Inductively Coupled Plasma Spectrometry 1996

Methods for the Examination of Waters and Associated Materials

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Inductively Coupled Plasma Spectrometry 1996

Methods for the Examination of Waters and Associated Materials

This booklet contains two parts. These are:

(i) Inductively Coupled Plasma Atomic Emission Spectrometry, which supersedes the corresponding chapter in "Emission Spectrometric Multi-element Methods of Analysis for Waters, Sediments and other materials of interest to the water industry 1980, HMSO in this series;

(ii) Inductively Coupled Plasma Mass Spectrometry.

Only limited performance data are available for the procedures described in this booklet.

Contents

About this series

Introduction

This booklet is part of a series intended to provide authoritative guidance on recommended methods of sampling and analysis for determining the quality of drinking water, groundwater, river and seawater, waste water and effluents as well as sewage sludges, sediments and biota. In addition, short reviews of the more important analytical techniques of interest to the water and sewage industries are included.

Performance of methods

Ideally, all methods should be fully evaluated with results from performance tests reported for most parameters. These methods should be capable of establishing, within specified or pre-determined and acceptable limits of deviation and detection, whether or not any sample contains concentrations of parameters above those of interest.

For a method to be considered fully evaluated, individual results encompassing at least ten degrees of freedom from at least three laboratories should be reported. The specifications of performance generally relate to maximum tolerable values for total error (random and systematic errors), systematic error (bias), total standard deviation and limit of detection. Often, full evaluation is not possible and only limited performance data may be available. An indication of the status of the method is shown at the front of this publication on whether or not the method has undergone full performance testing.

In addition, good laboratory practice and analytical quality control are essential if satisfactory results are to be achieved.

Standing Committee of Analysts

The preparation of booklets in the series 'Methods for the Examination of Waters and Associated Materials' and their continuous revision is the responsibility of the Standing Committee of Analysts. This committee was established in 1972 by the Department of the Environment and is managed by the Drinking Water Inspectorate. At present, there are nine working groups, each responsible for one section or aspect of water quality analysis. They are:

1.0 General principles of sampling and accuracy of results
2.0 Microbiological methods
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General non-metallic substances
6.0 Organic impurities
7.0 Biological monitoring
8.0 Sewage treatment methods and biodegradability
9.0 Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, in co-operation with the working group and main committee. The names of those members associated with this booklet are listed at the back of the booklet.

Publication of new or revised methods will be notified to the technical press. An index of methods and the more important parameters and topics is available from HMSO (ISBN 0 11 752669 X).

Every effort is made to avoid errors appearing in the published text. If, however, any are found please notify the Secretary.

Dr D WESTWOOD
Secretary

27 December 1995

Warning to users

The analytical procedures described in this booklet should only be carried out under the proper supervision of competent, trained analysts in properly equipped laboratories.

All possible safety precautions should be followed and appropriate regulatory requirements complied with. This should include compliance with The Health and Safety at Work etc Act 1974 and any regulations made under the Act, and the Control of Substances Hazardous to Health Regulations 1988 SI 1988/1657. Where particular or exceptional hazards exist in carrying out the procedures described in this booklet then specific attention is noted. Numerous publications are available giving practical details on first aid and laboratory safety, and these should be consulted and be readily accessible to all analysts. Amongst such publications are those produced by the Royal Society of Chemistry, namely 'Safe Practices in Chemical Laboratories' and 'Hazards in the Chemical Laboratory', 5th edition, 1992; by Member Societies of the Microbiological Consultative Committee, 'Guidelines for Microbiological Safety', 1986, Portland Press, Colchester; and by the Public Health Laboratory Service 'Safety Precautions, Notes for Guidance'. Another useful publication is produced by the Department of Health entitled 'Good Laboratory Practice'.

A Inductively Coupled Plasma Atomic Emission Spectrometry

A1 Introduction

The development of inductively coupled plasma atomic emission spectrometry (ICP-AES) has arisen in response to the need for a solution analysis technique combining the sensitivity and precision of atomic absorption spectrometry with the capability for simultaneous multi-element determination. Although high temperature arc and spark plasmas have been used for the multi-element analysis of solid materials before the advent of ICP, their structures made them unsuitable for the injection of liquid samples.

In 1961, Reed [1, 2] described the first dynamic or flowing ICP. This plasma did not require electrodes, and its robustness for sample introduction was demonstrated by its use for high temperature crystal growing. Greenfield *et al* [3, 4] recognised the analytical potential of ICP operating in an annular configuration. Wendt and Fassel [5] were also experimenting with a laminar flow "tear drop" shaped ICP. Subsequently, Scott *et al* [6] described the medium power (1–3 kW) 18 mm annular plasma now favoured in modern analytical instruments. The importance of employing the correct plasma operating conditions was also demonstrated by Dickinson and Fassel [7] and this theme was further investigated by Boumans and deBoer [8, 9]. Although much of the early work was aimed at development of the ICP source, work on industrial analysis was carried out [10–12].

The pioneering work outlined above demonstrated the analytical advantages of the technique. Subsequent development of commercial instruments has led to ICP-AES becoming one of the preferred techniques for multi-element analysis of samples in solution. Many more advances have since been made following the original drafting of this manuscript.

A2 Plasma Emission Spectrometry

A2.1 Formation of a Plasma

An ICP is formed by coupling the energy of a radio-frequency (rf) magnetic field (1–3 kW power at 27–50 MHz) to free electrons in a suitable gas. The gas, usually argon, is contained in a plasma "torch" constructed from a high temperature resistant material, for example, fused silica, that is transparent to the rf radiation. The magnetic field is produced from a 2- or 3-turn water-cooled copper coil placed around the upper part of the torch. The initial electron "seeding" of the gas is provided by a spark discharge.

A single free electron is immersed in a gaseous cloud of neutral atoms, exposed to an oscillating magnetic field. The electron is accelerated during the first half of the cycle and describes an elliptical path around the magnetic field lines. Because the induced electro-motive force (emf) and the electron motion (current) are in phase, the loading of the generator is resistive and there is an efficient power transfer. Where no collisions occur before the field changes direction, the induced emf and electron motion become out of phase during the second half of the cycle and the power transfer falls to zero. For electrons in a gas at atmospheric pressure, the electron collision frequency (approximately 10^{10} s^{-1}) is much higher than the applied field frequency (approximately 10^{7} s^{-1}) typically used for ICP and therefore the electrons undergo numerous collisions during each half cycle; this interrupts the out-of-phase motion and allows efficient power transfer. Each elastic collision transfers a small amount of momentum, from the electron to a neutral gas atom, in proportion to the ratio of the colliding masses so that energy is gained by the electrons in a series of steps with frequent small reversals. Eventually some electrons attain energies equivalent to the ionisation potential of the gas, at which point they may undergo inelastic collisions

and cause further ionisation. An equilibrium is rapidly reached in which the rate of electron production is balanced by losses due to recombination and diffusion, and a stable plasma results.

Macroscopically, this process is equivalent to the heating of a conductor by an rf field, the resistance to eddy current flow producing Joule heating. The field does not, however, penetrate the conductor uniformly and therefore the largest current flow and heat dissipation occur in the periphery of the conductor. This so-called "skin" effect, coupled with a suitable gas flow geometry, produces an annular or doughnut shaped plasma. Electrically, the coil and plasma form a transformer with the plasma acting as a one turn secondary coil of finite resistance.

A2.2 Spatial Structure and the Emission of Spectral Lines from the ICP

The temperature distribution in a typical annular ICP is shown in Figure A1 [13]. This confers on the source almost ideal properties for the vaporisation, atomization and excitation of samples in solution. Given sufficient velocity, a particle of sample, as aerosol, will penetrate the base of the plasma and be constrained by the high temperature plasma ring to pass through the central channel. The injection velocity is typically 7 ms^{-1} and therefore the particle will be exposed to a temperature of approximately 6000K for a period of a few milli-seconds. Experimental evidence has shown that this is sufficient to provide 100% atomization efficiency for particles having diameters of less than 10 μm. The confinement of the sample aerosol to the axial channel limits the interaction between the introduction of the sample and the coupling of power to the plasma. This contributes greatly to the robustness of ICP in accepting sample aerosols without significantly modifying the ICP.

Before attempting to define the optimum operating parameters, it is necessary to have a qualitative knowledge of the structure of the central channel of the ICP. This can be achieved by examination of the fate of an aerosol particle as it traverses the plasma. As a particle approaches and enters the base of the plasma, evaporation occurs followed by dissociation of the water and solute components to yield free atoms. The energy requirements of these processes, particularly the dissociation of water, delay the temperature rise of the central channel, but then accelerate again due to the release of free hydrogen which has a thermal conductivity an order of magnitude higher than that of argon, the gas normally used in the plasma.

Once dissociation is complete, the first sign of low energy atomic emission is observed, but this quickly disappears as the rapid increase in temperature leads to ionisation which is partially offset by the increasing inflow of electrons from the plasma ring. The resulting structure of the central channel is shown in Figure A2. The terminology commonly used to describe this structure was first proposed by Koirtyohann *et al* [14]. An excellent way of viewing this structure is to nebulise yttrium into the plasma; in this case, the initial radiation zone is characterised by the red atomic emission, this gives way to a strong blue ionic emission in the hotter normal analytical zone, with the red atomic emission again returning in the cooler regions of the tail flame. The actual positions of the different zones are determined by the operating conditions, particularly the applied power and sample carrier gas flow rate, the quality and particle size distribution of the sample aerosol, the solvent vapour loading and the matrix components of the sample. It is normal to use the top of the load (induction) coil as the reference point for determining vertical locations in the plasma, but Anderson *et al* [15] have advocated using the normalised spatial emission profiles of spectral lines to provide an internal plasma reference point.

The principles of emission spectrometry in general [16] and plasma spectrometry in particular [17, 18] have been extensively covered in the literature. The equation describing the spectral radiance, B, of an assembly of atoms contained in a source in local thermal equilibrium having an absolute temperature (T) is:

$$B = \frac{1}{4\pi} h\nu_0 \frac{NL}{Z(t)} g_k A_{ki} \exp(-E_k/kT) \quad (Wm^{-2}sr^{-1}) \qquad (1)$$

where h is Planck's constant (Js)
ν_0 is the frequency of the emitted photons (s^{-1})
N is the number of atoms per unit volume (m^{-3})
Z(t) is the partition function

g_k is the statistical weight of the k_{th} state
A_{ki} is the Einstein transition probability for spontaneous emission (s^{-1})
L is the optical depth of the source (m)
E_k is the excitation energy of the k_{th} state (J)
k is the Boltzmann constant (JK^{-1})

This equation expresses the linear relationship that exists between the spectral radiance and the concentration of free atoms in the source which underpins the calibration of the emission intensity for analytical purposes. Equation (1), however, is based on the assumption that all photons emitted escape from the source and are available for detection, ie the source is assumed to be optically thin. In fact, this assumption is only valid when the product of the number density, N, and the optical depth, L, is small. As the product (NL) increases, there is a greater probability that emitted photons will be absorbed by unexcited atoms. This process of "self-absorption" degrades the proportionality between emission intensity and atomic concentration, producing a characteristic curvature of the calibration graph towards the concentration axis. The effect on the spectral profile of an emission line is shown in Figure A3. A point is eventually reached where the emission intensity at the line centre ceases to be dependent on the atomic concentration and, over this limited region of the spectrum, the source approximates to a black body whose radiance may be described by Planck's law and is a function of temperature only. Further increases in the emission intensity occur only in the wings of the line and it may be shown [17] that the intensity becomes proportional to $(NL)^{1/2}$. Thus the full calibration curve for the emission technique when plotted on logarithmic scales comprises an initial linear portion of unity slope followed by a region of curvature leading once again to a linear portion of slope 0.5. Such a curve is only obtained if the spectral bandpass of the measuring instrument can accommodate the very broad spectral lines that may occur at high analyte concentrations. Normally, this is not the case and the calibration curvature is more severe. Increased curvature, or even a negative slope in the calibration curve may occur if the source is inhomogeneous with respect to temperature along the viewing axis. The self-absorption caused by atoms in the cooler regions of the source is concentrated at the line centre, with the result that there is a decrease in the emission intensity over the central portion of the spectral line. This phenomenon is known as "self-reversal".

From Figure A2, the analyte atoms are confined to a narrow central channel through the plasma thereby minimising the optical depth, L. Furthermore, the external heating of this channel produces an almost flat temperature profile in the normal analytical zone (where the analyte emission is normally viewed). Self-absorption and self-reversal are therefore minimised with the result that the linear portion of the calibration curve extends upward typically 6 orders of magnitude from the detection limit.

The temperature distribution along the central channel of the ICP is reflected in the types of emission that are observed, as illustrated by the description of the spatial emission profile of yttrium. This characteristic profile has important implications for the use of ICP for spectrometric analysis in establishing optimum operating parameters and for the selection of spectral lines. Two concepts are useful in understanding the spatial emission profile: that of the "norm temperature" and a division of spectral lines into "hard" or "soft" lines as proposed by Boumans [19].

Equation (1) contains two terms which are temperature dependent, the partition function Z(t) and the exponential Boltzmann term. The partition function describes the change in the relative population of the excited states with temperature, and therefore increases with temperature, as does the exponential term. Initially, the exponential term increases at the greater rate and therefore the intensity of the spectral line rises. As the excited states become more populated, the increase in Z(t) accelerates and the intensity due to the transition begins to decrease. For elements of low ionisation potential there will also be a significant population of the excited states of the first ionic state. Thus, there is a temperature at which the emission intensity of a particular spectral line reaches a maximum and this is known as the "norm temperature". The Bouman's classification divides lines according to their difficulty of excitation, with lines having excitation potentials below approximately 4.5 eV being termed "soft lines" and those above, "hard lines".

For soft lines, it has been shown that low in the plasma, in the vicinity of the initial radiation zone, the peak in the spatial emission profile correlates with the norm temperature [20]. Thus, in this region of the central channel the excitation is essentially thermal in nature. A consequence of this is that both the position and magnitude of the spatial emission peaks for the soft lines are strongly dependent on the operating conditions and the matrix components of the sample, and these dependencies are reflected in emission observed from the normal analytical zone. These dependencies may be summarised as follows:

(a) an increase in applied power enhances the emission and shifts the peak lower in the plasma;

(b) an increase in the sample carrier flow rate reduces the emission intensity and shifts the peak higher in the plasma; and

(c) the presence of an increasing concentration of an easily ionisable element enhances the emission and shifts the peak lower in the plasma, but higher up in the vicinity of the normal analytical zone the enhancement is much less [21]. This is not an ionisation interference in the classical sense and the normal technique of buffering the source to reduce the problem is inappropriate.

For hard lines, the position of the peak of the spatial emission profile is remarkably constant, even for lines having widely different excitation characteristics. Thus, low wavelength (less than 300 nm) atomic lines and all ionic lines peak at approximately the same position in the plasma in the region of the normal analytical zone. This stability of the spatial emission pattern is reflected in the effect of parametric changes and the composition of the matrix. These may be summarised as follows:

(a) an increase in the applied power produces an increase in the emission intensity, but the position of the peak in the plasma changes very little;

(b) an increase in the sample carrier gas flow produces a small but significant upward shift in the spatial emission peak and a reduction in intensity; and

(c) an increasing concentration of easily ionisable elements causes a depression in the vicinity of the spatial emission peak, but an enhancement lower in the plasma with the result that there is a cross-over region where the effect of this is minimised.

These characteristics point to an essentially non-thermal excitation environment in the normal analytical zone. For more information on excitation mechanisms see reference [22].

The responses of the spectral emissions to parametric changes are reflected in changes in the zone structure of the plasma which occur as follows:

(a) an increase in the power causes the zones to shift downwards and there is an expansion of the normal analytical zone;

(b) an increase in the injector flow rate causes the zones to shift upwards;

(c) an increase in the outer flow causes a slight reduction in the overall plasma diameter and a small downward shift of the zones; and

(d) an increase in the intermediate flow moves the body of the plasma slightly upwards.

These descriptions of the structure of the central channel and the characteristic emission patterns are central to the successful analytical application of ICP and provide the basis for optimising the source, see section A6.2.

A3 Instrumentation

The instrumentation required for ICP-AES is shown diagrammatically in Figure A4 and comprises three basic units: the source, a spectrometer and a computer for control and data analysis.

A3.1 The source

The source unit includes the rf generator, the plasma torch and gas flow control system, and the sample introduction system.

A3.1.1 Radio-frequency generators

A number of different designs of rf generator are available and they are categorised according to whether they use a crystal oscillator and power amplifier to drive the local coil, or whether the load coil is part of a free-running rf oscillator. The type used is not particularly important in terms of analytical performance, except that the crystal controlled oscillators should have automatic tuning if organic solvents or hydride generation are to be used, or if the frequent ingress of small quantities of air to the sample introduction system is anticipated. Failure to provide automatic re-tuning under these circumstances will cause the plasma to be extinguished. Most commercial generators operate at 27.12 MHz, but it has been shown that plasmas operated at 40–50 MHz provide a higher signal-to-background ratio (SBR) in the emission spectrum [23].

An ICP can be sustained on powers down to a few hundred watts but, in order to operate the plasma to its full analytical potential, particularly if organic solvents are to be used, or if the plasma is to be operated on gases other than argon (for example air or nitrogen), a power output of up to 2000 watts (2 kW) is desirable. The precision of the ICP-AES technique under normal operating conditions is of the order of 1%. A typical emission line might show a response to power variation of 1–5% for each percent change in power, and therefore power stability and regulation of the power output with respect to the supply voltage is important. A stability figure of 0.1%, sustainable over a typical working day, is required if frequent re-calibration is to be avoided. The power unit should be sufficiently well screened to prevent interference with other equipment.

A3.1.2 Torches

The plasma is sustained in a plasma torch which consists of three concentric fused silica tubes arranged to provide a suitable gas flow geometry. Figure A5(A) shows a torch [24] which provides the annular plasma configuration essential for spectrochemical applications. Three gas flows were used in this torch, an outer or "coolant" flow introduced tangentially between the two outer tubes, an intermediate or auxiliary "plasma" gas also introduced tangentially between the injector and intermediate tube, and a central injector flow ("carrier" gas) to inject the sample aerosol through the base of the plasma. The torch used 10–35 litre min^{-1} of argon gas for the intermediate flow and 20–70 litre min^{-1} of nitrogen for the coolant flow and operated at powers up to 8 kW. An injector gas flow operated with a flow of 2–3 litre min^{-1} argon was used for aerosol introduction which was carried out with a modified atomic absorption nebuliser and spray chamber system.

Subsequent developments have led to a reduction in torch size and a corresponding reduction in gas consumption and operating power. Most modern instruments use a torch similar to that shown in Figure A5(B) [6]. Such torches will run at optimum performance at powers of approximately 1 kW, with an outer argon flow of approximately 10 litre min^{-1} and an injector flow rate of 1 litre min^{-1}. An intermediate flow may be used, but it is not necessary for successful plasma operation. This torch requires a high degree of concentricity and most are fabricated in one piece from fused silica. A problem with this form of construction is that erosion of the injector tube tip, or of the outer tube in the vicinity of the plasma, may necessitate replacement of the whole torch due to relatively minor local damage. This problem may be circumvented by use of a demountable torch as shown in Figure A5(C). The body supporting the outer fused silica tubes is made of ceramic-loaded polytetrafluoroethylene (PTFE) to provide thermal stability, and the sample introduction tube and injector mounting are made of PTFE. Gas is introduced tangentially through an array of holes for the outer flow, and other tangential holes for the intermediate flow. A very important feature of this torch is the use of 3 mm thick ground fused silica tubes which are shaped to produce smooth gas flow patterns. The fused silica is very robust so the injector and intermediate tubes endure almost indefinitely. The outer tube has a useful lifetime of approximately 1–2 years and may be replaced simply by plugging in a new one without dismantling the torch or removing it from the load coil. An additional feature of this torch is that it incorporates a sheathing flow for the injector flow [25]. This helps to minimise deposition on the tip of the injector when introducing solutions with a high solids content and it has also been found to improve the sensitivity of determination for the alkali metals [26].

Although there is a general consensus on the overall design of the torch, there are still variations in the type of injector used. Figure A6(A-C) shows three commonly used designs and these can be classified according to the degree of turbulence that exists in the aerosol stream as it enters the plasma. Design 6(A) provides a turbulent aerosol stream, whereas design 6(C) produces laminar flow. Design 6(B) represents an intermediate case. Figure A6(D) is a schematic of the injector tube used in the demountable torch; it incorporates two further features, a 20^{0} (full angle) inlet taper and a tapered injector tip. This design offers several advantages. The laminar flow appears to produce an easier penetration of the fireball and a greater concentration of the injector flow along the axis. This could be a disadvantage when aerosols or slurries are introduced to the plasma because the mixing between the hot gas (in the fireball) and cooler gas (in the central channel) may be somewhat slower. However, for normal solutions, and particularly for organic solvents where it is desirable to prevent diffusion of the solvent vapour into the fireball, the laminar flow injector is superior. The tapered tip reduces salt deposition on the top surface of the injector and also prevents the build-up of carbon deposits when organic solvents are used [27]. The low-angle inlet taper prevents excessive deposition of aerosol particles at the inlet and its remoteness from the plasma stops deposits from being baked onto the silica surface.

Torches are best left undisturbed unless there is a noticeable deterioration in analytical performance. Cleaning may involve an overnight soak in concentrated nitric acid, and some brushing of the injector tip or the outer wall may be necessary to remove solid deposits. Ablation and devitrification of the outer tube may eventually lead to arcing of the plasma through the wall onto the coil. This can usually be repaired and may be avoided by the addition of a fused silica "bonnet" (see Figure A5(D)) between the coil and the torch.

The observed shape of the plasma is determined to a large extent by the entrainment of the surrounding air. Extended torches have therefore been used, to exclude air and permit the determination of nitrogen using the 386.1 nm NH band-head [28], and to reduce the background emission from the OH band [29].

The gas consumption and power requirement of ICP have been shown to be dependent on the annular gap between the intermediate and outer tube [30]. For example, a torch having an annular gap of 0.3 mm can be operated successfully with an outer flow of 3 litre min^{-1} with an applied power of 0.3 kW. The requirement for good concentricity, however, places severe dimensional constraints on such designs and the practical limit appears to be about 0.4 mm. A high efficiency torch [31] using approximately 6 litre min^{-1} argon shows evidence that the structure of the plasma and excitation conditions may be slightly different from those obtained with conventional designs. An alternative approach to reducing gas and power consumption is to reduce the torch size [32].

A3.2 Sample Introduction

The ICP can accept samples in vapour, liquid, or solid forms and systems have been described for the introduction of each type of sample. The robustness of the ICP for sample introduction is one of its great strengths, and modifications to the method of sample introduction can be the simplest way of enhancing the performance of the technique for specific applications.

A3.2.1 Nebulisation

The vast majority of analyses are carried out using pneumatic nebulisation for sample introduction and, although satisfactory for many applications, it is often stated that this is the weakest link in ICP instrumentation. Sharp [33] has discussed this topic and the information given here is limited to practical matters relating to the principal types of nebuliser.

A typical nebuliser/spray chamber combination, operating at a gas flow rate of 1 litre min^{-1}, pressure of 30 psig (approximately 21000 Nm^{-1}) and using 2 $mlmin^{-1}$ of aqueous sample, will deliver to the plasma, approximately 20-30 mg of aerosol, with a maximum particle diameter of about 10 μm, and an accompanying 17 mg (assuming that the nebulising gas is saturated at 20 ^{0}C) of water vapour per litre of gas. This technique of sample introduction has a number of disadvantages.

(a) Because pneumatic nebulisers produce polydisperse aerosols and require a spray chamber to remove the large particles, the analyte transport efficiency can be poor, approximately 1%.

(b) The process of nebulisation is affected by the physical properties of the solution (temperature, surface tension and viscosity) and the presence of particulate matter, and therefore a degree of matrix matching is necessary between samples and standards. The sample flow rate to the nebuliser is also affected, but this may be controlled independently by a pump.

(c) Fluctuations in the rate of aerosol production are a principal source of noise in the optical signal.

(d) The presence of dissolved solids at concentrations in excess of 5000 μgml^{-1} particularly salts close to saturation, or particulate matter, notably cellulose fibres, can lead to partial blockage of the nebuliser or a cessation of operation. Temporary perturbations of the production of aerosol may result in undetected analytical errors.

In spite of these drawbacks, the simplicity and convenience of the nebulisation technique and its excellent performance in most circumstances makes the procedure very popular.

Figure A7(A, B, and C) shows the three principal types of pneumatic nebuliser. The concentric (A(7A)) and cross-flow (A7(B)) nebulisers are self-priming whereas the Babington nebuliser (A7(C)) requires a pump to deliver the solution. The glass concentric nebuliser is probably the most widely used and with care provides stable and trouble-free operation. Its principal disadvantages are its fragility and the fineness of the liquid-carrying capillary (internal diameter, about 0.3 mm) and of the annular gas orifice (thickness, about 0.02 mm). Blockages are commonly due to accumulation of salt particles in the annular gas orifice, and to physical obstruction of the liquid capillary, usually by fibres attaching themselves to the wall at the tube exit. Recessed-tip versions of the concentric nebuliser have been reported which enable highly concentrated salt solutions to be handled without salting-up of the gas orifice [34]. Other necessary precautions are to ensure an adequate washing of the nebuliser between samples and to prevent the passage of excessive quantities of air which can promote drying of the tip and crystal formation. The use of argon saturated with water vapour also helps to prevent salt formation, and in extreme cases, periodic injections of water into the gas line clean the nebuliser without the need to interrupt the plasma. A blocked nebuliser can be cleaned by soaking, by back-flushing (either orifice) with a syringe, or by ultrasonic cleaning in acid and/or a surfactant. Mechanical cleaning should only be used as a last resort and then only soft materials should be used, for example a camel hair brush or nylon fishing line. The glass construction precludes the use of hydrofluoric acid, solutions containing concentrated fluoride ion, or strongly alkaline solutions.

