Liquid-sample introduction in plasma spectrometry

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Plasma-spectrometry techniques, namely inductively coupled plasma atomic emission spectrometry (ICP-AES) and plasma-based mass spectrometry (MS), are the most commonly used in analytical laboratories for elemental analysis in a wide variety of samples. In these techniques, the quality of the analysis strongly depends on appropriate selection of the sample-introduction system. For liquid samples, it basically comprises a nebulizer, which transforms the bulk solution into an aerosol, and a spray chamber, which modifies the characteristics of this aerosol and transports it to the plasma base through an injector tube. Sometimes, a desolvation system is incorporated to reduce the solvent load into the plasma. This article describes the different components of the sample-introduction system, emphasizing their main advantages and drawbacks. A review of the processes that affect the aerosol between generation and reaching the plasma is also included.

Keywords: Desolvation system; Inductively coupled plasma atomic emission spectrometry (ICP-AES); Inductively coupled plasma mass spectrometry (ICP-MS); Nebulizer; Spray chamber

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1. Introduction

Plasma-spectrometry techniques, namely inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS), are widely used in the analytical laboratories, mainly because of their low limits of detection (LOD), high sensitivity, precision and analytical throughput. In these techniques, the analytical response depends directly on the number of analyte atoms present in the plasma and, therefore, on the analyte concentration in the sample. In ICP-AES, the radiation generated is finally measured using an appropriate detection system. In ICP-MS, analyte ions are extracted from the plasma and then directly registered.

The main goal of a sample-introduction system is to introduce the maximum amount of analyte into the plasma in the most suitable form. A great variety of devices have been designed so far to introduce liquid, gas and solid samples into the plasma [1–4]. The appropriate selection of the sample-introduction system is a critical step when particular analytical figures of merit are required. Moreover, some kinds of interference can be minimized or even eliminated by a judicious selection of the sample-introduction system [5,6].

2. Description of the liquid sample-introduction system

Usually, the sample is supplied as a liquid solution because of its homogeneity, ease of handling and the possibility of preparing calibration standards. In this case, the main components of the sample-introduction system are (Fig. 1):

(i) a nebulizer, which spreads out the liquid bulk generating an aerosol;
(ii) a spray chamber, which filters the aerosol and transports it to the plasma;
(iii) a desolvation system to reduce the mass of solvent reaching the plasma; and,
(iv) an injector tube to introduce the aerosol into the plasma base.

2.1. Nebulizers

The aerosol-generation process (i.e., nebulization) requires the supply of energy to a liquid bulk by means of a nebulizer [7]. The characteristics of the aerosols are greatly dependent on the amount of available energy and on the efficiency of the energy transfer. Usually, nebulizers have been classified on the basis of the type of energy employed. Thus, aerosols can be originated:

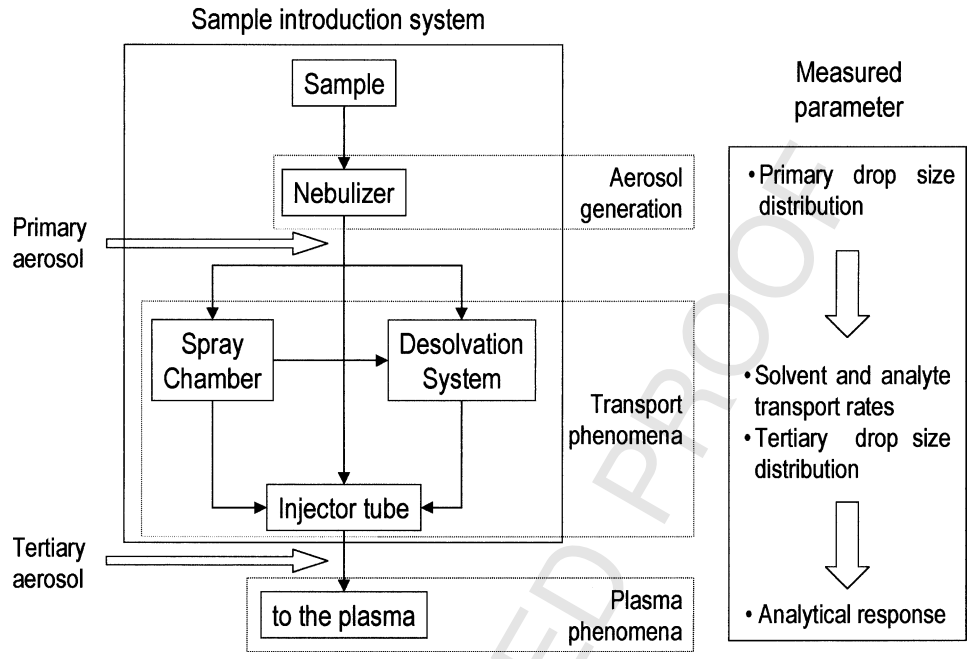

Figure 1. Scheme of the sample-introduction system in plasma spectrometry.

