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An Ultrasonic Nebulizer for Microliter Samples in Inductively Coupled Plasma Emission Spectrometry

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Synopsis. A batch type ultrasonic nebulizer is constructed for 300-μl samples to produce an aerosol for more than 60 s. Desolvation facilities are not used. The internal standard method is employed to compensate for the instability of nebulization.

The most common method for introducing samples into an inductively coupled plasma (ICP) is the pneumatic nebulization of aqueous or organic solutions. Although ultrasonic nebulizers were extensively used in the early stage of the development of the ICP,[1,2] they were gradually replaced by pneumatic nebulizers mainly due to cumbersome operation procedures in conjunction with desolvation apparatus. Olson *et al.*[3] reported an ultrasonic nebulizer which provided rapid and convenient sample change capability and a long term stability but it is still not widely accepted.

Recently considerable attention has been paid to the microliter sample injection into the ICP by conventional pneumatic nebulization[4,5] or electrothermal vaporization.[6,7] Ultrasonic nebulizers are inherently suited for the nebulization of microliter samples because they can nebulize solutions quite efficiently. Though many types of ultrasonic nebulizers have been reported in the literature,[8–12] none of them were particularly intended to be used for microliter samples. Hoare and Mostyn[8] designed a multicell ultrasonic system in which each sample cell could be rotated in turn to locate in the focussed ultrasonic beam, but they did not mention explicitly the sample size required.

We have constructed a batch type ultrasonic nebulizer with easily exchangeable cells for microliter samples. Simultaneous multielement analysis can be performed with a conventional signal integrator without modification by using 300-μl sample solutions.

Experimental

Apparatus. A Shimadzu 1-m grating spectrometer (GE-100) equipped with a three-channel detector unit (M-4),[5] a three-channel integrator (ES-603) and a 27 MHz ICP generator (ICPS-2H) were used. The entrance and exit slitwidths of the spectrometer were set to 20 and 40 μm, respectively. The ICP was operated at a forward power of 1.2 kW and argon flow-rates of 10, 1.0 and 0.8 l min^{-1} were used for the outer, intermediate and carrier gas, respectively.

Ultrasonic Nebulizer (Fig. 1). An ultrasonic transducer for a household electronic humidifier (Mitsubishi Electric Co.) mounted at the bottom of the cooling water chamber was driven by a 1.72 MHz transistor oscillator. The sample cell was a glass tube (11.5 mm i.d., 25 mm long) with a thin bottom plate (0.15 mm thick microscope cover glass, stuck with an epoxy resin adhesive). Two sample cells were mounted in a sliding cell holder so that they were rapidly exchanged without disturbing the nebulization. A polyethylene buffle made of a sealing cap of a reagent bottle was placed on the top of the cell to prevent large aerosol droplets from reaching the fog chamber. Carrier gas was introduced tangentially at the top of the cell so that the aerosol produced was effectively mixed with the carrier gas. Both the top plate of the sliding cell holder and the cooling water chamber were made of Teflon to make the holder slide smoothly without a leak of cooling water. A 35-ml fog chamber was designed so that the condensed aerosol would not flow into the sample cell and contaminate a new sample. The aerosol was introduced into the ICP without any desolvation facilities.

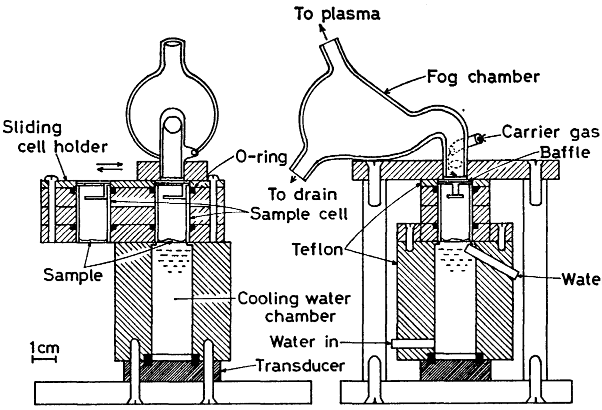

Fig. 1. Schematic diagram of the ultrasonic nebulizer for microliter samples.

