrogen. The two flow rates were optimised by a simple factorial process in which signal size was measured at four different aeration flow rates, each one with six different laminar flow rates. The results are shown in Fig. 5, from which the

Table 2. Optimisation of the forward microwave power

Incident microwave power/W	Peak area (arbitrary units)	Peak height (arbitrary units)
18	130	0.16
25	283	0.21
32	504	0.26
40	756	0.27
48	- results too 'noisy' to be meaningful	

Fig. 5 Effect of argon flow rates on mercury atomic fluorescence



following general comments may be made. The higher the laminar flow rate, the greater was the confinement of the mercury in the area in front of the EDL and slit. At certain flow rates "pinching" occurred some distance above the fluorescence zone and vertical expulsion of the mercury was retarded. This effect further increased the residence time of the mercury in the light path and enhanced signals resulted.

For a given laminar flow rate, the higher the carrier gas flow rate the smaller the signal, since the residence time of the mercury in the light path was reduced by the increased driving force of the carrier stream.

At very low carrier flow rates (0.3 $l.min^{-1}$ or less), insufficiently vigorous agitation caused the mercury to reach the fluorescence zone as a series of "plugs", resulting in deformed peaks and poor precision. This effect became more pronounced as the volume of solution in the reduction cell increased after each subsequent injection. Although peak area was only slightly affected peak height and shape were markedly altered, the peak width at half-height increasing with the volume of solution in the reduction cell.

The laminarity of the two gas flows was observed visually by placing two Dreschel bottles, one containing dilute ammonia solution, the other dilute hydrochloric acid, in series in each of the gas streams alternately. When the evolved ammonium chloride was passed through the capillary tubes only, at the optimum flow rate for maximum signal size, the "pinching" effect was clearly visible some 3-4 cm above the top of the laminar flow device. When the ammonium chloride was passed through the reduction cell only, a regular, vertical flow of gas past the EDL and slit was observed up to 3 cm above the laminar flow device. The "pinching" effect of the laminar flow then caused the ammonium chloride to eddy slightly in the space between the EDL and the slit before slowly diffusing away vertically. Some experiments were performed using 3 mm internal diameter tubing to introduce the carrier gas into the reduction cell. Better results were, however, obtained using capillary tubing, since more vigorous agitation occurred and sharper, more reproducible peaks were observed.

The optimum flow rates were found to be 0.4 and 5.5 $l.min^{-1}$ for carrier and laminar flows respectively. Under these conditions the laminar stream eliminated the effects of draughts and prevented lateral diffusion of mercury vapour. Entrainment of atmospheric species which effectively quench mercury fluorescence was markedly reduced.

This resulted in a hundredfold improvement in the limit of detection over that obtained previously when flow rates of 3 $l.min^{-1}$ for both laminar and aeration flows were used. Further, signal size was approximately 12 times greater than that obtained with no laminar gas flow. Precision generally appeared slightly improved at higher laminar flow rates, typically 1-5% relative standard deviation (RSD) in the range 3-11 $l.min^{-1}$, compared with 6-26% RSD when operating without the laminar gas flow (Table 3).

2.4.1.3 REDUCTION CELL VOLUME

In the apparatus described previously a 25 ml flask was connected directly to the bottom of the laminar flow device, but the

Table 3. Effect of shielding gas

No shielding

Carrier gas, $\ell.min^{-1}$	0.4	0.9
Relative peak area	1	1.7
R.S.D.	18%	7%

With shielding, at
optimum flow of 5.5 $\ell.min^{-1}$

Carrier gas, $\ell.min^{-1}$	0.4	0.9
Relative peak area	11.5	3.5
R.S.D.	1%	5%

need frequently to empty the cell led to difficulty in realigning the optics of the system. In order to be able to remove the flask without disturbing the laminar flow device, the two were connected via a 450 mm length of polypropylene tubing (10 mm i.d.). Since this increase in dead volume did not result in any peak broadening a 100 ml flask was used instead of the 25 ml flask. Much broader peaks were observed and peak area decreased by approximately 20%. It was concluded that in the case of the 25 ml flask less diffusion of mercury vapour was occurring inside the flask and that the mercury vapour was travelling along the tube as a discrete plug. Consequently, the 25 ml flask connected to the laminar flow device via the polypropylene tubing was used for all subsequent work.

2.4.1.4 SAMPLE SIZE

The need for a small reduction cell placed constraints on the size of the sample used. Using 0.4 $l.min^{-1}$ of argon as carrier, excessive frothing occurred (causing large amounts of water vapour to enter the fluorescence zone) when the total volume of solution in the cell exceeded approximately 14 ml. Moreover, it became difficult for the argon to purge the mercury rapidly from the large volume of solution and peak broadening occurred. The concentration and volume of tin (II) chloride used were chosen in order to provide a large excess of Sn^{2+} over Hg^{2+} and sufficient volume to ensure rapid, efficient mixing. It was decided to use 3 ml of tin (II) chloride solution with an injection volume of 0.5 ml. This permitted up to 20 injections to be made before it became necessary to empty the cell. In practice the tin (II) chloride was replaced after 15-18 injections.

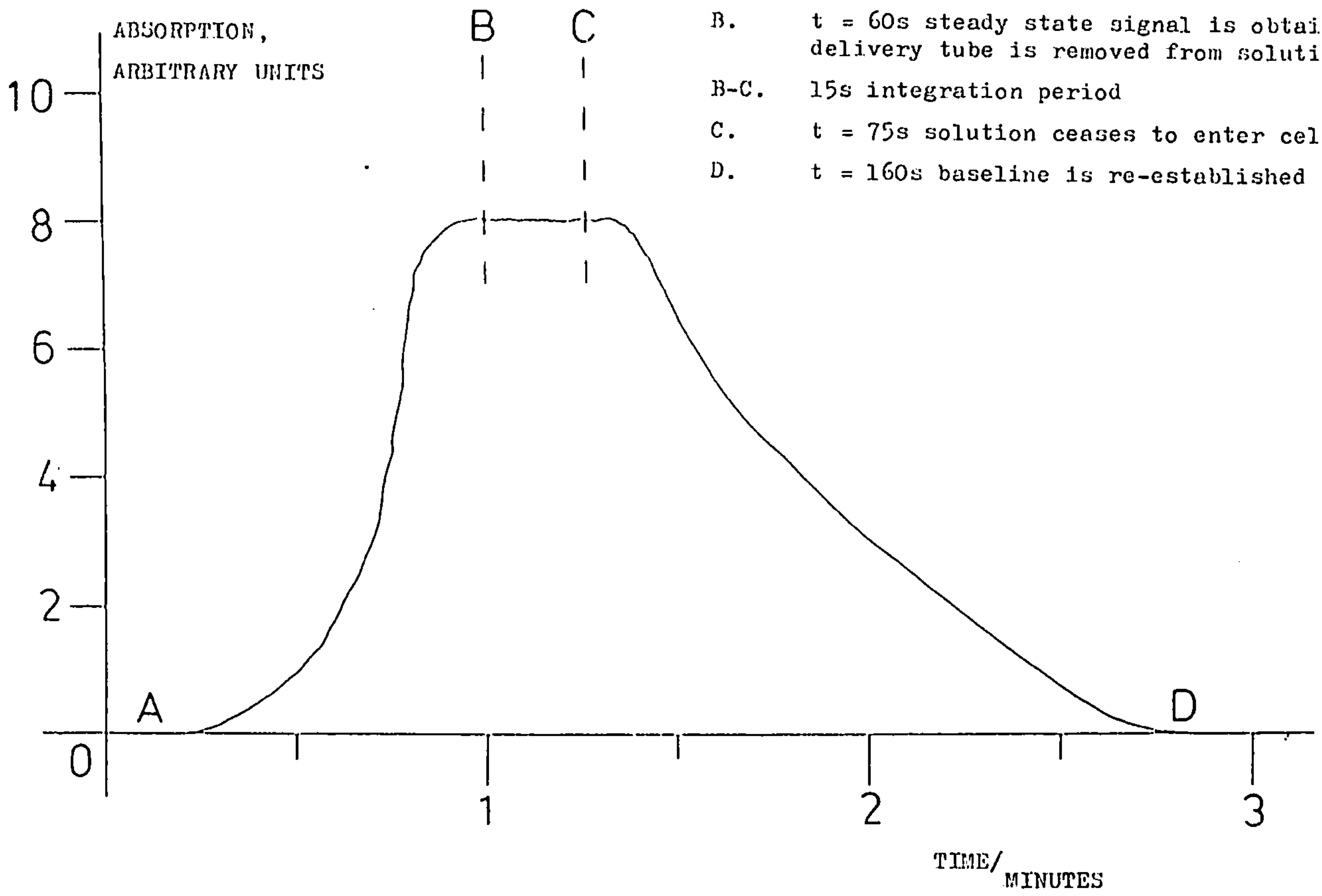
Injection volume precision was checked by injecting 11 aliquots of 0.5 ml into the cell on a precision balance and weighing each injection. Three different syringes were used and a mean relative standard of 0.6% obtained.

2.4.2 OPTIMISATION OF THE CONTINUOUS FLOW SYSTEM

The experiment to determine the optimum gas flow rates was repeated using the continuous flow system, and similar results were obtained. At carrier flow rates less than 0.3 $l.min^{-1}$ the mercury was purged somewhat irregularly from solution producing erratic signals. Having adopted 0.4 $l.min^{-1}$ as the preferred carrier flow rate the optimal laminar flow rate was again 5.5 $l.min^{-1}$.

The signal against time plot obtained from the continuous flow system was typical of an automated flow system as shown in fig. 6. Signal size was independent of both the flow-rate and concentration of the tin (II) chloride solution in the ranges 2.5 to 25 $ml.min^{-1}$ and 5 to 40% m/v respectively. The signal increased linearly with the flow-rate of sample (or standard) up to a maximum of 30 $ml.min^{-1}$, above which it became difficult to drain the cell sufficiently rapidly. Flow-rates of 2.5 $ml.min^{-1}$ of tin (II) chloride solution (10% m/v as the dihydrate) and 7.0 $ml.min^{-1}$ of sample/standard were chosen to minimise the volume of reagent and sample required, consistent with acceptable signal size. Using these flow-rates the rise time, as shown in fig. 6, was about 60s and the sample delivery tube contained sufficient residual solution to allow a 15s integration time on the spectrometer to be used with removal of the tube from the sample solution upon commencement of the integration. Consequently

Fig. 6 Typical signal versus time plot for the continuous flow system



A. t = o tube is placed in sample solution

B. t = 60s steady state signal is obtained and delivery tube is removed from solution

B-C. 15s integration period

C. t = 75s solution ceases to enter cell

D. t = 160s baseline is re-established

the amount of sample consumed was about 7 ml. Residual mercury was purged from the cell and the base-line re-established about 2 minutes after solution ceased to enter the cell. Total analysis time was 2 to 3 minutes per solution.

2.4.3 DETECTION LIMITS AND LINEAR CALIBRATION RANGES

2.4.3.1 MANUAL INJECTION TECHNIQUE

The detection limit (that concentration of mercury producing a signal equal to the mean of the blank plus twice the standard deviation of the blank mean) was 0.02 ng. ml^{-1}, i.e. for 0.5 ml injections, 0.01 ng.

At high concentrations of mercury little scale expansion was required and the effects of baseline drift were minimal. Precision was good, typically 1-3% relative standard deviation (RSD) down to concentrations as low as 3 $ng.ml^{-1}$. At very low concentrations of mercury, however, short-term fluctuations in the base-line coupled with high scale-expansion resulted in either premature or retarded tripping of the integrator and precision was degraded accordingly. If 10% is taken as the maximum tolerable RSD, the lower end of the useful working range of the method was 0.4 $ng.ml^{-1}$ i.e. 0.2 ng for 0.5 ml injections.

2.4.3.2 CONTINUOUS FLOW SYSTEM

The detection limit for the continuous flow system (again 2σ) was 0.043 $ng.ml^{-1}$. Precision, however, was generally improved, typically 2% RSD at 0.5 $ng.ml^{-1}$ compared with 7% RSD at 0.5 $ng.ml^{-1}$ for the manual injection technique. Taking 10% RSD as the maximum tolerable, the lower end of the useful working range of the method was 0.2 ng.ml^{-1}.

Analytical working curves were constructed for both methods using standard solutions of mercury prepared from a stock solution of 1000 μg.ml^{-1} of mercury. In each case the calibration plot was linear over approximately four orders of magnitude, from 0.4 ng.ml^{-1} (10% RSD) to 2000 ng.ml^{-1} (3% RSD). The calibration plot is shown in fig. 7 and the values in parentheses indicate the RSD at that concentration.

2.4.4. EVALUATION OF THE OPTIMISED SYSTEM

2.4.4.1 DETERMINATION OF MERCURY IN BARLEY SEEDS

The barley seeds had been coated with a seed dressing containing phenylmercury (II) acetate. The samples were digested using concentrated nitric acid (section 2.3.3.2, page 43) and the results for seven replicate determinations are shown in Table 4a. In this case an independent mercury content figure was not available and the accuracy of the method was checked using recovery tests. Known amounts of phenylmercury (II) acetate was added to six replicate samples of seeds and the mercury content determined as before (Table 4b). A reagent blank was also determined and the necessary correction made. The results demonstrate that no mercury was lost during digestion or transport to the atom cell.

Matrix effects were investigated by determining the mercury content

Fig. 7 Calibration plot for mercury at 253.7 nm

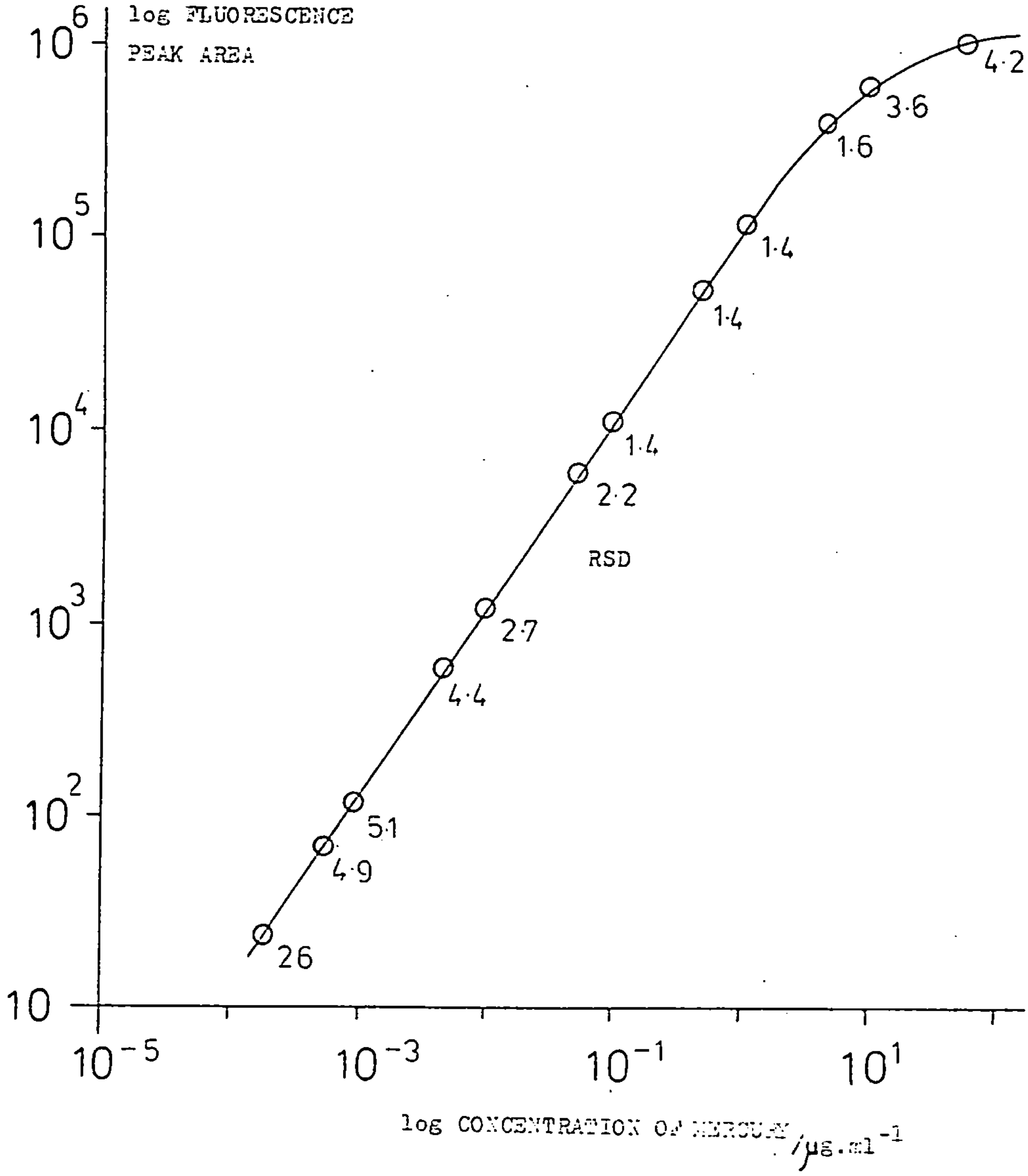


Table 4a

Mercury content of barley seeds

Replicate Number	1	2	3	4	5	6	7
Mercury Found ($\mu g.g^{-1}$)[a]	10.62	10.55	10.60	10.98	10.84	10.80	10.78

Mean = 10.74 $\mu g.g^{-1}$

Estimated standard deviation of the mean = 0.07 $\mu g.g^{-1}$

Relative standard deviation = 0.6%

[a] Each reported figure is the mean of 5 measurements of the same digest.

Table 4b

Recoveries of phenyl mercuric acetate (2.50 $\mu g.g^{-1}$ as mercury) added to barley seeds (containing 10.74 $\mu g.g^{-1}$ mercury).

Replicate number	1	2	3	4	5	6
Mercury found ($\mu g.g^{-1}$)[a]	13.22	13.31	13.23	13.24	13.18	13.23
% recovery	99.2	102.8	99.6	100.0	97.6	99.6

Mean recovery = 99.8%

[a] Each reported figure is the mean of 5 measurements of the same digest.

of a series of solutions each containing a fixed volume of the same standard solution and various known volumes of a seed solution of known mercury content. A plot of integrated signal area against concentration of mercury was linear, indicating the absence of matrix enhancement or suppression effects.

2.4.4.2 DETERMINATION OF MERCURY IN ORCHARD LEAVES

The accuracy of the method was then checked by analysing replicate samples of a standard reference material, S.R.M. 1571 Orchard leaves (National Bureau of Standards, Washington D. C., U. S. A.). The samples were digested overnight in concentrated nitric acid (section 2.3.3.2 page 43).

The results are given in Table 5 and show excellent agreement with the certified value and impressive precision.

2.5 CONCLUSIONS

In general the difficulty of preparing excitation sources offering a high signal-to-noise ratio has hindered the development of atomic fluorescence spectrometry. In the case of mercury, however, it is relatively easy to prepare suitable sources and, under suitable experimental conditions, the inherent advantages of atomic fluorescence (greater sensitivity and extended linear dynamic range) are available. In the work described several clearly identifiable factors have contributed to the sensitivity, precision or ease of operation of the method developed.

Table 5

Mercury content of orchard leaves

(NBS SRM 1571, certificate value 155 ± 15 $ng.g^{-1}$)

Replicate Number	1	2	3	4	5	6	7
Mercury Found ($ng.g^{-1}$)[a]	159	153	155	155	159	158	157

Mean = 157 $ng.g^{-1}$

Estimated standard deviation of the mean = 1.0 $ng.g^{-1}$

Relative standard deviation = 0.6%

[a] Each reported figure is the mean of 5 measurements of the same digest

Methods of producing mercury vapour by heating metal traps on which mercury has been collected after dissolution or combustion of the sample, generally prove more efficient in removing potential interferents. Such methods are, however, complex and expensive. In contrast the cold-vapour reduction/aeration technique is rapid, simple, cheap and robust. When strongly oxidising species are absent this procedure is equally free from interferences. Unnecessary dilution of mercury vapour by flame-gases is avoided using the flameless atom cell. This results in a higher instantaneous concentration of mercury in the optical path and enhanced sensitivity.

The long path-length atom-cells preferred in atomic absorption spectrometry are not necessary in atomic fluorescence spectrometry, where a suitable atom-cell is one in which the analyte atoms are contained in a relatively small volume close to both the excitation source and the entrance slit. The atom cell described is thus entirely suited for use with atomic fluorescence spectrometry. The geometry and positioning of the tube from which the mercury vapours are discharged ensures that all the mercury evolved reaches the optical path. The laminar flow of argon surrounding the atom cell prevents lateral diffusion of mercury allowing a windowless cell to be used, which eliminates the problems encountered with fogging of cell windows by water vapour. Since all the mercury evolved reaches the optical path a prime consideration is that of residence time, which is most dependent on carrier gas flow rate. The optimum residence time has been obtained by using the optimal combination of carrier and laminar gas flow rates. Vertical expulsion of the mercury from the optical path is retarded by turbulent mixing of the two gas flows above the fluorescence zone.

The increase in signal size of approximately 12, realised through use of the laminar flow of argon, is thought to be due to two separate effects. In addition to ensuring transport of the mercury through the optical path the sheathing gas prevents entrainment of the surrounding air. Oxygen and nitrogen are thus excluded from the atom cell and quenching of mercury atomic fluorescence by these species is prevented (it has been shown that the fluorescence signal is only 5% and 25%, in air and nitrogen respectively, of that obtained in argon). The use of sheathing gas also produces significant improvements in precision.

The calibration plot obtained is typical (91) of atomic fluorescence methods in which a line instead of a continuum excitation source has been used. At low mercury concentrations the response versus concentration plot is rectilinear, <u>i.e</u>. the slope = 1 and response is proportional to N, the number of atoms. At high mercury concentrations (2000 ng.ml^{-1} and greater) absorption of the fluorescent radiation by mercury atoms on the periphery of the atom cell causes a negative deviation from the expected analytical growth curve. This effect becomes more pronounced as the mercury concentration increases until a point is reached when the signal begins to decrease with increase in concentration. Beyond this point the trend continues until the slope of the plot reaches a value of $-\frac{1}{2}$ and response is proportional to $N^{-\frac{1}{2}}$, the reciprocal of the square root of the number of mercury atoms. Nevertheless, calibration is linear over approximately four orders of magnitude (0.4-2000 ng.ml^{-1}) and, while this is inferior to some reported atomic fluorescence and atomic emission (I.C.P.) linear dynamic ranges, it is considerably superior to typical atomic absorption linear calibration plots.

The vast majority of workers have reported methods in which excitation and collection of atomic fluorescence is achieved using conventional right-angle optics. Thus, the results obtained using 45° illumination are interesting since they suggest that 90° is a much less favourable angle of illumination. One reason, perhaps, why 90° has proved so popular is that this angle is most readily accommodated by the practical systems which have been used. Using illumination at 45° the level of specular reflection and background radiation entering the monochromator is much reduced. Consequently greater amplification of the signal with only a minimal increase in noise is achieved, resulting in greatly increased sensitivity.

The manual injection technique described provides good sensitivity, but is rather time-consuming and suffers from poor precision at very low levels of mercury due to the number of discrete variables and manipulations involved. In contrast the continuous flow system provides a rapid and convenient method with improved precision and a minimal loss in sensitivity. If the dead volume of the system could be substantially reduced, then the increased concentration of mercury in the carrier gas could result in even better sensitivity.

Thus atomic fluorescence spectrometry has provided a method which is both sensitive and precise for the determination of mercury and which extends over a wide linear calibration range. The gas-sheathed atom cell has enhanced this initial sensitivity both by constraining the mercury in the optical path and also by preventing entrainment of atmospheric species which are known to quench mercury atomic fluorescence. While the device described has been used in a conventional dispersive spectrometer, it is easily accommodated and should be suitable for installation in most instruments, including non-dispersive systems of the type recently reported (92, 93), but not yet widely available. The ease of analysis provided by the continuous flow system contributes toward the overall usefulness of this method when large numbers of samples, containing diverse matrices and widely varying amounts of mercury, are to be analysed.

Chapter 3. DETERMINATION OF MERCURY IN COAL

3.1 INTRODUCTION

Determinations of mercury in coal are fraught with a number of problems because of the highly intractable nature of the coal matrix, the volatility of mercury and the very low levels thought to be present (typically significantly less than 1 $\mu g.g^{-1}$. It has been proposed that instrumental techniques such as spark-source mass spectrometry (2, 21) and X-ray fluorescence (94) may be used to determine mercury in coal without sample dissolution, but this has not been widely confirmed. While such methods are relatively simple and rapid, good sensitivity and precision are not readily obtained and the results reported may be only semiquantitative. While whole coal may be irradiated in order to determine mercury by neutron activation analysis (95), it is frequently necessary to combust (22, 96) or digest (23, 97, 98) the coal later in order to concentrate the mercury prior to counting to obtain the necessary sensitivity. While offering good accuracy and precision, these methods are frequently very time-consuming and complex, requiring expensive, specialised instrumentation.

Most alternative analytical methods for coal entail prior destruction of the matrix. Recently, low temperature ashing (150°C) using radio-frequency excited oxygen at reduced pressure has been used to prepare coal samples for analysis. While the majority of metals are retained some of the more volatile may still be lost (22, 23). In addition, prolonged sample treatment times (typically 70 hours for a 0.5 g coal sample) are required, several samples are conventiently ashed simultaneously. Low temperature ash may also require further treatment, e.g. fusion or dissolution with hydrofluoric acid to bring it into a form suitable for analysis.

A few reports have appeared on methods of coal dissolution without prior ashing. A variety of oxidising acid mixtures and conditions have been used, typically under reflux, e.g. sulphuric acid/potassium permanganate (99), sulphuric acid/nitric acid (100), sulphuric acid/nitric acid/perchloric acid (101, 102), perchloric acid/periodic acid (103), sulphuric acid/hydrogen peroxide (104), aqua regia/potassium permanganate (105). Some of these methods may produce incomplete digestion or losses of volatile elements, especially mercury due to the vigorous digestion conditions. The use of PTFE lined digestion bombs is another alternative reported, and again a variety of acid mixtures has been used, e.g. aqua regia/hydrofluoric acid (106), fuming nitric acid/hydrofluoric acid (107). Combustion bombs in which the coal is burned in oxygen under high pressure have also been reported. After combustion the gases were absorbed in dilute nitric acid (108) and hydroxalymine hydrochloride/dilute nitric acid (109). These bombs present some handling difficulties (23, 105) and acid migration may result in damage to metallic components and losses of mercury.

Oxidative combustion and non-oxidative pyrolysis have been used to generate mercury vapour at temperatures reported variously between 600°C (110) and 850°C (111). The liberated mercury is removed by a small flow of gas, commonly oxygen, air or nitrogen and trapped on a series of gold frits (23, 111, 113) or collected in a suitable absorbing medium, commonly acidified potassium permanganate solution

(23, 110, 113, 114), or in a liquid nitrogen cooled trap (88). Some workers (110, 115) have experienced over-rapid combustion when using oxygen as the purge gas, while others have recommended the use of secondary combustion and ashing agents, e.g. silver and quartz wool (115), sodium carbonate (111), in order to prevent losses of mercury by adsorption on uncombusted carbonaceous materials and tars. Other workers using amalgamation methods have reported that similar auxilliary oxidising agents and catalysts, e.g. copper oxide (88), sodium nitrate (112), alumina and quartz wool (114), silver wool (23) and hot platinum wires (88), may be required to prevent smoke and organic vapours from obstructing amalgamation sites on the metal frits and from entering the absorption cell. Similar results have been observed by some workers collecting the mercury in acidic potassium permanganate solution where organic vapours and combustion products (23, 116), e.g. sulphur dioxide and oxides of nitrogen, have decomposed the collecting solution resulting in losses of mercury. In one variation (117) based on the above methods a sample of coal was combusted and the evolved mercury collected on the inner surface of a porous, gold-plated carbon tube. The tube was inserted in a carbon rod atomiser and the mercury determined by conventional electrothermal atomic absorption spectrometry. In another variation (118) the mercury released on combustion of the coal was collected on gold spherules from which it was subsequently removed by digestion with concentrated nitric acid in a heated autoclave. The mercury was electrolytically deposited onto carbon cathodes which were then inserted into a graphite tube and the mercury determined by electrothermal atomic absorption spectrometry. This latter method is somewhat time consuming, requiring at least twelve hours to ensure complete deposition of the mercury onto the carbon cathodes.

One review article by Schlesinger and Schultz (119) summarizes the advantages and limitations of several approaches to sample pretreatment while another by Lehmden et al (120) compares the results obtained for coal analysis using a variety of analytical techniques.

In this work investigations into the use of various oxidising acid mixtures as a means of dissolving coal samples for subsequent mercury analysis are described. The major requirement of a suitable method is that safe and reproducible liberation of the mercury from the coal is achieved in as short a time as possible while quantitatively retaining the mercury. In the methods examined attempts were made not only to digest the coal, but also to leach and to distil the mercury from the coal matrix.

In addition to the dissolution methods considered a more specific approach involving oxidative combustion and non-oxidative pyrolysis of coal as a means of releasing mercury was examined. As previously stated several workers have reported such methods though conflicting opinions exist especially regarding the choice of the combustion support gas and the need to include auxilliary oxidising agents and catalysts in the combustion train. As a result non-oxidative pyrolysis under nitrogen seemed to offer a method whereby mercury could be isolated from coal without the attendant hazards of explosive ignition. Potassium dichromate solution (due to its proven utility for storing dilute solutions of mercury) or potassium permanganate solution (by virtue of its previous applications) was used to collect the mercury evolved during pyrolysis (or combustion) of the coal. Subsequent determination of the mercury was achieved using the cold vapour atomic fluorescence system described in Chapter 2. The performance of the optimised system was evaluated by determining the mercury content of various coal and ash samples including the NBS bituminous coal, SRM 1632a.

3.2 EXPERIMENTAL

3.2.1 EQUIPMENT

All wet chemical digestions and distillations were performed using readily available laboratory glassware, i.e. a 2-necked, round-bottomed 250 ml flask and a B24 Quickfit double surface condenser. Reaction mixtures were heated using a Bunsen burner. The tube furnace (Carbolite Ltd., Sheffield) and pyrolysis train are shown in fig. 8.

3.2.2 REAGENTS

Unless otherwise stated, all reagents used were of analytical grade.

Nitric acid diluent and preservative for standards: 0.03% $^{m}/v$ potassium dichromate in nitric acid, 16 M.

Potassium dichromate solutions:

(i) for digestion experiments; 0.5% $^{m}/v$ in concentrated nitric acid.

(ii) for leaching experiments; 0.03% $^{m}/v$ in concentrated nitric acid.

(iii) for pyrolysis experiments; twelve solutions were prepared containing concentrated sulphuric acid (200 $ml.l^{-1}$) and concentrated nitric acid (100 $ml.l^{-1}$).

Hydroxylamine hydrochloride solution:

20% $^m/v$ in distilled deionised water, purified by a double extraction with dithizone (0.05% $^m/v$ in chloroform).

Concentrated nitric acid.

Concentrated sulphuric acid.

Concentrated hydrochloric acid.

Concentrated hydrofluoric acid.

Concentrated perchloric acid (60 and 72% $^m/v$).

Hydrogen peroxide (100 vols, 30% $^m/v$).

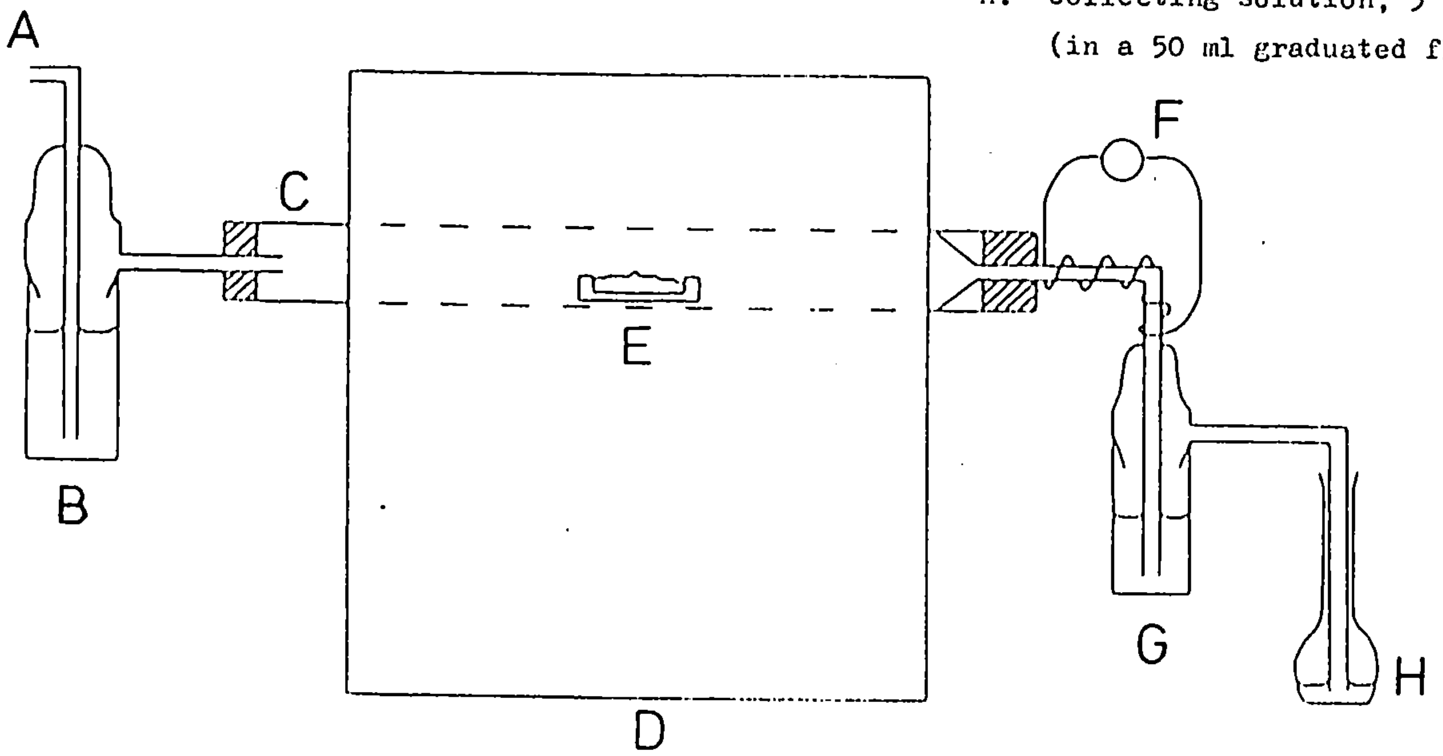
Boric acid solution (saturated solution, 6% $^m/v$).

Potassium perchlorate solution (g. p. r).

Potassium iodide.

Fig. 8 Schematic diagram of coal pyrolysis system

A. Nitrogen inlet, 300 ml.min^{-1}
B. Scrubbing solution, 50 ml.
C. Fused silica tube
D. Furnace
E. Fused silica boat, containing powdered coal
F. Heating tape and power supply
G. Collecting solution, 20 ml
H. Collecting solution, 5 ml
(in a 50 ml graduated flask)



3.2.3 PROCEDURES

3.2.3.1 WET DIGESTIONS

SULPHURIC ACID/NITRIC ACID

Powdered coal (1.0 g) was added to the digestion flask containing concentrated sulphuric acid (7 ml) and concentrated nitric acid (3.5-7 ml). The mixture was refluxed gently for approximately 90 mins. Further small aliquots (0.5 ml) of nitric acid were added over a period of 90 mins (total volume added 3.5 ml). After cooling the solution and residues were transferred, with washings, to a 50 ml graduated flask.

SULPHURIC ACID/HYDROGEN PEROXIDE

Powdered coal (0.2 g) was added to the digestion flask containing concentrated sulphuric acid (10 ml). The mixture was heated to 80°C and maintained at this temperature for 1-2 hours. Hydrogen peroxide was added dropwise until the solution cleared or until a maximum of 5 ml had been added. In an alternative method concentrated nitric acid (5 ml), was added to the sulphuric acid at the beginning of the digestion and the hydrogen peroxide added as before.

After cooling, the solution and residues were transferred with washings to a graduated flask (25 or 50 ml).

NITRIC ACID/POTASSIUM DICHROMATE

Powdered coal (1.0 g) was added to the digestion flask containing potassium dichromate solution (0.5% $^{w}/_{v}$ in concentrated nitric acid, 20 ml). The mixture was refluxed gently for 1½-2½ hours. If potassium perchlorate solution was to be added the mixture was cooled after approximately 90 mins and the reagent added <u>via</u> the second neck of the flask. After heating for a further 90 mins. the mixture was cooled and the solution and residues transferred with washings to a 50 ml graduated flask.

PERCHLORIC ACID

(i) with nitric acid pretreatment.

Powdered coal (0.5 g) was added to the digestion flask containing potassium dichromate solution (0.5% $^m/v$ in concentrated nitric acid, 5 ml). If used, potassium iodide (0.1 g) was added at this point. The mixture was heated gently for 10-15 mins after which perchloric acid (60 or 72% $^m/v$, 25 ml) was added and the mixture refluxed gently for ½ to 1½ hours. When cool the solution and residues were transferred, with washings, to a 50 ml graduated flask.

(ii) without nitric acid pretreatment.

Powdered coal (0.5 g) was added to the digestion flask containing perchloric acid (60 or 72% $^m/v$, 30 ml). If used, potassium iodide (0.1 g) was added and the mixture heated until effervescence began and the reaction became vigorous and self-sustaining. Heating was discontinued until effervescence subsided whereupon the mixture was refluxed until dissolution occurred (section 3.3.1.4, p.79). After cooling, the solution and residues were transferred with washings to a 50 ml graduated flask.

NITRIC ACID/HYDROCHLORIC ACID/HYDROFLUORIC ACID

Powdered coal (0.5 g) was placed in the P.T.F.E. bomb liner, to which concentrated nitric acid (6 ml) and concentrated hydrochloric acid (3 ml) were added. The bomb was then sealed and heated in an oven maintained at 135 ± 10°C for 1½ hours. After cooling in air for

45 mins and in iced water for 30 mins, the bomb was opened, concentrated hydrofluoric acid (5 ml) added and the bomb reheated to 135°C for a further 1½ hours. After cooling as described above excess hydrofluoric acid was destroyed with saturated boric acid solution (6% ^{m}/v, 50 ml). The solution was then transferred with washings to a 100 ml graduated flask.

If incomplete digestion of the coal occurred an aliquot of the solution was filtered through glass wool and analysed in addition to the unfiltered solution.

3.2.3.2 LEACHING

NITRIC ACID/HYDROCHLORIC ACID

Powdered coal (1.0 g) was added to the digestion flask containing concentrated hydrochloric acid (30 ml) and potassium dichromate solution (0.03% ^{m}/v in concentrated nitric acid, 7.5 ml) and refluxed gently for 1 hour. After cooling the mixture was filtered through glass wool into a 50 ml graduated flask and made up to volume with flask and residue washings.

3.2.3.3 DISTILLATION

NITRIC ACID/SULPHURIC ACID

Powdered coal (1.0 g) was placed in the digestion flask containing concentrated nitric acid (30 ml) and concentrated sulphuric acid (60 ml) and heated vigorously without reflux for 1-2 hours. The evolved mercury was collected in potassium permanganate solution (1% ^{m}/v in sulphuric acid, 10 ml, 1 M) in a 25 ml graduated flask.

The air condenser was washed into the flask and excess potassium permanganate solution destroyed using hydroxylamine hydrochloride solution (20% $^{w}/v$, added dropwise until the purple colour was discharged).

3.2.3.4 PYROLYSIS AND COMBUSTION PROCEDURES

PYROLYSIS AND COLLECTION IN POTASSIUM DICHROMATE SOLUTION

Powdered coal (2.0 g) was weighed into a fused silica boat, previously cleaned by heating to 1000°C in a stream of nitrogen. The boat was inserted into a fused silica tube (25 mm i.d., 500 mm long) located in the cavity of the tube furnace. A Dreschel bottle (to act as scrubber) and the collecting vessel (a 25 ml graduated flask) were filled with 50 ml and 20 ml of the appropriate collecting solution. The scrubber was then connected to the front of the pyrolysis train and the collecting vessel to the end (fig. 8). The delivery tube was maintained at 150°C by a heating tape to prevent condensation of water and/or organic vapours on the glassware. The furnace was heated to 800°C (about 40 mins at 20°C min^{-1}) during which time nitrogen (300 ml. min^{-1}) was flushed through the tube to sweep the evolved mercury into the collecting solution. On reaching 800°C the furnace was switched off and allowed to cool to approximately 400°C (about 1 hour). The side arm was rinsed with concentrated nitric acid ($\leqslant$ 5 ml) which was added to the collecting solution. A reagent blank was prepared by pyrolysing an empty boat.

PYROLYSIS FOLLOWED BY COLLECTION IN POTASSIUM PERMANGANATE SOLUTION

Method 1

This procedure was similar to that described above but included the following modifications:

(i) potassium permanganate solution(1% $^{m}/v$ in sulphuric acid, 1M) was used as the scrubbing and collecting solution, 50 ml and 15 ml respectively.