(i) by the kinetic energy of a high-velocity gas stream (pneumatic nebulizers) or of the liquid itself (hydraulic nebulizers);
(ii) as the result of mechanical energy applied externally through a rotating (rotating nebulizers) or vibrating device (ultrasonic nebulizers); or,
(iii) as a result of the mutual repulsion of charges accumulated on the surface (electrostatic nebulizers).

2.1.1. Pneumatic concentric nebulizers. This is the most common method for aerosol generation. Attending to the geometry of the interaction between the gas and liquid streams, pneumatic nebulizers can be classified in two main groups:

(i) pneumatic concentric nebulizers (PCNs), for which the interaction takes place concentrically; and,
(ii) cross-flow nebulizers (CFNs), for which the liquid-gas interaction occurs perpendicularly.

Fig. 2 shows the scheme of some of these nebulizers. PCNs (Fig. 2a) are widely used because of their simplicity, robustness, ease of use and low cost. Nevertheless, they have some drawbacks, especially their low transport efficiency (typically about 2% in ICP-AES) and their tendency to get clogged when using high salt-content solutions.

To overcome this drawback, different nebulizer designs have been developed. Most of them are of the cross-flow type (based either on the Babington principle, such as the V-groove (VGN), the cone-spray, the Hildebrand grid nebulizers, etc.) or based on modifications of the conventional PCNs [8].

In PCNs, the interaction between liquid and gas streams can be improved by reducing the cross-sectional area of the gas and/or liquid outlet and/or the width of the liquid-conduction walls. Nevertheless, a lower gas cross-section implies a higher gas pressure to keep the same gas flow. In line with these considerations, a new pneumatic nebulizer, which works at high gas and liquid pressures, the so-called single-bore high-pressure pneumatic nebulizer (SBHPPN) (Fig. 2d), has been developed [9].

In recent years, much effort has been devoted to the development of new, more efficient aerosol-generation systems. Of these so-called high-efficient nebulizers, the thermal, hydraulic and ultrasonic are the most used. In general terms, the analytical performance of the high-efficient nebulizers is superior to that of the conventional pneumatic ones [10]. However, these nebulizers also suffer from some drawbacks: (i) they are more expensive;

(i) they are more difficult to use; and,
(ii) some of them require a desolvation unit to avoid the negative effects of an excessive solvent load to the plasma.

2.1.2. Thermal nebulizers. The so-called thermospray, or thermal nebulizer (TN), comprises a narrow-bore stainless-steel tube, electrically heated to just above the boiling point of the solvent. This nebulizer can be

