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Application of an electrospray-interface as a new nebulizer for inductively coupled plasma atomic emission spectrometry

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Abstract—An electrospray nebulizer was constructed for possible use as an interface for micro-HPLC and ICP–AES. The sample uptake rate was 10 μl min^{-1}. To allow the transport of the aerosol to the plasma, the highly positively charged droplets produced by the electrospray were neutralized. To test the performance of the interface, methanol and methanol/water (8:2, v/v) solvent test solutions of metal–acetylacetonates were nebulized. Concentration detection limits obtained with this interface were worse than those obtained with thermospray or conventional pneumatic nebulizers. However, due to the low uptake rate, the absolute detection limits were considerably lower. No signal drift was observed when nebulizing the methanol test solution over 1 h. The extra-column peak broadening caused by the interface is not satisfactory and only acceptable when coupling to a micro-HPLC packed column with an inner diameter no smaller than 1 mm.

1. Introduction

Interest is growing in the application of atomic emission spectrometry (AES) detectors to micro-separation systems. Inductively coupled plasma (ICP) and microwave-induced plasma (MIP) may be valuable detectors in micro high performance liquid chromatography (micro-HPLC) and the latter one in capillary zone electrophoresis (CZE).

Such hyphenated techniques require the use of nebulizers as interfaces that are compatible with the column effluent flow rates. In micro-HPLC with microbore columns, liquid flow rates are in the range of 5–200 μl min^{-1}, whereas in CZE these are even below 1 μl min^{-1}. So far, the lowest flow rate for which a microconcentric pneumatic [1, 2] or thermospray nebulizer [3] has been shown to operate effectively is 120 μl min^{-1}. For a frit-type nebulizer even a flow rate down to 50 μl min^{-1} has been used [4, 5].

In recent years, micro-HPLC [6–9] and CZE [10, 11] have successfully been coupled to mass spectrometry (MS) by an electrospray (ES) probe.

In this paper we report on an ES interface that enables coupling of micro-HPLC to ICP–AES. Preliminary results of some test solutions are given. These solutions were either fed continuously or flow-injected to the ES-nebulizer, from which the aerosol was transported into the ICP. Liquid flow rates were 10 μl min^{-1}.

2. Apparatus and Techniques

The principle of the ES technique is the dispersion of a liquid, emanating from a capillary, into fine droplets under the influence of a strong electric field. Under such conditions an electrophoretic charge separation mechanism takes place [12]. The liquid surface becomes enriched in electric charge and thus unstable due to electrostatic repulsion forces. Provided that

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the applied voltage and thus the field strength is high enough, the liquid is drawn into a cone shape at the end of the capillary. A fine mist of droplets is emitted from the tip of the cone [13]. TAYLOR [14] has described the cone shape for an equilibrium situation, when the electrostatic pressure is balanced by the pressure caused by surface tension.

The analytical performance of an ES is, among other parameters, dependent on the dimensions (diameter and shape) of the capillary [15], the applied voltage, the liquid flow rate and the conductivity and surface tension of the liquid [16].

In coupling of the ES interface to MS, the spray capillary is kept at a positive potential of some kilovolts in most cases [7–10]. The MS end plate serves as the counter electrode and is kept at ground potential or at a positive potential of some volts. Ions, originating from the "electrosprayed" droplets are sampled through a small orifice in the end plate. For fundamental studies of the ES process [15, 16], a planar counter electrode is used, which is kept at ground potential as well.

For the coupling to ICP and MIP, a droplet transporter to the plasmas through tubing of considerable length is required. However, droplets produced by ES initially carry a high charge and move towards any grounded object available [17]. In order to transport a droplet through the tubing, the droplet charge must be neutralized before. MEESTERS *et al.* [17], facing the same problem when studying the ES for the purpose of the production of fine aerosols, performed a neutralization of positively charged droplets by negatively charged ions, generated by a corona discharge process around a negatively charged needle-shaped electrode, which was placed opposite the spray capillary. A neutral aerosol was obtained, which could easily be transported perpendicular to the spray axis by an aerosol carrier gas. A third, ring-shaped electrode was required on the spray axis in order to stabilize both the droplet production and the neutralization mechanism [17]. The ring-shaped electrode was kept at ground potential.

