

3 Instrument options

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3.1 Introduction

This chapter is mainly directed at the reader using ICP-MS systems with solution introduction. It is not intended as a detailed survey of all 'add-ons' for ICP-MS instrumentation nor as a detailed description of the theory of operation of these devices. The inductively coupled plasma source, its associated devices (nebuliser, spray chamber etc.) and the interface components can be readily modified by a user with some experience. Modification of the mass spectrometer, instrument electronics or system software is however, generally not a possibility for most ICP-MS users and for this reason will be omitted. It is advisable to consult the manufacturers before making any modifications to instrumentation, as this may invalidate the guarantee and can cause expensive damage.

The items considered will be:

- (i) nebulisers, types in use, principles of operation, free running or pumped, analytical characteristics;
- (ii) spray chambers, purpose of a spray chamber, types in use, temperature stabilised;
- (iii) plasma torches, types in use, principles of operation;
- (iv) sampling cones and skimmer cones, different designs, orifice diameters, materials of manufacture.

3.2 Nebulisers

3.2.1 Introduction

The sample introduction into the ICP, including nebulisation, is a critical part of the analytical process in ICP-MS. The great majority of ICP-MS analyses are carried out on liquid samples, however a gas stream is needed to get the sample into the plasma. The most convenient method for liquids to be introduced into the gas stream is as an aerosol from a nebuliser. A variety of methods can be used to produce an aerosol, such as the action of a high speed gas jet across the tip of a small orifice or the use of an ultrasonic transducer.

During the development of the nebuliser for optical spectroscopy it was

found that the addition of a spray chamber (section 3.3) placed after the nebuliser could remove some of the large droplets produced, and thereby improve the stability of the spectral emission. So effective were the early crude devices that apart from manufacturing refinements, they are still used today in flame emission and atomic absorption spectrometers.

The most commonly used nebuliser designs for analytical atomic spectrometry are 'pneumatic' and 'ultrasonic' (Sharp, 1988a and references 3-15 therein), although other types such as electrostatic (Bailey, 1984), thermospray (Vestal and Ferguson, 1985), jet impact (Doherty and Hiestje, 1984) and mono-dispersive generators (Berglund and Liu, 1973; Lindblad and Schneider, 1965) have been used. Solid samples may be introduced as aerosols, using sputtering devices, and some work has been carried out using fluid beds for powder sample introduction (Ng *et al.*, 1984). The introduction of solid samples is discussed in chapter 10. A detailed description of the mechanism of operation and operating characteristics of pneumatic nebulisers for analytical atomic spectrometry has been given by Sharp (1988a).

Very few of the more novel devices for solution sample introduction have been used on ICP-MS instruments, with pneumatic nebulisers in almost universal use for routine analysis. To date there are no nebulisers which have been designed specifically for use on ICP-MS instruments and this situation is likely to remain since the liquid sample introduction requirements of ICP-MS and ICP-AES systems are essentially the same. Equally the practical problems associated with the operation of the nebulisers such as unstable operation, blockage and poor efficiency, apply equally to both ICP systems.

Essentially three types of pneumatic nebuliser are used in ICP-MS; the concentric flow (Meinhard, 1976), the cross flow (Kniseley *et al.*, 1974) and the Babington type nebuliser (Suddendorf and Boyer, 1978). These are shown schematically in Figure 3.1.

3.2.2 Concentric nebulisers

Probably the most widely used ICP nebuliser is the one-piece Meinhard glass concentric nebuliser (Meinhard, 1976), shown in Figure 3.2. It can be obtained as a general purpose nebuliser with limited salt tolerance, in a high salt tolerance design, and for applications that require a low nebuliser gas flow. For ICP-MS, a nebuliser gas flow of $0.75-1.00 \text{ l min}^{-1}$ is typical, which is produced from a line pressure of 165 kPa (24 lb per square inch) at which the 'free running' uptake of water is about 0.6 ml min^{-1} .

3.2.2.1 Mode of operation Most concentric nebulisers are self-actuating and self priming, i.e. solutions are drawn up by the pressure drop generated as the nebuliser gas passes through the orifice. This mode of operation is called 'free-running'. The viscosity of the solution and the vertical distance through

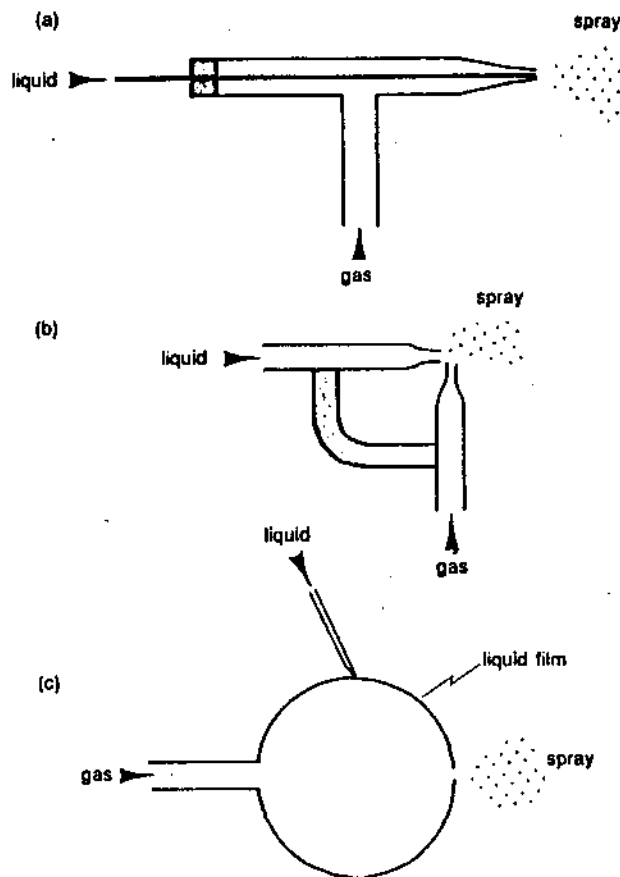


Figure 3.1 Schematic diagram of three types of pneumatic nebuliser. (a) Concentric flow, (b) cross flow, (c) Babington type. After Sharp (1988a).

which the liquid is lifted (the 'head') affect the rate of liquid transfer. The alternative and more common method is to meter the solution to the nebuliser using a peristaltic pump. This has a number of advantages which are described by Thompson and Walsh (1989).

- (i) The head effect is eliminated.
- (ii) Viscosity effects are reduced.
- (iii) Metering uptake with a pump limits air which can be introduced and reduces the risk of the plasma becoming unstable.
- (iv) The liquid uptake may be varied separately from the gas flow rate.
- (v) The pump speed may be increased between samples in order to reduce flush-out time.

The main disadvantage of using a peristaltic pump is that it may contribute to poor precision. To achieve the flow rate required it is best to use a narrow bore pump tube and fast rotation of the rollers. The narrow bore tubing reduces the size of the successive liquid pulses and the high pump speed is needed to obtain the required sample uptake.