A final point of practical concern is the connection of the liquid supply tubing to the nebuliser which has a large bore glass inlet tube. A suitable method [35] employs a platinum capillary set in silicone rubber adhesive to reduce the large dead volume.

The cross-flow nebuliser (Figure A7(B)) offers similar analytical performance to the concentric flow design and requires the same basic care. Various materials are used for its construction, including sapphire, glass and inert plastics. The most critical mechanical feature is the relative alignment of the liquid-carrying capillary and the gas orifice, and therefore a rigid design is essential. The liquid carrying capillary generally has an internal diameter not exceeding 0.5 mm and that of the gas orifice is usually 0.1—0.2 mm. Liquid capillaries of less than 0.3 mm internal diameter are prone to blockage. The cross-flow nebuliser is slightly less prone to blockage than concentric types, and when this does arise it is usually the liquid capillary which is obstructed. Salting-up can occur on the side of the liquid carrying capillary facing the gas orifice, this results in the formation of a salt bridge and ultimately perturbation of the gas flow. Most cross-flow nebulisers operate at relatively low pressure (20-40 psig, approximately 14000—28000 Nm^{-1}), but an all-glass high-pressure (200 psig, approximately 1400000 Nm^{-1}) design offers some advantages in terms of efficiency and analytical precision [36]. A drawback of this device is that it needs a separate gas control system.

Very concentrated solutions, or those containing significant quantities of suspended solids, for example, slurries can be determined using a nebuliser based on the Babington principle [37]. The essential feature of this design is that the liquid is not confined to a narrow capillary but is conducted to the gas orifice along an open slot or V-groove (Figure A7(C)) [33, 38–42]. The key factor is the efficiency of the gas-liquid mixing and, if this is satisfactory, the performance of the device will equal or exceed those of concentric or cross-flow nebulisers. The problem of achieving satisfactory gas-liquid mixing has been addressed in the "Conespray" nebuliser (Figure A7(D)) and employs a conical sapphire nozzle into which liquid is introduced by the action of gas jet entrainment. Lower analyte transport efficiencies can be overcome by increasing the sample feed rate.

Other kinds of nebulisers have been investigated and have been shown to offer specific advantages, but often these are outweighed by factors that reduce their convenience of operation. The ultrasonic nebuliser is perhaps the best example of these [43, 44]. It produces a very fine aerosol (particle diameters of less than 2 μm) and therefore high transport efficiency, and enables the injector flow rate and nebulisation rate to be varied independently. Set against these advantages are: the rather unstable production of aerosol leading to increased noise, the need to de-solvate the sample aerosol to avoid excessive solvent loading of the plasma, relatively slow sample changeover times, and a gradual deterioration in the interface that couples the ultrasonic energy to the solution.

The frit nebuliser is by far the most efficient pneumatically-powered device, producing droplets of the order of 1 μm in diameter [45]. However, the fine pores of the frit (4–8 μm in diameter) are prone to progressive blockage, and memory effects for elements having a high affinity for glass, for example, boron have been reported [44]. Frit nebulisers may have some advantages in delivering organic solvents to the plasma where the small particle size will aid pre-plasma evaporation and therefore lead to reduce vapour loading if the vapour is re-condensed on the spray chamber walls [46]. A nebuliser which uses a pair of 100 μm mesh platinum gauzes instead of a frit [47] has been used. This device is intermediate between a frit and a Babington nebuliser and offers some modest improvements in efficiency with good sample handling characteristics.

The thermospray nebuliser, originally designed as an interface for liquid chromatography—mass spectrometry (LC-MS) [48], has been used in ICP-AES and, like the ultrasonic nebuliser, offers improved efficiency and does not depend on the injector flow as the energy source for nebulisation [49]. Nebulisation occurs through the adiabatic expansion of a superheated liquid held under pressure in a capillary tube by the action of a pump.

An obvious drawback of the design is the requirement to use narrow capillaries (approximately 150 μm) to sustain a high pressure without excessive liquid flow. A promising application of the thermospray is the interfacing of HPLC to ICP-AES where the chromatographic column acts as an effective pre-filter for the nebuliser [50].

The principal function of the spray chamber is to remove the large aerosol droplets (greater than 10 μm) from the spray produced by the nebuliser. It should, however, accomplish this with a minimum loss of the small droplets, permit rapid changes from one sample to another without memory effects, and provide for free drainage of the waste solution without causing pressure pulsations which can be reflected in noise on the optical signal. Temperature control of the spray chamber can result in improved precision (depending upon the magnitude of fluctuations in ambient temperature). Cooling of the spray chamber is the principal method employed for controlling the solvent loading of the plasma when organic solvents are used [51].

The most satisfactory spray chambers are those incorporating a simple impact wall with a minimum impendence low dead volume path for the aerosol take-off. Take-off tubes greater than 8 mm in diameter allow free drainage of any aerosol or vapour that condenses out at the chamber exit. The double-pass spray chamber, [6], see Figure A8(A), is the most commonly used, but often has unnecessarily large dead volumes. An alternative design is shown in Figure A8(B). Cyclonic chambers have also been used which claim to provide improved efficiency compared with the double-pass chamber [52]. Free drainage of chambers is essential and this is assisted

by occasional nebulisation of a surfactant to ensure that the walls of the chamber are "wetted" by the solvent. The surfactant will also improve performance of the constant head device which is normally used to drain the excess liquid from the chamber. If a multi-channel pump is used to feed the nebuliser, one channel can be used as an effective and pulse free method of draining the chamber. Such a configuration may also be used to re-circulate the analyte to improve the efficiency, although some designs of re-circulatory spray chambers use self priming concentric nebulisers feeding directly on the drained solvent pool [53, 54].

The use of a peristaltic pump to feed the nebuliser has a number of advantages. It minimises variations in the feed rate caused by changes in the viscosity of the solution and by changes in the static head between the nebuliser and the sample reservoir. Nebulisers produce a very modest suction and the liquid carrying capillary is easily obstructed. If a pump is used to supply the sample, such an obstruction will cause an immediate rise in the pressure up to about 30 psig (approximately 210000 Nm^{-1}) which will often clear the blockage. Additionally, the pump may be reversed to back-flush the nebuliser for cleaning. Furthermore, the pump enables the sample flow rate to be controlled independently of the nebuliser gas flow rate. Most nebulisers provide improved efficiency at low liquid flow rates which may also be accompanied by improved signal-to-noise ratio leading to lower detection limits. A free-running nebuliser draws in copious quantities of air through an empty liquid feed tube which may de-stabilise the plasma and lead to salting-up of the nebuliser. The pump minimises the ingress of air and therefore avoids problems if the solvent reservoir should inadvertently empty. Additionally, a pump greatly simplifies automation of the sample handling and is an essential component for techniques such as flow-injection and hydride generation. There are, however, some disadvantages, but these can be minimised with appropriate precautions. Peristaltic pumps produce surges in the flow which are reflected in the optical signal. These are minimised by using a multi-roller pump run close to its maximum speed with narrow bore pump tubing. The important consideration is the ratio of the period of signal variation to the measurement period. The extra plumbing associated with the use of a pump may slow down the change-over time between samples. Perversely, this problem becomes more acute when high efficiency nebulisers requiring very low liquid feed rates are used (for example, frit nebulisers). Problems have been encountered with the adsorption of transition metals, for example, copper and iron from water samples with low acidity onto solvent resistant pump tubing. The effect is not consistent and is influenced by the past history of the tubing. An effective solution to the problem is to add ethylenediaminetetraacetic acid to the samples and standards to preferentially complex the susceptible elements.

A3.2.2 Chemical Vapour Generation

The direct introduction of the analyte in vapour form offers the potential for achieving 100% transport efficiency and therefore improved sensitivity; a separation of the analyte from the matrix and a consequent reduction in interferences; and avoids the problems associated with nebulisation. The techniques used are modifications of those previously developed for use in atomic absorption spectrometry, namely the cold vapour technique for mercury, hydride generation for arsenic, bismuth, germanium, lead, antimony, selenium, tin and tellurium, and the generation of volatile chlorides and organometallic compounds. The necessity for modification arises because the ICP is not tolerant of high levels of molecular vapours, for example, hydrogen, as these quench the plasma and may cause an impedance mismatch with the generator causing the plasma to be extinguished. Higher power levels (2–2.5 kW) are usually employed to accommodate greater levels of hydrogen input, but the essential step is to limit the production of hydrogen to a suitable level. This is usually accomplished by generating the hydrides in a continuous flow apparatus which enables the rate of reaction to be controlled.

The use of continuous flow hydride generation has been extensively studied [55–57, see also ref 35, Chapter 6] and methods have been developed for a range of geological samples [58–60], waters [61] and plant materials [62]. Optimisation studies have been carried out [63–64] and a mathematical model of hydride generation which describes the factors affecting the shape and magnitude of the analytical signal has been reported [65–67].

The chemical vapour generation of species other than hydrides is not widely used, but some useful applications have been reported. For example, the determination of dissolved organic carbon in water by oxidation with copper oxide and conversion to carbon dioxide [68]; dissolved carbonate by conversion to carbon dioxide [69]; sulphide in waters by conversion to hydrogen sulphide [70] and molybdenum by nebulisation of a solution of butan-1-ol containing molybdenum as $Mo(CO)_6$ [71].

A3.2.3 Electrothermal Vaporisation

The simplest method of improving the sensitivity of ICP techniques is to bypass the nebulisation step and introduce the analyte directly into the plasma. A number of techniques have been developed including electro-thermal vaporisation (ETV), direct sample insertion devices, based on graphite cuvettes or metallic filaments; arc or spark sampling for conducting materials; and laser ablation. Developments in all of these techniques are regularly described in the literature.

The technique most relevant to liquid samples is ETV which has been comprehensively reviewed [72]. The use of ETV for sample introduction provides approximately an order of magnitude improvement in detection limits for elements that are readily vaporised. There is also the potential for the elimination of interferences, either through the use of an ashing step, or by time gating the measuring system to coincide with the appearance time of the analyte [73]. Unless it is imperative to achieve lower detection limits, the operational disadvantages of ETV preclude it from routine use. The selective vaporisation encountered with ETV may be advantageous in removing certain interferences, but it also accounts for a loss of sensitivity for refractory elements. This problem may be overcome [74] by the addition of 0.1% trifluoromethane to the argon gas preferentially to form volatile halides. It is important to stress that complete atomization is not necessary and is probably disadvantageous because of the loss of free atoms to the containing vessel walls. A molecular vapour, or better still a micro-particulate, exhibits superior transport properties and selenate or sulphide ions can be added to samples to promote aerosol formation [75]. Other factors including condensation have been considered [76], and the addition to the carrier gas of halocarbon or hydrocarbon vapours which, through pyrolysis, can provide a carrier aerosol for the analyte.

The signal from ETV sample introduction is transient, and this complicates the use of automatic background correction by wavelength scanning. Furthermore, the rapid heating of the injector gas flow causes volumetric expansion of the gas and a decrease in background emission intensity as the resultant pressure pulse passes through the plasma. It has been suggested [77] that the containment cell volume should be minimised so that the pressure pulse is sharp and decays before the analytical signal develops. Uniform heating of the furnace is necessary to avoid multiple peaks in the emission signal and a close coupling of the furnace with the torch minimises transport losses.

Direct sample insertion devices offer an economic alternative to ETV, but the thermal mass of the substrate limits the maximum temperature attainable so that refractory materials are not efficiently vaporised. Set against this drawback are the simplicity of the device and the removal of interference effects caused by differential transport of analytes. Although the ETV approach is the more readily automated, an automatic direct sample insertion system has been described [78].

A3.3 Spectrometers

The most important features of a spectrometer for ICP-AES are its resolution, light throughout, stability, and stray light performance. Unfortunately, high resolution is not compatible with high light throughout (for dispersive spectrometers) and stability, and a compromise is necessary. It must be stressed that this compromise is entirely determined by the type of samples that are to be analysed. For samples generating line rich spectra, for example, metallurgical, nuclear, or rare earth materials, high resolution should be the first regard to both minimise interferences and conserve practical detection limits [79]. Agricultural and environmental samples are generally less demanding in this respect. Instruments to be used for such samples require moderate resolution, but with high light throughput and stability, and good stray light characteristics to cope with high concomitant matrix levels.

The largest contribution to the physical line width of spectral lines emitted from an ICP is Doppler broadening and since the Doppler half-width is inversely proportional to the square root of the atomic mass, there is a progressive reduction in line width for heavier elements. Thus, for example, the light elements beryllium (Be II 313.107 nm) and boron (B I 249.773 nm) have line widths of 6.2 pm and 5.0 pm respectively, whereas the heavy elements molybdenum (Mo II 202.030 nm) and gold (Au II 200.081 nm) have line widths of 1.2 pm and 0.9 pm [79]. This simple picture is complicated by the fact that many spectral lines exhibit hyperfine structure due to the effect of nuclear spin or to the pressure of isotopic components. The hyperfine structure is not normally resolved by analytical instruments and can result in the occurrence of quite broad spectral lines. This effect has been observed for lines of bismuth, cobalt, europium, holmium, indium, lanthanum, lutetium, manganese, niobium, lead, praseodymium, platinum, rhenium, antimony, tantalum, terbium and vanadium [79]. For example, the reported physical line widths of lanthanum (La II 398.852 nm), niobium (Nb II 309.418 nm) and holmium (Ho II 347.426 nm) are 14.6, 14.8 and 21.2 pm respectively. Even these line widths do not approach the apparent line widths caused by self absorption.

An ideal spectrometer would have a spectral bandpass equal to the width of the line under study and would be capable of resolving lines separated by this wavelength interval. For the lines emitted from an ICP, a resolving power in excess of 10^5 would be required to meet this criterion. Many ICP spectrometers have a theoretical resolving power of this order, but the practical resolving power is always determined by the slit-width [80]. A narrow slit (for example, 3 μm) set to provide diffraction-limited performance will pass such a small flux that the attainable signal-to-noise ratio and detection limit will be limited by the shot noise. Opening the slit will increase the light flux, but the noise will increase only as the square root of the light flux with a consequent gain in the signal to noise ratio and detection limit. The limit to this improvement is set by the increasing contribution from flicker noise (which is proportional to the signal intensity) which for the ICP limits the attainable signal to noise ratio to approximately 200. Thus for measuring the background emission, or lines for which there are no problems of spectral interference, the minimum practical slit width is that which permits the instrument to be operated under flicker noise limited conditions. The effects on slit width and therefore on the practical resolution of meeting this requirement become increasingly severe for wavelengths below 250 nm. Provided that the light flux is adequate, the minimum slit width is set by the constraints of mechanical stability. In most practical situations, there will be a need to minimise spectral interferences and the working slit width will be a compromise between resolution and light throughput. Typical slit widths vary between 20 and 50 μm depending upon the type of instrument and the particular application.

The majority of spectrometers used in commercial ICP systems are of the single channel scanning type, or of the multi-channel fixed wavelength type. Figure A9 is a schematic diagram of a typical scanning spectrometer using the Czerny-Turner mounting. Figure A10 shows the optical configuration of a typical multi-channel spectrometer using the Paschen-Runge mounting. The detailed designs of these spectrometers have been described elsewhere [35, 18 (Part I)] and here discussion will be limited to their operational characteristics. The basic requirements for any spectrometer for ICP-AES are that the wavelength coverage extends from below 200 nm to 800 nm and that the detection system is linear over a range of 10^6, which covers the operating range of most photomultiplier tubes (anode currents 1—10^6 nanoamps) and encompasses the linear dynamic range of the ICP (10^5). A number of elements, notably aluminium, arsenic, mercury, phosphorus and sulphur have their best analytical lines below 200 nm and for these an evacuated spectrometer is required.

Several factors must be considered before an objective choice can be made between a scanning and multi-channel system [81, 82]. The following is a list of the operating characteristics of each type.

A3.3.1 Multi-Channel Spectrometers

The advantages may be summarised as follows:

(i) Speed of analysis. Because all the analyte lines are monitored simultaneously, the speed of analysis is limited mainly by the sample changeover time.

(ii) Minimal sample consumption. Multi-element determinations can be performed on a small volume of sample, or on microsamples if ETV or HPLC are used for sample introduction.

(iii) Accuracy and stability of wavelength setting. The use of fixed slits and a modern thermally stable construction ensure that the correct wavelengths are measured. The stability of the wavelength setting provides good analytical precision (0.5-1.0% relative standard deviation) for routine measurements.

(iv) Flexibility of background correction mode. Most modern multi-channel spectrometers incorporate a scanned entrance slit or spectrum shifter to enable simultaneous scanning of all the programmed spectral lines. This feature, together with the ability to quantify, simultaneously, elements causing spectral interference, permits both automatic (off-peak) and on-peak background correction.

(v) Ease of applying matrix corrections. Rotational interferences caused by matrix components can be compensated for without time penalty by the simultaneous determination of the concentrations of the interfering elements and the application of suitable corrections.

(vi) Ease of implementing internal standardisation. The simultaneous measurement of reference lines can in specific circumstances compensate for changes in instrument performance (see section A6.2).

The disadvantages are:

(i) High cost relative to single channel spectrometers.

(ii) Inflexibility. The suite of lines to be used should be chosen in advance of installation and subsequent modification is difficult and expensive. There may be no facility for moving to another line if a new sample type renders a line unusable because of its sensitivity, or the occurrence of spectral interferences.

(iii) Moderate resolution. The requirement to maintain good optical stability imposes limitations on the slit width that can be used in a multi-channel spectrometer. Typically, entrance slits of 20 μm and exit slits of 50 μm are used which, for a spectrometer having a reciprocal linear dispersion of 0.8 nm mm^{-1}, in the first order yields a bandpass of 0.04 nm. This imposes limitations on the use of automatic background correction and on the ability of the instrument to minimise spectral interferences.

For these reasons, multi-channel spectrometers are normally employed where high sample throughput is required and the elements to be determined are known in advance of purchase. A particular ability of multi-channel instruments is the provision of multi-element determinations on micro samples provided that an appropriate sample introduction procedure is used.

A3.3.2 Single-Channel Scanning Spectrometers

The advantages include:

(i) Flexibility. All the spectral lines for each element are available for selection to meet the requirements of a particular application.

(ii) High resolution. Because wavelength selection is achieved dynamically, narrower slits, for example, 20 μm, can be used leading to improved resolution. The consequences of this are reduced spectral interferences and improved detection limits, most noticeably in the presence of spectral interferences [79]. A reduced optical bandwidth provides improved signal-to-background ratios which could translate directly into improved detection limits compared with multi-channel spectrometers, even in situations where there are no spectral interferences [83]. Unfortunately, the uncertainty in dynamic wavelength selection and the difficulties in extracting the true net line intensity from a wavelength scan have meant that the detection limits obtained on the two types of system for aqueous standards are similar.

(iii) Ease of automatic background correction. The total signal and background signal are measured separately and the net analyte signal calculated by difference. Background correction is therefore automatic and can be extended to work in the presence of spectral interference, either by implementation of a suitable software algorithm, or by intervention of the analyst following graphical display of the data.

(iv) Lower cost relative to multi-channel spectrometers.

(v) Survey analysis. It is possible to scan the entire spectrum of the ICP and, using software-based reference tables, produce a "total analysis" on a semi-quantitative basis.

The disadvantages are:

(i) Speed of analysis. The sequential measurement of spectral lines involving slewing to the line, peak location and measurement imposes a time penalty in proportion to the number of elements determined. Modern instruments have extremely rapid wavelength drives and can, by economising on the measurement time, perform rapid survey analyses, but at the expense of precision.

(ii) Higher sample consumption. This is a direct consequence of (i) above and occurs in proportion to the number of elements determined.

(iii) Inability to implement internal standardisation. Whereas matrix correction can be achieved by time separated measurements, internal standardisation requires the simultaneous measurement of the reference line(s).

Since the manuscript was orininally drafted, the disadvantages identified here, and in the previous section, have decreased.

Scanning spectrometers have therefore found application in situations where sample throughout is not the principal criterion, where the range of elements determined varies widely from sample to sample, and in some applications where there has been a paramount need to minimise spectral interferences.

An instrument combining the merits of scanning and multi-channel spectrometers has obvious advantages. The simplest approach is to add a separate scanning monochromator system viewing the plasma along a different axis. The advantages are that the best features of each type of spectrometer are available, but such "two-box" solutions are expensive. A simpler alternative is to provide a separate scanning or "(N + 1)" channel within the frame of the multi-channel spectrometer. The resolution of such systems is inevitably poorer than that achieved by stand-alone scanning spectrometers, but the engineering is more compact and the standard electronics of the multi-channel spectrometer can be used to process the signal from the roving channel.

The optical geometries of a combination spectrometer are shown in Figures A11 and A12. In this system, the emitted light in the centre of the aperture of the primary optics is passed to the multi-channel spectrometer and the light which falls outside the aperture of this spectrometer is intercepted and passed to the scanning spectrometer. A feature of this instrument is that the scanning spectrometer is of a hybrid design. It uses the same frame type as a multi-channel spectrometer, but the individual exit slits are replaced by an array of 255 equally spaced (2 mm) exit slits etched into a mask. In operation, the entrance slit is moved (±1 mm) along the Rowland circle so that the analytical line is brought into coincidence with one of the exit slits. Detection is by one of two photomultiplier tubes (optimised for red and blue response) which can be positioned behind the appropriate exit slit by means of a movable carriage. Advantages of the design are that scanning to any wavelength can be achieved within 2 seconds, and that the performance is closely matched to that of the coupled multi-channel spectrometer.

The majority of ICP-AES systems use spectrometers of the type previously described, but two alternative spectrometer designs are available that offer both high resolution and good light throughput. They are the echelle spectrometer and the Fourier transform (FT) spectrometer. The theoretical resolution of a grating is determined by the product of the total number of rulings and the order of diffraction. Conventional spectrometers usually operate in the first or second order, but an echelle spectrometer is set up to employ orders of 50–100. To maintain an adequate light throughput, a coarsely ruled blazed grating is used. The penalty of such a configuration is the overlapping of spectral orders that occur in the focal plane of the instrument. In a conventional spectrometer, 400 nm in the first order corresponds with 200 nm in the second, and 133 nm in the third, etc, and 400 nm in the hundredth order corresponds with 396 nm in the ninety-ninth order. Thus, whereas order overlap is not a serious problem at low orders and is reduced by the judicious use of filters, it is a serious problem at high orders. Two approaches have been used to overcome this difficulty.

In the first (see Figure A12) a prism is used as a secondary disperser to sort the orders so that the spectrum has a 2-dimensional configuration, each line accommodating the spectrum of a given order. The second approach employs a coarse monochromator as a pre-filter to limit the spectral bandpass to one order at a time. Instruments with a 2-dimensional spectral display can be used with a slit mask to function as multi-channel spectrometers, or with a programmable single slit to mimic a conventional scanning spectrometer. The pre-filter spectrometer operates in a manner entirely analogous to that of a conventional monochromator. Both systems are capable of matching or exceeding the resolution performance of low order grating instruments and of providing bandwidths (0.002 nm) approaching the physical line width.

The ideal spectrometer would have unlimited and variable resolution, high accuracy wavelength setting, simultaneous recording of all wavelengths in the spectrum and high light throughput. Such are the properties of Fourier transform spectrometry which have been reviewed [84]. Unfortunately, when applied to noise limited sources such as ICP, the multiplex advantage becomes a severe disadvantage in that temporal fluctuation (noise) from strong spectral components in the source become transformed to spectral features (side bands) and base-line noise in the transformed spectrum. The result is a poorer signal to noise ratio for weak lines and a loss of detection power. This problem may be circumvented by the use of a pre-disperser to limit the optical bandwidth, but the invaluable ability to simultaneously record the entire sample spectrum is lost.

A4 Analytical Characteristics

A4.1 Element Coverage

The ICP is suitable for the determination of most elements in the periodic table with the exceptions of the halogens, the inert gases and those gases found in air which are freely entrained into the plasma in the normal analytical zone. Emission lines for the halogens in the near infra-red have been reported [85], but the detection limits are poor. Air may be excluded from the plasma, as indicated earlier, by the use of a torch with an extended outer tube and this approach has been used for the determination of nitrogen [28, 86]. A list of lines commonly used in analysis by ICP-AES is given in Table A1.

