

A low-powered microwave thermospray nebulizer for inductively coupled plasma atomic emission spectrometry

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A novel microwave thermospray nebulizer (MWTN), using a TM₀₁₀ resonant cavity as the energy coupling device, is described in this paper. The nebulizer consists of a knotted PTFE capillary (od, 1.3 mm, id, 0.5 mm) and a thinner quartz outlet capillary located in a TM₀₁₀ cavity. A microwave power of 60 W is enough to nebulize the sample solution. Because of the big diameter of the PTFE capillary, a peristaltic pump, instead of the necessary high-pressure pump in a traditional thermospray nebulizer, could be used to transfer the solution. The nebulizer was successfully coupled to an inductively coupled plasma atomic emission spectrometry (ICP-AES) instrument. The effect of various parameters, such as the nature and concentration of the medium, carrier gas flow rate, sample uptake rate and so on, on the emission intensity of Fe, Mg, V and Cu was studied. Compared with a pneumatic nebulizer, the detection limits for Cu, Fe, Mg, and V were improved by a factor of 2–4.

Since the introduction of thermospray (TSP) in 1978,¹ it has attracted more and more attention from the spectrochemical community and is thought to be an ideal method² for sample introduction. Because it generates very fine hot primary aerosols, it is possible for a high percentage of analyte to reach the atomization cell. The combination of ICP-AES with a TSP gives a much better analytical performance than with a conventional pneumatic nebulizer (PN) in terms of sensitivity for most elements. TSP has been widely applied to atomic emission spectrometry,^{3–6} mass spectrometry^{7–9} and as an interface between liquid chromatography and AES or MS.^{10–13}

Up to now, most studies on TSP made use of thermal conduction to heat a quartz or stainless-steel capillary to generate aerosols. If a stainless-steel capillary is used, there will be a problem of corrosion when a strong acid medium is used. With such a heating method, there exists a heat gradient from the capillary wall to the center of the liquid stream within. If the liquid contains a relatively large amount of analyte or the temperature is not controlled strictly, the analyte will deposit on the capillary wall. As a result, it is difficult to use such a thermospray technique to analyze sample solutions with a high salt content or a slurry.^{3,4}

Microwave heating is related to dipole rotation and ion migration. The quartz (or PTFE) capillary wall is almost transparent to the microwave, so the whole liquid column in the capillary will be heated by the microwave at the same rate. Therefore, there is no heat gradient from the wall to the center of the liquid stream. The deposition of analyte on the wall will, hence, be minimized. Moreover, the solvent vapor will mix well with the remaining liquid and, theoretically, the droplet diameter distribution of the aerosols produced will be much narrower. To avoid local overheating, in most studies on TSP, the capillary diameter is very small (0.025–0.2 mm). While with microwave heating, the capillary diameter can be up to 1 mm.¹⁴ Therefore the microwave thermospray nebulizer (MWTN) can work at a lower liquid pressure, and be used to analyze sample solutions with high salt contents or even slurries.

Recently, Bordera *et al.*¹⁵ reported the use of a focused microwave oven as the heating device for TSP. The analytical performance is satisfactory compared with a pneumatic nebulizer. However, since the size of focused microwave

oven is big, the combination of the system with a commercial spectrometer is somewhat inconvenient. In addition, because the sample volume is small, the microwave energy could not be absorbed by the sample efficiently and a microwave forward power of 300 W is needed to produce enough aerosol. Jin *et al.*¹⁴ tried various microwave resonant cavities as microwave heating devices. Because a wide quartz capillary (id 1.0 mm) was used and the microwave irradiation length was very short (about 10 mm), only a small part of the tested solution could be heated to become a vapor. Therefore, the spray efficiency was not obviously improved and the emission intensities for several elements were similar to those obtained with a pneumatic nebulizer.

In this paper, a TM₀₁₀ microwave resonance cavity was used to concentrate the microwave energy. Because the efficiency of the resonance cavity was better than that of a focused microwave oven, the power needed to generate the spray was much reduced. A knotted PTFE capillary prolonged the irradiation length of the nebulizer. A forward power of about 60 W was enough to generate very fine aerosols. Moreover, the system size was reduced, which made it easy to be coupled with a spectrometer. The low powered microwave thermospray system was coupled with an ICP-AES, and a comparison between it and a system with a pneumatic nebulizer was carried out. The preliminary results showed that it could provide obvious, more intensive emission. However, due to the unsatisfactory precision at present, the detection limits for some elements were improved by only a factor of 2–4.

