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RESEARCH ARTICLE

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Studies on injector pump-ultrasonic nebulizer feeding sample system for MPT-AES

Abstract The feeding-sample system used by microwave plasma torch atomic emission spectroscopy (MPT-AES) is the pneumatic nebulization system; its efficiency, however, is not good. A newly built injector pump–ultrasonic nebulizer combination feeding-sample system has been designed. Its performance was tested and compared with that of the pneumatic nebulization system. It can be concluded that the newly built feeding-sample system can increase the spectral line intensity by about two to three times and decrease the detection limit by about 2 to 10 times. Moreover, this newly built system can reduce the time taken washing the sample cell from 30 min or so to about 10 min.

Keywords injector pump–ultrasonic nebulizer, MPT-AES, pneumatic nebulization system

1 Introduction

The microwave plasma torch (MPT) has many applications in analysis methods; for example, MPT and atomic absorption, atomic fluorescence [1], mass spectrometry [2], chromatography [3] used together are all extremely successful. At present, the main application of microwave plasma torch–atomic emission spectroscopy (MPT-AES) includes pneumatic nebulization [4–5] and ultrasonic nebulization [6–10]. In ultrasonic nebulization, the analysis solution is transported to a quartz piezoelectric transducer surface, which transforms the electrical energy into high-frequency vibration. This causes the sample solution to disperse aerosol of small droplet size and narrow drop size, then the aerosol is led continuously into the plasma by the carrier gas. Because the droplet produced by ultrasonic nebulization is thin and because of the high efficiency of aerosol generation and transport, it is a good sample introduction for a mass spectrometer. In early ultrasonic nebulizers, the majority used the intermittent-type sample introduction. Because these used continuous sample introduction, the atomizer piezo-electric crystal plate easily burns down. The present ultrasonic nebulizer solves this problem. Although commercial ultrasonic nebulizers have been in the market for years, their expensive price (US$12,000～20,000/set) has hindered their further use.

Some research teams are attempting to improve the situation. Jin et al. [11] reported one kind of ultrasonic nebulizer by modifying cheap domestic humidifiers. The short-term performance of this nebulizer is satisfactory, but its long-term accuracy is poor because the sample solution is consumed easily and the coupling water temperature gradually rises, which hinders nebulization efficiency. Clifford et al. [12] also reported a similar equipment that can be used either as an intermittent nebulizer or a continuous one. But this kind of equipment needs a big spray chamber that requires longer cleaning time (approximately 6 min). Petrucci and Loon [13] described an improved continuous ultrasonic nebulizer whose cleaning time is about 25 s～30 s.

In this research work, a set of intermittent-type ultrasonic nebulizers were developed. This system includes an ultrasonic nebulizer and a sample introduction system. The sample introduction system pumps through the multichannel valve and the syringe pump pours and discharges the sample solution into the sample chamber. It uses a degassed water circulation unit to keep the coupling water temperature constant, which results in improved performance of the ultrasonic nebulizer.

2 Experimental

2.1 Reagents and instrumentation

According to the standard method, standard mix stock

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solutions (1 mg ml^{-1}) of cadmium, copper, magnesium, calcium, and sodium were prepared. The blank solution is double distilled water.

The MPT-AES is a product of Changchun Jilin University–Little Swan Instruments. The injection pumps and the ultrasonic nebulizer were assembled by us. The injection pumps were from Jihua Medical Apparatus and Instruments. Argon purity was 99.99% (Changchun Oxygen Factory).

2.2 The design of the ultrasonic nebulizer

The pneumatic nebulization system is shown in Fig. 1. The high flow rate carrier gas enters the nebulizer from the entrance (3) to form the negative pressure in the capillary vessel terminal and the solution is extracted from the nebulizer cavity body through the drive pipe (2). Then, the solution is pulled and hits the thin droplet from the spray outlet (4) blowout.

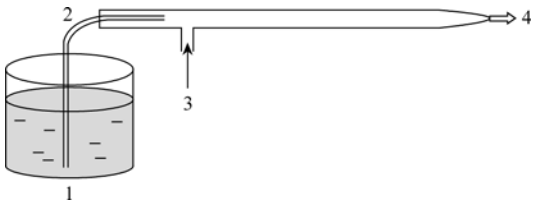

Fig. 1 Schematic diagram of a concentric pneumatic nebulizer.
(1) Sample cell; (2) sample tube; (3) carrier gas entrance; (4) spray outlet.