A4.2 Detection Limits, Precision and Dynamic Range

Detection limits in ICP-AES are usually defined as the concentration yielding a net line signal equal to n times the standard deviation of the background signal (σ_B). The value of n is usually taken as 2, or 3 and the sometimes quoted "limit of determination" corresponds to n = 10. If a 2σbasis [87] is adopted, the detection limit, C_L is defined by

$$C_L = \frac{2\sigma_B}{S} \tag{2}$$

where S is the sensitivity, ie the slope of the linear calibration curve relating signal strength to concentration. For a given concentration C, the equivalent net line intensity is I_c and hence the sensitivity is given by

$$S = \frac{I_c}{C} \tag{3}$$

and introducing the background intensity I_B, equation 2 becomes

$$C_L = 2\sigma_B \frac{I_B}{I_B} \frac{C}{I_c} \tag{4}$$

or

$$C_L = \frac{2\sigma_B}{I_B} \frac{C}{SBR} \tag{5}$$

where SBR is the signal-to-background ratio. An ICP operating under flicker noise limited conditions should achieve a relative standard deviation of the background signal of 0.01 so that equation (5) becomes

$$C_L = 0.02 \frac{C}{SBR} \quad (6)$$

From which it can be seen that the detection limit should correspond to a signal to background ratio of 0.02. In practice this will vary depending upon whether the background is pure continuum radiation, or is structured because of the presence of spectral lines or bands [79]. Another quantity, derived directly from equation (6) and often quoted is the background equivalent concentration (BEC) corresponding to the concentration required to yield a signal to background ratio of unity.

For small signals (SBR of less than 1), the noise is principally that due to the variation in the background so that to a first approximation the standard deviation of the net line signal remains fairly constant for concentrations below the BEC. However, the relative standard deviation gradually improves with increasing concentration as the line strength increases. At concentrations above the BEC, the standard deviation increases in proportion to the net signal so that the relative standard deviation becomes constant at a value of approximately 0.01. This situation is shown graphically in Figure A13.

Detection limits for ICP-AES using pneumatic nebulisation for sample introduction vary from approximately 0.1 $ngml^{-1}$ for elements such as calcium, barium, magnesium, manganese and strontium up to approximately 100 $ngml^{-1}$ for elements such as arsenic, potassium, phosphorus, lead, selenium and uranium. An order of magnitude improvement is attainable for many elements using ETV and a similar improvement is achieved by the use of hydride generation for the elements arsenic, bismuth, germanium, lead, tin, selenium and tellurium. A list of detection limits for ICP-AES is given in Table A2. These are generally attainable using aqueous standards but may be severely degraded for real samples. The linear dynamic range of ICP-AES is 3 to 6 orders of magnitude, depending upon the detection limit for the particular element [88]. Curvature is produced either by self absorption above 1000 μgml^{-1}, or there is the possibility that a matrix effect will occur which produces a "self-induced" curvature of the calibration line [89]. Matrix effects are dependent upon the operating conditions and therefore it can be anticipated that the onset of calibration curvature will depend on the instrument settings [90]. The dynamic range for most elements, therefore, extends from approximately 1000 μgml^{-1} down to the detection limit.

Ideally, the detection system should not impose a limit on the dynamic range, but in one respect this is unavoidable. A spectrometer set up to produce flicker noise limited performance on a particular line typically operates with a photomultiplier tube anode current, derived from the background, of 100-1000 nanoamps. The maximum tube current is typically 10^5—10^6 nanoamps and so, in the worst case, only 3 orders of magnitude of linear response are available. This difficulty can be resolved by reducing the voltage on the photomultiplier tube, reducing the slit-widths (if practical) or selecting a different line.

A.5 Interferences

The increasing popularity of ICP-AES for elemental analysis owes much to the remarkable degree of freedom from interferences. Nevertheless, interferences do occur and they are normally divided into two classes, translational (or additive) and rotational (or multiplicative) interferences. Translational interferences are proportional to the concentration of the interferent and independent of the concentration of the analyte. A given concentration of the interferent produces a signal that is additive to the analyte signal and causes a simple translation of the calibration curve along the response axis as shown in Figure A14. Rotational interferences occur when the effect of a given concentration of the interferent is to multiply the analyte signal by a constant factor. The factor is independent, to a first approximation, of the concentration of the analyte and the effect is to produce a rotation of the calibration curve about the origin (see Figure A14). Translational interferences are caused by spectral overlaps and by stray light in the spectrometer, whereas rotational interferences are caused by more general matrix effects.

A5.1 Spectral Interferences

The total signal produced by a spectrometer observing an ICP is the summation of the signals due to the background continuum radiation, spectral lines from atoms and ions, molecular bands, stray light within the spectrometer and the photomultiplier

tube dark current. The background continuum is derived from recombination radiation (dominant below 500 nm) and from Bremsstrahlung radiation (dominant above 500 nm) which is caused by the local acceleration and deceleration of electrons as they pass in the vicinity of the slower moving plasma ions.

Spectral interference can conveniently be divided into three classes as illustrated in Figure A15. These are:

(i) line overlap, in which the interfering line shares a common portion of the spectrum with the analyte line;

(ii) line interference, in which the interfering line intrudes into the spectral bandpass of the spectrometer; and

(iii) background interference, in which there is a general change in the intensity of the background continuum, or in which the wing of an intense neighbouring spectral line intrudes into the bandpass of the spectrometer.

Theoretically, the wings of any spectral line extend to infinity on the wavelength axis so that these divisions are arbitrary, but they are valuable because they reflect the appropriate methodology for correction.

The practical significance of line overlap is that its effect cannot be completely removed by improved instrumentation, ie higher resolution. The severity of the interference depends on the relative intensity of the two lines and on the degree of overlap. Most spectrometers operate with a spectral bandpass 3-4 times the physical line width so that even partially overlapped lines will be completely unresolved.

The simplest way of dealing with line overlap is to choose another line, but where this is inappropriate, the total apparent analyte signal must be corrected for the contribution from the interfering line. Clearly, the success of this approach depends on the relative magnitude of the correction, which ideally should be less than 10% of the total intensity. Any correction must decrease the relative precision and have an adverse effect on the detection limit. The greatest error arises from the uncertainty in the correction factor which is typically of the order of 5% [91]. This translates to an increase in the detection limit of approximately 10% of the magnitude of the background correction [92].

Two methods are available for making corrections, either blank subtraction, or cross-calibration of the contribution from the interfering element at the analyte wavelength (sometimes referred to as "on-peak" correction). Blank subtraction is only applicable when the samples have a known and constant concentration of the interfering element. The cross-calibration method involves preparing a calibration curve for the interferent at the analyte wavelength and then, during analysis, using an interference-free line to measure the concentration of the interfering element. Clearly, this procedure is more efficiently carried out on a multi-channel spectrometer. Although it might be anticipated that the cross-calibration curve should in all cases be linear, in practice some curvature is usually present requiring a quadratic curve to fit the experimental data. This is a contributory factor to the uncertainty in the calculated correction. An important point to note is that this form of background correction depends on a prior knowledge that the interference exists.

Line interference is caused by the inability of the spectrometer to resolve neighbouring spectral lines. Increasing the resolution will therefore both decrease the severity of the interference and potentially provide a dramatic improvement in the detection limit. The ability to control resolution is limited to scanning spectrometers, where the options of using narrower slits, or a higher order spectrum are available.

Two methods of background correction may be used to reduce the effects of line interference. The cross-calibration procedure, described previously, is most appropriate for multi-channel spectrometers, but for scanning spectrometers, automatic background correction (sometimes referred to as "off-peak" correction) may be possible. This is the process of scanning the spectrum and extracting the net analyte signal intensity from the data. Its success depends on the ratio of the intensities of the analyte and interfering lines and on the degree of resolution achieved by the spectrometer. Where the resultant overlap is slight, measurement of the background on the side of the spectral line away from the interfering line may be perfectly adequate. The difficulty of making an accurate background correction increases substantially

when the interfering line makes a significant contribution at the central wavelength of the analyte line. Many of the techniques for resolving overlapping spectra depend on fitting intensity data to a model curve; Gaussian or Voigt profiles are most applicable to isolated spectral lines generated by ICP [79, 93–96]. However, the observed profile from a spectral scan is the convolution of the physical line profile and the instrument function. Thus, from a knowledge of the physical line shapes and the instrument function, simulated overlapping spectra can be generated and tested for goodness of fit to the experimental data. From this, individual contributions of the analyte and interfering line can be estimated. This form of background correction is more complex than the cross-calibration procedure, but it has the considerable advantage that a prior knowledge of the existence of an interference is not necessary. The background correction algorithm should in this instance be capable of detecting the presence of unsuspected interfering lines which can subsequently be identified.

Computer-based techniques are available for the resolution of overlapping spectra. However, considerable care is necessary in developing algorithms for peak detection and background correction. A common effect of a poorly resolved spectral interference is to shift the peak of the resultant spectral profile. Unless the peak detection algorithm is sufficiently rigorous, it may simply fit a single profile to the shifted peak and the interference will pass undetected.

Background interference may be caused by:

(i) the wings of strong spectral lines, for example, calcium (Ca II 396.847 nm) on aluminium (Al I 396.153 nm);

(ii) the presence of molecular band-heads generated from sample components, for example, CN, NO and OH bands;

(iii) increases in the intensity of the recombination continuum, for example, from the presence of aluminium in the spectral region below 220 nm; or

(iv) stray light, for example, from high levels of calcium and magnesium.

So varied are these causes that background correction techniques depending on prior knowledge of the existence and source of the interference are not applicable. Automatic background correction works extremely well and is only complicated by the occasional necessity to allow for a sloping baseline. The relative magnitude of the interference is the most important consideration and, where the factor by which the background intensity changes exceeds an order of magnitude, there will be a significant loss in detection power.

A5.2 Matrix Interferences

The rotational interferences that occur due to the presence of a matrix in the analyte solution are derived from two sources: the effect that the matrix has on the structure and excitation conditions of the plasma, and its effect on the sample introduction process. Systematic studies of matrix interferences have been carried out [91–94] and discussed.

It is important to emphasise that the observed level of interference will vary between instruments, and is particularly dependent upon the imposed operating conditions. The approximate levels in Table A2 are those for a 27 MHz ICP instrument operating under optimised conditions for multi-element analysis (see section A4). Consideration of the data published in the literature suggests the following.

(i) Interferences generally occur as suppressions of the emission intensity and increase with the total excitation potential (ionisation plus excitation) of the analytical line. In the case of some low excitation potential lines, for example, lithium (Li 670.78 nm), the interferences may be positive, but the magnitude is small, generally being less than 5%.

(ii) The magnitude of the interference caused by a particular matrix correlates with the sum of its ionisation energy plus its dissociation energy, termed the "matrix energy demand" [94].

(iii) The effect of an increasing concentration of matrix element on the relative sensitivity of a particular analyte is characterised by a decaying exponential curve. The initial slope and degree of curvature are dependent on the total excitation potential of the line as shown schematically in Figure A16. The occurrence of

a change in the slope in the concentration range 1500-2500 μgml^{-1} is characteristic of a high matrix demand element such as calcium. It can be seen from this figure that in the majority of cases where the level of interfering matrix does not exceed a concentration of 1000 μgml^{-1}, the level of interference will be generally less than 5%.

(iv) As a consequence of the asymptotic nature of the interference curve, the interference caused by a composite matrix is less than the sum of the individual effects. Although this outcome makes it difficult to build a predictive model of matrix effects, in a limited practical sense it implies that provided calibration solutions are approximately matched to the samples in terms of the major components (particularly those of high matrix energy demand), the analytical errors will be small (less than 5%). This condition will be met by using multi-element calibration standards containing realistic levels of the major sample components. It is particularly important to include appropriate concentrations of the fluxing agent in standard solutions used to calibrate analyses employing fusion in the sample preparation stage. The high concentration of the flux will minimise the effects of variation in the concentration of other sample components. The solvent is the major matrix component and therefore samples and standards must be approximately matched in acid type and concentration.

Considerable effort has been devoted to studying the mechanism of matrix interferences in ICP, particularly the effects of easily ionisable elements. The observed interferences due to the presence of easily ionisable elements are not attributable to simple shifts in the ionisation equilibria as those that occur in flame spectrometry. Ionisation buffering is not therefore appropriate for use in ICP-AES. Matrix interferences may be explained by the occurrence of small reductions (up to 100K) in the plasma temperature. For a local thermal equilibrium plasma, a knowledge of the temperature change would allow an accurate prediction of changes in line intensity. However, the ICP is known to exhibit non-local thermal equilibrium behaviour for states coupled to the groundstate by resonance lines [22] and for states having a total excitation potential close to the ionisation potential (15.4 eV) of argon which are subject to "charge-transfer" excitation [95].

A5.3 Physical Effects

The introduction of samples into the ICP by nebulisation involves conduction of the sample along the sample uptake tube, conversion of the liquid to an aerosol, and conduction of the aerosol through the spray chamber and torch injector into the discharge [33]. Taking each of these stages in turn it is possible to identify the sample properties that affect them:

(i) Conduction of liquid along the uptake capillary

For self-priming nebulisers, the sample flow rate is determined by the nebuliser suction, by the difference in static head pressure between the nebuliser and sample, by the hydrodynamic resistance of the transport tubing and by the effective viscosity of the sample solution. Variation in these quantities will affect the instrumental response. A simple example is the modification of the effective viscosity by the presence of fibres and particulate matter in the sample solution. However, the use of a peristaltic pump will provide a constant flow of sample more or less independent of the sample properties.

(ii) Nebulisation

The important properties influencing nebulisation are the solution viscosity and surface tension and there will be secondary effects caused by the presence of particles and fibres.

(iii) Transport of the aerosol to the plasma

The principal factors affecting this process are the solvent volatility and the evaporation factor [51] which determine the total solvent loading and the ratio of liquid aerosol flux to vapour flux. These factors are important for organic liquids and cooling of the spray chamber, and/or the use of a condenser may be necessary to control the solvent loading.

One of the practical consequences of these observations is that it is necessary to produce samples and standards in similar solvents (for example, acid) approximately matched in molarity [96]. Furthermore, where the samples contain high concentrations of solutes that might affect the bulk solution properties, for example, brines, surfactants, organic liquids, dissolved polymeric materials, the standards must be similarly constituted.

A6 Data Handling

The information content of the signals provided by an ICP spectrometer is far greater than the singular concentration derived for each element. Making use of this additional information and presenting it in ways that are of value to the analyst can be of great benefit.

A6.1 Calibration

Careful studies of the calibration curves derived from ICP-AES have shown them to be linear over a range of 5–6 orders of magnitude. As previously indicated, this range generally extends from about 1000 mgl^{-1} down to the detection limit, although curvature may be evident at lower concentrations for the very sensitive lines of elements such as calcium (Ca II 393.366 nm) and magnesium (Mg II 279.553 nm). In practice, curvature may be observed for a variety of reasons as follows (see also Figure A14).

(i) Curvature towards the concentration axis at high concentrations:

- self absorption due to a high optical density,
- a matrix effect from the analyte itself or from other major components in the standard solution,
- saturation of the detector or signal processing electronics.

(ii) Curvature away from the concentration axis at low concentrations:

- a significant blank concentration of the analyte in the solution used to dilute the standards.

(iii) Curvature towards the concentration axis at low concentrations:

- loss of the analyte to the container walls, pump tubing or suspended particulate matter, or due to precipitation.

For linear calibration graphs, two standards should, in theory, be adequate, but in practice it is better to over specify the curve and fit the data in order to average both the random errors and systematic errors in the concentrations of the standards. An approach can be to adopt (n + 4) standards, where n is the order of the curve fitted to the data. Most curve-fitting algorithms use the least squares procedure for finding the "best" line, but some care should be exercised using this approach in which the computer will attempt to minimise the absolute sum of the squares of the differences of the data points and fitted line. In an ICP calibration curve, the standard deviation remains approximately constant (equal to the standard deviation of the background signal) for the first two orders of magnitude increase in concentration above the detection limit. Least squares fitting will therefore give equal weighting to the data points in this concentration range and produce a satisfactory calibration line. However, above the background equivalent concentration (BEC), the standard deviation increases in proportion to the signal. Therefore, the deviations from the true calibration line at a concentration of two orders of magnitude above the BEC will be two orders of magnitude greater than at the BEC. Least squares fitting, therefore, will give undue weight to the data points of highest concentration and largely ignore the data points at the low concentration. This problem may be overcome by weighting the fit, or by transforming the data to logarithmic scales whereby the deviations will be rendered equal at all concentrations. To summarise, calibration curves on linear axes are appropriate for concentration levels below the BEC, and logarithmic scales can be used for concentrations above the BEC when least squares methods are used to estimate the best straight line [97].

A useful feature that can be added to curve fitting software is the facility for reporting the percentage deviations of each standard from the fitted line. This is of considerable value for detecting standards that do not contain the correct concentration of

the analyte. Least squares methods are susceptible to the effects of data outliers and for this reason more robust methods based on the so-called "fuzzy logic theory" are gaining acceptance [98].

Multi-element instrument calibration is time-consuming and it is impractical to repeat the entire process as a means of correcting for instrument drift. Drift arises from a variety of causes, but manifests itself as a translation or rotation of the calibration curve. A commonly used drift correction procedure is illustrated in Figure A17. It involves recording a low and a high signal for every analytical line using a minimum number of multi-element calibration solutions immediately after the full calibration is completed. The solutions used may be standards, but the procedure does not depend on knowing the concentration of the analyte elements. The same solutions are re-run each time the curve needs to be updated. From Figure A17 it can be seen that the change in gain factor G which causes curve rotation is given by

$$G = \frac{I_H - I_L}{I'_H - I'_L} \tag{7}$$

where I_H, I'_H are the initial and final signals for the high concentration solution and I_L, I'_L are the corresponding signals for the low concentration solution. A change in the zero level causes a translation of the curve, D, given by

$$D = I'_L(1 - G) - LE \tag{8}$$

$$\text{where } LE = I'_L - I_L \tag{9}$$

and therefore the corrected intensity I for a recorded intensity I′ becomes

$$I = I'G - D \tag{10}$$

The preparation of multi-element calibration solutions is not a trivial problem and the two main factors which should be taken into account are:

(i) the presence of other analytes in the material used to prepare initial single element stock solutions prior to mixing: this is a particular concern if attempts are made to make multi-element standards by mixing single element standards for atomic absorption analysis; and

(ii) the compatibility of the analytes and their solvent in the mixed solution (for example, silver in hydrochloric acid, lead in chromate solution).

A6.2 Optimisation

The performance of an ICP system, both in terms of the detection limit and the freedom from interferences, is strongly influenced by the operating parameters. The effects of individual parametric changes, however, are not independent; the optimum power determined at fixed levels of the other parameters will vary each time one or all of them are changed. The most important operating parameters for ICP are power, observation height and injector flow rate; with outer flow, intermediate flow and sample uptake rate being of secondary importance. Mapping the complex multi-variate response surface associated with these parameters would take many measurements and is impractical for routine optimisation.

Often, instruments operated under so-called "optimised conditions" are, in fact, operated under arbitrary conditions that happen to meet a defined level of performance. The establishment of a true optimum both improves the data quality and provides an unambiguous statement of "best" performance, and therefore enables comparisons of procedures or instruments even though they are different.

The most widely used optimisation technique is based on implementation of the "Variable Step Simplex" algorithm [99] although alternative techniques are described [104]. A simplex is a geometric figure in factor space having N + 1 vertices, where N is the number of parameters to be optimised. The response of the instrument is recorded at the parametric setting corresponding to each vertex and then these responses are ranked. The procedure involves reflecting the simplex through its centroid away from the vertex of worst response towards the factor space of best response. This produces a new vertex which is used to generate a new simplex and

the old worst response is discarded. The procedure is terminated when additional simplexes produce no significant improvement in performance. The rate of convergence is influenced by the selection of the size of the initial simplex and it is usual to adopt the procedure [100] which produces a large initial simplex encompassing the majority of factor space. Optimisation then proceeds by a series of contractions and reflections of the simplex.

The first step in optimisation is to define the objective variable by which performance will be estimated. Two commonly used variables are the signal-to-background ratio (SBR) [83, 100–103] and the relative freedom from interference. For a single analytical line, convergence is usually quite rapid, occurring in 20–25 vertices. Figure A18 shows the results in terms of the best and worst response at each step recorded for the optimisation of the calcium (Ca II 393.36 nm) line for minimum interference in the presence of a synthetic matrix. The initial conditions produced some results with relatively low levels of interference (about 3%), but other vertices represented unacceptably high levels. Gradually, convergence occurs and the level of interference falls to about 1%.

Optimisation becomes more difficult when conditions suitable for simultaneous multi-element analysis are sought. Simultaneous optimisation of the SBR of hard and soft lines will produce a slow convergence because the conditions for each are different. The average SBR of these groups could be used as the objective variable, but additional criteria may be specified, for example, so that a balanced improvement for all lines is achieved. In practice, it is found that optimisation of the SBR, or interference performance, of a single or group of hard lines for example, cadmium (Cd II 226.5 nm), tin (Sn II 202.1 nm) will produce the most suitable conditions for multi-element analysis. Inspection will then show that the plasma is being viewed in the normal analytical zone where efficient excitation and maximum freedom from interference occurs.

Once optimisation is complete, it is important to carry out a local search in factor space, say over a range of 10% from the optimum, to ensure that each parameter is indeed optimised. This implies that the slope of the response surface will be zero leading to maximum instrument stability. The topography of the response surface is important in this context and occasionally slight relaxations of the optimum settings may yield improved stability.

A6.3 Internal Standardisation

Under ideal conditions, ICP is a stable source in space and time and therefore internal standardisation should be of no particular benefit and could cause a slight loss in precision because of the propagation of statistical error in the rationing step. Unfortunately, departures from ideality in ICP performance can occur because of changes in the performance of the nebuliser, drift in the nominal values of the operating parameters and effects induced by the matrix. Where these departures result in a significant loss in precision or accuracy, internal standardisation can be of benefit.

The essential criterion in selecting internal standards is that the variances in their signals show a positive correlation with the variances of the analyte signals. In conventional arc spectrometry this was achieved by selecting lines with similar excitation characteristics, and such lines were termed homologous pairs. For ICP-AES it has been found more effective to choose internal standard reference lines which reflect changes in the parametric settings of the source which affect most analyte lines in a similar sense, though in varying magnitude. Two schemes have been particularly successful in this respect [105–108]. In one scheme, about 5% of the plasma radiation incident on the main spectrometer is split from the beam and passed through two photometers, one monitoring the scandium (Sc II) line at 424.638 nm and the other, the argon background emission at 450 nm. The internal reference signals derived from these observations have been shown to compensate both random noise, resulting in improved precision, and drift caused by changes in the performance of the nebuliser. In another scheme, two internal standard lines are chosen; one of low excitation potential, for example, lithium (Li 670.78 nm) or rubidium (Rb 780.02 nm) whose variance has been shown to correlate with variations in the sample introduction process, and a high excitation potential line, for example, zinc (Zn II 202.55 nm) or cadmium (Cd II 226.50 nm) whose variance correlates with changes in the power

coupled to the plasma. Correction coefficients are calculated for each analyte line and it has been shown that both random and systematic errors are compensated. The most important benefit from the latter scheme is not the improvement in precision that is obtained (typically a factor of 2), but its ability to reduce matrix effects which can produce errors of greater than 10%. A reduction in rf power would notionally have a similar effect and therefore an internal standard that reflects changes in applied power will similarly reflect the effects of an added matrix and may be used for their compensation. An alternative to deriving software correction factors from internal standards is to use them for interactive instrument control, and preliminary experiments of this type have been reported [109].