(ii) hydroxylamine hydrochloride solution (20% $^{m}/v$) was added dropwise to the collecting solution to destroy excess potassium permanganate.

If the coal was to be combusted, rather than pyrolysed, the nitrogen purge gas was replaced with air (100-300 ml. min^{-1}).

Method II

This procedure is similar to that described in 'I' above, but uses the more oxidising and acidic collecting solution described in section 3.2.2, page 68. In addition the single collecting vessel was replaced with two vessels in series, containing 20 ml and 5 ml of collecting solution.

DETERMINATION OF MERCURY

The apparatus, operating conditions and procedures used for the determination of mercury are given in Chapter 2 (section 2.3.3.3,(ii), page 44).

3.3 RESULTS AND DISCUSSION

3.3.1 DIGESTION OF COAL USING WET CHEMICAL METHODS

3.3.1.1 NITRIC AND SULPHURIC ACIDS

First attempts involved carefully heating the mixture on a water bath to initiate the reaction followed by more vigorous heating with a flame. When this proved unsuccessful subsequent mixtures were heated immediately with a Bunsen burner. The initial reaction proceeded smoothly and, after further small additions (0.5 ml, total volume added 3.5 ml) of nitric acid had been added during digestion, solutions of coal were eventually obtained. These solutions contained precipitated silica and were coloured bright yellow due to the presence of Fe^{3+}. Unfortunately dissolution times were frequently in excess of three hours and digestion was often incomplete. Attempts to minimise these effects were made by including more nitric acid in the initial mixture to make the conditions more oxidising. No significant reduction in dissolution time was observed, even for mixtures in which the initial ratio of acids had been reversed. As the amount of nitric acid was increased excessive frothing occurred and the mixture was blown into the condenser, which then became difficult to wash prior to collecting the coal solution quantitatively. Moreover, because of the strenuous reflux conditions used the nitric acid could not be distilled off (as in BS 1016) without loss of mercury also. Consequently the solutions obtained from mixtures containing large amounts of nitric acid were often deep brown coloured and it was difficult to tell when and if digestion was complete. The concentrations of nitric and sulphuric acids in the final digests were approximately 1-3 M. After subtraction of the appropriate reagent blank the results obtained indicated that signal size and precision were not significantly affected by the concentration of either nitric or sulphuric acid.

The results overall, however, were not encouraging. Recoveries of mercury from SRM 1632a were invariably low (typically 30-50%), dissolution times were lengthy and problems of incomplete digestion were encountered.

3.3.1.2 SULPHURIC ACID AND HYDROGEN PEROXIDE

Using the recommended temperature of 80°C this method invariably produced incomplete digestion of the coal. Modifying the reaction conditions by: increasing the amount of acid and/or hydrogen peroxide; adding the coal as two 0.1 g portions; heating for prolonged periods (up to 3 hrs); using prolonged heating with elevated temperatures (150°C), failed to achieve complete digestion of the coal.

Both filtered and unfiltered solutions were analysed with recoveries of mercury from SRM 1632a typically 20-40%. The initial reaction conditions were modified to include nitric acid (5 ml conc.) and the hydrogen peroxide was then added as before. Similar results were obtained and the method was deemed unsatisfactory.

3.3.1.3 NITRIC ACID AND POTASSIUM DICHROMATE

Using this method the coal samples underwent very subdued, reluctant reaction and no significant dissolution occurred. In one experiment the mixture was cooled and potassium perchlorate solution (15 ml) was added as an auxilliary oxidising agent. Although the reaction initiated on subsequent heating was noticeably more vigorous, digestion of the coal was still incomplete as evidenced by the large amount of coal remaining unreacted in the flask.

3.3.1.4 PERCHLORIC ACID

It was felt that the potential explosive hazards associated with the use of perchloric acid could be overcome by pretreatment of the coal with concentrated nitric acid, in order to oxidise the more reactive organic components. Perchloric acid of two different strengths (60 and 72% $^{m}/v$) was used and in each case incomplete dissolution of the coal occurred when nitric acid was included in the digestion procedure. The same result was obtained when 60% perchloric acid was used without nitric acid. However, when 72% perchloric acid was used without nitric acid pretreatment, rapid and complete dissolution of the coal was observed. Using the stated quantities the mixture was heated gently with a Bunsen burner until the reaction became vigorous and self-sustaining (10-15 mins). Heating was reapplied after effervescence had subsided and complete dissolution was achieved after a total reaction time of about 30 mins.

Recoveries of mercury from SRM 1632a, however, were low, in the range 20-50%, but were greatest for samples in which the coal had been fully digested. For these latter samples the losses were presumed to be due to volatilisation of the mercury at the elevated temperatures required to reflux concentrated perchloric acid (approximately 210°C). Experiments in which lower temperatures were used failed to digest the coal whilst others, in which excess potassium iodide was added to the mixture in order to prevent losses of mercury through formation of the relatively involatile $[HgI_4]^{2-}$ complex ion, were also unsuccessful.

3.3.2 LEACHING OF MERCURY USING NITRIC ACID AND HYDROCHLORIC ACID

Mercury is thought to exist in coal predominantly as the sulphide, which is appreciably soluble in aqua regia (hydrochloric acid/nitric acid, 4:1). Thus attempts were made to leach the mercury from the coal matrix without completely dissolving the coal.

The mixture described was heated gently (80-100°C) for approximately 30 mins. Potassium dichromate was included in the nitric acid (0.03% $^{m}/v$) for two reasons, firstly to retain the evolved mercury (as with the standard solutions), and secondly to oxidise any organic materials which may have interfered in the atomic fluorescence detection of mercury. Both filtered and unfiltered solutions were analysed but low recoveries of mercury were obtained (less than 20%) even when prolonged heating (up to 90 mins) and/or elevated temperatures (up to 150°C) were used.

These reagents were then used in experiments with a PTFE lined digestion bomb. The method employed was typical of those using such bombs in that carbonaceous material was destroyed using hydrochloric acid/fuming nitric acid and siliceous material using hydrofluoric acid, the use of which introduced the following drawbacks: strenuous safety precautions, sometimes very time consuming, were required due to the extremely corrosive nature of hydrofluoric acid; saturated boric acid solution was required to neutralize excess hydrofluoric acid, thereby further diluting the sample solution and possibly increasing reagent contamination; special high density PTFE bomb liners were required to minimise acid migration which might otherwise have resulted in mercury losses or damage to the bomb; polypropylene or PTFE volumetric vessels were required.

The results obtained with the bomb were not encouraging. Sample throughput times were typically four to five hours and the method seemed limited by the need to use small samples (0.5 g) or less, producing sample concentrations of 1% $^{w}/v$ or less. Even after prolonged cooling copious volumes of oxides of nitrogen were released upon opening the bomb. Frothing and leakage of the contents also occurred, leading to losses of mercury.

Clearly these approaches to sample digestion were unsatisfactory and there seemed no simple way to overcome these shortcomings. Thus it was decided to try to exploit, rather than combat, the volatility of mercury, and to distil the mercury from the coal followed by collection in a suitable collecting medium.

3.3.3 DISTILLATION OF MERCURY

This method was found to be unsuitable since gaseous decomposition products, evolved during the reaction, were carried over with the mercury. The potassium permanganate was reduced to manganese dioxide which tended to plate out on the glassware, thereby decreasing the ability of the solution to absorb mercury and causing low recoveries.

Because of the potential safety hazards involved in using perchloric acid without reflux (when dehydration and fuming may occur), distillation using this acid was not attempted. Other acid mixtures were not used in distillation experiments since the problems of incomplete digestion encountered previously were expected to prevent release of mercury from the coal.

It was decided therefore to investigate non-oxidative pyrolysis and oxidative combustion as methods of releasing mercury from coal.

3.3.4 NON-OXIDATIVE PYROLYSIS

Replicate samples of a base coal were pyrolysed at 800°C in a stream of nitrogen (scrubbed by passing through a small volume of collecting solution) and the evolved mercury collected in each of a series of solutions containing potassium dichromate in nitric acid. The acid strengths were 1.6, 5.0 and 16 M. Each acid solution was used to make four solutions containing 0.03, 0.3, 3.0 and 5.0% $^{m}/v$ potassium dichromate. In some cases (strong acid and/or high potassium dichromate concentrations) it was difficult to dissolve the potassium dichromate without prolonged immersion in an ultrasonic bath. The results were compared (Table 6) to determine which solution was most efficient for collection of the mercury. A reagent blank has been subtracted in each case.

The results are generally inconclusive though high acid concentrations appear to be favoured. Four samples of SRM 1632a were pyrolysed and the evolved mercury absorbed in the four strong acid solutions of potassium dichromate. The apparent recoveries obtained for the 0.03, 0.3, 3.0 and 5.0% $^{m}/v$ solutions were ca 200, 180, 300 and 280% respectively. The reasons for these high recoveries were not immediately apparent though several possible causes were identified, which were:

(i) the pyrolysis boats contained varying amounts of mercury;

(ii) mercury contamination of the nitric acid and/or potassium

Table 6. Fluorescence signal as a function of nitric acid and potassium dichromate concentrations

Potassium dichromate concentration, % m/v	acid molarity 1.6	acid molarity 5.0	acid molarity 16
	Fluorescence signal/arbitrary units		
0.03	2051	1417	4554
0.30	1774	2659	4260
3.0	5503	3113	5767
5.0	3457	2826	5691

dichromate;

(iii) the highly acidic potassium dichromate solutions were leaching mercury from the glassware used;

(iv) mercury in the purge gas was not effectively removed by the scrubber;

(v) organic pyrolysis products not oxidised by the potassium dichromate solution were undergoing broad band molecular fluorescence at and around the analytical line.

In order to eliminate each of these effects the following steps were taken:

(i) the pyrolysis boats were heated to 1000°C in a muffle furnace supplied with a small flow of nitrogen, (the boats were then stored in concentrated nitric acid in a closed container);

(ii) the potassium dichromate was heated to 420°C (melting point 398°C) under a stream of nitrogen in a muffle furnace and stirred to remove any mercury (the cleaned potassium dichromate and nitric acid solutions were analysed for mercury content which was found to be less than 0.5 $ng.ml^{-1}$ for both solutions).

(iii) the glassware used was cleaned and stored in concentrated nitric acid in a closed container;

(iv) a solution of potassium permanganate in dilute sulphuric acid was used to scrub the purge gas;

(v) the fluorescence spectrum was scanned in the region 240-265 nm while pumping first standard solution and secondly sample solution. No significant differences in the line profiles were observed indicating the absence of broad band molecular fluorescence.

After taking all the above precautions recoveries of mercury from SRM 1632a were still high, typically 120-200%. In view of the failure to identify the reasons for these high recoveries the potassium dichromate solution was rejected. The basic pyrolysis procedure was retained but potassium permanganate solution (1% $^{m}/v$ in sulphuric acid, 1 M) was used as the purge gas scrubber and mercury collecting solution. The problems encountered in distillation experiments using this solution were again apparent. Organic pyrolysis products reduced the potassium permanganate to manganese dioxide which plated out on the glassware thereby decreasing the ability of the solution to absorb mercury, causing low recoveries. Some experiments were performed in which the coal was combusted by using air as the purge gas. There was evidence of over rapid combustion causing sputtering of coal from the silica boat and sudden discharges of gaseous products through the collecting solution. These effects combined to yield low recoveries of mercury. In an attempt to control the rate of combustion the purge gas flow rate was reduced from 300 to 100 ml.min^{-1}. The heating rate, which was slow anyway, was maintained at 20°C min^{-1}. No significant increase in recovery of mercury was observed.

The problem of low recoveries was partially overcome by returning to nitrogen as the purge gas, increasing the concentration of potassium permanganate (from 1% to 5% $^{m}/v$) and adding concentrated nitric acid to the collecting solution making it both more oxidising and more acidic. Using this method recoveries of mercury were approximately 94% of the certified figure. When the collecting solution was placed in 2 bubblers in series, containing 20 ml and 5 ml respectively, quantitative recoveries of mercury were obtained. The method was also applied to the determination of mercury in other coal and ash samples having independently determined mercury levels. The results for SRM 1632a and the other samples are given in Table 7.

3.4 CONCLUSION

The determination of mercury in coal has posed several fundamental analytical problems in terms of the intractability of the matrix, the volatility of mercury and the low levels typically present in coal. While instrumental techniques, in which prior destruction of the matrix was avoided, have been reported, the consensus of opinion has favoured isolation and collection of the mercury prior to analysis. In the work described the efficiency of a number of wet chemical digestion mixtures has been evaluated and compared with the performance of systems in which thermal release of the mercury was followed by collection in a suitable absorbing medium.

In general the results obtained for the various acid mixtures used are disappointing. Except when using concentrated perchloric acid complete, reproducible dissolution of the coal is not readily achieved. When dissolution does occur the reaction times are usually in excess of three hours (30 min. for perchloric acid) and elevated temperatures (200°C) necessary. Low mercury recoveries are invariably obtained, indicating that mercury is lost during digestion, presumably through volatilisation. Possibly this is because some of the mercury is present as the sulphide which readily oxidises and decomposes to elemental mercury and even strenuous reflux appears unable to retain the mercury formed in such hot, oxidising conditions. The addition of potassium dichromate to ensure the presence of Hg^{2+} in solution (and to assist oxidation of the matrix) fails to prevent

TABLE 7

Results of Mercury Determinations on Various Coal and Ash Samples

Coal	Mercury found/ ng g^{-1}	Independent Analysis	
		Mercury quoted/ ng g^{-1}	Method
NBS SRM 1632a	134.1[a]	130 ± 30[b]	AAS and NAA
NCB A	140	<400	NAA
NCB B	175	<500	NAA
Coal Ash	**Mercury found/ µg g^{-1}**	**Mercury quoted/ µg g^{-1}**	**Method**
BCRA Ash	202	195	CVAFS

a. Mean of nine replicate coal samples with each of these solutions analysed nine times. Standard deviation 3.1 ng g^{-1}, relative standard deviation 2.7%.

b. Certificate value.

AAS = Atomic absorption spectrometry

NAA = Neutron activation analysis

CVAFS = Cold vapour atomic fluorescence spectrometry volatilisation losses. Similarly adding excess potassium iodide fails to retain mercury as the $[HgI_4]^{2-}$ complex ion.

Had one or more of the dissolution methods proved satisfactory, typical coal sample solution concentrations were likely to have been in the range 0.5-2% $^m/v$ (0.6-2.6 $ng.ml^{-1}$ mercury). The determination of such low levels of mercury is, however, well within the scope of the detection system described (typically 10% R.S.D. at 0.4 $ng.ml^{-1}$).

Since none of the experiments involving direct dissolution and leaching of the coal satisfies the requirements for a suitable method an alternative approach is required and one in which the volatility of mercury can successfully be exploited appears attractive.

The problems of the reactivity of the sample decomposition products experienced in distillation experiments are aggravated in attempts to pyrolyse coal, since pyrolysis produces more smoke, volatile organic vapours and sulphur dioxide than does distillation of mercury from solution. The low recoveries of mercury observed when coal is combusted may be due to adsorption of mercury on carbonaceous matter deposited on the walls of the tube following over-rapid burning of the sample. Although the success of subsequent pyrolysis experiments is due primarily to the modifications made to the collecting solution, the use of two collecting vessels in series and a heating tape to prevent condensation in the side arm both assisted in ensuring quantitative collection of the mercury. Depletion of the available potassium permanganate is allevaited by increasing the concentration 5-fold, while adding nitric acid to the solution assists in oxidising some components of the smoke which may otherwise react with the potassium permanganate. The collecting solution described gives quantitative recoveries of mercury for the only coal available having a certified mercury value. Good agreement with the independent analysis of other coals was also obtained and the solution is expected to be sufficiently oxidising for a range of coal types, e.g. sub-bituminous and brown coals.

The use of the argon-sheathed atom cell and cold-vapour atomic fluorescence spectrometry, together with the reproducible pyrolysis conditions and the continuous flow system, provides more than adequate precision for coal analysis (2.7% relative); this is especially so when the inherent sampling problems of coal are considered. The large linear working-range for mercury in coal (5 ng g^{-1} to 25 μg g^{-1}), with a detection limit of 1.13 ng g^{-1} using a 2 g sample, could be even further improved by varying the sample size taken or the amount of collecting solution.

Analysis time is presently 2 to 3 minutes per solution, but the time consuming step involves the slow heating and cooling rates of the furnace available. A smaller, more versatile furnace with more rapid heating and cooling rates should markedly reduce the overall analysis time of approximately 1½ hours per sample. This would make the method even more suited to the routine determination of mercury in coal and fly ash, with its probable extension to coal tar and related materials.

Chapter 4. DETERMINATION OF ARSENIC AND SELENIUM BY ATOMIC ABSORPTION AND ATOMIC FLUORESCENCE SPECTROMETRY USING CONTINUOUS HYDRIDE GENERATION

4.1 INTRODUCTION

As with mercury the last 15 years has witnessed a much-increased interest in the determination of low levels of arsenic and selenium in a variety of samples. Traditionally, routine determinations of arsenic have been performed using variations of the method first reported by Gutzeit (121) in 1879. In this method arsenic was determined by volatilizing the element as arsine (AsH_3) and comparing the colouration formed upon discs of dry paper impregnated with mercury (II) chloride with that obtained using known amounts of arsenic. The method lacks precision and it is doubtful whether the accuracy exceeds 10% of the true value. On the whole, spectrophotometric procedures based on molybdenum blue (100) or silver diethylthiocarbamate (122) have proved superior. Both possess good sensitivity and precision, but exhibit poor selectivity and are prone to interferences. Selenium has been determined spectrophotometrically by fluorimetric methods using 3,3'-diaminobenzene (123) and 2,3 diaminonapthalene (DAN) (124, 125). The use of DAN, however, has certain disadvantages including the need to purify the reagent and to perform the analysis promptly due to the unstable nature of the piazselenol complex. Furthermore, DAN is chemically related to highly carcinogenic compounds. Selenium continues to be determined colourimetrically using dithizone (126).

Because of the limitations mentioned these methods have largely been superseded, partly by instrumental techniques (e.g. spark-source mass spectrometry (2), X-ray fluorescence (94) and neutron activation analysis (127) - see section 5.1), but more frequently by atomic spectroscopic methods (see below), which generally offer greater freedom from interferences and improved sensitivity.

4.2 DETERMINATION OF ARSENIC AND SELENIUM USING ATOMIC SPECTROSCOPIC TECHNIQUES.

Of the atomic spectroscopic techniques available hydride generation/atomic absorption is the most widely used. In this method the sample is mixed with a suitable reductant after which the gaseous covalent hydride is purged from solution by a stream of gas and delivered to the atom cell. The advantages of this method include quantitative transfer of the analyte to the atom cell and separation of the analyte from the matrix which reduces chemical interferences.

Godden and Thomerson (128) have reviewed the wide variety of approaches reported for the determination of several metalloid elements by hydride generation/atomic spectrometry. Conflicting opinions (129, 130) exist regarding the selectivity and efficiency of the various reductants used. Many authors (129, 131, 132) have preferred sodium tetrahydroborate (III) solution. Others have used mixtures of titanium (III) chloride/magnesium powder (133) and potassium iodide/zinc powder/tin(II) chloride (130, 134, 135).
Advantages claimed for sodium tetrahydroborate (III) are speed of hydride evolution, simplicity, higher conversion efficiency, lower blank levels and the co-evolution of hydrogen which helps to purge the hydrides. Interferences from reducing mixtures containing tin (II) ions have been reported (136). Collection devices, particularly

balloons (129, 137), for storing the hydrides prior to transfer to the atom cell proved advantageous when the analytical signal was measured by peak height methods and slower reductants, e.g. zinc, were used. Most recent systems (25, 138) have excluded collecting devices by sweeping the hydrides directly to the atom cell. Methods involving injections of discrete samples were initially reported but, while sample may be conserved in this way, such systems prove tedious when large numbers of samples are to be analysed. Several workers have reported automated systems for the generation of arsine and hydrogen selenide in which the reductant and sample were pumped to a reduction cell (27, 28, 29, 139, 140, 141) prior to atomic absorption spectrometry. The merits claimed for these systems are speed in analysis, improved precision and greater freedom from interferences (29) compared to manual injection.

Flames and tubes (either flame (19, 138) or electrically heated (25, 142, 143)) have been used to generate free atoms from the gaseous hydrides. The high absorbance of the air/acetylene flame (144) at the arsenic and selenium resonance lines (193.7 and 196.0 nm respectively) results in poor signal to noise. In contrast the argon or nitrogen/hydrogen/entrained air diffusion flames are markedly more transparent at these wavelengths and have found many applications (129, 130, 145). The problems of compound formation interferences sometimes encountered using these cool flames are largely overcome when gaseous samples of covalent hydrides are introduced directly into the flame. Many authors have reported using heated quartz tubes as the atom cell, which improved sensitivity by eliminating flame absorption and increasing residence times. Graphite tube atomisers have also been used (29) though interference effects are apparently more pronounced.

When increased sensitivity is required this may be achieved using hydride generation followed by atomic fluorescence spectrometry. Both dispersive (146) and non-dispersive (147, 148) systems have been used to determine arsenic and selenium and impressive detection limits are quoted. The use of a miniaturised argon/hydrogen flame has also been described (149).

Atomic emission spectrometry using the inductively coupled plasma has also been used to determine arsenic (150) and selenium (151). The analytes are introduced as the hydrides and advantages analogous to those obtained when using atomic absorption spectrometry are gained. Of the alternative atomic spectroscopic techniques available for the determination of arsenic and selenium electrothermal atomic absorption spectrometry is currently the most widely used. The popularity of this technique for these elements stems from the fact that the use of flames is avoided and the problems of low signal to background at the analytical lines of interest are reduced. However, scattering of source radiation by particulate matter in the furnace tube is more severe at these short wavelengths and for many matrices high and variable matrix absorption is unavoidable. Consequently background correction is highly desirable. Methods in which the sample is injected into the furnace manually can prove tedious and part- or fully-automated systems, which generally offer improved precision are more widely reported. Nevertheless the methods can be time-consuming (5-10 minutes for 5 replicates per solution) especially when prior addition of matrix modification agents is necessary to prevent losses of volatile elements such as arsenic and selenium.

In addition, sample preparation and control of experimental conditions requires careful attention if reproducible results are to be obtained. Despite these apparent limitations the inherently good sensitivity of the technique has been exploited to good effect by workers (152, 153, 154) determining arsenic and selenium in a variety of matrices.

Our requirement was for a simple yet sensitive hydride generation system suitable for routine analytical determinations. The continuous flow system (section 2.3.1, page 35), was retained was the basis of the method and the hydride generation system developed by Thompson et al (155) was modified for our purposes. Sodium tetrahydroborate (III) solution was chosen as the reductant for the reasons outlined above. Since flames represent a well understood and simple to operate class of atom cell, a small argon/hydrogen/entrained air flame was adopted as being favourable for atomic fluorescence but also applicable to atomic absorption. Argon was chosen as the support gas because of its low fluorescence quenching characteristics.

4.3 EXPERIMENTAL

4.3.1 EQUIPMENT

The apparatus used for the determination of mercury was modified by adding a 28-turn auto-analyser mixing coil (2.5 mm i.d.) between the peristaltic pumps and the reduction cell. The two solution streams entered the coil via a "Y" shaped adaptor and this premixing of the reductant and analyte solutions resulted in partial generation of the hydride prior to entry into the reduction cell. The intimate mixture of spent solution plus hydride was released into the top of the reduction cell, which now functioned largely as a gas/liquid separator, while a stream of argon, introduced via a capillary, was directed into the incoming mixture. This arrangement promoted efficient stripping of the hydride from the spent solution which was taken to waste through the constant-head drainage tube. The hydride was then swept by the flow of argon to the base of the burner, where it was mixed with a small flow of hydrogen prior to decomposition in the flame (Fig. 9).

The burner consisted of a borosilicate glass tube (8.5 mm i.d., 100 mm high) with inverted "Y" side-arms (5 mm i.d., 35 mm long) to act as gas inlets. This was located vertically in the spectrometer, replacing the burner/nebuliser assembly, and at the focal length of the entrance slit lens.

Arsenic and selenium hollow cathode lamps were used as spectral sources for atomic absorption measurements. The light beams were focussed on the atom-cell through a zoom lens located between the source and the burner. Atomic absorption measurements were then made in the volume 0 - 10 mm above the burner using the spectrometer optical system. Arsenic and selenium electrodeless discharge lamps were used as line sources for atomic fluorescence measurements. These were arranged so that the volume 0 - 25 mm above the burner was irradiated, the fluorescence radiation passing through the entrance slit to the monochromator. Atomic fluorescence was excited using front-face illumination with a source/atom-cell/slit angle of 45°.

Atomic absorption and atomic fluorescence were measured at 193.7 and 196.0 nm for arsenic and selenium respectively. For atomic fluorescence the spectrometer was operated in the "emission" mode and a spectral bandpass of 2.0 nm was used in all work. The steady-state signals obtained were sampled using the spectrometer integrator. Instrumentation and operating conditions were given in Table 8.

4.3.2 REAGENTS

Unless otherwise stated the reagents used were of analytical grade.

Sodium tetrahydroborate (III) solution.

Prepared by dissolving sodium tetrahydroborate (III) (Fisons Scientific Apparatus, Loughborough, Leicester, 1 g G. P. R.) in sodium hydroxide solution (100 ml, 0.1 M). Solutions prepared this way remained usable for 2 - 3 days.

Arsenic and selenium standard solutions.

Arsenic and selenium standard solutions were prepared by serial dilution of stock solutions of 1000 $\mu g.ml^{-1}$ (Hopkin and Williams, Chadwell, Heath, Essex). Working standards, typically in the range 1 - 100 $ng.ml^{-1}$ were prepared using the diluents described below.

Hydrochloric acid diluent solutions.

Arsenic solution diluent was prepared by dissolving sodium iodide (10 g) in hydrochloric acid (1 litre, 5 M). Selenium solution diluent was prepared by dissolving sodium bromide (10 g) in hydrochloric acid (1 litre, 5 M).

Fig. 9 Continuous flow system for the generation of gaseous hydrides

A. Peristaltic pump, 2.5 $ml.min^{-1}$ sodium tetrahydroborate (III) solution

B. Peristaltic pump, 7.0 $ml.min^{-1}$ sample or standard solution

C. 28 turn mixing coil (2.5 mm i.d.)

D. Gas/liquid separator

E. Drain, to waste

F. Argon carrier gas inlet, 120 ± 10 $ml.min^{-1}$

G. Hydrogen inlet, 180 ± 10 $ml.min^{-1}$

H. Borosilicate glass tube burner

I. Argon/hydrogen/entrained air flame atom cell

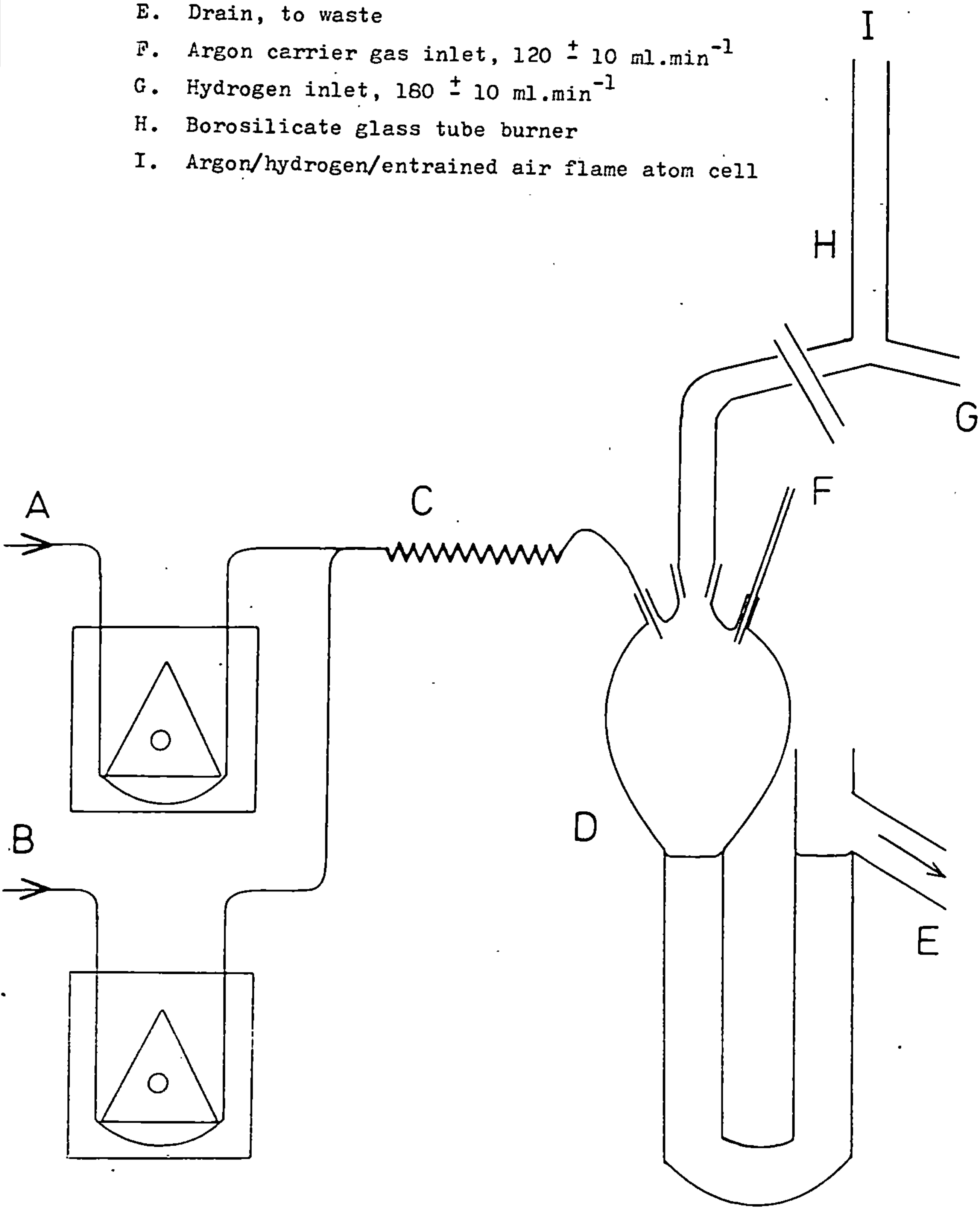


Table 8

INSTRUMENTATION AND OPTIMUM OPERATING CONDITIONS

Component	Model	Supplier	Operating Conditions
Excitation Sources; Atomic absorption	Arsenic and Selenium Hollow Cathode Lamps	S.J. Juniper & Co Harlow, Essex	As 4 mA; Se 4 mA
Atomic fluorescence	Electrodeless discharge lamps		As 37W; Se 64W
Microwave Cavity	Broida ¼ wave cavity, 210L, powered by a Microtron 200 Mark III microwave generator	Electromedical Supplies Wantage Oxon	
Peristaltic Pumps	Schuco Minipumps Mark III and Mark IV	Schuco Scientific Halliwick Court Place, Woodhouse Road, London.	Mark III, (reductant) 2.5 mℓ min^{-1} Mark IV (standard) 7.0 mℓ min^{-1}
Spectrometer	IL 151	Instrumentation Laboratories Lexington, M.A., USA	

Spectrometer operating conditions

Function	aas		afs	
	As	Se	As	Se
Mode	Atomic absorption		Atomic emission	
Photomultiplier voltage	800	800	900	800
gain	x2	x2	x2	x5
wavelength/nm	193.7	196.0	193.7	196.0
band pass/nm	2.0		2.0	
integration period/s	4 x 4		4 x 4	

4.3.3 PROCEDURES

4.3.3.1 PRESERVATION OF STANDARDS

The arsenic (III) and selenium (IV) calibration standards were stabilised by dilution with the hydrochloric acid solutions of sodium iodide and sodium bromide respectively. When the solutions were stored in borosilicate glassware these diluents prevented losses of arsenic and selenium for several days at 100 $ng.ml^{-1}$ and lower and several weeks at 500 $ng.ml^{-1}$ and higher.

4.3.3.2 DETERMINATION OF ARSENIC AND SELENIUM

Zero the instrument when pumping sodium tetrahydroborate (III) solution and hydrochloric acid solutions into the gas/liquid separator. Replace the acid diluent with the sample or standard solution. Using the spectrometer integrator measure the atomic absorption or atomic fluorescence, of either arsenic or selenium at the appropriate wavelength, once a steady state signal has been obtained (approximately 45 seconds later).

4.4 RESULTS AND DISCUSSION

4.4.1 OPTIMISATION OF THE SYSTEM

4.4.1.1 GAS FLOW RATES

The optimum gas flow rates were identified by a simple factorial process. Hydrogen and argon flow rates were examined in the range 0.05 to 1.2 $l.min^{-1}$. The process was repeated at several different burner heights, for both arsenic and selenium using atomic absorption and atomic fluorescence spectrometry. Typical results are shown in

Fig. 10. The optimum flows were those causing least dilution of the hydrides. When using very low flows of hydrogen, 0.1 $l.min^{-1}$ and less, pulsing from the peristaltic pumps caused the very small flame to fluctuate. Low flows of argon, 0.1 $l.min^{-1}$ and less, purged the hydrides only slowly from the gas/liquid separator. Both effects caused poor precision. The gas flows producing the greatest signals with acceptable precision were 120 ± 10 and 180 ± 10 $ml.min^{-1}$ of argon and hydrogen respectively.

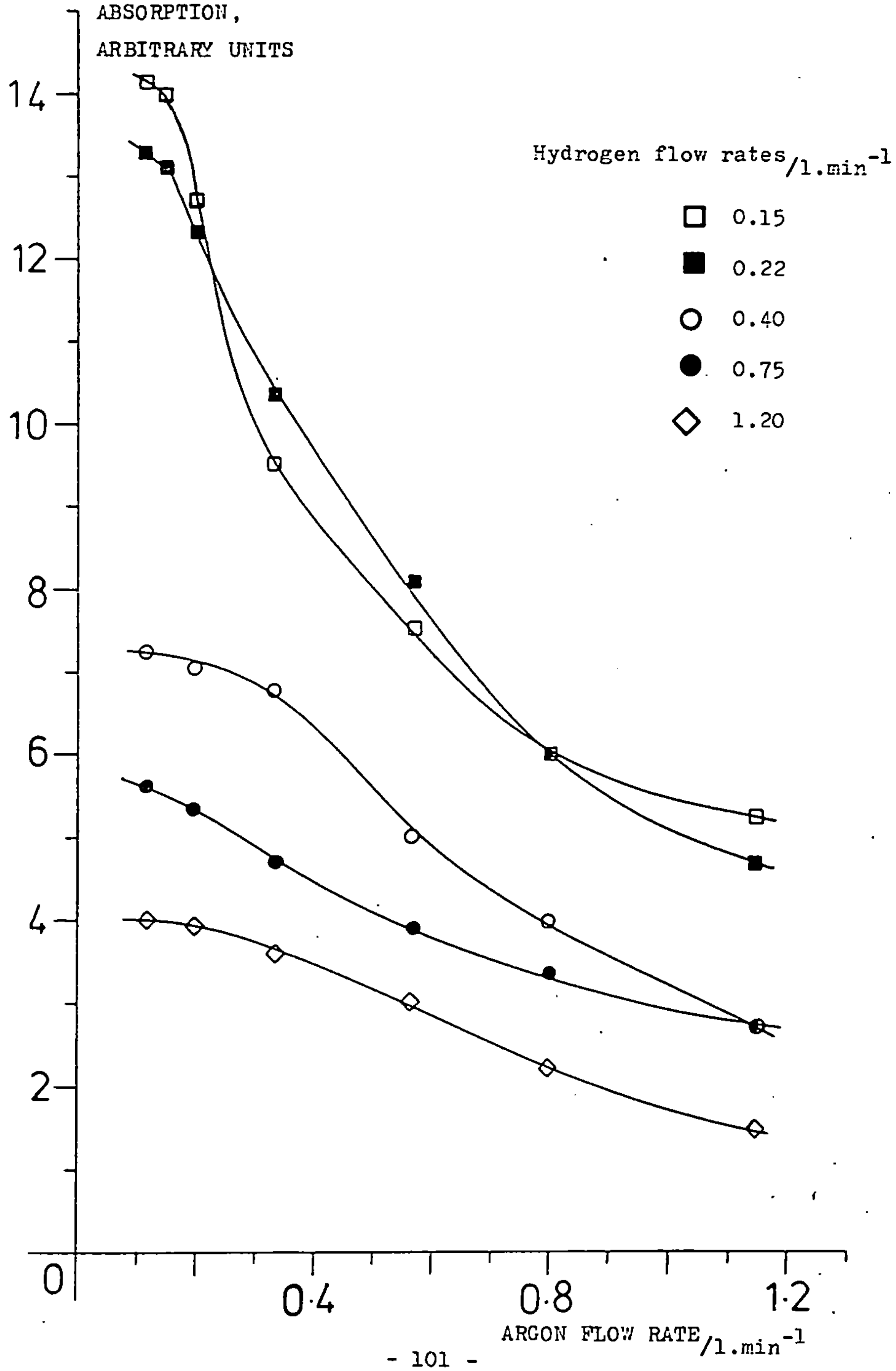
4.4.1.2 CONTINUOUS FLOW SYSTEM

Signal size was relatively insensitive to variations in sodium tetrahydroborate (III) solution concentration and flow-rate. The signal increased linearly with the flow-rate of sample up to a maximum of 30 $ml.min^{-1}$ above which it became difficult to drain the cell sufficiently rapidly. Flow-rates of 2.5 $ml.min^{-1}$ of sodium tetrahydroborate (III) solution and 7.0 $ml.min^{-1}$ of sample solution were chosen to minimise reagent and sample consumption, consistent with acceptable signal size.

4.4.1.3 SODIUM TETRAHYDROBORATE (III) AND HYDROCHLORIC ACID SOLUTION CONCENTRATIONS

Different concentrations of sodium tetrahydroborate (III) and hydrochloric acid solutions were investigated in the range 0.5 to 4% $^{w}/v$ and 1 M to 7 M respectively. For arsenic little variation in signal size with pH was observed though for selenium an optimum hydrochloric acid concentration of 5 - 6 M acid was clearly identified. The reagent concentrations chosen were designed to minimise over vigorous reaction while ensuring rapid and efficient generation

Fig. 10 Optimisation of argon and hydrogen flow rates for the determination of arsenic by atomic absorption spectrometry



of the hydrides. Since arsine is produced equally readily from As (III) and As (V) in strongly acidic solution ($pH < 4$) and selenium sensitivity is enhanced in strong acid, 5 M was chosen as the preferred hydrochloric acid concentration, for which the optimum sodium tetrahydroborate (III) solution was 1% $^{w}/v$. Aqueous solutions of sodium tetrahydroborate (III) were stable for only a few hours but this problem was readily overcome by preparing solutions in dilute sodium hydroxide solution (0.1 M).

4.4.1.4 BURNER DESIGN

The very short path-length, 8.5 mm, though suitable for atomic fluorescence spectrometry, could be considered less favourable for atomic absorption spectrometry than a long path-length burner. As all the sample reaches the atom cell the consideration should, however, be of residence time and efficiency of irradiation. This design, the simplest possible construction, has been found to give very satisfactory performance. In further experiments the evolved hydrides were swept into the expansion chambers of conventional air/acetylene and nitrous oxide/acetylene burners. After a similar optimisation of the gas flows the longer path lengths did produce somewhat larger absorption signals. Signal to noise, however, was much reduced, more so for the air/acetylene burner than for the nitrous oxide/acetylene burner and this work was not continued.

The optimum optical arrangement for absorption was obtained by placing the burner at the focal length of the entrance slit lens with the top of the burner blocking the lower half of the light beam from the hollow cathode lamp. The width of the light beam, at the burner, was then set equal to the diameter of the burner using the spectrometer zoom lens. This corresponded closely to the optical focus.

4.4.1.5 OPTIMISATION OF ATOMIC FLUORESCENCE SIGNALS

The volume 0 - 25 mm above the burner was irradiated, again using illumination at 45° in preference to the conventional 90° illumination. In this arrangement the burner was located at the focal length of the entrance slit lens (instead of adjacent to it) and advantages similar to those gained in the determination of mercury were observed, i.e. much lower levels of background radiation and specular reflection reaching the monochromator, enabling greater signal amplification with a minimal increase in noise and also more efficient collection of the atomic fluorescence.

When the power to the electrodeless discharge lamps was varied the graphs obtained of integrated fluorescence signal against forward microwave power were linear from 18 W (lowest available setting) up to 55 W and 67 W for arsenic and selenium respectively. The selenium signal was stable at high power, though above approximately 40 W the arsenic signal became very noisy. The power settings yielding consistently acceptable signal to noise ratios were approximately 37 W and 64 W for arsenic and selenium respectively.

4.4.1.6 DETECTION LIMITS AND LINEAR WORKING RANGES

The following flow rates ($ml.min^{-1}$) were used to determine arsenic and selenium using hydride generation/atomic absorption and atomic fluorescence spectrometry:

hydrogen	180 ± 10
argon	120 ± 10
sodium tetrahydroborate (III)	2.5
sample or standard	7.0

Using these conditions the detection limits and linear working ranges shown in Table 9 were obtained. A relative standard deviation of 10% was taken as the lower limit of the useful working range of the methods and the corresponding concentrations are also shown in Table 9.

