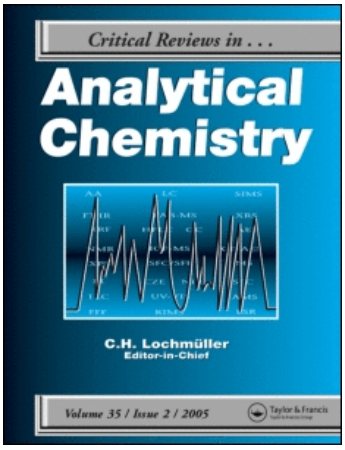

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Thermospray Sample Introduction to Atomic Spectrometry

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Thermospray Sample Introduction to Atomic Spectrometry

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ABSTRACT: Thermospray aerosols are generated by forcing a liquid sample through a capillary tube that is heated to partially vaporize the solvent, resulting in a blast of vapor that converts the remaining liquid to droplets. The droplet size character of thermospray aerosols can be electrically varied by changing the temperature and degree of solvent vaporization of the liquid stream. The primary droplets produced by thermospray under optimal conditions are smaller on average then those produced by pneumatic nebulizers, particularly of the types used for inductively coupled plasmas (ICPs). Solvent vaporization is enhanced for smaller particles and higher temperatures, with both aspects leading to faster size reduction due to solvent evaporation than would occur with pneumatic sample introduction at room temperature. As smaller droplets are more efficiently transported through sample introduction systems, the use of thermospray aerosol generation provides higher analyte transport, higher sensitivity, and lower LODs than pneumatic sample introduction with most atomic spectrometric detectors. Factors that affect the extent of improvement are the operating temperature of the thermospray vaporizer, the temperature of the spray chamber, the presence or absence of a desolvation system, the diameter of the capillary, and the liquid sample flow rate. The absence of desolvation results in degradation of excitation conditions within ICPs, and in smaller improvements in analytical peformance with ICP atomic emission spectrometry (ICP-AES). Smaller capillary exit diameters provide better performance. Specific LOD improvements with thermospray sample introduction compared to pneumatic sample introduction vary, but typically are a factor of 15 to 25 times lower when desolvation is used with thermospray, and when both systems operate at comparable flow rates. Matrix effects are generally higher with thermospray sample introduction than with pneumatic sample introduction, but are comparable to those reported for ultrasonic nebulization. Thermospray systems have been shown to provide LODs an order of magnitude lower than that obtained with pneumatic sample introduction, even in the presence of high dissolved solids, such as 3000 μg/ml Ca. Thermospray capillaries as small as 25 to 50 μm can operate effectively at optimal conditions with high dissolved solids content samples, without problems of capillary clogging.

Thermospray sample introduction has most often been applied to ICP-AES, but also has been studied with ICP-mass spectrometry, flame atomic absorption, and even graphite furnace atomic absorption. The principle applications of thermospray sample introduction to ICP-AES to date have been to environmental analyses, and for detection of discrete samples resulting from flow injection and liquid chromatography. For discrete sampling methods, the advantages are the low extra-column volumes of thermospray systems, which minimize dispersion, and improved sensitivity, which counteracts the effects of unaviodable dispersion, particularly during chromatographic separations.

KEY WORDS: thermospray, aerosol techniques, particle size distribution, inductively coupled plasma-atomic emission spectrometry, inductively coupled plasmas-mass spectrometry, flame atomic absorption, limits-of-detection, matrix effects, environmental analysis, flow injection analysis, metal speciation.

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I. INTRODUCTION

Determinations of the concentrations of elements in matter are extremely important to the characterization and prediction of the properties of any material. Techniques based on measurements of optical photons or ions from, or interacting with, an atomized gas-phase version of the material are perhaps the most widely used for this purpose. Such *atomic spectrometric* methods are widely performed using flames or plasmas,[1,2] which are used for the high-temperature decomposition, atomization, and excitation/ionization of analytical samples. These samples for atomic spectrometry are most commonly in liquid form because of the practical ease of sample dilution, sample handling, and standards preparation that liquid solutions allow. However, bulk liquid samples or streams are not directly compatible with flames and plasmas. To facilitate sample-source interaction, aerosol techniques are commonly employed to disperse the sample within a carrier gas that is injected into the flame/plasma. Energy from the source is then used to dry the analyte-containing droplets (i.e., the solvent is removed via evaporation), vaporize the resulting dry particles, and decompose the subsequent molecular species to atoms and ions. As the solvent and dissolved solids must be rapidly vaporized prior to signal measurement, aerosols are excellent media for these processes by virtue of the high surface-area-to-volume ratios, and therefore high vaporization rates, that they provide. Furthermore, as excessive amounts of solvent can lower the temperature of the flame/plasma source such that the steps prior to signal measurement may be inefficient, rapid solvent vaporization and removal *prior* to the source can be performed using aerosol interfacing methods.

Aerosol sample introduction methods are employed for almost all practical analyses with flame atomic absorption (FAA), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS). Currently, these are the major atomic spectroscopic methods,[3] particularly for metallic elements, along with graphite furnace atomic absorption spectrometry (GFAAS) for which aerosol interfaces are not commonly employed.

Despite such wide application with atomic spectrometric methods, the aerosol interface is generally considered to be the weak link in the experiment, substantially limiting the analytical capabilities of each method. As such, substantial research has been devoted to the development of new strategies for aerosol interfacing and to a greater understanding of fundamental aerosol sample introduction phenomena. Aerosol techniques also have been developed for other analytical applications. One example of this is *thermospray*, as developed by Vestal and co-workers,[4] for coupling liquid chromatography to mass spectrometry (LC-MS). The purpose of this paper is to review fundamental and applied aspects of sample introduction to atomic spectrometry based on aerosol generation by thermospray, which has also shown particular capability to alleviate the traditional sample introduction limitations to atomic spectrometry.

II. BACKGROUND

Much of the current knowledge and terminology of conventional aerosol sample introduction has been summarized clearly by Browner.[5] A typical aerosol sample introduction system for atomic spectrometry is shown in Figure 1. Aerosol is generated by a component called a *nebulizer* and contained within a *spray chamber*. An important characteristic of aerosols produced by any source is particle size. Aerosols can generally be considered to be either polydisperse or monodisperse, in terms of the distribution of particle sizes present within the aerosol. Aerosols from most nebulizers consist of particles having a considerable range of sizes, i.e., they are polydisperse. For analytical applications, the initial distributions of aerosol particles produced by nebulizers have been termed *primary aerosols*.[6]

Since particle sizes characterize aerosols produced by nebulizers, it is useful to consider some of the ways by which aerosol particle size distributions are depicted. One characteristic of aerosols is that they consist of numerous, discrete particles. Consequently, one way to evaluate aerosols is in terms of the number of particles as a function of size. In addition, different particle sizes can contain significantly different fractions

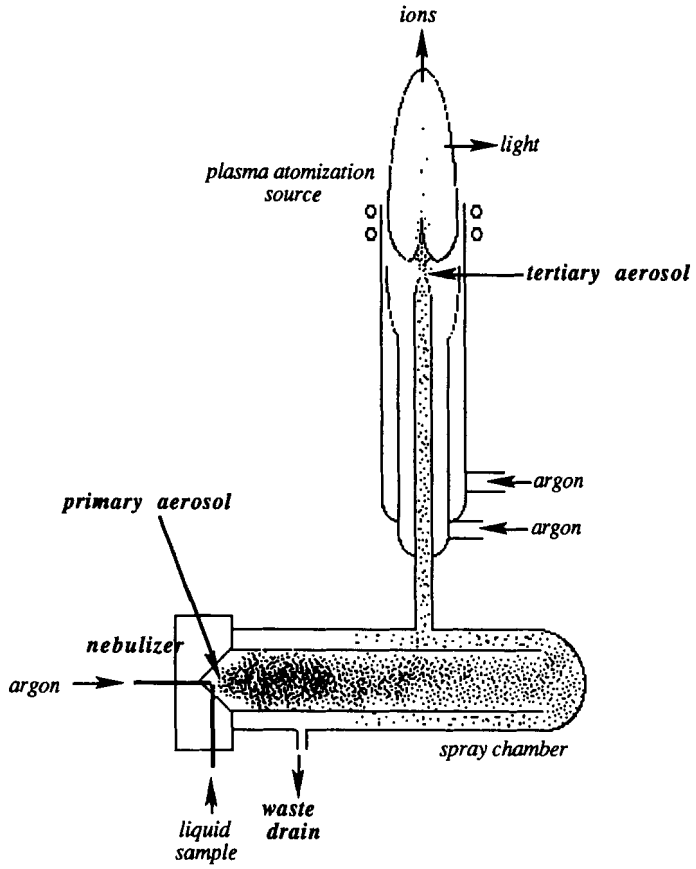


FIGURE 1. Typical aerosol sample introduction system.

of the sample volume (or mass) distributed in the aerosol cloud. For example, a 0.1-μm diameter droplet contains only 0.1% of the volume of a 1-μm droplet. Figure 2 depicts a theoretical size distribution evaluated on number and volume bases.

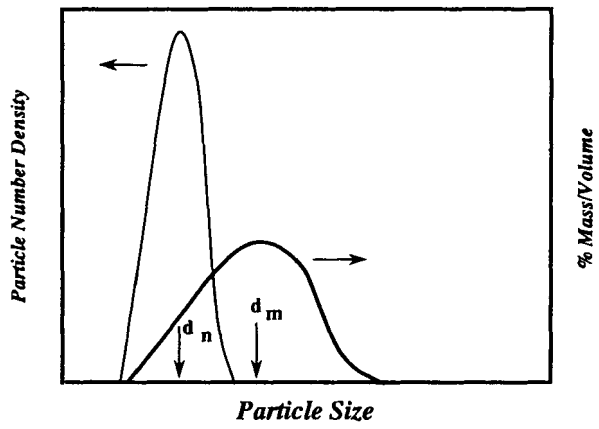


FIGURE 2. Comparative number and mass size distribution data for example aerosol.

To simplify representation of particle size distributions, average or median sizes are commonly used to describe polydisperse aerosols. Some commonly used values are the number mean diameter (d_n), which is the particle size that bisects the total number of particles within the distribution; the Sauter mean diameter (d_s), which is the size that bisects the surface-area-to-volume ratio of the distribution; and the mass median diameter (d_m), which represents the median size based on the total aerosol mass. For most polydisperse aerosols of interest to sample introduction for chemical analysis, $d_n << d_s \sim d_m$. Since d_m represents the distribution of mass within the aerosol and signals produced by atomic spectrometric methods are related to analyte mass, this value and the often comparable d_s are usually the preferred mean/median values for representing analytical aerosols. Also labeled in Figure 2 are d_n and d_m.

Within instrumentation, *primary aerosols* are subjected to many phenomena that act to modify

the droplets prior to interaction with the analyte detector such that the size distribution is highly dynamic. Aerosols reaching the detector are called *tertiary aerosols* (Figure 1) and typically have dramatically different size distributions from primary aerosols as a result of these modification processes. Solvent evaporation causes particle size decreases; since evaporation is a surface phenomenon, evaporation rates are highest for the smallest particles, which have the highest surface-area-to-volume ratios. Particle coagulation, especially prominent in dense aerosols and turbulent aerosol formation stages, causes particle size increases. Turbulence within a spray chamber causes impaction of larger particles with surfaces, leading to generally undesirable analyte losses and a shift of the aerosol distribution to smaller sizes. Other processes, such as gravitational settling and centrifugal effects, can be important sources of analyte loss and inefficiency depending on the specific configuration of the instrument. In any case, particle size plays a major role in determining the efficiency of analyte transport to most detectors. For any analyte concentration, the product of this efficiency and the sample input rate to the nebulizer determine the analyte mass flux to the source, and therefore the mass of analyte available per unit time for signal production.

Pneumatic nebulizers are by far the most common means for aerosol generation with atomic spectrometry. These nebulizers employ a high-velocity gas jet to blast a liquid stream into aerosol droplets. Many geometric configurations of pneumatic nebulizers have been employed, but the most common designs are cross-flow and concentric arrangements of the gas and liquid flows.