Figure 2 is a cross-sectional view of the ultrasonic nebulizer. The ultrasonic wave source (1) produces the ultrasonic wave through the transmission medium (2) (constant temperature is needed to avoid evaporation) to the vibration surface that the high polymer thin film produces. This causes the solution in the sample chamber under the thin film vibration function to create a thin fog from the spray outlet (5) blowout. The sample tube (7) and waste tube (8) connects to the sample chamber base. Their function is for the introduction of the solution to the sample chamber and disposal of the effluent from the sample chamber. The compensating pipe (9) apertures are distanced from the sample chamber base and control liquid level at a certain height; the excess solution is discharged through it. Sample chamber volume is about 40 ml. It is filled with just 7～8 ml (approximately) of the sample solution, i.e., 1/5–1/6 of the sample chamber, in order to achieve good nebulization effect. The sample solution is replaced after approximately 2 min. Under this condition, 0.8 l • min gas flow rate may produce 0.9 g • min of aerosol. Comparing this with the ordinary pneumatic nebulizer (output, 0.06 g • min aerosol), the aerosol can be produced 15 times faster, Which may therefore enhance the sensitivity by more than one magnitude compared to the pneumatic nebulizer.

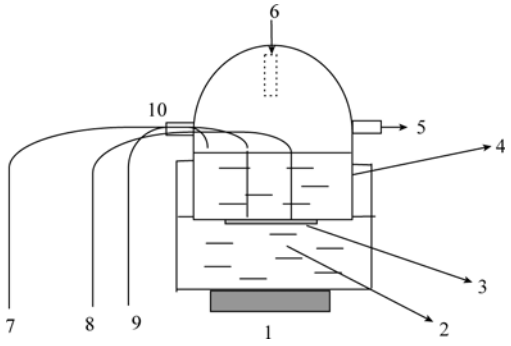

Fig. 2 Section plane diagram of the ultrasonic generator.
(1) ultrasonic generator; (2) transmission medium; (3) transducer (polymer membrane); (4) sample chamber and resolution; (5) spray outlet; (6) carrier gas entrance; (7) sample tube; (8) waste tube; (9) compensating pipe

The injection pump–ultrasonic nebulizer combination feeding-sample system is shown in Fig. 3. The sample introduction System was designed to control the introduction of the sample solution and discharge into the sample chamber. The sample introduction system mainly includes a syringe pump, a three-way valve, and three one-way valves. The injection pumps through the triple valve (14), which is distinguished from the three one-way valves (9–11). When the syringe pump is pushed down, the one-way valve entrance connected to it turns on the sample solution admission valve. When the syringe pump pours into it, the one-way valve outlet opens to let the solution be discharged. The one-way valve (9) controls the introduction of the sample solution to the ultrasonic atomizer sample chamber. Then, when the one-way valve (10) discharge exceeds, it establishes the volume of the sample solution in advance. The one-way valve (11) controls the discharge of the sample solution into the sample chamber. To test, the syringe pump was turned off and the ultrasonic atomizer discharges the droplet into the heating tube (2). The steam, together with the sample, enters the cooling tube (5) and the water was discharged from the freeing port (17). Then, the sample aerosol enters the microwave plasma torch. After the test had been completed the syringe pump was turned on and the connected one-way valve (11) discharges the excess sample solution. After waiting for the waste liquid to be discharged completely, distilled water (7～8 ml) is poured into the sample chamber through the one-way valve (9). Then, the ultrasonic nebulizer system was started for approximately 2 min and discharged the waste liquid. The cleaning process was repeated twice.