Experimental

Instrumentation

Fig. 1(a) shows the schematic diagram of the microwave thermospray nebulizer (MWTN) system used in this study. Fig. 1(b) shows the construction of the nebulizer. A laboratory built microwave resonance cavity (TM₀₁₀ cavity) was used as the microwave heating device. The MWTN consists of a knotted PTFE capillary (id, 0.5 mm; od, 1.3 mm; about 300 mm long) and a short narrow quartz capillary (about 15 mm long; id, 0.075 mm), which was fixed at the outlet of the

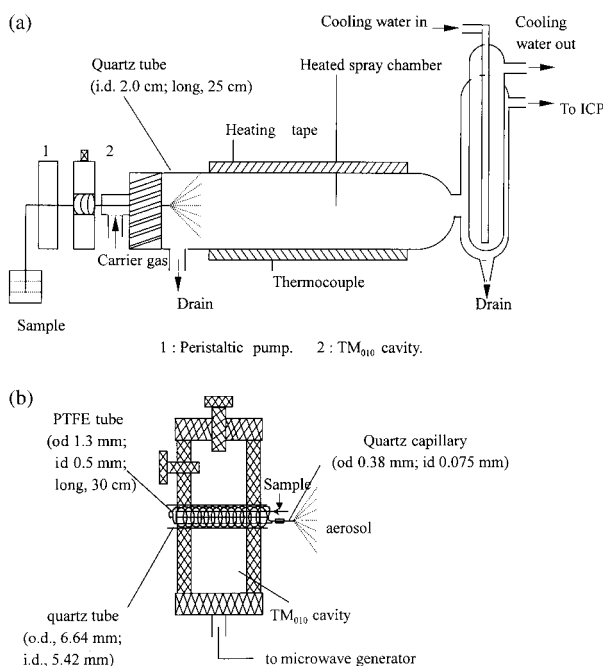


Fig. 1 Schematic diagram of the microwave thermospray system. (a) Block diagram of thermospray system; (b) main part of microwave thermospray system.

PTFE capillary by means of a PTFE union. Hereinafter, the small narrower quartz capillary is called the outlet capillary. The knotted PTFE capillary was placed in the central hole of the cavity, where the sample solution was heated and a thermospray was produced at the end of the quartz outlet capillary. The aerosols produced then entered into the heated spray chamber.

The sample in an acid solution was pushed through the PTFE capillary by the peristaltic pump of the ICP spectrometer. When the sample passed through the microwave irradiation zone, the sample solution was heated above the boiling point of water (solvent). Part of solvent would become vapor. However, because the outlet capillary restricted the passage of the vapor and the remaining solution, the pressure inside the nebulizer capillary was raised. When the mixture of solvent vapor and the remaining solution was forced out of the outlet capillary, the vapor expanded with very high velocity due to the sudden pressure reduction. This made the remaining solution become a very fine aerosol. The aerosol was carried into the heated spray chamber with a carrier gas. It was shown that when the carrier gas flow rate was 1.0 L ml^{-1} , the temperature of the aerosol leaving the spray chamber was about 130°C . After being condensed by a condenser with tap water, the dry aerosol was introduced into the plasma. Owing to the characteristics of the material used (PTFE, quartz), the

MWTN can deal with solutions of high acidity. Because only the outlet capillary is narrow, the pressure inside the PTFE capillary is not as high as in a traditional TSP system. Therefore, a peristaltic pump, which was a component of the ICP spectrometer, was enough to push the sample through. No high pressure pump was needed.

In this study, the original pneumatic nebulizer of an ICP-AES was replaced with the MWTN system. The detailed operation conditions of the ICP-AES are listed in Table 1.

Reagents

The acids, HCl, H_2SO_4 , HNO_3 and HClO_4 , were all commercially guaranteed reagents. Multi-element solutions were made from standard stock solutions of 1.0 mg ml^{-1} by dilution with corresponding acid and de-ionized water. Cu, Fe, Mg, V of 0.5 mg L^{-1} , were tested in this study.

Results and discussion

Effect of acid nature and concentration on emission intensity

Because the microwave heating depends strongly on the dipole rotation and ion migration, if there are not enough ions in the sample solution the heating rate is low, and the solution cannot be heated to a temperature sufficient for nebulization after it passes through the microwave radiation zone. For example, pure water reaches only about 50°C when it leaves the nebulizer when a microwave power of 60 W is applied. In this study, some acid was added into the test solution to increase the number of ions in it, thus the heating rate was raised and fine aerosols were formed at the exit of the outlet capillary.