One of the major advantages of these nebulizers is their great simplicity. However, pneumatic sample introduction significantly limits the performance of atomic spectrometric methods in a variety of ways. The aerosols produced by pneumatic nebulizers under conditions compatible with flames or plasmas are highly polydisperse.[5] The fraction of aerosol particles that is too large to produce a useful signal and/or would lead to large matrix interferences is typically 90 to 95% in the case of flames, or 99% in the case of inductively coupled plasmas.[6] These aerosol particles are removed by the accompanying spray chamber and lost to waste (Figure 1). As a result, the flux of analyte mass into the source is one to two orders of magnitude lower than the flux into the sample introduction system, leading to limited sensitivity and inefficiency. One effect of reduced sensitivity will be poorer lower limits of detection (LODs) than would be anticipated for a more efficient process. In addition, these pneumatic sample introduction techniques are known to introduce noise to the measurement process, degrading precision and further degrading LODs that might be obtained. Importantly, the analytical performance of well-designed pneumatic nebulizers of different geometric type is largely invariant; that is, the analytical figures of merit for the overall atomic spectrometer are generally within about a factor of 2, regardless of the type of pneumatic nebulizer employed.[7-10] Thus, there appears to be a fundamental limitation to the performance of pneumatic nebulizers. This likely results from the fact that for any experiment, the flow of gas for the nebulizer is constrained to that for stable performance of the source, limiting the energy available for aerosol formation to the amount supplied by that limiting flow of gas.[11]

Among alternatives to pneumatic sample introduction, ultrasonic nebulization (USN) has been of long-standing interest.[5] In this case, the liquid sample flows across the surface of an ultrasonic transducer powered by an RF power supply. Aerosol formation is thought to occur as a result of cavitation or geyser formation, and it has long been assumed that USN aerosols are highly monodisperse.[12] Recently, Browner has shown that the particle size distributions for *tertiary* USN aerosols only appear monodisperse if viewed as a number distribution;[13] these studies have indicated that when viewed as a function of mass, *primary and tertiary* USN aerosols provide broader particle size distributions than even pneumatic nebulizers. However, when USN aerosols are desolvated (i.e., the aerosols flow through a heated chamber followed by a condenser), enhanced LODs are obtained, particularly with ICP sources. Typically, LODs for ICP-AES using USN with desolvation are about a factor of 10 lower than those obtained by conventional pneumatic sample introduction.[14,15] A further advantage of USN for ICPs is the fact that the aerosol formation process is disengaged from the aerosol injection flow rate.

With pneumatic sample introduction to ICPs, the aerosol generation gas flow also is used to inject the aerosol into the plasma; as this gas flow will significantly influence the aerosol characteristics *and* the plasma operation, it is not known whether optimum flows employed are indeed a compromise of one or both of these factors.

Despite the improved LODs observed with USN sample introduction to ICPs, such systems have not gained wide acceptance, primarily as a result of the high cost of the complete system (RF power supply, transducer, and desolvation system), larger matrix effects, lack of long-term stability and reliability, long washout times, memory effects, and large dead volumes for discrete sampling methods,[16] although Fassel and Bear have recently disputed some of these reservations.[17]

III. THERMOSPRAY

A. Aerosol Generation Processes

When liquid is pumped through a capillary tube and heated uniformly along the length of the tube, a significant temperature gradient must exist from entrance to exit as the liquid temperature is raised from ambient. If the energy input to the tube is sufficient to cause partial vaporization of the liquid, the fraction of vapor produced from the liquid also will increase as the exit of the tube is approached. Vapor exiting the capillary will be of sufficiently high velocity to convert the remaining liquid to an aerosol, perhaps by the same surface stripping mechanisms postulated to cause droplet formation with pneumatic nebulizers.[5] Overall, this describes the process of thermospray, as depicted in Figure 3A. As suggested in this figure, such a thermospray system is conceptually similar to a concentric pneumatic nebulizer (Figure 3B), with the primary distinctions being that for thermospray (1) the nebulizing gas results from the liquid sample itself and is therefore not a permanent gas; (2) the aerosols are formed at higher temperatures; (3) the liquid sample and aerosols are partially desolvated at formation as a result of the thermospray process; and (4) the liquid and gas flows are not separated by a physical boundary prior to the exit of thermospray vaporizers. Invariably, the capillaries employed with thermospray have internal diameters less than 150 μm; moderately high pressures are required to pump solutions through such capillaries. Consequently, pumps of the type used for HPLC are typically used with thermospray.

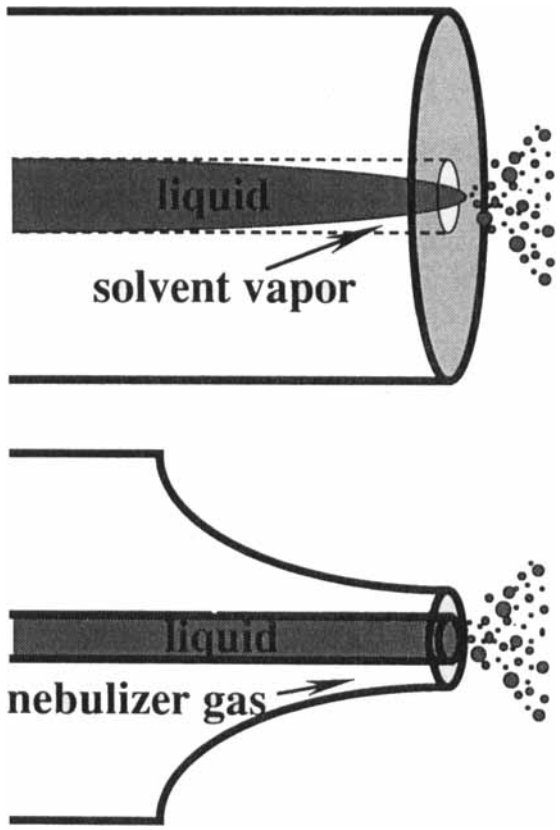


FIGURE 3. Conceptual depiction of thermospray aerosol generation (top), with comparison to concentric pneumatic nebulization (bottom); not to scale.

If the inlet temperature (T_1) and the outlet temperature (T_2) of a thermospray vaporizer are monitored, a characteristic plot of T_1 vs. T_2 can be obtained as exemplified by Figure 4. At low temperatures, increases in power input to the vaporizer cause both the inlet and outlet liquid temperatures to increase at comparable rates. An inflection point is observed for conditions that initiate vaporization at the outlet. Beyond this point, increases in applied power over a considerable range cause the inlet temperature to rise, while the outlet temperature does not change significantly. This is so because the outlet consists of an equilibrium

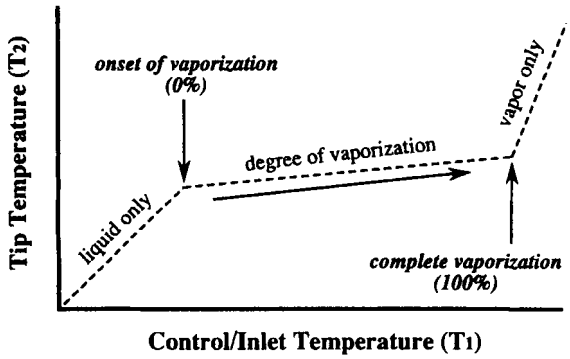


FIGURE 4. T_1 vs. T_2 plot for typical thermospray vaporizer.

mixture of liquid and vapor; as long as some liquid remains unvaporized at the outlet, the outlet temperature cannot exceed the boiling point for the solvent. At higher powers, a second inflection point is observed, corresponding to the point where solvent vaporization at the outlet is complete. Increasing the power input to the vaporizer beyond this point causes the vapor temperature to rise, while the point of complete vaporization retreats farther toward the inlet of the capillary tube. The region of the curve from the first to the second inflection point corresponds to increasing fractions of solvent vaporization at the exit, conditions where an aerosol is formed, and thus the range of conditions generally of interest for sample introduction. The fraction of solvent vaporized determines the liquid-to-gas flow ratio at the exit of the capillary and is an important determinant for the properties of the aerosols that result. Vestal has provided an excellent fundamental description of thermospray.[4]

Figure 5 shows four frames for the tip of a thermospray vaporizer at different temperatures. Frame a is for a temperature before the first inflection point in Figure 4, providing no solvent vaporization and simply a liquid stream. In frame b, the temperature has been adjusted to just above the first inflection point. A small degree of solvent vaporization is provided, resulting in the formation of a relatively coarse aerosol as evidenced by the large droplets in the lower portion of the frame. Frame c shows aerosol produced with an intermediate degree of vaporization; a dense aerosol is produced and comparison to frame b shows the absence of the large droplets at the higher temperature. In frame d, the vaporizer is heated to near complete vaporization and the aerosol density appears reduced as the aerosol is shifted to smaller sizes, which scatter visible light less efficiently. So, Figure 5 visually shows that the particle size distribution of thermospray aerosols can be electrically varied by changing the vaporizer temperature and thereby the degree of solvent vaporization and the amount of solvent vapor available for aerosol formation. Higher temperatures and fractions of solvent vaporized also increase the extent of analyte desolvation within the vaporizer.

B. Aerosol Size Measurements

Direct measurements of primary thermospray aerosols have been made using a laser Fraunhofer diffraction technique.[18] For these studies, thermospray aerosols were found to be highly polydisperse, as depicted in Figure 6. These data were obtained just beyond the tip of a relatively large internal diameter thermospray capillary (150 μm) by current standards. The size distributions are seen to shift to smaller droplets as the exit temperature is increased from 130 to 145 to 165°C. Number median diameters for these thermospray aerosols were typically 2 μm, compared to values greater than 10 μm measured using the same particle measurement technique for primary aerosols produced by a wide range of pneumatic nebulizers.[8] As the measurement distance from the thermospray vaporizer tip was increased to 25 mm, further decreases in size were observed.[18] Clearly, solvent evaporation with thermospray is initially enhanced by the higher temperature of these droplets. However, it is important to note that these measurements were made for thermospray aerosols sprayed into the open atmosphere; size distribution modification processes will be significantly affected by the presence of an enclosing spray chamber and the geometry, temperature, solvent vapor pressure, and absolute pressure of that chamber.

As indicated above, size distributions of aerosols change dynamically during transport through an aerosol interfacing system, such that the tertiary aerosols reaching the detector are dramatically different from the primary aerosols. Indirect measurements of tertiary thermospray aerosols (i.e., aerosols that have been processed through a

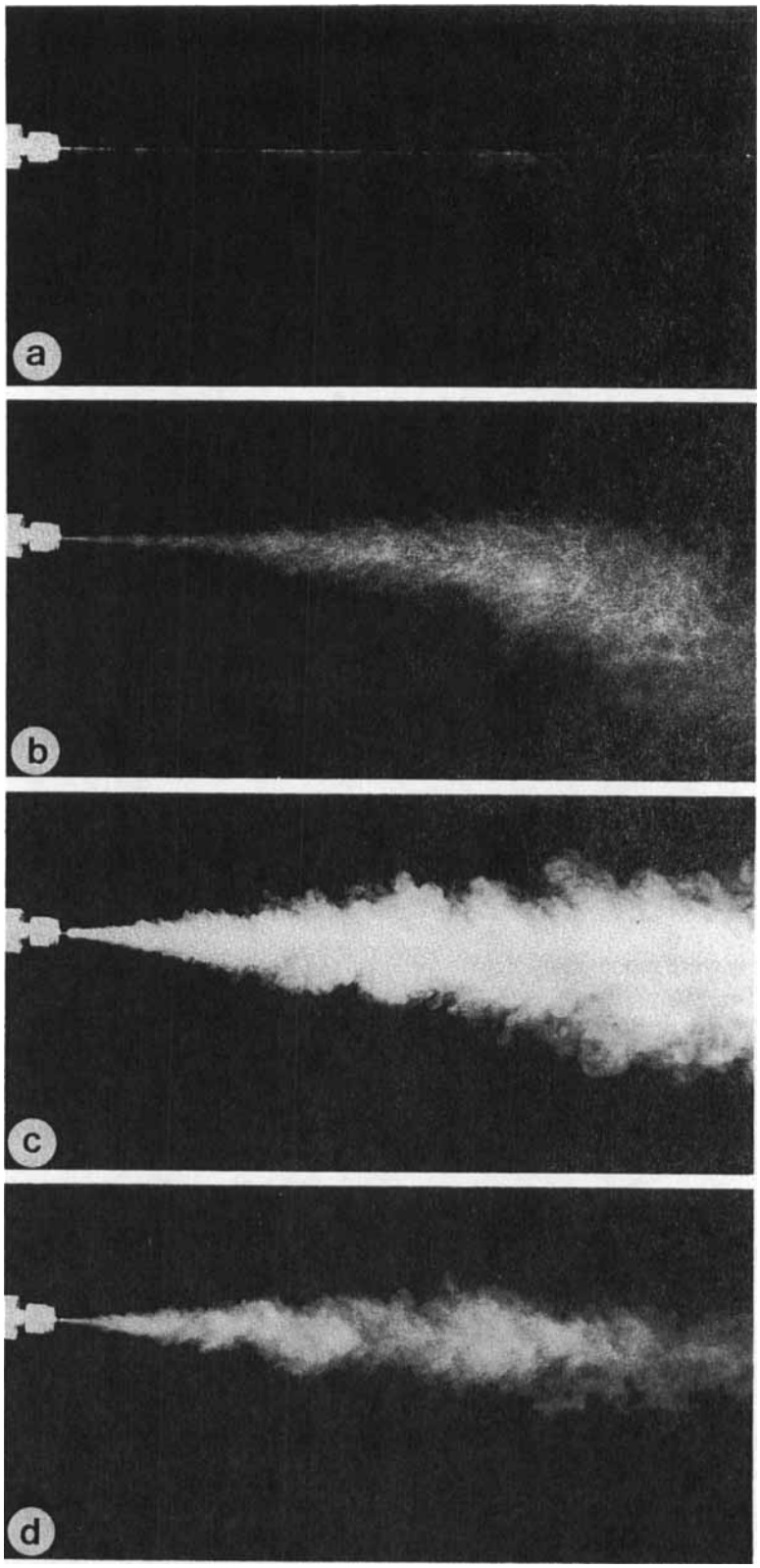


FIGURE 5. Effluent from a 50-μm fused silica aperture thermospray vaporizer for different degrees of solvent vaporization: (a) prior to solvent vaporization; (b) just above temperature for onset of vaporization; (c) intermediate degree of vaporization; (d) nearly complete solvent vaporization. Note that the droplets in (b) are visibly larger and gravitationally settle in the lower right hand corner, compared to c and d.