The effect of two different tube sizes to achieve the desired flow of 0.5 ml min^{-1} is shown in Figure 3.3, where the ICP-MS response for

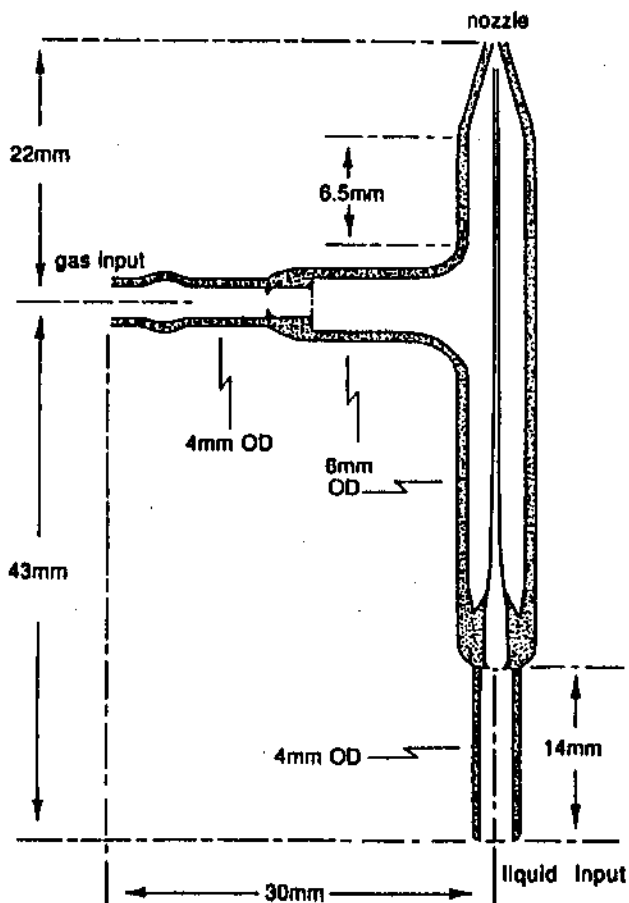


Figure 3.2 Meinhard concentric glass nebuliser. From Meinhard (1976).

100 ng ml^{-1} In was monitored at $115 m/z$. With the 1 mm tubing (Figure 3.3a) regular spikes in the analyte signal are produced at a frequency of about 1 Hz, corresponding to the pump roller period rate. A smaller bore tubing of 0.38 mm shows only a general noise level (Figure 3.3b) without the pulse and this is similar to that obtained if the nebuliser is allowed to aspirate freely (Figure 3.3c). An additional advantage of using fine bore tubing is that it reduces uptake and wash-out time. Pump tubing is normally made of PVC and linked to the nebuliser by a length of PTFE tubing. PVC tubing is suitable for most aqueous applications, but organic solvents require tubing made from much more expensive materials such as Viton.

The variation of analyte signal response as a result of pumping a Meinhard nebuliser at different flow rates can be seen in Figure 3.4. Signal increases linearly with uptake rate up to about 0.3 ml min^{-1} . Beyond this point response changes little and it will be seen that the free aspiration or natural uptake occurs midway along the plateau. As a consequence flow rates as low as 0.2 ml min^{-1} can be used, which is particularly useful if sample volumes are limited. Where very little sample is available, a recirculating system of the type described by Hulmston (1983) or Isoyama *et al.* (1990) may be used. Recirculating systems may enrich the sample and give memory effects. In

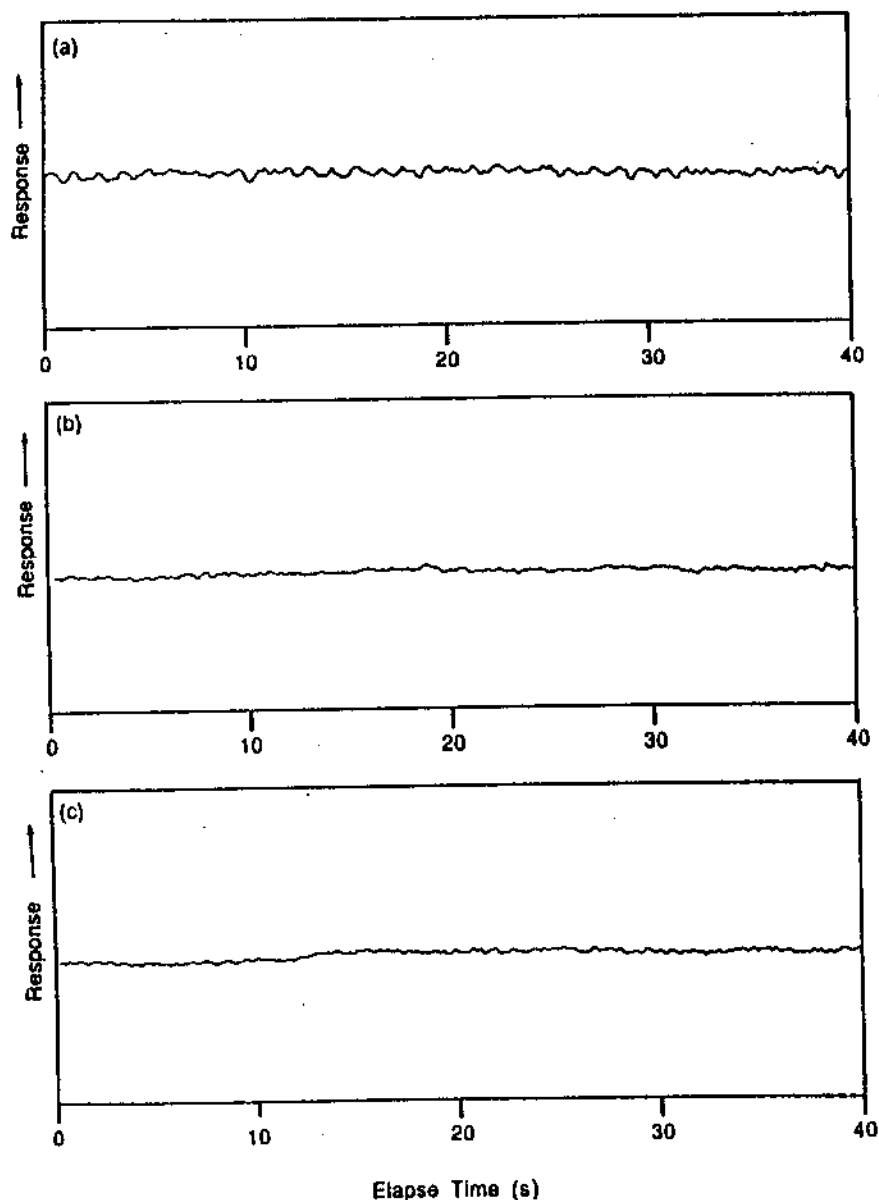


Figure 3.3 Comparison of short term signal stability with a Meinhard nebuliser for 100 ng ml^{-1} In solution, aspirated at 0.5 ml min^{-1} . Full scale deflection $25\,000 \text{ counts s}^{-1}$. (a) 1 mm i.d. tube pumped, (b) 0.38 mm i.d. pumped, (c) free running.

general they have been little used, but may be worth pursuing for isotope ratio measurements.