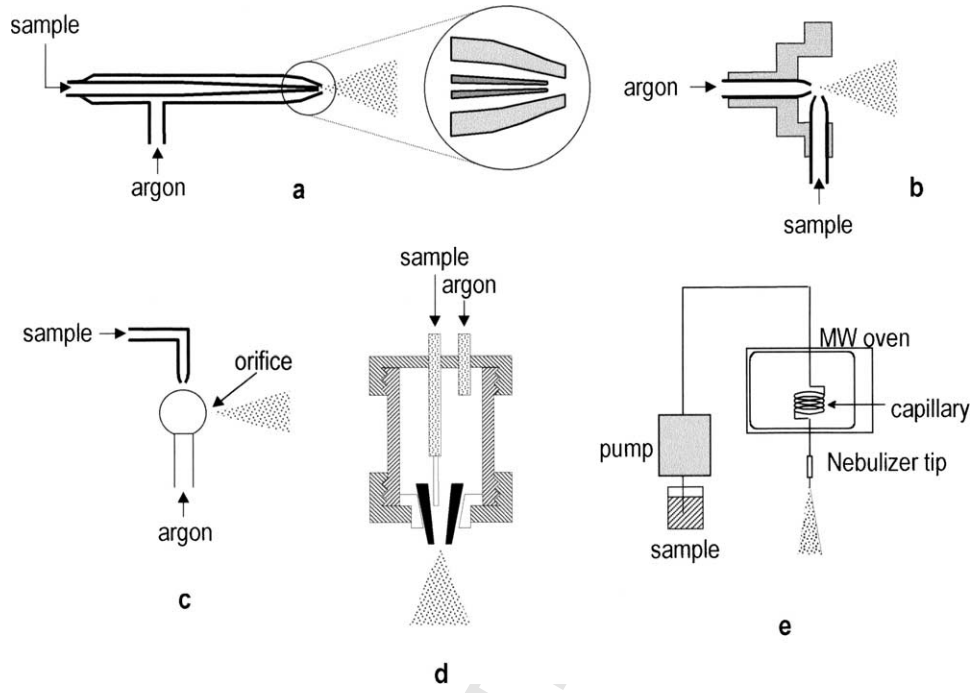

Figure 2. Pneumatic nebulizers: (a) concentric; (b) cross-flow; (c) Babington; (d) single-bore high-pressure pneumatic; (e) microwave thermal.

considered pneumatic in nature, since nebulization takes place by interaction between the liquid stream and a gas stream generated through the evaporation of a fraction of the solvent [11]. The main drawback of the TN is that it is not well suited to work with acidic or high salt-content solutions and slurries.

Recently, a new microwave thermal nebulizer (MWTN) (Fig. 2e), based on sample heating by means of microwave radiation, has been presented by Bordera et al. [12]. This nebulizer features many of the advantages of the TN and overcomes some of its limitations: no corrosion problems; lower working pressure; suitable for high salt-content solutions; etc.

2.1.3. Hydraulic high-pressure nebulizers. In the hydraulic high-pressure nebulizer (HHPN), the aerosol is generated when a high-velocity liquid jet, which emerges from a narrow orifice (10–30 μm i.d.), impacts on a solid surface placed in front of the nebulizer nozzle. Its analytical behavior compares favorably with that of a PCN [13]. Nevertheless, it shows several drawbacks mainly because of the deterioration of the nozzle.

2.1.4. Ultrasonic nebulizers. In ultrasonic nebulizers (USNs), the solution is pumped to the surface of a piezoelectric transducer. As a consequence of the interaction between the ultrasonic waves and the liquid film, a very fine aerosol is obtained. With this nebulizer, improvements in detection limits up to 10-fold are achieved when it is coupled to a desolvation system.

2.2. Aerosol-transport phenomena

After the aerosol is generated (''primary aerosol''), before it reaches the plasma (''tertiary aerosol''), it suffers some modifications that change its original characteristics. All the processes that take place along the spray chamber or desolvation system are known as ''aerosol-transport phenomena'' [14]. The final effects of these processes are:

(i) a reduction in the amount of aerosol reaching the plasma;
(ii) a decrease in the turbulences associated with the aerosol-production process;
(iii) a thermal and charge equilibrium; and, finally,
(iv) a reduction in the aerosol mean-particle size.

As a result, a more suitable aerosol for the plasma source is obtained. Some of these phenomena are discussed below in Sections 2.2.1 to 2.2.4.

2.2.1. Solvent evaporation. Solvent evaporation appears when the gas is not saturated with solvent vapor, causing a decrease in the aerosol-droplet diameter. Several factors influence the extent of the evaporation rate:

(i) the solvent nature, since volatile solvents evaporate faster;
(ii) the droplet diameter, since the evaporation rate is higher for the finest droplets;
(iii) the droplet composition. Thus, the higher the salt concentration of the solution, the lower is

the droplet-evaporation rate. This fact is because of the decrease of the partial pressure vapor of the solvent at the surface of the droplet; and, finally,

(iv) the temperature difference between the droplet surface and the surrounding gas and the velocity at which the droplet environment is renewed.

2.2.2. Nucleation. Droplet formation and growth through condensation of the vapor on an appropriate surface is known as 'nucleation'. This process is the opposite of evaporation, since its effect is to increase the mean size and the number of the aerosol droplets. Nucleation depends on the saturation ratio (i.e., the ratio between the partial gas vapor pressure and the saturation vapor pressure) in the droplet environment. It takes place when saturation ratios higher than 1 are achieved. For a given saturation ratio, nucleation depends on the original droplet diameter and on the aerosol composition.