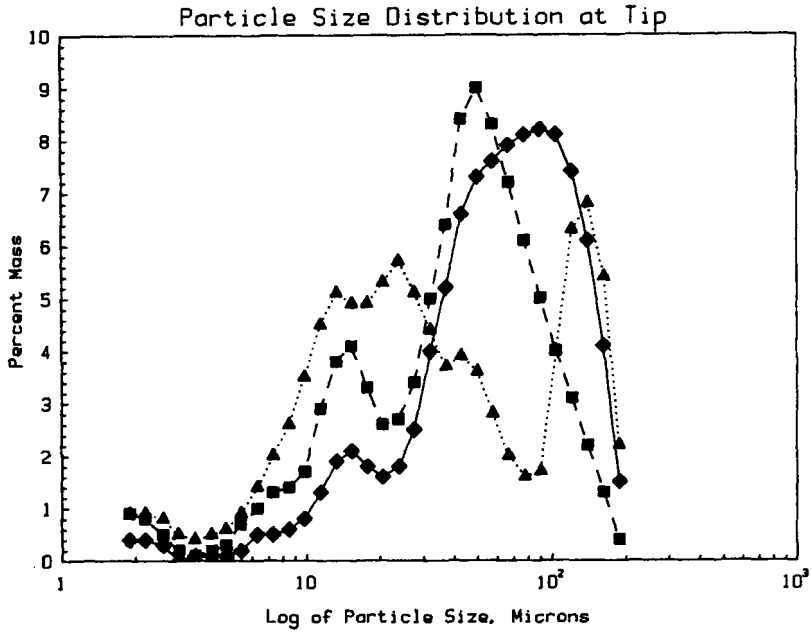
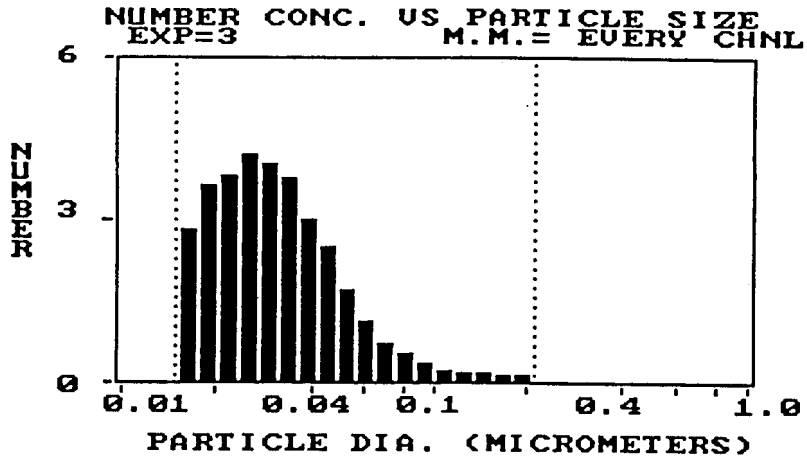


FIGURE 6. Primary aerosol particle size data for thermospray obtained using laser Fraunhofer diffraction for a low temperature (diamonds), intermediate temperature (squares), and a high temperature (triangles); 150-μm i.d. stainless steel capillary, 1-ml/min water. (From Koropchak, J.A.; Winn, D.H. *Appl. Spectrosc.* **1987,** *41,* 1311. With permission.)

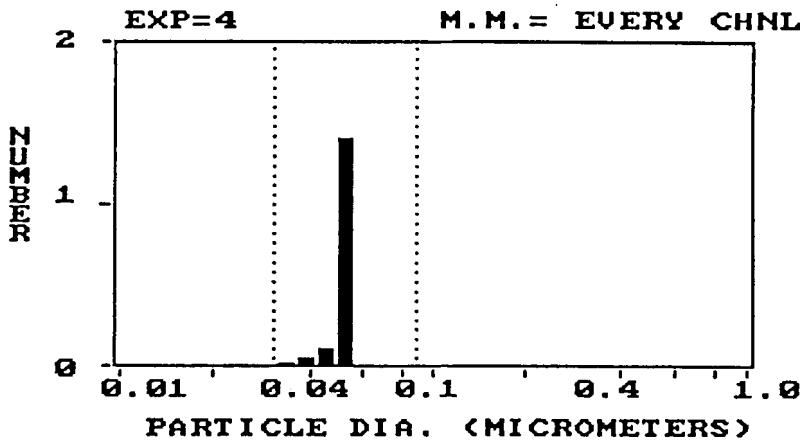
spray chamber) also were made using a light scattering approach.[19] In this case, the aerosols contained a moderately high concentration of nonvolatile salt and were evaporated to dryness (desolvated) prior to measurement. The sizes of the original particles were calculated using the following relationship:

$$D_D = D_I(C/\rho)^{1/3} \quad (1)$$

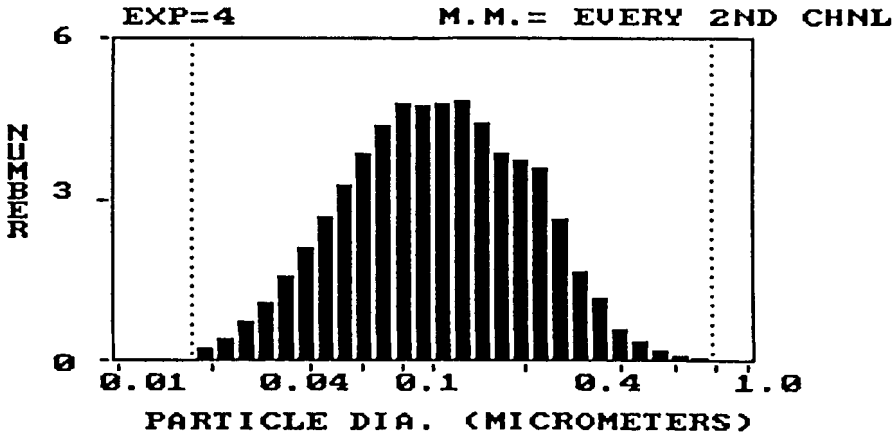
where D_D is the diameter of the desolvated droplet, D_I is the initial droplet size, C is the nonvolatile solute concentration, and ρ is the solute density. One conclusion of this study was that thermospray produced a greater abundance of small particles than pneumatic nebulizers. Measurements of aerosols processed through a membrane diffusion desolvation apparatus were made by Wilkes[20] using a differential mobility particle size analyzer (DMPS); this study also concluded that thermospray provided a larger number of small particles than did a concentric pneumatic nebulizer. Zarrin and co-workers[21] also measured desolvated tertiary aerosols from several nebulizer types using DMPS, which can measure particles down to 10 nm in diameter. Figure 7 shows the results of these measurements. Although different spray chambers, different dissolved solids levels, and different solvents were used in each case, comparison of the data for the pneumatic nebulizer (a), and the thermospray nebulizer (c) is not unreasonable. These graphs indicate that the *desolvated thermospray aerosols actually are larger than the desolvated pneumatically generated aerosols.* This is so in part because with thermospray the analyte is preconcentrated in the liquid phase prior to aerosol formation as a result of the solvent vaporization required for thermospray aerosol generation. If the primary aerosols formed are comparable in size for both pneumatic and thermospray nebulizers, desolvated thermospray aerosols must be larger because the concentration of dissolved solids at aerosol formation is higher with thermospray. However, it also is notable that the y-axis is an order of magnitude larger for the



a) Pneumatic Nebulization of 10^{-3} gr/ml NaCl Solution



b) Electrospray, 1.25 x 10^{-4} gr/ml Sucrose Solution



c) Thermospray, 2 x 10^{-4} gr/ml Caffeine in 75:25 Acetonitrile:DI-Water

FIGURE 7. Particle size data for desolvated aerosols from (a) a pneumatic nebulizer; (b) electrospray; and (c) thermospray obtained using a differential mobility particle sizer (DMPS). (From Zarrin, F.; Kaufman, S.L.; Socha, J.R. *J. Aerosol Sci.* **1991,** *22,* S343. With permission.)

thermospray size distribution, so that the *number* of particles measured for the thermospray system is much larger than for the pneumatic system. As the particles also are larger, the total dissolved solids mass (e.g., including analyte) transported as aerosol also is much larger with thermospray. This result would predict that thermospray sample introduction should be much more efficient at transporting dissolved solids mass than pneumatic sample introduction.

Another approach to the measurement of tertiary thermospray aerosols was based on the use of a *cascade impactor* for the collection of aerosols containing a moderate concentration of a test analyte such as Cu.[22] The analyte mass collected on each stage was analyzed separately to provide a distribution analyte mass as a function of particle size. A typical set of particle size data comparing pneumatic sample introduction to thermospray with 150- and 50-μm capillaries is shown in Figure 8. Clearly indicated in this figure is a substantially higher mass of analyte transported in the aerosol for the thermospray systems operating with analyte solution input at the same rate as for the pneumatic system.

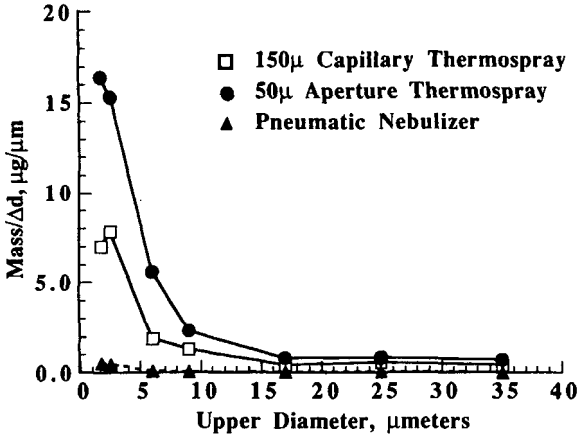


FIGURE 8. Particle size data for desolvated aerosols collected using a cascade impactor. Analyte mass (Na) over the size window for each stage (Δd) vs. upper diameter for each range. Masses were collected from the same initial analyte mass input to each nebulizer.

Considering the conceptual similarities between thermospray and concentric pneumatic nebulizers, it is conceivable that aerosol generation by such pneumatic nebulizers would provide a means for modeling thermospray aerosol generation. Unfortunately, although pneumatic nebulizers have been studied for over a century, aerosol generation by these methods is not well understood. Perhaps the best available model was derived by Nukiyama and Tanasawa[22] as described by the following equation:

$$\mathbf{d}_s = 585\left[\frac{\sigma^{0.5}}{c\rho^{0.5}}\right] + 597\left[\frac{\mu}{\rho\sigma^{0.5}}\right]^{0.45}\left[1000\frac{Q_l}{Q_g}\right]^{1.5} \quad (2)$$

where ρ, σ, and μ are the density, surface tension, and viscosity of the liquid, respectively; c is the velocity difference between the gas and liquid flows; Q_l and Q_g are the volumetric liquid and gas flows, respectively. The d_s predicted is for *primary aerosol*. Unfortunately, this model was empirically derived using particle sizing methods that are limited to the accurate measurement of particles larger than 5 to 10 μm; as indicated in Figure 6 and many measurements of pneumatic aerosols,[5] aerosol particles smaller than this size range comprise a very significant fraction of the *primary aerosols* for most nebulizers at typical operating conditions and very often the major portion of *tertiary aerosols* reaching detectors, as indicated in Figure 8. Thus, the Nukiyama-Tanasawa equation (Equation 2) is not typically an accurate indicator of *absolute* particle sizes produced by nebulizers. The equation *is*, however, often useful for predicting *trends* for the effects on d_s of operating parameters or physical characteristics.