4.5 CONCLUSION

Because of its greater sensitivity, relative to conventional atomic absorption methods, hydride generation/atomic absorption has become the method of choice for the determination of hydride forming elements. The success of the technique is due to a number of factors all of which contribute to the sensitivity available.

When a suitable reductant is used and efficient stripping of the evolved hydrides achieved, quantitative transfer of the analyte, from solution to the atom cell is possible. The analyte, now in the form of a simple gaseous compound, is readily decomposed, allowing the hydride to be introduced directly into the flame. Thus undue dilution of the analyte through inefficient nebulisation processes is avoided and enhanced sensitivity results. When using air/acetylene flames traditional atomic absorption methods for the determination of arsenic and selenium suffer from poor sensitivity due to absorption by the flame at the wavelengths of interest. Since the

TABLE 9

DETECTION LIMITS AND WORKING RANGES FOR THE DETERMINATION OF ARSENIC AND SELENIUM

	Limits/ng mℓ$^{-1}$ Arsenic	Limits/ng mℓ$^{-1}$ Selenium
Atomic absorption spectrometry		
Limit of detection (2σ)	0.8	0.5
Linear calibration range	2.5 - 150	1.5 - 100
Lower limit of working range*	5.0	2.5
Atomic fluorescence spectrometry		
Limit of detection (2σ)	0.34	0.13
Linear calibration range	1.0 - 50	1.0 - 50
Lower limit of working range*	2.0	1.0

* The lower limit of the working range is taken to be the level at which the relative standard deviation has risen to 10%

hydride is easily decomposed once separated from the matrix, the air/acetylene flame can be avoided in favour of a cooler, less luminous flame. Thus, hydrogen-based diffusion flames have been extensively used as atom cells in hydride generation/atomic absorption methods, mainly due to the low background and absorption characteristics in the spectral region immediately above 190 nm.

By choosing an atom cell with suitable geometry this type of flame is well suited for use with atomic fluorescence spectrometry. Argon is usually preferred to nitrogen as the support gas because of its lower cross-section for quenching of atomic fluorescence. The relatively low temperature also results in reduced quenching and reduced thermal expansion with minimal dilution of the analyte atoms in the atom cell.

In the work described each of the parameters expected to exert the greatest effect on sensitivity and precision has been investigated. The sodium tetrahydroborate (III) solution is shown to be a rapid and efficient reducing agent for the generation of arsenic and selenium hydrides. Premixing of the solution streams prior to their entry into the gas/liquid separator promotes efficient reduction. The geometry of the burner and the optimum gas flow rates combine to generate a miniature flame which is suitable for both atomic absorption and atomic fluorescence measurements. The excellent sensitivity obtained using atomic absorption spectrometry with such a short pathlength is due to the way in which the hydride is introduced to the atom cell. Quantitative transport of the gaseous analyte to the atom cell is readily achieved using only a small flow of argon and undue dilution by flame gases is avoided. The analyte atoms are contained in a small volume (approximately 1 cm^3) which results in efficient irradiation, while the low gas flows promote increased residence times. Using longer path length burners failed to produce any increase in sensitivity due to the high gas flow rates required to support the flame, which resulted in dilution of the analyte and short transit times through the atom cell.

The apparatus, though extremely simple, offers competitive sensitivity using atomic absorption spectrometry. Atomic fluorescence spectrometry, disappointingly, gives only a small advantage in detectability (a factor of approximately three) and no gain in linear working range. Both of these problems are thought to be due to the difficulties in operating the sources in a suitably intense manner. Thermostatting of the sources could be expected (156) to extend the lower end of the fluorescence working ranges considerably.

The inexpensive pumps allow continuous generation of the hydrides, thus improving precision by eliminating discrete variables, and accuracy, by unambiguously defining the background level. By using an autosampler the system could be fully automated.

Chapter 5. DETERMINATION OF ARSENIC AND SELENIUM IN COAL

5.1 INTRODUCTION

A number of reports has appeared on the determination of arsenic and selenium in coal using a variety of techniques and approaches. Both elements have been determined in whole coal using spark-source mass spectrometry (157) (semiquantitatively, (2)) and X-ray fluorescence (22, 94). Using the latter, poor accuracy, due to spectral interferences, has been reported (22) though the use of sophisticated computing techniques has enabled some workers (94) to overcome both spectral and matrix interferences, permitting calibration with aqueous solutions. However, careful preparation of the sample appears necessary in order to ensure the homogeneous particle size reportedly desirable. Neutron activation methods (95, 97, 158, 159, 160, 161) have also been applied to the analysis of whole coal samples. Several workers have reported good agreement between experimentally obtained and certified arsenic and selenium values when analysing standard coals. While lengthy sample pretreatment procedures are avoided, problems of limited sensitivity and poor precision may be encountered when the concentration of arsenic or selenium is very low, typically 2 $\mu g.g^{-1}$ or less. In addition most of the reported neutron activation methods require that the activity of the sample be allowed to decay for lengthy periods, both for safety reasons and to reduce interferences, and this may prove a major analytical disadvantage. Arsenic and selenium have been determined in low temperature coal ash using spark source mass spectrometry (162) and neutron activation analysis (22). While the ash is relatively easily obtained the methods used for subsequent dissolution of the ash, and the chemical treatment of the solutions obtained, appear extremely tedious. Many workers using neutron activation methods have preferred to dissolve (127, 163) or combust (96) the sample after irradiation in order to remove potential interferences and to preconcentrate arsenic and selenium before counting.

Feasability studies (164) have recently been performed using heavy-ion induced 'K', 'L' and 'M' X-rays to excite trace metal spectra of coal and biological samples. Whereas proton-induced X-ray emission methods are more widely reported, methods using heavy-ion induced X-rays are attracting interest because of the greater sensitivity available with these higher energy X-rays. Although potentially capable of simultaneous multi-element analysis this technique appears limited by the complex spectra produced.

The lower volatilities of arsenic and selenium relative to mercury have been exploited by several workers who have reported methods of sample dissolution using oxidising acids at elevated temperatures. Various geological samples (rocks, soils or sediments) were digested using mixtures of aqua regia (165), nitric acid/perchloric acid (147), nitric acid/perchloric acid/hydrochloric acid (166), and nitric acid/perchloric acid/hydrofluoric acid/potassium permanganate/potassium persulphate. Other workers have reported fusion of the sample with sodium hydroxide followed by digestion of the melt using nitric acid (167) and water (139). Similar approaches have been used to determine both arsenic and selenium in coal. After dissolution of coal using a mixture of perchloric acid/periodic acid, arsenic was determined colourimetrically (103) and by atomic absorption spectrometry using a sampling boat technique (168). Selenium has been determined using anodic stripping voltametry (169) after dissolution of coal using a mixture of nitric acid/perchloric acid/sulphuric acid. Using a similar mixture to digest coal, other workers have determined arsenic and selenium using gas/liquid chromatography with a microwave plasma atomic emission detector (170, 171) and electrothermal atomic absorption spectrometry (108, 172). High temperature ashing techniques have also been used to prepare coal samples for subsequent determination of arsenic and selenium. After treatment with a suitable ashing agent, either a solution of magnesium nitrate (173) or a mixture of magnesium oxide/sodium carbonate (108), powdered coal was ashed at temperatures between 450 and 500°C. The ash was treated with hydrochloric acid prior to analysis using hydride generation/atomic absorption spectrometry. A similar ashing temperature was reported (174) for coal samples which had been treated with a solution of magnesium nitrate/nickel nitrate to prevent volatilisation losses. Subsequent determination of arsenic (and antimony) was performed using electrothermal atomic absorption spectrometry.

While the hydride generation/atomic absorption spectrometric technique is currently proving popular for the determination of low levels of arsenic and selenium, the analysis of 'real' samples has been shown to suffer from a wide variety of interferences, e.g. valency state (175, 176), pH (177), certain metals (28, 178, 179) and anions (28, 178). Several authors (180, 181) have reported similar interferences when using hydride generation/atomic fluorescence spectrometry. Numerous approaches have been used to eliminate or to reduce these interferences to tolerable levels. Successful methods have involved the use of masking agents (182) or separation of the analytes from the interfering species by coprecipitation on metal hydroxides (183, 184).

In this work a method is described in which concentrated perchloric acid is used to digest coal prior to analysis for arsenic and selenium using hydride generation/atomic absorption and atomic fluorescence spectrometry. Potential interferences are investigated, identified and overcome using a simple method in which arsenic and selenium are separated from the matrix by a coprecipitation step using lanthanum (III) hydroxide. After this step arsenic and selenium are determined using the hydride generation methods described in Chapter 4.

A second method for arsenic (arising from the interference studies) is described in which solvent extraction is used to separate arsenic from the perchloric acid digest prior to determination using electrothermal atomic absorption spectrometry.

Feasability studies on the determination of arsenic in low temperature coal ash are also discussed.

5.2 EXPERIMENTAL

5.2.1 EQUIPMENT

Coal digestions were carried out using routinely available laboratory equipment, including: a two-necked, round-bottomed flask (250 ml); a B24 (Quickfit) double-surface condenser and a Bunsen burner, tripod and gauze.

Precipitation of lanthanum (III) hydroxide was performed by mixing the appropriate solutions in a centrifuge tube (100 ml, PTFE) which, after cooling, was inserted into a heavy-duty centrifuge (M.S.E. Super Minor centrifuge, M.S.E. Scientific Instruments, Manor Road, Crawley, Sussex). The continuous flow system and atom cell described previously were used to determine arsenic and selenium by hydride generation/atomic absorption or atomic fluorescence spectrometry.

In experiments where the arsenic was removed from the perchloric acid matrix by solvent extraction, subsequent determination was performed using a full-automated electrothermal atomic absorption procedure. Instrumentation and operating conditions are given in Table 10.

Ash samples were prepared for analysis by ashing powdered coal under radiofrequency excited oxygen at reduced pressure. Experimental conditions are given in Table 11. Subsequent determination of the arsenic was performed using electrothermal atomic absorption spectrometry (see Table 10 for details).

Silica residues (obtained on the dissolution of coal with perchloric acid) were analysed qualitatively using both X-ray fluorescence and X-ray diffraction. The equipment and operating conditions used are described in Table 12.

Table 10

Instrumentation and optimum operating conditions used in the determination of arsenic by electrothermal atomic absorption spectrometry

Component	Model	Supplier	Operating Conditions
Spectrometer	PE 272	Perkin Elmer Post Office Lane Beaconsfield Bucks	Atomic absorption PMT voltage 620 V wavelength 193.7 nm spectral bandpass 0.7 nm
Autosampler	AS 1	"	Sample volume 20 µℓ 4 replicates per sample.
Recorder	056	"	1 cm.min^{-1}; 10 mV f.s.d.
Sources	As hollow cathode lamp	"	7.5 mA
	deuterium arc	"	4 mA
Furnace	HGA 76B	"	See below

Furnace Operating Conditions

Cycle parameter	dry	char	atomise
temperature (°C)	150	1250	2700
time (s)	20	15	8
gas flow (mℓ.min^{-1} argon)	50	50	stopped
recorder	no	no	yes

Table 11

Instrumentation and operating conditions used in the preparation of low-temperature coal ash

Plasma generator:	Nanotech Plasma Prep P100 Supplied by Nanotech Thin Films Ltd., Sedgley Park Trading Estate, Prestwich, Manchester.
Operating conditions:	Forward power; 115 ± 5 W Reflected power; *ca*. 5 W Oxygen flow rate; 20 ± 2 mℓ.min^{-1} Sample size; 0.05 - 0.5 g coal Ashing time; various, typically between 24 and 90 hours.

Table 12

Instrumentation and operating conditions used in the analysis of silica using x-ray fluorescence and x-ray diffraction

X-ray fluorescence:	Link Systems MECA 10 energy-dispersive x-ray fluorescence analyser, fitted with a KEVEX 0100 pulse height analyser subsystem for data processing.
Anode settings:	Voltage, 45 kV; current, 10 mA.
Targets:	(a) molybdenum (b) barium titanate.

The samples were mounted on a small PTFE block and irradiated through a vacuum path for 1000 seconds.

X-ray diffraction

X-ray films were exposed in a Debye-Scherrer camera using iron-filtered cobalt Kα radiation, (6.93 keV).

5.2.2 REAGENTS

Unless otherwise stated all reagents used were of analytical grade.

Hydride generation

Sodium tetrahydroborate (III) solution,

1% $^{m}/v$ in sodium hydroxide solution, 1 M.

Lanthanum (III) chloride solution

Prepared by dissolving lanthanum (III) chloride (10 g) in distilled, deionised water (100 ml).

Ammonium hydroxide solution

Prepared by diluting concentrated ammonia solution (S. G. 880) with an equal volume of distilled, deionised water.

Hydrochloric acid diluent solutions for arsenic and selenium standard solutions

(i) Sodium iodide solution

Prepared by dissolving sodium iodide (10 g) in distilled, deionised water (100 ml).

(ii) Sodium bromide solution

Prepared by dissolving sodium bromide (10 g) in distilled, deionised water (100 ml).

Solvent extraction

Hydrogen peroxide (100 vols., 30% $^{m}/v$)

Saturated bromine solution

Prepared by adding bromine (5 ml) to distilled, deionised water (100 ml).

Sodium iodide solution

Prepared by dissolving sodium iodide (20 g) in distilled, deionised water (100 ml).

Diethylammonium diethyldithiocarbamate solution

Prepared by dissolving diethylammonium diethyldithiocarbamate (BDH Chemicals, Poole, Dorset; 0.5 g) in chloroform (100 ml).

Copper solution

Prepared by dissolving copper foil (0.50 g) in dilute nitric acid (500 ml, 4 M) and diluting to 1 litre with distilled, deionised water. The resulting solution contained 500 $\mu g.ml^{-1}$ copper in 2 M nitric acid.

Arsenic standard solutions

Arsenic standard solutions were prepared by serial dilution of a stock solution containing 1000 $\mu g.ml^{-1}$ of arsenic (Hopkin and Williams, Chadwell Heath, Essex). Working standards, typically 0.015 - 0.15 $\mu g.ml^{-1}$, were prepared using the copper solution as diluent.

All coal digestions were performed using concentrated perchloric acid (72% $^{m}/v$). Low temperature coal ash was leached using the copper solution described above.

5.2.3 PROCEDURES

5.2.3.1 DISSOLUTION OF COAL USING CONCENTRATED PERCHLORIC ACID

Powdered coal (0.7 g), was added to the digestion flask and a double surface condenser fitted to the B 24 neck of the flask. Concentrated perchloric acid (35 ml, 72% $^{m}/v$) was added <u>via</u> the second neck of the flask, which was then stoppered and the flask swirled repeatedly to ensure mixing and thorough wetting of the coal. The mixture was heated gently using a Bunsen burner until effervescence began (5 - 10 mins). At this point the reaction became vigorous and self-sustaining. Heating was discontinued until effervescence subsided (5 - 10 mins), whereupon the mixture was heated strongly until complete dissolution of the carbonaceous matter was observed. The mixture was then refluxed for approximately 10 mins and allowed to cool, yielding a sample solution in 45 mins or less. When more concentrated sample solutions were required the mixture was cooled after the initial effervescence had ceased and a second portion of coal (0.3 - 0.7 g) added via the second neck of the flask. The procedure was then continued as described above and the total reaction time was typically 1 hour. After cooling, first in air and secondly in an ice/water mixture, the solution and silica residues were transferred with condenser and flask washings (10 - 12 ml, 5 M hydrochloric acid) to a graduated flask (50 ml). As a safety precaution iced water (approximately 200 ml) was placed in a separating funnel, fitted in the vertical arm of a Quickfit 'Ͱ' shaped two way adaptor located in the top of the condenser. In certain experiments when smouldering and/or ignition of the coal was observed, the iced water was immediately discharged into the reaction flask to cool and quench the mixture.

5.2.3.2 SEPARATION OF ARSENIC AND SELENIUM BY CO-PRECIPITATION WITH LANTHANUM (III) HYDROXIDE

An aliquot of the perchloric acid digest (10 - 20 ml) was transferred to a PTFE centrifuge tube (100 ml capacity) and lanthanum (III) chloride solution added (2 ml, 10% $^m/v$). Sodium iodide solution (1 ml 10% $^m/v$) or sodium bromide solution (1 ml, 10% $^m/v$) was added for arsenic or selenium determinations respectively. After mixing, ammonium hydroxide solution (25 - 50 ml, 50% $^m/v$) was poured quickly into the mixture. For arsenic determinations the solution was cooled by immersion in cold water. For selenium determinations the solution was allowed to cool in air (10 - 15 mins), the heat of neutralisation being used to assist reduction of selenium (VI) to selenium (IV). The lanthanum (III) hydroxide precipitate was separated from the bulk of solution by centrifuging at approximately 3000 r.p.m. for 2 - 3 minutes. A second aliquot (1 ml) of lanthanum (III) chloride solution was added and the mixture centrifuged as before. The supernatant liquor was carefully discarded and the precipitate dissolved in a minimum of hydrochloric acid (5 M, containing 1% $^m/v$ sodium bromide or sodium iodide for selenium or arsenic determinations respectively). The resulting solution was transferred to a graduated flask (10 - 25 ml) and made up to volume again, using the appropriate hydrochloric acid diluent. The solution was then analysed for arsenic or selenium by hydride generation/atomic absorption or atomic fluorescence spectrometry (section 4.3.3.2, page 99).

5.2.3.3 SOLVENT EXTRACTION OF ARSENIC FROM COAL DIGESTS

An aliquot of the perchloric acid digest (10-20 ml) was placed in a small beaker (50 ml) and hydrogen peroxide solution (1 - 2 ml) added. The solution was heated gently until effervescence ceased and, after cooling, extracted with diethylammonium diethyldithiocarbamate solution (2 x 10 ml, 0.5% $^m/v$ in chloroform). The organic phase was discarded and a second aliquot (1 - 2 ml) of hydrogen peroxide solution was added, followed by saturated bromine water (1 - 2 ml). After boiling to dispel the bromine the solution was cooled, sodium iodide solution (1 ml, 20% $^m/v$) added and the mixture allowed to stand for 10 mins. The solution was then extracted with the diethylammonium diethyldithiocarbamate solution (2 x 5 ml) and the aqueous phase discarded. The organic phase was then extracted with the copper solution (2 x 5 ml, 500 $\mu g.ml^{-1}$ copper in nitric acid, 2 M). This solution was then analysed for arsenic by electrothermal atomic absorption spectrometry using the instrumentation and operating conditions described in Table 10.

5.2.3.4 LOW TEMPERATURE ASHING OF COAL SAMPLES

A sample of powdered coal (typically 0.5 g) was spread thinly on a cover glass which was then placed in the sample chamber of the ashing unit. After evacuation of the chamber a small flow of oxygen (20 $ml.min^{-1}$) was introduced, the forward power set to approximately 100 W, and the plasma initiated. The forward power was increased to a nominal setting of 115 W and the plasma tuned to produce a minimum of reflected power (typically 5 W). The sample was allowed to ash in the oxygen plasma for a period ranging between twenty four and ninety hours. On completion of the ashing cycle the oxygen supply was switched off and the pressure in the sample chamber slowly allowed to rise to atmospheric. The ash was then mixed with the nitric acid solution of copper (15 ml of 500 μg.ml^{-1} copper in 2 M nitric acid) and heated at 80°C for 30 mins. The suspension was allowed to cool to approximately 30°C and then filtered directly into a graduated flask (25 ml). The precipitate was washed and the solution made up to volume with the same copper solution. Arsenic was determined by electrothermal atomic absorption spectrometry using the instrumentation and operating conditions described in Table 10.

5.3 RESULTS AND DISCUSSION

5.3.1 DISSOLUTION OF COAL USING CONCENTRATED PERCHLORIC ACID

The results of previous experiments using perchloric acid had shown that it was possible to dissolve the carbonaceous content of coal rapidly and reproducibly. However, since perchloric acid enjoys a rather dubious reputation (due mainly to its explosive hazards when improperly handled) it was decided first to determine whether or not the reagent could be used safely on a routine basis.

During initial attempts to digest coal the ratio of volume of acid per unit weight of coal was varied in order to determine which proportions yielded rapid and safe dissolution of the coal while preventing undue dilution of the sample solution. It was found to be essential to wet the coal thoroughly but, wherever possible with a minimum of agitation. If the acid and coal were not intimately mixed small inclusions or 'pockets' of dry coal tended to react rather vigorously during preliminary heating of the mixture. In some cases when the ratio of acid to coal was low (typically 20 ml:1 g or less) these inclusions tended to persist to the stage of vigorous heating of the mixture and ignition of the coal occurred. Similarly, when the coal and acid mixture was shaken too vigorously prior to heating a thin layer of coal dust was seen to collect on the inside of the flask above the level of the acid. During heating of the mixture this coal dust was seen to smoulder, suggesting imminent ignition. When this happened the iced water stored in the separating funnel in the top of the condenser was immediately discharged into the flask to quench the mixture and prevent potential explosion. The minimum acid to coal ratio necessary to minimise these problems was 40:1, though in practice 50:1 was preferred.

The sample solution concentrations were of the order of 1.4% $^{m}/v$. This concentration represented arsenic concentrations of 130 and 5 $ng.ml^{-1}$ and selenium concentrations of 36 and 12 $ng.ml^{-1}$ for SRM's 1632a and 1635 respectively. While these levels were measurable with the proposed detection systems, the precision obtainable for both arsenic and selenium in SRM 1635 was unlikely to exceed 10% (relative). Consequently sample solution concentrations were increased by adding more coal during digestion. This proved to be a relatively simple task and increased the time taken for sample dissolution by only 15-20 mins.

5.3.2 DIRECT DETERMINATION OF ARSENIC AND SELENIUM IN PERCHLORIC ACID DIGESTS USING HYDRIDE GENERATION/ATOMIC ABSORPTION AND ATOMIC FLUORESCENCE SPECTROMETRY

Initial attempts to determine arsenic and selenium directly in the perchloric acid digests of standard coals using the hydride generation methods described resulted in low recoveries of both elements (typically 80%). Four possible causes were suspected, which were:

i) losses through volatilisation due to the elevated temperatures required to reflux concentrated perchloric acid (200-210°C);

ii) adsorption of arsenic and selenium on the silica precipitated during digestion of the coal;

iii) depletion of the available reductant concentration due to reaction between perchloric acid and sodium tetrahydroborate (III) solution;

iv) interferences during generation of the hydrides by certain transition metals, notably copper and nickel.

5.3.3 IDENTIFICATION OF INTERFERENCES

To identify which one (or more) of these possible causes was responsible the following strategy was adopted:

a) to separate and analyse the silica for arsenic and selenium content;

b) to develop an alternative and independent method for the determination of arsenic and selenium in the coal digests. (If quantitative recoveries were obtained then volatilisation losses could be discounted)

c) to prepare standard solutions containing perchloric acid and dilute hydrochloric acid and to compare the signal against that of standards made up in dilute hydrochloric acid only;

d) if a) above indicated that arsenic and selenium were retained during digestion, to separate both of the analytes from the interferents in the perchloric acid matrix prior to determination using the hydride generation technique.

After digestion of two coal samples the silica was filtered from both solutions (Nucleopore, 0.8μm) and taken for analysis by both X-ray fluorescence and X-ray diffraction. The results of the X-ray diffraction confirmed that the material was largely quartz combined with small amounts of kaolinite and alumina. The X-ray fluorescence results were more interesting, both samples yielding spectra in which peaks due to arsenic were observed (detection limit 5 $\mu g.g^{-1}$). Selenium was not observed in either spectrum but this was probably because the maximum levels of selenium anticipated in the silica were below the detection limit of the method (5 $\mu g.g^{-1}$). The silica was returned to each of the solutions and the samples refluxed for 10-15 minutes. After a second filtration the silica was again examined using X-ray fluorescence, which this time showed that the arsenic had been desorbed. After analysis of the solutions using hydride generation/atomic absorption spectrometry the recoveries of arsenic were still low (typically 80%) and this possible mechanism of interference was discounted. The X-ray fluorescence spectra are shown in Figs 11, 12 and 13.

<u>Fig. 11</u> X-ray fluorescence examination of residues remaining after digestion of NBS SRM 1632a (bituminous coal) using concentrated perchloric acid

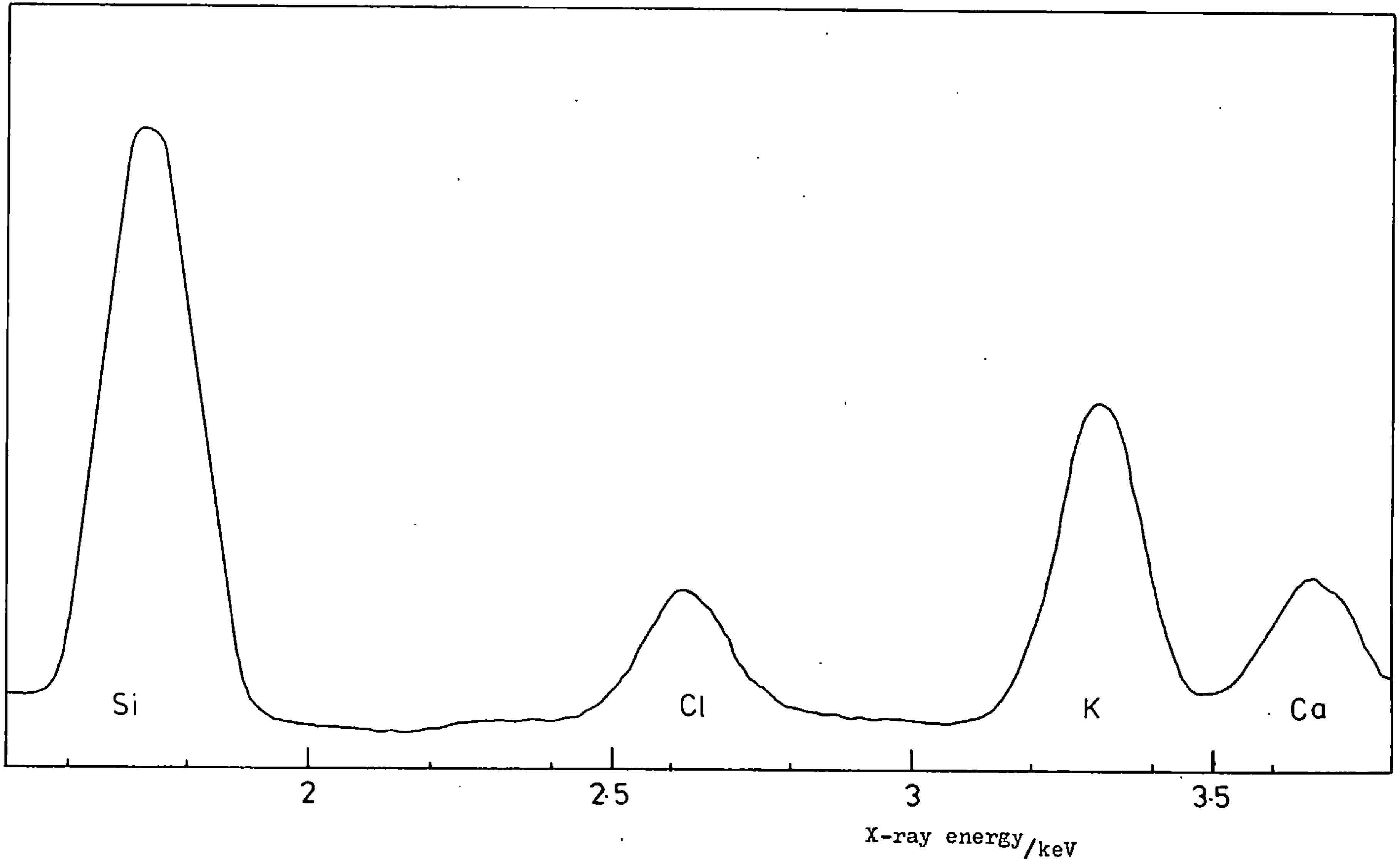


Fig. 12 X-ray fluorescence analysis of silica residues from perchloric acid digestion of NBS SRM 1632a; (a) before refluxing; (b) after refluxing

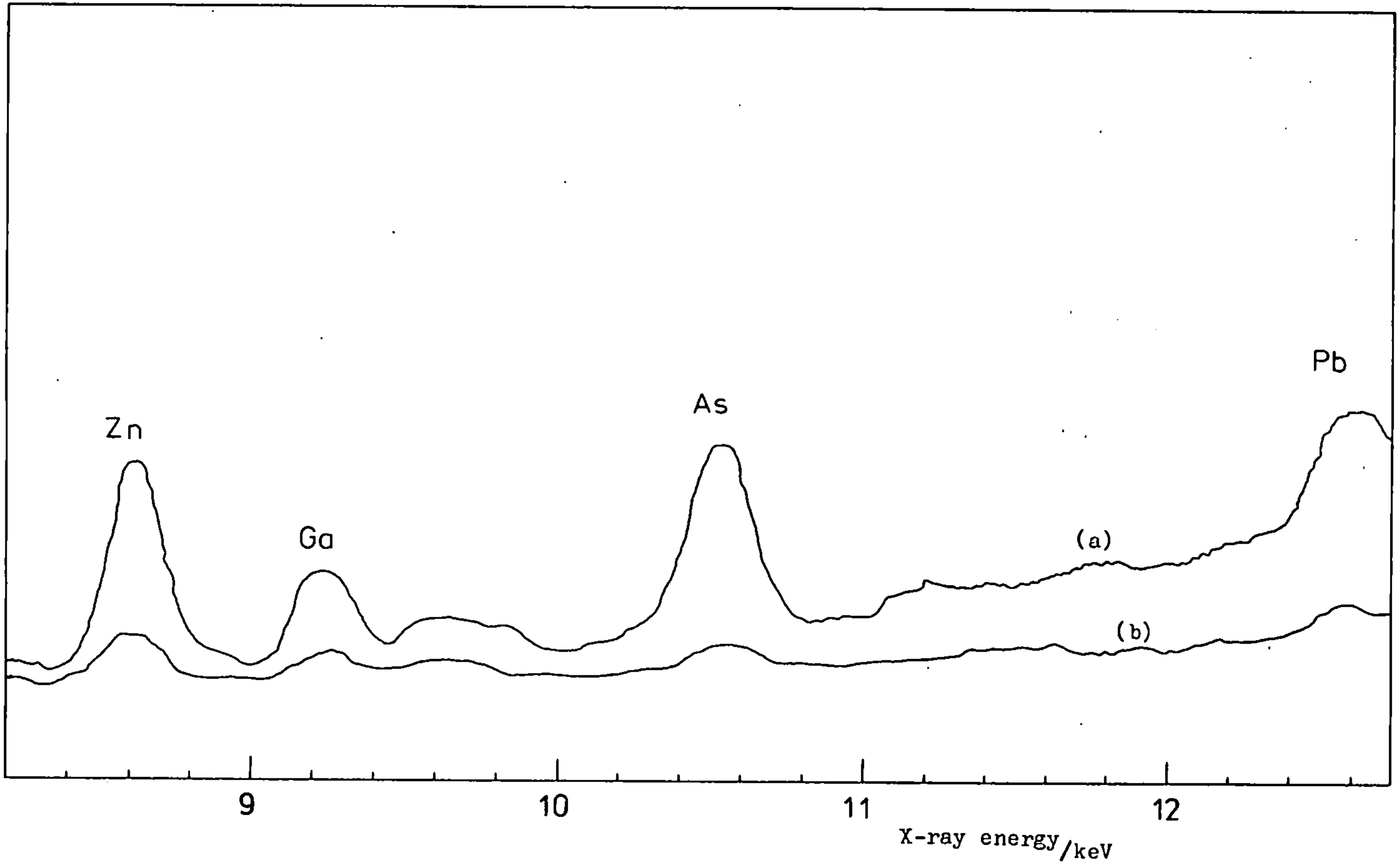
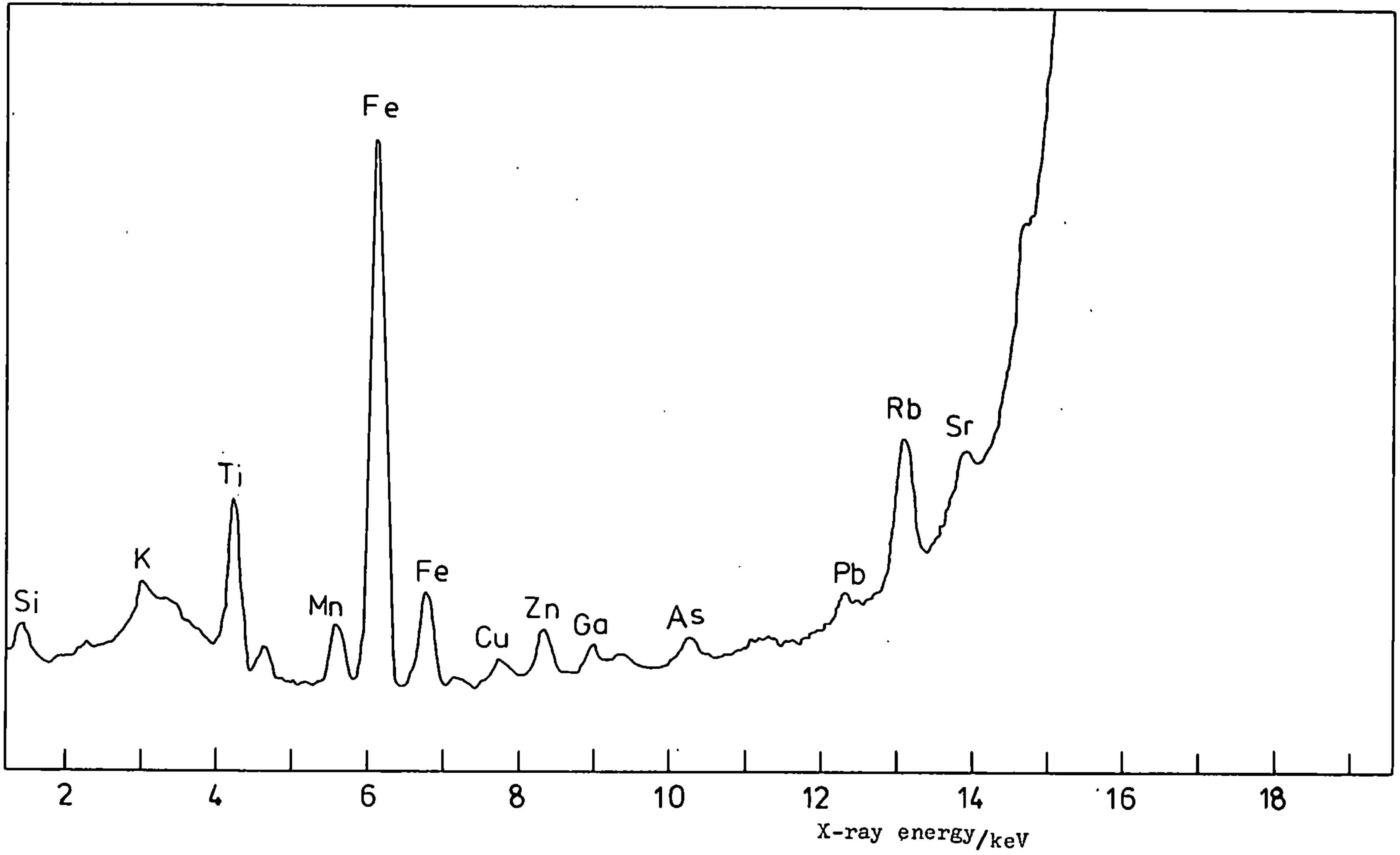


Fig. 13 Broad spectrum X-ray fluorescence scan of silica residues from perchloric acid digestion of NBS SRM 1632a



5.3.3.1 DETERMINATION OF ARSENIC USING SOLVENT EXTRACTION/ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

In respect of (b) it was decided to determine arsenic using a technique not involving hydride generation. Due to the low levels of arsenic anticipated (10-100 $ng.ml^{-1}$) electrothermal atomic absorption spectrometry was selected. Again, direct analysis of the perchloric acid digests using this method was impracticable due to severe attack on the carbon tubes during the atomisation stage. Consequently a method was developed in which the arsenic was removed from the matrix by a solvent extraction/back extraction procedure prior to determination using the carbon furnace. In the method described (185, 186)(section 5.2.3.3, page 119) hydrogen peroxide was added to the coal digest to convert all the arsenic to the pentavalent oxidation state. The first extraction with diethylammonium diethyldithiocarbamate solution was included to remove transition metals which may otherwise have been co-extracted with arsenic (III) or subsequently have interfered with the carbon furnace determination, but not pentavalent arsenic. The arsenic was then reduced to the trivalent oxidation state with sodium iodide solution and removed from the perchloric acid by a second extraction with diethylammonium diethyldithiocarbamate solution. Potassium iodide solution is not suitable since large amounts of insoluble potassium perchlorate are precipitated which collect at the interface of the two phases during the second extraction and hamper separation. Sodium perchlorate is readily soluble and causes no such problems. Arsenic was subsequently stripped from the organic phase by back-extraction with an aqueous solution of copper, which was chosen because of its higher formation constant than arsenic with diethylammonium diethyldithiocarbamate (186).

Analysis of the solutions obtained by this procedure using electrothermal atomic absorption spectrometry gave recoveries of arsenic of 101 ± 4% (three determinations).

The same solutions when analysed using the hydride generation/atomic absorption method gave recoveries of approximately 80%.

This approach was not repeated for selenium due to the difficulties encountered in identifying a complexing agent with which selenium could be simply and selectively extracted from the coal digests.

From the results of these experiments it appeared increasingly likely that the low recoveries of arsenic and selenium obtained using the hydride generation methods were due to interferences during generation of the hydrides. Thus, some method of separating the arsenic and selenium from these interferents was required. While quantitative removal of arsenic from the perchloric acid matrix had been achieved using the solvent extraction procedure, the solutions used for analysis contained large amounts of copper (500 $\mu g.ml^{-1}$). Copper has been widely reported to interfere in hydride generation methods, probably through compound formation with the analytes, in this case copper arsenide and copper selenide. Analysis of these copper containing solutions by hydride generation/atomic absorption spectrometry gave very low recoveries of arsenic, typically 50%. Other metals which displace arsenic from the diethylammonium diethyldithiocarbamate complex (_e.g_. mercury, palladium and silver) are also reported to interfere in hydride generation methods and these were not investigated. In addition simultaneous isolation of arsenic and selenium was not possible using the solvent extraction procedure described. Extraction of selenium required adjustment of the pH of the solution to approximately 5.5, but this would have been suitable for the extraction of arsenic also. However, the iodide added to reduce arsenic (IV) to arsenic (III) also reduced selenium (IV) and (VI) to selenium metal which was not extractable using diethylammonium diethyldithiocarbamate. Further experiments designed to co-extract arsenic and selenium simultaneously were not performed due to the difficulty in identifying a reducing agent powerful enough to reduce arsenic (V) to arsenic (III), yet mild enough to reduce selenium (VI) to selenium (IV) and no further (and which would not produce a precipitate when added to the perchloric acid digests). Rather an alternative method was sought and the simultaneous removal of arsenic and selenium from coal digests was soon successfully achieved using a variation of one of a number of reported methods in which both these, and other hydride forming elements, were co-precipitated on lanthanum (III) hydroxide from ammoniacal solution. The efficiency of the procedure was evaluated by determining arsenic and selenium in a series of standard solutions, some of which contained the trace metals thought to be responsible for the low recoveries observed.

5.3.3.2 EFFICIENCY OF THE CO-PRECIPITATION STEP

Various 'synthetic' coal solutions were prepared containing the trace transition metals present in SRM 1632a (chromium, copper, iron, lead, manganese, nickel, vanadium and zinc, as well as arsenic and selenium). Two solutions contained these metals in their 'natural' (in coal) concentration ratios and were made up in solutions of hydrochloric acid (5 M) and a mixture (1:1) of hydrochloric acid

(5 M) and concentrated perchloric acid. Two other solutions were prepared using similar acids but contained the metals other than arsenic and selenium at a concentration of 10,000 $ng.ml^{-1}$ of each other metal. When measured using hydride generation/atomic absorption spectrometry both sets of solutions gave apparently low recoveries of arsenic and selenium, (typically 80-90%) relative to solutions made up in hydrochloric acid (5 M) and containing no transition metals. The solutions containing 10,000 $ng.ml^{-1}$ of transition metals gave slightly lower recoveries than the solutions directly representative of SRM 1632a. The results are given in Table 13. Although rigorous attempts to identify specific metals were not made,the effects of copper and nickel in particular were investigated. Solutions of both arsenic and selenium containing copper or nickel (SRM 1632a concentration ratios) were analysed directly using hydride generation/ atomic absorption spectrometry. In each case recoveries were low, typically 90% and 80% for nickel and copper containing solutions respectively. When the lanthanum (III) hydroxide procedure was carried out in ammoniacal solution using a single precipitation arsenic was recovered quantitatively, but only 93 ± 2% of the selenium was recovered. Quantitative recoveries of both elements were obtained using the double precipitation procedure described.