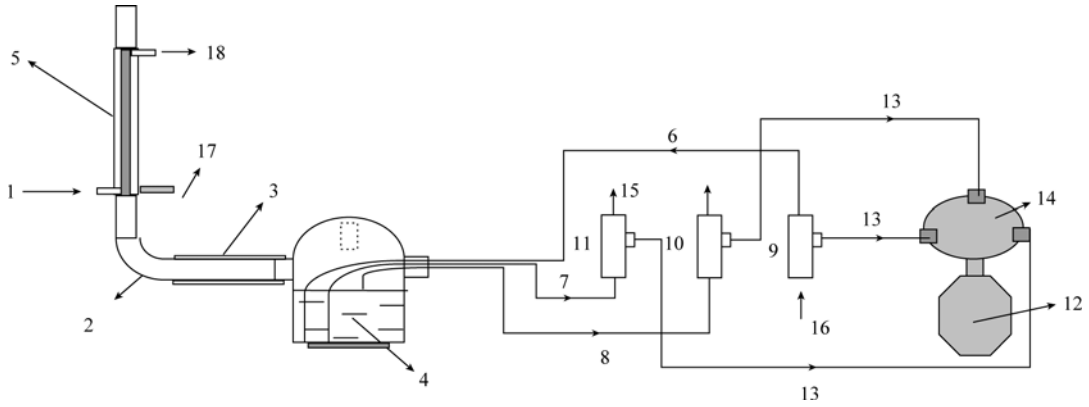

Fig. 3 Injection pump-ultrasonic nebulizer combination feeding-sample system.
(1) cooling water inlet; (2) heating tube; (3) heating tape; (4) sample cell; (5) cooling tube; (6) sample pipe; (7) waste pipe; (8) compensating pipe; (9–11) one-way valve; (12) injection pump; (13) linkage pipe between one-way valve and injection pump; (14) triple valve; (15) Exhaust outlet; (16) sample inlet; (17) freeing port; (18) cooling water outlet

2.3 The parameters for instrumentation

The support gas and carrier gas of the MPT-AES is Ar. The carrier gas flow rate is 0.7 ml/min, support gas flow rate is 0.6 ml/min and the negative high pressure of the multiplier phototube is 650 V. The heating pipe temperature is 350 °C, the heating pipe is inclined at a 15° angle and the medium water temperature is 8 °C。

3 Results and discussion

3.1 The influencing factor of the ultrasonic nebulizer system performance

3.1.1 The influence of sample chamber liquid level

The sample solution was a standard solution (1 mg/l) of Cu. When the sample solution was introduced into the sample chamber, the liquid level height rose, with an interval of 30 s to carry on the sample determination, which was done 42 times. The obtained data are shown in Fig. 4. As can be seen in Fig. 4, the solution liquid level was reduced while the sample signal intensity value also changing along with it. The signal intensity gradually increased then maintained at an invariable platform intensity. Afterwards, the intensity decreased gradually. This shows that the solution volume influenced the signal emission; the solution volume whether excessive or minimal can cause the signal strength to be reduce (7–13 ml).

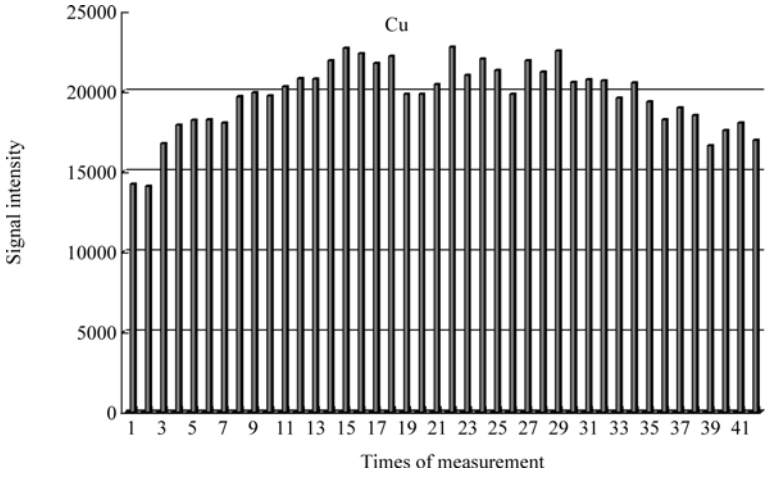

Fig. 4 Effect of height of liquid level (the emission intensity of copper with an increasing nebulizing interval of 30 s was recorded at each volume)

3.1.2 Heating pipe angle of tilt influence

The sample solution was a standard solution (1 mg • l^{-1}) of Cu. The sample introduction sample chamber and the liquid level altitude controlled to the best position; the angle of tilt of the heating pipe was changed (upwardly to incline by 15° or lower). The result is shown in Fig. 5. The heating pipe upwardly inclines, which was higher than that shown in Fig. 5.