In order to consider the application of the Nukiyama-Tanasawa equation to thermospray, it is possible to predict the gas flow rate at any operating temperature to be the product of the fraction of liquid vaporized (f) at that temperature and the flow of gas that would result for 100% vaporization (Q_g), and the liquid flow rate at the outlet to be the product of $(1-f)$ and the input liquid flow.[18] This provides a new version of the Nukiyama-Tanasawa equation for thermospray as follows:

$$\mathbf{d}_s = 585\left[\frac{\sigma^{0.5}}{c'\rho^{0.5}}\right] + 597\left[\frac{\mu}{\rho\sigma^{0.5}}\right]^{0.45}\left[1000\frac{(1-f)Q_l}{fQ_g}\right]^{1.5} \quad (3)$$

The term c′ is the velocity difference between the liquid and gas flows as calculated by Equation 4,

$$c' = \frac{Q_l}{A}\left(\rho \Delta V_v - 1\right) \qquad (4)$$

where A is the cross-sectional area of the vaporizer and ΔV_v is the specific volume of vaporization, which for water at atmospheric pressure is 26.2 cm^3/g.

Comparison of the calculated results of this model with measured d_s values obtained from laser Fraunhofer diffraction is shown in Figure 9. The trends observed for the measured and calculated data are quite similar, although the experimental data are shifted to higher degrees of vaporization. These differences may result from the differences in the particle measurement procedures used by Nukiyama and Tanasawa vs. those used today, or more likely from imprecise knowledge of the degree of vaporization used for the x-axis of the measured data. It is possible that refinement of this model might provide a more accurate predictor for the thermospray process. A more satisfying model based solely on fundamental physical principles is not currently available for thermospray or pneumatic nebulization.

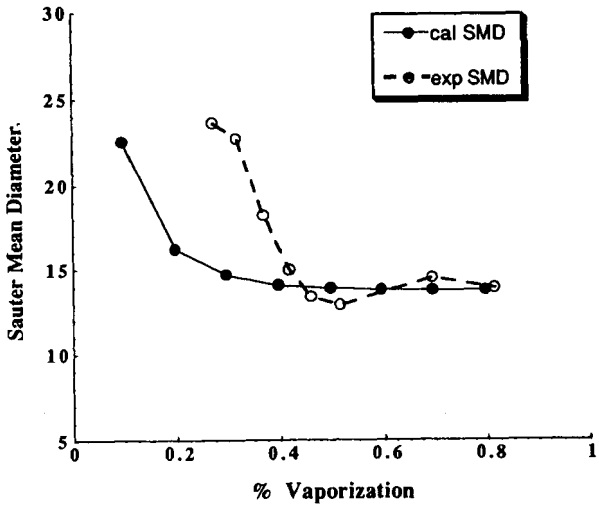


FIGURE 9. Sauter mean diameter (d_s) vs. degree of vaporization for thermospray measured using laser Fraunhofer diffraction (dashed line) and calculated using Equation 3 (solid line). (From M.S. thesis of D.H. Winn, Southern Illinois University, Carbondale, **1987**.)

Despite the limitations of this model for thermospray vaporization, it is possible to predict trends for the effects of changes in the physical construction and operation of thermospray vaporizers on the particle size characteristics of resultant aerosols. One significant effect predicted by this model is a reduction in particle size for decreasing capillary diameters. Although no direct measurements of *primary aerosols* produced by thermospray as a function of capillary diameter have been reported, it is important to note that improvements in sensitivity for both thermospray LC-MS[23] and thermospray ICP-AES[24] have been reported for decreasing exit capillary diameters. Furthermore, measurements of analyte mass in *tertiary aerosols* have demonstrated large increases in transport efficiency for smaller capillary diameters at fixed liquid flow rates, as indicated by Figure 8. These effects infer that decreasing capillary diameters indeed reduce the mean diameters of aerosol particles produced by thermospray.

C. Thermospray Aerosol Generation Methods

The primary basis for the generation of thermospray aerosols is the input of energy into a liquid capillary flow. This has been accomplished by a variety of means. The original work with thermospray by Vestal and co-workers used rapid heating with a CO_2 laser[25] or an oxy-hydrogen flame.[26] Although these techniques were somewhat successful, control of the vaporization process was poor, such that reproducibility and applicability to real analyses were less than adequate. Most, if not all, current thermospray work is conducted using capillary tubes that are heated electrothermally. Within this class of systems, heating of the capillary is performed by either direct or indirect means. The indirect process is generally conducted by the use of cartridge heaters imbedded in a large mass heating block. This approach has the advantage of providing more gradual heating and vaporization of the solvent than the laser or flame methods described above. As a result, much greater reproducibility and stability were obtained, as particularly observed with LC-MS experiments.[4]

The most common method currently available for generating thermospray involves the direct electrothermal heating of the capillary through which the liquid sample flows. In this case, the length of capillary heated is, in general, significantly longer than that for the indirect electrothermal method; therefore, the heating process is even more gradual than all of the methods described above. The more gradual heating appears to provide much greater control and stability to the degree of vaporization. As this factor directly determines the characteristics of the aerosols produced, it is clear that such control should lead to enhanced stability of signals with detectors used with thermospray, and therefore improved analytical performance. Stable control of the degree of vaporization also is likely to minimize the possibility for capillary clogging via deposition of nonvolatiles, especially for LC-MS experiments where the degree of vaporization is often set to be 95% or more.

Direct heating also allows for the adequate use of feedback control of the vaporizer temperature(s). If the response of the control circuitry is sufficiently fast, feedback provides a means of compensating for slight variations in the liquid flow rate. As the capillaries employed for thermospray typically have sufficiently small internal diameters (≤150 μm) that high pressure is required for maintenance of liquid flow rates employed for appropriate analytical experiments (0.5 to 2 ml/min), high-pressure pumps of the type employed for HPLC are generally required for liquid flow metering. As these pumps are usually reciprocating piston types that do exhibit flow pulsations, such compensation for flow variations is desirable. Vestal and Fergusson have described a triac-controlled system that is commonly employed for many current thermospray experiments.[27]

For the most part, capillaries used for thermospray generation are often 1.6-mm outer diameter stainless steel tubes of appropriate inner diameter. Fused silica capillaries also are used by some workers. With fused silica capillaries, the heating process is less direct, as the fused silica tube is inserted into a stainless steel tube or heater block that is directly heated. An advantage to fused silica capillaries is their chemical resistance to samples and mobile phases containing halides, which corrode stainless steel.

The model for thermospray aerosol generation described earlier suggested that one means of reducing particle size with thermospray aerosols would be to reduce the internal diameter of the capillary employed. One way to do this with either stainless steel or fused silica is simply to choose smaller internal diameter capillaries. However, if sample/mobile phase flow rates on the order of 1 ml/min are to be employed, the pressures required are excessive for significant lengths of capillary with internal diameter less than about 75 μm. It is subsequently possible to split off or reduce the sample flow; however, as detectors such as ICPs and mass spectrometers are mass sensitive, the reduction in mass input may offset any gains in particle size that might be achieved with smaller diameters.

In order to overcome this seemingly insurmountable compromise, it has been demonstrated that only the exit diameter for the capillary needs to be reduced to improve performance.[24] A simple way to do this is to crimp the exit of a standard capillary partially closed. This procedure is quite difficult considering the small internal dimensions involved. Alternatively, sapphire jewel[23] and laser-drilled steel disk[24] apertures have been mounted to the exit of standard capillaries. Enhanced performance with thermospray ICP-AES[24] and often with LC-MS[23] has been demonstrated with apertures as small as 25 μm. More recently, a similar approach with fused silica capillaries was demonstrated where short lengths of small internal diameter fused silica were laser-fused to the exit of larger diameter capillaries.[28]

IV. THERMOSPRAY LC-MS

Before discussing the use of thermospray with atomic spectrometry, it will be useful to briefly describe the ways it is used for coupling HPLC to MS: (1) thermospray aerosols are sprayed into a vacuum chamber where ions may be formed by one of a variety of processes; and (2) thermospray aerosols are generated at atmospheric pressure for use in particle beam interfacing.

A. Thermospray Ionization

As indicated earlier, thermospray was originally developed by Vestal et al.[25–27] as a means of interfacing liquid chromatography to mass spectrometry and was the first highly successful and widely used LC-MS method. Thermospray LC-MS has found wide application, particularly in the areas of biochemical, biomedical, and biotechnological science.[4]

The primary goal of interfacing techniques for liquid chromatography to mass spectrometry is to efficiently remove the mobile phase from the analyte prior to the main vacuum system of the mass spectrometer. The reason for this lies with the fact that vaporization of the 1 to 2 ml/min of mobile phase would result in a volumetric flow of greater than 1 to 2×10^3 atm ml/min, or over 3 orders of magnitude higher molecular flow than would be provided by a capillary gas chromatography experiment. Although vacuum pumps for mass spectrometers can accommodate the flow of a gas chromatograph, the flow from a liquid chromatograph would overwhelm even the largest vacuum systems typically available with MS, resulting in unacceptably high pressures within the MS. Aerosol techniques overcome this problem because mobile phases in LC are typically more volatile than are analytes, and aerosols provide a means of preferentially volatilizing the mobile phase prior to the main part of the MS vacuum system. The solvent vapors can be subsequently removed from the analyte by one of a variety of methods before reaching the main vacuum chambers of the mass spectrometer.

The first successful LC-MS system based on thermospray involved the direct spraying of thermospray aerosols into a preliminary vacuum chamber pumped by a mechanical pump.[25] Part of the material within this chamber was extracted into the MS through a skimmer cone located downstream from the thermospray aerosol plume. A major discovery of early work was that with mobile phases containing ammonium acetate and with the vaporizer operating with about 95% vaporization, ions for certain species are formed directly during this process.[26] The ionization is thought to result from the fact that aerosol formation with solutions containing dissolved ions gives rise to particles that have a high probability of having excess charge based on the rapid separation of the droplet from the bulk liquid. The distribution of charge among the population of droplets is Gaussian. Solvent evaporation of these charged liquid droplets leads to increasingly high electric fields that are thought to give rise to ion production by ion evaporation, the process considered to be primarily involved with direct ion formation with thermospray.[4] The primary ions produced by thermospray may be subsequently modified by ion molecule reactions occurring within the gas phase, giving rise to the ions collected and measured by the mass spectrometer. Both positive and negative ions are formed and the choice of ion polarity to monitor is a significant function of the type of molecule under study. In general, the predominant ions formed by the direct thermospray ionization process are protonated or deprotonated molecular ions [MH^+ or $(M\text{-}H^+)^-$], or molecular adduct ions (e.g., MNH_4^+ or MH_3O^+) and thus provide a means for the determination of analyte molecular weights.

Since the direct thermospray process is not universal as an ionization means, an electron beam and/or Townsend discharge also are common within thermospray interfaces as methods to promote chemical ionization (CI) of molecules that are not directly amenable to thermospray ionization. As with other CI methods, fragmentation of molecular ions is generally low and thus structural information derived from mass spectra generated in these modified modes of thermospray operation is often minimal. A major strength of thermospray LC-MS appears to be the ability to determine the molecular weight of many types of molecules. However, identification of species is limited by the lack of structural information resulting from the minimal fragmentation generally obtained.

B. Thermospray Particle Beam Methods

An alternative to the thermospray interfacing/ionization methods for LC-MS are the so-called particle beam techniques.[29] With these techniques, aerosols also are used to provide a means for efficient vaporization of mobile phase solvent.