5.3.4 DETERMINATION OF ARSENIC AND SELENIUM IN COAL

The perchloric acid/lanthanum (III) hydroxide coprecipitation method was then used to prepare sample solutions of SRMs 1632a and 1635. Arsenic and selenium were subsequently determined using hydride generation/atomic absorption and atomic fluorescence spectrometry. The results are given in Tables 14, 15, 16 and 17. In attempts to increase the recovery of arsenic from SRM 1635 the concentrations of both the lanthanum (III) chloride and ammonium hydroxide solutions were increased. The arsenic values for SRM 1635 were not increased, but the results were within the NBS quoted range and were deemed acceptable.

A range of non-standard coals was analysed for arsenic and the results obtained were compared with results obtained independently (187) using British Standard B.S. 1016 and neutron activation analysis. The results are shown in Table 18.

5.3.5 PREPARATION AND ANALYSIS OF LOW TEMPERATURE COAL ASH

The recommended ashing time for a 0.5 g coal sample was seventy hours, with intermittent shut down and stirring of the ash. This was considered to be unacceptable if the method was to be used on a routine basis. Consequently experiments were performed in which the weight of coal taken and the ashing times were varied in order to find the optimum conditions for rapid preparation of the ash. The ash leachates were analysed for arsenic by carbon furnace atomic absorption spectrometry (see Table 10) and the results are shown in Table 19.

The results suggest that the sample needs to be ashed for more than twenty-four hours if quantitative leaching of the arsenic from the ash is to be achieved. In one experiment the ash was not filtered from the leachate and an ash slurry was analysed instead. The recovery of arsenic was within 6% of the value obtained for the filtered leachate though precision was worse, presumably due to light scattering in the furnace by ash particulates. Nevertheless, the results demonstrate that the method permits the analysis of arsenic in coal with adequate accuracy and precision provided that sufficient time is allowed for ashing of the sample.

The ash was also analysed by X-ray fluorescence before and after leaching. The results (Figs 14 and 15) indicate that arsenic is effectively leached from the ash using the method described.

Table 13

A comparison of the responses obtained from various solutions with and without the trace metals present in SRM 1632a as measured using hydride generation/atomic absorption spectrometry.

	% recoveries of arsenic and selenium			
	As	Se	As	Se
Nominal concentrations/ng.mℓ$^{-1}$	20	20	100	100
Solutions*:				
a	100	100	100	100
b	103	97	102	99
c	86	90	90	89
d	86	90	91	84
e	79	83	84	80
f	82	80	83	80

All arsenic and selenium solutions contained sodium iodide and sodium bromide (1% m/v) respectively.

* a 5M hydrochloric acid containing arsenic and selenium

b 5M hydrochloric acid/concentrated perchloric acid (1:1) containing arsenic and selenium

c 5M hydrochloric acid containing: arsenic, (20 ng.mℓ$^{-1}$); chromium, (70 ng.mℓ$^{-1}$); copper, (35 ng.mℓ$^{-1}$); iron, (2,000 ng.mℓ$^{-1}$); lead, (25 ng.mℓ$^{-1}$); manganese, (60 ng.mℓ$^{-1}$); nickel, (40 ng.mℓ$^{-1}$); selenium, (5 ng.mℓ$^{-1}$); vanadium, (90 ng.mℓ$^{-1}$); zinc, (60 ng.mℓ$^{-1}$).

d 5M hydrochloric acid/concentrated perchloric acid (1:1) with the metals as in 'c' above.

e 5M hydrochloric acid containing: arsenic, (20 ng.mℓ$^{-1}$); selenium, (5 ng.mℓ$^{-1}$); chromium, copper, iron, lead, manganese, nickel, vanadium and zinc (10,000 ng.mℓ$^{-1}$).

f 5M hydrochloric acid/concentrated perchloric acid (1:1) with the metals as in 'e' above.

TABLE 14 Determination of Arsenic in SRM 1632a

National Bureau of Standards

Standard Reference Material 1632a, Bituminous Coal

Quoted Arsenic Content = 9.32 ± 1 μg.g^{-1}

Arsenic found μg.g^{-1}

	a.a.s.	a.f.s.
	9.13	
	9.36	
	9.44	
	9.34	
	9.30	
	9.66	
	9.66	
	9.12	
*both analyses on same solution	9.02*	9.13*
		9.57
		9.02
		9.49
		9.12
mean	9.34 μg.g^{-1}	9.27 μg.g^{-1}
standard deviation	0.23 μg.g^{-1}	0.25 μg.g^{-1}
relative standard deviation	2.43%	2.66%

TABLE 15 Determination of Arsenic in SRM 1635

National Bureau of Standards

Standard Reference Material 1635, Sub-bituminous Coal

Quoted Arsenic Content = 0.42 ± 0.15 $\mu g.g^{-1}$

Arsenic found $\mu g.g^{-1}$

	a.a.s.	a.f.s.
	0.31	
	0.31	
	0.33	
		0.35
		0.32
		0.36
		0.31
		0.33
mean	0.32 $\mu g.g^{-1}$	0.30 $\mu g.g^{-1}$
standard deviation		0.02 $\mu g.g^{-1}$
relative standard deviation		7%

TABLE 16 Determination of Selenium in SRM 1632a

National Bureau of Standards

Standard Reference Material 1632a, Bitumous Coal

Quoted Selenium content = 2.6 ± 0.7 µg.g^{-1}

Selenium found µg.g^{-1}

	a.a.s.	a.f.s.
	2.48	
	2.59	
	2.67	
	2.51	
	2.59	
	2.53	
	2.67	
		2.59
		2.70
		2.68
		2.65
		2.63
mean	2.58 µg.g^{-1}	2.64 µg.g^{-1}
standard deviation	0.08 µg.g^{-1}	0.05 µg.g^{-1}
relative standard deviation	2.9%	1.9%

TABLE 17 Determination of Selenium in SRM 1635

National Bureau of Standards

Standard Reference Material SRM 1635, Sub bitumous Coal

Quoted Selenium Content 0.9 ± 0.3 $\mu g.g^{-1}$

Selenium found $\mu g.g^{-1}$

	a.a.s.	a.f.s
	0.97	
	0.89	
	0.86	
	0.89	
		0.93
		0.91
		0.93
		0.87
		0.88
mean	0.90 $\mu g.g^{-1}$	0.90 $\mu g.g^{-1}$
Standard deviation	0.03 $\mu g.g^{-1}$	0.03 $\mu g.g^{-1}$
relative standard deviation	5%	5%

Table 18

A comparison of the arsenic levels determined in this work with independent analyses on six coal samples

	Arsenic values/µg.g^{-1}				
	This work	Independent analyses			
	Hydride generation/ a.a.s.	Neutron Activation	B.S.1016	E.T.A.A.S.	
Sample				a	b
1	18.5	28.0	16.7	17.7	-
2	16.7	20.0	14.1	22.7	12.0
3	17.3	32.0	13.2	22.7	16.0
4	8.4	11.3	7.0	14.3	12.5
5	4.6	-	2.9	6.7	4.8
6	15.2	-	10.8	13.5	8.9

a Calibrated with aqueous solutions matched for nickel and magnesium content

b Calibrated with aliquots of slurried coal (sample 1) assuming an arsenic content of 16.7 µg.g^{-1}.

Table 19

Recovery of arsenic from low temperature coal using electrothermal atomic absorption spectrometry

National Bureau of Standards

Standard Reference Material 1632a, Bituminous Coal[a].

	Ashing time/hours	
	24	72
Sample weight/g	As found $\mu g/g^{-1}$	
0.050	7.4 ± 1	10.0 ± 0.4
0.200	6.5 ± 1	9.18 ± 0.4*
0.500	6.0 ± 1	9.14 ± 0.4

* Arsenic found by analysis of slurry 8.8 ± 1.3 $\mu g.g^{-1}$

[a] Certificate value, 9.32 ± 1 $\mu g.g^{-1}$.

Fig. 14 X-ray fluorescence analysis of low temperature coal ash from NBS SRM 1632a (a) before, and (b) after leaching with dilute nitric acid

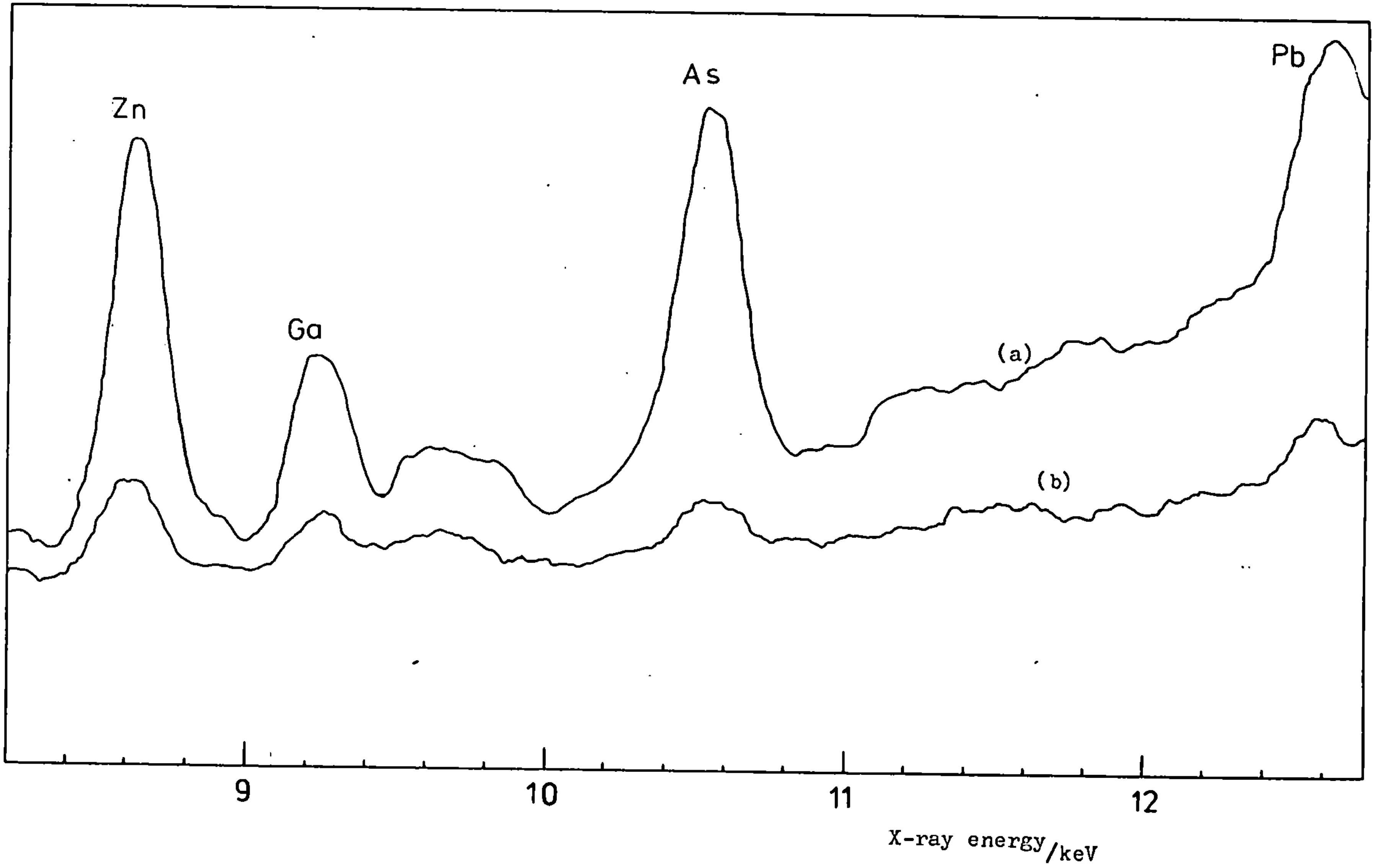
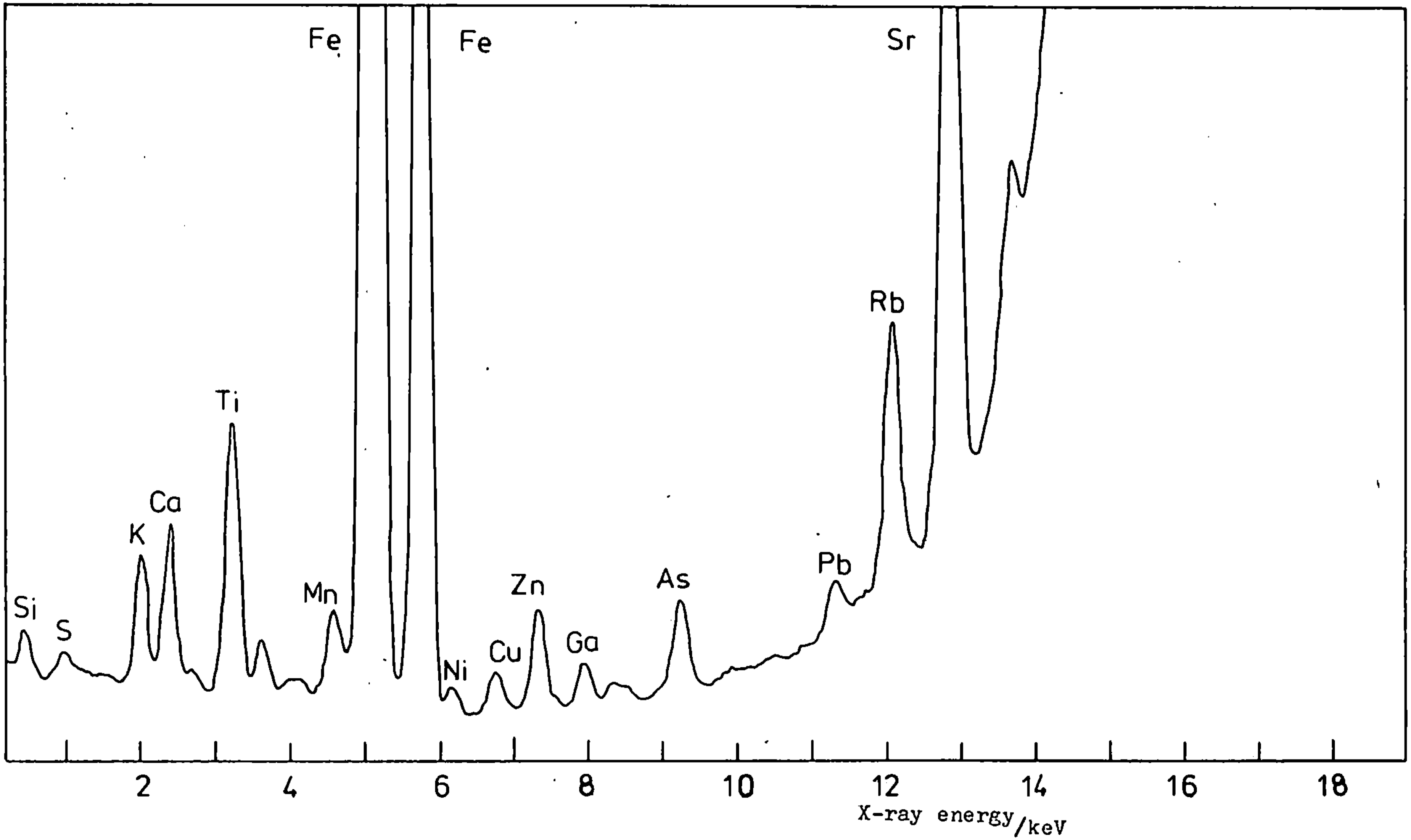


Fig. 15 Broad spectrum X-ray fluorescence scan of low temperature coal ash from NBS SRM 1632a



5.4 CONCLUSIONS

The determination of arsenic and selenium in coal has recently been reported by several authors and a noteworthy feature of the literature is that no single technique has proved to be either analytically superior to or noticeably more popular than the others. Several instrumental techniques have been used to determine these elements in whole coal but problems of limited sensitivity and poor precision have induced other workers to use lengthy ashing or combustion procedures in order to overcome these problems. Equally popular are methods in which the coal has been dissolved or wet ashed prior to the determination of arsenic or selenium. Numerous ashing aids, digestion mixtures and detection systems have been reported. In the work described here coal is taken into solution using concentrated perchloric acid. Arsenic and selenium are removed from interferents by coprecipitation on lanthanum (III) hydroxide prior to determination using hydride generation/atomic absorption and atomic fluorescence spectrometry.

The perchloric acid digestion procedure is seen to be a very simple and efficient method for the dissolution of coal. The elevated temperatures required to reflux concentrated perchloric acid (200-210°C) have incurred no losses by volatilisation of either arsenic or selenium. The strenuous reflux conditions used also minimise undesirable emission of perchlorate fumes. Thus the tendency towards dehydration of the acid, which may subsequently introduce potential explosive hazards, is avoided. When used as recommended this method is completely safe and reliable showing no tendencies towards ignition and/or over-vigorous reaction. It has been used regularly throughout this phase of the practical work to dissolve numerous coal samples, of widely varying compositions in a rapid and reproducible manner.

Some workers (170) have experienced problems of adsorption of selenium on precipitated silica when dissolving environmental samples using a mixture of nitric, perchloric and sulphuric acids. Such problems have been avoided in this work by refluxing the coal digest to desorb arsenic and selenium from the residual silica.

Direct analysis of the perchloric acid digests using the proposed hydride generation methods fails to yield quantitative recoveries of arsenic and selenium. The results of a series of experiments have indicated that these low recoveries are due to inhibition by certain transition methods (probably nickel and copper) during generation of the hydrides. A possible explanation is that species such as copper arsenide, copper selenide, nickel arsenide and nickel selenide are precipitated during mixing of the sodium tetrahydroborate (III) and sample solutions, when the pH of the solution rises sharply. Thus, appreciable amounts of both arsenic and selenium are made unavailable for reduction and low recoveries result. The large excess of lanthanum (III) ions added during the precipitation step ensures that arsenic and selenium are preferentially precipitated with the lanthanum while the copper and nickel remain in solution as their alkali soluble ammine complexes. Overall the coprecipitation step is much more rapid and simple than the solvent extraction procedure (see below) and in addition is capable of isolating arsenic and selenium simultaneously.

The solvent extraction procedure has helped to confirm the efficiency of the perchloric acid digestion. However, while quantitative separation of arsenic from the perchloric acid digests is possible, the method, like many solvent extraction methods, is tedious and time consuming. Nevertheless, its usefulness should not be underestimated and if a suitable reducing agent, one capable of reducing arsenic (V) to arsenic (III) and selenium (VI) to selenium (IV), can be identified, then simultaneous extraction of arsenic and selenium should be possible. Because of the non-standard nature of many of the hydride generation systems reported many workers will continue to determine arsenic and selenium by electrothermal atomic absorption spectrometry, which is a well-characterised and standard technique. Thus, this method may well prove attractive to those laboratories not equipped with hydride generation equipment. Similarly, it may be possible to use the coprecipitation method to isolate arsenic and selenium and then simply to dissolve the precipitate in dilute nitric acid (instead of dilute hydrochloric acid) prior to determination using electrothermal atomic absorption spectrometry. Lanthanum has been used (188) successfully as a matrix modifier to prevent premature volatilisation of arsenic during determination using electrothermal atomic absorption spectrometry.

Of the two methods described, coprecipitation followed by hydride generation/atomic absorption or atomic fluorescence spectrometry is preferred because of its overall simplicity and ease of operation. Analysis time per solution is approximately one minute, whereas the electrothermal atomic absorption method requires 5-10 minutes (approximately $1\frac{1}{2}$-2 mins per replicate, 4 or 5 replicates per solution). The latter also requires considerably more care when setting the experimental and operating conditions.

The results of the coal analyses are encouraging in terms of accuracy and precision. Values obtained for both elements in both standard coals using hydride generation/atomic absorption and atomic fluorescence spectrometry are within the NBS quoted ranges. The value obtained for arsenic in SRM 1635 is towards the lower end of the NBS quoted range. The certified value is based upon figures obtained by determinations performed using atomic absorption spectrometry and photon activation analysis. Authors (158, 159, 160, 189) determining arsenic in SRM 1635 using instrumental activation methods have reported average values substantially higher than the NBS value, and often with poorer precision. This is probably because such low concentrations are close to the detection limits of the methods used but possibly there may be some interferences. Consequently, a certificate value based on results obtained using these techniques may be biased towards the high end of the range.

The use of the miniature flame as the atom cell and atomic absorption or atomic fluorescence spectrometry, together with the reproducible digestion conditions and continuous hydride generation provides a suitably accurate and precise method for the determination of arsenic and selenium in coal. Interferences during generation of the hydrides are readily overcome using a simple and rapid coprecipitation procedure. The detection limits of 58 and 36 $ng.g^{-1}$ by atomic absorption spectrometry and 25 and 10 $ng.g^{-1}$ by atomic fluorescence spectrometry for arsenic and selenium respectively are adequate for typical arsenic and selenium levels in coals. When extra sensitivity is required these detection limits can be improved by a factor of 2 - 3 by increasing the amount of coal dissolved per digestion (though correspondingly longer digestion times are required).

Finally, the potential of the low temperature oxygen plasma ashing technique as a suitable method for preparing coal samples for subsequent determination of arsenic and selenium has been investigated. At the moment the time-consuming step is the time required to effect ashing of the sample. Recent studies (190) have shown that, under suitable experimental conditions, ashing times of three hours are sufficient to prepare coal samples for analysis. The inherent simplicity of this method makes it very effective, and if this can be coupled with such short sample preparation times, the capital outlay for such instrumentation should be justifiable.

Chapter 6. THE DETERMINATION OF TRACE METALS IN COAL USING THE METHOD OF SLURRY ATOMISATION IN AN INDUCTIVELY COUPLED PLASMA

6.1 INTRODUCTION

The direct atomisation of solid or slurried samples would appear to offer a rapid method for the analysis of intractable matrices which might normally require pretreatment using lengthy digestion or combustion procedures. Traditionally arc and spark optical emission spectrometry has been an important technique for the analysis of solid samples. The technique is most successful when analysing conducting materials, the sample being used as one of the electrodes. Non-conducting materials have been analysed, usually in powdered form and after mixing with graphite (or occasionally copper) powder to make the sample more conducting. Arc and spark emission spectrometry is, however, fraught with a number of problems. It is usually necessary to calibrate using standards with compositions closely resembling those of the samples. Matrix interferences and irreproducible arc conditions may cause poor precision, a problem more evident when analysing powdered, non-conducting samples. In general these techniques are better suited to the analysis of bulk sold samples (e.g. metals) than to powders. In contrast atomic absorption and inductively coupled plasma atomic emission spectrometry offer good sensitivity, precision and relative freedom from chemical interferences. It is not surprising therefore that there has been a gradually increasing interest in the application of these techniques to the analysis of solid and slurried samples.

A comprehensive review (191) describing the various approaches to the direct analysis of solid samples using atomic absorption spectrometry contains many references to both theoretical considerations and practical applications. Another review (192) deals more generally with atomic emission and atomic fluorescence as well as atomic absorption spectrometry.

Methods using flames for atomisation of solid samples (193, 194, 195) have tended to produce results lacking sensitivity and precision. Such methods are not widely reported. Since the early experiments of L'Vov and co-workers (196) on the analysis of solid samples using electrothermal atomic absorption spectrometry this technique has been widely used to determine a range of elements in a variety of sample matrices (191, 197, 198, 199). Powdered samples have also been analysed directly using the inductively coupled plasma. Fluidised beds (69) and hollow, demountable sample-holders (70) have been used to effect sample introduction. The major analytical problems associated with these techniques have been: sample segregation; erratic sample introduction rate; selective volatilisation; non-specific absorption; insufficiently rapid or complete destruction of the matrix and/or incomplete volatilisation and atomisation of the analyte. Some or all of these effects may combine to a greater or lesser extent to produce relatively poor sensitivity and precision. However, when only semi-quantitative results are required such methods are generally rapid and the loss in accuracy may be made tolerable by the gain in speed of analysis. More recently laser ablation has been used to volatilise samples for subsequent analysis using spark emission spectrography (200) and inductively coupled plasma emission spectrometry (201). In the latter method the samples were collected on adhesive tape prior to volatilisation and a fully-automatic multi-element analysis was performed every ten seconds. While good precision was reported for several elements, the small amount of sample actually reaching the atom cell (typically 1 μg) resulted in poor precision (10-25% RSD) for other elements. Disadvantages of these techniques include problems due to sample inhomogeneity and the relatively poor shot-to-shot reproducibility of existing lasers.

Of increasing popularity is the analysis of slurries, i.e. powders suspended in either aqueous or organic solvents. In early work (202) flame atomic emission spectra were obtained by aspirating a soil sample suspended in a 1:1 mixture of isopropanol and glycerol. Later workers determined alkali metals in plants (203) and rocks (204) using analogous techniques. A significant contribution to the field of slurry analysis was the paper by Willis (205). In this work a study was made of the factors influencing the atomisation efficiencies of several metals when suspensions of geological materials were sprayed into a flame for analysis using atomic absorption spectrometry. Perhaps the most prominent feature of the work was the conclusion that only particles of 12 μm or less contributed appreciably to the absorption signal and that atomisation efficiency increased rapidly with decrease in particle size. Some workers (206, 207) have attempted to overcome the problems encountered with flames by using electrothermal atomic absorption spectrometry. Thixotropic thickening agents were used to produce stable suspensions and the authors concluded that particle sizes of up to 25 μm were tolerable. Since these studies it has become apparent that the potential for the direct analysis of slurried samples may be limited by the complexity of the untreated matrix. In the case of electrothermal atomisation methods problems of non-specific absorption are significant while blocking of the sample capillary or burner slot are problems encountered when using conventional burner/nebuliser assemblies. Although less sensitive than electrothermal atomisers, typical burner/nebuliser systems are generally more convenient to operate and capable of more rapid sample throughput. Much work has been performed on the development of nebuliser and burner systems capable of handling samples with high salt concentrations and high levels of suspended solids.

Development and subsequent characterisation of a unique nebulisation principle by Babington (208) has revolutionised sample introduction techniques. The advantage of this type of nebuliser is that the sample is no longer required to pass through a very narrow capillary (ca. 0.35 mm). Instead the sample flows through a relatively broad tube (up to a few mm) and is delivered to a narrow orifice through which argon issues at close to supersonic velocity. Shattering of the sample stream by the argon allows direct generation of high-density, finely-dispersed aerosols from a variety of complex materials. Using this type of nebuliser in combination with a wide-slot, high-solids burner, copper and zinc have been determined in whole blood, milk, urine and seawater using atomic absorption spectrometry (209). Several authors have subsequently reported modified versions of this nebuliser. The argon used for nebulisation was discharged from a narrow orifice located in a 'V' groove which had been cut along one end of the nebuliser body. Sample was allowed to trickle down this groove and the greater contact established between sample and gas resulted in more efficient nebulisation. These nebulisers have been used in the analysis of samples containing high salt concentrations and/or high levels of suspended solids, e.g. various steels (210), liquid foodstuffs (211), and sludge and biological samples (212).

Slurries of homogenised animal tissue samples have been nebulised using similar apparatus, prior to determination of copper, zinc and manganese using atomic absorption (213) and d.c. plasma atomic emission (214) spectrometry. An advantage claimed for the latter detection system was that the sample was introduced to the atom cell via a much larger orifice. Thus problems of burner blockage were eliminated enabling continuous sample introduction instead of pulsed nebulisation.

Despite these obvious advances, flame atomisation efficiencies in slurry nebulisation techniques are still low, typically 20% of those of aqueous solutions of equivalent concentration. A recent study (71) has compared the use of flame, electrothermal and inductively coupled plasma atomisation techniques for the analysis of slurries. The authors conclude that for flame atomisation pulsed nebulisation was necessary to avoid blockage of the nebulisation system, and for inductively coupled plasma atomisation a high-solids nebuliser is essential. Atomisation efficiency in nebuliser based systems is shown to be dependent on sample transport efficiency, particle size, atomisation temperature and sample matrix. For analytical determinations it is reportedly necessary to grind the sample to less than 10 μm particle size and to use standards which are closely matched to the samples. For electrothermal atomisation particle size effects are reportedly significant only above 25 μm, when sampling becomes the major source of error.

Some work has been performed on the direct analysis of whole coal slurries using atomic absorption spectrometry. The results discussed in a preliminary report (215) are generally inconclusive except for the suggestion that calibration using standardised slurries instead of aqueous solutions may be necessary. A second, more comprehensive report (216) and a further paper (217) have discussed the effects of several parameters (e.g. slurry concentration, viewing height and flame composition) on analytical performance. Relative to aqueous solutions typical slurry atomisation efficiencies were 20 ± 6%. Calibration was achieved using slurries of several different coals, the metal levels of which had previously been determined using conventional ashing/dissolution atomic absorption procedures. However, significant deviations from linearity were observed for the slurry calibration plots and two possible causes were discussed. Firstly different coals may contain significantly different amounts of mineral matter which may dictate the grinding characteristics of the coal and hence influence the final particle size distribution. If the size of a particle is related to the composition of that particle, then segregation of the sample has occurred and certain size fractions may be relatively enriched or depleted in one or more of the analytes. Secondly coals with different compositions may undergo different atomisation processes. Thus under identical experimental conditions the response per unit concentration of analyte may vary from coal to coal.

Analytical methods based on slurry atomisation techniques have several advantages to offer, particularly in terms of speed in analysis and prevention of possible contamination during pretreatment of the sample. However, the complexities of this approach are apparent. If these limitations can be eliminated or reduced to tolerable levels, either by the refinement of existing methods, or by the development of new techniques, then such methods would be of particular interest to those involved in the analysis of coal.

The inductively coupled plasma offers an atom cell of higher temperature (relative to flames) and, under certain conditions, longer residence times. These effects should combine to promote complete matrix destruction and analyte atomisation. Hence it may be possible using the inductively coupled plasma, to achieve equivalent sensitivity for slurry and aqueous concentrations.

To date no-one has been able to define unambiguously the precise excitation mechanisms responsible for the emission spectra observed using an inductively coupled plasma. Recent work (218) has led to an appraisal of the extent of local thermal equilibrium in the all-argon plasma. The results of these and other studies (219, 220) indicate that local thermal equilibrium does not exist in the all-argon plasma, which has led to the suggestion of a non-thermal excitation mechanism involving collisions between the analyte and metastable argon species (the so-called Penning ionisation). This idea is particularly attractive since the excitation energies of the metastable argon levels of 11.55 and 11.71 eV correspond well with the excitation energies of singly ionised species found in the plasma.

The situation for the nitrogen-cooled plasma, however, is somewhat different. In this plasma there appears to be a tendency for the nitrogen to quench the metastable argon species, and local thermal equilibrium may be more closely approached. Removal of these metastable argon species from the plasma would result in a decrease in the amount of energy available for sample excitation. Consequently the intensity of ion lines may be reduced while the intensity of atom lines should be less affected.

This work describes the development of a method for the analysis of coal samples using direct slurry atomisation in an inductively coupled plasma. The performance of both nitrogen-cooled and all-argon plasmas was optimised for aqueous solutions (for cadmium) and coal slurries (for manganese) using the variable step size simplex procedure (221, 222) as recently reported for the inductively coupled plasma (223). The effects on sensitivity and precision of slurry concentration, sample pumping rate and particle size are also investigated. The performance of a PTFE "Babington-type" high-solids nebuliser for the generation of sample aerosols from coal slurries is evaluated.

6.2 EXPERIMENTAL

6.2.1 EQUIPMENT

A schematic diagram of the instrumentation used in this work is shown in Fig. 16.

The plasma torch (see reference 61 for details of construction) was mounted concentrically in a three-turn, water-cooled, copper induction coil. Radiofrequency power was supplied to the coil by a 5kW, 27 MHz free-running generator (Radyne R50P, Radyne, Wokingham, England).

Gases were supplied to the torch by a purpose-built 'gas-box'. Five rotameters in this box allowed direct switching of the plasma from 'start up' to 'running' conditions. The coolant gas flow was equipped with a switching facility enabling either argon or nitrogen to be selected as the coolant gas. All three gas flows (coolant, plasma and injector) were controlled at the gas-box allowing the optimum operating conditions to be selected.

The analyte was introduced into the plasma in the form of an aerosol which was produced using a PTFE 'high-solids' nebuliser (Fig. 17; see reference 224 for details of construction). During this work the nebuliser was force-fed using a small peristaltic pump (Schuco Mini Pump Mark IV, 60 r.p.m., Schuco Scientific, Halliwick Court Place, London). This was necessary in order to provide a constant head of sample as this type of nebuliser has no natural uptake action.

The larger aerosol droplets produced were removed using a laboratory-constructed double-pass spray chamber (Fig. 18) and the resulting analyte aerosol was transported through the central injector tube of the torch into the plasma. In later experiments, when high pumping-rates were used to deliver coal slurries to the nebuliser, a recycling spray-chamber (Fig. 19) was used to conserve sample solution.

An inverted image of the plasma was projected 1:1 onto the 25 µm entrance slit of the monochromator using a quartz lens, 7.5 cm focal length. The spectroscopic emission lines of interest were isolated using a 0.5 m Ebert scanning monochromator (Jarrell Ash (Europe), Le Locle, Switzerland). The radiation was then focussed via a 25 µm exit slit onto a photomultiplier tube (Hamamatsu R106, operated at 500 v). The signal from the photomultiplier was amplified using a linear picoammeter (L M 10, Chelsea Instruments Ltd., London), and fed into a three-pen potentiometric chart recorder (Type MC 641-32, Watanabe Instrument Corporation, Japan).

Coal samples for preliminary slurry investigations were ground using a Tema Laboratory Disc Mill (Model T100, Siebtechnik, Mulheim, West Germany). Subsequent samples were ground using a McCrone Micronising Mill (McCrone Research Associates Limited, 2 McCrone Mews, Belsize Lane, London NW3).

Coal ash solutions were analysed for selected trace metals using an Instrumentation Laboratories I.L 151 atomic absorption spectrometer (Instrumentation Laboratories Inc., Lexington, Massachusetts, U. S. A.).

Particle size distributions were determined using a Coulter Counter Model T A II Multichannel Particle Counter, (Coulter Electronics, Northwell Drive, Luton, Beds.). Proprietory Coulter electrolyte and dispersant were used to suspend the samples which were sized using a counting tube with a 140 μm orifice.

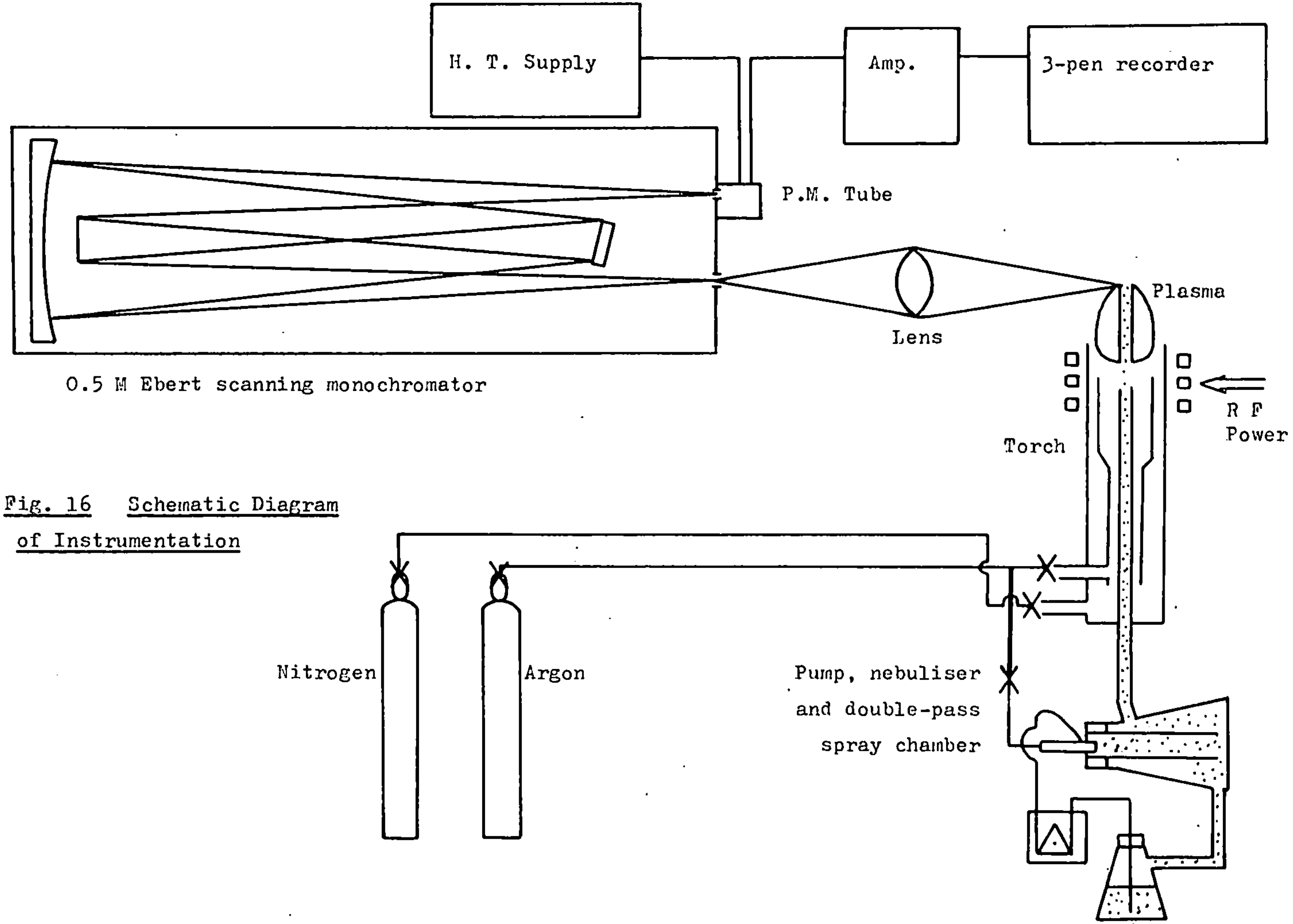
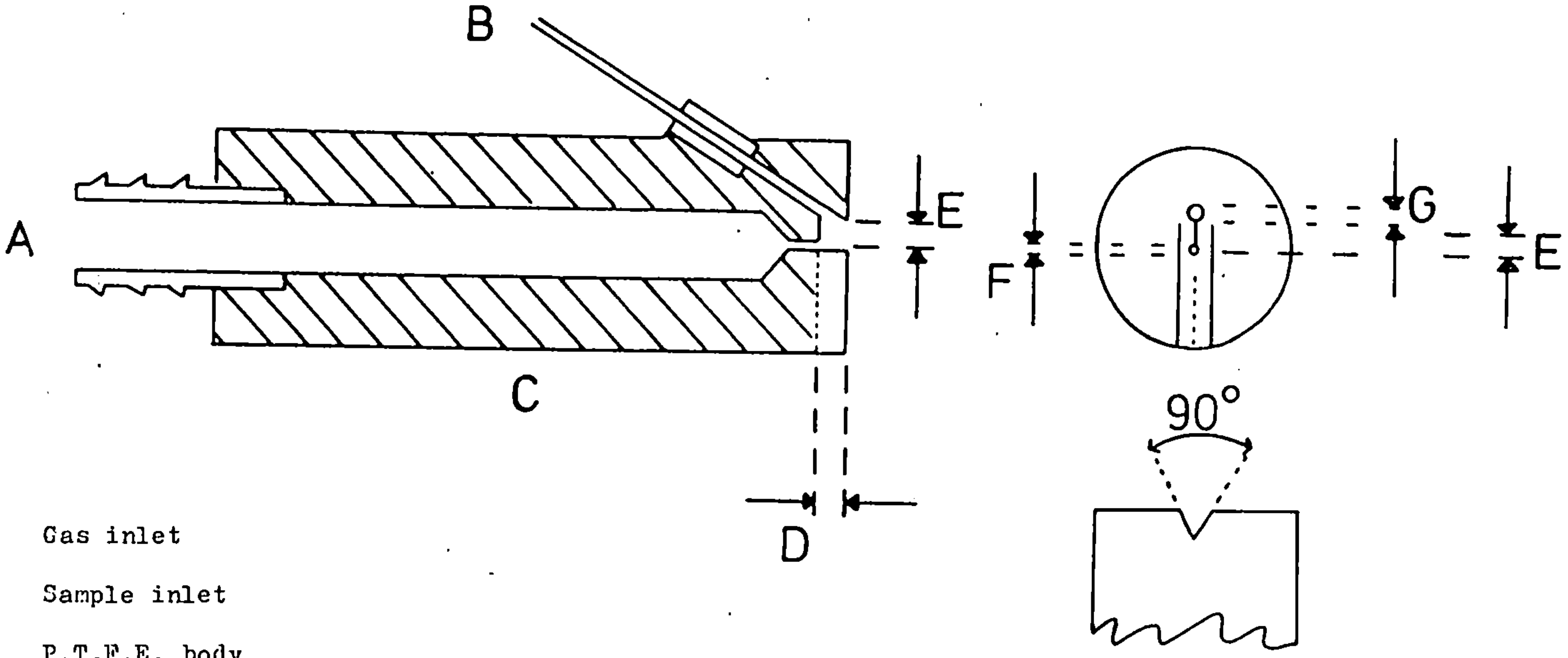


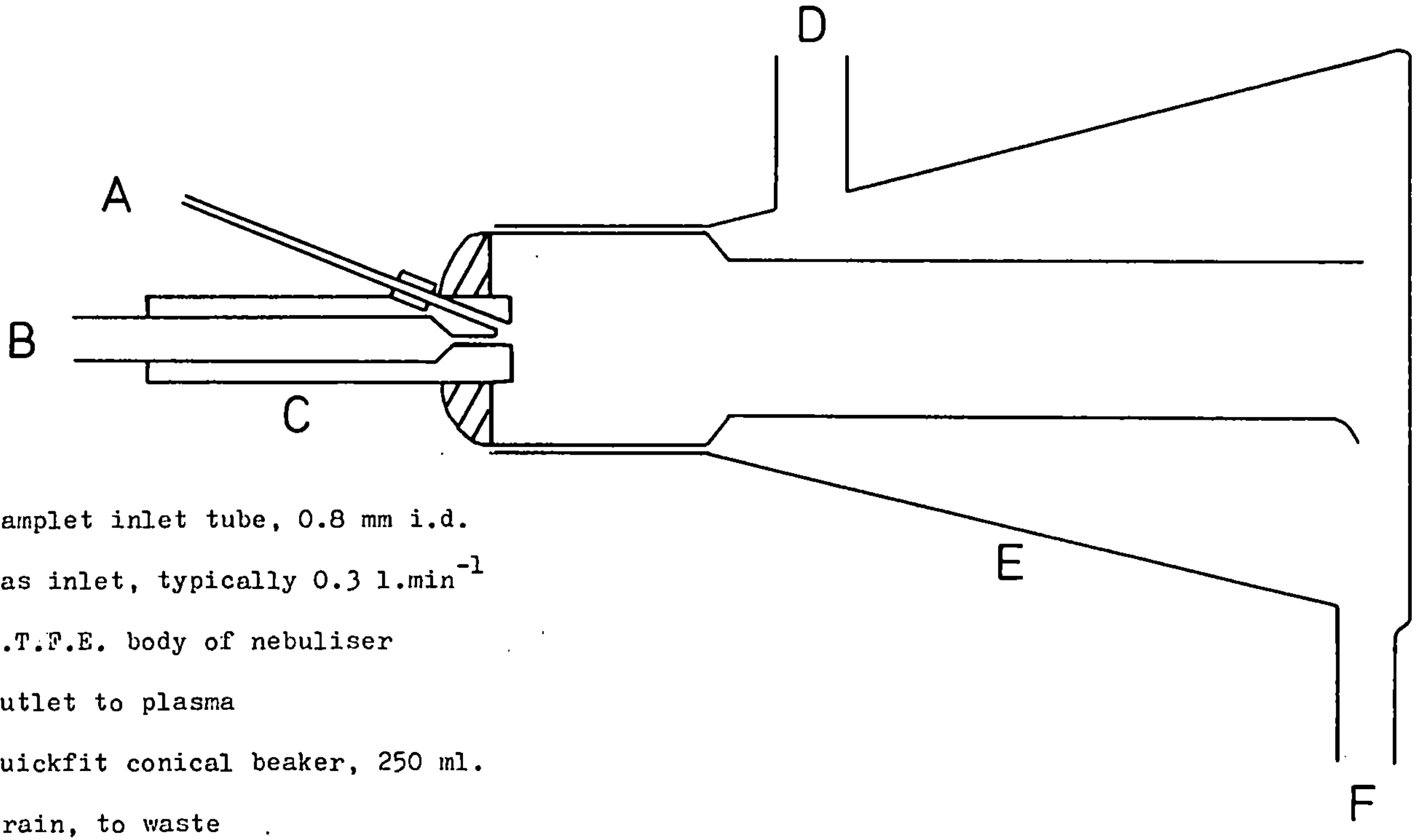
Fig. 16 Schematic Diagram of Instrumentation

Fig. 17 P.T.F.E. high solids nebuliser



A	Gas inlet
B	Sample inlet
C	P.T.F.E. body
D	1 mm
E	1 mm
F	0.4 mm
G	1 mm

Fig. 18 Double pass spray chamber



A Samplet inlet tube, 0.8 mm i.d.