Table A1 Common wavelengths used in ICP-AES

Element	Note	Wavelength nm	Typical Limit of Detection μgl^{-1}	Interference
Aluminium		167.08	5–100	Mn, V, Fe
		308.215	8–40	Mg, V
		309.3		
		394.4		
		396.152	11–30	V, Ca
Antimony	(4)	206.833	40–100	Al,Cr,Fe,Ni,Ti V
		217.58	70	Al,Fe,Ni
		252.8		
		259.80		
Arsenic	(4)	189.0		Cr,Fe,Mg,Mn,V
		193.696	30–50	Fe,Ca
		193.759	10–100	Al,Fe,V
		197.3	100	Al, V
		228.81	30–100	Cd
		233.527		Fe,V,Ni
		278.0	50–700	
Barium		233.527	3–10	Fe,V,Ni
		455.403	0.5–5	Cr,Ni,Ti
		493.409	3	Fe
Beryllium		234.86	0.6–2	Fe,Ti
		313.04	0.1–2	V,Ti
		313.107	2	Ti
Bismuth	(4)	223.1	10–30	Cu,Ti
		306.77	12	Fe,V
Boron		208.959	5	Al,Fe
		249.678	3–30	Co,Fe (less than 249.773)
		249.773	0.6–30	Fe
Cadmium		214.44	20	Al,Fe
		226.502	2–20	Fe,Ni
		228.802	3–20	As,Al,Fe,Ni
Calcium		181.45		
		315.889	100	Co,Cr,Fe
		317.933	1–50	Fe,Cr,V
		393.366	0.1–1	
		396.8	5	Fe,V
		445.478	400	

Element	Note	Wavelength nm	Typical Limit of Detection μgl^{-1}	Interference
Carbon	(1)	193.09	200	Al,Mn,Ti
		247.86	500	Fe,Cr,Ti,V
Cerium		413.77	100	Ca,Fe,Ti
Chromium		205.552	4–30	Fe,Mo,Al,Cu,Ni
		267.716	5–30	Mn,V,Fe,Ti
		283.563	5	Fe,Mo,Mg,V
		284.325	10	
		425.43		
Cobalt		228.616	3–20	Cr,Fe,Ni,Ti
		238.89	5–10	Fe,V
		343.35		
Copper		224.7	15	Fe
		296.12		
		324.754	0.3–5	Ca,Cr,Fe,Ti
		327.396	10	Ca,Fe,Ni,Ti,V
		510.55		
Gallium		294.364	100–	
Germanium		209.42	100–	
Gold		242.78	25	
		267.58	25	
Indium		230.61	100	Fe,Mn,Ni,Ti
		303.9	200	Cr,Fe,Mn,V
Iron		233.38		
		238.207	6–40	Cr,V
		239.56		
		249.33		
		259.940	1–20	
Lanthanum		379.5	20	Ca,Fe,V
		398.8	6–20	
		408.67	20	Ca,Cr,Fe
Lead		220.351	30–50	Al,Cr,Fe
		280.2	30–200	
		283.31	200	Fe,Cr,Mg
		405.78	7–300	
Lithium		670.784	3–10	V,Ti
Magnesium		279.079	20–30	Cr,Fe,Mn,Ti
		279.553	0.5	Fe,Mn
		280.27	1	Cr,Mn,V
		285.213	3–10	Fe,Cr,V
		518.36		
Manganese		257.610	0.4–5	Fe,Al,Cr
		263.82		
		293.306	20	

Element	Note	Wavelength nm	Typical Limit of Detection μgl^{-1}	Interference
Mercury	(4)	184.950		
		194.23	20	Al,V
		253.65	100	Fe,Mn,Ti
				Al,Fe
Molybdenum		202.032	7–30	
		281.6	20	Cr,Fe,Mg,Mn,Ti
		317.03		
		379.82	1–10	
		386.4	0.6	
Nickel		225.39	50	
		231.604	7–20	Co,Fe
		341.48	80	
Nitrogen	(2)	174.3		
		174.5		
Niobium		316.34	60	Ca,Cr,Fe
		319.5		
Palladium		340.46	70	Fe,Ti,V
Phosphorus		177.50		
		178.287	20–100	
		213.62	20-80	Cu,Al,Cr,Fe,Ti
		214.9	50–100	Cu,Al
		253.57	20–200	Cr,Fe,Mn,Ti
Platinum		214.4	30	Al,Fe
		265.9	80	Fe,Mg,Cr,V,Mn
Potassium		404.72	40000	Ca,Fe,V (mg in
		766.490	80–3000	2nd order) Ti
		769.90	400	Cr,Ti
Rhodium		343.46	60	
Rubidium		780.0	200	Ti
Scandium		361.364	0.05–2	Cr,Cu,Fe,Ti
Selenium	(4)	196.026	50–80	Al,Fe
		196.090	20–100	Al,Fe
		204.0	120	Al,Cr,Fe,Mn
Silicon		250.690	40	
		251.61	5–120	Cr,Fe,Mn,V
		288.158	20–150	Cr,Fe,Mg,V
		390.55		
Silver		328.068	5–10	Fe,Mn,V
		338.29	20	Cr,Ti
Sodium		330.23	5000	Cr,Fe,Ti
		588.995	20–150	Ti
		589.592	6–200	Fe,Ti,V
Strontium		407.771	0.2–2	Cr,Fe,Ti
		421.552	10	
		460.733	70	

Element	Note	Wavelength nm	Typical Limit of Detection μgl^{-1}	Interference
Sulphur	(3)	180.73	80	
		182.036	50–200	
		469.4	5000	
Tantalum		226.23	40	Al,Fe
Tellurium	(4)	214.2	20–50	Al,Fe,Ti,V
Thallium		190.86	50	Al,Ti
Tin		189.989	7–50	
		283.999	150	Al,Cr,Fe,Mg,Mn, Ti,V
		317.50	250	
		333.00		
Titanium		334.940	3	Ca,Cr,Cu,V
		336.121 (336.09)	5	
		337.279	10	Ni,V
Tungsten		207.91	20-100	Al,Cu,Ni,Ti
		239.71	150	
Uranium		263.55	500	Ca,Fe,Mg,Mn,Ti,V
		385.96	400	Ca,Cr,Fe
Vanadium		290.882	5–10	Fe,Mo,Mg,Cr
		292.402	0.5–10	Fe,Mo,Ti,Cr
		309.31	0.3–10	Al,Cr,Fe,Mg
		310.230	10	Fe,Ti,Ni
		311.071	3–10	Fe,Mn,Ti
Zinc		202.55	2-15	Al,Cu,Fe,Ni,Ti,V
		213.856	1-15	Cu,Ni,Al,Fe,Ti,V
		239.71	High	
		330.25		
		334.50		
Zirconium		339.189	10	Cr,Fe,Ti,V
		343.8	20	Ca,Cr,Fe,Mn,Ti
		349.6	5-25	Hf,Mn,Ni,Ti,V

Notes

1. Rarely determined by ICP-AES due to problems with argon purity and impurities in the air.
2. Rarely determined by ICP-AES due to problems with air.
3. Different analytical working curves for volatile and non volatile substances.
4. Hydride or cold vapour generation similar to atomic absorption spectrometry can be used and greatly lowers the limit of detection.

Table A2 Detection limits for ICP-AES for a 27 MHz plasma

Element	Ionization State. Wavelength nm	Detection limit μgl^{-1}
Ag	I 328.068	4.0
Al	I 308.215	18.0
	I 396.152	11.0
As	I 193.696	50.0
B	I 182.59	
	I 249.773	3.1
Ca	II 317.933	9.4
	II 393.366	0.18
Cd	II 226.502	2.8
Co	II 228.616	5.1
	II 238.892	5.7
Cr	II 267.716	5.1
Cu	I 324.754	2.3
Fe	II 259.940	1.7
Hg	I 184.960	–
	II 194.227	25
K	I 766.49	80
Li	I 670.780	19
Mg	II 279.079	20
Mo	II 202.030	7.4
	I 379.830	5.3
	I 313.259	11
Na	I 588.995	30
Ni	II 231.604	7.1
P	I 178.287	100
	I 213.618	73
Pb	II 220.353	40
S	I 182.040	50
Se	I 196.026	71
Si	I 251.611	9.1
	I 288.158	18
Sn	II 189.926	25
Ti	II 337.280	3.7
V	II 290.882	6.8
Zn	I 213.856	1.7

ICP-AES data abstracted from refs 110 and 111.

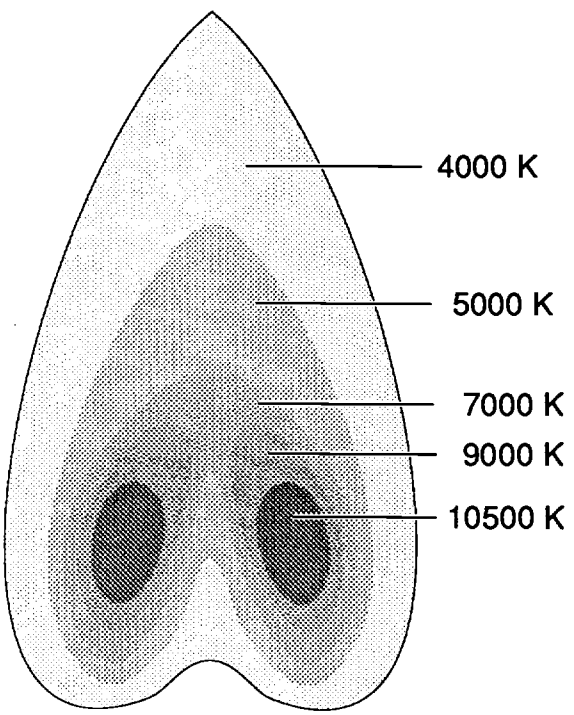

Figure A1 Approximate Temperature Distribution (Kelvin) in a Medium Power (1–2 kW) ICP.

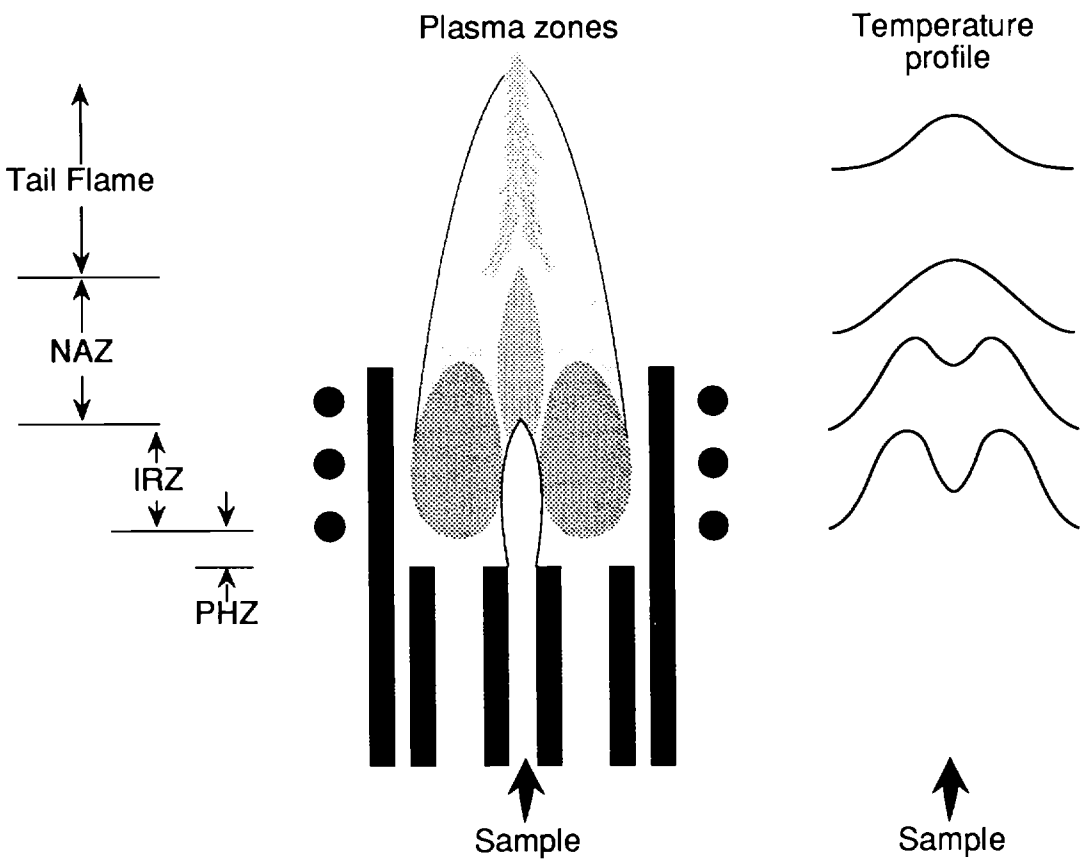

Figure A2 Axial Channel Emission Zone Structure of an ICP

PHZ = pre-heating zone
IRZ = initial radiation zone
NAZ = normal analytical zone

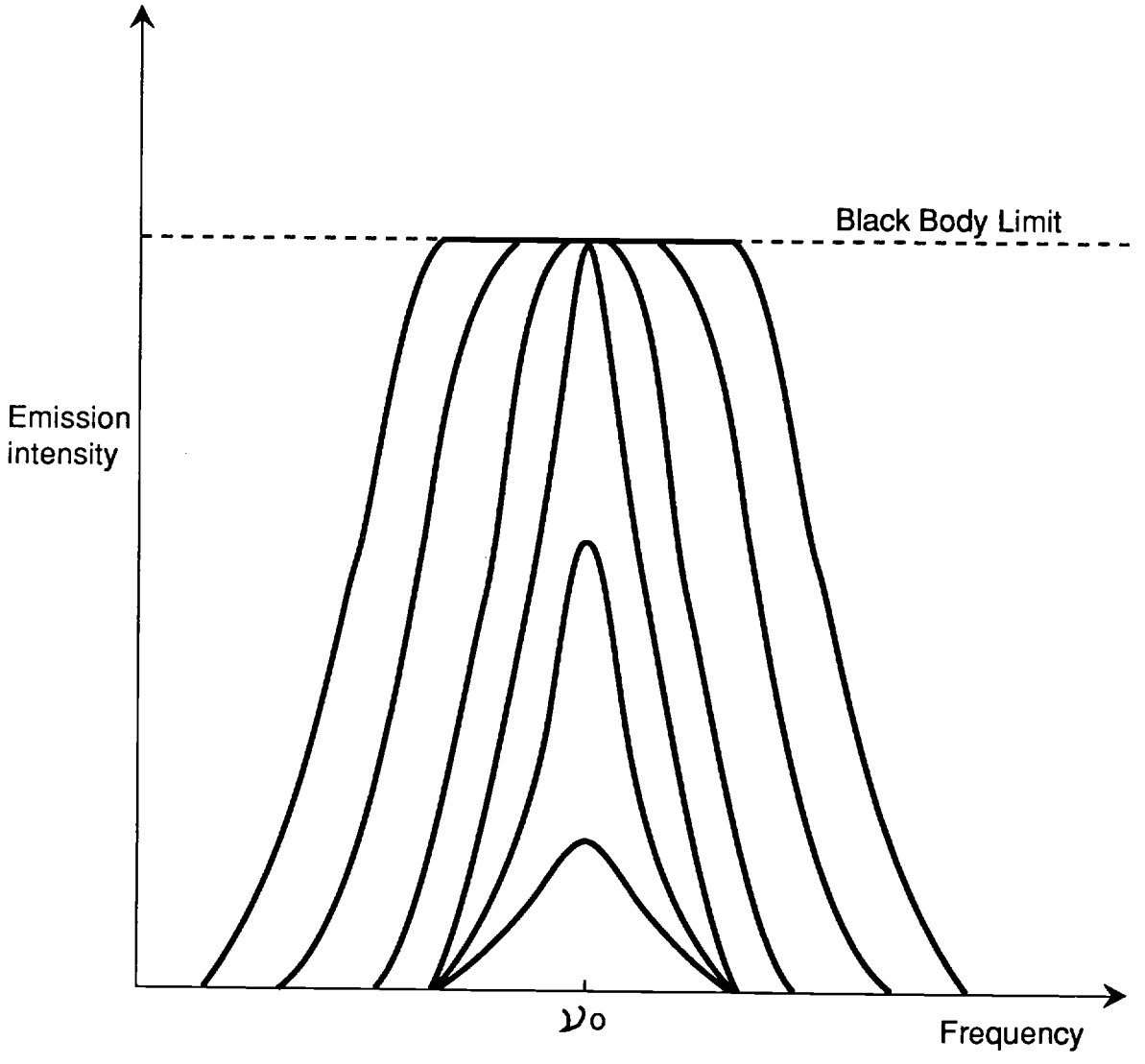

Figure A3 Effect on Spectral Line Profile of Varying the Concentration of the Analyte.

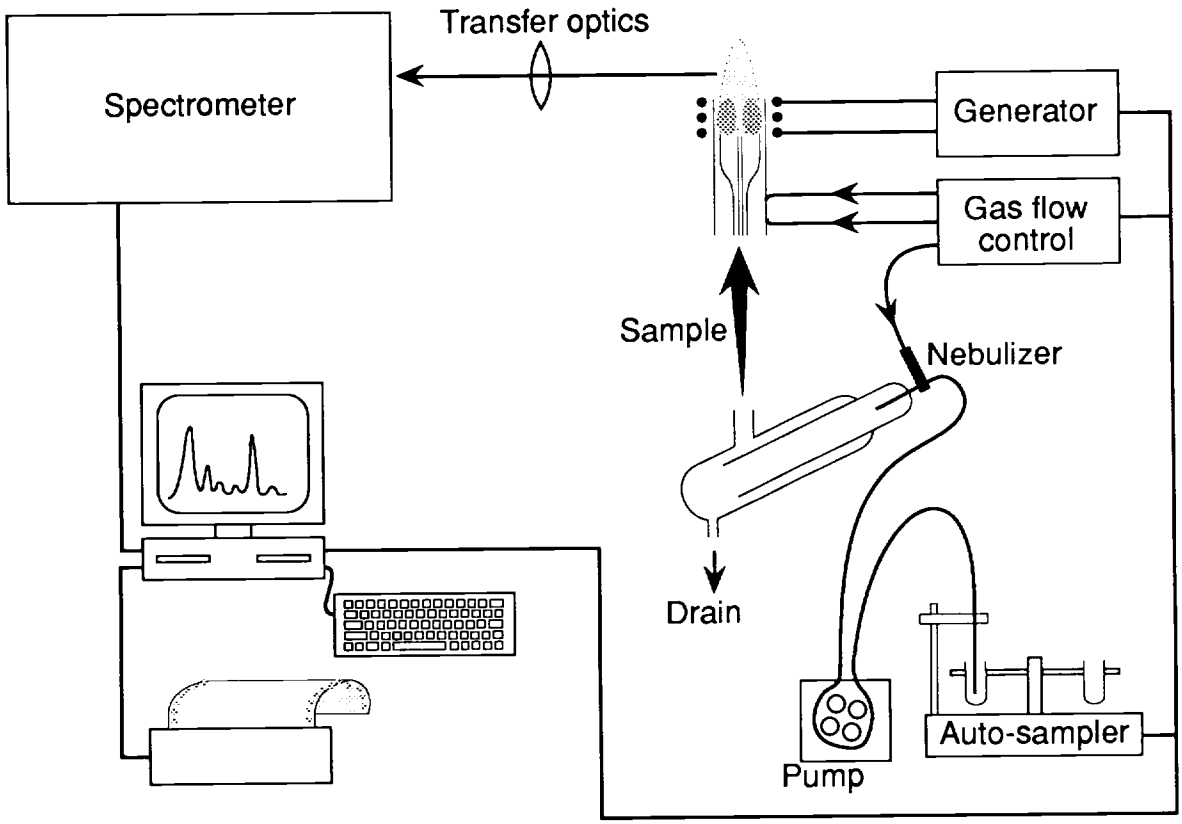

Figure A4 Schematic Diagram of an Inductively-Coupled Plasma Optical Emission System.