If the solvent vaporization is complete, the liquid aerosol flow will have been converted to a flow of solvent vapor, and dry particles will be comprised of the less volatile species, which generally include the analyte. These particles can be focused to a beam and separated from solvent vapor and carrier gas within a momentum separator. The principles of the momentum separator are identical to those employed with jet separators for GC-MS (gas chromatography-mass spectrometry), except that the momentum differences with the particle beam are much larger and therefore this approach can be much more efficient. Once the gas phase species have been removed, the particles are injected to the ion source of the mass spectrometer where flash vaporization and ionization can occur. A major advantage to this approach for LC-MS is that electron impact ionization (EI) can be used, allowing the fragmentation, structural information, and qualitative identification that EI provides.

As one means of aerosol formation, thermospray can be employed for the first step in the particle beam process, and the application of thermospray for this purpose has been developed.[29a] However, at this point it is uncertain whether or not thermospray is a particularly advantageous aerosol source for this technique.

V. THERMOSPRAY SAMPLE INTRODUCTION TO INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

The primary motive for employing a different aerosol source, such as thermospray, for sample introduction to atomic spectrometry is to improve the analytical figures of merit for the technique. With ICP-AES, sensitivity and LODs are of primary interest. In this section, we review the data that are currently available regarding the analytical performance of thermospray with ICP-AES and highlight factors of importance to the operation of thermospray systems that influence performance.

A. Sensitivity and Limits of Detection

Invariably, studies of the use of thermospray sample introduction to ICP-AES have demonstrated improvements in sensitivity and LODs. The specific levels of improvement for these characteristics vary substantially from one experiment to another, however. Factors that influence sensitivity and LODs include thermospray operating temperature, thermospray capillary diameter, spray chamber temperature, and sample flow rate.

1. Thermospray Operating Temperature

With any thermospray apparatus, one of the primary operating parameters to routinely optimize is the vaporizer temperature, which controls the degree of solvent vaporization. Figure 6 revealed that increasing the operating temperature of a thermospray vaporizer will shift the aerosol particle size distribution to smaller sizes. In addition, it was indicated earlier that an aerosol spray chamber acts as a particle filter with a specific cut-off diameter. It follows then that increasing the temperature of a thermospray vaporizer will increase the fraction of analyte transported to the ICP and also increase the signal produced, by increasing the fraction of analyte in particles below the cut-off diameter of the spray chamber. The typical trend to signal and analyte transport vs. thermospray temperature is indicated in Figure 10. Signal and analyte transport increase, reach

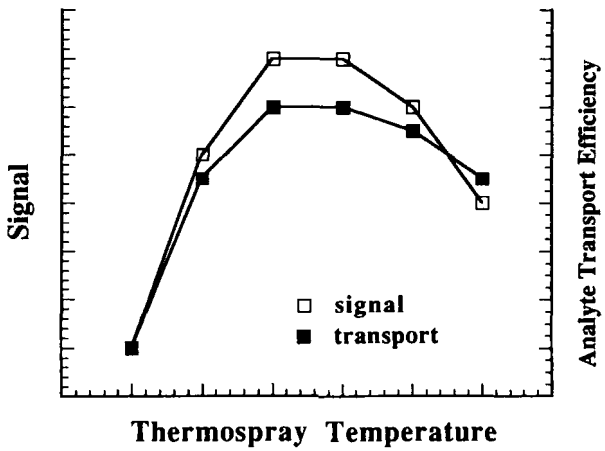


FIGURE 10. Signal and analyte transport as a function of thermospray operating temperature.

a maximum, and subsequently decline. It has been estimated that the degree of vaporization at which the optimum occurs is typically 50 to 60%.[18] Although smaller particles will be produced at higher temperatures (and percent vaporizations), analyte transport is attenuated. Thermospray systems employed for particle beam LC-MS experiments provide optimal operation with fractions vaporized comparable to those for ICP spectrometry.[20] Interestingly, optimum conditions for thermospray ionization LC-MS occur with nearly complete solvent evaporation.[4]

One reason for the attenuated analyte transport at higher vaporization fractions with ICP experiments that has been suggested is that at higher degrees of vaporization, analyte deposition within the vaporizer occurs.[18] Another possibility is that under these conditions, the extent of particle charging increases, resulting in more analyte losses due to electrostatic effects.[20] Since particle charging is a *necessity* for thermospray ionization LC-MS and mass spectrometers are designed to handle charged particles, this might partially explain the difference in optimal operation for each experiment. In addition, particle losses due to diffusion, which increases as particle size decreases, might also increase if particle sizes become *too small.*

One factor affecting the absolute value for the optimum temperature for any thermospray system is the solvent composition of the liquid stream. Clearly, volatile solvents will require lower absolute temperatures to reach the same degree of vaporization.[18] Furthermore, more volatile solvents will have higher vapor pressures and will lead to higher solvent loading within the plasma, perhaps resulting in reduced plasma excitation conditions.[30] Consequently, without also providing for adequate solvent removal, optimum thermospray conditions might be compromised to those providing reduced plasma solvent loading.

Another consideration with regard to thermospray temperature optima is that absolute values *are not necessarily* comparable from one design to another. This results from the fact that the temperature measurement position relative to the aerosol itself and the heat transfer characteristics of the devices vary significantly for the designs reported to date. Small variations in temperature characteristics may even occur between different vaporizers of the same design. However, the trends as indicated above *are* universally observed with the systems reported to date.

2. Aerosol Spray Chamber Temperature and Desolvation

There are basically two trains of thought regarding the operating temperature of the chamber into which the aerosol is sprayed. The first considers that ICP temperatures are lowered by excess solvent, leading to decreased excitation and compromised performance. As thermospray systems also can transport solvent efficiently, particularly as vapor, such sample introduction can significantly cause these effects. One way to reduce solvent vapor loading is to cool the spray chamber to enhance condensation prior to the ICP.

The second approach to the control of spray chamber temperature is to consider that thermospray aerosols are formed at temperatures and pressures well above ambient. The thermospray jet thus cools during adiabatic expansion, leading to supersaturation of the gas phase with solvent vapor. This solvent can easily recondense on particles, leading to undesirable particle growth and large particle losses during the initial, turbulent stage of the aerosol interfacing. This process can be opposed if sufficient heat is added to the spray chamber. The solvent vapor can subsequently be removed by a condenser after dissipation of the turbulence. This approach also reduces solvent loading to the ICP to avoid plasma temperature reduction.

Ambient temperature (i.e., comparable to conventional systems employed with pneumatic nebulizers) or cooled spray chambers have been adapted for use with thermospray by a variety of workers with reasonable success. Meyer et al., in the first report of the study of thermospray with ICP-AES, found LODs with a thermospray system improved by two to six times relative to pneumatic sample introduction with both nebulizers using the same spray chamber without

temperature control.[31] A conventional 150-μm internal diameter (i.d.) thermospray vaporizer was used in these studies. One difference between the operation of the two nebulizers was that the sample flow rate was 1.0 ml/min with the pneumatic nebulizer, while this flow was limited to 0.5 ml/min with thermospray. The first work of Elgersma and Maessen employed a standard double-pass spray chamber at ambient temperature with a 25-μm i.d. fused silica capillary thermospray vaporizer.[32] Despite operating with only 0.12-ml/min sample flow rate, LODs obtained with the thermospray system were nearly identical to those obtained with a pneumatic sample introduction system operating with 15 times the sample flow (1.8 ml/min).

The first work by Vermeiren et al. with thermospray ICP-AES involved the use of a 180-μm i.d. vaporizer with a water-cooled spray chamber and found LODs improved by a factor of 5 on average compared to pneumatic sample introduction for the 14 elements studied.[33] Work by de Loos-Vollebregt has consistently been performed using spray chambers cooled to between 14 and 20°C; the studies revealed LODs better than those for pneumatic sample introduction by a factor of 2 to 5, despite operating at substantially lower sample flow rates (0.3 to 0.6 ml/min) than the comparative pneumatic system (≥ 1 ml/min).[34–35] However, despite the use of a cooled spray chamber for the reduction of solvent vapor loading, de Loos-Vollebregt reported that excitation temperatures for ICPs operating with their thermospray sample introduction system were only about 5700 K, compared to 6150 K with pneumatic sample introduction.[36] Furthermore, electron number densities were about 50% lower with the thermospray system. Clearly, a cooled spray chamber alone does not prevent solvent loading and reduced plasma excitation when thermospray sample introduction is employed.

The largest improvements in LODs have been reported when heated spray chambers were employed. Typically, the spray chamber is heated to between 100 and 150°C, which is comparable to temperatures used with desolvation systems for ultrasonic nebulization. Koropchak and Winn[37] reported the use of a 150-μm i.d. stainless steel capillary thermospray vaporizer inserted downward into a vertically oriented cylindrical spray chamber and found sensitivity improved by a factor of 2 when the spray chamber was heated to an outlet surface temperature of 110°C, compared to the unheated case. Overall, LOD reductions of up to a factor of 10 were reported for the elements studied, compared to pneumatic sample introduction operating at the same sample flow rate; part of the LOD improvement resulted from lower background noise. A later study showed that analyte transport efficiency increased from about 10% with an unheated spray chamber to over 20% when the spray chamber was heated with this sytem.[18] Even higher transport efficiences were later reported for improved vaporizers.

Another observation with the use of fully heated spray chambers with thermospray has been that lower aerosol carrier flow rates and viewing heights than are typical for pneumatic sample introduction have provided optimum response.[18,24,28,37] This contrasts with other thermospray reports. Maessen has reported similar observations for dry sample introduction to ICP-AES using electrothermal vaporization.[38] Long and Browner also reported that dry sample introduction to ICP-AES provides optimum response at lower viewing heights.[39] This suggests that aerosol desolvation is quite effective with these fully heated spray chamber thermospray systems.

Recently, Coetzee and Robinson[40] used a thermospray apparatus similar to that described by Koropchak and Winn.[37] With a 130-μm i.d. stainless steel vaporizer, 0.1 ml/min sample flow, and a spray chamber heated to 200°C, the authors claimed that sensitivities were improved by a factor of 8 compared to pneumatic sample introduction.

Vermeiren et al.[41] investigated the use of a completely heated spray chamber, but found the system to provide unstable performance. The rationale for this instability was that large droplets striking the spray chamber walls were flash vaporized, causing fluctuations in gas flow to the plasma. The large droplets in this case probably resulted from the fact that a vaporizer having a 180-μm i.d. was used in this case; as will be described, the appearance of these droplets is minimized with smaller diameter capillaries. Subsequently, they used a spray chamber of the type reported by Goulden and Anthony,[42] employing

an unheated portion surrounding the turbulent aerosol formation region, followed downstream by a heated region. A condenser for vapor removal followed. With this system, the sensitivity of ICP-AES with thermospray sample introduction was found to increase by a factor of about 2.5 with an increase in spray chamber temperature from 70 to 180°C. At the same time, analyte transport increased from about 4 to over 11%. For optimum stability, the temperature was maintained between 130 and 140°C. Overall, LODs reported were on average 15 times lower for the thermospray system than for pneumatic sample introduction.

Maessen and co-workers[43] recently also investigated the effect of spray chamber temperature with their fused silica capillary thermospray vaporizer, depicted in Figure 11. This system is conceptually similar to that employed by Vermeiren et al.[41] and differs from that of Koropchak and Winn[37] only in that the first few centimeters are not directly heated in this case. Using a 50-μm i.d. capillary and a sample flow rate of 0.4 ml/min, signals increased for most elements as the aerosol temperature, as monitored by the temperature control thermocouple, was increased from 60 to about 100°C. Using 100°C, LODs for 12 elements were 3 to 25 times better than those reported by Winge[44] for pneumatic sample introduction operating at a 1-ml/min sample flow. The absolute value of the optimum spray chamber temperature is probably lower here than in the other cases as surface temperature was measured in those cases, as opposed to the *aerosol* temperature monitored in this case.