B. Gas inlet, typically 0.3 l.min^{-1}

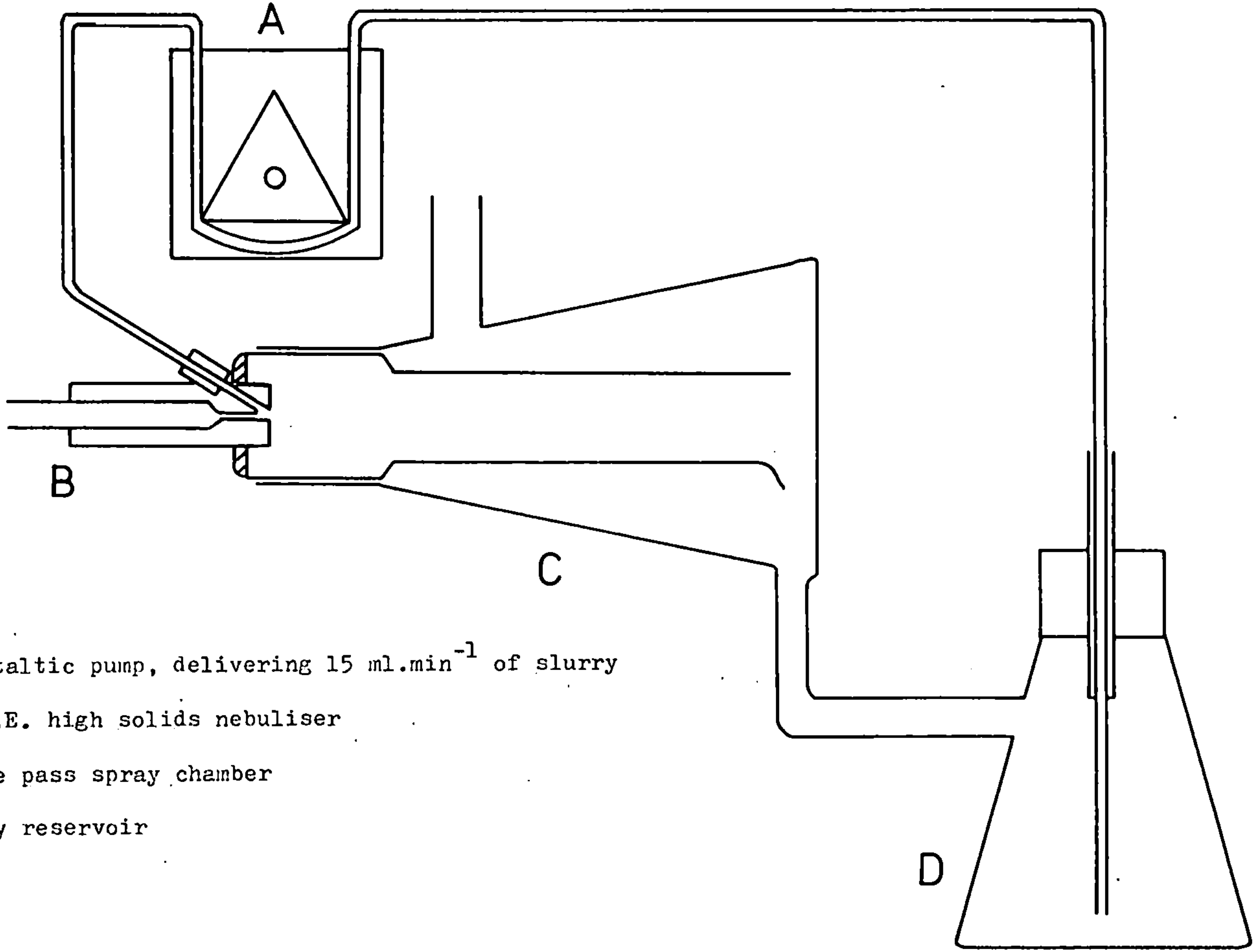
C. P.T.F.E. body of nebuliser

D. Outlet to plasma

E. Quickfit conical beaker, 250 ml.

F. Drain, to waste

Fig. 19 Recycling nebulisation system



A. Peristaltic pump, delivering 15 ml.min^{-1} of slurry

B. P.T.F.E. high solids nebuliser

C. Double pass spray chamber

D. Slurry reservoir

6.2.2 REAGENTS

Calibration standards for both atomic absorption and inductively coupled plasma methods were prepared by serial dilution of stock 1000 $\mu g.ml^{-1}$ solutions of chromium, copper, iron, manganese, nickel, vanadium and zinc (B.D.H. Chemicals, Poole, Dorset). For slurry analyses dilutions were made using a stock diluent of Triton X-100 solution (B.D.H. Chemicals, 1% $^{v}/v$).

The following analytical grade reagents were used in the coal ash dissolution procedure:

- concentrated hydrochloric acid;
- concentrated nitric acid;
- concentrated hydrofluoric acid;
- saturated boric acid solution (6% $^{m}/v$ in distilled, deionised water).

6.2.3 PROCEDURES

6.2.3.1 ANALYSIS OF COAL USING FLAME ATOMIC ABSORPTION SPECTROMETRY

Coal samples were ashed and the ash dissolved using the American National Standards Institute/American Society for Testing Materials method ANSI/ASTM D 3683-78 (225). Using this method coal ashed at 500°C was dissolved with aqua regia and hydrofluoric acid. Saturated boric acid solution was used to neutralise excess hydrofluoric acid. The solutions obtained were analysed for chromium, copper, iron, manganese, nickel, vanadium and zinc using atomic absorption spectrometry. The spectrometer operating conditions used were those recommended by the instrument manufacturer.

6.2.3.2 GRINDING OF COAL SAMPLES

The samples as received had been ground to pass a -250 mesh sieve (60 µm). For the particle size investigations 40 g of one coal sample was ground using the Tema Laboratory Disc Mill. After grinding the whole of the sample for approximately two minutes, the sample was tipped into a series of sieves and the different size fractions isolated by manual agitation of the sieves. The particle size ranges were: 250-125 µm, 125-106 µm, 106-63 µm, 63-53 µm, 53-38 µm and less than 38 µm. Portions of each fraction were used to prepare the coal slurries (4% $^{m}/v$) which were used to assess the effect of particle size on emission signal.

For the slurry simplex optimisation procedures a second 40 g portion of the same coal sample was ground in four 10 g portions using the Tema Laboratory Disc Mill. After screening the powder produced, those particles not passing through a 38 µm sieve were combined and ground repeatedly until all of the sample had been reduced to less than 38 µm in diameter. All the particles were combined and a coal slurry (4% $^{m}/v$, 1 litre total volume) prepared using the whole of the sample. This slurry was used during optimisation of the all-argon and nitrogen-cooled plasmas. Coal samples were prepared for quantitative analysis using the McCrone Micronising Mill. Typically 5 g of sample were dry-ground for approximately 30 mins. A total of 30 g of each coal was ground in this way and the samples were mixed thoroughly prior to the removal of the portion (10.0 g) with which the slurries(10% $^{m}/v$) were prepared.

6.2.3.3 SELECTION OF SPECTRAL LINES AND MEASUREMENT OF EMISSION SIGNALS

The spectral lines used were selected following an appraisal of:

(i) the signal to background ratio available at that line in the concentration range of interest;

(ii) the freedom from spectral interferences, particularly iron emission lines.

This was performed using mixed calibration standards containing each of the metals of interest (1.5, 3.0 and 4.5 $\mu g.ml^{-1}$ of cadmium, copper, lead, manganese, nickel, vanadium and zinc), each solution containing 1000 $\mu g.ml^{-1}$ of iron.

Quantitative emission measurements were made using an all-argon plasma employing two different sets of operating conditions. These conditions are shown in Table 20. As a result of this appraisal, copper, iron, manganese and nickel were determined using the atom line conditions, while vanadium was determined using the ion line conditions. Chromium, lead and zinc were not determined.

In order to ensure accurate measurement of the background under the analyte signals the emission spectrum was scanned continuously across a few nanometers either side of the analytical lines. To improve the precision of the measurements the lines were scanned at least three times for each of the standards and samples.

Plasma operating conditions were optimised for:

(i) cadmium in aqueous solutions using both all-argon and nitrogen-cooled plasmas at the cadmium 228.8 nm atom line ;

(ii) cadmium in aqueous solution using a nitrogen-cooled plasma at the cadmium 214.4 nm ion line;

(iii) manganese in coal slurries using both all-argon and nitrogen-cooled plasmas at the manganese 403.1 nm atom line.

The variable step-size simplex method, as previously applied to the inductively coupled plasma by Ebdon et al (223), was used to optimise plasma performance.

Table 20

Preferred operating conditions for observation of atomic and ionic emission lines in an all-argon plasma

Parameter	atom lines	ion line
Coolant gas flow /$\ell.min^{-1}$	8.7	5.0
Plasma gas flow/$\ell.min^{-1}$	14.0	14.0
Injector gas flow/$\ell.min^{-1}$	0.58	0.37
Power/kW	0.50	0.54
Observation height/mm above load coil	26	18

These conditions were used to determine :			
	copper	327.4 nm	vanadium 290.9 nm
	iron	372.0 nm	
	manganese	403.1 nm	
	nickel	341.8 nm	

6.3 RESULTS AND DISCUSSION

6.3.1 OPTIMISATION OF PLASMA PERFORMANCE FOR THE DETERMINATION OF CADMIUM

Initial studies were directed towards the determination of cadmium. Simplex optimisation procedures (using the criterion of signal to background ratio, SBR) were performed for aqueous solutions using the cadmium 228.8 nm atom line operating both all-argon and nitrogen-cooled plasmas. The optimum values obtained for the various flow-rates, power settings and observation heights are given in Table 21. Confirmation that these values were representative of the true optima was obtained using the method of univariate searches (223, 226, 227). In this procedure n - 1 of the n variables were held constant and SBR was evaluated throughout the range of the remaining variable. The results are shown for the all-argon plasma in Figs 20-24, and for the nitrogen-cooled plasma in Figs 25-29.

The shaded areas on these figures represent the final ranges of the values permitted for these variables at the termination of the simplex. The greatest differences between the two plasmas were noticed for the coolant flow-rates, power settings and observation heights. For the all argon plasma an elongated, conical fireball extending approximately 5 cm above the load coil was observed. For the nitrogen-cooled plasma the low coolant-flow and the quenching effect of the nitrogen combined to generate a more compact and intense fireball extending only 1-2 cm above the load coil. As a result lower observation heights were preferred for this plasma. The higher power preferred for the nitrogen-cooled plasma is in agreement with the reported results of other workers (223, 228).

The absolute emission signal in the optimised nitrogen-cooled plasma was approximately three times more intense than in the optimised all-argon plasma. However, the greater background of the nitrogen-cooled plasma resulted in a much reduced SBR ratio (0.024) relative to the all-argon plasma (SBR 0.34). These results were in keeping with the general trends outlined previously. In order to investigate this approach further, the cadmium ion line at 214.4 nm was optimised using a nitrogen-cooled plasma. As the simplex procedure progressed it became increasingly clear that SBR's were relatively insensitive to the nitrogen flow rate. At very low flows of nitrogen, SBR increased as the plasma approximated more closely to an all-argon plasma. A plot of SBR versus nitrogen flow rate is shown in Fig. 30. Point B is correctly identified as providing the maximum SBR within the initial limits of the simplex. Nitrogen flow rates lower than those at point A produced unstable plasmas and were outside the limits of the simplex. The results are in keeping with the suggestion that ion line emissions should be more intense in an all-argon plasma. At the end of these experiments it was concluded that the sensitivity available for cadmium with the instrumentation to hand (detection limits <u>ca</u>. 1 $\mu g.ml^{-1}$) was insufficient to determine cadmium at the levels typically present in coal (<u>ca</u>. 0.2 $\mu g.g^{-1}$). It was decided therefore that initial investigations into slurry analysis would be performed on the determination of manganese, an element considerably more plentiful in most coals.

Table 21

Optimum operating conditions for the determination of cadmium using all-argon and nitrogen-cooled plasmas

	Plasma type	
Parameter	all-argon	nitrogen-cooled
Coolant gas flow/ℓ.min^{-1}	4.6 (Ar)	3.2 (N_2)
Plasma gas flow/ℓ.min^{-1}	10.9	11.4
Injector gas flow/ℓ.min^{-1}	0.31	0.31
Power/kW	0.60	1.0
Observation height/mm above load coil.	20	13
SBR for an aqueous solution of 1 μg.mℓ$^{-1}$ of cadmium	0.340	0.024

SBR measured at the cadmium 228.8 nm atom line.

<u>Fig. 20</u> Cd (I) 228.8 nm Univariate search: Coolant flow - all-argon plasma

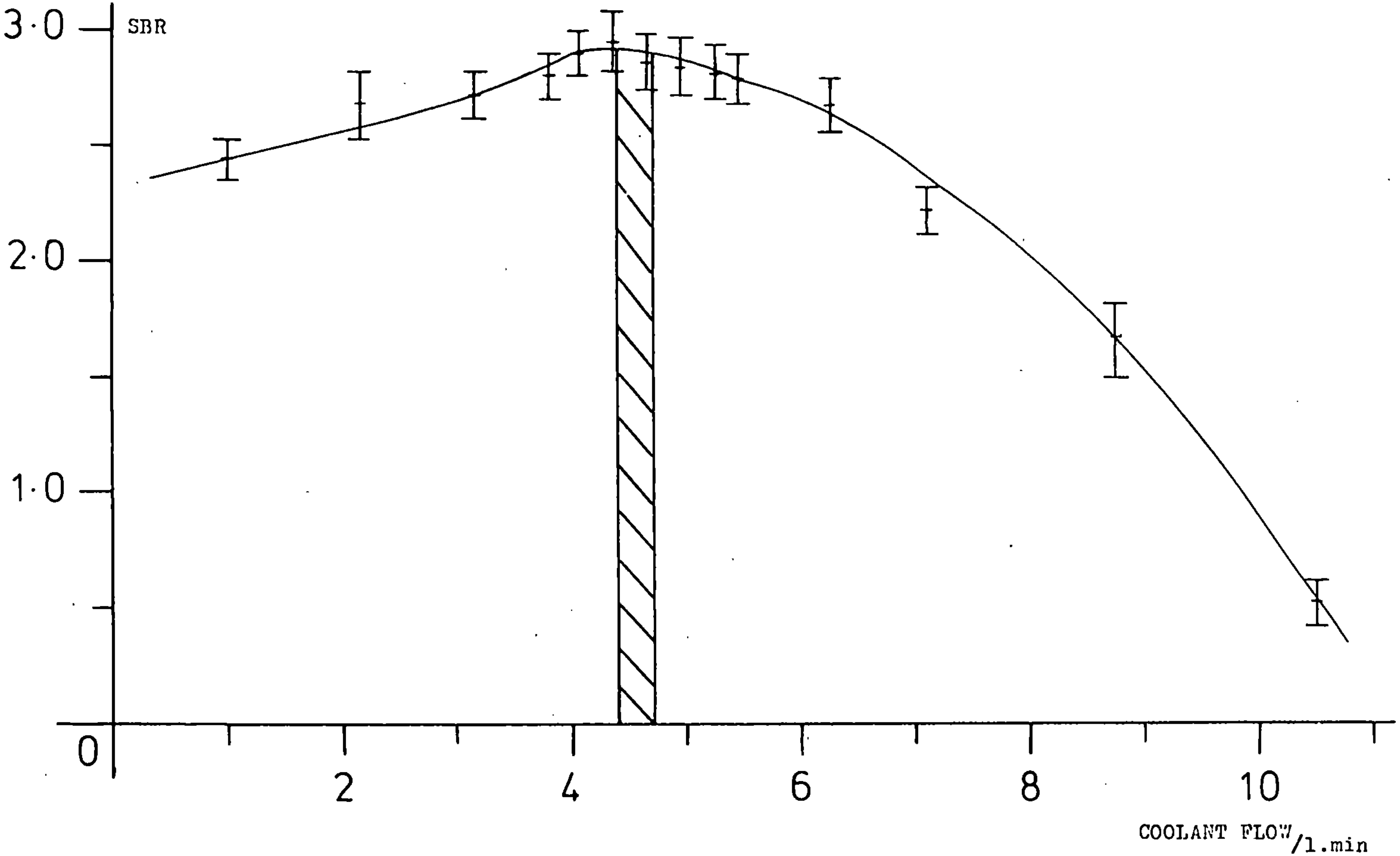


Fig. 21 Cd (I) 228.8 nm Univariate search: Plasma flow - all-argon plasma

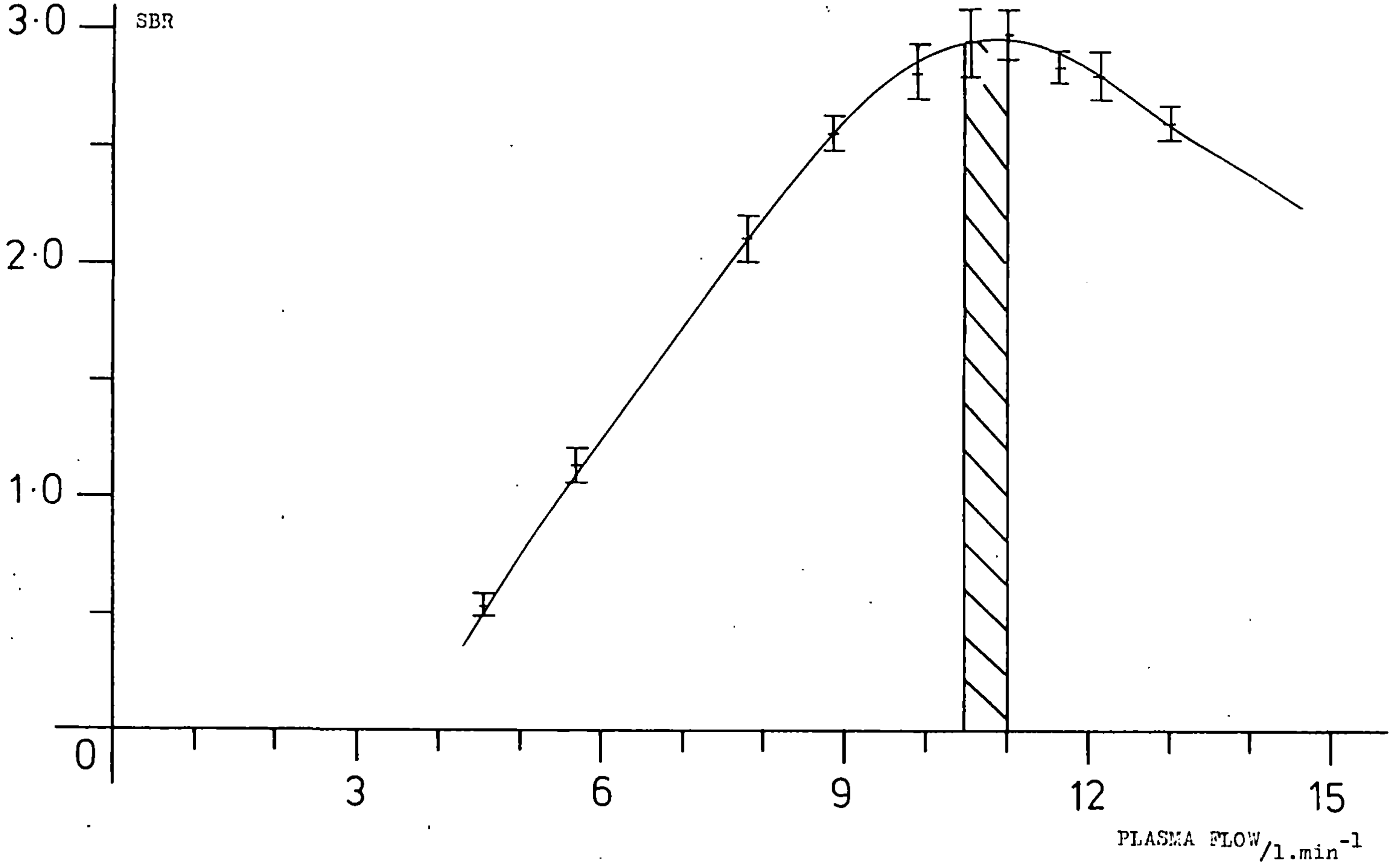


Fig. 22 Cd (I) 228.8 nm Univariate search: Injector flow - all-argon plasma

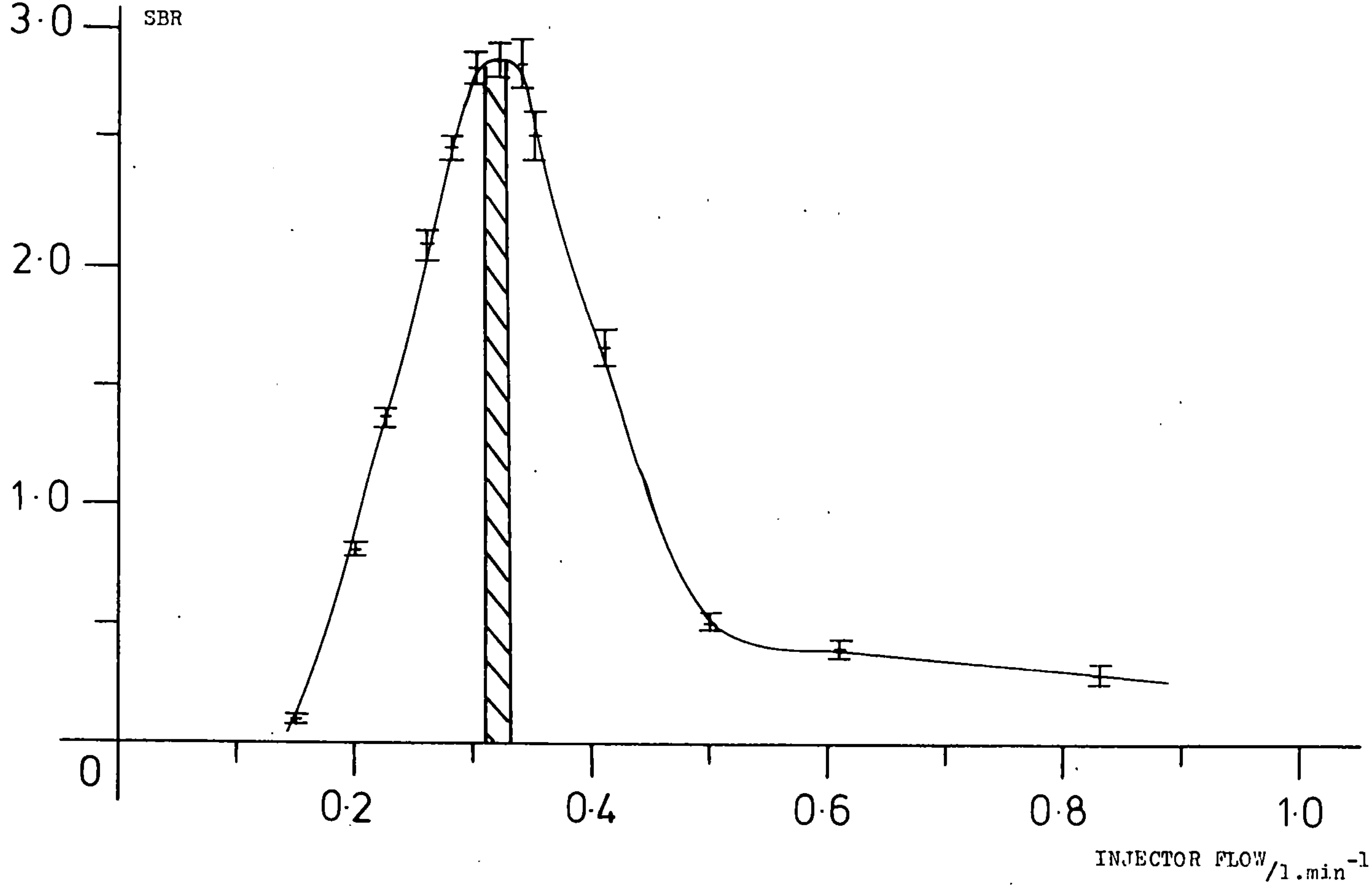


Fig. 23 Cd (I) 228.8 nm Univariate search: Viewing height - all-argon plasma

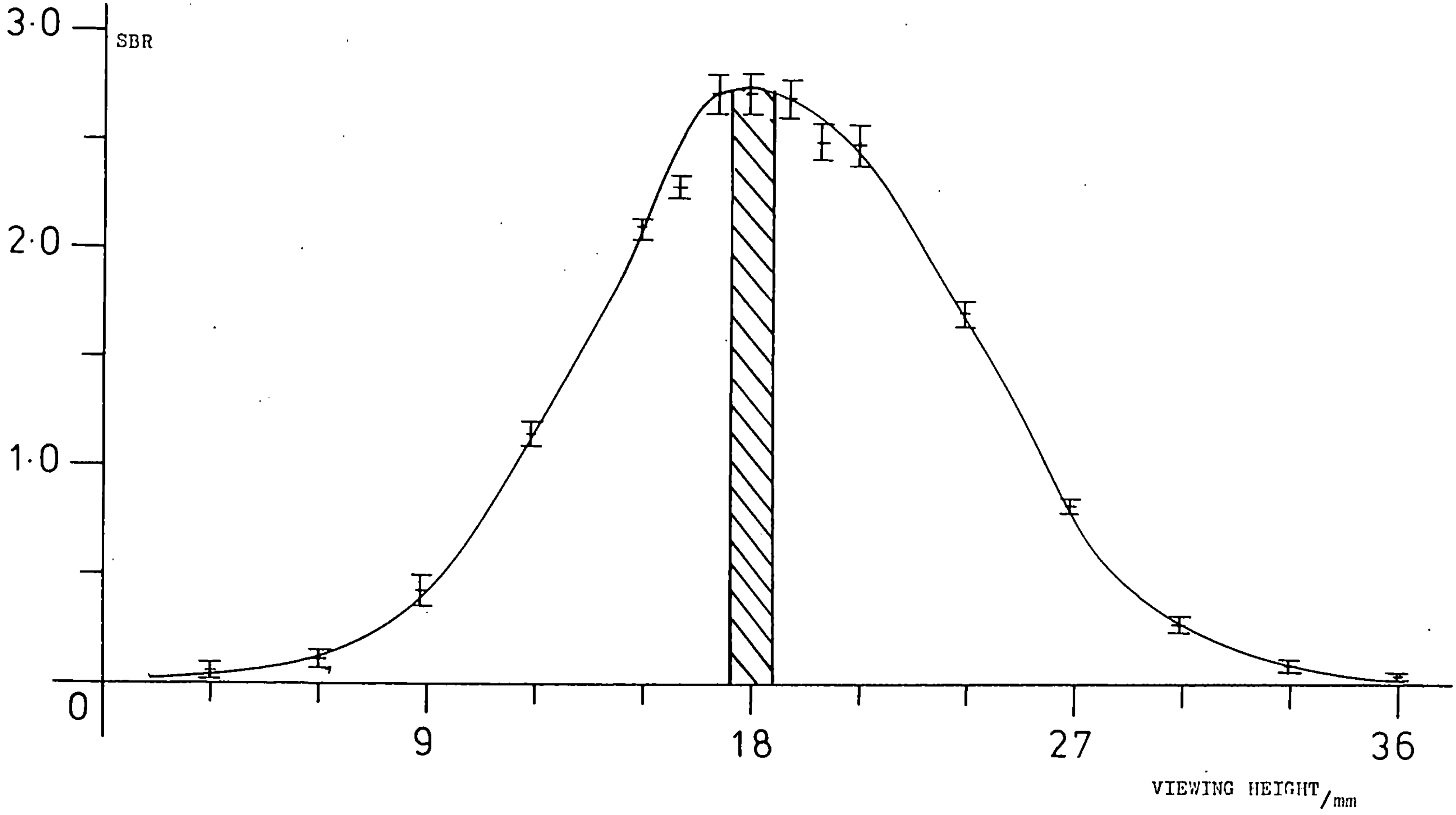


Fig. 24 Cd (I) 228.8 nm Univariate search: Power - all-argon plasma

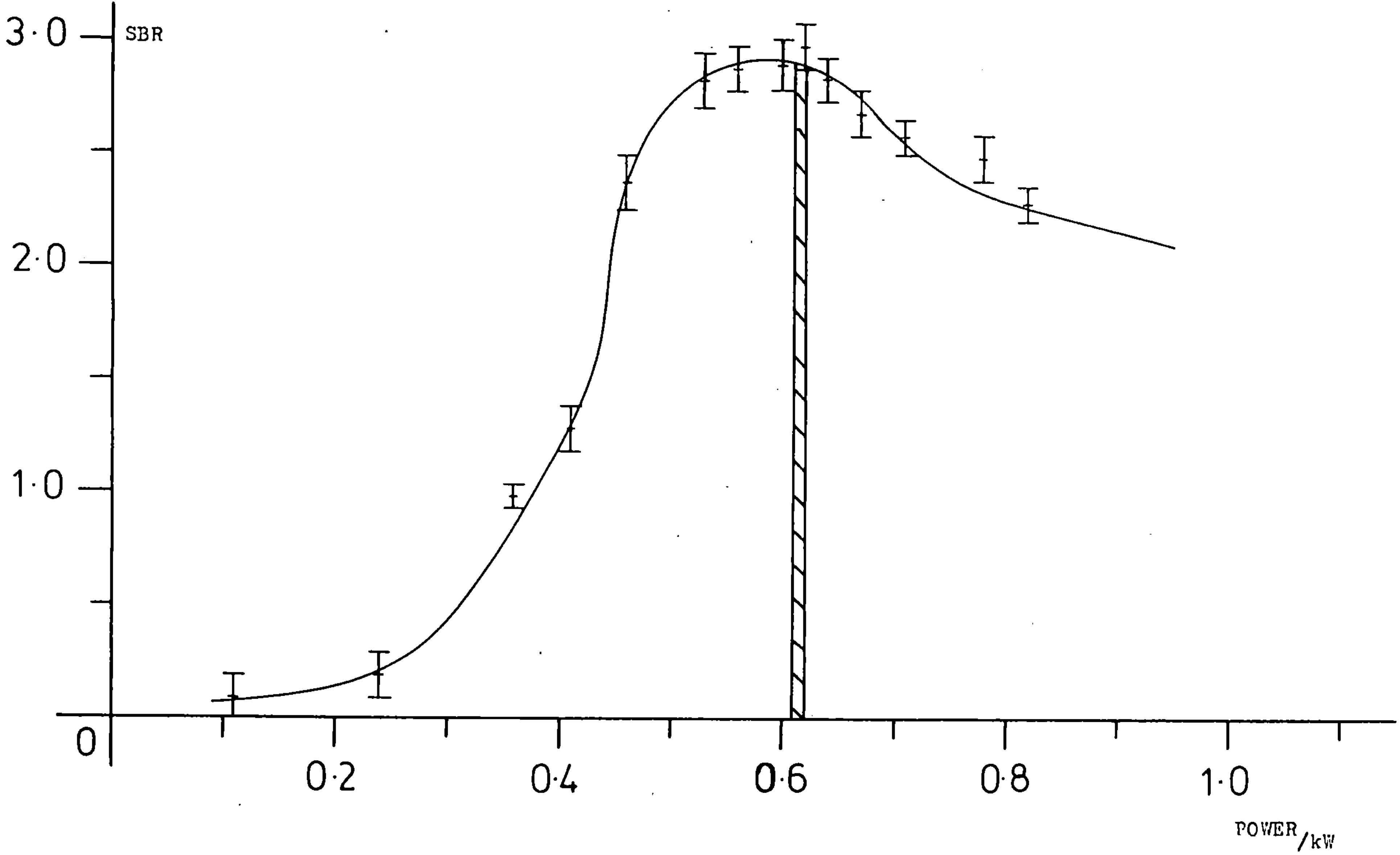


Fig. 25 Cd (I) 228.8 nm Univariate search; Nitrogen coolant flow - nitrogen cooled plasma

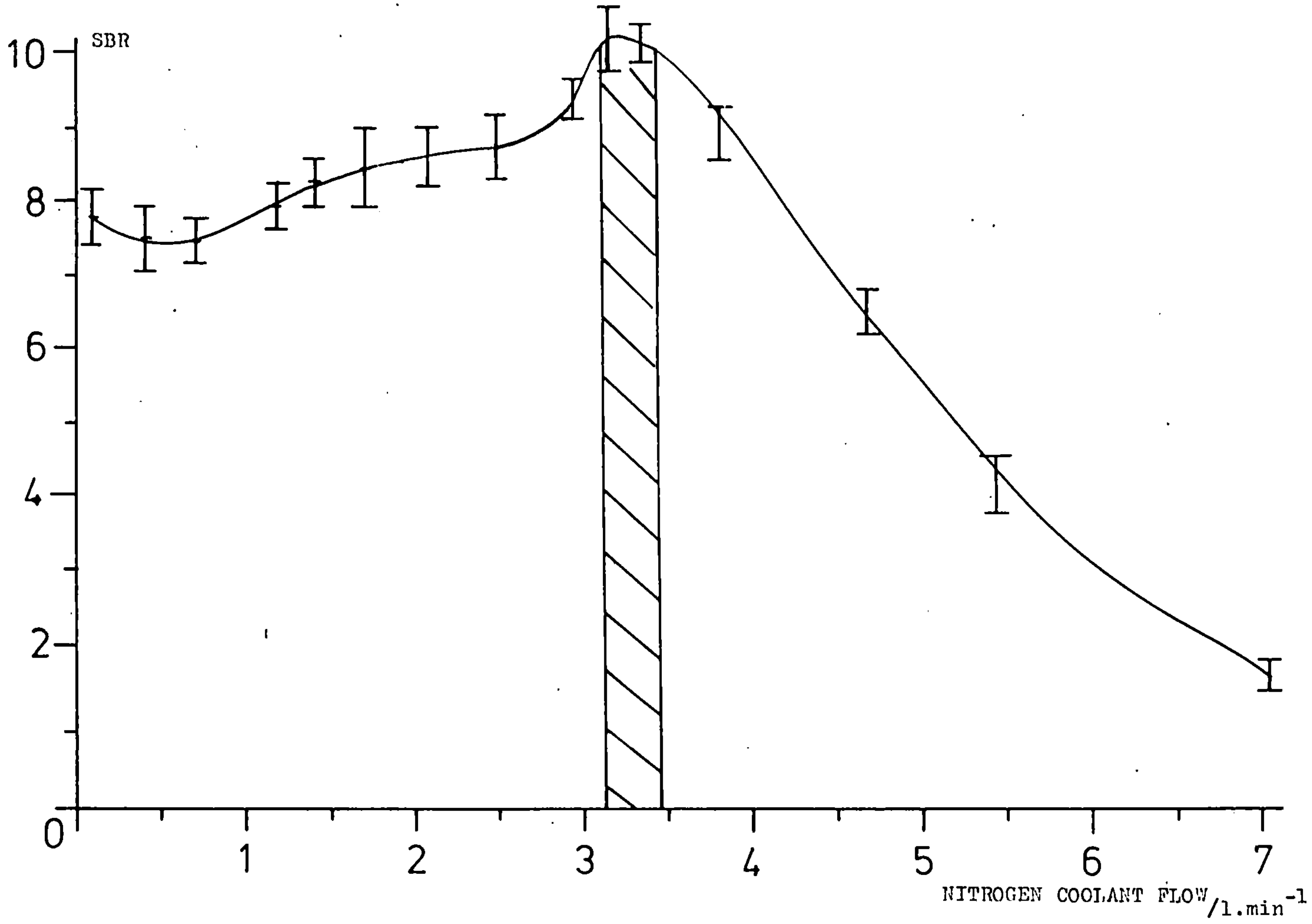


Fig. 26 Cd (I) 228.8 nm Univariate search; Plasma gas flow - nitrogen cooled plasma