3.2.2.2 Blockage Nebuliser blockage may occur for two reasons. The first may be caused by suspended solids getting stuck in the narrow (about 0.3 mm diameter) central sample uptake capillary. This is likely in samples which contain significant amounts of suspended solids, but the risk can be minimised by filtering or centrifuging the sample. Nebuliser blockage may be prevented by using a fine uptake tube, similar in diameter to the nebuliser capillary, so that material collects in the tubing, which can be readily replaced. Blockages can be dealt with by a number of methods such as forcing liquid or gas back-

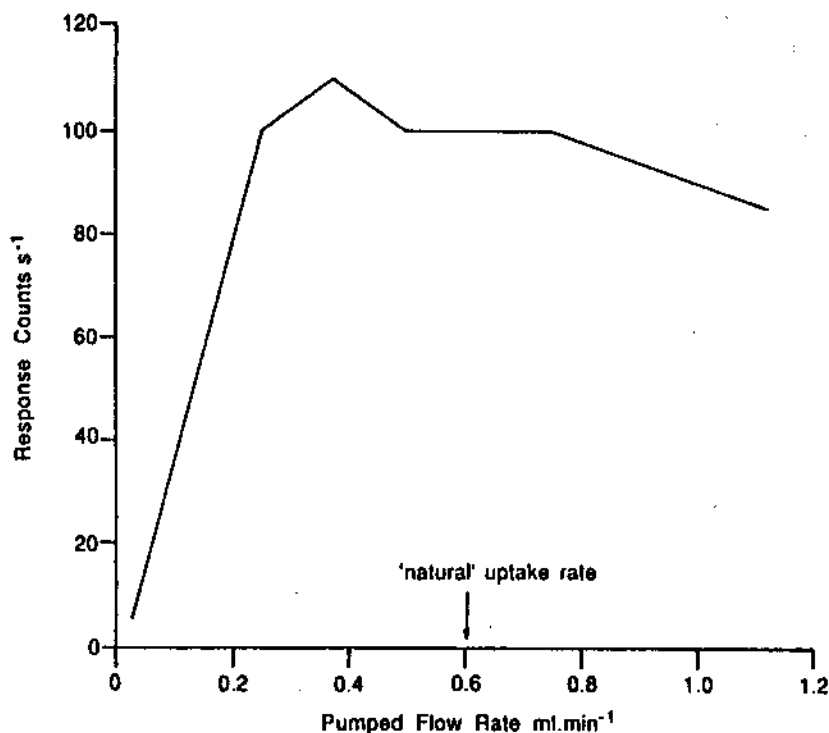


Figure 3.4 The effect of pumping a Meinhard nebuliser at increasing flow rate. The natural uptake rate of 0.6 ml min^{-1} does not exactly correspond to maximum response.

wards along the capillary (backflushing), chemical dissolution or mechanical treatment, where a fine wire is pushed down the capillary to dislodge the blockage. These techniques have to be used with extreme caution as it is very easy to inflict permanent damage on the device. Ultrasonic cleaning of the nebuliser must not be carried out as this will usually damage the glass capillary.

The second type of blockage is caused by dried solute from a sample of high dissolved solids content partly obstructing the orifices. This interferes with the operation of the nebuliser and may reduce the signal. This effect has been explained by Sharp (1989a). Some droplets fall back on to the face of the nebuliser adjacent to the gas annulus. If the deposited solution contains salt close to saturation, the cold dry gas from the nebuliser causes sufficient cooling and evaporation to initiate crystal formation along the gas annulus of the nebuliser. This eventually stops the nebulisation. However, before this point is reached, introduction of distilled water can gradually reverse the salting process, but once nebulisation has stopped, mechanical removal or washing of the nebuliser is required. A number of authors (Burman, 1981; Gustavsson, 1979; Walton and Goulter, 1985) have proposed wetting of the gas stream to reduce evaporation. This can be effective for ICP-AES, however, it could lead to problems in ICP-MS where high aerosol water content causes high levels of polyatomic ions (see section 3.3). Regular washing of the gas annulus can prevent salt deposits building up, but the most effective method is to use the high salt tolerance nebuliser (Baginski and Meinhard, 1984).

Blockage of the annular gas orifice can occur if dust particles or fibre particles get into the gas supply lines. This type of blockage is almost impossible to correct, so it is imperative that the gas lines are disturbed as little as possible.

3.2.3 Cross-flow nebulisers

Much of the general behaviour of concentric nebulisers is also shown by cross-flow designs. They are less prone to blockage and salting up, but these can still occur as the sample solution is pumped through a capillary. Early ICP-MS work used the cross flow, but the lack of a readily available commercial type led to manufacturers supplying concentric, and more recently, high solids nebulisers.

The operation of the cross-flow nebuliser is similar to that of a scent spray, where a horizontal jet of gas passes across the top of a vertical tube. The reduced pressure that is generated draws liquid up the tube where at the top, it is disrupted into a cloud of fine droplets. These devices are capable of 'free running' but may not be self-priming. For this reason, it is normal to use a peristaltic pump.

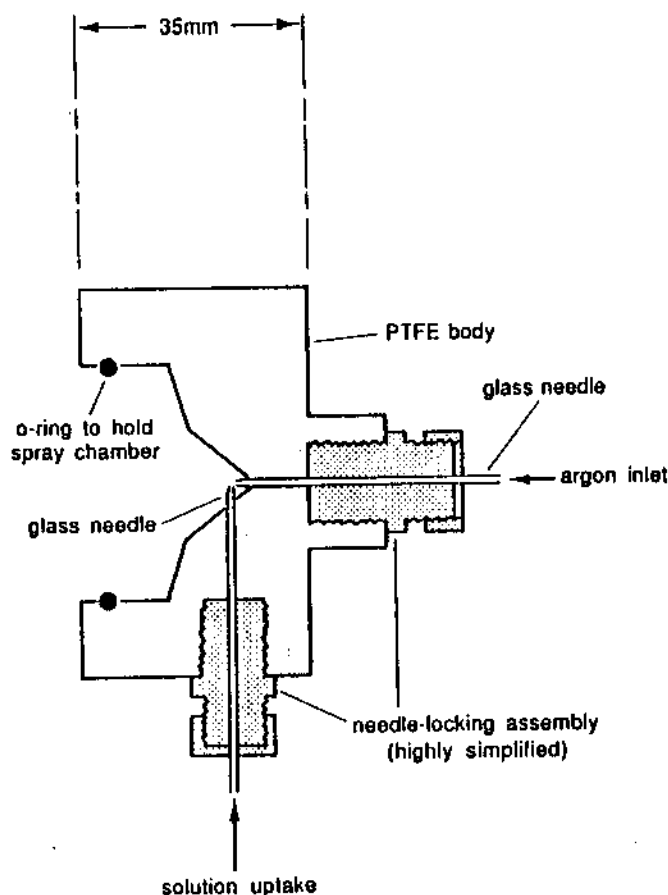


Figure 3.5 Simplified diagram of an adjustable, glass capillary cross flow nebuliser. From Kniseley *et al.* (1974).

Among the early models was the nebuliser designed by Kniseley *et al.* (1974), which had adjustable capillaries for both gas flow and sample uptake (Figure 3.5). These models were, however, prone to misalignment. Current models of cross-flow nebulisers have bodies constructed of Ryton or polypropylene and fixed capillaries of glass or sapphire. A 'fixed geometry' cross-flow nebuliser made of a hard, dense plastic material such as Ryton, with sapphire capillaries, is useful for introducing corrosive liquids that would damage an all glass nebuliser. During the later stages of development of ICP-MS in the United Kingdom, Gray and Date (1983) used a fixed geometry cross-flow nebuliser manufactured by the Jarrel-Ash Company (now Thermo-Electron). This type of cross-flow nebuliser has been in use in the authors' laboratory for a number of years in preference to a Meinhard nebuliser, because of the rugged construction and relative ease with which they can be cleaned. It is a very satisfactory alternative to concentric design. If blocked it can be cleaned by pushing a fine wire down the liquid capillary, or forcing the gas flow up the liquid capillary by blocking the exit face of the nebuliser. Fixed cross-flow nebulisers are not damaged if cleaned in an ultrasonic bath.

Gray and Williams (1987b) and Williams (1989) found that the performance of the ICP-MS instrument was very similar when using either a cross-flow or Meinhard nebuliser. Other types of cross-flow nebuliser are available such as the MAK (Anderson *et al.*, 1981). These, however, have not found widespread use.

3.2.4 Babington type nebuliser

The original device developed by Babington (1973) allowed a film of water to flow over the surface of a sphere. Gas forced through an aperture beneath the film produced an aerosol. The essential feature of this type of nebuliser is that liquid flows freely over a small aperture, rather than passing through a fine capillary and thus has a great tolerance to high dissolved solids. Since the delivery of the sample is not constrained by a capillary, slurries can be nebulised (Williams *et al.*, 1987; Ebdon *et al.*, 1988). They are not self-priming or self-aspirating and therefore must be pumped.