3. EXPERIMENTAL

3.1. *General set-up*

In the present study, an ES interface similar to the system described by MEESTERS *et al.* [17] was firstly constructed. According to the criteria established by these authors, the dimensions of the spray chamber were as follows: length 10 cm, inner diameter 8 cm, and height 17.5 cm. Droplets were generated at a positively charged capillary and discharged by ions, produced at a negatively charged needle. Argon, the usual aerosol carrier gas of an ICP–AES system, was originally chosen as the transporting gas. Thus the spray chamber was completely filled with argon. When a high voltage was applied, a spark discharge occurred at a field strength that was lower than that required for the onset of the spray mode. Argon had to be replaced by a molecular gas, in which the breakdown potential was higher [18]. Air, nitrogen and oxygen were employed for this purpose. Oxygen had been used as a discharge suppressing gas in the negative ion operation mode of the ES [19], but was not suitable in our application, because large droplets were formed instead of a fine aerosol. In nitrogen and air a proper spray operation was possible.

However, the air or nitrogen flow was limited with respect to a stable operation of the ICP. It was too low for an efficient transport of the aerosol out of the spray chamber. But then a satisfactory aerosol transport efficiency and a proper spray operation could be achieved when air or nitrogen were added just around the spray capillary and the discharge needle. With this arrangement spark discharge was successfully suppressed. Argon was used to carry the neutralized droplets out of the spray chamber.

Air was preferred to nitrogen as an electrode-flushing gas, because air was more suitable as a nebulizer gas component in order to oxidize CN molecules [20], which are formed when organic matter is introduced into the ICP.

3.2. *Interface chamber*

Figure 1 shows the design of the interface chamber that was finally used for experiments. The spray chamber material was glass. The choice of the dimensions (length 5 cm, inner diameter 4 cm, height 11 cm) followed two considerations: first, it had been found in preceding experiments (Section 3.1) that bigger spray chamber dimensions resulted in a better spray performance and through this a higher detection power. On the other hand, the contribution of the interface to extra-column peak broadening in coupling with separation techniques should be as small as possible. This should be achieved by a small spray tube with a low dead volume.

The spray capillary and the discharge needle were mounted on Teflon holders (10 mm outer

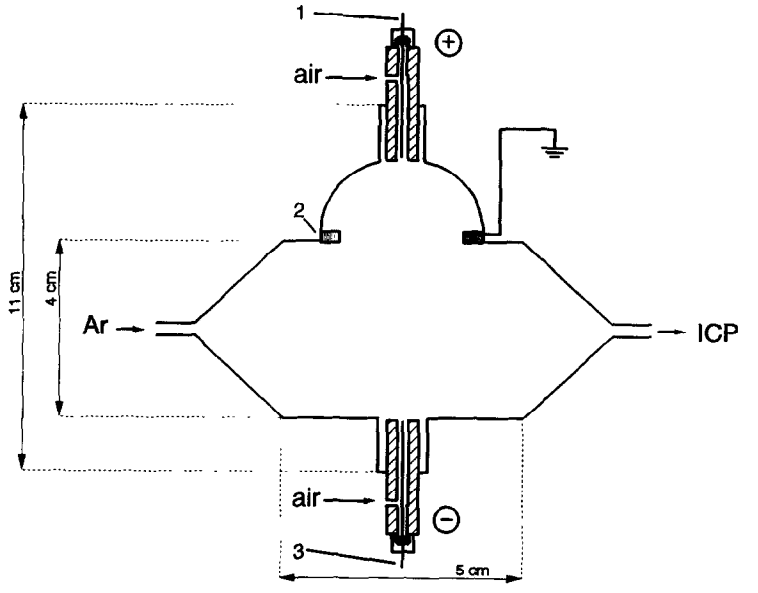

Fig. 1. Schematic drawing of the interface chamber: (1) spray capillary; (2) ring electrode; (3) discharge needle.

diameter) by means of a ferrule. The Teflon holders fitted by a screw cap into the electrode housings of the glass spray tubes. A 3 mm bore was drilled into each holder, so that air could be added coaxially to the spray capillary and the discharge needle, respectively. Thus the electrodes were embedded in an air stream. The flow of pure air was controlled with a flow controller (Model 8744; Brooks, Veenendaal, The Netherlands) and split into two streams, one to the spray capillary and the other to the discharge needle. The electrode distances could be varied within a few centimetres, but were practically fixed at 2 cm capillary/ring distance, and 5 cm ring/needle distance. Argon was added perpendicularly to the spray direction. The aerosol left the spray tube at the opposite end of the Ar supply. It was conducted to the ICP-torch through a polyethylene tubing with an inner diameter of 6.5 mm and a length of approximately 40 cm.

The high voltage region containing the ES-device was electrically isolated in an interlocked plexiglass box.