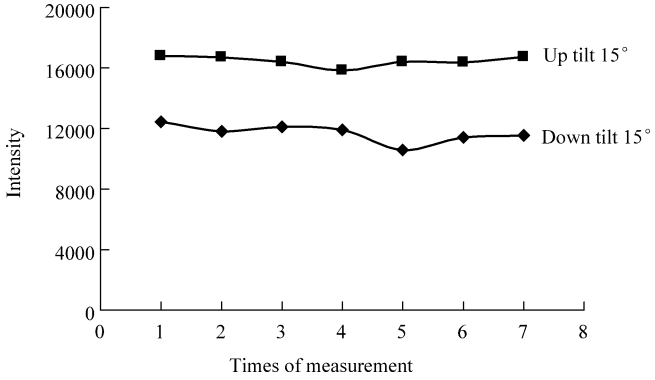

Fig. 5 Effect of angle of heating tube (the emission intensity of copper with an increasing nebulizing interval of 1 min was recorded)

3.1.3 Transmission medium temperature to sample signal influence

As can be seen in Fig. 2, the energy of the ultrasonic wave is transferred to the high polymer thin film through the transmission medium (2), causing the sample solution to be nebulized. The transmission medium temperature was increased along with the increase in nebulizer operating time, which causes the determination of the sample signal to become stable. The rubber tube was bent to a spiral-shape to put in the transmission medium. The temperature of the circulating water system was kept constant to ensure that the temperature of the transmission medium would remain constant in this research. The signal emission of 1 mg/l Cu was inspected when the temperature of the circulating water system increased from 6 °C to 15 °C. Obtained data are shown in Fig. 6. Along with the drop in circulating water temperature, the Cu emission rate stability was increased. In order to give attention to both the sample emission rate, and the stability, the temperature of the transmission medium was kept at 8 °C. As shown in this experiment, the

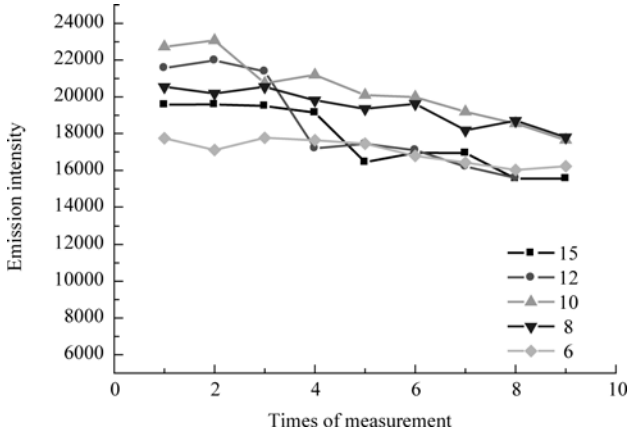

Fig. 6 Effect of temperature of conduct medium (the emission intensity of copper with an increasing nebulizing interval of 1 min was recorded)

transducer produced stable ultrasonic wave when the transmission medium temperature was low, which results in stable sample transmitting message. When the temperature of the transmission medium dropped to 6 °C, the emission rate of the sample decreased. It is believed that the temperature significantly affects the ultrasonic wave energy output of the transducer.

3.1.4 Carrier gas flow rate to sample signal influence

The sample solution was a standard solution (1 mg • l^{-1}) of Cu. When the carrier gas flow rate was, 0.8, 0.7, and 0.6 ml/min, the carrier gas flow rate had a weak influence on the sample signal. The measurement result is shown in Fig. 7.

Carrier gas flow rate has no effect on the sample emission, but in the sample chamber, the solution liquid level, the heating pipe angle of tilt, and the change in the temperature of the transmission medium have a tremendous influence on the sample emission. From this, the equipment structure and the exploitation conditions of the injector pump–ultrasonic nebulizer combination feeding-sample system were determined: (1) when the sample solution is introduced into the sample chamber, the solution has to adjust to the equilibrium height to maintain invariably the sample signal intensity; (2) the heating pipe must be inclined; (3) room temperature must be kept stable.