The original Babington nebuliser design showed extensive memory effects as the solution was allowed to wet the entire face of a sphere. Suddendorf and Boyer (1978) proposed constraining the liquid in a V-groove and introducing gas from a small hole in the bottom of the groove (Figure 3.6). This made a significant improvement to memory effects, although Babington type nebulisers do still have worse memory effects when compared to concentric or cross-flow designs. There are now a number of similar systems available, however, the two most commonly used in ICP-MS are probably the V-groove nebuliser produced by Van der Plas products (Ripson and de Galan, 1981) and the Ebdon nebuliser (Ebdon and Cave, 1982).

The main advantage of the V-groove nebuliser is its resistance to blockage.

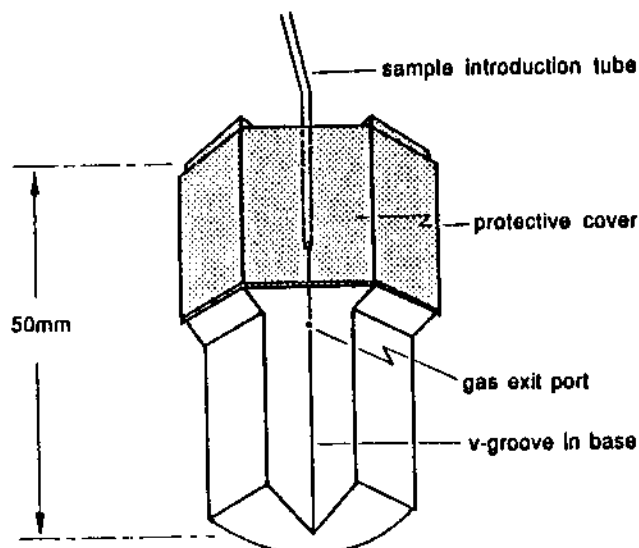


Figure 3.6 Suddendorf and Boyers' (1978) Babington type nebuliser.

However, it is not an optimum geometry for aerosol generation, which is evident from the coarser particle size distribution and lower efficiency (Sharp, 1988a). These disadvantages are not necessarily translated into a degradation of analytical performance, since the spray chamber (section 3.3) is the principal determinant of particle size reaching the plasma. If necessary an increased supply of liquid can be used to overcome inefficiency in nebuliser performance.

3.2.5 Frit type nebuliser

Concentric and cross-flow nebulisers only produce about 1% of droplets of the correct size to conduct to the plasma. This source of inefficiency has attracted some attention. An alternative design is the frit nebuliser (Layman and Lichte, 1982) which produces droplets of mean size $1\ \mu\text{m}$. The design is essentially the same as the Babington types, but with a fine glass frit matrix in place of a V-groove. The V-groove device optimises resistance to blockage at the expense of gas-liquid mixing efficiency (particle size distribution), whereas the frit provides excellent gas-liquid mixing but at the expense of poor sample handling characteristics, i.e. the nebuliser is prone to clogging and salting up and exhibits poor clean out characteristics.

A variation on the frit type nebuliser is the Hildebrand grid nebuliser (Figure 3.7) which uses a fine mesh grid positioned in front of the gas stream. Sample flows over the grid and nebulisation takes place from the wetted surface. Brotherton *et al.* (1989) used this nebuliser for analysis of high matrix solutions with ICP-MS and compared the performance of the nebuliser to that of a Meinhard. They concluded that the limiting factor in introducing salt solutions was not the grid nebuliser itself, but the ICP-MS interface, which begins to block up with the introduction of high salt solutions.

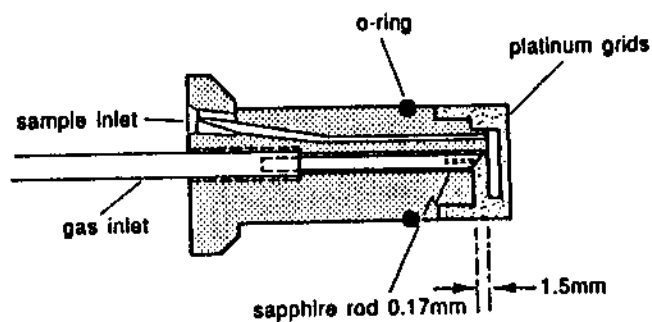


Figure 3.7 Simplified diagram of Hildebrand grid nebuliser. Front platinum grid is 100 mesh \times 0.061 mm thickness. Rear grid is of the same mesh size and 1.5 mm thickness. After Brotherton *et al.* (1989).

3.2.6 Ultrasonic nebuliser (USN)

This method of aerosol generation was used in the development of both ICP-AES (Wendt and Fassel, 1965) and ICP-MS (Houk *et al.*, 1980). Solution is fed to the surface of a piezoelectric transducer operated at a frequency of between 0.2 and 10 MHz. The longitudinal wave, which is propagated at right angles to the surface of the transducer towards the liquid-air interface, produces pressure that breaks the surface into an aerosol. There is a very high efficiency of production with this type of device, which is independent of gas flow. Thus more analyte can be transported to the ICP at a slower nebuliser gas flow rate than that used with pneumatic nebulisers. This potentially gives a considerable increase in sensitivity, and improvement of detection limits, since the analytes have a longer residence time in the plasma. However, the increased efficiency does allow a greater quantity of water to enter the plasma, producing a cooling effect, which is counter-productive for analyte ionisation. For ICP-MS it is essential that the aerosol is desolvated since high solvent loadings lead to high levels of interference ions (see section 3.3). This is normally achieved using a heated tube to evaporate the water droplets and a condenser to remove the resulting water vapour. The remaining solute particles then enter the plasma.

For simple aqueous matrices, detection limits with USNs are usually an order of magnitude better than with pneumatic devices. Tingfa *et al.* (1990) compared the multi-element detection limits for ICP-MS using a USN with those of a pneumatic nebuliser, and showed an improvement factor of between 8 and 200, depending on the element. In samples with a complex matrix, the background signal from the matrix also grows and leads to increased levels of spectral and non-spectral interferences. They generally have the longest wash-out times of most nebuliser types.

Apart from the analytical limitations of the USN, the high cost of commercial systems is prohibitive for most laboratories (approximately £10 000) as USNs require a separate RF source. In addition, the devices tend to be unreliable due to their complexity. Despite these drawbacks, one

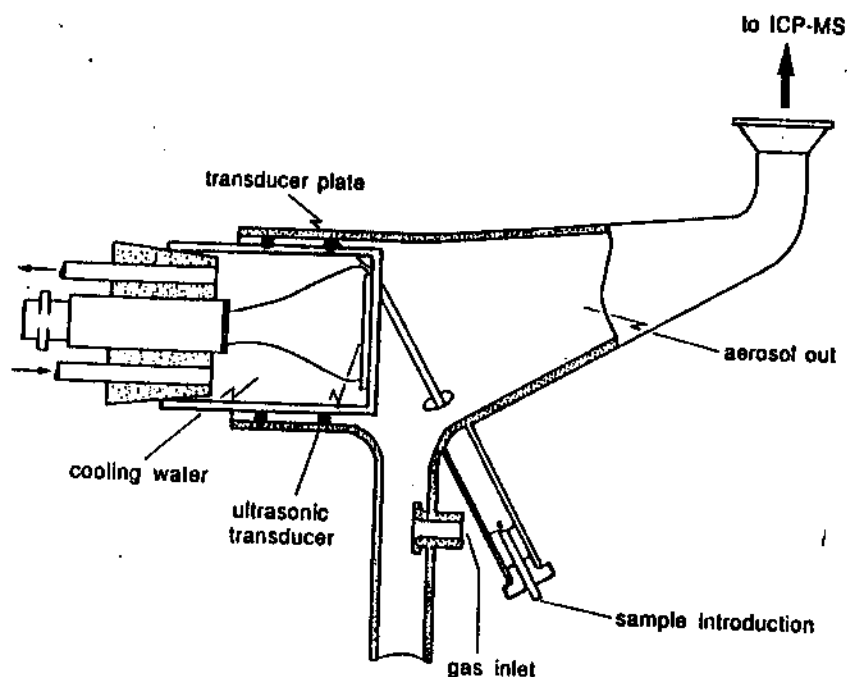


Figure 3.8 Schematic diagram of a continuous-flow ultrasonic nebuliser. After Fassel and Bear (1986).