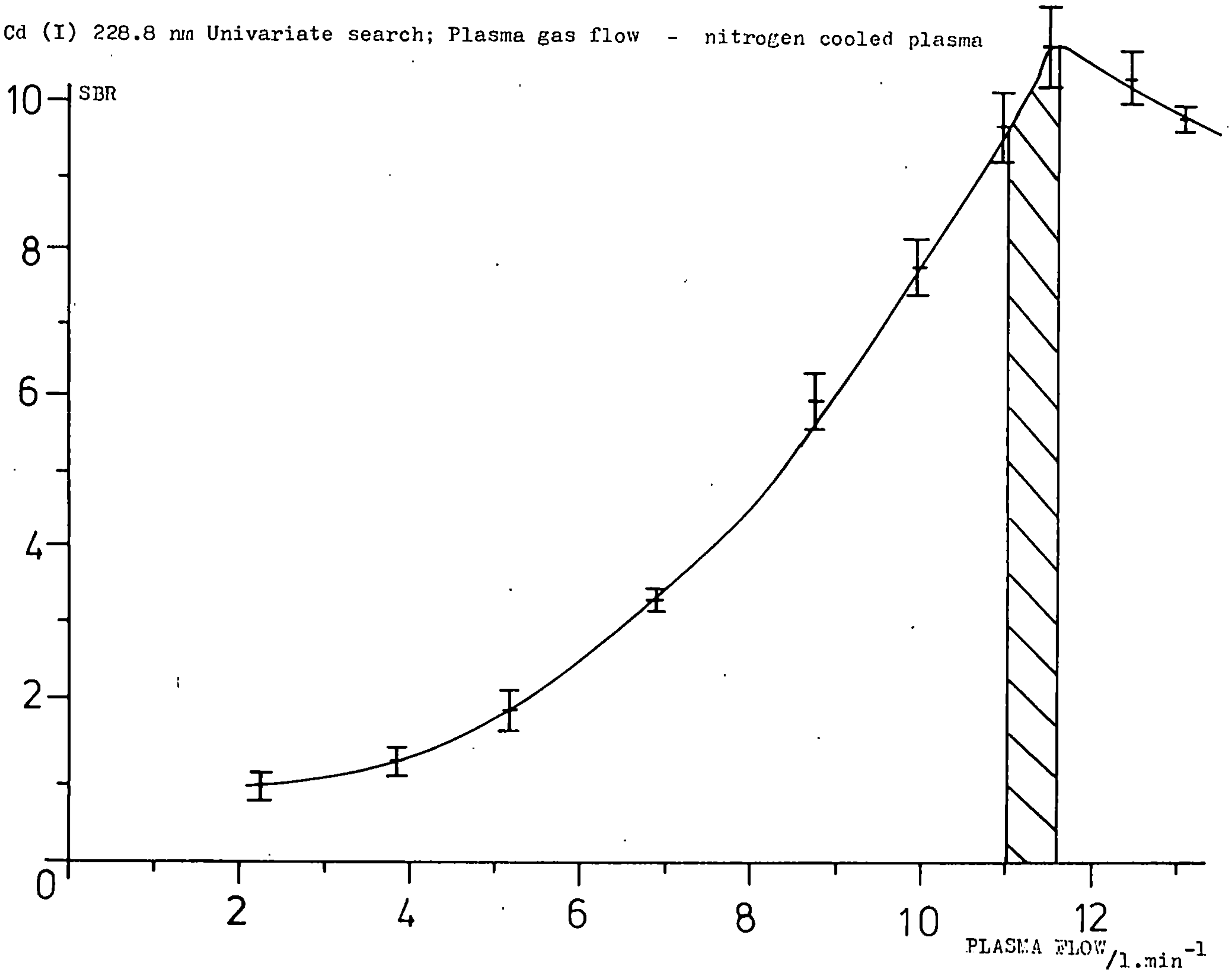


Fig. 27 Cd (I) 228.8 nm Univariate search; Injector flow - nitrogen cooled plasma

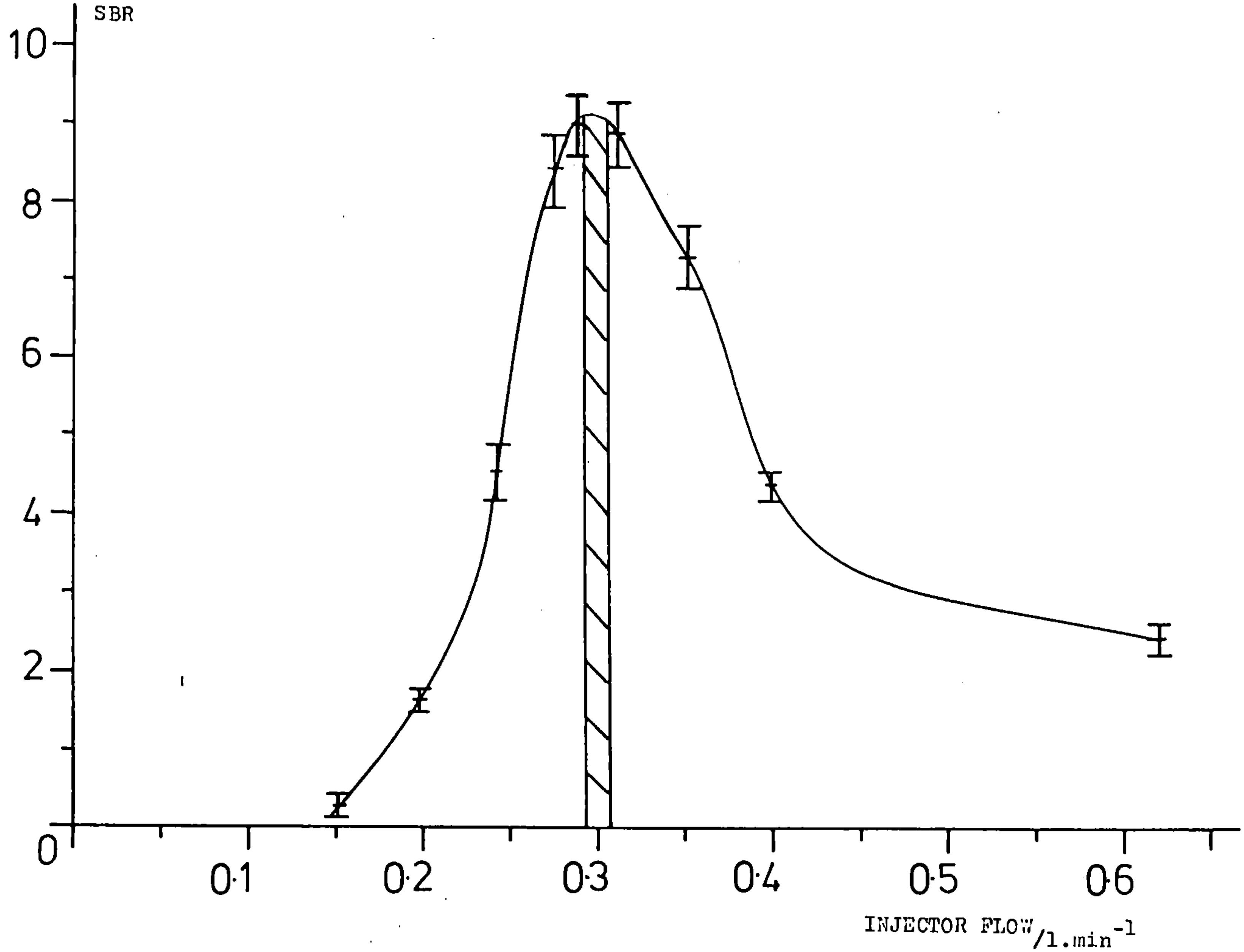


Fig. 28 Cd (I) 228.8 nm Univariate search; Viewing height - nitrogen cooled plasma

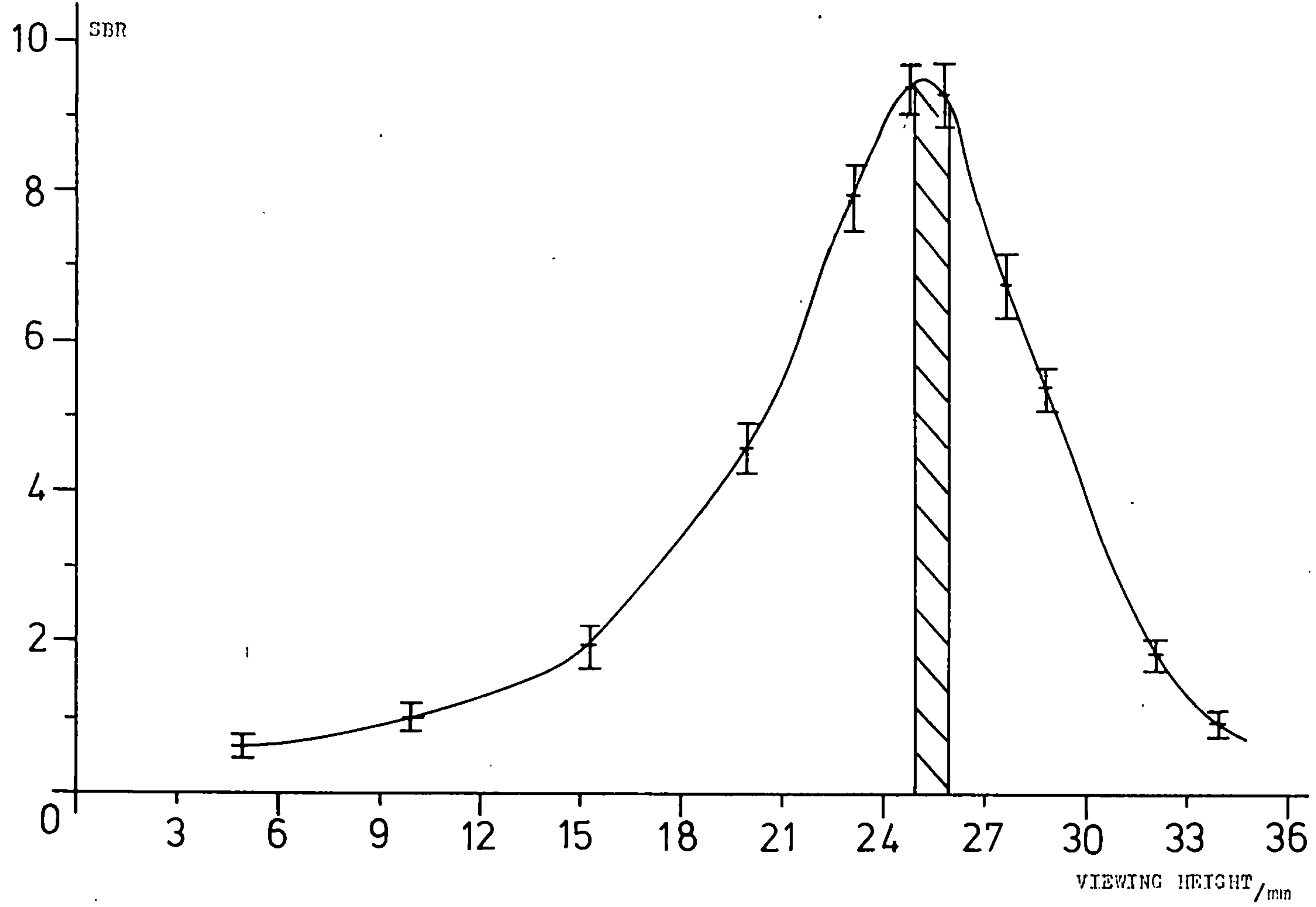


Fig. 29 Cd (I) 228.8 nm Univariate search; Power - nitrogen cooled plasma

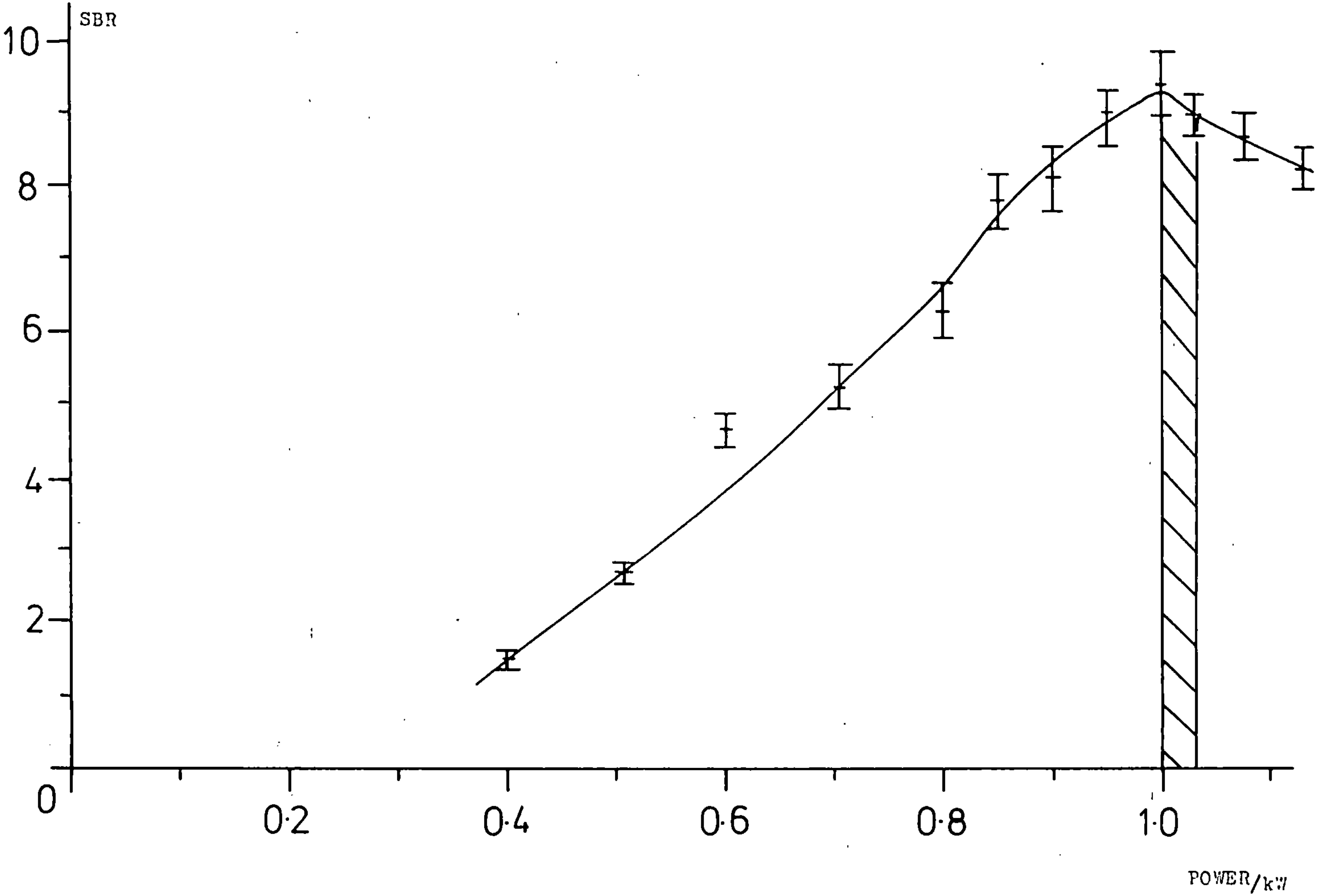
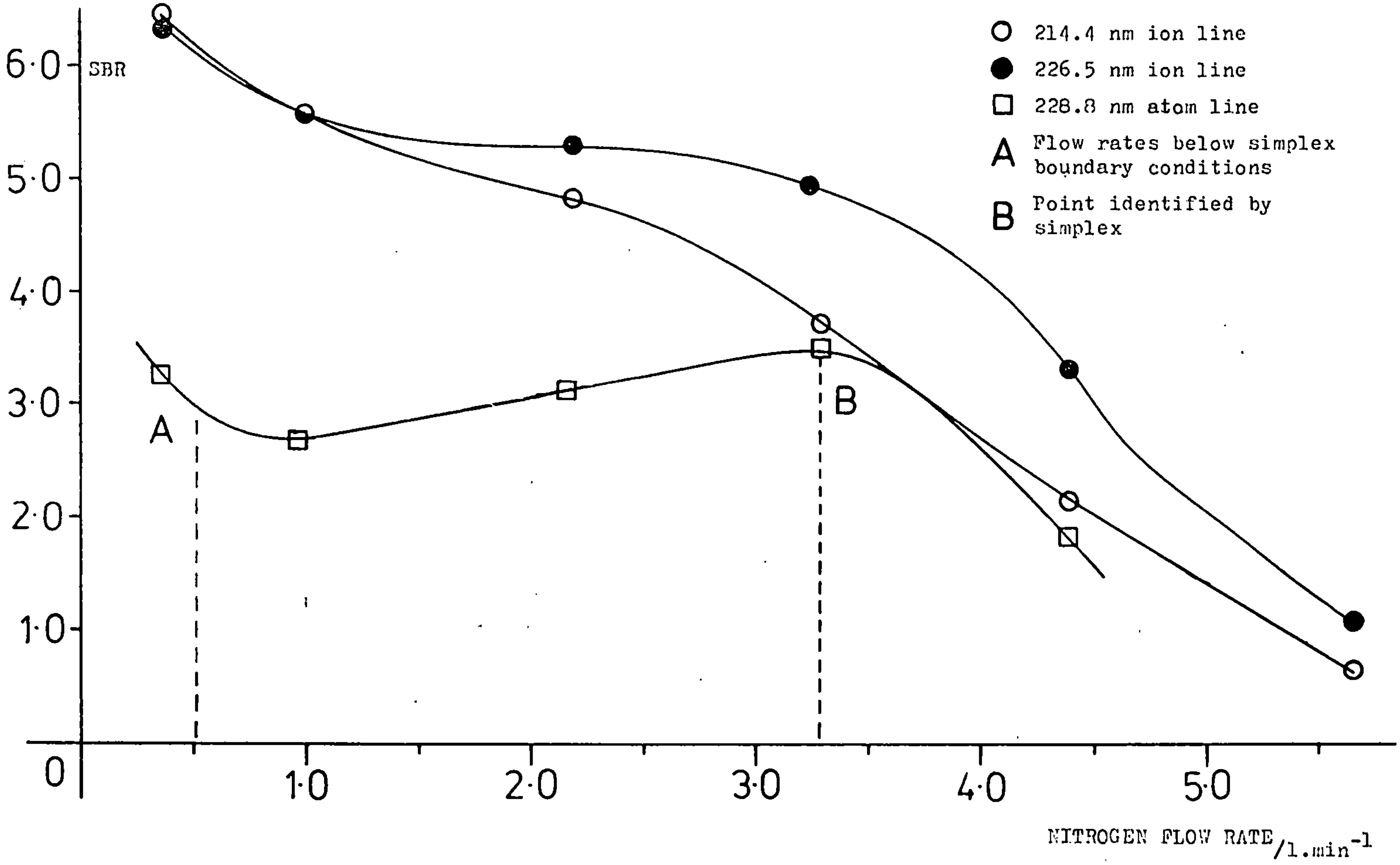


Fig. 30 Variation of cadmium ion line and atom line SBR's with increase in nitrogen coolant flow rate



6.3.2 OPTIMISATION OF PLASMA PERFORMANCE FOR SLURRY ATOMISATION

The initial operating conditions selected were those reported previously (227) when this instrumentation had been used to determine manganese in a range of metallurgical samples. The parameters investigated were those considered likely to have the greatest effect on SBR, i.e. slurry concentration, sample pumping rate and particle size. Slurry concentrations and sample pumping rates were varied in the ranges 1-25% $^{m}/v$ and 0.67-5.0 ml.min^{-1} respectively. Particle sizes were in the ranges 250-125 µm, 106-63 µm, 63-53 µm, 53-38 µm and <38 µm. Both types of plasma were used and the results are shown in Figs 31-43. From these results the following general conclusions were drawn.

For the all-argon plasma, SBR increased rectilinearly with increasing slurry concentration up to approximately 20% $^{m}/v$. Deviation from linearity was approximately 5% at 25% $^{m}/v$. For the nitrogen-cooled plasma SBR increases linearly (slope = 0.4) up to slurry concentrations of approximately 10% $^{m}/v$. While the absolute emission signal was greater in the nitrogen-cooled plasma, the increased background level again resulted in inferior SBR and this is reflected in Figs 31-43.

The signal to background ratio increased with increase in sample pumping rate, more so for the all-argon plasma than for the nitrogen-cooled plasma which showed little change in SBR at sample pumping rates greater than 2.0 ml.min^{-1}. For the all-argon plasma, as the slurry concentration was increased, the range of linearity of response was extended to higher pumping rates.

Particle size was a critical factor in determining the magnitude of the emission signal. Particles less than 38 µm produced the largest signals, while those in the range 38-53 µm produced signals at least twice the size of particles in the range 53-63 µm. Particles greater than 70 µm contributed very little to the overall SBR, probably due to insufficiently rapid and/or complete atomisation of such relatively large particles.

To ensure that the responses from different particle size fractions were not due to segregation of the sample during grinding, samples from each size fraction were analysed for manganese content using flame atomic absorption spectrometry (section 6.2.3.1, page 163). The results showed no significant differences between the various size fractions. An average value of 90 ± 1.5 $\mu g.g^{-1}$ was obtained and this agreed fairly well with an independent analysis figure of 99 $\mu g.g^{-1}$, determined by neutron activation analysis.

Fig. 31 SBR as a function of sample pumping rate for a 1% $^{m}/_{v}$ coal slurry

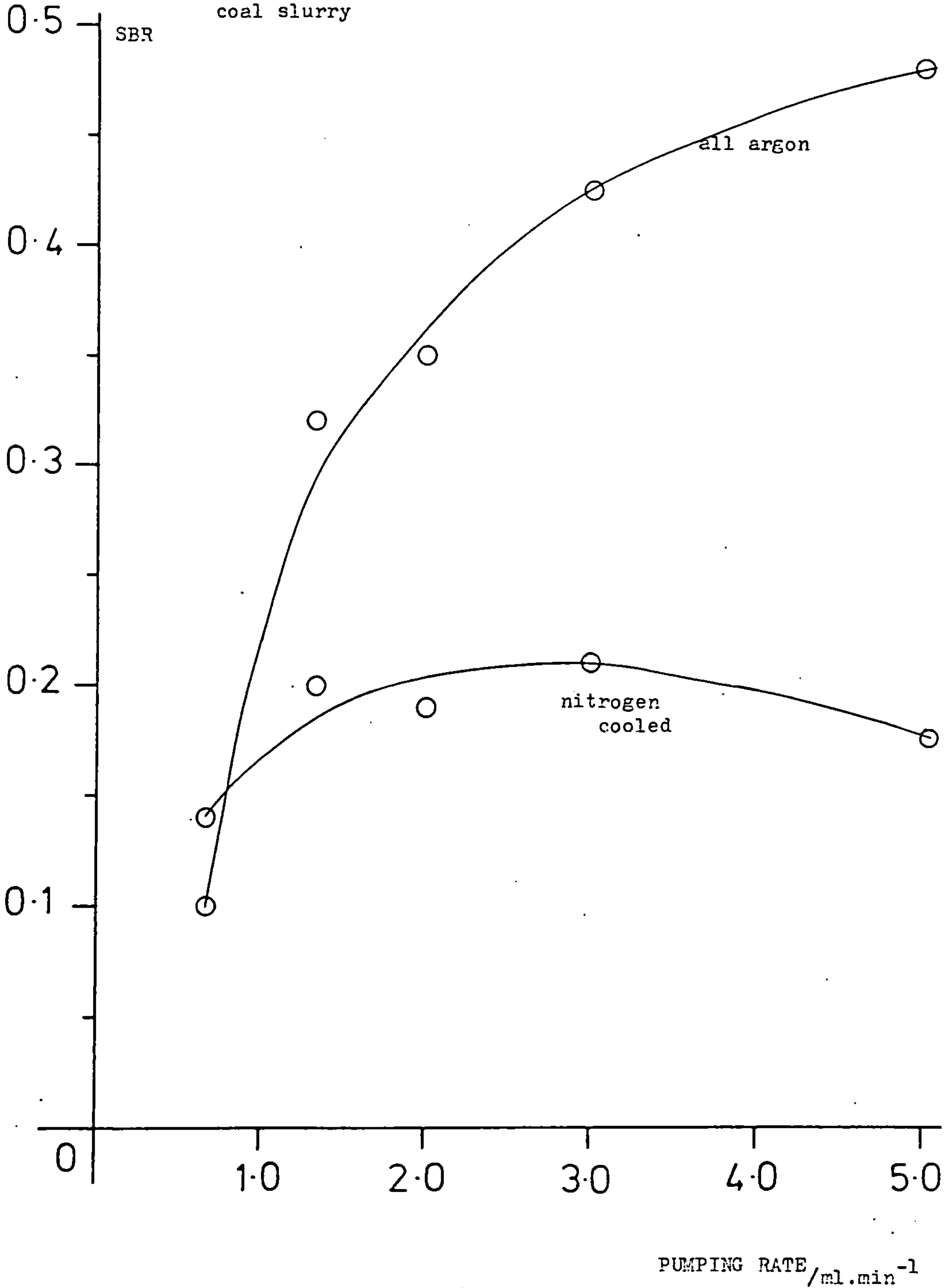


Fig. 32 SBR as a function of sample pumping rate for a 4% $^m/v$ coal slurry

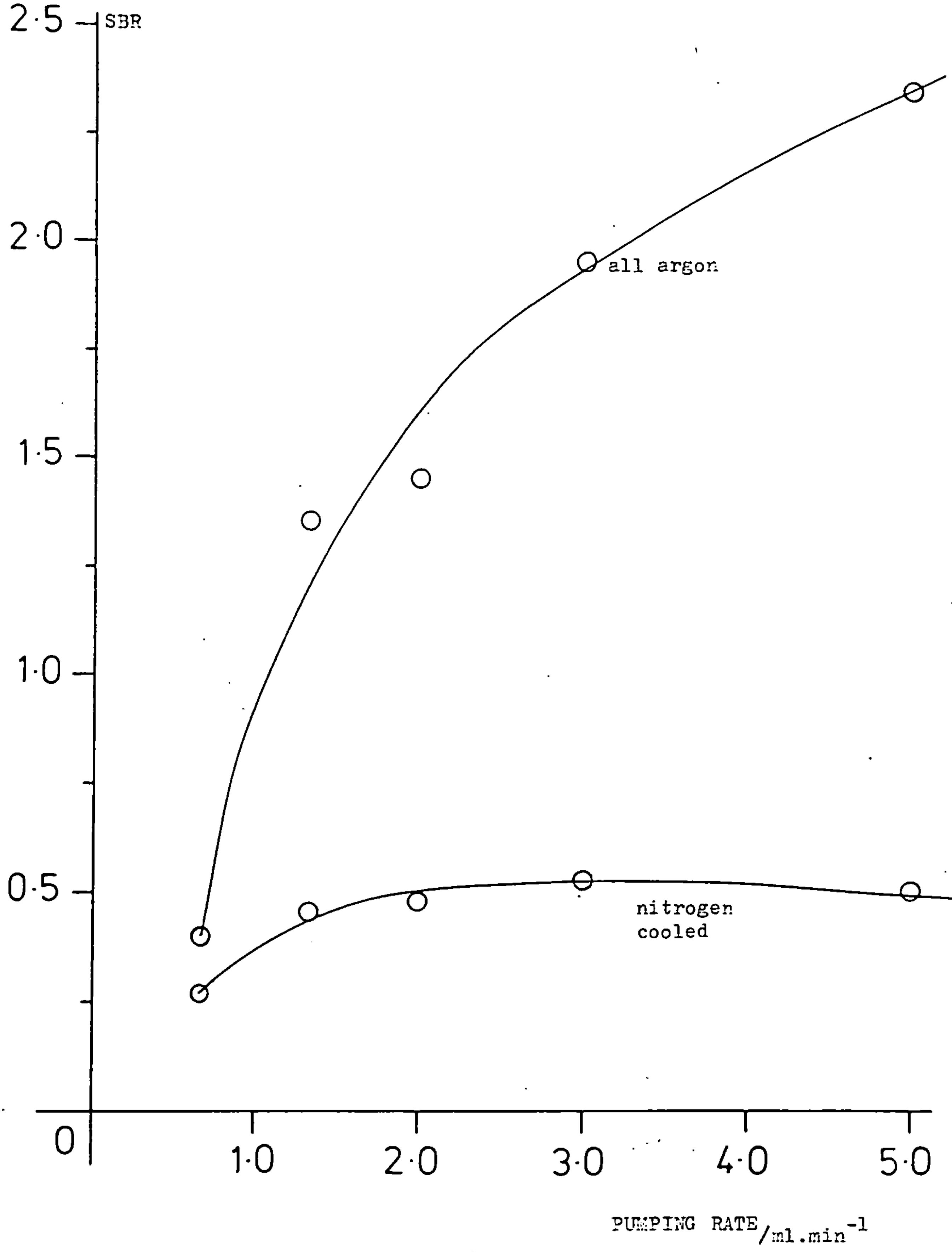


Fig. 33 SBR as a function of sample pumping rate for a 10% $^m/v$ coal slurry

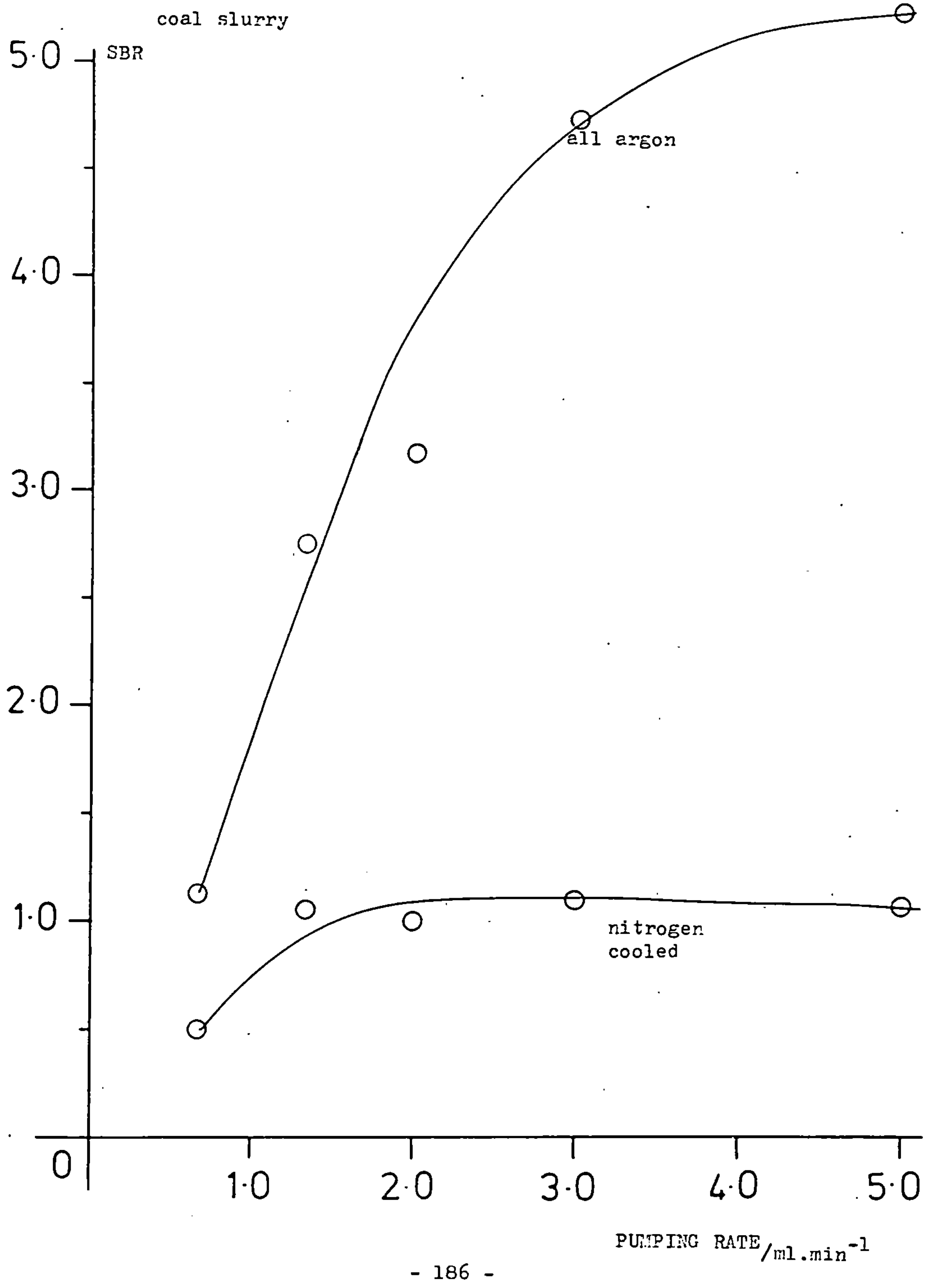


Fig. 34 SBR as a function of sample pumping rate for a 25% $^m/_v$ coal slurry

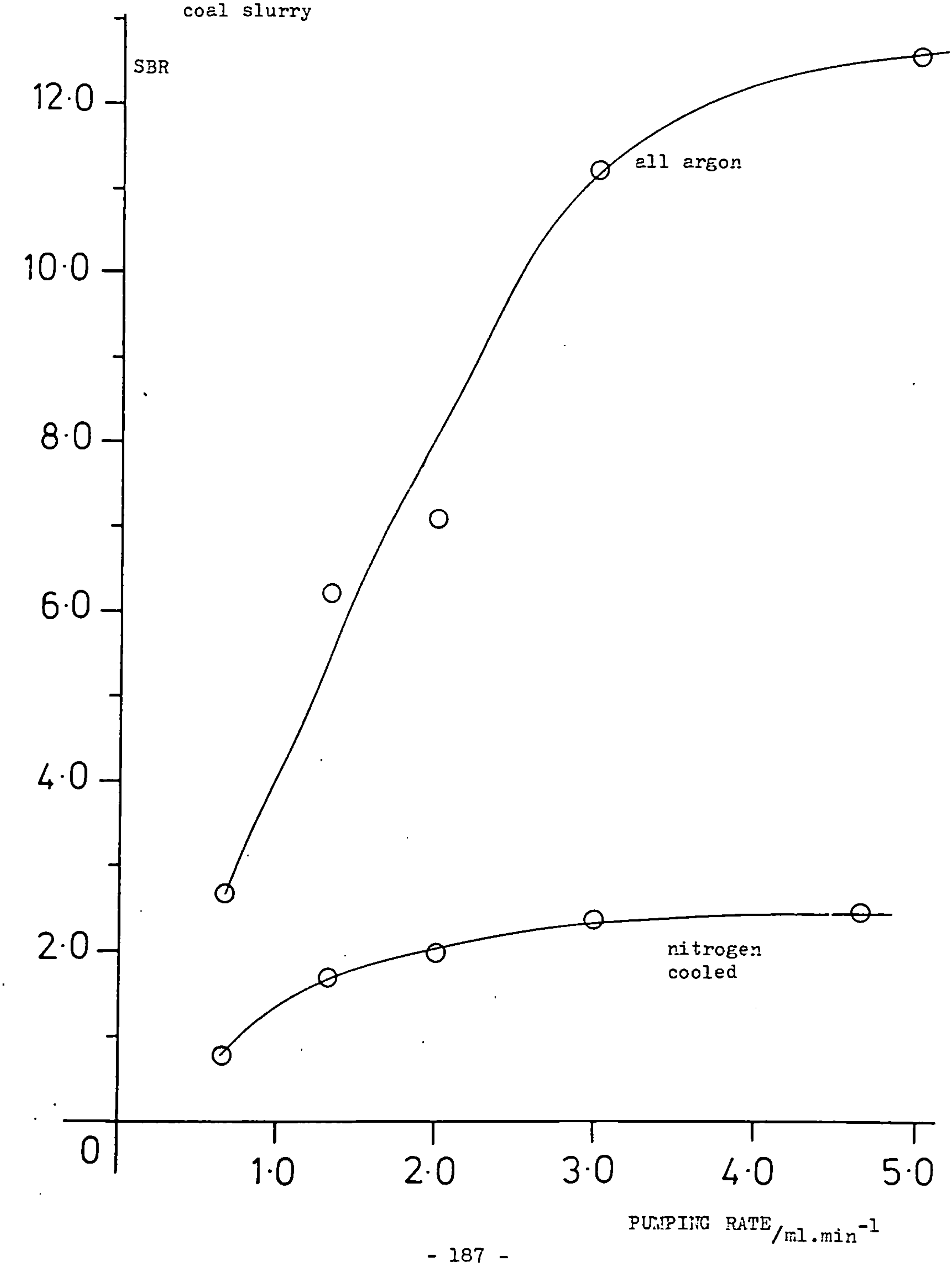
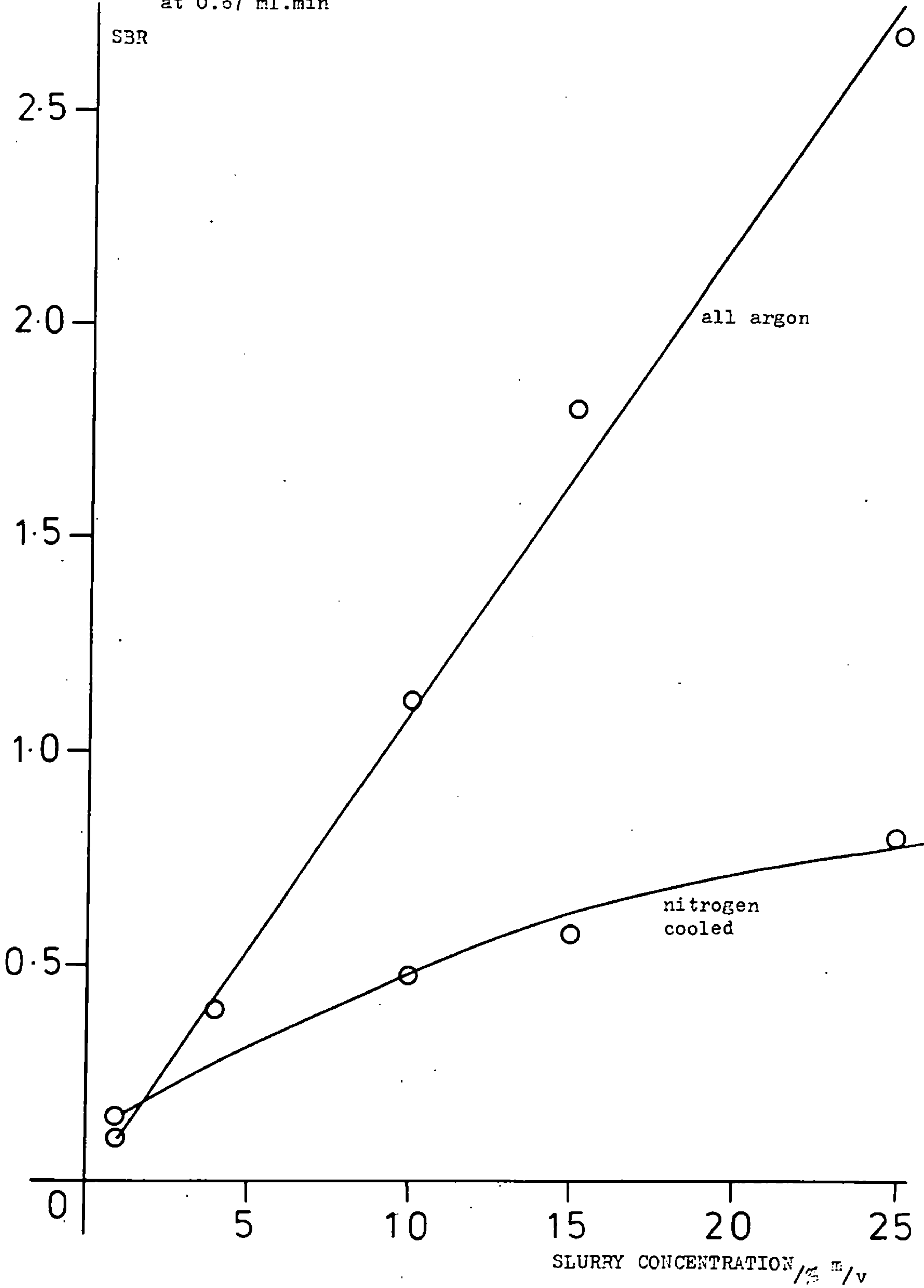


Fig. 35 SBR as a function of slurry concentration, pumping sample at 0.67 ml.min^{-1}



<u>Fig. 36</u> SBR as a function of slurry concentration, pumping sample at 1.4 $ml.min^{-1}$