2.2.3. Coagulation. The net effect of this phenomenon is an increase in the droplet diameter because of collisions with other droplets and, therefore, a decrease in the number of droplets contained in a given aerosol volume. The origin of these collisions lies in the different motion of the droplets contained in the aerosol. Coagulation rate increases with the magnitude of the difference between droplets velocities.

2.2.4. Impact losses. In this case, a fraction of the aerosol particles or droplets collide against the walls of some of the components of the sample-introduction system. Therefore, a reduction in the number of aerosol droplets and a decrease in the aerosol mean size result. Depending on the main mechanism of droplet collision, the impact losses can be divided into three main groups:

(i) gravitational settling. The gravitational field is responsible for droplet removal from the aerosol stream. On taking into account the range of diameters of the aerosols used in plasma spectrometry, it can be stated that this mechanism is not significant in comparison with those remaining;

(ii) turbulence deposition. Because gas turbulences can act in any spatial direction, the study and the characterization of this mechanism is really difficult. The rate of turbulent deposition losses is proportional to the square of the drop diameter and the acceleration suffered by the droplet when a force acts on it; and,

(iii) inertial deposition. In some instances, the sample-introduction system includes an impact surface placed along the aerosol path to remove the coarsest droplets. When the aerosol reaches this surface it is forced to change its trajectory (Fig. 3). Because of its lower inertia, a small droplet is more likely to follow any sharp trajectory change than a coarse one. A large droplet requires a longer time to accommodate its trajectory to the new path than a smaller one. Therefore, large droplets are more likely to impact against the surface walls.

2.3. Spray chambers

The main function of the spray chamber is to filter the aerosol generated by the nebulizer (primary aerosol), so as to allow the smallest droplets to be conducted towards the plasma. It is recognized that, when less of 5% of the analyte nebulized is transported to the plasma, the spray chamber, rather than the nebulizer (i.e., conventional pneumatic nebulizers), determines the characteristics of the aerosol injected into the plasma [15].

Spray chambers (Fig. 4) can be classified into:

(i) double-pass (DPSC), so-called Scott type or reverse-flow type;

(ii) cyclonic (CSC), which includes several modifications such as vortex type, Sturman-Master or vertical rotary; and,

(iii) single-pass or cylindrical type, also called direct spray chamber.

2.3.1. Double-pass spray chambers. The DPSC is the most widely used design. As can be seen in Fig. 4a, it comprises two concentric tubes. The aerosol is introduced in the inner tube and, after turning back at its end, leaves the spray chamber through an upper exit. A fraction of the droplets is removed from the primary aerosol stream by collision against the inner-tube walls. Another benefit of the inner tube is damping of the turbulences associated with the nebulization process which, otherwise, would degrade the signal stability. In

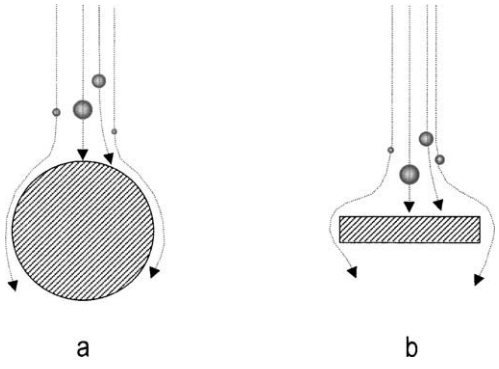

Figure 3. Paths of particles of different sizes around: (a) a spherical or cylindrical surface; (b) a flat surface.