research group at Ames laboratory uses a USN (Figure 3.8) developed by Fassel and Bear (1986) for much of their ICP-MS investigations (Jiang *et al.*, 1987; Jiang and Houk, 1988; Jiang *et al.*, 1988).

3.3 Spray chambers

3.3.1 Principles

Aerosol transport efficiency is defined as the percentage of the mass of nebulised solution that actually reaches the plasma. For this percentage to be high and for rapid desolvation, volatilisation and atomisation of the aerosol droplets when they reach the plasma, a nebuliser must produce droplets of $< 10 \mu\text{m}$. However, pneumatic nebulisers produce aerosols with a broad distribution of droplet diameters up to $100 \mu\text{m}$. The primary task of the spray chamber is to remove large droplets (i.e. $> 10 \mu\text{m}$) from the gas stream and deliver them to waste. As the gas flow carrying the aerosol enters the spray chamber, it undergoes sharp changes in direction which the larger droplets cannot follow. These droplets strike the walls and subsequently run to waste. The spray chamber ensures that only droplets small enough to remain in suspension in the gas flow are carried into the plasma. With most pneumatic nebulisers this means a loss of about 99% of the sample solution. Readers interested in the theory and dynamics of spray chambers are directed to the excellent review on the subject by Sharp (1988b).

3.3.2 Operation

The search for an ideal spray chamber has led to a variety of designs being proposed and evaluated. The most common formats are those employing flow reversal cyclonic action and impact beads. Droplets leaving the 'ideal' spray chamber should be $< 10\mu\text{m}$ in diameter and have a small size distribution. They should also have a high analyte mass flux and transport efficiency, a low wash-out time and good pressure-temperature stability. These quantities are dependent on the sample and gas flow rates. Some of these criteria are met by the double pass (flow reversal) system (Figure 3.9) developed by Scott *et al.* (1974). Various versions of this basic design are widely used in ICP-MS instruments. A number of alternative spray chamber designs (cyclonic or impact bead) are available and used in ICP-AES, but their use on ICP-MS instruments has been limited. Spray chambers may be constructed of glass, polyethylene, PTFE or Ryton. Allenby (1987) described the use of a PTFE spray chamber on an ICP-MS instrument, used to determine trace elements in uranic materials which had been dissolved in hydrofluoric acid. Solutions containing up to 2% of fluoride were aspirated into the chamber with no deleterious effects to the spray chamber. Commercially produced inert spray chambers are widely available for analysis of solutions which are corrosive to glass.

Removal of waste solution has to be carried out in a way that retains a small positive pressure in the spray chamber to drive the aerosol through the injector tube. This can be achieved simply by dipping the drain tube into the waste container, however, the pressure will change slightly as the container fills with this arrangement. Drains should be designed so that the liquid runs away smoothly through devices such as fritted glass discs or capillaries. Liquid build-up in the chamber must be avoided, as this causes pressure changes resulting in signal drift and leads to extended memory effects. Pumping away

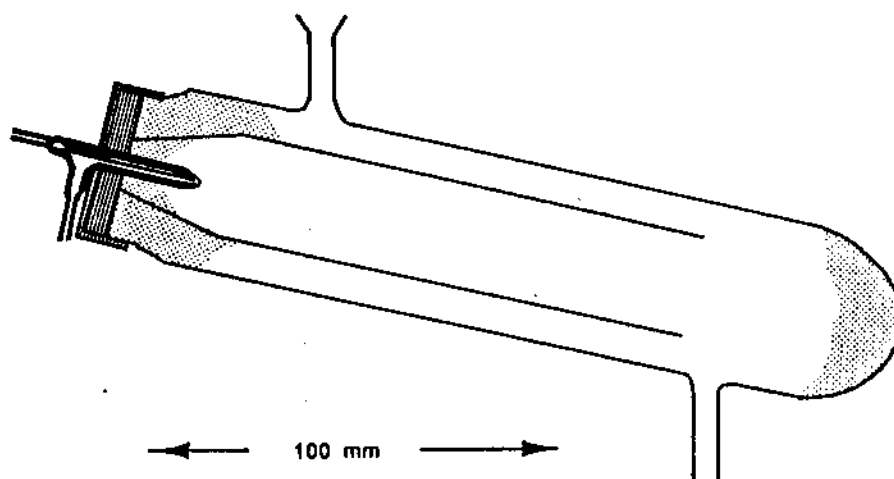


Figure 3.9 Double pass spray chamber as described by Scott *et al.* (1974). The shaded area is dead volume where aerosol remains after the sample solution has been removed. Excessive dead volume can lead to increased wash-out times.

waste solution is a convenient method, particularly if a second channel is available on the pump used to supply the nebuliser.

The wide dynamic response, high throughput of samples and excellent sensitivity of ICP-MS are of little value if the sample introduction system is subject to memory effects. The time taken for sample wash-out between samples may have a major influence on the total time required for analysis, particularly in some isotope ratio determinations. Certain elements are very troublesome, particularly those which are volatile, such as Br and Hg. These are retained on the glassware, particularly on the injector tip of the torch, for a long period of time, even if they are introduced at low levels (10 ng ml^{-1}). Most elements, however, do not present such a problem and typical clean out times are between about 60 and 180 s.

Different designs of nebuliser can critically affect wash-out time. A comparison of wash-out times for a Meinhard and a de Galan nebuliser under the same operating conditions is shown in Figure 3.10. The response for $100 \text{ ng ml}^{-1} \text{ In}$ in $1\% \text{ HNO}_3$ was monitored using the $115 m/z$ setting. The sensitivity was about $1.5 \times 10^6 \text{ counts s}^{-1} \text{ per } \mu\text{g ml}^{-1}$. After a steady signal rate was obtained, the uptake tube was placed in a washing solution of $2\% \text{ HNO}_3$. With the Meinhard nebuliser the signal decayed to about 1% of the original rate after about 8 s, 0.1% in 35 s and has returned to background levels in about 1 min (Figure 3.10a). The wash-out time for the de Galan V-groove is much longer than that of the Meinhard (Figure 3.10b) of the order of 165 s to reach 1% of the original signal. This is probably because