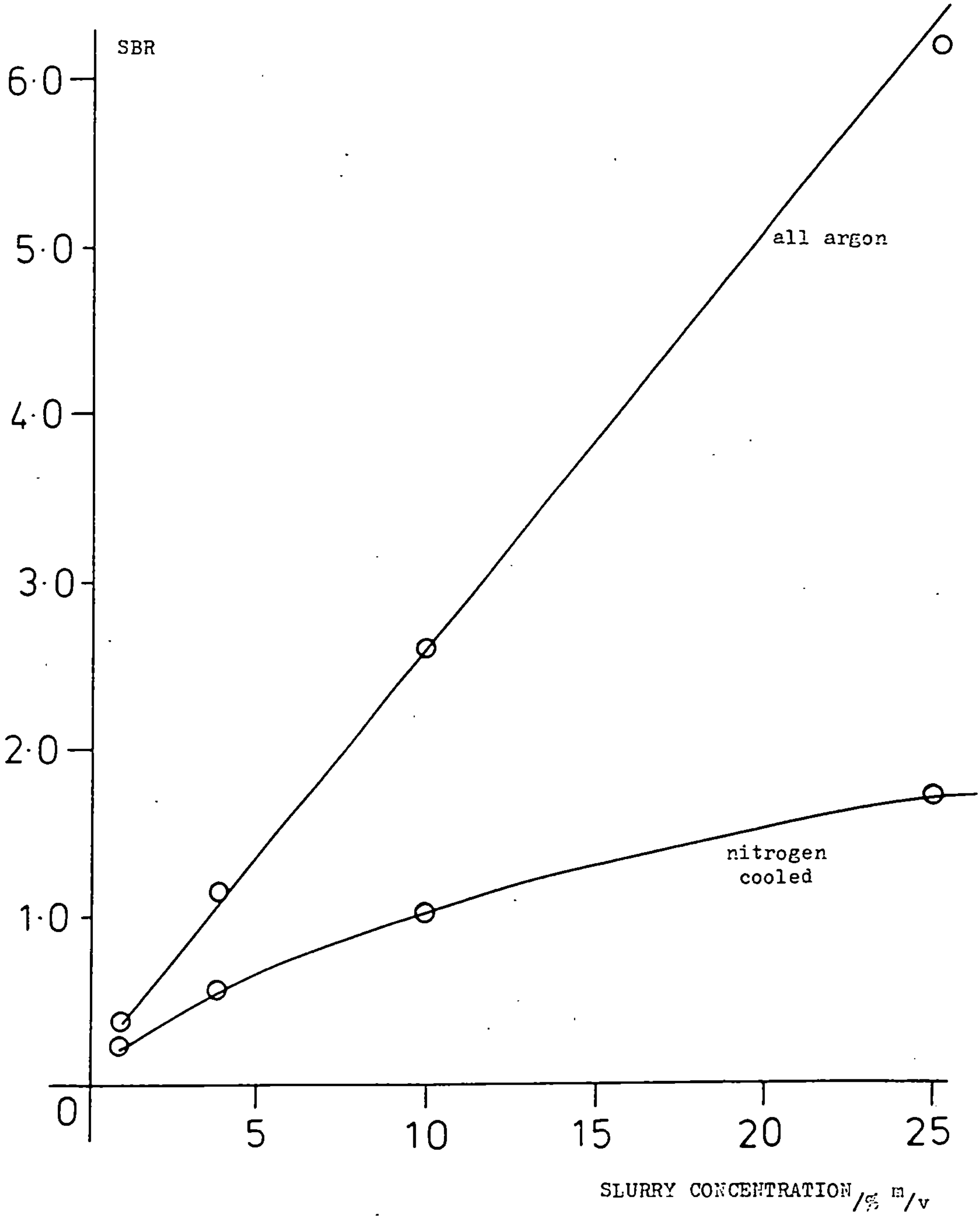


Fig. 37 SBR as a function of slurry concentration, pumping sample at 2.0 $ml.min^{-1}$

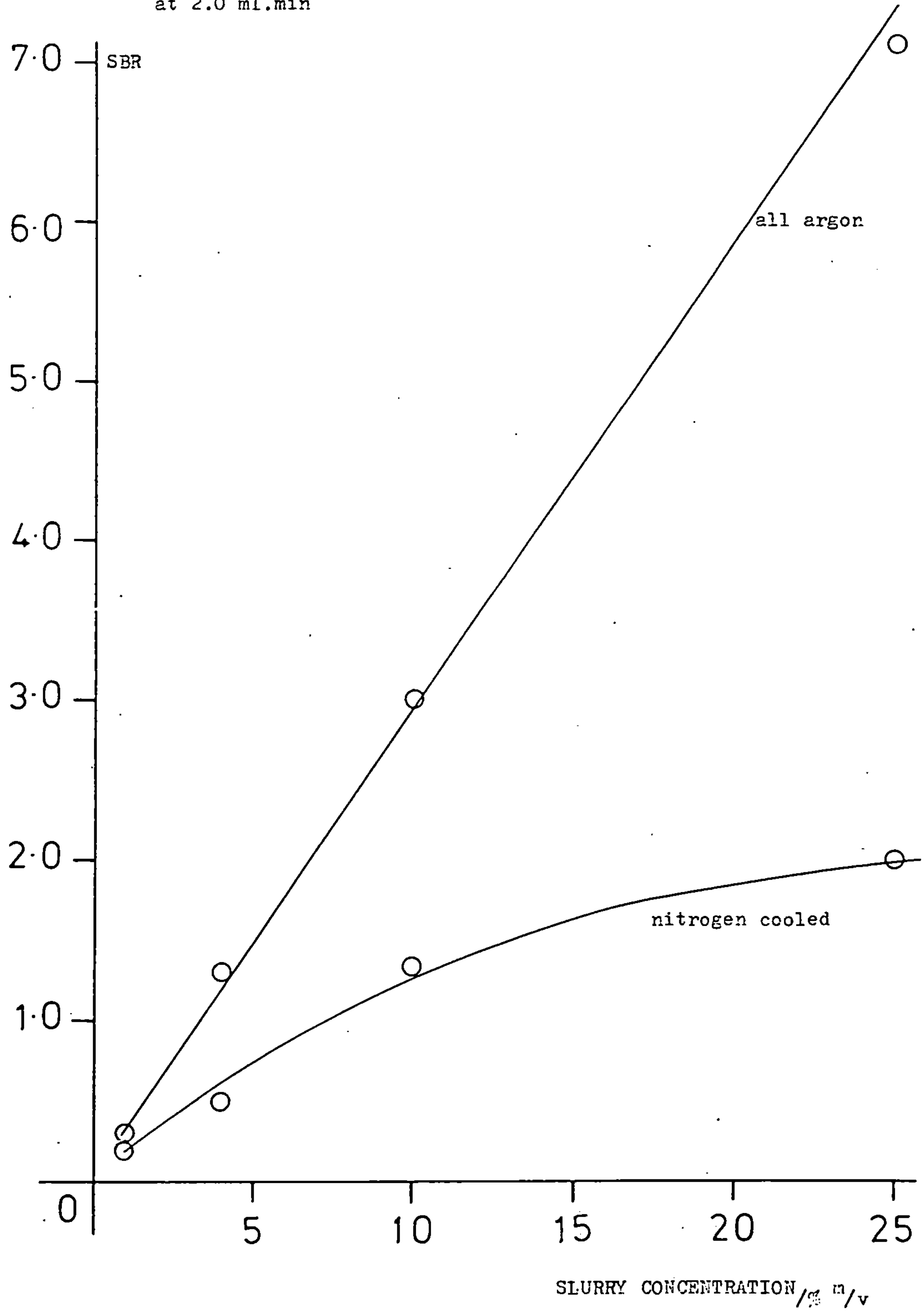


Fig. 38 SBR as a function of slurry concentration, pumping sample at 3.0 $ml.min^{-1}$

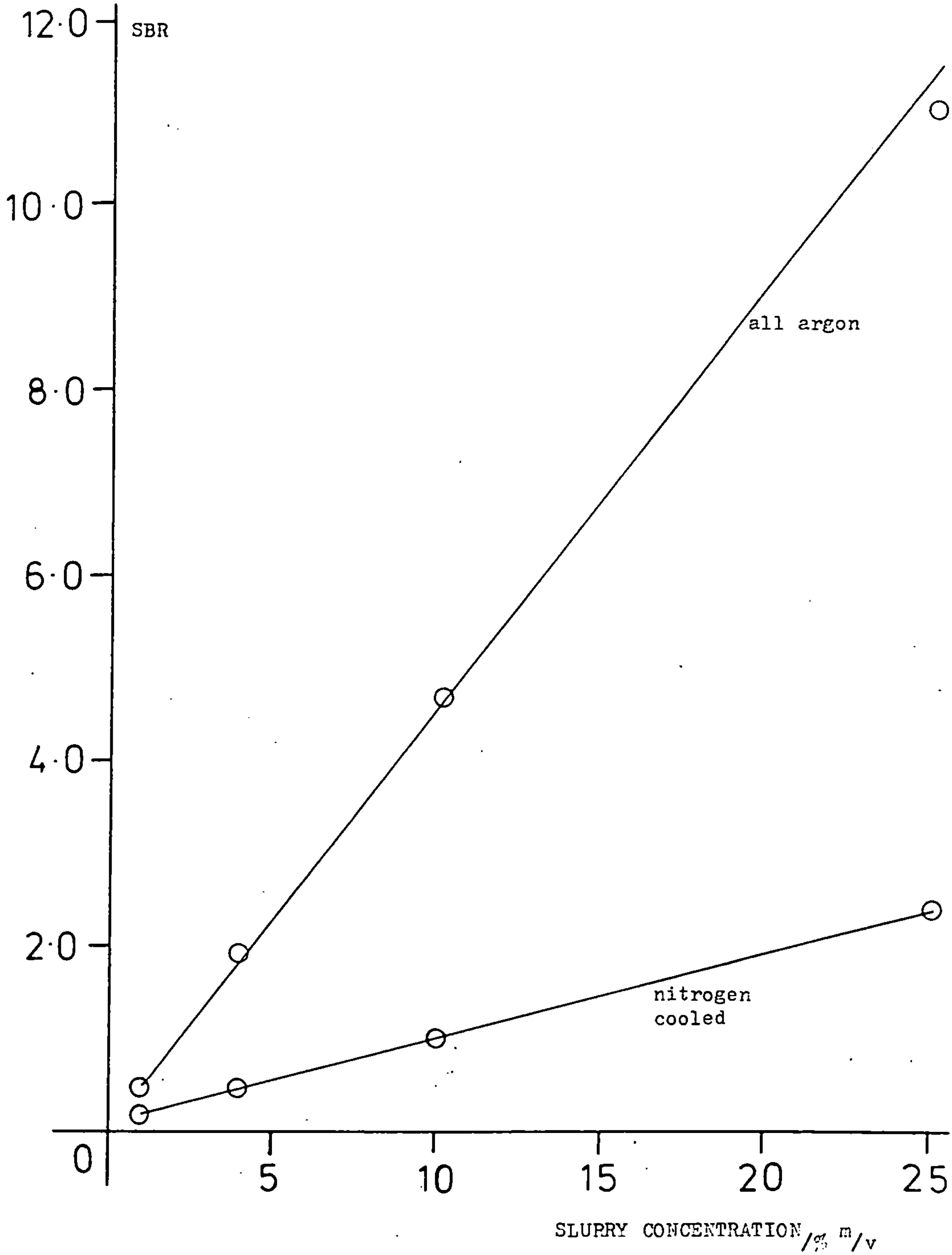


Fig. 39 SBR as a function of slurry concentration, pumping sample at 5.0 ml.min^{-1}

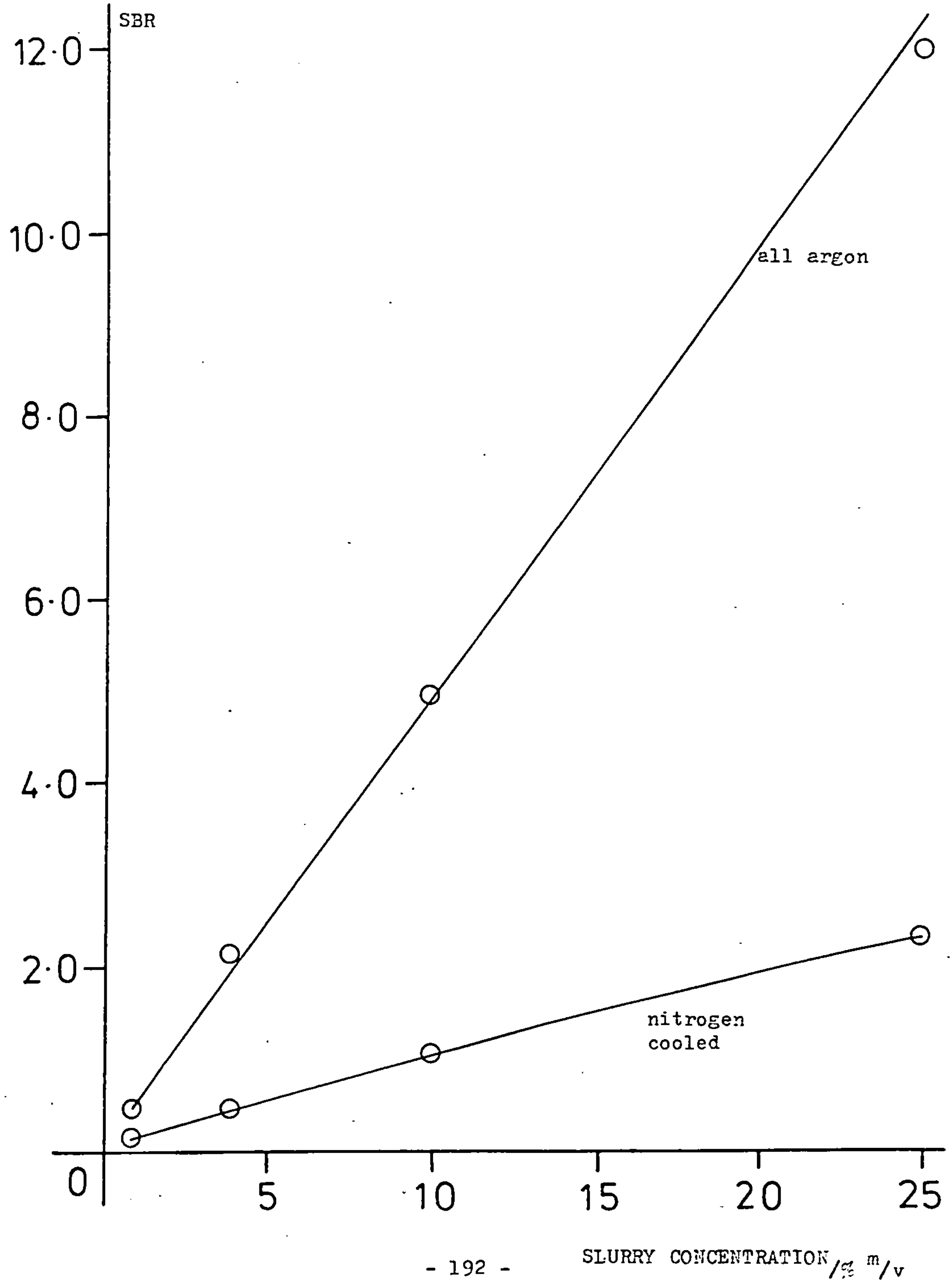


Fig. 40 SBR as a function of particle size, pumping a 1% m/v slurry at 2.0 ml.min^{-1}

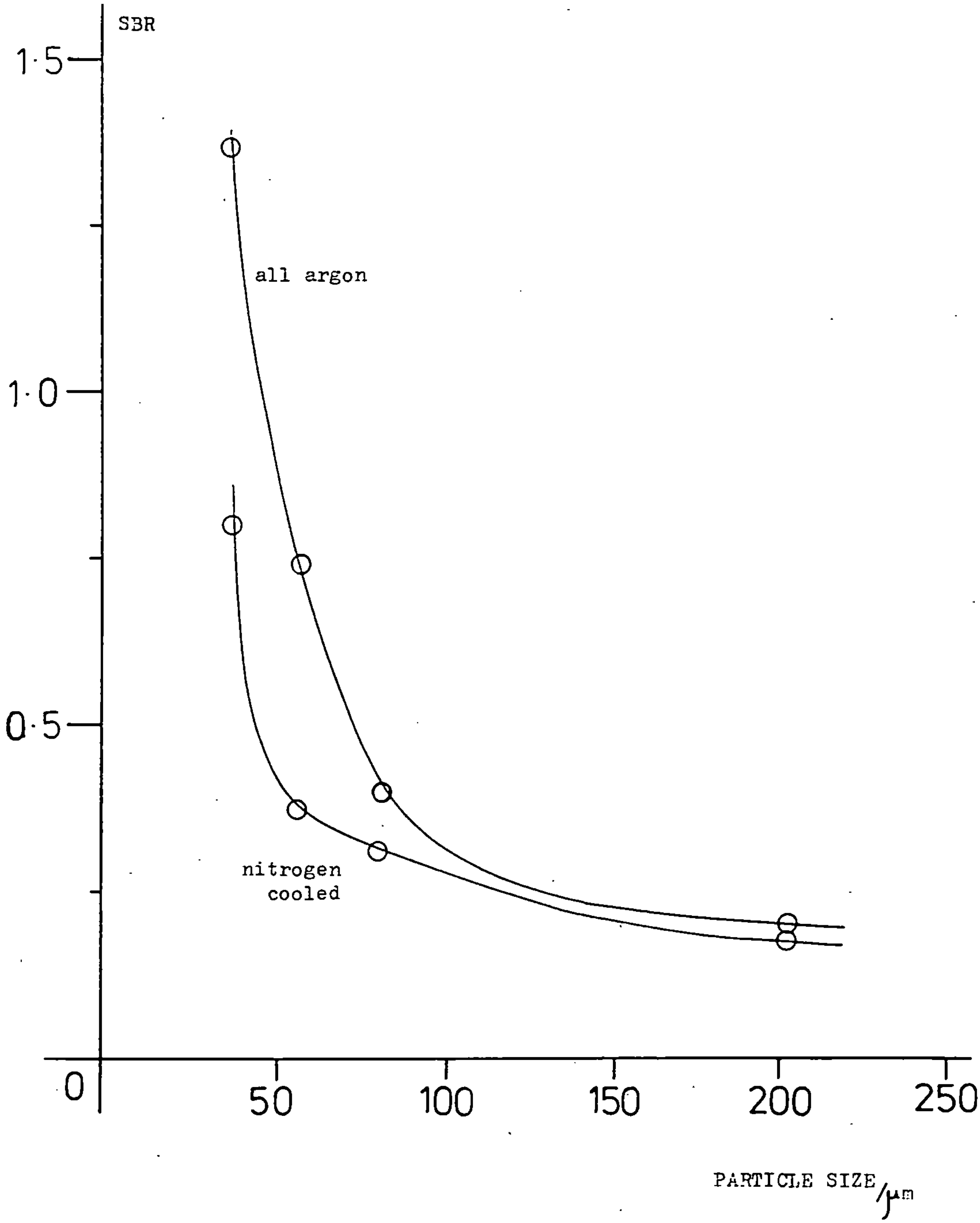


Fig. 41 SBR as a function of particle size, pumping at 4% $^m/v$ slurry at 2.0 ml.min^{-1}

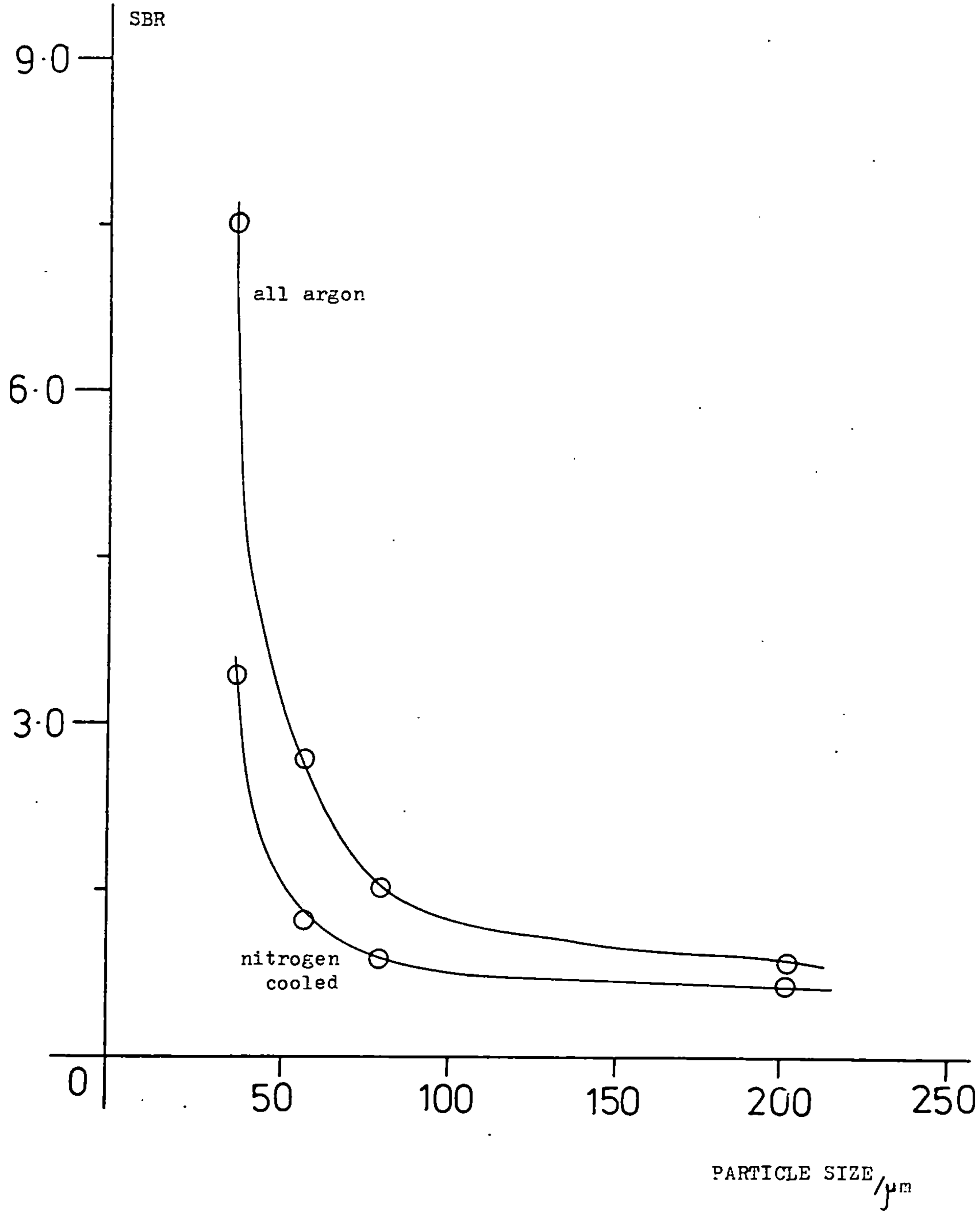


Fig. 42 SBR as a function of particle size, pumping a 1% $^{m}/v$ slurry at 5.0 ml.min^{-1}

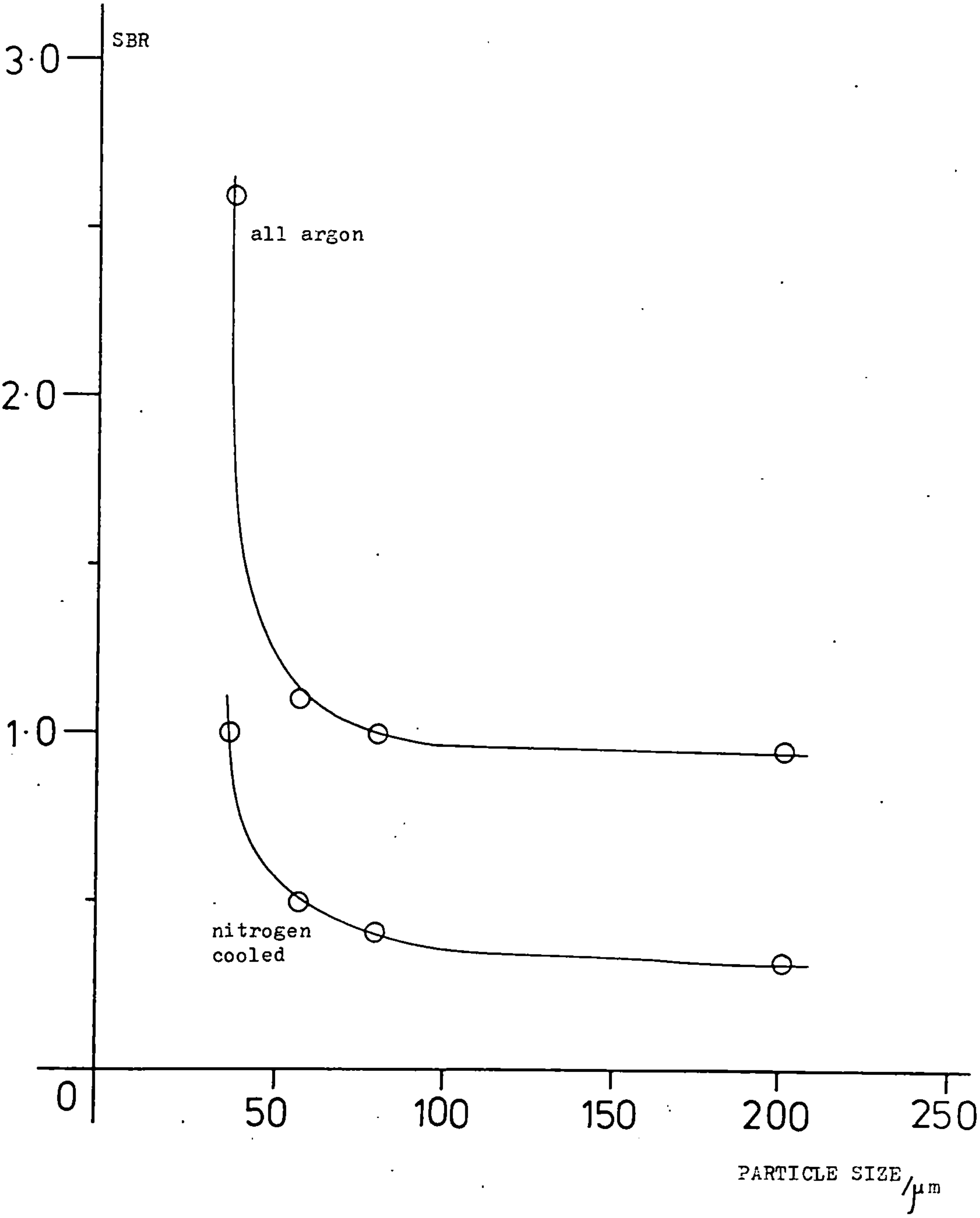
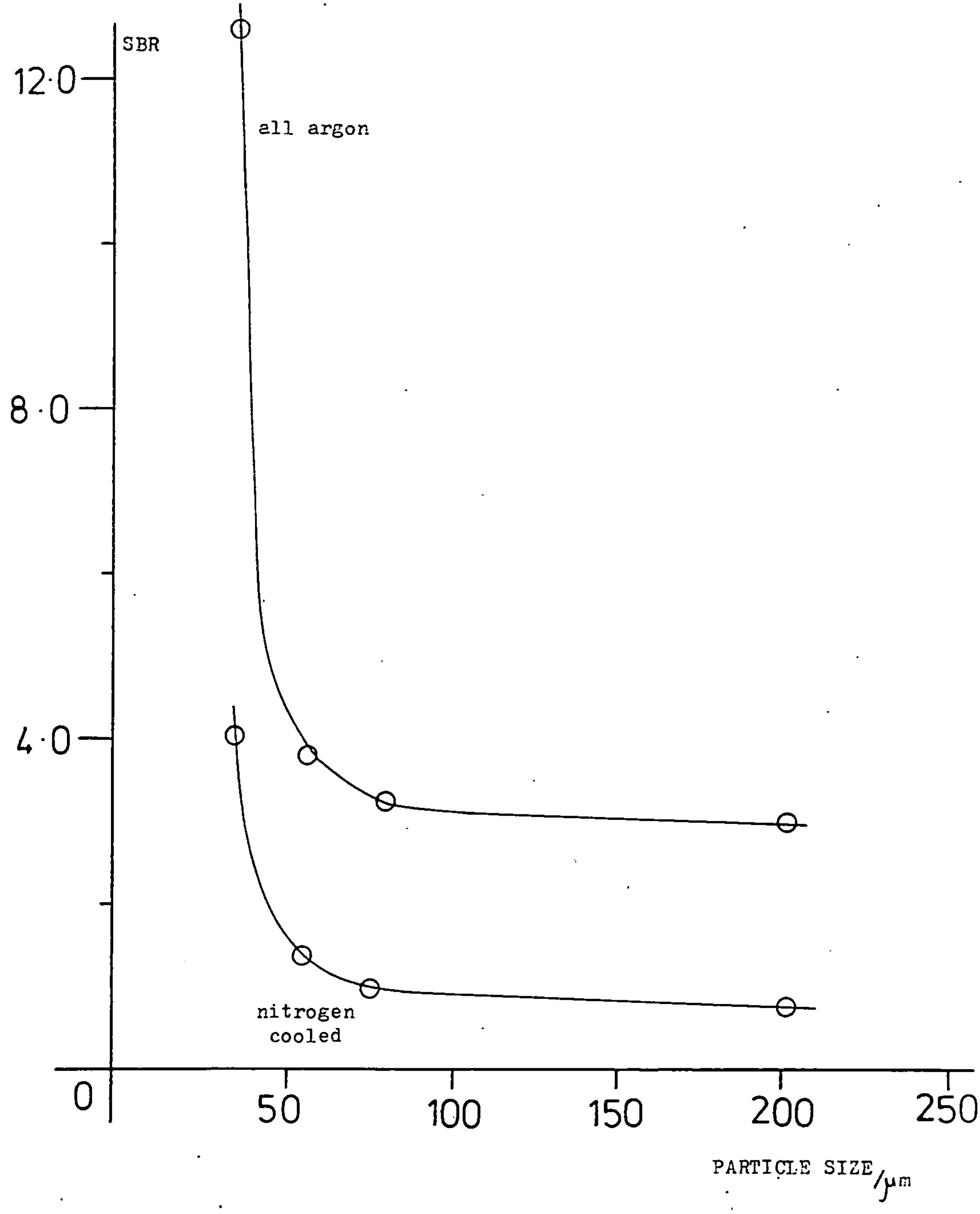


Fig. 43 SBR as a function of particle size, pumping a 4% $^{m}/_{v}$ slurry at 5.0 ml.min^{-1}



Plasma performance for slurry atomisation was then optimised using the variable step size simplex procedure. The SBR was measured at the 403.1 nm manganese atom line in both all-argon and nitrogen-cooled plasmas. A slurry concentration of 4% $^{m}/v$ and a sample pumping rate of 2.0 $ml.min^{-1}$ were chosen in order to minimise consumption of slurry while producing acceptable signal size. The coal sample was ground and sieved repeatedly until all the particles passed through a 38 μm sieve. Particle size analysis showed that approximately 5% (by number) of the particles were smaller than 10 μm.

The optimum conditions for both plasmas are given in Table 22. Again the all-argon plasma gave better results in terms of SBR because of the low background observed. Under the optimum conditions the apparent concentration of manganese in the coal, as determined using aqueous calibration standards in the all-argon and nitrogen-cooled plasmas, was 48.6 and 36.6 $\mu g.g^{-1}$ respectively (compared to 90 $\mu g.g^{-1}$ by a.a.s.). These concentrations represent atomisation efficiencies (relative to aqueous solutions) of 60% and 40% for the all-argon and nitrogen-cooled plasmas respectively. It was decided at this point to use the all-argon plasma for all subsequent experiments because of the better SBR's available relative to the nitrogen-cooled plasma. A comparison of the optimal conditions for the determination of manganese in coal slurries and aqueous solutions using an all-argon plasma is shown in Table 23. Several significant and inter-related

Table 22

Optimum operating conditions for the determination of manganese by direct atomisation of whole coal slurries

Parameter	Plasma type all-argon	 nitrogen-cooled
Coolant gas flow/ℓ.min^{-1}	2.65(Ar)	4.0(N_2)
Plasma gas flow/ℓ.min^{-1}	13.3	13.3
Injector gas flow/ℓ.min^{-1}	0.35	0.38
Power/kW	0.29	0.40
Observation height/mm above load coil	34	33.5

SBR measured at the manganese 403.1 nm atom line, using a 4% m/v coal slurry (particles smaller than 38 μm), pumped at 2.0 mℓ.min^{-1}.

Table 23

Optimum operating conditions for the determination of manganese in aqueous solution and in whole coal slurries using an all-argon plasma

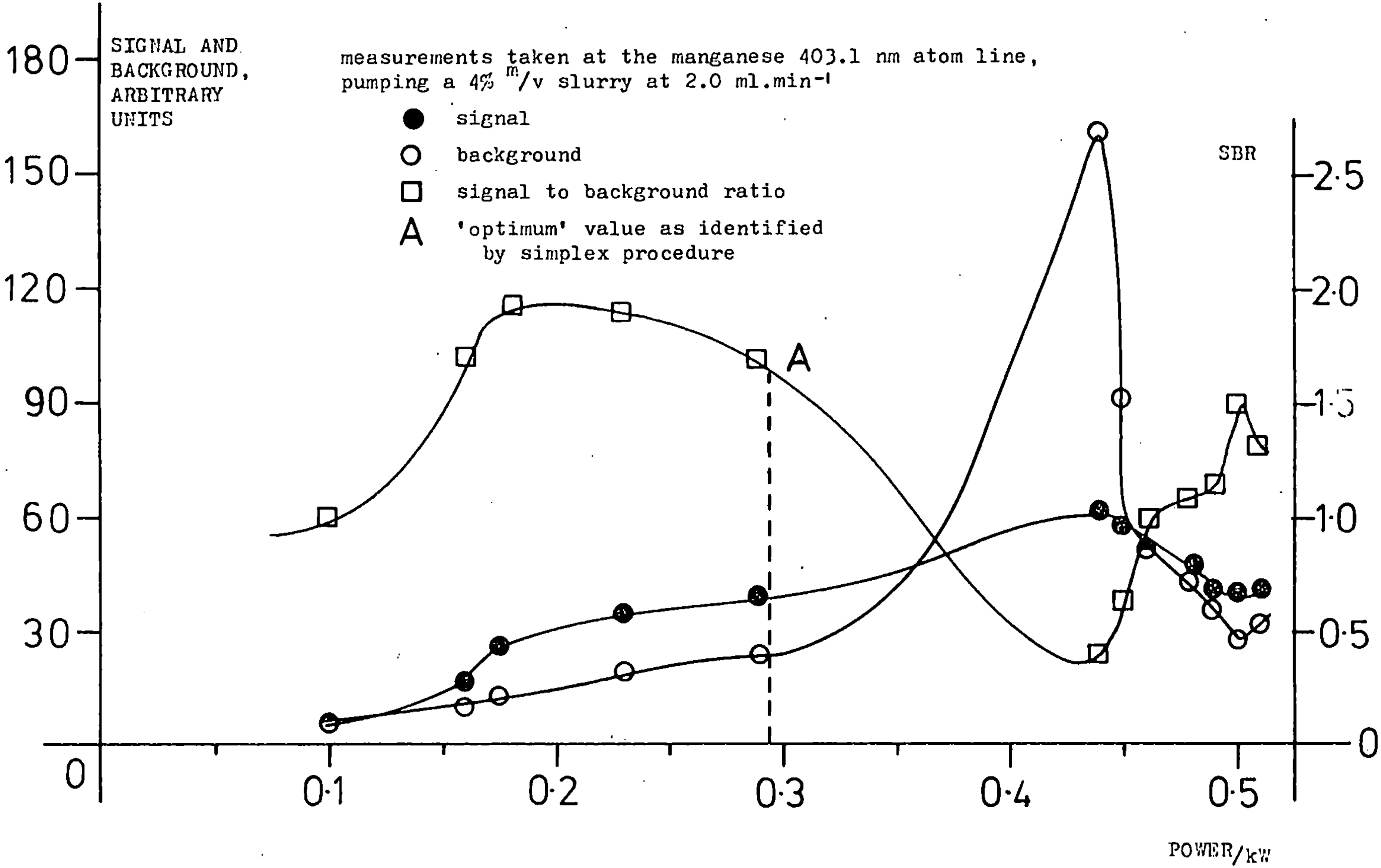
	Sample type	
	aqueous solution	whole coal slurry
Parameter		
Coolant gas flow/ .min^{-1}	8.7	2.65
Plasma gas flow/ .min^{-1}	14.0	13.3
Injector gas flow/ .min^{-1}	0.58	0.35
Power/kW	0.50	0.29
Observation height/mm above load coil	26	34

SBR measured at the manganese 403.1 nm atom line.

features were apparent. The height of observation above the load-coil was somewhat higher for slurries than for aqueous solutions. Although the plasma gas flows were similar, the coolant and injector gas flows were markedly lower for slurries. The outcome of a combination of these factors was a shift towards longer residence times in the atom cell. This effect would be expected to promote more efficient matrix destruction and analyte atomisation. That lower power was preferred for slurry atomisation is perhaps surprising. It was thought that this may have been the outcome of having optimised the operating conditions for signal to background. Whereas the background increases linearly with increasing power, this may not be so for the analyte emission signal. If this is the case then a point will be reached when the background is increasing more rapidly than the signal and for slurry atomisation this point appears to be reached at relatively low power. This was confirmed by performing a univariate search to identify the optimum power (Fig. 44).

It was felt that the atomisation efficiency of the all-argon plasma (60%) might be improved if the proportion of particles in the sample less than 10 μm could be increased. Five coal samples including two standard coals were ground using specialised equipment (McCrone Micronising Mill) which was expected to reduce the majority of the sample to less than 10 μm in diameter. When the particle size distributions were evaluated, however, the results were disappointing. At most only 45% of the particles were smaller than 10 μm, although for all the samples at least 95% of the particles were smaller than 25 μm. Wet grinding of the samples using water or more especially acetone would be expected to produce more particles smaller than

Fig. 44 Univariate search for optimum power: slurry atomisation using simplex optimised conditions



10 µm. Using water, however, losses of water soluble trace metals components are possible, while acetone would alter the sample composition by removing moisture from the coal. For the coals examined a direct correlation between moisture and ash content and the ease of grinding was apparent and this is demonstrated in Table 24. As the moisture content decreased and the ash content increased, then the number of particles smaller than 10 µm increased. The possible effects of this trend on atomisation efficiency are discussed in the following section.

Table 24

Correlation between ash and moisture content and the apparent ease of grinding of the five coals analysed

Coal	% moisture	% ash	% (by number) of particles smaller than 10 µm
NBS SRM 1632a (bituminous coal)	2.2	22.2	45.1
NCB C	3.4	21.6	42.2
NCB B	5.9	17.5	39.6
NCB A	9.4	4.6	31.8
NBS SRM 1635 (sub-bituminous coal)	18.8	4.3	28.5

Moisture and ash contents determined using NCB standard methods.

Particle size distributions evaluated using Coulter Counter.

6.3.3 ANALYSIS OF COAL SLURRIES BY DIRECT ATOMISATION IN AN INDUCTIVELY COUPLED PLASMA

The ground coal samples were used to prepare slurries (10% $^m/v$ in aqueous 1% $^v/v$ Triton X-100) and attempts were made to determine selected trace metals by direct atomisation these slurries in an inductively coupled plasma. Problems were immediately encountered due to the high levels of iron in the samples which resulted in numerous intense iron emission lines. Many of the analytical lines preferred for the determination of the desired elements in typical aqueous samples were interfered with by these iron emissions. In addition, different coals containing different amounts of iron were susceptible to these spectral interferences to varying degrees.

Consequently a range of analytical emission lines was investigated for each of the elements of interest. Each line was evaluated in terms of sensitivity (SBR) and relative freedom from spectral interferences. Both atom and ion emission lines were examined using the plasma operating conditions given in Table 20. The analytical lines fulfilling these requirements to the greatest extent were selected for the analytical procedures to follow. Vanadium gave better results using ion lines and typical ion line operating conditions. Copper, iron, manganese and nickel gave better results using atom lines and typical atom line conditions (Table 20). Since the simplex optimisation procedures for slurries had been performed using an atom line (manganese 403.1 nm), the feasibility of determining these latter elements using the optimised slurry operating conditions was investigated. While the SBR available for manganese was sufficient to determine this element at typical levels in coal slurries, the SBR's for copper and nickel were very low. This phenomenon highlights the variations in the atomisation processes occurring in the plasma fireball. Using conditions optimised for aqueous solutions of manganese, several other metals (in addition to manganese) gave easily measureable emissions when atomised from coal slurries. However, when conditions specifically optimised for the determination of manganese in coal slurries were used the metals other than manganese gave only very small emission signals when atomised from coal slurries. Simplex optimisation of each of the emission lines selected for the determination of copper, iron and nickel would have produced individual sets of operating conditions specific for each metal. From these sets it may have been possible to formulate a single set of compromise conditions suitable for the analysis of all three metals. This process could have been repeated for vanadium to establish compromise conditions for analyses using ion lines. However, such a comprehensive investigation was outside the scope of this work. Since adequate SBR's had been obtained for copper, iron, manganese and nickel using the atom line conditions given in Table 20, these conditions were adopted for the analysis of these elements. Vanadium similarly gave poor SBR's using the optimised slurry operating conditions and these elements were determined in coal slurries using the ion line conditions given in Table 20.

Earlier studies had shown that SBR increased with sample pumping rate (Figs 31-34). Using a 10% $^{m}/v$ coal slurry the optimum sample pumping rate was 15 ml.min^{-1}. To prevent undue waste of sample slurry the recycling spray chamber (Fig. 19) was used throughout.

In addition to the coals analysed a portion of the ash obtained from SRM 1632a was used to prepare a slurry (ca. 2% $^m/v$, which, when calculated as a weight of whole coal represented a slurry concentration of 10% $^m/v$). The results obtained for the five coals and the ash are shown in Tables 25-29, together with the apparent atomisation efficiencies (i.c.p. slurry atomisation values as a percentage of the flame a.a.s. values). Correlation plots of these results are given in Figs. 45-49.