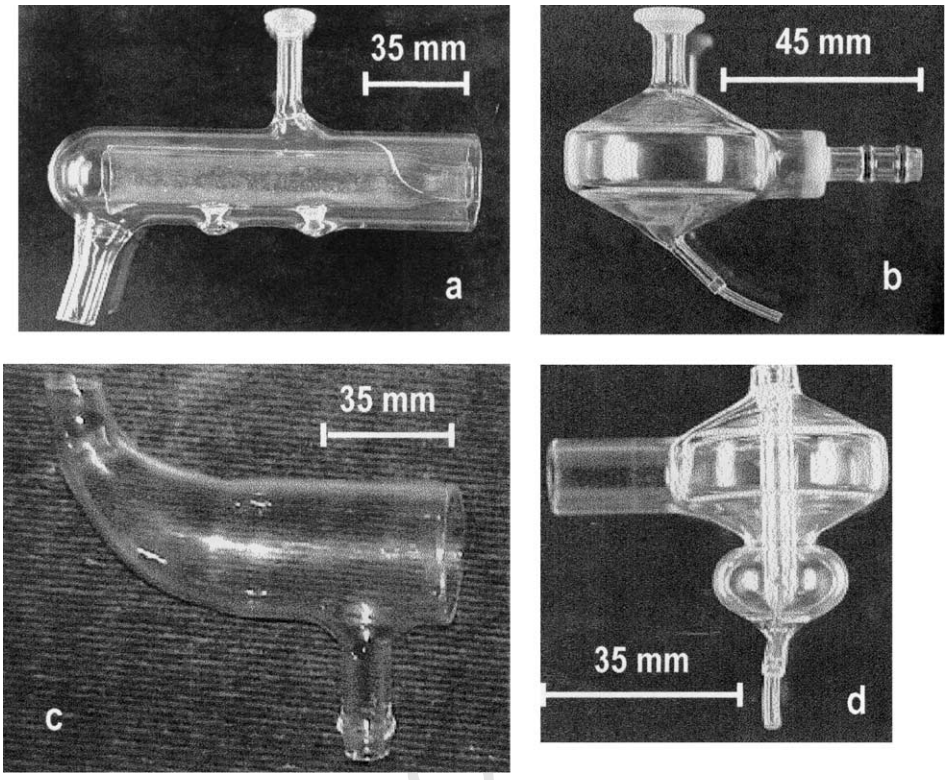

Figure 4. Different designs of spray chamber: (a) double pass; (b) cyclonic; (c) single pass; (d) Genie.

addition, the 180° change in direction of the aerosol flow promotes the inertial elimination of those droplets that cannot modify their direction (i.e., large droplets). This also contributes to the reduction in the aerosol-drop mean size in a very efficient way.

This spray chamber design has inner volumes (called dead volumes) that are not easily renewed by the nebulizer gas. The presence of these volumes increases the wash-out time (i.e., the time required by the system to achieve 1% of the steady-state signal) of the system between samples.

2.3.2. Cyclonic spray chambers. In the CSC (Fig. 4b), the aerosol is introduced tangentially to the main body. The aerosol path inside a CSC is not really clear, but it has been stated that the aerosol describes a double concentric spiral movement. In a design like that shown in Fig. 4b, the aerosol generated inside the spray chamber moves downwards in an external spiral movement, close to the spray-chamber walls. When the droplets reach the bottom of the chamber, a second inner spiral carries the aerosol towards the top of the spray chamber [16]. This complicated flow dynamic generates turbulences inside the spray chamber that promote the droplet selection process by collision against the inner walls of the spray chamber. It has been reported that centrifugal losses are not relevant in this design [15].

Several studies have been performed comparing the analytical behavior of the two most common spray chamber designs in ICP-AES (DPSC and CSC) [17]. In general terms, the DPSC produces finer tertiary aerosols than the CSC. As a result of the worse filtering action, the CSC affords higher analyte and solvent transport rates to the plasma than the DPSC, thus usually causing improvements in the analytical figures of merit.

The wash-out times are lower for the CSC than for the DPSC. This can be explained by taking into account the smaller inner volume of the CSC and the fact that the solution deposited on the spray-chamber walls can be easily removed in the CSC.

2.3.3. Single-pass spray chambers. Another spray chamber design also described in the literature is the single-pass or direct spray chamber (see Fig. 4c). This design is used with systems that do not require a strong filtering action of the aerosol. It must be borne in mind that, with this chamber, a significant fraction of the aerosol reaches the plasma and, hence, a desolvation system is highly recommended.

2.4. Desolvation systems

To reduce the solvent load going into the plasma and, therefore, different spectral and non-spectral interferences, several desolvation systems have been proposed.

The simplest device used to control the solvent load going into the plasma comprises a thermostated spray chamber. In this design, the solvent vapor generated inside the spray chamber is removed from the aerosol stream. It is specially interesting when coupled to a thermospray nebulizer or when using volatile solvents.

Most of desolvation systems, the so-called two-step desolvation systems (TSDSs), comprise a first heating step, in which the solvent is totally or partially evaporated from the aerosol droplets, and a second step, in which solvent vapor is removed from the aerosol stream. The desolvation conditions determine the fraction of solvent and analyte transported.