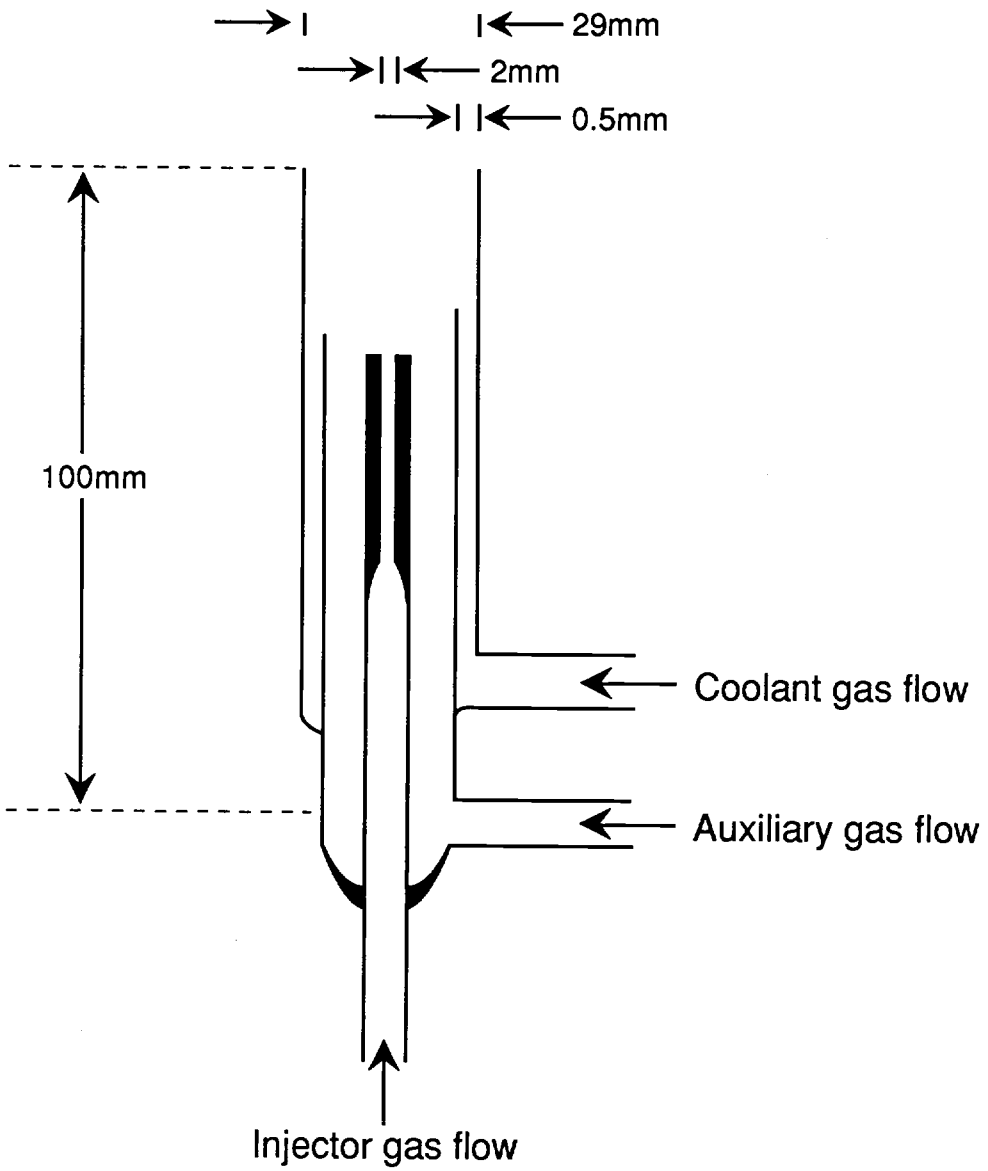

Figure A5 Plasma Torches for ICP-AES

A—Greenfield Torch

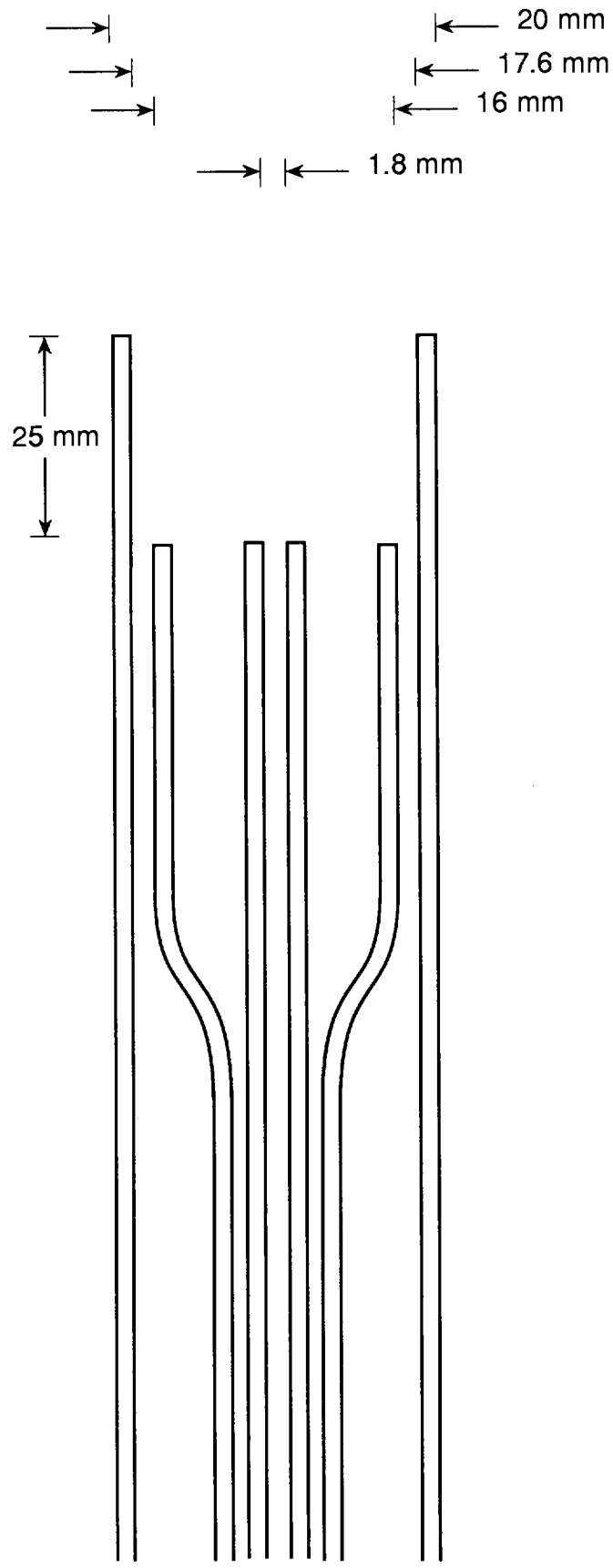

Figure A5 Plasma Torches for ICP-AES

B—Scott-Fassel Torch

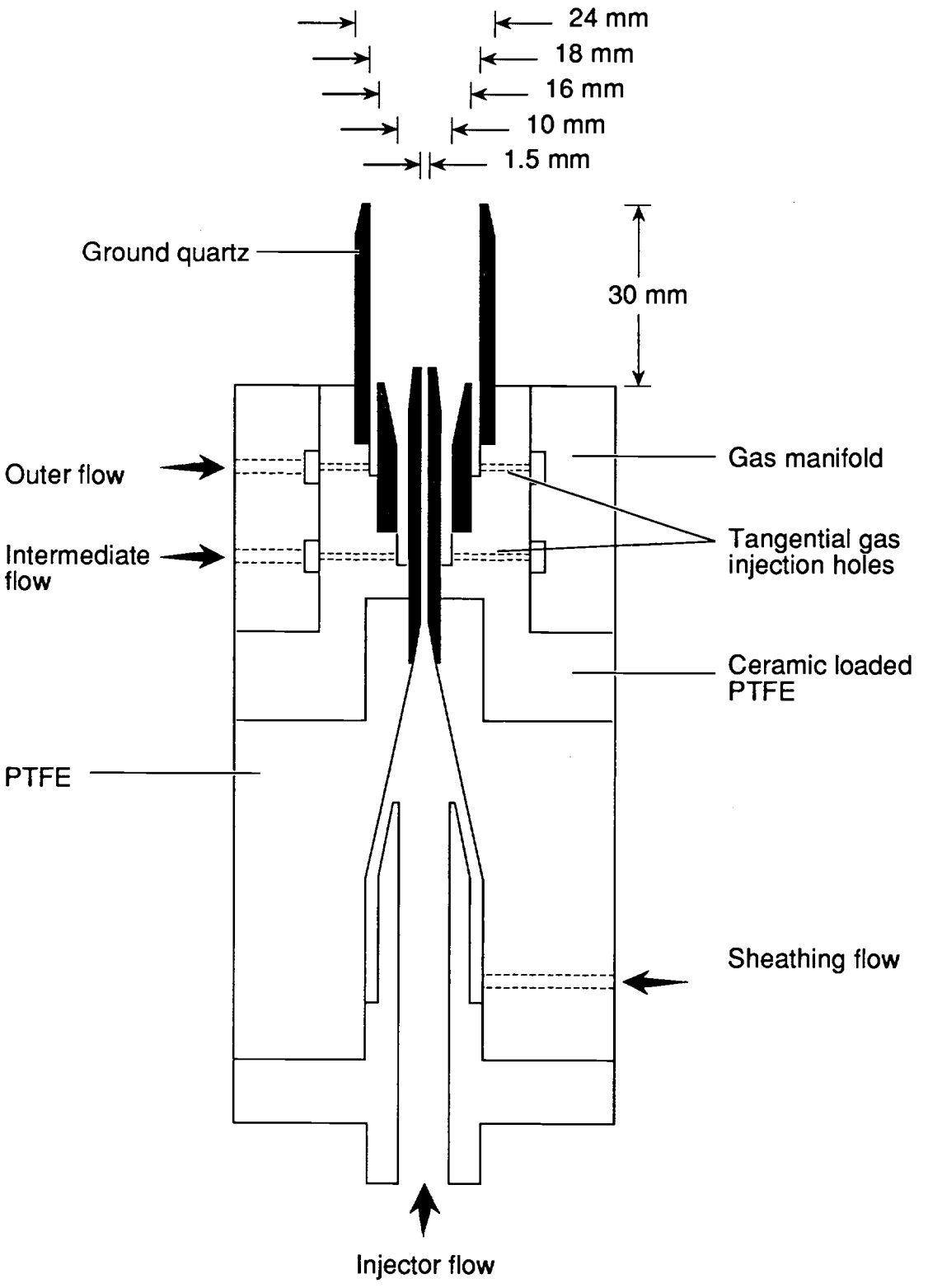

Figure A5 Plasma Torches for ICP-AES

C—Demountable Torch

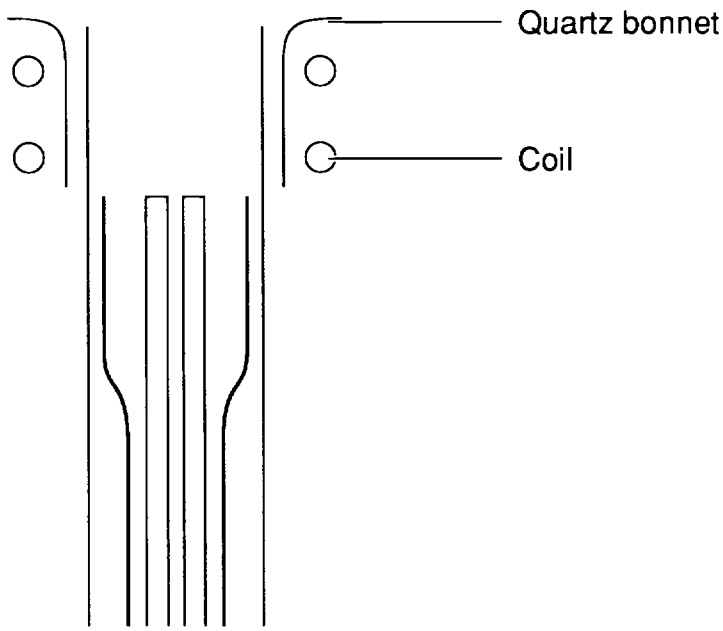

Figure A5 Plasma Torches for ICP-AES
D—Quartz Bonnet

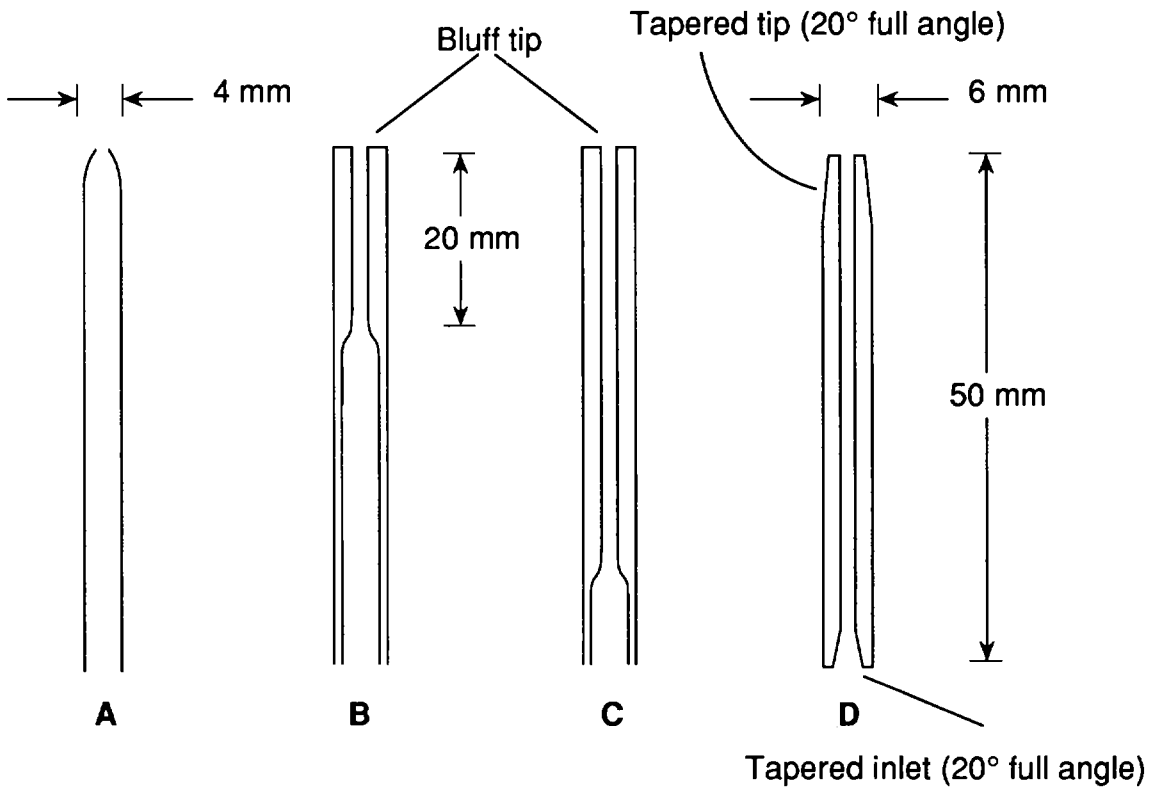

Figure A6 Commonly Used Injector Designs for ICP Torches

A—turbulent flow tapered injector
B—intermediate laminar/turbulent flow injector
C—laminar flow capillary injector
D—streamlined laminar flow injector

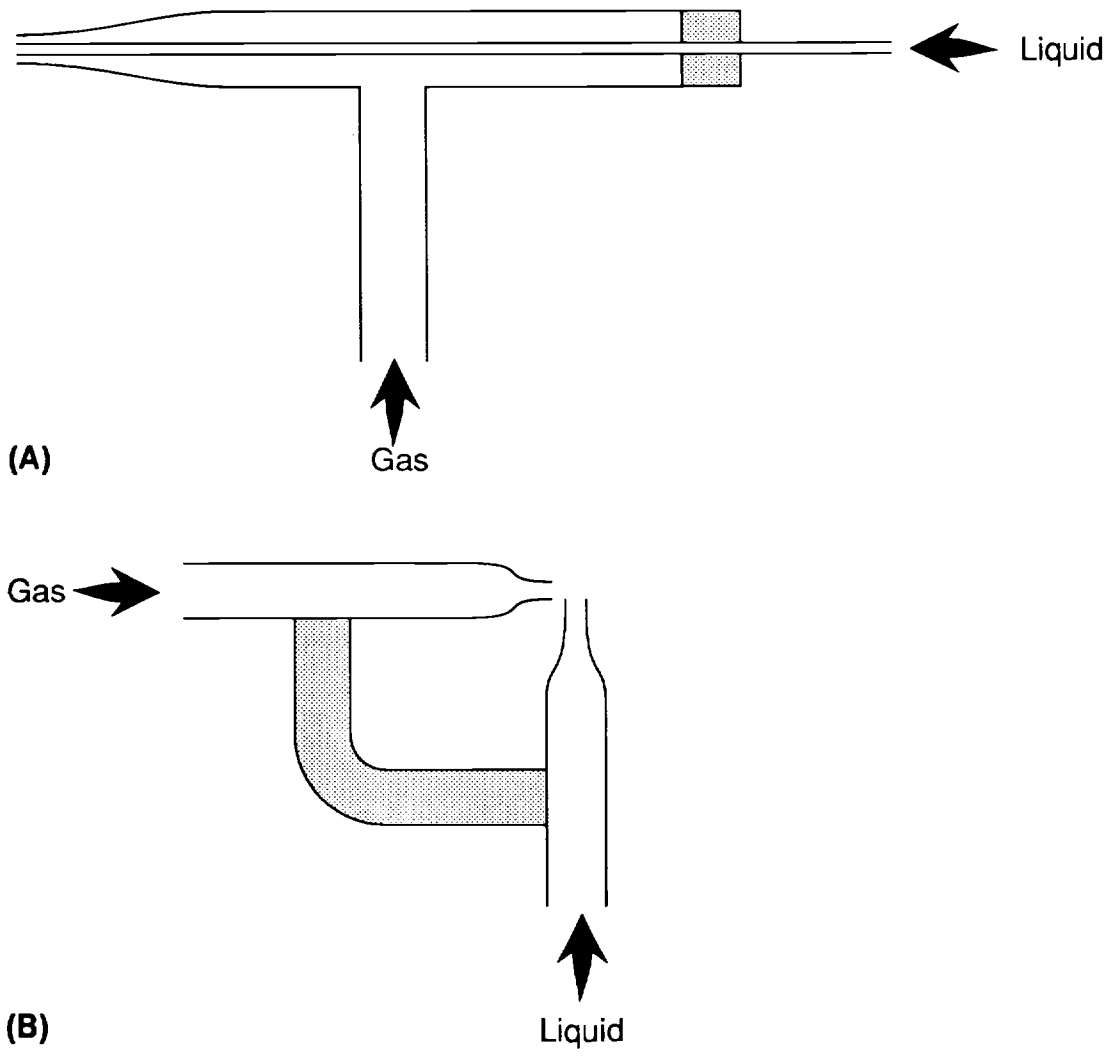

Figure A7 Pneumatic Nebulisers Used for ICP-AES

A—glass concentric nebuliser
B—fixed geometry cross-flow nebuliser

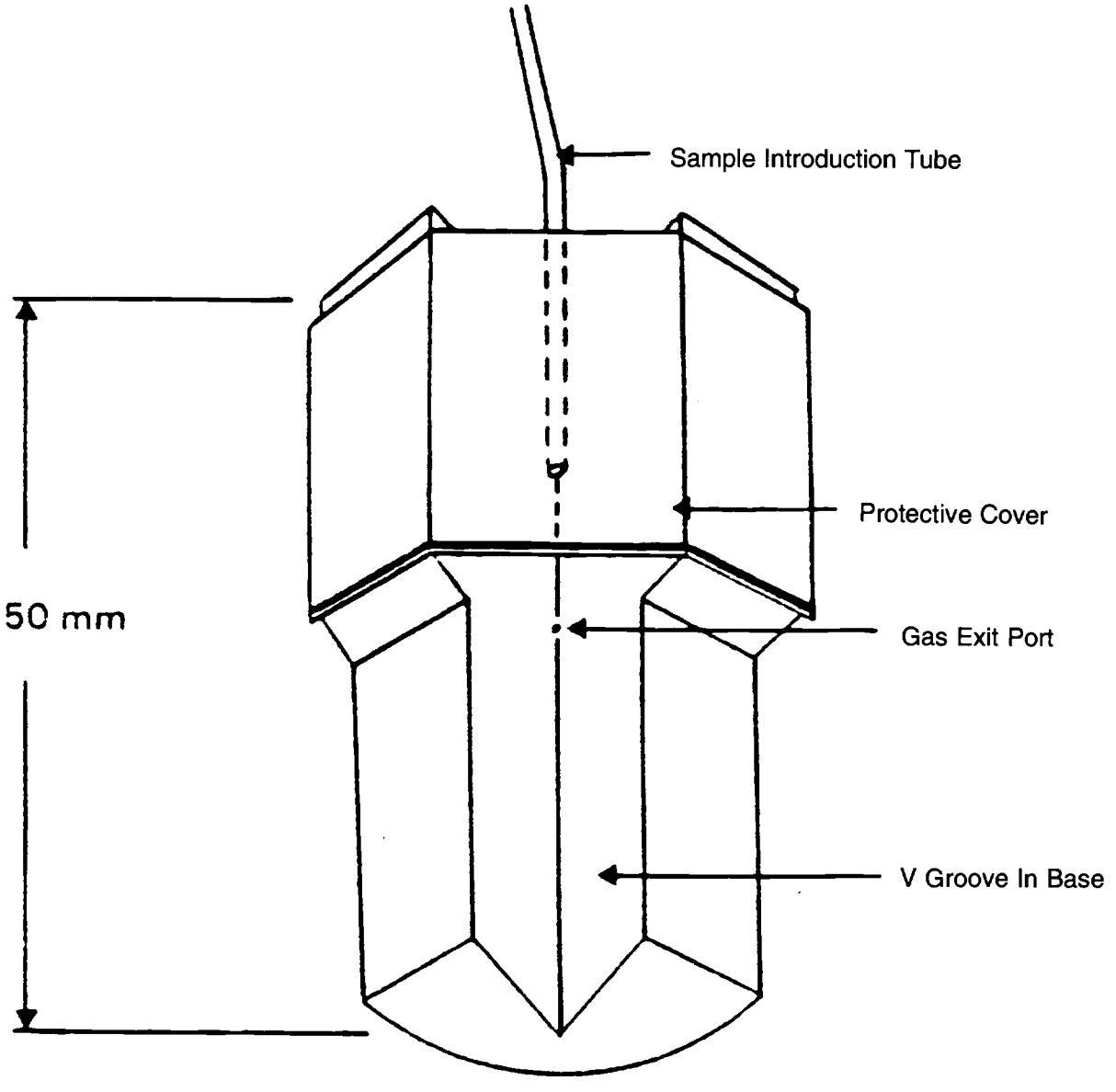

Figure A7 Pneumatic Nebulisers Used for ICP-AES

C—v-groove Babington nebuliser (redrawn with permission from R.F. Suddendorf and K.W. Boyer, Anal. Chem. 50, 1769 (1978))

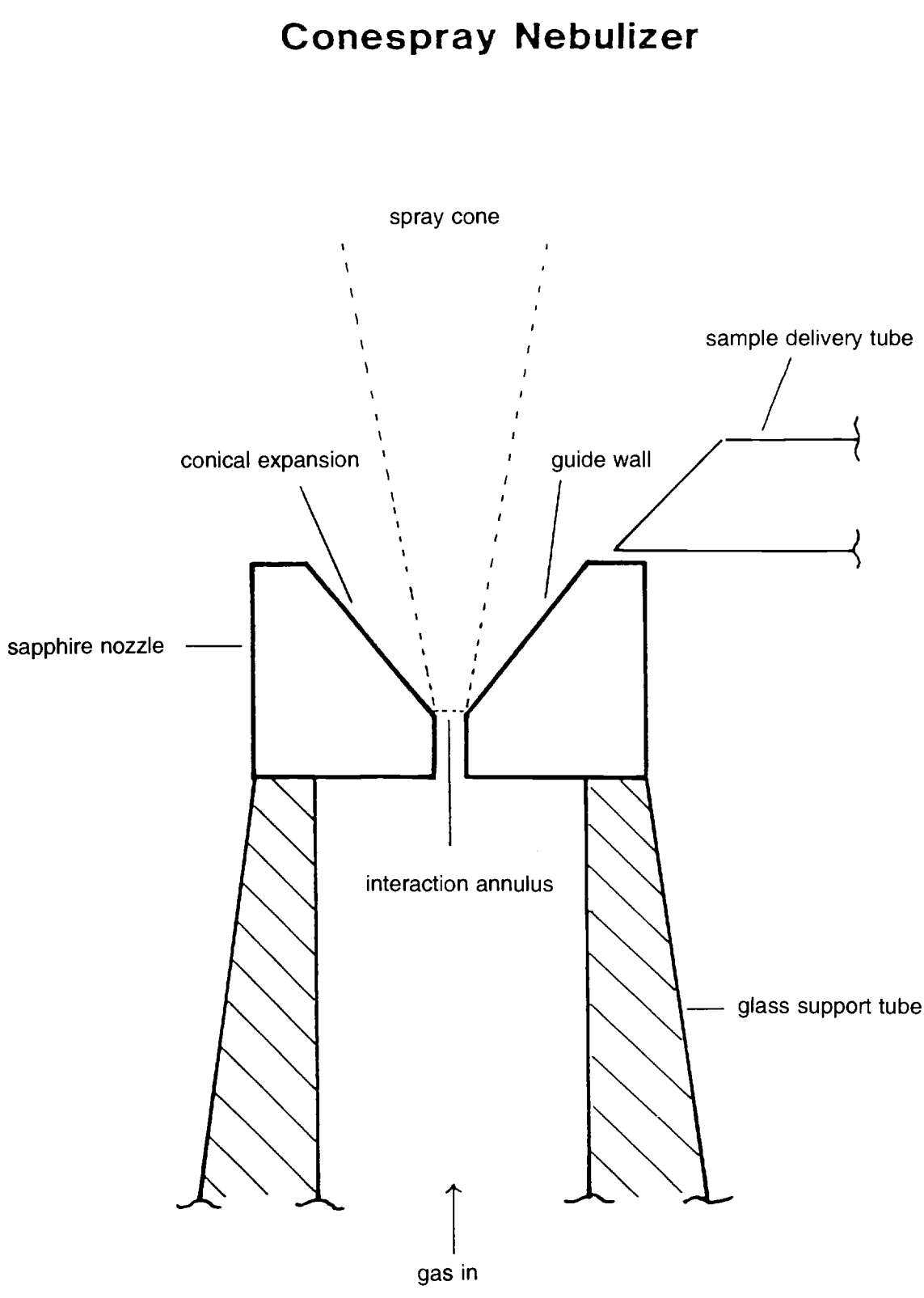

Figure A7 Pneumatic Nebulisers Used for ICP-AES

D—conical jet 'Conespray' nebuliser (redrawn with permission from B.L. Sharp, J. Anal. At. Spectrom., 3, 613 (1988)

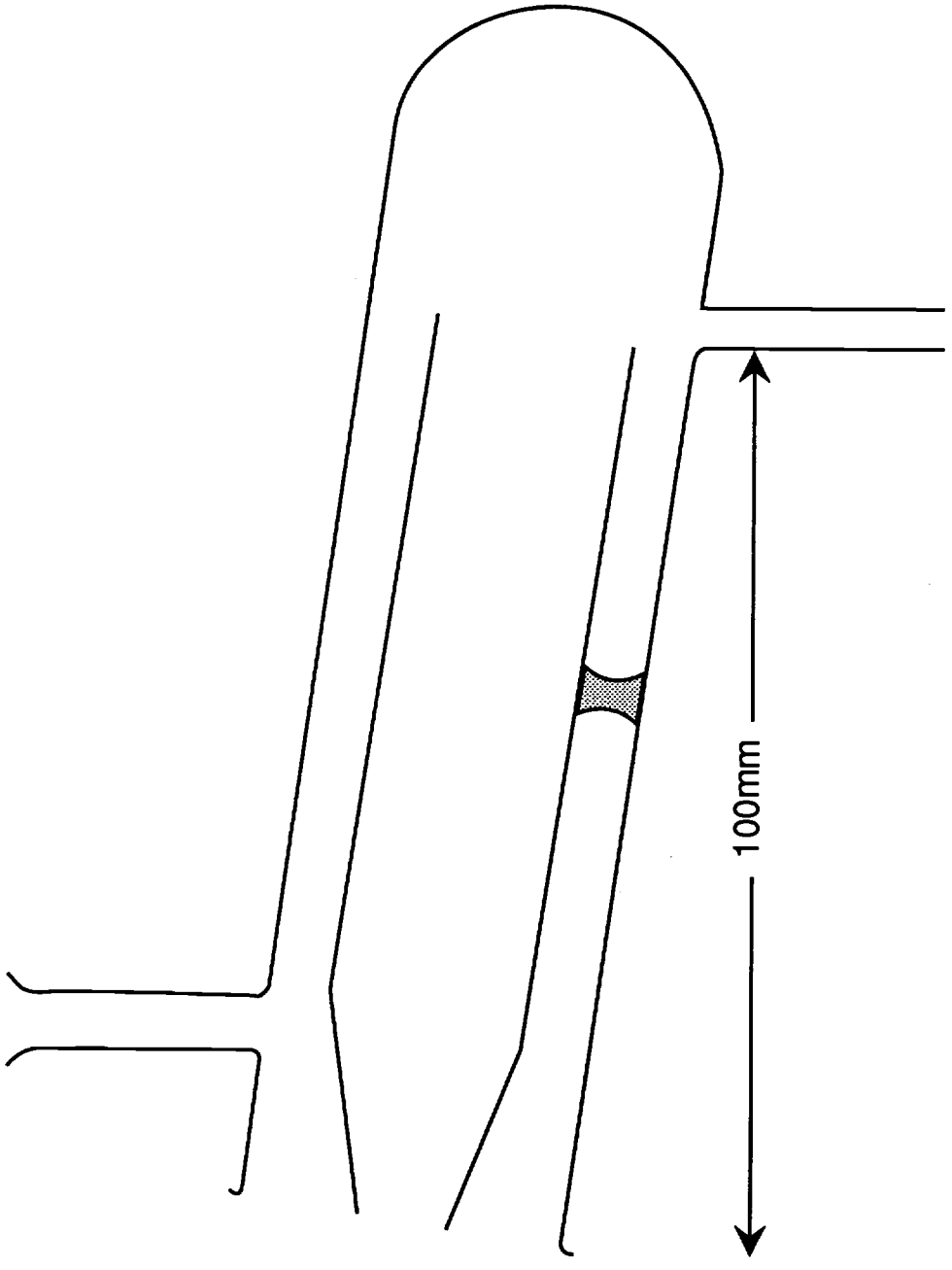

Figure A8 Spray Chambers for ICP-AES

A—Scott double pass chamber

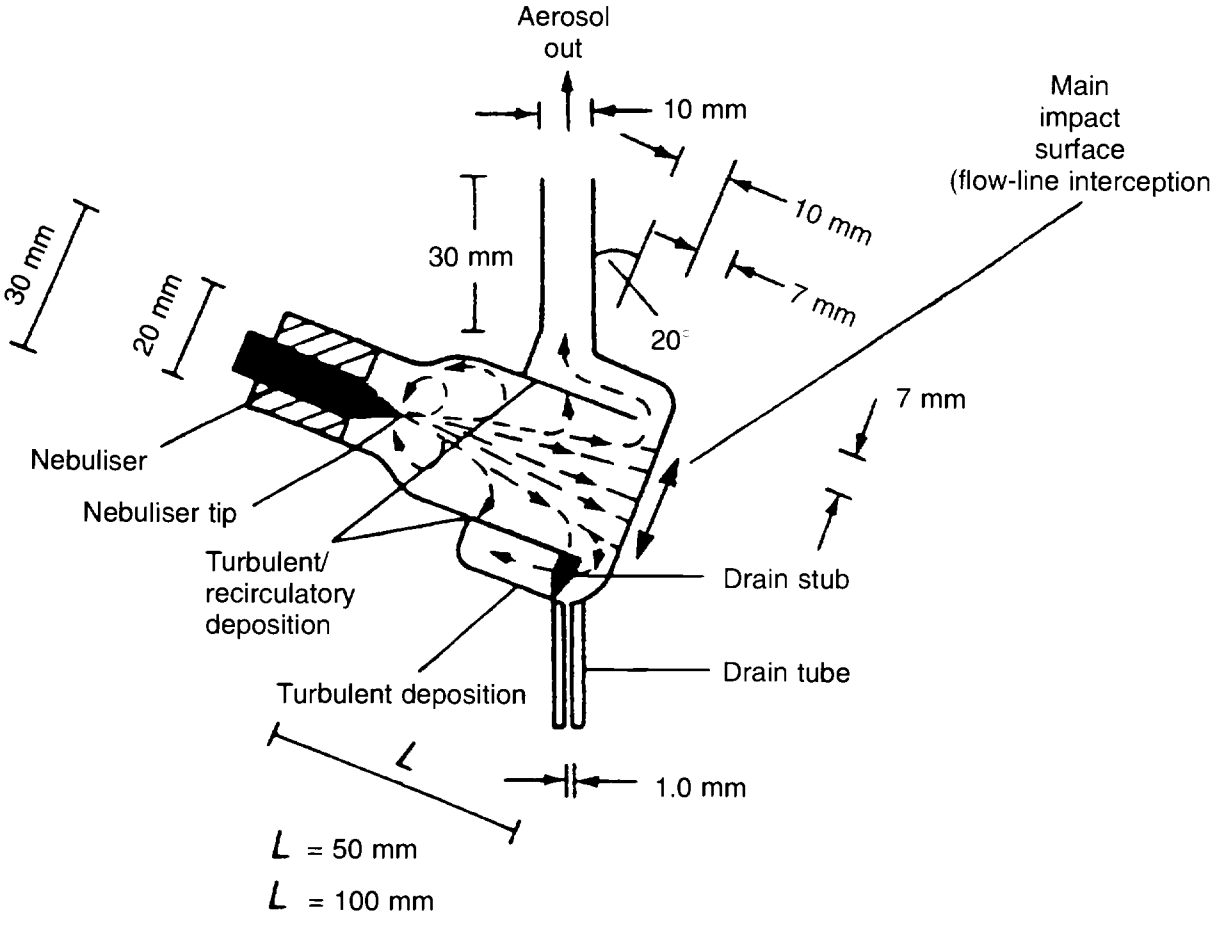

Figure A8 Spray Chambers for ICP-AES

B—low dead volume double pass chamber (redrawn with permission from B.L. Sharp, J. Anal. At. Spectrom., 3, 613 (1988))