Quantitative measurements of peak intensities were taken by making replicate scans across the analytical lines used. The appropriate background contribution was subtracted to yield the net emission signal. Since high background levels were observed at most of the wavelengths of interest, relatively high attenuation (typically 100 mV-1v full-scale deflection on the recorder) was required. Consequently the peaks measured were often small in relation to the overall background signal. An estimate of the precision available was made by measuring the maximum and minimum values possible for each peak as well as the value considered to represent the mean peak height. By this method the variance of the mean peak height measurements was found to be approximately ± 25%. However, the values measured for the maximum and minimum peak heights had not been refined to exclude any contributions from spurious noise peaks. After elimination of very high and very low measurements (of maximum and minimum peak height respectively), the variance of the measurements was estimated to be approximately ± 15%. After taking into account the relatively small variations in background level the overall precision for three replicate measurements was estimated to be approximately ± 12%. The uncertainty of the flame atomic absorption results was typically ± 5-10%.

Results were obtained for copper, iron, manganese, nickel and vanadium. As a basis for the discussion of these results reference is made to Table 24. The order of 'grindability' of the coals (measured in terms of the number of particles smaller than 10 μm) is: SRM 1632a > C > B > A > SRM 1635. Thus, if atomisation efficiency is simply and most directly affected by particle size, the atomisation efficiencies observed for these coals should follow a similar order. This trend was not observed for the coals analysed and the results obtained for copper, nickel and vanadium showed that atomisation efficiencies were biased in favour of those slurries containing the highest concentrations of small particles. For copper and vanadium, good agreement was observed between the values determined experimentally (flame atomic absorption and slurry atomisation) and the NBS certificate values for the standard coals analysed. When the non-standard coals were analysed for copper and vanadium the agreement between the values determined using flame atomic absorption spectrometry and slurry atomisation was generally less satisfactory. The discrepancies were random and no single coal was dientified as giving consistently high or low results using the slurry atomisation method. The results for the determination of nickel imply that there has been some contamination and/or segregation of the sample. This is demonstrated by the consistent discrepancy between the values determined experimentally for SRM 1632a (<u>ca</u>. 39 $\mu g.g^{-1}$ using flame atomic absorption spectrometry and slurry atomisation) and the NBS certified value (21.4 $\mu g.g^{-1}$). Overall the results obtained for

Table 25

Determination of Copper

atom line conditions, 327.4 nm.

A comparison of the values determined using flame atomic absorption spectrometry (f.a.a.s.) and inductively coupled plasma slurry atomisation (i.c.p.s.a.)

	technique		
	f.a.a.s.	i.c.p.s.a.	NBS certificate value
Sample slurry	concentration of copper/μg.g^{-1}		
SRM 1632a	17.5	17 (97)	16.5
SRM 1632a ash		17.9 (105)	
SRM 1635	4.7	4.6 (98)	3.6
NCB A	27	18 (67)	
NCB B	36	26 (72)	
NCB C	52	53 (102)	

Values in parentheses indicate apparent atomisation efficiencies relative to values obtained using f.a.a.s.

Fig. 45 Correlation of results obtained for Copper in coal using flame a.a.s. and i.c.p. slurry atomisation

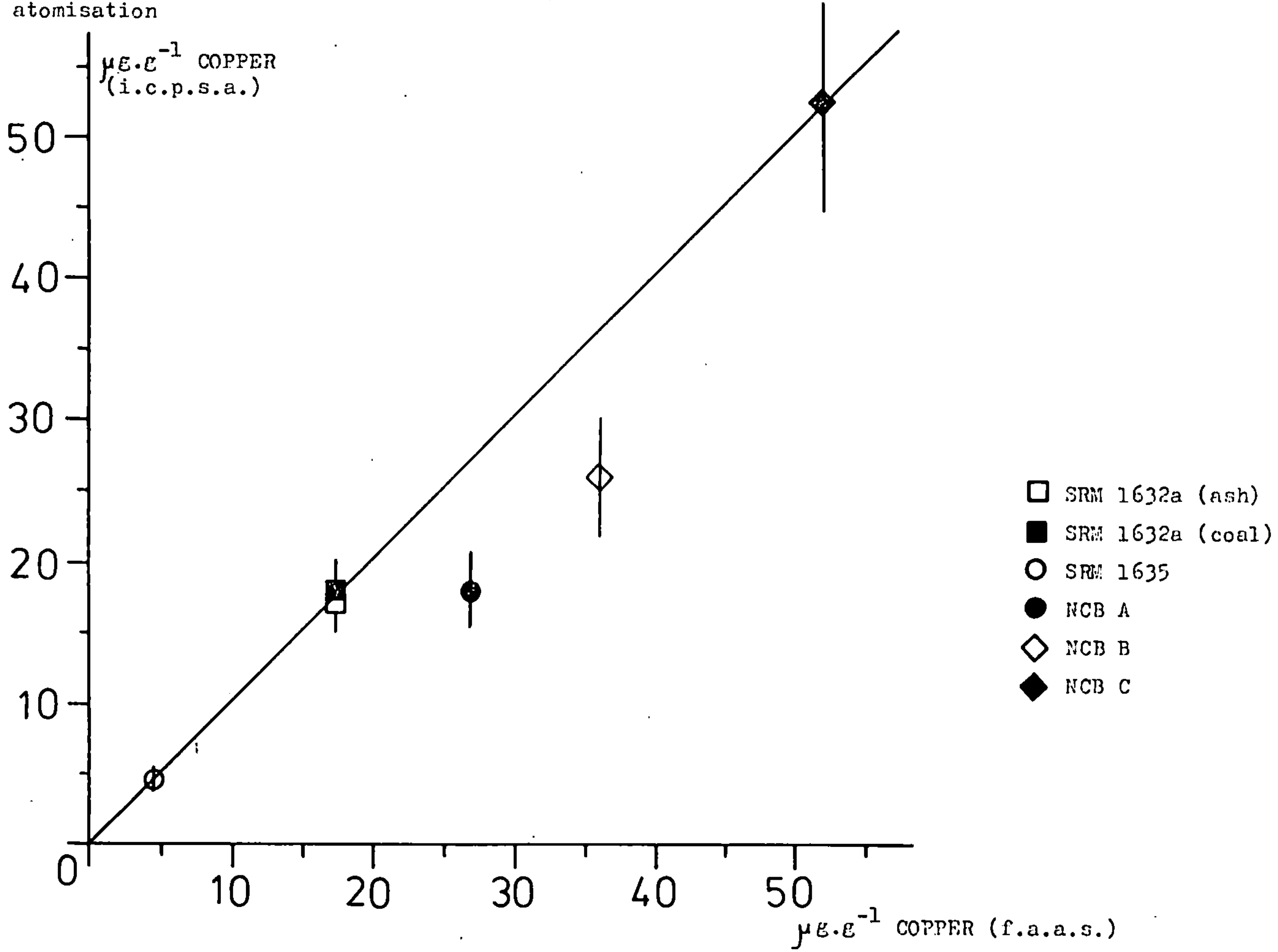


Table 26

Determination of Nickel

atom line conditions, 341.5 nm

A comparison of the values determined using flame atomic absorption spectrometry (f.a.a.s.) and inductively coupled plasma slurry atomisation (i.c.p.s.a.)

Sample slurry	technique f.a.a.s.	i.c.p.s.a.	NBS certificate value
	concentration of nickel/µg.g^{-1}		
SRM 1632a	42	39 (93)	19
SRM 1632a ash		39 (93)	
SRM 1635	7	17 (243)	1.7
NCB A	33	38 (115)	
NCB B	61	57 (93)	
NCB C	56	56 (100)	

Values in parentheses indicate apparent atomisation efficiencies relative to values obtained using f.a.a.s.

Fig. 46 Correlation of results obtained for Nickel in coal using flame a.a.s. and i.c.p. slurry atomisation

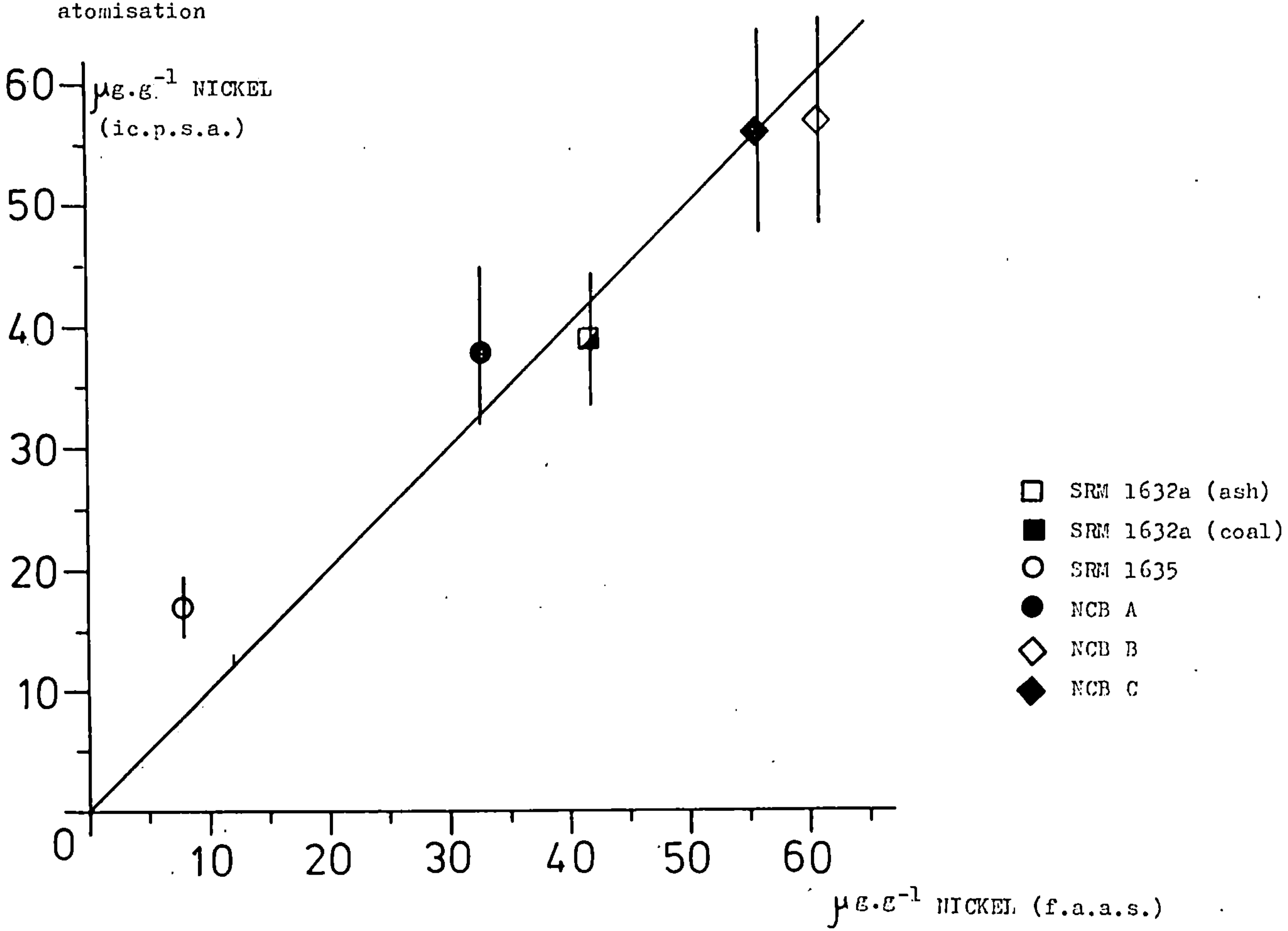


Table 27

Determination of Vanadium

ion line conditions, 290.9 nm

A comparison of the values determined using flame atomic absorption spectrometry (f.a.a.s.) and inductively coupled plasma slurry atomisation (i.c.p.s.a.)

	technique		
Sample slurry	f.a.a.s.	i.c.p.s.a.	NBS certificate value
	concentration of vanadium/$\mu g.g^{-1}$		
SRM 1632a	42.5	51 (120)	44
SRM 1632a ash		53 (125)	
SRM 1635	5.7	5.4 (95)	5.2
NCB A	20	20 (100)	
NCB B	37	53 (143)	
NCB C	44	73 (166)	

Values in parentheses indicate apparent atomisation efficiencies relative to values obtained using f.a.a.s.

Fig. 47 Correlation of results obtained for Vanadium in coal using flame a.a.s. and i.c.p. slurry atomisation

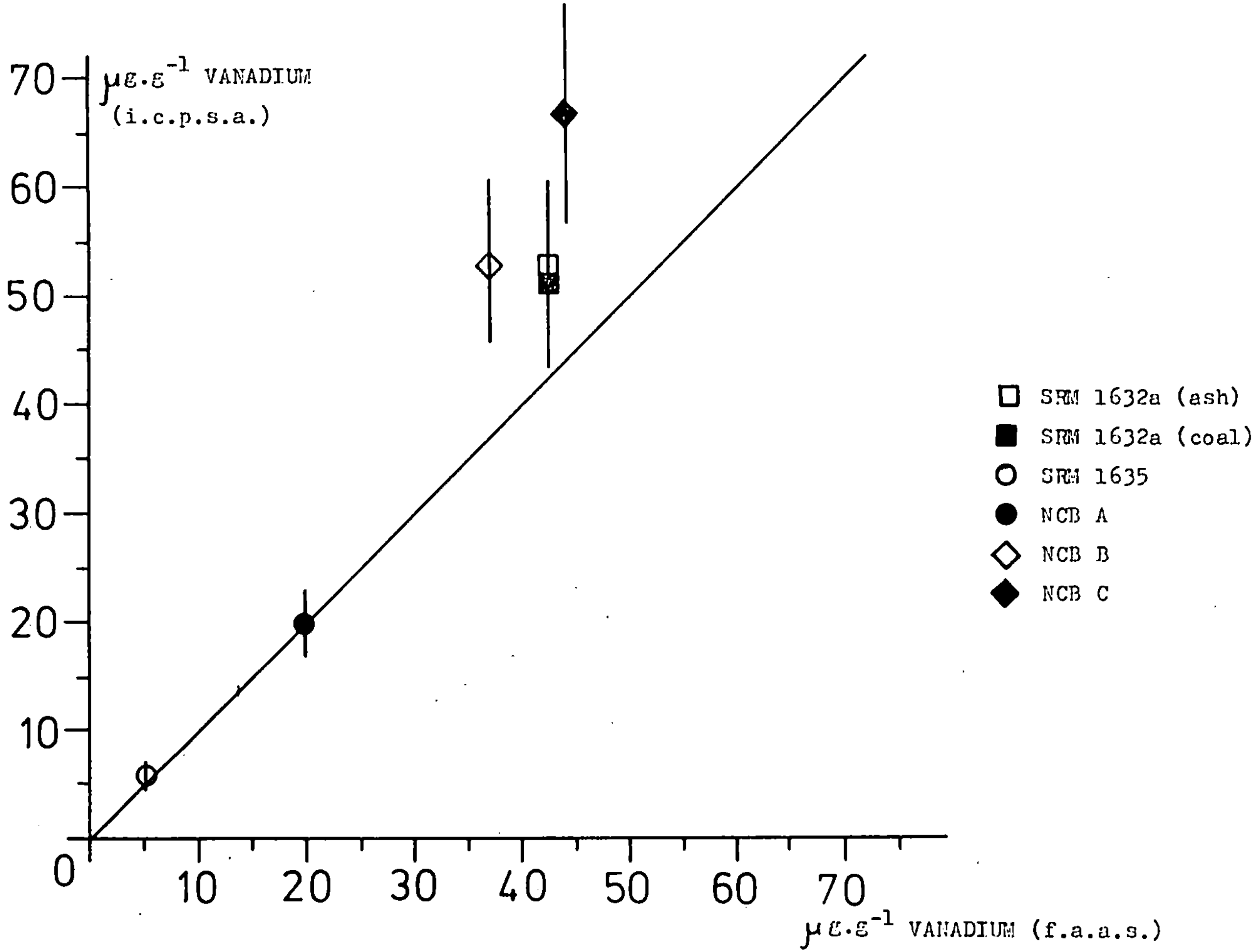


Table 28

Determination of Manganese

atom line conditions, 403.1 nm

A comparison of the values determined using flame atomic absorption spectrometry (f.a.a.s.) and inductively coupled plasma slurry atomisation (i.c.p.s.a.)

	technique		
	f.a.a.s.	i.c.p.s.a.	NBS certificate value
Sample slurry	concentration of manganese/$\mu g.g^{-1}$		
SRM 1632a	21.5	42 (195)	28
SRM 1632a ash		18 (84)	
SRM 1635	28.3	8.5 (30)	21.4
NCB A	34	48 (141)	
NCB B	73	96 (132)	
NCB C	194	128 (66)	

Values in parentheses indicate apparent atomisation efficiencies relative to values obtained using f.a.a.s.

Fig. 48 Correlation of results obtained for Manganese in coal using flame a.a.s. and i.c.p. slurry atomisation

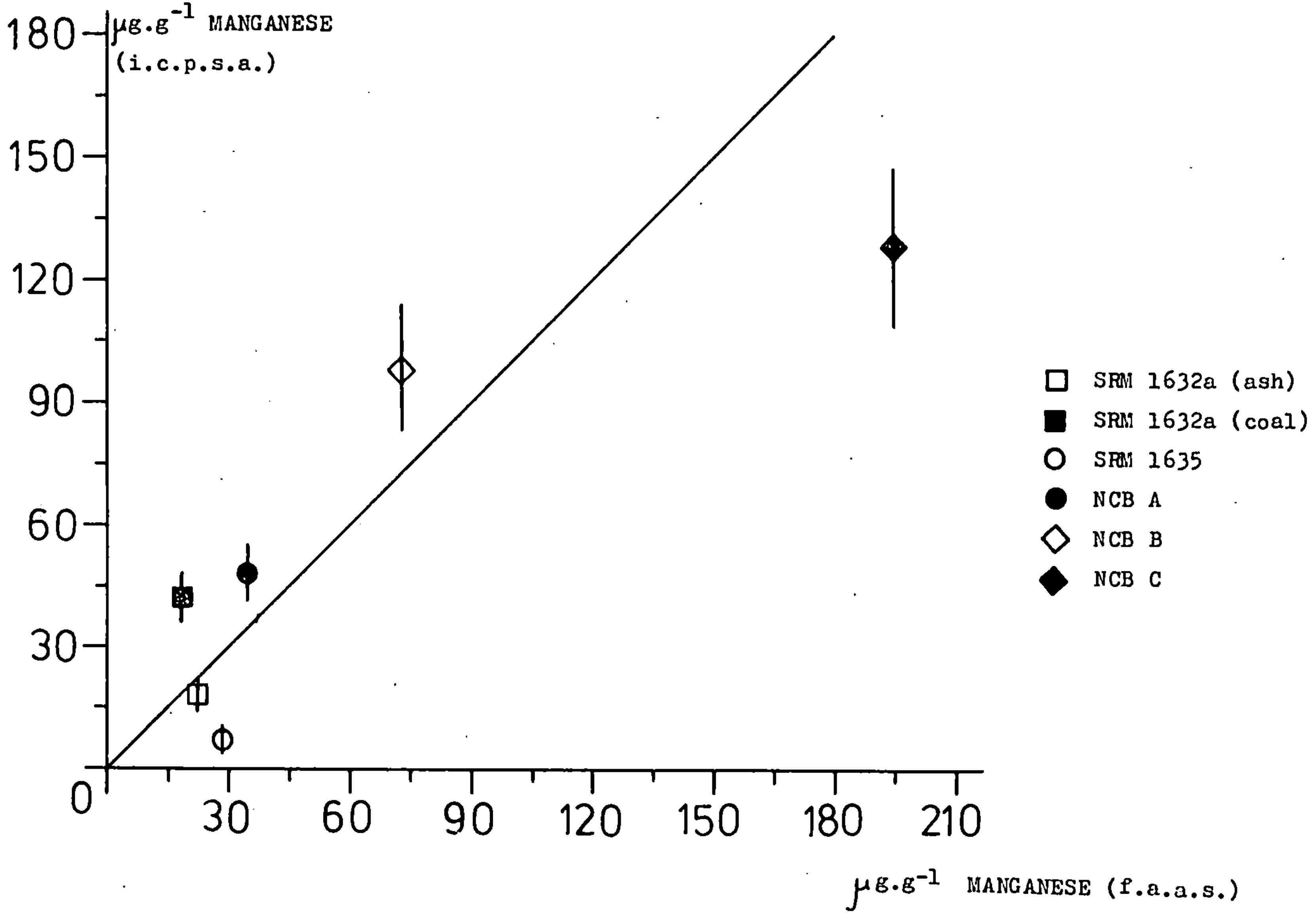


Table 29

Determination of Iron

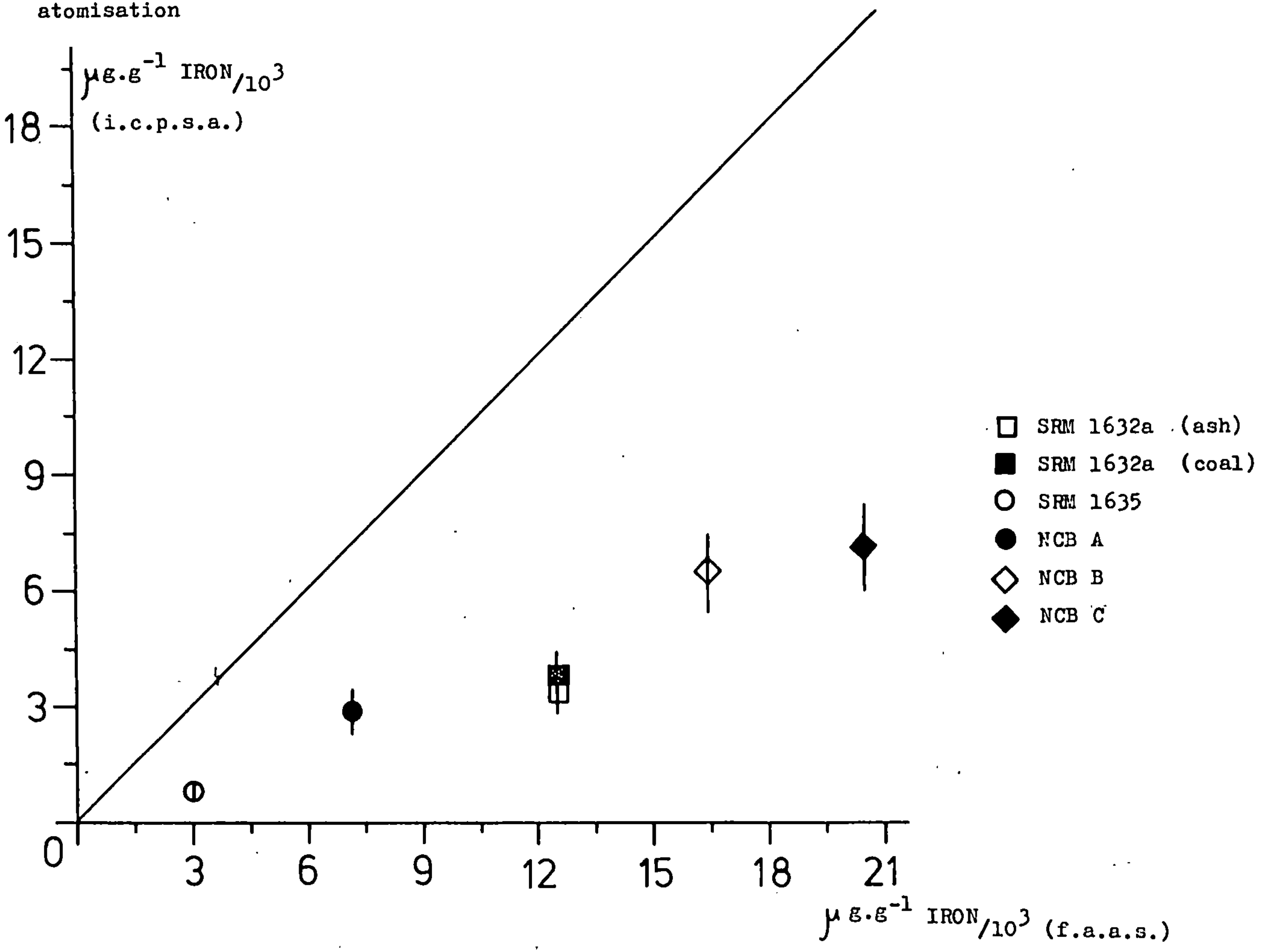
atom line conditions, 372.0 nm

A comparison of the values determined using flame atomic absorption spectrometry (f.a.a.s.) and inductively coupled plasma slurry atomisation (i.c.p.s.a.)

	technique		
	f.a.a.s.	i.c.p.s.a.	NBS certificate value
Sample slurry	concentration of iron/$\mu g.g^{-1}$		
SRM 1632a	12,560	3,830 (30)	11,100
SRM 1632a ash		3,416 (27)	
SRM 1635	3,070	736 (25)	2,390
NCB A	7,160	2,910 (41)	
NCB B	16,340	6,542 (40)	
NCB C	20,550	7,088 (34)	

Values in parentheses indicate apparent atomisation efficiencies relative to values obtained using f.a.a.s.

Fig. 49 Correlation of results obtained for Iron in coal using flame a.a.s. and i.c.p. slurry atomisation



nickel using flame atomic absorption spectrometry and slurry atomisation showed good agreement for all the coals except SRM 1635, which gave consistently high results using the slurry atomisation technique. The results obtained for manganese are disappointing and shows poor agreement between the values determined using flame atomic absorption spectrometry and slurry atomisation. The reasons for the variable recoveries are unclear and any attempts to correlate atomisation efficiency with particle size distribution are meaningless.

The low recoveries of iron were attributed initially to the high levels of iron in the atom cell causing self absorption of the signal or saturation of the photomultiplier tube. Both suggestions were discounted when dilutions of one slurry (10 and 200 fold) failed to produce results significantly different (± 5%) to the parent slurry. The reasons for the poor atomisation efficiencies observed for iron (relative to other elements) are unclear. One possibility is that the iron is contained in coal as relatively large inclusions of oxides and sulphides. Grinding of the sample reduces these inclusions to the same size as the coal particles, but, since such material is considerably more refractory than coal, atomisation may be slow or incomplete.

During nebulisation of the slurries, droplets of aerosol impinging on the bottom of the spray chamber and partly nebulised slurry were returned to the sample reservoir. It has been suggested by some authors that only particles smaller than 10 μm contribute appreciably to the analyte emission signal. Furthermore if the order-sorting effect of the spray chamber results in selective transport of very small particles to the atom cell, then the slurry recycled to the sample reservoir would be relatively depleted in these particles. In combination these two effects would be expected to cause some deterioration in signal size since successive portions of slurry nebulised into the plasma would contain progressively fewer smaller particles. Unfortunately the absolute weight of slurry reaching the plasma during typical analysis times was very small and any deterioration would have been very small. No significant decrease in signal size was observed, even after prolonged nebulisation of one coal slurry. There is some evidence to suggest that, for the range of particle sizes investigated (ca. 2-30 μm), atomisation efficiencies appear to be independent of the particle size distribution of the samples. Other authors discussing these parameters have been concerned largely with the analysis of refractory geological materials. It may be that the small particle sizes reportedly necessary for efficient atomisation of these materials are not necessary for coal. Since more than 95% (by number) of the particles present in all the coal samples analysed were smaller than 30 μm, this value may be closer to any critical particle size than is 10 μm.

This feature may be related both to the composition of the materials undergoing atomisation, and the rates at which the processes occur. Since atomisation of refractory materials (e.g. ash) should be slower than for coal long residence times and very small particles may be necessary to ensure complete atomisation. For coal a two stage atomisation process may be suggested. Firstly the relatively large carbon particles are ashed or pyrolysed in the plasma fire-ball, leaving behind smaller particles of ash, which are subsequently atomised. The overall time scales for the slow atomisation of ash particles and the two-stage atomisation of coal particles may be comparable. Attempts were made to confirm this mechanism by scanning the emission spectrum of a coal slurry in order to locate molecular bandheads due CN radicals (359, 388 and 422 nm), CH radicals (432 nm) and C_2 radicals (474 and 517 nm). With the exception of weak CH radical emissions at ca. 432 nm none of these bands was observed. In all probability this was due to dissociation of any reaction products by the high temperatures in the atom cell.

Good agreement was observed between the results obtained for the analysis of the SRM 1632a coal slurry and the ash slurry produced from this coal. This is interesting when the particle size distributions of these two samples are considered. From Table 20 it is seen that the low-ash coals produce fewer small particles on grinding than do high-ash coals. Thus it may be postulated that the relatively large particles left after grinding are largely carbonaceous in composition. Subsequent ashing of the coal removes carbonaceous material so the number of these large particles should be reduced, i.e. the ash should contain a higher percentage of small particles than the coal from which it was produced. Particle size analysis of the ash from SRM 1632a confirms this in that only 45% of the original coal particles were smaller than 10 μm, whereas 75% of the ash particles were smaller than 10 μm (Table 30). Hence better atomisation efficiencies might be expected for the ash slurry than for the coal slurry. If however the postulated atomisation mechanism is correct equivalent efficiencies for coal and ash slurries might be understandable. A comparison of the values determined for the two slurries revealed that the manganese and iron values again showed no consistency, both elements in fact giving lower recoveries for the ash slurry (85% and 43% of the coal slurry figure for iron and manganese respectively). For copper, nickel and vanadium (those elements giving the best results overall) the differences between the ash and coal slurry values were not significant, ± 5%.

Table 30

Particle size distributions of NBS SRM 1632a and the ash produced from this coal.

Upper limit of particle size range/μm		% Occurrence coal	% Occurrence ash
2.52		0.5	3.2
3.17		2.3	7.8
4.00		4.2	11.0
5.04		5.9	12.9
6.35		10.1	14.7
8.00		10.9	13.4
10.08		11.2	11.6
12.70		11.3	9.6
16.00		14.4	8.2
20.16		12.1	4.9
25.40		10.4	1.9
32.00		6.7	0.8
	Totals	100	100

	coal	ash
% of particles smaller than 10 μm	45.1	74.6

6.4 CONCLUSIONS

The atomisation of whole coal slurries using the high temperature atom cell available with the inductively coupled plasma has been investigated. The method has been found to show considerable promise for the determination of trace metals in coal. While preparation and introduction of the sample into the plasma have been found to be simple and rapid, analytical problems of a more fundamental nature have been encountered.

Traditionally problems of nebuliser and burner blockage are encountered when samples containing suspended solids or high salt concentrations are analysed using conventional flame techniques. A significant contribution to the avoidance of such problems has been made by the modified Babington-type nebuliser used throughout this work. Blocking of this nebuliser is avoided by introducing the slurry into the nebulising gas stream <u>via</u> a relatively wide diameter tube (<u>ca</u>. 0.8 mm i.d., compared to <u>ca</u>. 0.35 mm for typical Meinhard nebulisers). This type of nebuliser does not function by generating a Venturi effect at the gas/liquid interface and consequently has no natural uptake mechanism. Accordingly a constant head of sample is maintained at the nebuliser tip using a small peristaltic pump. With this arrangement the nebuliser has been found to give excellent service for a wide range of slurry concentrations (up to 25% $^{w}/v$), introduced at high sample pumping rates (15-20 $ml.min^{-1}$) and containing relatively large particles (maximum particle size 105 μm).

Excessive consumption of slurry when pumping sample at 15 $ml.min^{-1}$ is avoided using a gastight recycling system in which slurry aerosol droplets impinging on the walls of the spray-chamber and partly nebulised slurry are returned to the sample reservoir <u>via</u> the spray chamber drain. If only a limited amount of sample is available lower pumping rates (typically 0.5-2.5 $ml.min^{-1}$) can be used, though at the cost of a loss of sensitivity (typically 20%).

At the present time the major analytical problems are associated with the restricted freedom of line selection. Two independent factors are responsible for these problems. Firstly the long residence times identified by the simplex procedure involve viewing the plasma high above the load coil (typically 34 mm). While the level of background radiation should be relatively low at this height, sufficient time may have elapsed to allow extensive recombination of metal ions and electrons so that emissions at atom lines should be more intense than at ion lines. Attempts to exploit the greater sensitivity of some of the ion lines available for the elements determined necessarily involve looking lower in the more energetic regions of the plasma tailflame. This in turn reduces the residence time (and possibly the degree of atomisation) of the sample, and increases the level of background radiation. Both effects combine to produce inferior SBR's and no gain in analytical performance is obtained. Thus, due to the extended residence times required to ensure complete atomisation of the slurry particles, the use of some potentially sensitive ion lines is precluded.

Secondly, as a result of spectral interferences from iron, many of the preferred atom lines are unavailable. While alternative lines may be found, the sensitivities of these lines may be insufficient to allow determination of the desired metals at levels typical in coal slurries. The poor resolving power of the monochromator available in this work serves only to aggravate these problems. On way to overcome these problems might be to determine the iron content of each coal and then to prepare calibration standards with accurately matched matrices for each individual slurry. However, this necessarily requires an atomisation efficiency of 100% for iron so that the amount of iron added to each set of standards can be determined accurately. The results obtained for iron indicate that this approach is not as yet feasible.

From the results of the experiments performed it has become clear that spectral interferences pose the major analytical problems in this method. Where interference-free lines can be found the application of simplex optimisation techniques should assist in identifying the experimental conditions which will enable the sensitivity of such lines to be exploited fully. Clearly there is much scope for expanding the simplex optimisation work already carried out here, not only in continuing similar optimisation experiments on a wider range of elements and spectral lines, but also to investigate the analytical potential of new systems (e.g. an all-nitrogen plasma has recently been reported)(229).

Recent developments (230, 231) in I.C.P. instrumentation appear to favour the more flexible computer controlled scanning sequential spectrometers in preference to direct reader simultaneous detection systems. Sequential systems no longer require analyses to be performed using a single set of compromise operating conditions, since operational parameters can be changed to suit each element in turn. Therefore it is logical to extend the role of the computer to include manipulation of the plasma controls (i.e. gas flows, power and viewing height). Such a system should be ideally suited to simplex optimisation studies and would give information not only about the fundamental mechanisms of plasma systems, but also for general analytical work, where optimisation of operating parameters for different elements in various matrices could be achieved rapidly and efficiently.

The results of the optimisation studies carried out here suggest that the all-argon plasma is more suited to the determination of trace metals in coal slurries than is the nitrogen-cooled plasma. This enables a lower power (and hence less expensive) generator to be used. The argon plasma produces only a low background with relatively few molecular bands, and a potentially wider range of sensitive spectral lines is available. Unfortunately the matrix background from coal slurries interferes with many of the preferred analytical lines. If a direct reading spectrometer is used to measure the emission signal, the highest possible resolution must be used to eliminate or minimise matrix interferences on the fixed set of analytical lines available. If a more flexible scanning monochrometer is used spectral interferences can often be overcome by using different spectral lines, or compensated for using wavelength scanning techniques (as in this work). In either case a monochromator of high resolving power will assist considerably in successfully overcoming interferences of this kind.

In conclusion, the potential for the rapid analysis of whole coal slurries using the inductively coupled plasma is clearly demonstrated. Analysis times are reduced from typically 1½-2 working days (say for five elements determined in one coal sample using flame atomic absorption methods) to less than ½ of a working day, including the time taken to grind the sample. Elimination or avoidance of spectral interferences (perhaps involving variable step-size simplex techniques) will enhance considerably the utility of the method which should be applicable to a wide range of coals and related materials, e.g. ashes and coke.

When this method is used in conjunction with the methods described previously for mercury, arsenic and selenium an overall strategy for the determination of a wide range of trace elements in coal is available, thus enabling the construction of significant trace metal balances in and around coal-utilising power plants.

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LECTURES AND MEETINGS ATTENDED

(i) Selected lectures from the C.N.A.A. M.Sc. in Instrumental Analytical Chemistry.

(ii) Department of Chemistry 'Analytical Discussion Group' (Sheffield City Polytechnic; weekly from May 1978 until December 1980; Chairman of the above, January-December, 1980).

(iii) Department of Environmental Sciences 'Chemistry of Natural and Polluted Environments Research Group' (Plymouth Polytechnic; weekly from January until October 1981).

(iv) Department of Chemistry Research Colloquia (Sheffield City Polytechnic; fortnightly from May 1978 until December 1981).

(v) Sheffield Modern Methods of Analysis (Metallurgical and Engineering) Group (British Iron and Steel Research Association Headquarters, Sheffield; bimonthly from May 1978 until December 1980).

(vi) Instrumentation Laboratories Inc., IL User Group Meetings, Post House Hotel, Leeds; November 1978 and July 1980.

MEETINGS OF ROYAL SOCIETY OF CHEMISTRY AND RELATED BODIES

(CHRONOLOGICAL ORDER)

(i) North East Region R.I.C. and Atomic Spectroscopy Group 'Problem Areas in Atomic Absorption', Gateshead, October 25, 1978.

(ii) Atomic Spectroscopy Group, joint meeting with the Board of Annual Reports on Analytical Atomic Spectroscopy and the Sheffield Modern Methods of Analysis Group, 'Sixth Annual Reports on Analytical Atomic Spectroscopy Symposium', Sheffield, January 4th 1979.

(iii) North East Region R.I.C. with Sheffield and District C.S./R.I.C. 'A Century of Achievement in Metallurgical Analysis', Sheffield, January 17th 1979.

(iv) Analytical Division 'Research and Development Topics in Analytical Chemistry', Edinburgh, July 4th/5th, 1979.

(v) Atomic Spectroscopy Group, joint meeting with Western Region R.I.C., 'Plasma Emission Spectroscopy', Bristol, November 21st, 1979.

(vi) Atomic Spectroscopy Group, joint meeting with North East Region R.I.C., 'Competitive Spectroscopies in Metallurgical Analysis', Sheffield, December 5th, 1979.

(vii) Atomic Spectroscopy Group, joint meeting with the Board of Annual Reports on Analytical Atomic Spectroscopy, 'Seventh Annual Reports on Analytical Atomic Spectroscopy Symposium', Sheffield, March 27th, 1980.

(viii) Analytical Division 'Research and Development Topics in Analytical Chemistry', Canterbury, April 1st/2nd, 1980.

(ix) Atomic Spectroscopy Group with North West Region R.S.C., 'Industrial Applications of Atomic Absorption Spectroscopy', Lancaster, September 16th, 1980.

(x) R.S.C. Autumn Meeting: Analytical Division Symposium on 'Trace and Ultra-Trace Analysis', Cardiff, September 23rd-25th, 1980.

(xi) Industrial Division, joint meeting with North East Region R.S.C., 'Industrial Hygiene Monitoring', Sheffield, December 3rd, 1980.

(xii) Atomic Spectroscopy Group, joint meeting with North East Region R.S.C., 'Plasma Emission Spectroscopy', Middlesborough, March 11th, 1981.

(xiii) Atomic Spectroscopy Group, joint meeting with the Board of Annual Reports on Analytical Atomic Spectroscopy, 'Eighth Annual Reports on Analytical Atomic Spectroscopy Symposium: Quality Assurance and Atomic Spectroscopy', Sheffield, April 2nd, 1981.

(xiv) Royal Society of Chemistry Annual Chemical Congress: Analytical Division Symposium; 'Matrix and Sensitivity Problems in Analysis', Guildford, April 7th-9th, 1981.

(xv) Analytical Division 'Research and Development Topics in Analytical Chemistry', Salford, June 30th/July 1st, 1981 (Paper presented at this meeting).

In addition to these lectures and meetings a period of 3 months (May - July 1980) was spent at the London Research Station of the British Gas Corporation. Duties during this period involved the development of general analytical methods for the analysis of coal, particularly using carbon furnace atomic absorption spectrometry.

PUBLICATIONS

In print

'Determination of sub nanogram amounts of mercury by cold vapour atomic fluorescence spectrometry with an improved gas sheathed atom cell'

Anal. Chim. Acta, 1981, 128, 45.

(with L. Ebdon and K. W. Jackson)

In press

(i) 'Determination of mercury in coal by non-oxidative pyrolysis and cold vapour atomic fluorescence spectrometry'

Accepted by 'The Analyst' and in press.

(ii) 'Determination of volatile trace metals in coal by analytical atomic spectrometry'

Accepted by 'Analytical Proceedings' and in press.

(iii) 'A simple and sensitive continuous hydride generation system for the determination of arsenic and selenium by atomic absorption and atomic fluoresence spectrometry'

Accepted by 'Anal. Chim. Acta' and in press.

PAPERS PRESENTED

Invited

'The determination of mercury by cold-vapour atomic fluorescence spectrometry using an improved argon-sheathed atom cell.' Presented at a joint meeting of Sheffield City Polytechnic and Sheffield University Analytical Discussion Group with Sheffield Modern Methods of Analysis (Sheffield Metallurgical and Engineering) Group, Sheffield, November, 1979.

'The determination of volatile trace metals in coal by analytical atomic spectrometry.' Presented at a Faculty of Environmental Science Research Symposium, Plymouth Polytechnic, Plymouth, September 1981.

Submitted

'The determination of volatile trace metals in coal by analytical atomic spectroscopy.' Presented at 'Research and Developments in Analytical Chemistry', Analytical Division, Royal Society of Chemistry, Salford, June 1981.

OTHER PROFESSIONAL ACTIVITIES

(i) Member of the Analytical Division, Royal Society of Chemistry, 1977 onwards.

(ii) Fellow of the Society of Chemical Industry, 1978 onwards.

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