Aerosol heating can take place in the spray chamber or in a glass extension tube placed at the exit of the spray chamber. Usually, the walls of the aerosol conduction tube are heated by a heating tape wounded round it. Heat is transferred to the aerosol droplets by a conduction/convection mechanism. It gives rise to temperature gradients as well as turbulences and contributes to increases in the background and signal noise as a result of pressure fluctuations caused by the sudden and violent evaporation of droplets impacting against the hot walls [18]. Moreover, the analyte contained in these droplets remains adhered to the walls, causing the analyte transport rate to decrease and memory effects to become more significant. All these factors degrade the analytical response.

Aerosol heating can also be accomplished by absorption of radiation, such as infrared (IR) [19] or ultraviolet-visible (UV-VIS) [20], instead of convection/conduction. Recently, a microwave desolvation system (MWDS), based on microwave aerosol heating, has been developed (Fig. 5) and its behavior evaluated both in ICP-AES and ICP-MS [21,22]. In general, aerosol radiative heating is faster than resistive heating and reduces, but does not completely eliminate, the drawbacks of the latter.

Vapor removal is usually carried out by condensation on cold surfaces. This is the simplest way to reduce the solvent load going into the plasma. However, its effectiveness is hampered because of nucleation, since a given fraction of the droplets formed by nucleation is not removed, contributing to an increase in the solvent load going into the plasma. The extent of nucleation can be reduced by carrying out condensation in two steps at two different temperatures. Vapor removal from the aerosol stream can also be done through membrane extraction [23]. This mechanism reduces nucleation. However, it shows a limited capability for vapor removal (i.e., its vapor removal rate is not as high as that of condensation systems).

2.5. Diagnostics

An ideal liquid sample-introduction system must fulfill the following requirements:

(i) high analyte-transport efficiency. This parameter is defined as the amount of analyte reaching the plasma relative to the amount of analyte introduced into the sample-introduction system;
(ii) low solvent-transport efficiency, so as to avoid plasma deterioration and interferences caused by the solvent;
(iii) good reproducibility;
(iv) low memory effects, thus allowing high analytical throughput;
(v) robustness, i.e., stability of the system against changes in the sample matrix; and,
(vi) ease of handling and low maintenance cost.

To achieve these requirements, all the components of the sample-introduction system should work as efficiently as possible. Points (i) and (ii) are directly related

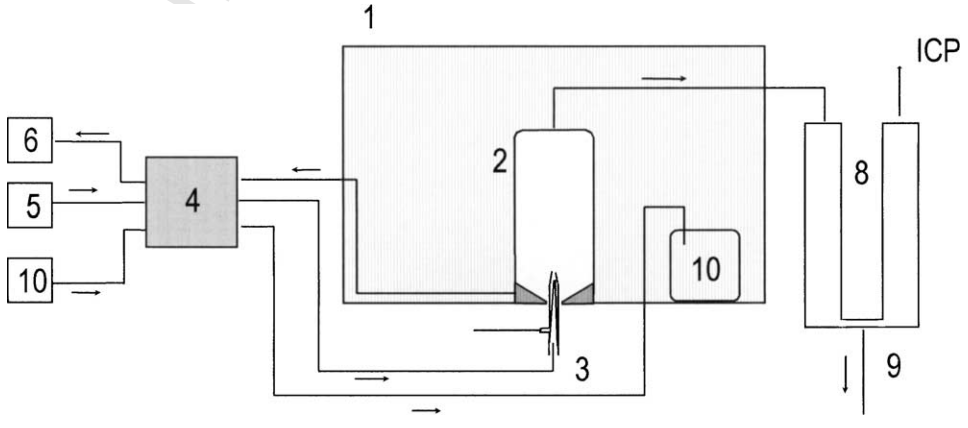

Figure 5. Experimental setup of the microwave desolvation system: (1) microwave oven; (2) spray chamber; (3) nebulizer; (4) peristaltic pump; (5) sample; (6) spray chamber drain; (7) aerosol conduction; (8) condensation unit; (9) condensation unit drain; (10) water to prevent magnetron damage.

to the characteristics of the primary aerosols and to the transport phenomena that take place along the pathway to the plasma.

2.5.1. Nebulizer diagnostics. The ideal nebulizer would have the following characteristics, among others:

(i) low sample consumption;
(ii) the ability to nebulize a wide range of solution types (solutions with high solid or salt contents without clogging or premature failure, acids, organics, etc);
(iii) simplicity of use;
(iv) ruggedness; and,
(v) low cost.