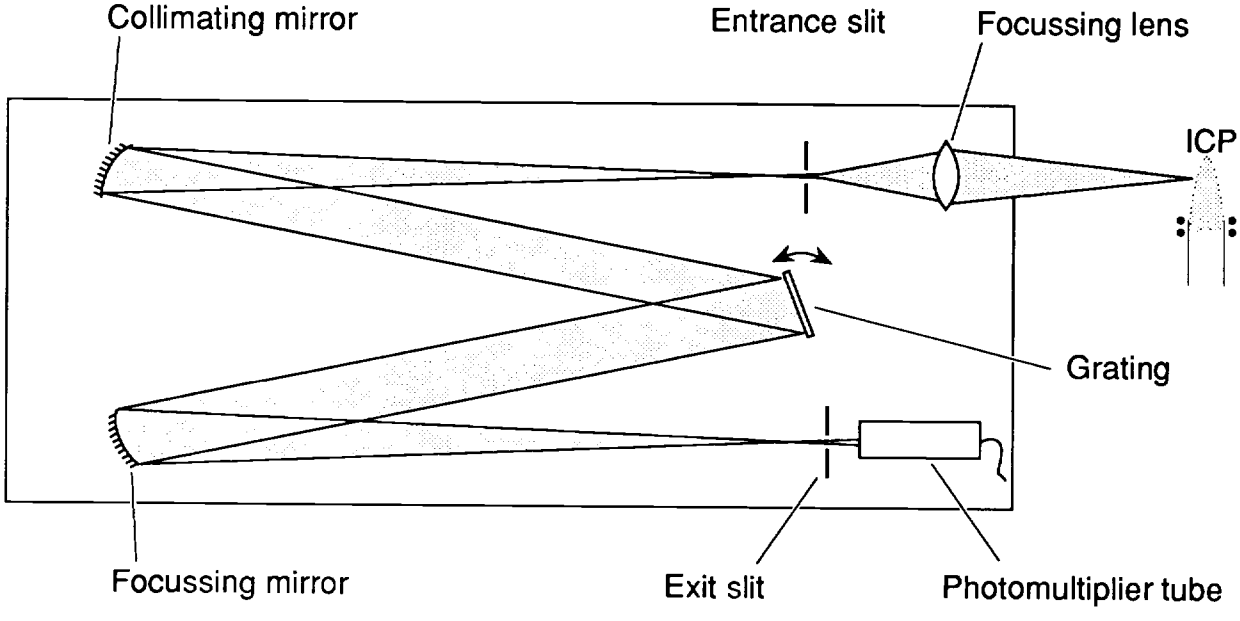

Figure A9 Single Channel Scanning Spectrometer Based on the Czerny-Turner Optical Configuration.

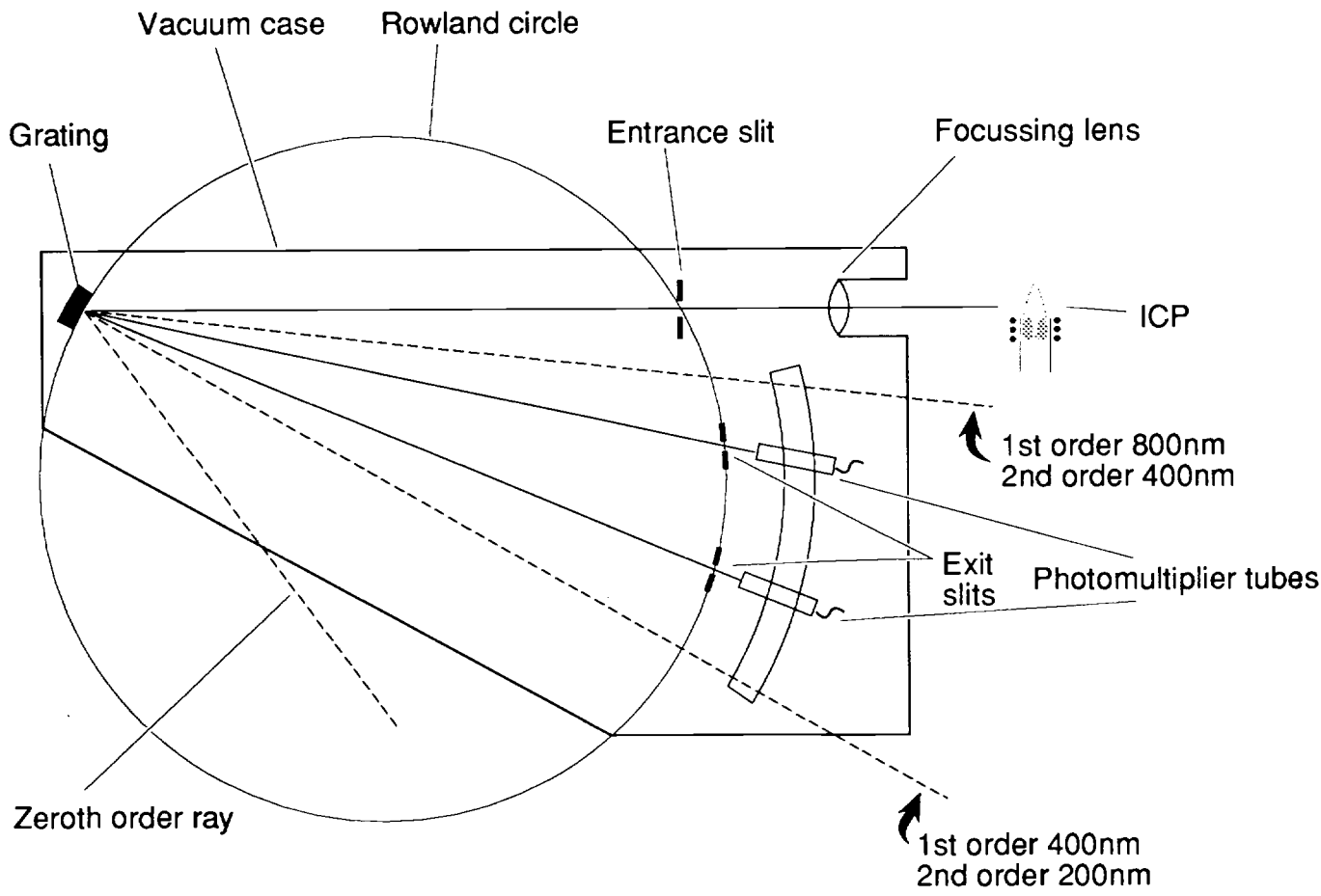

Figure A10 Multi-channel Simultaneous Spectrometer Using the Paschen-Runge Optical Configuration.

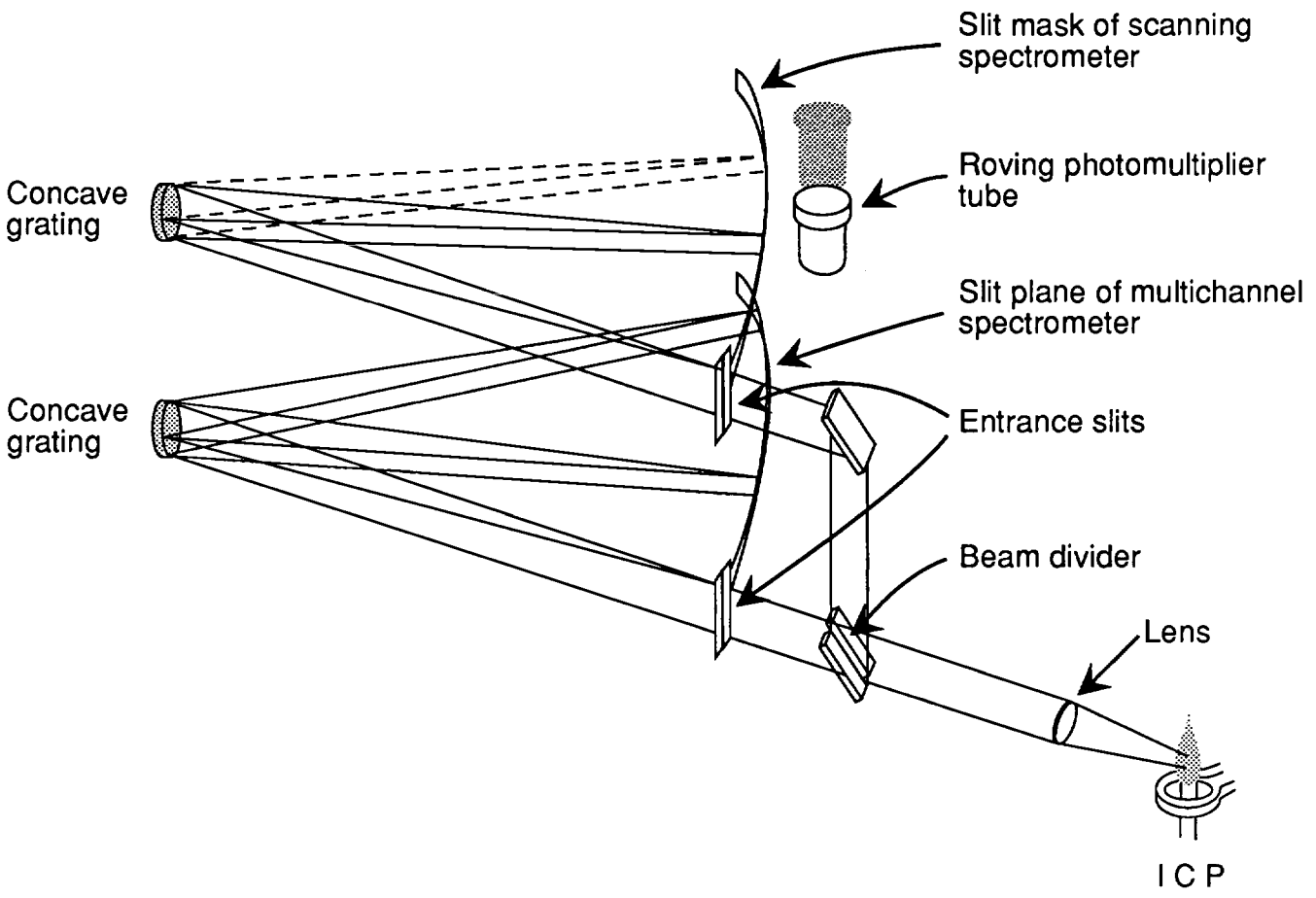

Figure A11 Optical Configuration of a Combination Multichannel/Scanning spectrometer (courtesy of Fisons Instruments).

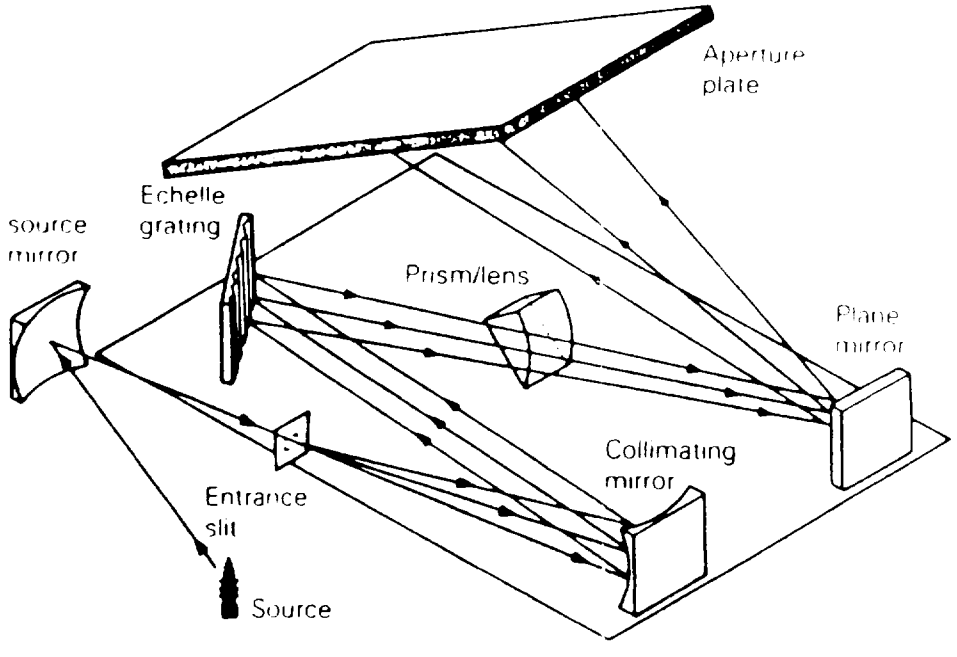

Figure A12 Optical Configuration of an Echelle Spectrometer with Post-Grating Prism Order Sorter (courtesy of Unicam Analytical Systems).

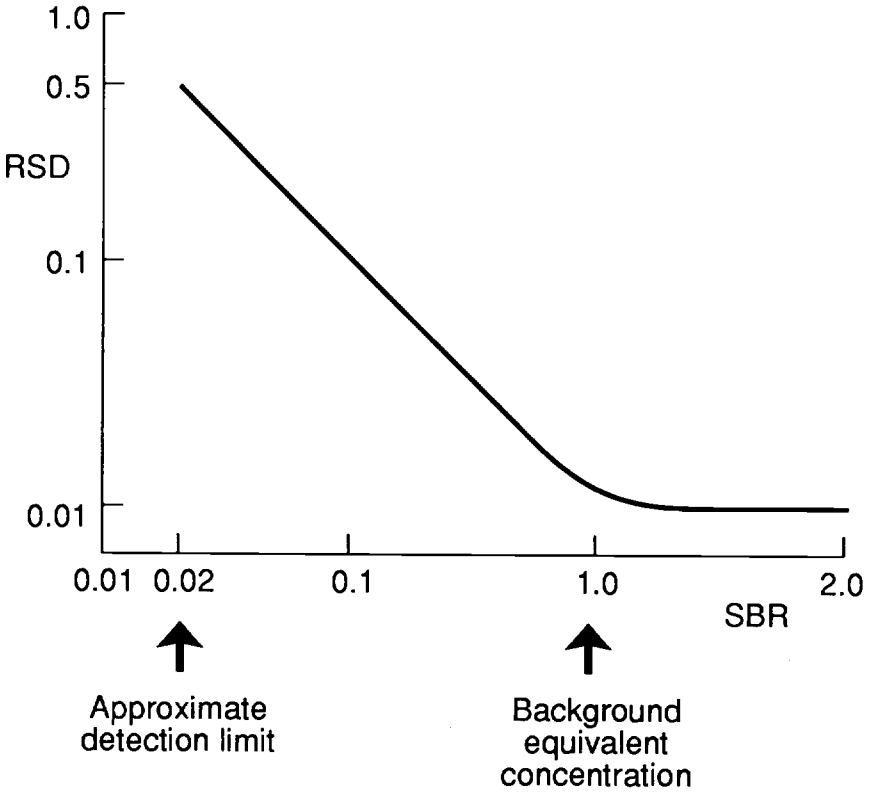

Figure A13 Relationship between Relative Standard Deviation and Analyte Concentrations.

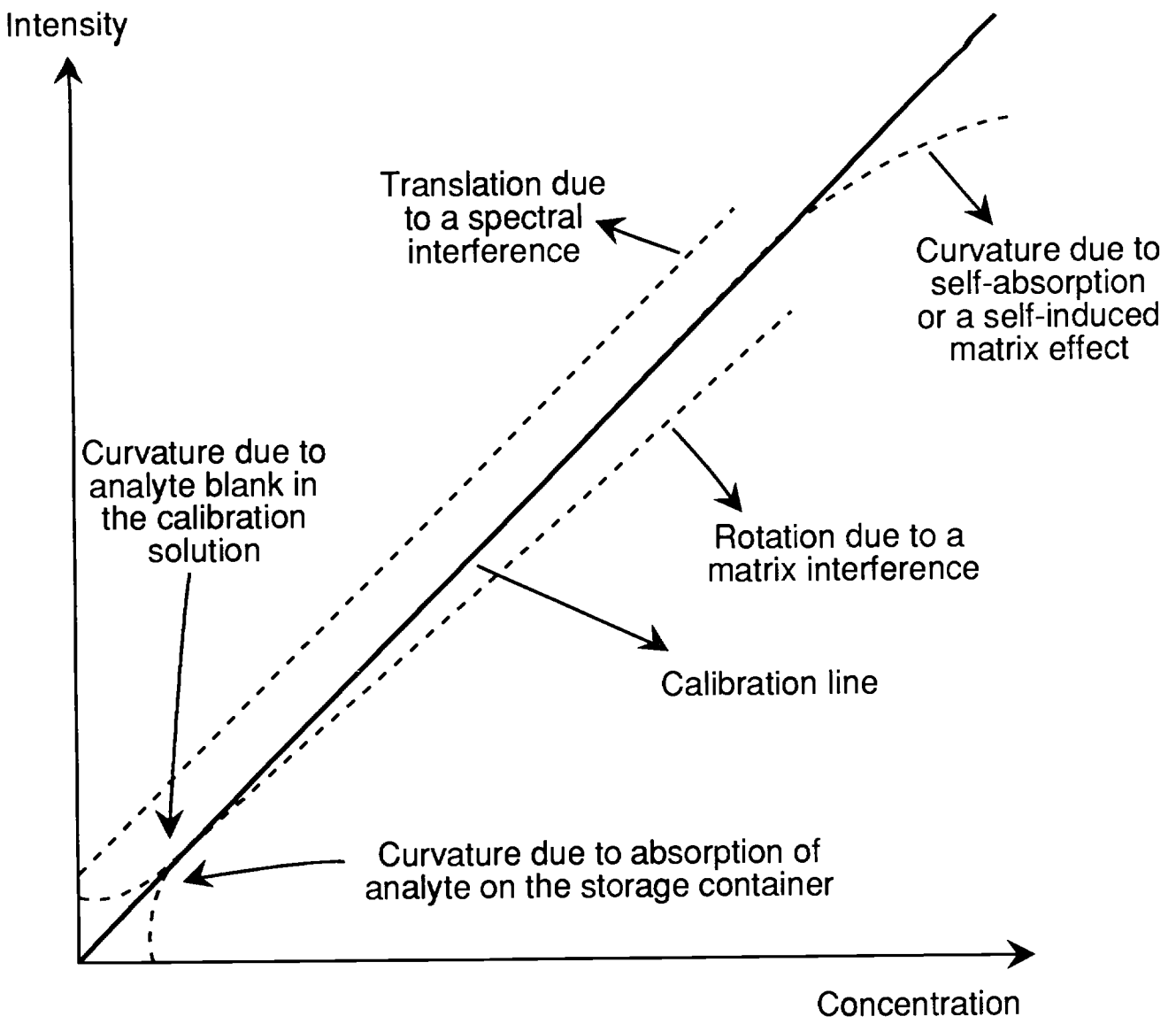

Figure A14 Calibration Curves obtained in ICP-AES.

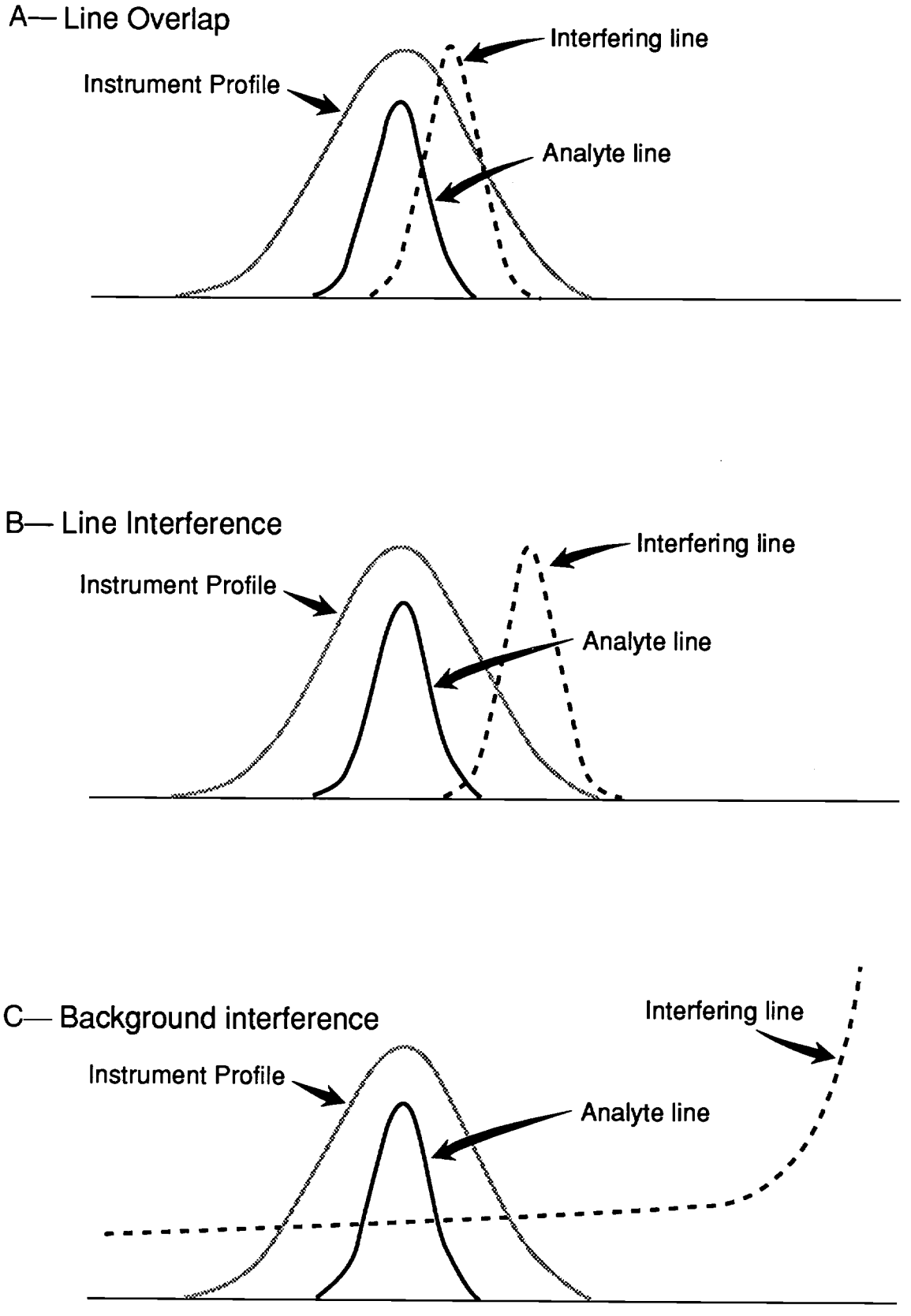

Figure A15 Types of Spectral Interference Encountered in ICP-AES

A—line overlap
B—line interference
C—background interference

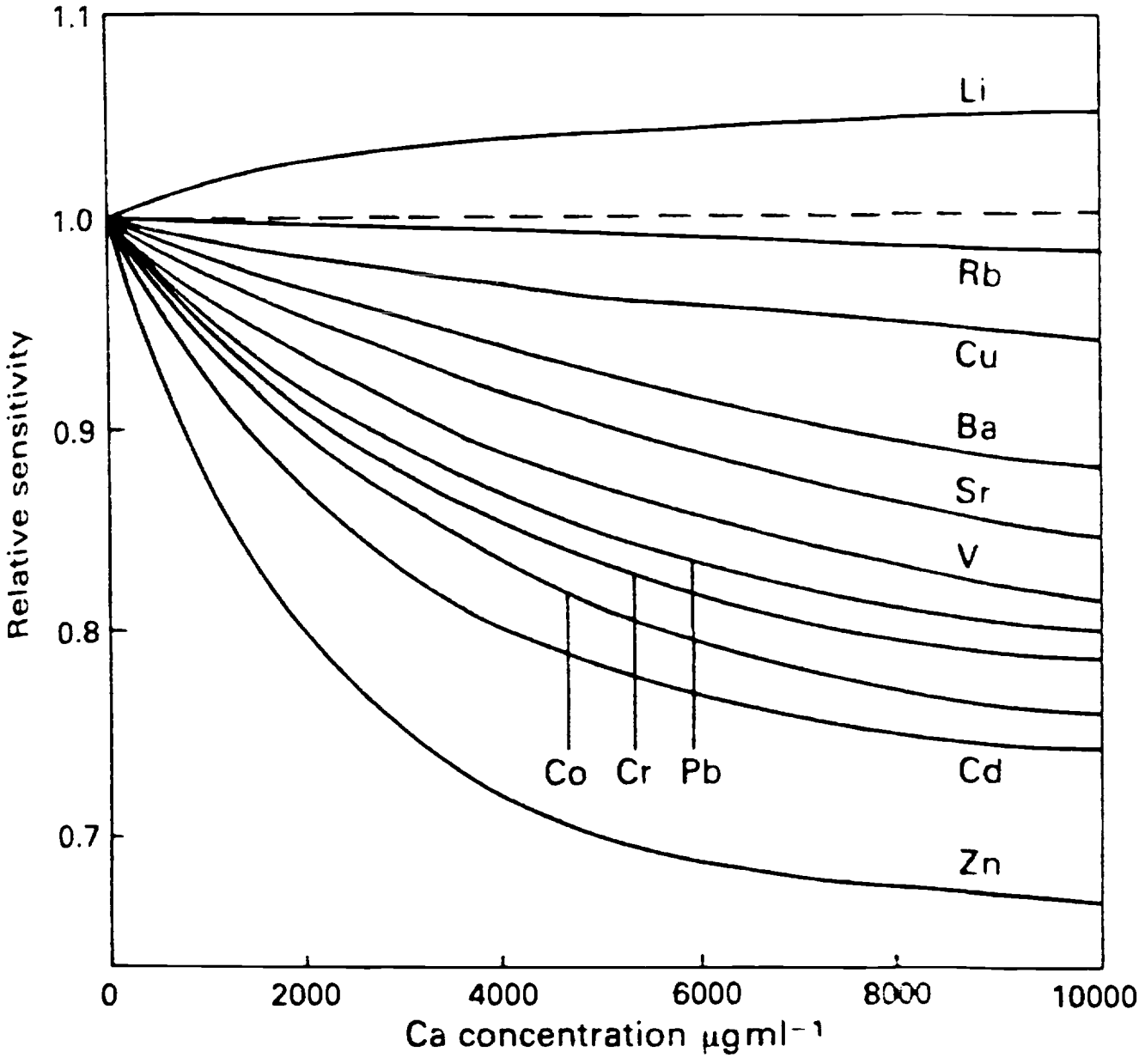

Figure A16 The Effect of Increasing Matrix Concentrations (Ca matrix) on the Rotational Interference for Lines of Varying Excitation Potential (redrawn with permission from M. Thompson and M.H. Ramsey, Analyst, 110, 1413 (1985)).