All of these data demonstrate the importance of spray chamber temperature and desolvation on sensitivity performance with thermospray sample introduction. Performance better than pneumatic sample introduction can be obtained even without spray chamber heating. The work of de Loos-Vollebregt et al.,[36] however, clearly shows that efficient aerosol desolvation is required with thermospray sample introduction to avoid degradation of excitation conditions within the plasma. This is not surprising, as an aerosol system efficient at transporting analyte also will be efficient at transporting solvent unless some means for preferential solvent removal (desolvation) is employed. The solvent will, in part, be in aerosol form; since thermospray aerosols are at high temperatures, the saturation vapor pressure also will be higher than pneumatic sample introduction unless that temperature is reduced. The spray chamber temperature also will influence the fraction of analyte transported, with higher temperatures providing higher analyte transport and therefore higher signals as long as solvent is removed to avoid plasma loading. The largest improvements in LODs are observed when spray chamber

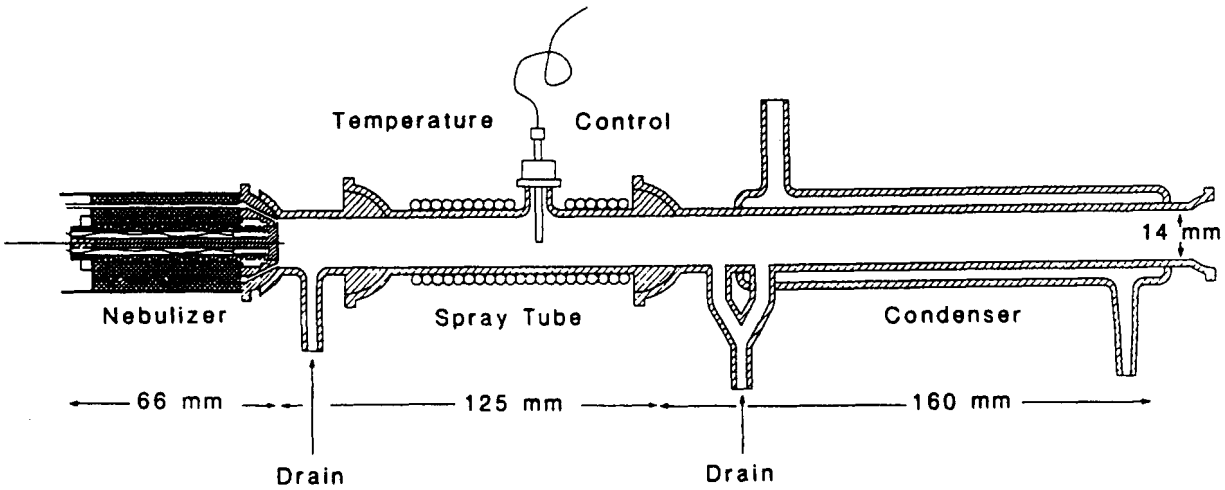


FIGURE 11. Spray chamber for thermospray with unheated initial region followed by heated region. (From Elgersma, J.W.; Balke, J.; Maessen, F.J.M.J. *Spectrochim. Acta.* **1991,** *46B,* 1073. With permission.)

heating and desolvation are employed with thermospray.

It also is likely that subtle aspects to the design of the spray chamber heating apparatus can affect the way the system operates. The work of Vermeiren et al.[41] and Maessen et al.[43] avoided heating the initial aerosol formation region, presumably due to concern for aerosol deposition and flash vaporization in this turbulent region. In our work, such deposition is not problematic, perhaps for one or more reasons: (1) the aerosol is introduced downward into a vertically oriented spray chamber, reducing any contribution from gravitational settling within the chamber; (2) the aerosol carrier is introduced concentrically, acting as a sheath flow boundary; and/or (3) with our optimal vaporizers, very large aerosol particles are visibly absent.

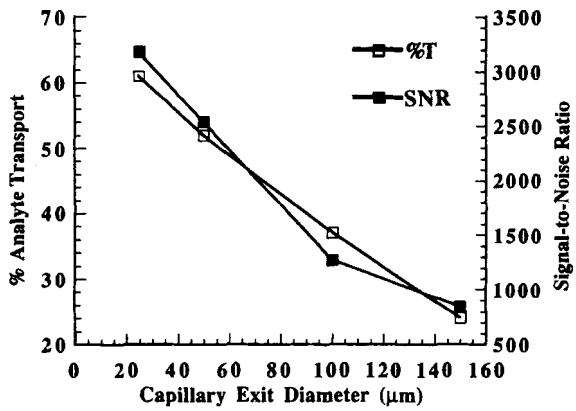


FIGURE 12. Analyte transport efficiency and SNR as a function of capillary exit diameter with stainless steel thermospray vaporizers; laser-drilled apertures for diameters less than 100 μm.

3. Capillary Diameter

The earlier discussion of aerosol formation processes with thermospray suggested that improved aerosol characteristics will be achieved when smaller capillary diameters are employed. Several studies have documented the influence of capillary diameter with thermospray ICP-AES. Koropchak and Aryamanya-Mugisha used varying diameter laser-drilled apertures affixed to the end of stainless steel vaporizers[45] as a means to study this; they found that both analyte transport and signal-to-noise ratio increased dramatically as the exit diameter of the capillary decreased[24] down to 25 μm, as shown in Figure 12, as predicted. For the smallest diameter capillaries, over 50% analyte transport was reported. Size distribution data determined using a cascade impactor showed that the improvements in transport and signals resulted from increases in analyte mass with aerosol particles less than 2 μm in diameter. In addition, the optimum operating temperature for the vaporizer also increased as the aperture diameter decreased. These results were confirmed by de Loos-Vollebregt et al.,[35] who studied capillary tubes of fixed internal diameter. Signal-to-background ratios for 0.4-ml/min sample flows increased dramatically as the capillary internal diameter was reduced in stages from 150 to 50 μm; optimum vaporizer temperatures also increased as diameter decreased.

More recently, similar results also have been reported by Koropchak and co-workers for a fused capillary system employing fused silica apertures for capillary exit size reduction.[28] Using a 50-μm exit aperture and a sample flow rate of 1.6 ml/min, sensitivities and LODs for the elements studied were 15 to 20 times lower than those obtained for pneumatic sample introduction. LOD improvements were derived solely from enhanced sensitivity; no reduction in background noise was observed during this study. In addition, improved response was observed for apertures down to 50 μm, but no further improvements were obtained for 25- or 20-μm apertures, suggesting that some aspect other than the nebulizer was the limiting factor to overall system response.

These results clearly indicate that smaller thermospray capillaries are preferred for best detection with ICP-AES and that only the exit diameter needs to be small. Although it might be suspected that plugging would be frequent with capillaries as small as 25 μm i.d., no reports to date have suggested so. In our laboratory, we have routinely observed that continuous sample introduction of even 10% dissolved solids does not lead to problems of capillary clogging if the vaporizer is operated at the optimal temperature. We find that capillary clogging is rare with rea-

sonably filtered samples and is usually an indication of another problem, such as operation at a vaporizer temperature above the optimum. This leads to a higher than optimum degree of vaporization and, apparently, deposition of dissolved solids within the capillary. For systems whose power input is fixed or temperature compensation is slow, variations or pulsation in sample flow also will cause temporal variations in the exit degree of vaporization and may lead to capillary clogging regardless of capillary diameter. A well pulse-dampened sample flow is therefore preferred for routine thermospray operation. For discrete sampling applications, an on-line filter beyond the sample injector is recommended, as particulates may be introduced to the flow stream due to mechanical wear within the injector. Interestingly, efforts in our lab to study stainless steel apertures smaller than 20 μm have been largely unsuccessful due to fairly rapid clogging.

4. Liquid Sample Flow Rate

With any sample introduction system and ICP-AES, the signal produced (S) can be expressed as

$$S = R \varepsilon_t F C \qquad (5)$$

where ε_t is the analyte transport efficiency, F is the sample flow rate, C is the analyte concentration, and R, the responsivity, is the accumulation of factors that affect the signal produced per unit mass analyte. Factors that may affect R include instrumental aspects, plasma operating conditions, and plasma excitation conditions, which may be affected by factors such as solvent loading as indicated above or particle size.[46,47] If we assume that R is constant, the signal per unit concentration (i.e., the slope of the calibration curve or sensitivity) will depend on the product of ε_t and F. Sample introduction systems that operate with high transport efficiency at high sample flow rates without degrading R will provide the highest sensitivity.

Thermospray systems have been shown to provide high analyte transport efficiencies. Several reports have included the effects of sample flow rate. Koropchak and Winn reported that the signal for their system with a 150 μm capillary increased linearly from 1 to 1.5 ml/min, while higher flow rates up to 3 ml/min resulted in a gradual decrease in response.[18] Higher operating temperatures were required to optimize the signal at higher flow rates. Similar results were reported by de Loos-Vollebregt for a wide range of capillary diameters, except that measurements with smaller diameter capillaries (e.g., 50 μm) were limited to about 0.4 ml/min.[35] Elgersma et al.[43] also observed substantial signal increases as the analyte flow rate to their 50-μm fused silica capillary was increased from 0.12 to 0.4 ml/min. With a fused silica aperture (50 μm) thermospray system, it was observed that optimized signals increased from 0.8 to 2.2 ml/min; at higher sample flow rates, insufficient power was available from the power supply employed with this configuration to adequately vaporize the higher liquid mass fluxes.[28] The stability of signals also declined at the higher flow rates.

All of these studies show that thermospray systems provide higher signals at higher sample flow rates. Several factors can act to limit the flow rates that can be employed. First, efficient analyte transport at high sample flow rates also means high solvent transport, which will degrade R unless efficient desolvation is employed. Secondly, higher sample flow rates require more energy to reach the optimum degree of vaporization. In principle, there is no limit to the sample flow rate that is possible, as long as sufficiently large power supplies are available and appropriate heat transfer and vaporization rates can be achieved. The last consideration concerns the operating pressure of the sample supplying pump. For any selected flow rate, the pressure required to pump that flow is determined by the open cross-sectional area of the capillary and the length of that capillary. To use the smaller-diameter capillaries, which are most efficient, pressures exceeding the limits of most HPLC-type pumps would be required to pump milliliters per minute-level flows if the capillaries are greater than perhaps a few centimeters in length. In our laboratory, we have approached the latter problem by designing capillary systems having relatively large diameters (~150 μm) through most of the capillary length but having short limiting apertures (≤1

mm, or so) at the capillary exit. For example, the operating pressure of our fused silica aperture system with a 50-μm exit diameter was only 2.7 MPa (~400 psi) at an operating liquid flow rate of 1.6 ml/min.[28]

To summarize the effects of various operating parameters on sensitivity and LODs, Table 1 lists LODs for thermospray sample introduction to ICP-AES reported by various authors under a wide range of conditions.

B. Matrix and Dissolved Solids Effects

Matrix effects with thermospray sample introduction have been studied by several workers, and some general conclusions are that matrix effects are usually larger for thermospray sample introduction than for pneumatic sample introduction,[28,36,41,43,48] and matrix effects for thermospray systems employing desolvation increase as spray chamber (desolvation) temperatures increase.[41,43] Furthermore, when thermospray has been used with desolvation, most descriptions of interelement matrix effects have reported signal depressions.[28,41,43,48] Vandecasteele reported signal reductions of approximately 30% with 3000 μg/ml of Ca or Na nitrates.[48] With 10,000 μg/ml K matrices, Maessen reported that Mn signals were reduced by 20% at low spray chamber temperatures, but by 40% at high temperatures.[43] Maessen indicated that for the selection of spray chamber temperature, a compromise between optimum sensitivity and reduced matrix effects must be pursued.[43] When thermospray has been used with a cooled spray chamber, signal enhancements for Cd atom and ion lines were reported in the presence of easily ionized elements.[36] Signal depressions were observed for up to 8% levels of mineral acids with both thermospray and pneumatic sample introduction at comparable levels, except that the matrix effect from $HClO_4$ was lower for thermospray.[36] To reduce matrix effects with thermospray, de Loos-Vollebregt also investigated the use of end-on observation with a horizontally oriented ICP; however, this approach was not successful in reducing matrix effects.[34]

Matrix effects on analyte signal intensity with ICP-AES may arise from factors affecting the analyte transport rate to the plasma and/or from phenomena influencing the responsivity of the analyte within the plasma. A clear understanding of the latter *plasma effects* has not been established; with ICP-AES, almost all dissolved solids are known to give rise to signal depressions.[49] As thermospray systems transport higher fractions of the matrix as well as analyte to the plasma, it follows that such plasma effects should be higher with thermospray. Vermeiren has described the transport effects with thermospray as resulting from the fact that, with desolvation, the eventual dry particle size distribution increases with the dissolved solids content; as the transport also is size dependent, high dissolved solids can reduce transport.[41] The same authors provided data where the percent ε_t in the presence of 0.02 *M* $NaNO_3$ decreased from ~11 to 8% as the spray chamber temperature was increased. Electron micrographs of collected aerosols clearly indicated the increased particle sizes in the presence of the high dissolved solids.