Nonetheless, the key factor in the success of analysis is the production of an aerosol as fine and monodisperse as possible in order to improve aerosol transport to the plasma. Therefore, the diagnosis of a given nebulizer must be done in terms of the characteristics of the aerosols generated, since it influences both the signal and the noise. To this end, the aerosol droplet-size distribution (DSD) and the mean drop diameter are the parameters used most.

A good aerosol for plasma purposes would have a DSD with both mean drop size and width as small as possible. Ideally the DSD width would be zero, i.e., monodisperse aerosol, although, in general, polydisperse aerosols with droplets ranging from a few nm to 200 μm are generated.

Other parameters than must be considered in estimating the quality of an aerosol are:

(i) the aerosol yield., i.e., the fraction of the sample mass pumped to the nebulizer that is transformed into an aerosol. This parameter, which ideally should be 100%, depends on the nebulizer and the experimental conditions; and,
(ii) the aerosol cone angle, since a large cone angle increases the amount of aerosol that impacts against the side walls of the spray chamber.

2.5.2. Aerosol-transport-system characterization. An ideal aerosol-transport system (i.e., spray chamber and/or desolvation system) must have the following characteristics:

(i) the ability to transport as much analyte mass to the plasma as possible without degrading its excitation properties. Analyte and solvent transport rates (i.e., the amount of analyte and solvent that reaches the plasma per time unit, respectively) are the most widely used parameters to quantify the magnitude of the aerosol transport phenomena. Sometimes, analyte and solvent transport efficiencies are also employed;
(ii) production of a tertiary aerosol as fine as possible and less turbulent than the primary aerosol. Similarly to that for the primary aerosols, the DSD and mean size of the tertiary aerosols are parameters of great interest in characterizing the behavior of an aerosol-transport system. The DSD of the tertiary aerosols can be related to characteristics of the primary aerosols and the transport phenomena that take place along the aerosol-transport system;
(iii) similar behavior with samples of very different nature and composition;
(iv) minimization of memory effects. To this end, the wash-out time is the diagnostic parameter used most. Wash-out time depends on the design of the aerosol-transport system. The material also plays a significant role in terms of memory effects. Thus, for instance, it is well known that Pd shows long wash-out times because it is preferentially adsorbed onto polymer surfaces. Thus, when working with this kind of element, glass, instead of any polymer, is the preferred material; and,
(v) mechanical simplicity and low cost.

3. Low sample-consumption systems

The analysis of very small volumes of sample solutions is becoming one of the key research subjects in ICP-AES and ICP-MS, because of the great number of areas in which the sample size may be limited: semiconductors; clinical; geological; on-chip technology; liquid separation; spectroscopic coupled techniques; etc. In addition, low sample-consumption rates also mean a reduction in waste-management costs. One of the most accepted solutions proposed in these instances is to reduce the nebulizer-liquid uptake rates to the microliter per minute (μl/min)level.

Although conventional nebulizers can be used at rates under 1 ml/min, their design is not optimized for this purpose. Therefore, nebulizers specially designed to work efficiently at rates as low as 10 μl/min, the so-called micronebulizers (MN), are needed. Several pneumatic concentric micronebulizers have been described [2]:

(i) the high-efficiency nebulizer (HEN);
(ii) the MicroConcentric nebulizer (MCN);
(iii) the MicroMist (MM);
(iv) the direct-injection nebulizer (DIN); and,
(v) the direct-injection high-efficiency nebulizer (DIHEN).

Some others micronebulizers based on different principles, such as the micro-ultrasonic nebulizer or the oscillating capillary nebulizer, have also been proposed.