3.3. *Spray capillary, ring electrode and discharge needle*

The spray capillary (Fig. 2) was made by soldering two stainless steel (s.s.) capillaries with different diameters. A fused silica (f.s.) capillary (Poly-micro Technologies, Phoenix, AZ), through which liquid was supplied, was inserted into the spray capillary until it butted against the joint. To the other end of the spray capillary a union was soldered, in order to fix the f.s. capillary there by means of a Teflon ferrule and a nut. High voltage was applied to the liquid by contact with the s.s. capillary. The tip of the s.s. spray capillary was electropolished in such a way that it was conically shaped, but that the edge was still slightly blunt. The procedure was carried out for a few minutes at 6 V in an electrolyte bath containing 60% H_3PO_4 (85%), 20% H_2SO_4 (98%) and 20% water.

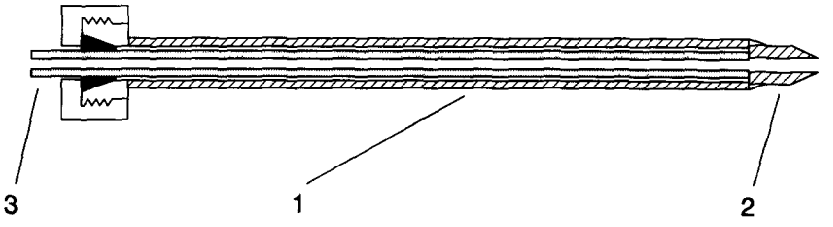

Fig. 2. Schematic drawing of the spray capillary: (1) stainless steel of length 8.5 cm, 500 μm i.d., and 650 μm o.d.; (2) stainless steel of length 1 cm, 100 μm i.d., and 470 μm o.d.; (3) fused silica, 50 μm i.d., and 375 μm o.d.

The s.s. ring electrode had the following dimensions: 3.2 cm i.d., 4 cm o.d., gauge 0.1 cm.

The discharge needle was made of a s.s. rod (diameter 0.5 mm). A pointed tip was obtained by electropolishing. Electropolishing was repeated frequently to keep the surface clean.

3.4. *Liquid feeding*

The test solutions were either fed continuously or flow injected to the interface. The liquid streams were pumped by a high precision constant flow pump (Model 300C; Gynkotek, Germering, F.R.G.) through a 2 μm in-line filter.

In the flow injection (FI) mode a sample injector (Rheodyne Model 7010, Catati, CA) was used. The f.s. tube, forming part of the spray capillary, was connected to the injector. This connection was made by inserting the f.s. capillary into a Teflon sleeve (3 cm, 0.5 mm i.d., 1.6 mm o.d.). The sleeve was fitted into the exit port of the injector, pushing the sleeve in as far as possible in order to avoid dead volume. Sleeve, and with that the f.s. capillary, were secured by a s.s. ferrule.

3.5. *Reagents and test solutions*

HPLC-grade methanol and sub-boiled water were used for test solutions. Prior to use, the solvents were filtered by vacuum suction over a 0.45 μm filter. Test solutions were prepared by dissolving Al-, Cu-, Mn-, and V-acetylacetonates (Baker, Deventer, The Netherlands) in methanol. In the experiments of methanol/water, methanol solutions of acetylacetonates were mixed with water in the volume ratio 8:2, and freshly prepared.

3.6. *Voltage supply*

Two high voltage supplies (Model HCN 14-12 500; FUG, Rosenheim, F.R.G.) were employed. A positive voltage was applied to the spray capillary and a negative voltage to the discharge needle. The ring electrode was kept at ground potential.

3.7. *ICP equipment, data acquisition and processing*

Jarrell Ash AtomComp model 975 ICAP multichannel equipment with a scanning monochromator was used. Specification of the main characteristics of the system are given elsewhere [21]. The original PDP-8 microcomputer for data acquisition had been replaced by computer-controlled individual integrators, multiplexed to a 12-bit A/D converter with a dynamic range $>10^6$. A spectrum shifter to move the spectral lines across the exit slit was built in. It consisted of a motor-driven refractor plate placed after the entrance slit. The shifter positions spanned 0.3 nm. In our experiments of continuous nebulization of test solutions it was used for measuring background signals (I_B) at wavelengths adjacent (−0.14 nm) to those of the analysis lines. For each analysis wavelength the gross line intensities (I_G) were consecutively measured ten times. The same procedure was subsequently employed for measuring the background intensities. Integration time of each measurement was 5 s. Net line intensities (I_N) were calculated as the difference between the ten available paired values for I_G and I_B. Time-scans were made of the transient signals in the FI-mode; measurement integration time was 3 s.