Matrix effects were studied with the fused silica aperture thermospray system and it was observed that the use of a smaller diameter aperture could reduce the level of interference from Na.[28] In a more detailed study, it was shown that transport effects could be substantially reduced by operating the vaporizer at a somewhat higher temperature than would be chosen for dilute solutions.[50] The percent reduction in analyte transport due to 2000 μg/ml Ca was lowered from 28% (or about that reported by Vermeiren, as above) to 5% using the higher temperature. Both reduction in capillary diameter and operation at higher temperature would be predicted to reduce primary particle size; smaller initial sizes would be less subject to transport losses due to matrix composition. These observations indicate that the bulk of matrix interferences with thermospray results from plasma effects derived from adding large amounts of the matrix to the plasma.

In the same study, it was observed that plasma effects could be reduced by careful adjustment of the aerosol carrier gas flow rate, although optimum flows varied from element to element; and for simultaneous multielement analysis, a compromise flow was chosen.[50] With the compromise conditions, LODs for a wide range of elements were increased in the presence of 3000 μg/ml Ca, but were on average within a factor of 1.7 of those

TABLE 1
Representative LODs (ng/ml) Reported by Various Groups for Thermospray Sample Introduction to ICP-AES

		LOD				
Element	λ (nm)	Ref. 35[a]	Ref. 31[b]	Ref. 43[c]	Ref. 41[d]	Ref. 28 and 50[e]
Sn	189.93		20			
As	193.69					11
Se	196.02					18
Mo	202.03		30			
Cr	205.55	4.2				
Zn	213.86	0.7			0.2	
Cd	214.44	1.4				0.11
Pb	220.35	17	70	2	5	2.4
Ni	221.65	3.0				
Bi	223.06	16				
Cd	226.50		3			0.32
Co	228.61		5		0.8	
Cd	228.80				0.3	
In	230.61	18				
Ni	231.60		10			
Ba	233.53		3			
Fe	238.20	3.3				
Ag	328.07	0.8			0.5	0.40
Co	238.89	2.7				
B	249.77	1.5				
Mn	257.61	0.4	1	0.3		
Fe	259.94		10			
Cr	267.72		10			0.30
Tl	276.79	49				9.5
Mg	279.55		1			
Mg	280.27			0.1		
Pb	283.31			23		
V	292.40		4			
Ga	294.36	39				
Bi	306.77		300			
Al	308.22		90	2		
Al	309.27	30				
Be	313.04	0.08	0.5			
Ca	315.89		20			
Cu	324.75	1.2		0.7	0.4	0.34
Ti	334.94		1			
Al	396.15				1.1	
Sr	407.77	0.05	1			
La	408.67			0.6		
Ce	418.66			5		
Nd	430.36			6		
Sm	442.43			3		
Ba	455.40	0.10		0.4		
Na	589.00			11		
Li	670.78			0.4		

[a] Cooled spray chamber (14°C), 50-μm i.d. fused silica vaporizer, 0.3-ml/min continuous sample flow rate.
[b] Room-temperature spray chamber, 150-μm i.d. s.s. vaporizer, 0.5-ml/min continuous sample flow rate, 3σ.
[c] Heated spray chamber (100°C aerosol), 50-μm i.d. fused silica vaporizer, 0.4- ml/min continuous sample flow, 3σ.
[d] Heated spray chamber (135°C), 180-μm i.d. s.s. vaporizer, 1.3-ml/min sample flow rate, 3σ.
[e] Heated spray chamber (145°C), 50-μm i.d. fused silica aperture vaporizer, 1.6-ml/min sample flow rate, 3σ.

obtained in the absence of Ca. Part of the LOD degradation resulted from higher background noise levels derived from higher background intensity levels in the presence of Ca. This approach of carrier flow and vaporizer temperature adjustment for minimization of matrix effects shows promise and is worth further investigation by other workers with different thermospray systems. It also is important to note that these studies were conducted using lower aerosol carrier flow rates and lower viewing heights indicative of dry aerosol introduction to the plasma, which may have substantially different general characteristics than those for measurements made in the normal analytical zone of ICP-AES with wet aerosols.

C. Other Figures of Merit and Considerations

Short- and long-term precision for measurements with thermospray sample introduction have been investigated and found to be comparable to those obtained with pneumatic sample introduction.[35] Furthermore, linear dynamic range has invariably been found to be essentially identical to that obtained with pneumatic sample introduction, except shifted to lower concentrations.

One practical consideration for thermospray is the effect of the composition of materials on performance. In this regard, blank contamination of Cr, Fe, and Mn from the use of stainless steel vaporizers has been reported.[41] The problem is worsened with samples containing halides, resulting from the corrosion of stainless steel by these species. Such problems are avoided by using fused silica vaporizers.

For conventional analyses using pneumatic sample introduction with ICP-AES, samples are generally pumped continuously into the nebulizer using a peristaltic pump. Sample turnaround is then determined as the time required to flush the flow and aerosol systems of analyte such that signal returns to baseline. Flow volumes in this case are small enough to result in fairly rapid sample turnaround. With thermospray, the sample must be pumped at high pressure through the vaporizer, invariably using an HPLC pump. To pump a sample continuously with thermospray, early studies involved placing the sample in the solvent reservoir for the pump. Unfortunately, these pumps have large volumes to flush, providing long sample turnaround times. To overcome this, most workers now use a flow injection approach. With large sample loops (e.g., 5 ml), this also has proven effective for rapid sequential multielement analysis.[28,41]

VI. THERMOSPRAY WITH OTHER ATOMIC SPECTROMETRIES

ICP spectrometric methods are perhaps the most inviting candidates for improvements in sample introduction since pneumatic sample introduction systems are particularly inefficient based on the limitations in injector gas flow rates imposed by the ICP. In principle, the same sensitivity advantages for ICP-AES should be obtained with ICP-MS. Several studies have investigated the use of thermospray with ICP-MS.

In the original paper describing the use of thermospray with ICPs, Meyer also employed a low-volume spray chamber to interface thermospray with ICP-MS.[31] Limited experiments indicated sensitivities for Cs and Tb that were 1.5 times those provided with pneumatic sample introduction, despite lower sample flows for thermospray (0.5 ml/min) vs. for pneumatic (1.0 ml/min).

In a recent study, Montaser compared the use of a thermospray sample introduction system having a membrane desolvation apparatus to ultrasonic nebulization with cryogenic desolvation, and pneumatic sample introduction with and without desolvation.[51] The membrane desolvation apparatus was one developed by Vestal for use with particle beam LC-MS.[52] The thermospray system utilized a 75-μm exit aperture for most of the studies; a smaller vaporizer tip provided higher sensitivity but unstable performance with this system. The authors reported LODs that were up to 60 times lower than those obtained for pneumatic sample introduction without desolvation, and up to 20 times lower than those for pneumatic sample introduction with desolvation. Undesirable oxide levels were lowest with the thermospray system using membrane desolvation. LODs for

the thermospray system and the ultrasonic system were within about a factor of 2 for all but 2 of the 12 comparative elements in this study — which were lower by 5 times for the ultrasonic system. It is likely that any differences in oxide levels and sensitivity between the thermospray and ultrasonic systems were primarily derived from the different desolvation systems used for each.

Nebulizers for flame atomic absorption operate at much higher gas flows than do nebulizers for ICPs, and have been found to be about 10% efficient at transferring sample to the flame, even with sample flows approaching 5 ml/min.[6] Consequently, any gain from the use of thermospray sample introduction with FAA would be expected to be lower than those observed with ICP methods. However, Choi and Robinson have reported LODs about 10 times better using a thermospray sample introduction system than with pneumatic sample introduction.[53]

Thermospray has also been investigated for use with GFAAS. Bank et al., provided a preliminary report on the development of instrumentation to periodically introduce thermospray aerosols into a graphite furnace.[54] Timing of the aerosol introduction coincided with flow injected 10-µl samples. The thermospray vaporizer was then withdrawn and the furnace temperatures were cycled in typical fashion. Signals comparable to conventional GFAAS were observed.

VII. APPLICATIONS OF THERMOSPRAY SAMPLE INTRODUCTION TO ATOMIC SPECTROMETRY

A. Environmental Analysis

One of the major advantages of thermospray for sample introduction to atomic spectrometry is the greater analyte transport efficiency at moderately high sample flow rates that can be obtained, leading to increased sensitivity and improved LODs. Measurements of metals in environmental samples often require lower LODs than can be obtained directly, especially with FAA and ICP-AES.

Vandecasteele et al. applied thermospray sample introduction to the determination of trace Cd, Pb, Cu, and Zn in natural waters with ICP-AES detection.[48] The overall method included preconcentration using a Chelex-100 column to provide preliminary enrichment factors of 30 times. LODs determined for the overall method were 0.02 ng/ml for Cd, 0.03 ng/ml for Cu and Zn, and 0.3 ng/ml for Pb. The metals in samples from several Belgian rivers were successfully determined using this method.

Koropchak and Roychowdhury used thermospray with ICP-AES to measure Cr in aerosols produced by an electroplating facility.[55] In this case, the aerosols were collected using a cascade impactor to determine the distribution of chromium species as a function of particle size. The chromium was further separated into various chemical forms using a reverse-phase liquid chromatographic process prior to analysis. As the chromium in the aerosol phase was rather low in concentration and the procedure involved separation of that chromium as a function of size and species, the added detection provided with thermospray reduced sample collection times by an amount corresponding to the LOD enhancement, a factor of 24 in this case. It was thought that the reduced sampling time also reduced the chance for alteration in the distribution of chromium among vairous oxidation states.

For analyses that are subject to regulatory agencies, such as the Environmental Protection Agency (EPA), methods employed must meet established criteria, especially with regard to LODs for EPA's Contract Laboratory Program. In many such analyses, ICP-AES is used for the simultaneous multielement analysis of most of the required 20 or so elements; while labor intensive, single element methods, such as graphite furnace atomic absorption, must be used for more difficult elements such as Pb, Tl, Cd, Se, and As. Recently, fused silica aperture thermospray was described for the analysis of samples derived the EPA's Toxicity Characteristic Leaching Procedure (TCLP) from concrete stabilized hazardous waste.[50] These samples typically contain large concentrations of Ca. LODs obtained for analytes in the presence of 1000 to 3000 µg/ml Ca were all below U.S. EPA required limits, while pneumatic sample introduction provided inadequate detection for half the key elements tested.

Comparison of LODs obtained for this sample intoduction system with and without Ca are listed in Table 2 with comparison to EPA required levels.

B. Discrete Sampling Methods: FIA and HPLC

With discrete sampling methods, a small volume portion of a sample is injected into a flow stream for subsequent analysis, reaction and detection, or separation of components with a chromatographic column. Several effects can limit the performance of these techniques — especially for trace analysis. First, dispersion of sample signals can occur if the sample flows through extraneous volume within the flow system. This results from the fact that these volumes typically experience laminar flow, as represented by a parabolic velocity distribution across the flow channel. Sample molecules evenly distributed across the channel attain different velocities, spreading and temporally diluting the band. This process is called *convective dispersion.* In addition, for LC separations, dispersion takes place on-column and the injected sample may be separated into several species, each of which must be of lower concentration than the total element concentration in the sample. Due to these factors, LODs for injected samples with FIA or HPLC are invariably much higher than they are for continuous sample introduction, and often inadequate. The sensitivity advantages of thermospray can offset the sensitivity losses inherent with discrete sampling methods. In addition, themospray techniques generally employ very low liquid flow volumes in a properly designed system, as small diameter capillaries are used. This minimizes dispersion which may occur within the liquid phase of the sample introduction system. Finally, it has recently been shown that once a discrete sample is converted to an aerosol, dispersion is much lower on a volume-to-volume basis compared to extra-column volume in the liquid phase.[56]

1. FIA

Many workers have preferred to emphasize using flow injection of samples with thermospray sample introduction to atomic spectrometry. In

TABLE 2
LOD (ng/ml) in the Presence of Calcium[a]

		Ca concentration (μg/ml)							
		0		1000		2000		3000	
	EPA req'd[d]	PN	FSApT	PN	FSApT	PN	FSApT	PN	FSApT
Ag	72	11	0.66	15	0.73	11	0.98	9.3	0.91
As	55	450	11	390	13	500	17	580	15
Cd[b]	66		0.11		0.20		0.26		0.28
Cd[c]	66	13	0.38	11	0.55	15	0.58	13	0.64
Cr	73	3.4	0.32	5.7	0.53	4.3	0.44	4.6	0.52
Cu	1300	7.7	0.42	7.7	0.63	4.7	0.60	5.6	0.51
Pb	21	61	3.0	116	5.3	110	6.3	167	7.9
Se	160	400	18	510	19	510	17	470	21
Tl	78	100	9.5	100	24	135	22	100	20

[a] All solutions in 1% HNO_3.
[b] Measurements at 214.4 nm.
[c] Measurements at 226.5 nm.
[d] Lowest values for several waste codes, current or proposed; from U.S. Code of Federal Register 40 CFR, paragraphs 268.41 and 268.43; and U.S. Federal Register, Volume 56, FR 41163, August 19, 1991.