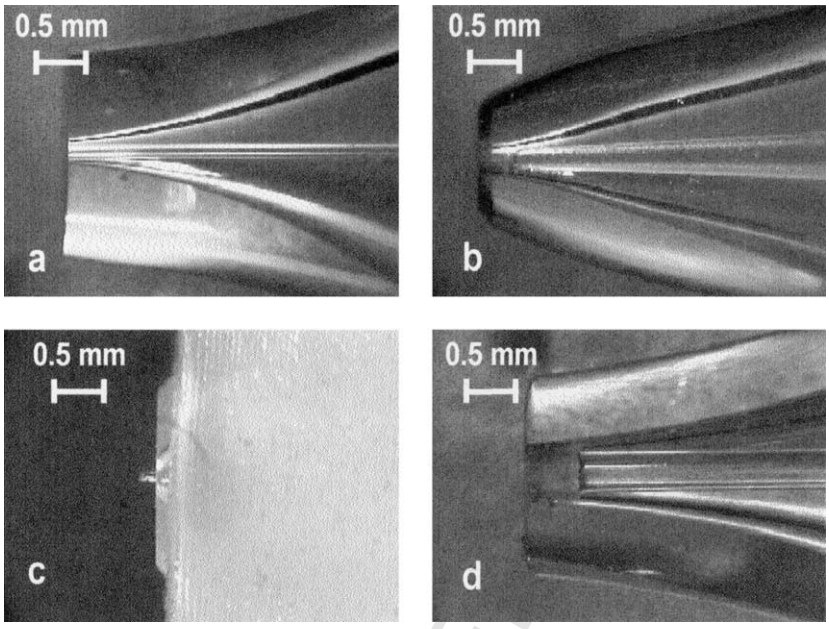

Figure 6. Images of different nebulizer tips: (a) high-efficiency; (b) MicroMist; (c) MicroConcentric; (d) conventional pneumatic concentric.

The HEN, MCN and MM are modified versions of a conventional PCN (Fig. 6) in which the liquid and gas cross-sectional areas and liquid capillary-wall thickness have been reduced (Table 1). As a consequence, the liquid-gas interaction is improved, so that primary aerosols are finer than those generated by a conventional nebulizer. Comparative studies [24] have indicated that the sensitivity obtained with a HEN operated at liquid-flow rates of about 50 μl/min is the same as that reported for a PCFN operated at around 1 ml/min. However, the HEN requires working at high pressures, thus needing a special gas-transport system.

The HEN, MCN and MM are normally employed in conjunction with a DPSC. Its inner volume must be reduced to work at very low liquid flow rates. Otherwise, large wash-out times would be required. Similarly, several low-volume spray chambers (LVSCs) have been developed. Among them, we can find the so-called Cinnabar and Genie. The Cinnabar is similar in design to the cyclonic (Fig. 4b), but its inner volume is about a half that of the conventional one (i.e., 19 ml instead of 40 ml). The Genie has a small sphere adapted at its bottom and an inner vertical centered tube (Fig. 4d). Its inner volume is about 29 ml. These spray chambers are reported to produce less severe matrix effects with inorganic species than the DPSC [25].

Table 1. Critical dimensions of different micronebulizers and a conventional pneumatic concentric nebulizer

Nebulizer	Gas-outlet cross-section area/mm^2	Liquid-capillary inner diameter/mm	Capillary-wall thickness/mm
Conventional	0.028	0.40	0.06
HEN	0.011	0.10	0.03
MCN	0.017	0.10	0.03
MM	0.025	0.14	0.05
DIHEN	0.0099	0.082	——

As mentioned above, a spray chamber produces primary aerosol losses. To avoid them, several authors have developed sample-introduction systems that do not include a spray chamber. Similarly, Greenfield and co-workers used a nebulizer to introduce samples directly into the ICP 30 years ago [26]. The DIN is a modified version of this device [27]. In this case, the aerosol is generated at the plasma base and no analyte is lost downwards. Recently, a new version, the DIHEN, has been developed, minimizing the cost and making it easy to operate. Apparently, these systems show a 100% analyte-transport efficiency. Because of this, their ICP-AES analytical figures of merit used to be better (i.e., shorter wash-out times, higher sensitivities and lower limits of detection) than for any of the three remaining pneumatic concentric micronebulizers coupled to a spray chamber.

One of the drawbacks of the DIN and DIHEN is that they become easily blocked when working with high salt-content solutions. To overcome this, a new version of the DIHEN provided with a wider liquid sample capillary, called the large-bore direct injection high-efficiency nebulizer (LB-DIHEN), has been described [28].

4. Conclusion

In ICP-AES and ICP-MS, the success of the analysis strongly depends on the selection of an appropriate

sample-introduction system. As has been shown, a wide variety of components of the liquid sample-introduction system have been developed to solve particular analytical problems. Several factors must be taken into account in making the selection of the most appropriate liquid sample-introduction system for a given application (see Table 2). Among them, the most important are:

(i) the required analytical figures of merit;
(ii) the sample matrix. The sample-introduction system must be selected to eliminate or at least to reduce matrix interferences. In addition, the sample-introduction system must be able to introduce a wide range of solution types (solutions with high solid or salt contents, acids, organics, etc.) into the plasma.
(iii) the available volume of sample.

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