3.8. *Detection limits*

The limits of detection were defined as concentrations that yield net line intensities equal to three times the standard deviation of the background signal. The detection limits (c_L) were estimated using the relation [22]

$$c_L = 3(\mathrm{RSD})_B\, c(\mathrm{SBR})^{-1} \tag{1}$$

where $(\mathrm{RSD})_B$ is the relative standard deviation of I_B and c the concentration of the test element yielding a measured signal-to-background ratio SBR.

4. Results and Discussion

4.1. *ICP and ES conditions*

Compromise measuring and operating conditions were found by varying the ICP-forward power, the measuring height above the induction coil, the total nebulizer gas flow rate and the air fraction while continuously nebulizing a methanol/water (8:2, v/v) test solution. The compromise ICP operating conditions and liquid flow rate are

Table 1. ICP operating conditions

Forward power	1.3	kW
Outer flow	20	l min^{-1} Ar
Intermediate flow	1	l min^{-1} Ar
Nebulizer flow	0.75	l min^{-1} Ar/air, air ratio 7%
Observation height above the induction coil	14	mm
Liquid flow rate	10	µl min^{-1}

listed in Table 1. Total nebulizer gas flow rate and air content had to follow ICP stability requirements [23, 24]. When a solution of methanol/water (8:2, v/v) was pumped to the ES capillary with a flow rate of 10 µl min^{-1} and the aerosol was introduced into the plasma at a forward power of 1.3 kW and a nebulizer gas flow rate of 0.75 l min^{-1}, the upper limit of the nebulizer gas air content was about 10%, before the plasma extinguished. A minimum air content of about 5% was required for a stable spray operation.

Voltages were adjusted to an optimum spray quality. The voltage ranged from +3.6 to +5.0 kV and from −1.9 to −4.7 kV, respectively. It should be noted that the spray conditions are affected by slight changes in liquid conductivity and electrode geometry [15]. In general, electrospray operation was more stable when the analytes were dissolved in pure methanol rather than in methanol/water (8:2, v/v). This can be explained by the fact that the surface tension of methanol is lower, and thus spray operation is facilitated.

4.2. *Detection limits and precision*

A test solution of analytes in methanol/water (8:2, v/v) was continuously nebulized at the ICP operating conditions, listed in Table 1. The concentration detection limits with the corresponding values of SBR and $(RSD)_B$ are summarized in Table 2. In addition, the precisions expressed in the relative standard deviation of I_N, $(RSD)_L$, are given. The analyte concentrations, with the exception of Al, were always taken as ≥100 times the detection limits, ensuring that measurement precisions were source flicker noise limited [22]. In Table 3, concentration detection limits obtained with our ES-interface are compared with values obtained with a thermospray interface [3] and a conventional pneumatic nebulizer [25]. One has to note particularly that the liquid flow rate in ES-experiments was only 10 µl min^{-1}, whereas it was 120 µl min^{-1} in thermospray experiments and 1.9 ml min^{-1} with the conventional pneumatic nebulizer. Nevertheless, the detection limit for Cu was in the same order of magnitude. For Al, Mn and V this was within a factor of 7 higher than values obtained with the pneumatic nebulizer.

Table 3 indicates the potential high sensitivity of this nebulizer with respect to absolute detection limits. We may assume that this is due to the narrow droplet size

Table 2. Performance of the electrospray interface by continuous test solution introduction:* +4.41 kV at the spray capillary; −2.09 kV at the discharge needle

Spectral line (nm)	$(RSD)_L$†	$(RSD)_B$†	SBR†	c†	c_L†
Al I 308.215	0.02	0.010	0.86	5000	174
Cu I 324.754	0.04	0.011	4.82	1000	7
Mn II 257.612	0.06	0.015	3.95	1000	11
V II 292.402	0.05	0.010	2.85	5000	53

* Flow rate of the methanol/water (8:2, v/v) test solution is 10 µl min^{-1}.

† $(RSD)_L$ and $(RSD)_B$ are the relative standard deviations of the net line and background intensity, respectively; c is the analyte concentration (ng ml^{-1}) which yielded a signal-to-background ratio of SBR; c_L is the detection limit (ng ml^{-1}).