For 0.5 mg L^{-1} Cu, Fe, Mg and V in different acid solutions with the same acid concentration (0.5 mol L^{-1}), the intensities of the elements in HClO_4 are similar to that in HCl. The intensities of different elements in HNO_3 do not show the same trend, and in H_2SO_4 the intensities are weaker than that in HCl solution. This phenomenon can be explained as follows: because the microwave heats the solution through dipole rotation and ion migration, there is a close relation between the ion number in solution and the microwave heating rate. When the acid concentrations in solution are the same, the ion number in solutions of HClO_4 , HCl, HNO_3 are the same, and the only difference is the anions. As a result, solutions in different media are heated at almost the same rate, and in turn the nebulization efficiencies are similar. The emission intensities of elements in HClO_4 , HCl and HNO_3 media are also similar. With the same acid concentration, the ion number in the solution of H_2SO_4 is the maximum among the four acids and therefore, the absorption of microwaves by the H_2SO_4 solution is more efficient than for the other three acid solutions, and the nebulization efficiency is higher. Meanwhile, the mean diameter of wet aerosols formed is smaller than that in other acids. Bordera *et al.*¹⁵ also drew a similar conclusion. However, the high nebulization and transfer efficiency would overload

Table 1 Operation conditions of the ICP-AES

ICP-AES spectrometer	Plasma 1000 Perkin-Elmer Co.
Monochromator	Ebert Type
Focal length	1.0 m
Grating	2400 grooves mm^{-1}
Optical resolution	0.012 nm
Wavelength	160–760 nm
Rf generator frequency	27.12 MHz
Forward power	1.0 kW
Carrier gas flow rate	1.0 L min^{-1}
Plasma gas flow rate	1.0 L min^{-1}
Cooling gas flow rate	15 L min^{-1}
Observation height	15 mm above the load coil
Peristaltic pump	Component of the spectrometer
Microwave generator	Lab-built, maximum output power: 70 W; frequency: 2450 MHz

the plasma. The presence of a large amount of H_2SO_4 in the plasma reduced the emission intensity of most elements. Therefore, when the acid concentrations are the same, the emission intensities of the elements in H_2SO_4 solution are less intensive than in the other three acids. Since HCl was less corrosive, HCl was selected as the solution medium throughout the study.

The emission intensities of some elements increase with the HCl concentration. Because, in this case, ion migration is a main mechanism of microwave heating, the more ions there are in solution, the faster the solution is heated, and the more rapidly the solution evaporates. Thus a higher pressure will be built up inside the solution vein. As in traditional TSP and pneumatic nebulization, a higher pressure and less solution will result in finer aerosols. In turn, the emission intensities increase with HCl concentration.

However, when the HCl concentration is $>0.5 \text{ mol L}^{-1}$, the rate of intensity increase slows down. The reason might be that a solution containing 0.5 mol L^{-1} HCl is enough to realize a thermospray of the solution at a given sample uptake rate and microwave power. Therefore, an increase in ions does not improve the nebulization to an obvious extent. In addition, too much acid getting into plasma will reduce the excitation ability of the plasma. As a result, the intensity curves level off when the HCl concentration is $>0.5 \text{ mol L}^{-1}$.

Thereafter, 0.5 mol L^{-1} HCl was chosen as the solution medium for all the experiments.

Effect of sample uptake rate

For traditional thermospray, sample uptake rate is a crucial factor affecting the detection power of the system. Due to the high pressure needed, it is difficult to obtain a higher sample uptake rate. Therefore, a thermospray with a flow rate of near 10.0 ml min^{-1} was considered as a revolution in atomic spectrometry.²

Fig. 2 shows the variation of relative emission intensities against the sample uptake rate. Limited by the experimental conditions, only sample uptake rates of $<1.2 \text{ ml min}^{-1}$ were studied. When the uptake rate went too high, the solution

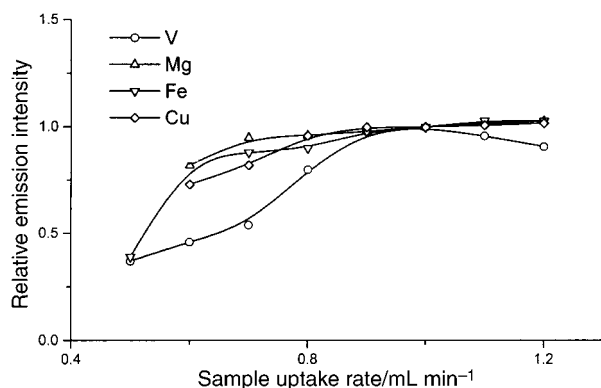


Fig. 2 Effect of sample uptake rate on the emission intensities of some elements: microwave power, 60 W; outlet capillary, $75 \mu\text{m}$ id; HCl concentration, 0.5 mol L^{-1} .