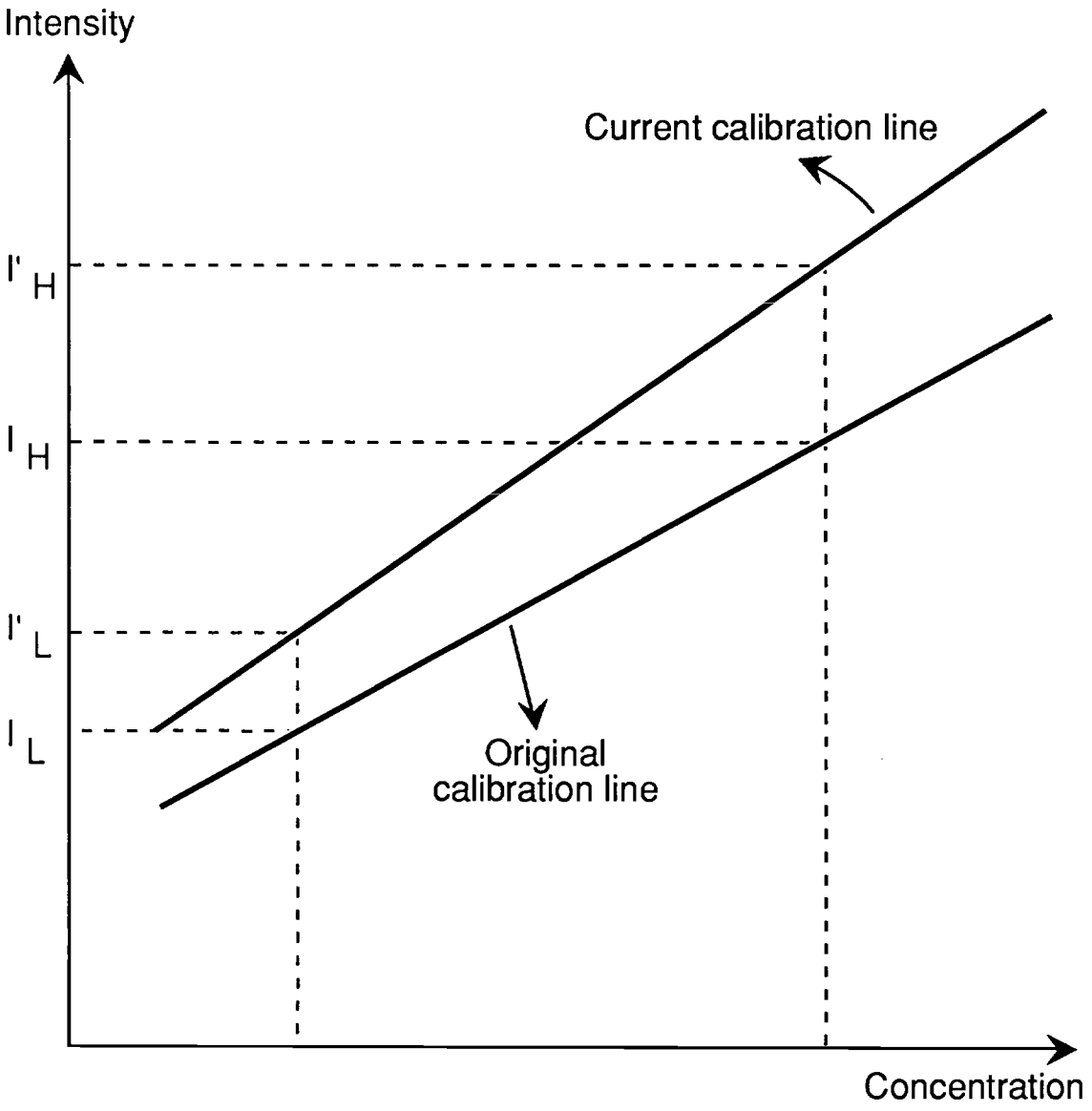

Figure A17 Graphical Representation of a Two Standard Drift Correction Procedure.

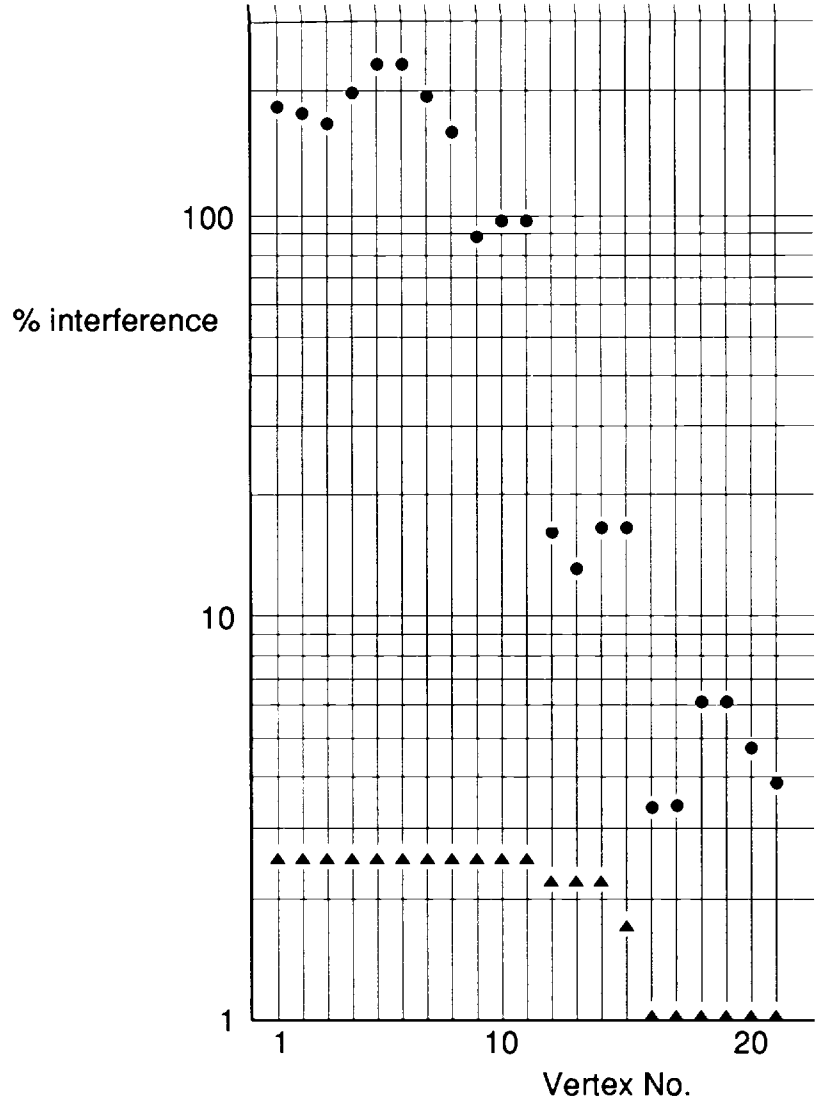

Figure A18 Graphical Representation of the Performance of the Simplex Optimisation in ICP-AES.

B The determination of trace elements in waters and associated materials by inductively coupled plasma—mass spectrometry (ICP-MS)

B1 Introduction

The determination of elements by ICP-MS is relatively new, although ICP-AES was developed many years ago and is now used routinely.

The evolution of plasmas as ion sources for mass spectrometry was pioneered in the early 1970s [112, 113]. The original system used a DC capillary arc plasma and small quadrupole mass analyser, but problems were encountered, which were attributable to the relatively low gas and ionisation temperatures (3500K) of the DC plasma.

ICP-MS is a rapid multi-element quantitative analytical technique similar to ICP-AES, but generally able to reach much lower limits of detection. The limits achievable for most elements are similar to those attainable by graphite furnace-atomic absorption spectrometry, a technique normally limited to single element determination. Each technique has its limitations for certain elements, and their interference effects differ.

As rapid determination of elements at low concentrations is a principal advantage of ICP-MS, the technique is very useful as a routine analytical tool in water analysis.

Although the range of elements covered in this method is limited, many others are capable of being determined with accuracy and without interference. Since the analysis is based on the measurement of individual isotopes, the technique may also be applied to isotope ratio determinations.

B2 Principle

The major components of the inductively coupled plasma-mass spectrometer are shown schematically in Figure B1.

The sample to be analysed, as a solution, is nebulised and dispersed into a stream of argon gas. This gas stream is injected into the core of a high temperature plasma sustained by radio frequency fields. Energy is transferred from the plasma to the sample, dissociating, atomising and ionising it in turn.

The plasma core containing the sample ions is extracted into a reduced pressure region through a small orifice in the 'sampling' cone. A portion of this extracted plasma passes through a further orifice in the 'skimmer' cone and there is a further drop in pressure. These two openings form the interface between the plasma and mass spectrometer. In order to maintain the high vacuum, a combination of vacuum pumps is used. Vacuum gauges are employed to monitor the pressures at different stages.

Behind the cones is a series of cylindrical electrodes designed to extract and focus the positively charged ions from the interface into the quadrupole mass filter, which transmits ions of a particular selected mass (or more accurately, the selected mass to charge ratio). This is followed by systems for measuring the number of ions arriving at the detector and for displaying the data.

The ion detection system consists of a channel electron multiplier followed by a suitable amplifier circuit. Each naturally occurring element has a unique and simple pattern of isotopes, allowing easy identification of the elements in the samples. Pulses from the detection system are fed to a microprocessor-controlled multi-channel analyser data acquisition unit or other data handling system. In the absence of interferents, the number of registered ions from a given isotope depends directly on the concentration of the relevant element in the sample. Accumulated data are transferred for storage and calculation.

B3 Performance characteristics

B3.1 This booklet describes a method for the determination of certain elements in raw, potable and waste waters. It may also be extended to sludges and sediments, but suitable digestion procedures may have to be undertaken prior to analysis (see Appendices 1 and 2). In addition, ICP-MS can also be used for high precision isotope dilution analysis, isotope finger-printing etc.

Determination of the following elements by ICP-MS is covered in this method:

Aluminium (Al)	Nickel (Ni)
Antimony (Sb)	Selenium (Se)
Arsenic (As)	Silver (Ag)
Barium (Ba)	Tellurium (Te)
Beryllium (Be)	Thallium (Tl)
Cadmium (Cd)	Thorium (Th)
Chromium (Cr)	Tin (Sn)
Cobalt (Co)	Titanium (Ti)
Copper (Cu)	Uranium (U)
Lead (Pb)	Vanadium (V)
Manganese (Mn)	Zinc (Zn)
Molybdenum (Mo)	

B3.2 Samples for analysis should ideally have a total dissolved solids content of less than 0.2% m/v. If necessary, the sample should be diluted appropriately.

B3.3 In order to avoid contamination and carry-over problems, samples known to have concentrations of the elements of interest at levels greater than 1 mgl^{-1} may have to be diluted before analysis.

B3.4 Calibration curves for most elements are often linear over a wide range of concentrations, but this should be determined for elements of interest in the types of matrices being analysed.

B3.5 Some precision and recovery data are given in Table B1 for certain elements. Limits of detection are given in Table B2.

B4 Interferences

There are a number of sources of interference which may cause errors in the determination of trace elements by ICP-MS.

B4.1 Isobaric Elemental Interferences

These interferences are caused by isotopes of other elements which form singly or doubly charged ions of the same nominal mass to charge ratio as that of the analyte of interest, and which cannot be resolved by the instrument. Most elements will have at least one stable isotope which is not overlapped by isotopes of other elements.

B4.2 Isobaric Molecular Ion Interferences

These interferences are caused by ions consisting of more than one atom which have the same mass to charge ratio as that of the isotope of interest, and which cannot be resolved by the instrument. They are usually derived from the plasma gas, the sample solvent or anionic matrix. Most common interferences have been identified [114] and are given in Table B3. The mechanisms of formation of molecular ions vary in significance with the matrix, instrument and operating conditions. Such interferences should be recognised, and when they cannot be avoided should be investigated or quantified. It may be necessary to analyse at least 2 isotopes of each analyte being determined.

B4.3 Physical Interferences

These interferences are associated with the physical process of sample analysis from sample uptake to transmission of ions through the ICP-MS interface. Viscosity and surface tension affect the sample uptake rate and aerosol formation. A peristaltic pump is normally used to transport the sample solution to the nebuliser. Its performance and efficiency of operation should be monitored. High levels of dissolved solids in the sample may lead to deposits forming on the sample and skimmer cones,

thus reducing the effective diameter of the orifices and therefore ion transmission. Internal standardisation with indium (or rhodium) is used in this method to compensate for many physical interference effects.

B4.4 Memory Effects

These influences result when elements in a previously run sample contribute to the signals measured in the following sample. In most cases, this occurs if high levels of an element pass through the system, although mercury can cause this problem at relatively low levels. Memory effects may result from sample deposition on the cones and from build up of material in the plasma torch, spray chamber and on plastic tubing.

The effects are usually reduced if adequate rinsing with dilute nitric acid (2% v/v) is carried out between samples.

B5 Hazards

Heat, vapours and fumes generated by the plasma can be hazardous and toxic. These should be extracted from the laboratory by means of an efficient exhaust system.

The plasma source emits radio-frequency radiation and intense ultra violet radiation. Personnel must be suitably protected from this radiation.

If liquid argon is used, the container should be kept undercover, outside, in a well-ventilated area.

Once the plasma has been extinguished, the torch, torch box, cones and cone housing may be very hot for a period of time. Care should be taken if these are to be touched.

Inherent in many instruments are safety interlock systems which are designed to shut down the instrument, or prevent it being operated, under certain circumstances.

Potentially lethal voltages are present within the torch box and radio-frequency generator. Power must be disconnected before these units are opened for service work.

Many of the concentrated standard solutions are toxic and exposure to them should be minimised.

Care should be taken when using acids and any other corrosive substances.

B6 Reagents

All reagents must be of sufficient purity that they do not give rise to significant interference during the analysis. This should be checked for each batch of material and verified by running procedural blanks with each batch of samples analysed.

The water used for blank determination and preparation of control samples should have negligible interferences in comparison with the smallest concentration to be determined.

B6.1 Water—Pure water must be used for the preparation of standard solutions, 'blanks' and for sample dilutions.
B6.2 Nitric Acid (d_{20} 1.42)—Analytical grade reagent
B6.3 Hydrochloric Acid (d_{20} 1.18)—Analytical grade reagent
B6.4 Ammonia (d_{20} 0.88)
B6.5 Hydrofluoric acid
B6.6 Standard Solution
B6.6.1 Stock Standard Solutions

Solutions of 1000 mgl^{-1} single element concentration can be used. It may be necessary to perform a scan of the individual standards at working concentrations to determine whether they are contaminated with other elements of interest.

Stock standard solutions from ultra high purity grade compounds or metals can be prepared or are commercially available. All salts should be dried for one hour at $105^{0}C$, unless otherwise specified.

Some metals, particularly those which form surface oxides may require cleaning prior to being weighed. This may be achieved by pickling the surface of the metal in acid solution, followed by drying.

a) Aluminium (1 ml ≡ 1000 μg Al): Dissolve 0.1 g of cleaned aluminium metal in 10 ml hydrochloric acid (B6.3) and 2 ml nitric acid (B6.2), heating to effect solution. Continue heating until the volume is reduced to 4 ml. Cool and add 4 ml water. Heat until the volume is reduced to 2 ml. Cool and dilute to 100 ml with water.

b) Antimony (1 ml ≡ 1000 μg Sb): Dissolve 0.1 g antimony powder in 2 ml 50% nitric acid and 0.5 ml hydrochloric acid (B6.3), heating to effect solution. Cool, add 20 ml water and 0.15 g tartaric acid. Warm to dissolve the white precipitate. Cool and dilute to 100 ml with water.

c) Arsenic (1 ml ≡ 1000 μg As): Dissolve 0.1320 g As_2O_3 in a mixture of 50 ml water and 1 ml ammonium hydroxide (B6.4). Heat gently to dissolve. Cool and acidify the solution with 2 ml nitric acid (B6.2). Dilute to 100 ml with water.

d) Barium (1 ml ≡ 1000 μg Ba): Dissolve 0.1437 g $BaCO_3$ in a mixture of 10 ml water and 2 ml nitric acid (B6.2). Heat and stir to effect solution and degassing. Dilute to 100 ml with water.

e) Beryllium (1 ml ≡ 1000 μg Be): Dissolve 0.1 g of cleaned beryllium metal in 5 ml hydrochloric acid (B6.3). Dilute to 100 ml with water.

f) Cadmium (1 ml ≡ 1000 μg Cd): Dissolve 0.1 g of cadmium metal in 5 ml 50% nitric acid, heating to effect solution. Cool and dilute to 100 ml with water.

g) Chromium (1 ml ≡ 1000 μg Cr): Dissolve 0.2827 g $K_2Cr_2O_7$ in a mixture of 10 ml water and 1 ml nitric acid (B6.2). Dilute to 100 ml with water.

h) Cobalt (1 ml ≡ 1000 μg Co): Dissolve 0.1 g of cleaned cobalt metal in 5 ml 50% nitric acid, heating to effect solution. Cool and dilute to 100 ml with water.

i) Copper (1 ml ≡ 1000 μg Cu): Dissolve 0.1 g of cleaned copper metal in 5 ml 50% nitric acid, heating to effect solution. Cool and dilute to 100 ml with water.

j) Indium (1 ml ≡ 1000 μg In): Dissolve 0.1 g of cleaned indium metal in 10 ml 50% nitric acid, heating to effect solution. Cool and dilute to 100 ml with water.

k) Lead (1 ml ≡ 1000 μg Pb): Dissolve 0.1599 g $Pb(NO_3)_2$ in 5 ml 50% nitric acid. Dilute to 100 ml with water.

l) Manganese (1 ml ≡ 1000 μg Mn): Dissolve 0.1 g of cleaned manganese metal in 5 ml 50% nitric acid, heating to effect solution. Cool and dilute to 100 ml with water.

m) Molybdenum (1 ml ≡ 1000 μg Mo): Dissolve 0.1500 g MoO_3 in a mixture of 10 ml water and 1 ml ammonium hydroxide (B6.4), heating to effect solution. Cool and dilute to 100 ml with water.

n) Nickel (1 ml ≡ 1000 μg Ni): Dissolve 0.1 g nickel powder in 5 ml nitric acid (B6.2), heating to effect solution. Cool and dilute to 100 ml with water.

o) Selenium (1 ml ≡ 1000 μg Se): Dissolve 0.1 g selenium powder in 2 ml 50% nitric acid and 0.5 ml hydrochloric acid (B6.3). Dilute to 100 ml with water.

p) Silver (1 ml ≡ 1000 μg Ag): Dissolve 0.1 g silver metal in 5 ml 50% nitric acid, heating to effect solution. Cool and dilute to 100 ml with water. Store in an amber glass container.

q) Thallium (1 ml ≡ 1000 μg Tl): Dissolve 0.1303 g $TlNO_3$ in a mixture of 10 ml water and 1 ml nitric acid (B6.2). Dilute to 100 ml with water.

r) Thorium (1 ml ≡ 1000 μg Th): Dissolve 0.1 g of thorium wire in 5 ml nitric acid (B6.2). Dilute to 100 ml with water.

s) Tin (1 ml ≡ 1000 μg Sn): Dissolve 0.1 g of cleaned granulated tin metal in 5 ml hydrochloric acid (B6.3), heating to effect solution. Cool and dilute to 100 ml with water.

t) Titanium (1 ml ≡ 1000 μg Ti): Dissolve 0.1 g of cleaned titanium metal in 5 ml hydrochloric acid (B6.3), adding one drop of hydrofluoric acid (B6.5) to effect solution. Dilute to 100 ml with water.

u) Uranium (1 ml ≡ 1000 μg U): Dissolve 0.1 g of uranium sheet in 5 ml nitric acid (B6.2). Dilute to 100 ml with water.

v) Vanadium (1 ml ≡ 1000 μg V): Dissolve 0.1 g of cleaned vanadium metal in 5 ml 50% nitric acid, heating to effect solution. Cool and dilute to 100 ml with water.

w) Zinc (1 ml ≡ 1000 μg Zn): Dissolve 0.1 g of cleaned zinc metal in 5 ml 50% nitric acid, heating to effect solution. Cool and dilute to 100 ml with water.

B6.6.2 Intermediate Mixed Standard Solutions (10 mgl^{-1})

These solutions may be prepared as mixed element standards in 5% v/v nitric acid or 5% v/v hydrochloric acid. Ensure chemical compatibility with the solutions prepared.

Standard Solution A

Aluminium	Molybdenum
Beryllium	Nickel
Cadmium	Thallium
Chromium	Thorium
Cobalt	Uranium
Copper	Vanadium
Lead	Zinc
Manganese	

This solution can be prepared by adding 5 ml of each of the 1000 mgl^{-1} stock standard solutions (B6.6.1) to 25 ml nitric acid (B6.2) in a 500 ml volumetric flask and making to the mark with water. This intermediate standard solution should be prepared freshly at monthly intervals.

Standard Solution B

Tin	Arsenic
Titanium	Selenium
Tellurium	Antimony

The solution can be prepared by adding 5 ml of each of the 1000 mgl^{-1} stock standard solutions (B6.6.1) to 25 ml hydrochloric acid (B6.3) in a 500 ml volumetric flask and making to the mark with water. This intermediate standard solution should be prepared freshly at monthly intervals.

Separate standard solutions of barium, silver and indium

The solution of indium is used as an internal standard. Barium and silver are known to cause problems by precipitation under certain circumstances.

Separate standard solutions are prepared. Add 5 ml of 1000 mg^{-1} stock standard solution (B6.6.1) to 25 ml nitric acid (B6.2) in a 500 ml volumetric flask and make to the mark with water. These intermediate standard solutions should be prepared freshly at monthly intervals.