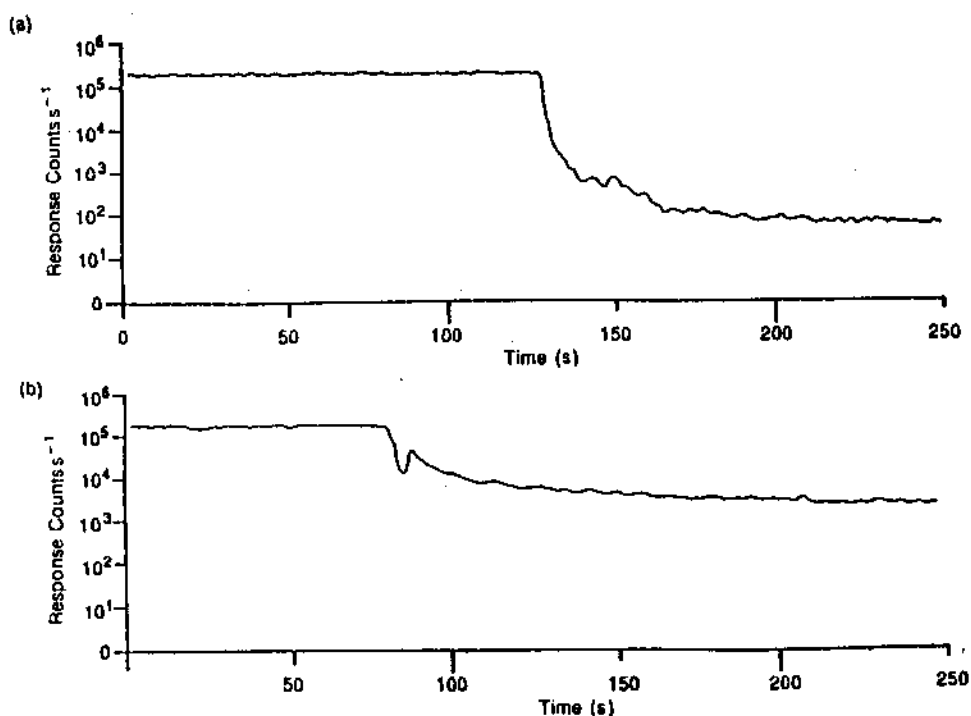


Figure 3.10 A comparison of wash-out characteristics for $100 \text{ ng ml}^{-1} \text{ In}$ for (a) Meinhard nebuliser and (b) de Galan V-groove nebuliser.

liquid is retained on the face of the nebuliser and drawn back into the groove. If high throughput is likely for an instrument, the wash-out characteristics must therefore be a major consideration during instrument operation and appropriate measure taken to assess wash-out times for individual elements. During an analysis run, it is advisable to monitor wash-out by choosing one of the elements in a suite under investigation, selecting the appropriate mass, and monitoring the signal decay until a suitable background level is achieved. This will depend on the level of the element(s) under investigation. The time period for the required signal decay to occur can then be used as a pre-set wash-out time. This is particularly important if an auto-sampler is to be used and time delays have to be programmed into the system to allow for wash-out. Increasing the pump speed to maximum between samples will not improve wash-out times of the spray chamber, but will reduce the time taken for washing solution or for the next sample to reach the nebuliser.

3.3.3 *Thermally stabilised spray chambers for ICP-MS*

During the early development of ICP-MS, water was identified as a major source of ions for the formation of polyatomic species. The advantages of carrying out analysis in the absence of water, with techniques such as laser ablation (Gray, 1985b), electrothermal vaporisation (Whittaker *et al.*, 1989) or arc nebulisation (Jiang and Houk, 1986) have been reported. Gray (1986a) calculated the population levels of H^+ , O^+ and Ar^+ in the plasma from the Saha equation along with those ions which are derived from common mineral acids such as N^+ , S^+ , Cl^+ and C^+ . Because of the high levels of these ions in the plasma it was suggested that only very low significant levels of polyatomic ions can be formed. Reducing the amount of water or solvent introduced into the plasma should reduce the levels of polyatomic ions. Stabilising the delivery of water vapour into the plasma should lead to a more reproducible signal for polyatomic ions. In addition, Gray *et al.* (1987) and Hutton and Eaton (1987) showed that ion energies may also be dependent on water loading of the plasma. For ICP-MS it is important that these remain stable, and at a low level, as they can critically affect instrument performance.

The variation of the $^{40}Ar^{16}O^+$ response with time and spray chamber temperature, using a pneumatic nebuliser is shown in Figure 3.11. Figure 3.12 shows the total amount of water from both vapour and aerosol entering the plasma at different temperatures assuming a 1% sample transport efficiency. For an instrument operating with the spray chamber temperature at $> 25^\circ C$, more water enters the plasma as vapour, than in the form of aerosol. Cooling the spray chamber causes much of the vapour to condense on the walls, significantly reducing the water input to the plasma. At about $10^\circ C$ the levels of both oxygen related (e.g. ArO^+) and other (e.g. $ArAr^+$) polyatomic ions are greatly reduced (Hutton and Eaton, 1987; Williams, 1989). In addition refractory oxide ions, doubly charged ions, energies and any corrosion

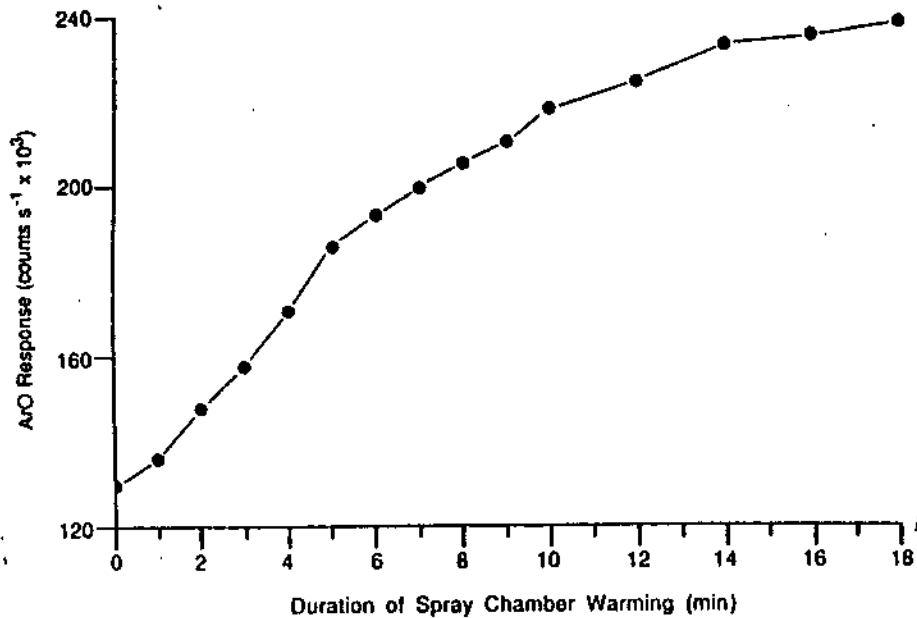


Figure 3.11 Variation of $^{40}\text{Ar } ^{16}\text{O}^+$ response with time and spray chamber temperature (spray chamber at 25°C at 0 min and 35°C after 18 min). From Williams (1989).