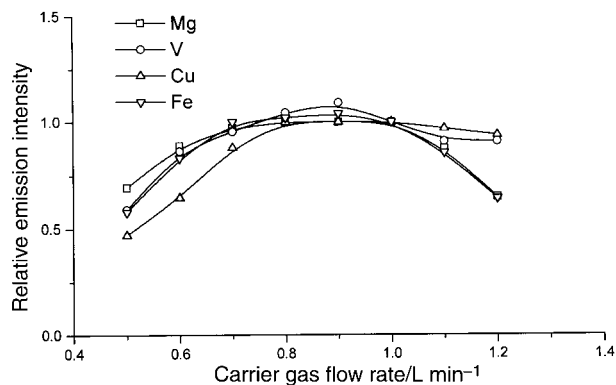


Fig. 3 Effect of carrier gas flow rate on emission intensities of some elements: microwave power, 60 W; outlet capillary, $75 \mu\text{m}$ id; HCl concentration, 0.5 mol L^{-1} .

leaked from the lab-built union between the PTFE and outlet capillaries.

It is shown in Fig. 2 that emission intensities of the four elements increase with the sample uptake rate. Once the sample uptake rate is higher than a necessary value, the amount of vapor produced is only dependent on the microwave power and acid concentration. The higher the sample uptake rate, the higher the pressure inside the PTFE capillary. Relative high pressure is favorable to the generation of fine aerosols. In addition, a higher sample uptake rate means more sample will be brought into the plasma. Therefore, the emission intensities increase with the increase of sample uptake rate. However, too much solution can cause the droplet size to become bigger during transfer, and also a higher sample uptake rate needs a higher microwave power. Meanwhile, because a large amount of water vapor was generated, a high efficiency condensing desolvation system was necessary for the MWTN. Since the emission intensity increase was no longer significant when the sample uptake rate increased above 0.8 ml min^{-1} , a 1.0 ml min^{-1} sample uptake rate was chosen in this study.

Effect of carrier gas flow rate

With TSP, the nebulization efficiency as well as the characteristics of aerosols produced are independent of carrier gas flow rate. Emission intensities of four elements against carrier gas flow rate are shown in Fig. 3. The carrier gas flow rate affects the intensities by affecting the amount of aerosol brought into the plasma per unit time and the residual time of the species in the central channel of the plasma. Also, the carrier gas flow rate can effect the transfer efficiency of aerosols. Based on the experimental results, the carrier gas flow rate in this study was set at 0.8 L min^{-1} .

Analytical figures of merits of the low-powered MWTN

Under the conditions chosen, the detection limits and precisions of an ICP spectrometer with the low-powered MWTN for iron, magnesium, vanadium and copper were determined and are listed in Table 2. The results obtained from the same spectrometer with a cross-flow nebulizer without

Table 2 Comparison of detection limits (DL) and relative standard deviations (RSD) of MWTN-ICP-AES and PN-ICP-AES for some elements

Element	Wavelength/nm	MWTN		PN	
		DL/ng ml^{-1}	RSD (%) ($n=11$)	DL/ng ml^{-1}	RSD (%) ($n=11$)
Fe	238.204	6.9	3.1	21	1.5
Mg	279.553	0.4	2	1.5	0.4
V	292.402	1.8	2.4	7	0.9
Cu	324.754	2	3.5	4	0.6

desolvation are listed also for comparison. The sample uptake rates were the same at 1.0 mL min^{-1} , and the carrier gas flow rates were 1.0 L min^{-1} . As can be seen, the detection limits for the elements studied were improved by a factor of 2–4. In fact, the emission intensities were usually improved by a factor of about 10; however, due to the unsatisfactory stability, the improvement factor for detection limits is not as great as that for emission intensity.

Conclusions and further studies

The preliminary results show that the low-powered MWTN can produce very fine aerosols. After sufficient and proper desolvation, it could be easily coupled to an ICP-AES spectrometer. It can provide much higher net emission intensities for most elements compared with a traditional pneumatic nebulizer, and can work with high acid concentration solutions. And because the inner diameter of the PTFE capillary used was rather wide, and only a short narrower quartz capillary was added, the pressure caused inside the nebulizer was not as high as in traditional thermospray. Therefore, a peristaltic pump is enough to push the sample through the nebulizer, while a high-pressure pump is necessary in traditional TSP. Instead of a microwave oven, a resonant cavity, TM_{010} cavity, was used as the heating device, thus, the nebulizer is not only highly efficient, but also small in size. In turn, it is easily combined with any commercial ICP spectrometer.

However, the precision is not satisfactory at present. Further studies will focus on the improvement of the stability and efficiency. No clogging was found for this nebulizer even when the matrix concentration (Na) was over 2000 mg L^{-1} . It shows a great potential in combining an on-line digestion system with the microwave thermospray and for the analysis of samples with high salt content such as sea water samples.

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