From Veber, M.; Koropchak, J.A.; Conver, T.S.; Herries, J. *Appl. Spectrosc.* **1992,** *46,* 1525. With permission.

part, this interest has derived from the relative ease in conducting flow injection with the high-pressure pumps required for thermospray aerosol generation vs. continuous sample introduction.

Several workers have carefully evaluated the use of thermospray sample introduction with flow injection analysis to ICP-AES. Laborda et al. studied dispersion in a flow injection mode with their thermospray sample introduction system and found post-injector dispersion to be small.[57] Elgersma et al. determined the volume variance for their system, as measured by the square of the half-width at 0.607 of the peak height; they concluded that the variance due to their thermospray system plus the ICP detector was about 4.5 μl^2 and quite small.[43] With 1-µl sample injections, signal-to-background ratios were as much as 5 times lower than for continuous sample introduction with thermospray sample introduction. Background relative standard deviations were higher due to limitations of the sample injector used in the 1-µl sample flow injection case such that concentration LODs were substantially higher than the continuous thermospray sample introduction case. Dispersion factors (D) were also measured. For a 120-µl/min flow rate, D was 1 with a 20-µl sample volume; that is, this volume provided a signal equal to that for continuous sample introduction at this flow rate. With a flow rate of 400 µl/min with their system, a sample volume of 80 µl gave a D of 1. However, peak signals increased for the sample volumes under study as the sample flow rate increased. Using the higher flow and sample volume, LODs of 3 to 25 times better than pneumatic sample introduction were obtained, despite background relative standard deviations, which were 3 to 4 times higher due to the injector.

In this laboratory, we have used thermospray in an FIA mode for the routine analysis of many different sample types to include wines for trace Pb determinations, bacterial culture media, natural waters, and digests of standard reference materials, paint chips, soils, bacterial centrifugates, etc.

2. HPLC-Atomic Spectrometry for Metal Speciation Studies

In many environments, metals can exist in a variety of chemical forms having different chemical properties. Study of the distribution of these chemical forms, or metal speciation, as opposed to determination of total metal concentrations, is a significant analytical challenge in many cases. One approach to this type of analysis that has been of substantial interest is to separate the species using LC, followed by selective metal detection using an atomic spectrometer. However, on-column and extra-column dispersion will significantly dilute the sample concentration, and each species will have a lower concentration than the total concentration. Consequently, injected concentration LODs for this approach will be substantially higher than those that can be attained with continuous sample introduction, and often above those required. In addition, preconcentration can distort the true distribution of species in many cases. As a result, techniques such as thermospray, which can dramatically improve sensitivity, can be particularly beneficial for coupling HPLC with an atomic spectrometer for metal speciation studies.

Koropchak and Winn described the use of reverse-phase ion pairing chromatographic separation of organotin compounds.[58] With a 150-µm i.d. thermospray vaporizer and sample introduction to ICP-AES, LODs for three tin species were 10 times lower than those obtained with pneumatic sample introduction.

Roychowdhury and Koropchak characterized their thermospray sample introduction system with a variety of elements and various species separated by several different LC techniques.[59] LODs for Cr species separated by ion chromatography or mobile phase ion-pairing chromatography were improved by factors of 24 or 36, respectively, for 50- and 25-µm aperture thermospray systems, as compared to pneumatic sample introduction. Values reported were even better than those reported for detection with ICP-MS.[60] Figure 13 compares chromatograms obtained with a thermospray and a pneumatic sample introduction system. For arsenic species separated by ion chromatography, relative response factors were improved by amounts comparable to those for chromium. However, for arsenite and dimethyl-arsinic acid, response for pneumatic and thermospray sample introduction was comparable. Thermal decomposition and subsequent vapor trapping within the desolvation system were thought to degrade the

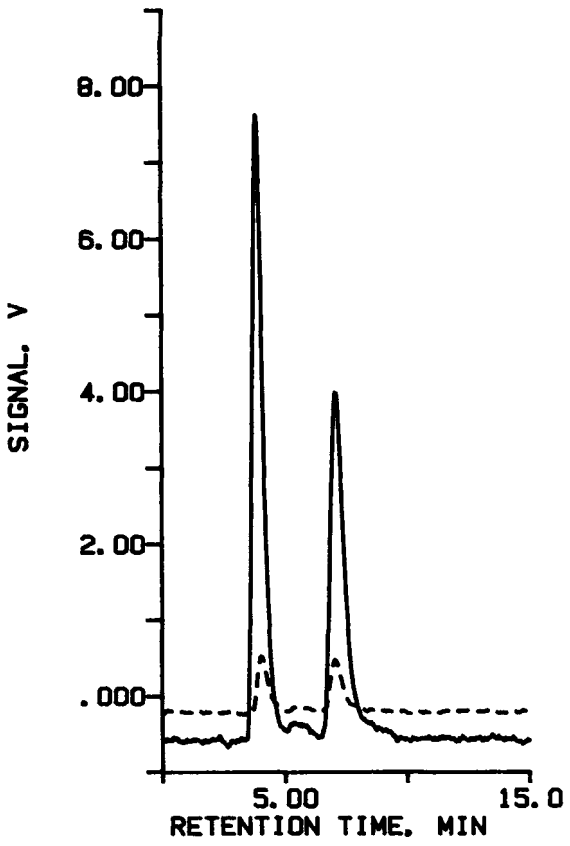


FIGURE 13. Chromatograms for separation of Cr(III) and Cr(VI) with 50-μm s.s. aperture thermospray (solid line) and pneumatic (dashed line) sample introduction. (From Roychowdhury, S.B.; Koropchak, J.A. *Anal. Chem.* **1990,** *62,* 485. With permission.)

enhancement for thermospray in these cases. For organometallic Fe species separated by size exclusion chromatography (SEC) with tetrahydrofuran (THF) as the eluent, LODs with a 50-μm aperture thermospray system were 50 times lower than with pneumatic sample introduction with a cooled spray chamber. For both nebulizers in this case, the standard system was followed by a cryogenic condenser for more efficient reduction of THF loading to the plasma. The particularly high LOD improvement observed for the SEC separation with thermospray was likely due, in part, to greater solvent removal efficiency with the combined thermospray-desolvation-cryogenic system compared to the pneumatic-spray chamber-cryogenic system. This thermospray system was used for the study of size- and species-dependent speciation study of Cr distributed within aerosols produced by chrome electroplating industries.[55]

Laborda et al. used their cooled spray chamber thermospray system to interface anion chromatographic separations of Se species with ICP-AES.[57] LODs were threefold better than with pneumatic sample introduction, and the thermospray system allowed operation with up to 75% methanol in the mobile phase, whereas the pneumatic system was limited to 25% methanol.

Maessen designed a low-consumption thermospray nebulizer for specific use with micro-HPLC and ICP-AES detection.[43] Robinson and Choi developed their thermospray interface with FAA for HPLC interfacing as well.[53]

A thermospray device was also used to couple HPLC to GFAAS for metal speciation studies.[61] Tin species were separated by cation exchange, and an LOD of 0.5 ng absolute (25 ng/ml) was reported. The system was used to determine tributyltin compounds in wood preservatives.

VIII. CONCLUSIONS AND FUTURE DIRECTIONS

Primary aerosols produced by thermospray are smaller in size, on average, than aerosols produced by pneumatic nebulizers, particularly of the type employed for sample introduction to ICP spectrometries. In addition, the primary thermospray aerosols are enriched in analyte since the thermospray generation process necessarily involves the vaporization of a substantial fraction of the sample solvent. Solvent vaporization is enhanced for smaller particles and higher temperatures, both aspects leading to faster size reduction due to solvent evaporation than would occur with pneumatic sample introduction at room temperature. These factors can combine to make thermospray systems extremely efficient at transporting nonvolatile solutes in aerosol form. In addition, thermospray systems can operate with high efficiency at relatively high sample flow rates (>1 ml/min), such that the analyte flux to a mass sensitive detector (such as an ICP) will be much higher than can be attained with pneumatic sample introduction. As a result, signals and LODs observed with thermospray are much im-

proved compared to pneumatic sample introduction.

Specific improvements reported with thermospray sample introduction to ICP-AES vary substantially, as affected by several system characteristics. Reducing the diameter of the vaporizer capillary has been shown to lead to improved transport, sensitivity, and LOD characteristics due to reduction in the sizes of primary aerosols. More importantly, it has been shown that only the exit diameter of the capillary needs to be small, allowing operation of the thermospray vaporizer at relatively high sample flow rates with acceptably small sample input pressures.

The largest variations in performance from laboratory to laboratory have resulted from differences in the extent of spray chamber heating and aerosol desolvation employed. Even with room-temperature or cooled spray chambers, enhanced LODs are observed based on the improved primary aerosol characteristics of thermospray compared to pneumatic neubulizers. However, higher analyte transport also implies higher solvent transport, unless some means for solvent removal is utilized. The work of de Loos-Vollebregt clearly shows that desolvation is required to avoid excessive solvent loading, lower plasma temperatures, and reduced excitation characteristics with thermospray-ICP-AES. Using a relatively cool initial spray chamber region followed by heated region and condenser for desolvation, as employed by Maessen and Vermeiren, perhaps a factor of 5 additional improvement in sensitivity is realized compared to using a cooled or unheated spray chamber. Using an entirely heated spray chamber as in our lab, somewhat larger improvements are realized, as heating the aerosol immediately after formation counteracts cooling, reduced solvent evaporation, and perhaps recondensation during expansion of the aerosol plume; these processes would lead to larger secondary particles being subject to loss mechanisms.

In addition to the generally observed benefit of higher sensitivity, thermospray sample introduction has been shown, in general, to provide larger matrix interferences. These effects have been derived from several processes. Without sufficient desolvation, the resultant lower plasma temperatures and electron concentrations would be predicted to give rise to lesser tolerance to the higher levels of dissolved solids input to the plasma. With desolvation, transport effects resulting from the influence of the matrix on desolvated particle size and plasma effects due to the higher transported levels of the matrix species are both important. Recent data with a fused silica aperture thermospray system have suggested that reduction of primary particle sizes by using smaller diameter capillaries and operation of the vaporizer at slightly higher temperatures can minimize transport effects. In addition, with efficient desolvation such that optimum viewing heights are low in the plasma, careful optimization of viewing heights and aerosol carrier flow rates appear to reduce the level of plasma effects. Further study of this phenomena may reveal compromise conditions comparable to the fortuitous "cross-over point" observed with pneumatic sample introduction, for which matrix interferences are minimized.[62]

Thermospray sample introduction has been applied beneficially to a wide range of practical applications. At this point, the only major limitation to the application of thermospray systems, compared with pneumatic systems, appears to be samples containing large particulates, to include slurries. In addition, only a few studies have investigated the use of thermospray with ICP-MS. As many recent studies have noted the importance of scrupulous water removal to minimize oxide interferences with ICP-MS, clearly efficient desolvation would be required for the successful application of thermospray to ICP-MS. In principle, the same level of improvement observed with ICP-AES should be attainable with ICP-MS.

One ultimate goal for research with aerosol sample introduction would be the development of a system that is 100% efficient in transporting analyte with high continuous liquid flow rates. In principle, there is no fundamental reason why this cannot be achieved! Some recent data suggest that with high-performance thermospray nebulizers, the aerosol source may no longer be the limiting factor in achieving this goal. New characterizations and new concepts with aerosol transport and desolvation may prove key to reaching 100% transport. Reductions in aerosol par-

ticle size with further improvements in thermospray vaporizers may still reduce matrix effects and perhaps improve responsivity, as several studies have indicated that responsivity is higher with smaller particle sizes.[46,47] In addition, new concepts to aerosol generation, taking advantage of the strengths of thermospray aerosol generation, may provide systems with even greater capabilities. For example, the nebulizing gas with thermospray (solvent vapor) is condensable and independent of the aerosol carrier gas flow. In principle, there is no limit to the volume of gas that could be generated and subsequently removed, assuming sufficient power for vaporization is provided. New vaporizers designed with this consideration in mind may provide completely new capabilities for thermospray, such as improved aerosol characteristics, self-aspiration, and the ability to deal with samples containing large particulates or even slurries.

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