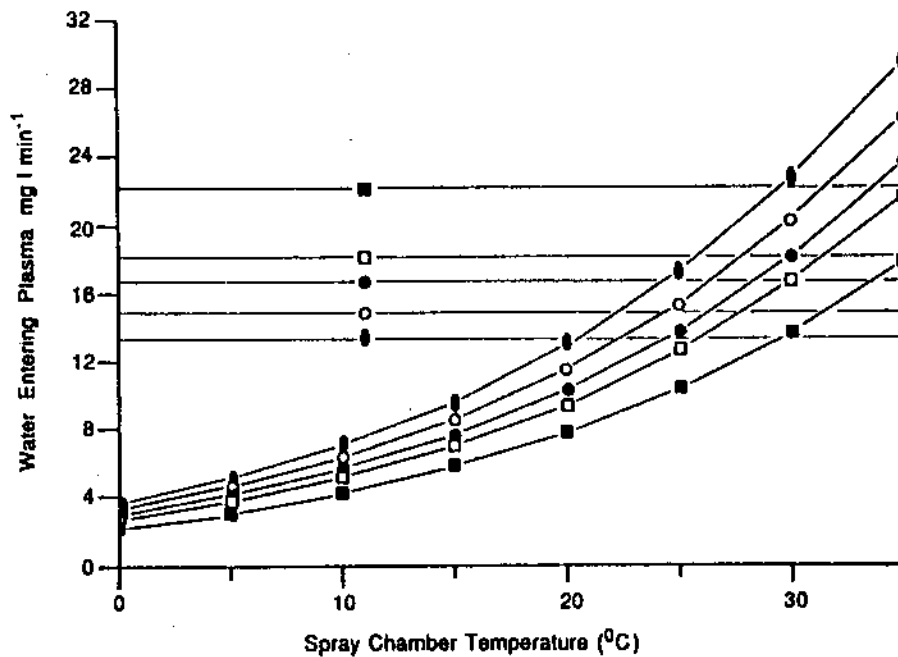


Figure 3.12 The mass of water entering the plasma is shown for five carrier gas flows. Horizontal lines represent aerosol component (assumed at 1% with no temperature effect) and curves represent vapour component. ■, 0.451 min^{-1} ; □, 0.551 min^{-1} ; ●, 0.61 min^{-1} ; ○, 0.671 min^{-1} ; ◐, 0.751 min^{-1} . After Williams (1989).

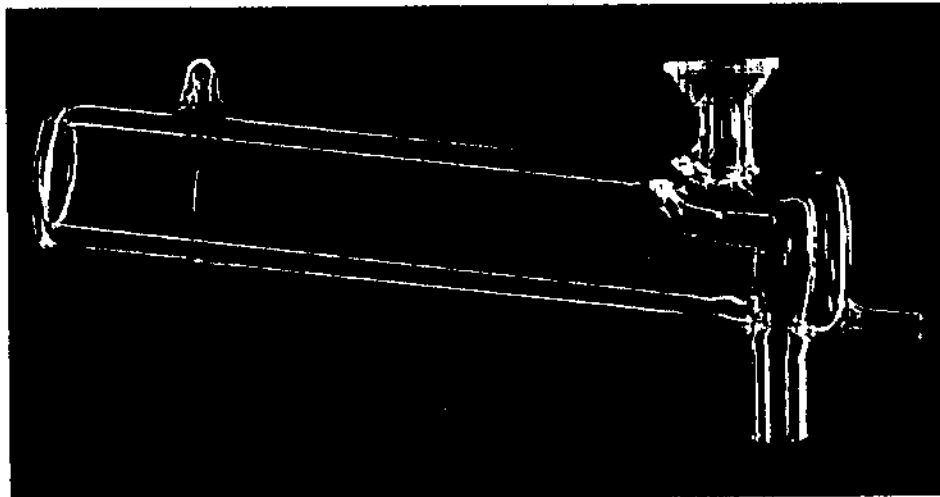


Figure 3.13 Surrey design water cooled single pass spray chamber. From Williams (1989).

products from sampling and skimmer cones are all reduced and maintained at a constant level.

The Scott double pass spray chamber is the type most commonly used with ICP-MS and ICP-AES instruments. A water jacketed version of this design is available and fitted to most ICP-MS systems. The only chamber designed specifically for an ICP-MS instrument has been described by Williams (1989) and is shown in Figure 3.13. This is a single pass type 125 mm long with a volume of some 60 ml. A single pass design has fewer internal surfaces and less dead space exposed to sample solution which reduces memory and wash-out times. A small baffle is placed directly below the outlet to prevent any large droplets accumulating at the outlet. A dripline path from the baffle to the waste outlet prevents pulsing from excess solution running to waste. A large aerosol outlet (10 mm) was found to avoid obstruction by condensation after a period of time. Wash-out times on Co for this spray chamber, using a Meinhard nebuliser, are < 10 s for the signal to decay to 1%, < 35 s to 0.1% signal decay and about 1 min to background.

The on-line effect of cooling the spray chamber from 35 to 11°C is shown in Figure 3.14. Here the level of $^{40}\text{Ar}^{16}\text{O}^+$ is reduced by more than a factor of 2, where ordinary tap water was used for cooling. In addition the levels of most other polyatomic species are reduced. A comparison of some oxygen based species found when introducing 1% solutions of nitric and hydrochloric acid is shown in Table 3.1. Concentrations are calculated relative to $10 \text{ ng ml}^{-1} \text{ Co}^+$. Depending on the species, the interferences were reduced by between 10% and 60%.

Thermally stabilised spray chambers are essential where organic solvents are used. The higher vapour pressure produces increased solvent loading in the ICP resulting in plasma instability. Temperature fluctuations in the spray chamber may have a significant effect on signal stability. Only small

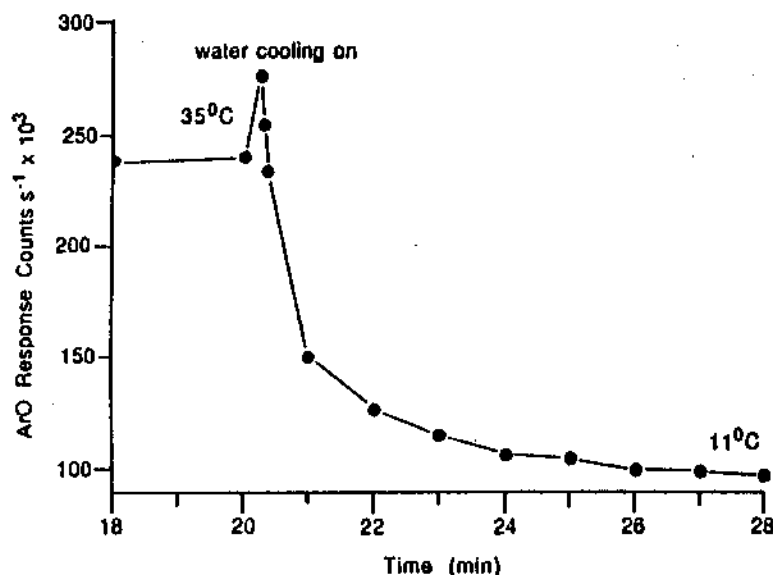


Figure 3.14 Variation of $^{40}\text{Ar } ^{16}\text{O}^+$ response with decreasing spray chamber temperature over a period of 10 min. The temperature was initially stabilised at 35°C before cooling to 11°C . From Williams (1989).

Table 3.1 Effect of cooling spray chamber temperature on oxygen containing polyatomic ion peaks*

Mass (m/z)	1% HNO_3		1% HCl	
	Uncooled	Cooled	Uncooled	Cooled
31	20.0	9.78	19.7	9.44
32	8030	2560	8270	2630
48	1.40	0.64	2.18	1.17
49	0.08	0.08	1.42	1.86
50	0.21	0.12	0.36	0.21
51	0.17	0.13	19.9	12.7
52	0.90	0.49	2.23	1.11
53	0.22	0.08	7.00	4.63
56	64.4	16.9	61.6	14.8
64	1.60	0.51	1.82	0.49
65	1.70	1.30	1.84	1.88
66	0.25	0.17	0.23	0.12
67	0.27	0.08	0.39	0.07
69	0.49	0.14	0.49	0.15

* Values are expressed as equivalent concentrations (ng ml^{-1}), referenced to 10 ng ml^{-1} Co. From Williams (1989).

temperature changes can drastically alter organic solvent loading of the carrier gas (Hutton, 1986). Operation of the chamber at $< 0^\circ\text{C}$ for the analysis of samples in volatile organic solvent such as white spirit, xylene, ethanol, acetone or chloroform is often necessary. To prevent freezing of recirculated cooling water, anti-freeze should be added. Maintaining temperatures of

<0°C when introducing aqueous solvents is inadvisable, as it may cause the aerosol and waste to freeze in the spray chamber and block it. /

3.4 Torches

3.4.1 Construction

Torches should be constructed to a high degree of accuracy using good quality quartz, an important feature for the stability and formation of the plasma. The injector tube diameter is generally about 1.5 mm. Narrower bore tubes are rarely used as they block easily, an important consideration when solutions containing high dissolved solids are to be analysed. They do, however, offer better plasma penetration. For high dissolved solids or slurry analysis, wider bore injectors (typically 3.0 mm) are often used, with little degradation in instrument performance.