Table 3. Detection limits obtained with the electrospray interface, a thermospray interface [3] and a conventional pneumatic nebulizer [25]

Spectral line (nm)	c_L (ng ml^{-1}) Electrospray	Thermospray	Pneumatic
Al I 308.215	174	5	45
Cu I 324.754	7	14	5.4
Mn II 257.610	11	1	1.4
V II 292.402	53	13	7.5
Test solution	Methanol/water (8:2, v/v)	Methanol/water (8:2, v/v)	Aqueous
Liquid flow rate (μl min^{-1})	10	120	1900

distribution of the aerosol [17], which results in a high analyte transport efficiency to the plasma [26].

The detection limits for Al, Mn and V were a factor of 1.5–2 lower than those obtained with a methanol test solution at the same operating conditions. This lowering has to be attributed to modified excitation conditions nebulizing the methanol solution. However, the spray was more stable in nebulizing methanol solutions.

4.3. *Long-term stability*

The long-term stability was measured both for a test solution of analytes in methanol/water (8:2, v/v) and in pure methanol. Concentrations of the analytes in both solutions were the same as listed in Table 2. The measuring procedure (Section 3.7) at the operating conditions (Table 1) was repeated every 5 min during a 1 h period. Nebulizing the methanol/water solution, the $(RSD)_L$ of the various spectral lines remained constant, but a drift was observed. The gross line intensities were 10–20% decreased at the end of the 1 h nebulization period, whereas the background intensities maintained the same level. In contrast, the methanol spray was very stable. No signal drift was shown after 1 h.

4.4. *Extra-column peak dispersion*

The contribution of the interface to extra-column peak broadening in coupling to a micro-HPLC system was investigated. To that end, various volumes of a test solution were flow injected into a solvent stream. A split-injection technique was applied to minimize dead volumes in the exit port of the sample injector, which was built into the system. For the same reason, the length of the f.s. capillary (25 cm, 50 μm i.d.), the connection between injector and nebulizer, was selected in such a way that its volume (0.5 μl) was smaller than the sample volumes introduced into the nebulizer. The injector was employed with various sample loops. The solvent stream was methanol at a flow rate to the nebulizer of 10 μl min^{-1}. The methanol test solution contained 10 μg ml^{-1} Cu. From the injected volumes 1, 2, 4, 7 and 10 μl reached the nebulizer and showed signal peaks with background-to-background intervals of 62, 87, 84, 120 and 132 s, respectively. From the results it appears that peak broadening of the first three peaks is mainly caused by dispersion effects of the interface plus detector, and to a lesser degree by sample injection volume.

The response curves obtained indicate a contribution to peak width by the interface plus measuring system of about 15 s, expressed as standard deviation (corresponding to the 60 s base-to-base width for the first peak). As the ICP itself is relatively fast responding, two effects may be held responsible for this contribution to peak width: dispersion in the liquid channels from the injector to the nebulizing point, and dispersion during the transport of the aerosol as discussed by WHALEY *et al.* [27]. The

former involves a 10 μl min^{-1} liquid stream, F_L, through a total volume, V_L, of 0.5 μl, and is unlikely to be significant, as V_L/F_L equals 3 s. The latter involves a 750 ml min^{-1} gas stream, F_G, through the spray chamber plus polyethylene tubing with a total volume, V_G, of about 75 ml, corresponding to V_G/F_G equalling 6 s. Thus, dispersion probably occurs during aerosol transport. The experimental value of 15 s is not satisfactory for most separation systems. It would be only acceptable when the interface is coupled to a microbore column (50 cm, 1 mm i.d.) with an eluent flow rate of 10 μl min^{-1}. Improvement in this respect is not easy, since as yet we have not succeeded in using smaller spray chambers.

The Cu emission signal of the 10 μl sample plug was at a steady state level for 30 s, whereas the rinse-out time required was about 60 s. No significant memory effect was observed.

5. Conclusions

An electrospray nebulizer was constructed for its possible use as an interface for micro-HPLC and ICP–AES. The sample uptake rate was 10 μl min^{-1}. A charged aerosol was produced by liquid dispersion in an electric field. The positively charged droplets were discharged by negatively charged ions. Concentration detection limits, obtained with this interface, were worse than those obtained with thermospray or conventional pneumatic nebulizers. However, the liquid flow rates and therefore the absolute mass detection limits were also considerably lower. No signal drift was observed when nebulizing a methanol test solution over 1 h. Contribution to peak width is still too high for many important applications.

Future work will aim to construct an interface that yields a smaller contribution to extra-column peak dispersion in coupling to micro-HPLC and to develop a wider application of ES in AES.

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