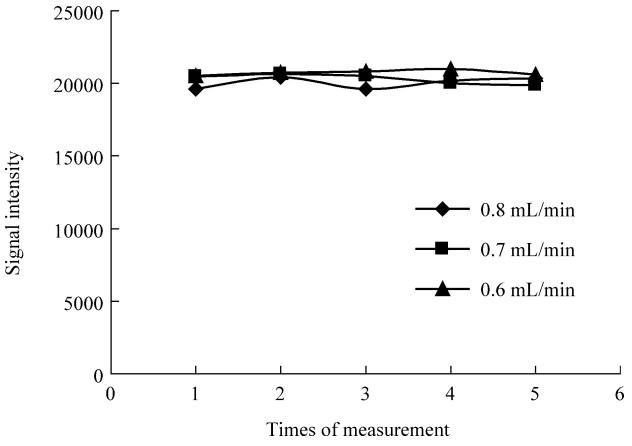

Fig. 7 Effect of flow velocity of carrier gas (the emission intensity of copper with an increasing nebulizing interval of 1 min was recorded)

3.2 Comparison between ultrasonic nebulization and pneumatic nebulization

The experimental conditions of the pneumatic nebulizer were optimized; support gas flow rate was 0.6 ml/min, carrier gas flow rate was 0.7 ml/min, and the negative high pressure of the multiplier phototube was 800 V. The experimental conditions of the ultrasonic nebulizer were optimized as stated above. Obtained results of 1 mg/l Cd, Cu, Mg, Ca, and Na are shown in Table 1. As can be seen, the obtained intensity of spectral line used by ultrasonic

nebulization was 2～10 times higher than that used by pneumatic nebulization, and the detection limits of the ultrasonic nebulizer were 2～10 times lower than that of the pneumatic nebulizer.

Table 1 Performance comparison of pneumatic nebulizer and ultrasonic nebulizer

Element	Nebulized method	Signal intensity					Blank signal intensity	Blank SD	Detection limit ($\mu g \cdot l^{-1}$)
		1	2	3	4	5			
Cd	U	16315	16934	17186	17130	16196	29.2	7.9	1.4
	P	9586	9341	9802	9671	9774	264	12.5	3.7
Cu	U	26013	26910	27188	25495	26119	30.8	3.5	0.5
	P	10793	10652	10327	11127	10897	502	19.3	5.4
Mg	U	25114	25318	24881	23802	25055	81.4	22.0	2.6
	P	9386	9882	9782	9671	10097	234	10.9	3.3
Ca	U	30256	29985	30628	29072	29641	141	4.3	0.4
	P	10581	10172	10789	9945	10391	40.6	9.4	2.7
Na	U	30482	29182	29451	31828	29644	88.1	3.1	0.3
	P	12268	12304	12562	11567	12005	22.7	6.9	1.6

U - Ultrasonic nebulizer**; P -** pneumatic nebulizer**; SD -** standard deviation**.**

3.3 Sample analysis

Under the experimental optimization condition, the determination of the actual sample uses the hair sample and the lubricating oil sample in the analysis; the accuracy of the analysis was confirmed by the element recovery.

3.3.1 Sample preparation

The hair sample (0.9 g) was accurately weighed in a quartz crucible and dry-ashed 30 min in a Muffle furnace at 800 °C. Then, the sample was dissolved in 2 ml of 2 mol • l^{-1} hydrochloric acid and the exces hydrochloric acid was removed from the sample solution. Then, the sample solution was diluted to 50 ml.

The sample lubricating oil sample (50 ml) was accurately measured in a quartz crucible. The sample was first carbonized at lower temperature on a sand bath and then incinerated for 30 min at 800 °C in a Muffle furnace. Then, the lubricating oil sample was treated just like the hair sample and diluted to 50 ml.

3.3.2 Analysis result

Table 2 shows two kinds of samples for measuring the concentration and recovery of the element. As can be seen from these data, the ultrasonic nebulizer system can increase the sensitivity of the MPT spectrometer.

Table2 Analytical results of two real samples

Element	Wavelength (nm)	Concentration ($\mu g \cdot g^{-1}$)			Recovery (%)
		Original	Added	Found	
Hair					
Mg	285.213	24.4	23.8	21.1	88.7
Cu	324.754	19.1	20.8	20.1	96.6
Zn	334.502	317	417	412	98.8
Fe	344.061	39.7	35.6	34.7	97.5
Ca	396.847	496	555	487	87.7
Oil					
Mn	259.373	14.2	10.0	9.01	90.1
Mg	285.213	0.50	1.00	1.03	103
Cu	324.754	5.74	5.00	5.52	110
Fe	344.061	16.1	20.0	18.9	94.5
Ca	393.366	3.33	2.50	2.27	90.8

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