There are various types of injector tube in use (see Thompson and Walsh, 1989) including tapered injector tip, capillary injector tip and complete capillary injector tip. Individual suppliers tend to favour a particular design for production reasons, unless a specific design is requested. The capillary tip injector is probably most commonly used, where the final 25 mm (approximately) of 3–4 mm diameter tube are at a diameter of 1.5 mm. A tapered injector tip tends to degrade in performance as the tip devitrifies and silica is lost.

3.4.2 Demountable torches

The plasma torch does not have to be of fixed configuration. It can be obtained partly demountable (i.e. with a removable injector tube) or fully demountable. Integral torches generally have better long term consistency although when they do finally degrade, replacement of the coolant tube has to be carried out by a glass blower. Replacement of injectors is generally not possible.

Fully demountable torches provide an easier (and cheaper) means of replacing devitrified parts, although they can be difficult to reconstruct. Partly demountable torches offer a good compromise and are used routinely on this author's ICP-MS instruments. This arrangement allows a range of injector diameters to be used (i.e. 1.5 mm for solution analysis and 3.0 mm for high dissolved solids and slurries), without the need to remove the torch from its assembly. In addition, materials other than quartz can be used for the injector tube. A particularly useful alternative is an alumina injector which allows HF solutions to be analysed.

Apart from overcoming the problems of injector blockage, when high dissolved solids or slurries are analysed, it has been found that a wider bore

injector (e.g. 3.0 mm) allows high dissolved solids solutions to be nebulised for longer periods of time before cone blockage occurs, compared with a standard 1.5 mm injector (Williams and Gray, 1988).

3.4.3 Alignment

The torch is normally mounted horizontally with the centre of the injector aligned on the axis with the sampling cone aperture. The final 25 mm of the coolant tube should be inside the load coil, such that the distance between the turn of the coil edge furthest from the sampling cone is 3–5 mm distant from the edge of the auxiliary tube. This positions the plasma correctly in the torch. The distance between the torch and sampling cone is usually between 10 and 15 mm as measured from the edge of the first turn of the load coil to the tip of the sampling cone. This static alignment method is generally satisfactory, however, a dynamic alignment method, such as the one described in chapter 2, is preferable.

3.4.4 Specialised torches

3.4.4.1 Torches for hazardous gases The trace element content of gases used in the micro-electronic industry has to be accurately determined to very low levels, as impurities can adversely affect the properties of the final products. These gases are extremely hazardous and specialised handling techniques must be employed with them. Some, such as trimethyl gallium, trimethyl aluminium, dimethyl zinc and silane are pyrophoric, i.e. they will spontaneously combust in air.

To allow these dangerous gases to be introduced into the ICP a special four gas inlet torch has been designed (Streusand *et al.*, 1990) which allows the addition of water *in situ* to hydrolyse the gas safely. In addition calibration standards can be added to the gas via the water.

3.4.4.2 Low flow torch Gordon *et al.* (1988) carried out a preliminary investigation of a torch externally cooled by water, which allowed coolant gas flows of only 2–3 l min⁻¹ to be used. Reasonable performance was found to be achievable, however, interference species (oxides, doubly charged etc.) were significantly higher.

A torch with a 9 mm diameter coolant gas tube has been characterised by Ross *et al.* (1990). An analytically useful plasma was supported by 850 W forward power (40.68 MHz RF frequency) and 8.7 l min⁻¹ total argon flow rate. Although the 9 mm source produced similar sensitivities, detection limits, doubly charged ion ratios and oxide ion ratios to a conventional plasma, the plasma sampling depth and sampling position had to be adjusted individually for each element in order to obtain maximum sensitivity.

3.4.4.3 Mixed gas and sheath gas torches A few workers have reported that the presence of a second gas in the Ar flow changes the fundamental properties of the plasma (Murillo and Mermet, 1989; Evans and Ebdon, 1989). The addition of a few percent of hydrogen as a sheath around the injector gas flow enhances the ionisation process in ICP-AES (Murillo and Mermet, 1989), and is attributed to the higher thermal conductivity of this diatomic gas. This leads to a more efficient transfer of energy with the plasma, resulting in improved desolvation, volatilisation and dissociation processes.

The use of mixed gas plasma, produced by adding a sheathing gas around the nebuliser gas, has been considered by Beauchemin and Craig (1990). Modifications were not made directly to the torch. To introduce the gas (H_2 or N_2) a sheathing device is inserted between the spray chamber and injector as shown in Figure 3.15. The addition of either gas reduced sensitivity but improved stability, resulting in generally improved detection limits. In addition, mass bias was decreased when mixed gases were used and lower nebuliser gas flow could be used. This final point shows potential for coupling a gas chromatograph to an ICP-MS instrument. The use of sheathing gases is not widespread at the moment as performance improvements are marginal, optimisation is complex and expensive extra gas flow control equipment is required.

A sheathing gas of argon was used by Lichte *et al.* (1987) in a specially designed four gas inlet torch. This allowed adjustment of the sample injection velocity into the plasma without affecting the performance of the nebuliser or the rate of total sample delivery. In addition this torch was water cooled to improve its lifetime.

To determine trace elements in organic based solution it is necessary to add a small amount of oxygen to the nebuliser gas flow to prevent the condensation of particulate carbon on the sampling cone orifice. Hausler (1987) analysed xylene solutions of organically bound metals using an addition of 2% oxygen to the argon flow, introduced between the spray chamber and injector. Hutton (1986) introduced 5–7% oxygen to the nebuliser

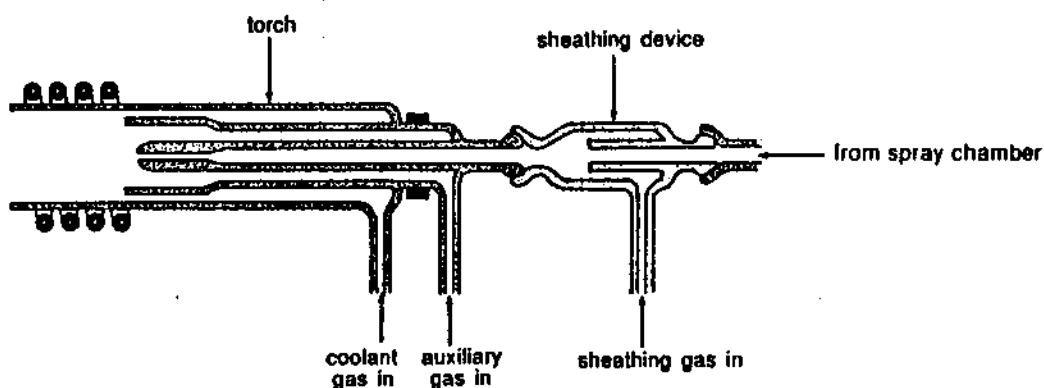


Figure 3.15 Schematic of the glassware arrangement used for the addition of a sheathing gas. After Beauchemin and Craig (1990).