B6.6.3 Calibration Standard Solutions

These solutions should be prepared freshly on each day of analysis at levels appropriate to the normal operating range of the instrument. They should be prepared in 1% v/v nitric acid. Examples of calibration standard solutions are:

(i) Calibration Standard Solution (a) (10 μgl^{-1})
Add 100 μl of the 10 mgl^{-1} standard solutions of interest (B6.6.2), plus 500 μl indium 10 mgl^{-1} internal standard solution (B6.6.2), plus 1 ml nitric acid (B6.2) to a 100 ml volumetric flask. Make to the mark with water. The indium concentration is 50 μgl^{-1}.

(ii) Calibration Standard Solution (b) (50 μgl^{-1})
Add 500 μl of the 10 mgl^{-1} standard solutions of interest (B6.6.2), plus 500 μl indium 10 mgl^{-1} internal standard solution (B6.6.2), plus 1 ml nitric acid (B6.2) to a 100 ml volumetric flask. Make to the mark with water. The indium concentration is 50 μgl^{-1}.

B6.6.4 Internal Standard Solution

An internal standard solution is added to the calibration standards, blanks and samples. It is used to monitor and to correct for fluctuations in matrix, instrumental drift, nebuliser and cone orifice blockages and aerosol transport effects.

One or more internal standards may be used. The levels of an element suitable as an internal standard should be negligible in the samples being analysed. The element should be easily ionised in the ICP and exhibit no unusual chemical effects, and be representative of the mass range under investigation. Examples of isotopes frequently used as internal standards are ^{115}In, ^{103}Rh, ^{89}Y and ^{45}Sc. The use of gas or polyatomic ion peaks as internal standards is not recommended.

B6.7 Analytical Quality Control Solutions

B6.7.1 'Spiked' Sample Solution

In order to monitor any bias in samples, a sample from each batch can be 'spiked' for example with 25 μgl^{-1} of the elements of interest, and their recoveries monitored. Into a clean 100 ml volumetric flask, add 250 μl of the 10 mgl^{-1} mixed standards (B6.6.2), 500 μl of the indium 10 mgl^{-1} standard (B6.6.2) and make up to volume with the acidified sample. If the samples are to be digested before analysis, a 'spiked' sample should be carried through that procedure.

B6.7.2 Reference Standard

An independent and externally produced quality control reference standard can be analysed with each batch of samples. This should have concentrations of elements at similar levels to those under investigation, and can be used to confirm the accuracy of calibration standard preparation.

B6.8 'Blank' Solutions

Three types of 'blank' solutions are required for this method.

B6.8.1 Calibration Blank Solution

This is used to establish the calibration graph, and if no digestion procedures are employed on the samples, can be used in blank subtraction calculations. This is prepared in 1% v/v nitric acid by adding 1 ml nitric acid (B6.2) and 500 μl indium 10 mgl^{-1} internal standard solution (B6.6.2) to a 100 ml volumetric flask and making up to the mark with water.

B6.8.2 Sample Preparation Blank

This is used to assess possible contamination from the sample preparation procedure and should be treated as a sample being carried through any digestion procedures. To a clean sample collection bottle, add 99 ml of water followed by 1 ml of the appropriate concentrated acid. This can be used in blank subtraction calculations when digestion procedures are involved.

B6.8.3 Rinse Blank (2% v/v Nitric Acid)

This is used to flush the instrument between samples in order to reduce memory interferences. Add 40 ml nitric acid (B6.2) to 1500 ml of water and make to 2000 ml with water.

B7 Apparatus

B7.1 Inductively Coupled Plasma Mass Spectrometer

B7.1.1 An instrument capable of scanning the mass range from 5-250 amu with a minimum resolution capability of 1 amu peak width at 10% peak height. The instrument may be fitted with a conventional or extended dynamic range detection system.

B7.1.2 A variable speed peristaltic pump for solution delivery to the nebuliser. When in operation, the pump tubes should be clamped so that there is no free movement of the solution to the nebuliser when the pump is stopped.

B7.1.3 A water-cooled spray chamber will be of benefit in reducing some types of interferences [115].

B7.1.4 Argon gas supply (high purity grade 99.99%).

B7.1.5 Because of the diversity of instrument hardware available, no detailed instrument operating conditions are provided. The analyst is advised to follow the operating conditions recommended by the manufacturer. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions satisfy the analytical requirements and to maintain quality control data verifying the instrument performance and analytical results.

Instrument operating conditions used to generate the performance data shown in Table B1 are given in Table B4.

B7.1.6 Where necessary, precautions should be taken to protect the electron multiplier from exposure to high ion counts. Changes in instrument response or damage to the multiplier may otherwise result. Samples possessing high concentrations of elements beyond the linear range and with isotopes falling within regions of interest should be diluted prior to analysis. Some regions of expected high intensity signals can be skipped over during data acquisition, and this will prolong the life of the electron multiplier.

B7.2 Assorted Apparatus

In the determination of trace levels of elements, avoidance of contamination and loss are of prime consideration. Potential contamination sources include insufficiently cleaned laboratory apparatus and general contamination within the laboratory environment. A clean laboratory work area designed for trace element sample handling should be used. Sample containers can introduce positive and negative errors in the determination of trace elements by:

a) contributing contaminants through surface desorption and leaching, or

b) depleting element concentrations through adsorption processes.

All re-usable apparatus (fused silica, polyethylene, polytetrafluoroethylene, etc) should be cleaned prior to use by thoroughly washing with detergent and water, followed by soaking overnight in 10% v/v nitric acid. This should be followed by rinsing with purified water.

B7.2.1 High density polyethylene sample bottles.
B7.2.2 Volumetric flasks for standard solutions.
B7.2.3 Variable or fixed volume mircopipettes with disposable plastic tips.

B8 Sample Collection and Preservation

Prior to collection of the sample, consideration should be given to the type of data required so that appropriate preservation and pre-treatment steps can be undertaken. Filtration and acid preservation should be performed at the time of sample collection, or as soon as possible after receipt.

Refer to the appropriate method is this series for individual elements before preservation is carried out. Certain determinations will require separate and specific preservation techniques.

For the determination of dissolved or soluble elements, the sample should be filtered through a 0.45 μm membrane filter. A portion of the sample should be filtered and then used to rinse the filter assembly. The filtrate should then be discarded. The required volume of sample should be filtered and the filtrate then collected. The filtrate is acidified to 1% with the appropriate acid immediately following filtration.

For the determination of total recoverable elements in aqueous samples, acidification to 1% with the appropriate acid is carried out immediately on collection. The sample need not be filtered prior to analysis, unless particulate matter remains and nebuliser blockage may occur.

If the sample contains an appreciable amount of particulate material, it should be carried through a suitable digestion procedure.

Following acidification, the sample can be held at room temperature prior to sample processing. Some elements are known to be lost if acidification is not carried out immediately and validation procedures should be undertaken to ascertain the extent to which this occurs.

Sludge and sediment samples may be analysed by this method if the total metal content is solubilised and diluted by a digestion procedure such as described in Appendix 2.

B9 Analytical Procedure

B9.1 Calibration and Standardisation

Set up the operating configurations of the instrument and data system according to the manufacturer's instructions.

If necessary conduct mass calibration and resolution checks using the mixed calibration standard solution B6.6.3 (ii).

The instrument should be calibrated for the analytes to be determined using calibration blank and standard solutions.

If necessary, the rinse blank should be used to flush the system between solution changes for blanks, standards and samples. Uptake times should allow equilibrium to be established before acquisition of data.

An internal standard, for example, (^{115}In) should be present in all standards, samples and blanks at an identical concentration. The concentration should be sufficient that good precision is obtained in the measurement of the isotope. In this method, the indium concentration in all solutions was 50 μgl^{-1}.

A stable analytical signal should be achieved before calibration can begin. This can be monitored using the internal standard signal. After the calibration has been established, it should be confirmed for all analytes.

To verify that the calibration of the instrument is maintained on a continuing basis, calibration blanks and standards should be analysed at regular intervals. The results of the analysis of the standards will indicate whether the calibration remains valid.

The response of the internal standard should be monitored throughout the analytical run and if unacceptable deviations occur, corrective action should be undertaken.

B9.2 Sample Analysis

For the determination of dissolved elements, to a 100 ml aliquot of the filtered, acid-preserved sample, add 500 μl of the internal standard solution (B6.6.2) and mix well. The sample is ready for analysis.

For new or unusual matrices, a semi-quantitative analysis can be carried out to screen the high element concentrations. Information gained from this may be used to prevent potential damage to the detector during sample analysis and to identify elements which have concentrations above the linear range. The sample should also be screened for the element(s) chosen for use as internal standards in order to prevent bias in the calculation of analytical data.

Flush the system with the rinse blank between samples.

Samples having concentrations higher than the established linear dynamic range should be diluted and re-analysed. Alternatively, the dynamic range may be adjusted by selecting an alternative isotope of lower natural abundance, provided that quality control data for that isotope have been established.

B10 Calculation of Results

The concentration of each element of interest in the sample can be determined, based on the calibration standards and taking into account any effects causing variation in the internal standard. The calibration blank values are subtracted from standards and samples where a digestion procedure has not been used. Where digestion has been carried out, the sample preparation blank (B6.8.2) should be subtracted.

B11 Analytical Quality Control

Analytical quality control samples serve to provide a daily check on results, and also to produce long term statistical data which can be used to assess method performance and to aid with the interpretation of results.

Analytical quality control in the determination of elements by ICP-MS can be carried out in the form of recovery tests on samples, and in the analysis of reference samples of known composition obtained from an external source.

In recovery tests, the efficiency of recovery should be noted.

Table B1 Standard deviations and recoveries of elements in waters

Type of Sample	Concentration (μgl^{-1})	Sw (μgl^{-1})	Recovery (%)
CADMIUM			
Standard	5.00	0.09	
Standard	45.00	0.36	
Tap Water	0.04	0.01	
Tap Water Spiked	25.05	0.23	100.3
River Water	0.00	0.00	
River Water Spiked	25.25	0.34	101.1
Sewage Effluent	0.10	0.06	
Sewage Effluent Spiked	23.18	0.28	92.6
CHROMIUM			
Standard	5.00	0.38	
Standard	45.00	1.85	
Tap Water	3.62	0.99	
Tap Water Spiked	28.68	1.64	100.5
River Water	3.38	0.91	
River Water Spiked	29.70	1.81	105.6
Sewage Effluent	3.35	0.41	
Sewage Effluent Spiked	27.49	1.57	96.8
COBALT			
Standard	5.00	0.22	
Standard	45.00	2.27	
Tap Water	0.57	0.17	
Tap Water Spiked	25.34	0.87	99.4
River Water	0.50	0.16	
River Water Spiked	27.30	1.33	107.5
Sewage Effluent	3.58	0.15	
Sewage Effluent Spiked	28.18	1.24	98.7
COPPER			
Standard	5.00	0.30	
Standard	45.00	2.40	
Tap Water	13.06	0.93	
Tap Water Spiked	37.25	1.60	97.1
River Water	4.27	0.32	
River Water Spiked	28.66	1.05	97.8
Sewage Effluent	12.04	0.78	
Sewage Effluent Spiked	34.44	1.48	89.9
LEAD			
Standard	5.00	0.18	
Standard	45.00	1.88	
Tap Water	0.82	0.09	
Tap Water Spiked	26.98	0.72	104.9
River Water	0.45	0.24	
River Water Spiked	27.57	1.42	108.7
Sewage Effluent	1.12	0.28	
Sewage Effluent Spiked	25.30	1.37	97.0

Type of Sample	Concentration (μgl^{-1})	Sw (μgl^{-1})	Recovery (%)
NICKEL			
Standard	5.00	0.33	
Standard	45.00	2.52	
Tap Water	4.38	0.38	
Tap Water Spiked	28.86	1.25	98.2
River Water	15.65	1.50	
River Water Spiked	41.04	2.32	102.0
Sewage Effluent	17.47	0.90	
Sewage Effluent Spiked	40.16	1.94	91.0
MANGANESE			
Standard	5.00	0.20	
Standard	45.00	1.70	
Tap Water	4.75	0.20	
Tap Water Spiked	29.71	0.89	100.1
River Water	24.92	0.98	
River Water Spiked	50.67	1.58	103.5
Sewage Effluent	21.93	0.58	
Sewage Effluent Spiked	46.14	1.92	97.3
ZINC			
Standard	5.00	0.30	
Standard	45.00	1.59	
Tap Water	13.40	0.56	
Tap Water Spiked	38.20	1.30	99.7
River Water	9.01	0.50	
River Water Spiked	33.43	1.20	98.0
Sewage Effluent	46.84	0.74	
Sewage Effluent Spiked	67.87	1.13	84.7

Sw is the within-batch standard deviation with 9 degrees of freedom.
The samples were 'spiked' with 25 μgl^{-1} of the element.
Data provided by the National Rivers Authority, Anglian Region.

Table B2 Limits of detection

Element	Isotope (amu)	Method LOD (a) (μgl^{-1})	Instrument LOD (b) (μgl^{-1})
Al	27		0.06
Ba	138		0.01
Be	9		0.03
Cd	114	0.04	0.006
Cr	52	0.06	0.03
Co	59	0.02	0.005
Cu	65	0.13	0.04
Pb	208	0.02	0.01
Mn	55	0.04	0.01
Mo	95		0.05
Ni	58	0.13	0.13
Ag	107		0.02
Te	128		0.04
Tl	205		0.003
Sn	118		0.007
Ti	47		0.16
U	238		0.002
V	51		0.01
Zn	66	0.27	0.04

(a) The method limit of detection is the minimum concentration of an element which can be identified, measured and reported with stated confidence (4.65 x Sw).

This was determined by analysis of a tap water matrix containing low concentrations of the analyte, with 9 degrees of freedom.

(b) The instrument limit of detection is the concentration equivalent of the analyte signal which is equal to 4.65 times the standard deviation of the blank signal at the selected analytical mass. There were 11 degrees of freedom.

Data provided by the National Rivers Authority, Anglian Region.

Table B3 Isobaric molecular ion interferences

Molecular Ion	Mass	Element Interferences (Elements covered in this method only)
Background Molecular Ions		
NH^+	15	
OH^+	17	
OH_2^+	18	
N_2^+	28	
N_2H^+	29	
NO^+	30	
NOH^+	31	
O_2^+	32	
O_2H^+	33	
$^{36}ArH^+$	37	
$^{38}ArH^+$	39	
$^{40}ArH^+$	41	
$^{36}ArO^+$	52	Cr
$^{38}ArO^+$	54	Cr
$^{40}ArN^+$	54	Cr
$^{40}ArNH^+$	55	Mn
$^{40}ArO^+$	56	
$^{40}ArOH^+$	57	
$^{40}Ar^{36}Ar^+$	76	Se
$^{40}Ar^{38}Ar^+$	78	Se
$^{40}Ar_2^+$	80	Se
Chloride		
$^{35}Cl^+$	35	
$^{37}Cl^+$	37	
$^{35}ClO^+$	51	V
$^{37}ClO^+$	53	Cr
$^{35}ClOH^+$	52	Cr
$^{37}ClOH^+$	54	Cr
$^{40}Ar^{35}Cl^+$	75	As
$^{40}Ar^{37}Cl^+$	77	Se
$^{35}Cl_2^+$	70	
$^{37}Cl_2^+$	74	
$^{40}ArO^{35}Cl^+$	91	
$^{40}ArO^{37}Cl^+$	93	
Sulphate		
$^{32}SO^+$	48	Ti
$^{34}SO^+$	50	V, Cr, Ti
$^{32}SOH^+$	49	Ti
$^{34}SOH^+$	51	V
$^{32}SO_2^+$, $^{32}S_2^+$	64	Zn
$^{40}Ar^{32}S^+$	72	
$^{40}Ar^{34}S^+$	74	
Phosphate		
PO^+	47	Ti
POH^+	48	Ti
PO_2^+	63	Cu
$^{40}ArP^+$	71	

Molecular Ion	Mass	Element Interferences (Elements covered in this method only)
Organics		
C_2^+	24	
C_2H^+, $^{12}C^{13}C^+$	25	
CN^+	26	
CO_2^+	44	
CO_2H^+, $^{13}CO_2^+$	45	
$^{40}ArC^+$	52	Cr
Group I and II Metals		
$^{40}ArNa^+$	63	Cu
$^{40}ArK^+$	79	
$^{40}ArCa^+$	80	Se
$^{40}ArLi^+$	47	Ti
$^{40}ArFe^+$	96	Mo
$^{40}ArCu^+$	103, 105	
$^{40}ArAg^+$	147, 149	

Table B4 Instrument Operating Conditions Used For Generation of Performance Data

Instrument	VG Plasma Quad PQ1
Plasma Forward Power	1.35 kW
Coolant Flow Rate	13.5 l min^{-1}
Auxiliary Flow Rate	0.45 l min^{-1}
Nebuliser Flow Rate	0.70 l min^{-1}
Solution Uptake Rate	0.88 ml min^{-1}
Spray Chamber Temperature	12 ^0C
Data Acquisition	
Detector Mode	Pulse counting, peak jumping
Peak Jump Dwell	50 msec
Peak Jump Sweeps	20
Points Per Peak	3
DAC Step Between Points	3
No. of Channels	2048
Sample Uptake Time Before Acquisition	80 sec
Rinse Time	120 sec

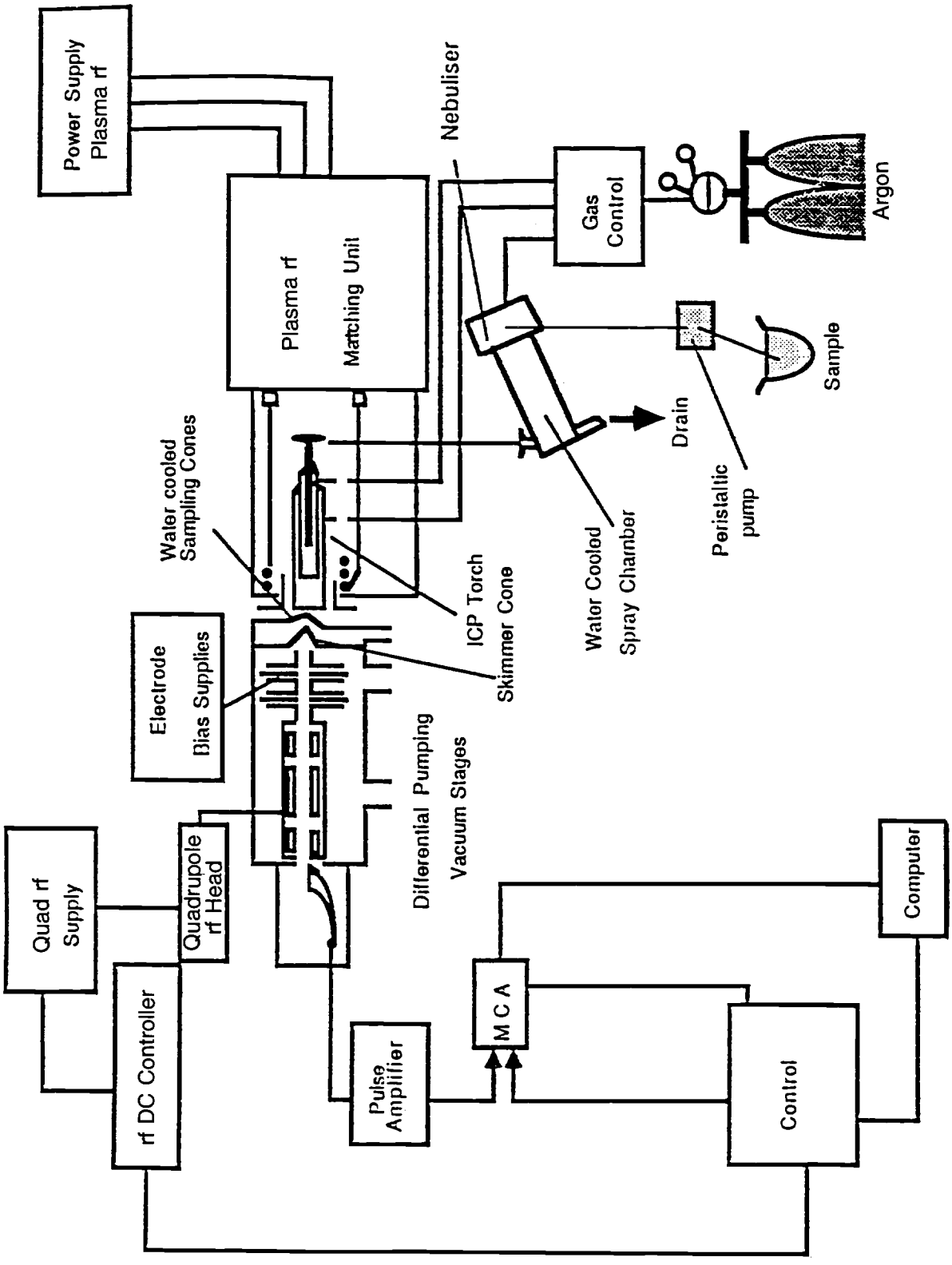

Figure B1 Schematic diagram of the inductively coupled plasma—mass spectrometer

Appendix 1: Preparation of Water Samples

General Principles

The determination of metals in water samples by ICP-MS relies on the presentation of the analytes in solution, or in a suspension sufficiently dispersed to mimic a solution. Most metal ions are held in stable form by the inclusion of acid.

The speciation of the metal should be determined, ie whether total, soluble or particulate fractions are required. These fractions can be separated using 0.45 μm membrane filters. This appendix describes the determination of 'total' and 'dissolved' fractions; 'particulate' can be treated as solid samples (see Appendix 2).

The unstable nature of many metal species in natural waters has implications for sampling techniques. It is preferable that any separation is carried out at the time of sampling, and that preservation reagents are added as soon as possible thereafter.

Procedures should be followed which avoid contamination of the sample, by minimising the amount of handling which samples receive prior to determination.

Sampling

General guidelines for sampling of water are given in previous publications in this series [116, 117). The following points are worth noting:

(i) For each sample, prepare a container, preferably of high density polyethylene. This should have been pre-cleaned by soaking in 10% v/v nitric acid for one to two days, and then rinsed with deionised water before use.

(ii) The sample should be representative of the body of water from which it was taken, and be clearly identified. The method of collection should not contaminate the sample.

(iii) The sample should be stabilised, if necessary, as soon as possible and kept free of contamination at all times.

(iv) Where multiple samples are needed (for example, for different elements), it is preferable to take these separately on site, avoiding sub-sampling later.

Filtration

For separation of 'dissolved' metals the sample should be passed through a membrane filter (0.45 μm pore size) as soon as possible after sampling.

Sample Preservation

Samples for the determination of the metals covered by this method should be preserved using dilute acid. A final acid concentration of 1% v/v, nitric acid or hydrochloric acid can be used. The particular acid used depends on the elements of interest.

The following elements can be preserved in nitric acid: Ag, Al, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Th, Tl, U, V, Zn

The following elements can be preserved in hydrochloric acid: As, Sb, Se, Sn, Te, Ti

Samples for total metal content should be acidified in the bottles used for collection.

Sample Digestion

Samples for the determination of the metals covered by this method may require digestion before analysis. Generally, filtered samples which have been acidified immediately will not normally require any digestion, though unfiltered samples generally will. A precise treatment cannot be prescribed for all sample types, and procedures should be defined locally, supported by any experimental work needed for validation of the method used. The following notes may, however, be useful.

Whatever digestion procedure is used, contamination risks are to be avoided. The sensitivity of ICP-MS often enables the analyst to dispense with risky pre-concentration techniques, (such as evaporation, ion-exchange, solvent extraction, etc.) A major

source of contamination arises during transfer of samples to intermediate digestion vessels. If, therefore, digestion can be carried out in the storage bottle, the risk of contamination can be reduced. This, of course, assumes that the storage bottle itself does not cause contamination, either during storage or digestion. A number of laboratories have adopted a method in which the sample is stored in a polyethylene container, and after the addition of acid is subjected to a period of exposure to the acid before analysis. This may be sufficient even at room temperate for some samples, though it may be necessary to heat the sample to about 80 ^{0}C for several hours in a thermostatically controlled oven [118]. Extraction of metals from particulate matter in samples by such methods may not be analytically valid. More severe digestion may be achieved by boiling samples in acid solution, perhaps with the inclusion of hydrogen peroxide, peroxy-disulphuric acid, etc. In practice, analysis following overnight digestion at 80 ^{0}C will normally be sufficient for samples containing only small amounts of finely divided particulate material.

Appendix 2: Dissolution Methods for Solid and Semi-Solid Samples

Introduction

A number of methods are available for extracting or digesting solid and semi-solid samples before analysis by ICP-MS (or ICP-AES). The exact procedure should be chosen carefully after consideration of several factors.

a) The purpose for which the analysis is required.

b) The range of elements which is required; open tube digestion or high temperature ashing procedures may not be appropriate if analytes such as mercury and arsenic are to be determined. Similarly, elements soluble with difficulty such as barium, silver, tin and titanium should only be determined following a chemical procedure which is appropriate.

c) The limit of detection which is needed to meet the requirements for which the analysis is being undertaken. A procedure which involves a large dilution ratio may be less attractive than one which avoids this.

d) The amount of solids which the method of preparation will introduce into the solution for analysis. ICP-MS normally requires solutions with low solids contents (although this requirement varies according to the nature of the matrix). A preparation method which introduces an appreciable amount of an inorganic salt into the sample solution, such as fusion with lithium metaborate, will result in the elevation of detection limits because of the consequent dilution which may be necessary.

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Plasma Source Mass Spectrometry
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Royal Society of Chemistry, London and Cambridge, 1990

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