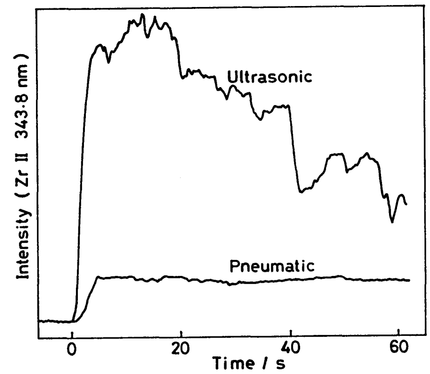

Fig. 2. Intensity-time curves for the Zr II 343.8 nm line.

The same intensity scale for the ultrasonic and pneumatic nebulizers. Zr: 1 μg ml^{-1}.

Solution. Standard solutions were prepared by dissolving reagent-grade salts or pure metals in appropriate mineral acids and diluting with water immediately before use.

Results and Discussion

Sample Volume. As the volume of the sample solutions in the cell was increased from 0 to 500 μl, the emission signals increased at first and then gradually decreased, with the maximum at about 300 μl, where the experiments hereafter were carried out.

Intensity-time Curves. Figure 2 shows intensity-time curves for the Zr II 343.8 nm line (1 μg Zr ml^{-1}) obtained with the present ultrasonic nebulizer and with a conventional pneumatic (concentric glass) nebulizer. In spite of the much smaller consumption of sample,

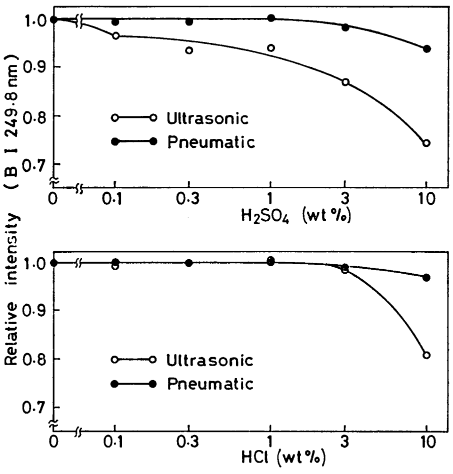

Fig. 3. Effects of acid concentrations on the intensity of the 249.8 nm line.
B: 10 μg ml^{-1}.

the signal intensity with the ultrasonic nebulizer is several times higher than that with the pneumatic nebulizer. The aerosol is produced for more than 60 s, so that a conventional signal integrator can be used without modification. Variation of the signal with time, however, is quite large as compared with that of the pneumatic nebulizer. Although various configurations of the fog chamber and sample cell were tried, the signal stability could not be improved.

Effect of Acid Concentrations. Generally the efficiency of the pneumatic nebulizer is known to be affected by acid concentrations[13] due to the variation of the viscosity of the solutions. The effects of sulfuric and hydrochloric acid concentrations on the emission intensity of the B I 249.8 nm line (10 μg B ml^{-1}) are shown in Fig. 3 for ultrasonic and pneumatic nebulizers. The efficiency of the ultrasonic nebulizer is affected more seriously than that of the pneumatic nebulizer by acid concentration.

Internal Standard Method. The instability of nebulization can be compensated to some extent by adopting the internal standard method. Though this method has not generally been applied in ICP emission spectrometry, it sometimes improves the precision of the analysis.[14] Yttrium was added as internal standard to the sample solutions and intensity-time curves of lines of various elements were compared with those of yttrium lines. The intensity-time curves of all the lines examined strikingly resembled each other irrespective of the excitation characteristics of the lines. Table 1 shows the relative standard deviations of intensities of various elements and those of ratios to the yttrium line intensities. In these experiments, each sample was nebulized for 10 s before the signal integration for 20 s. The determination was repeated 10 times for each sample. The use of the internal standard method reduced the relative standard deviation to less than 2%. The precision, however, is strongly dependent on the concentration level of the material being analyzed since the background fluctuation is not compensated by the internal standard method. Variation of the relative standard deviations with the change of titanium concentrations are shown in Table 2. The relative standard deviation of the intensity ratio increases rapidly below 0.1 μg ml^{-1} of titanium. Thus the detection limits cannot be improved.

TABLE 1. RELATIVE STANDARD DEVIATIONS (RSD) OF INTENSITIES AND INTENSITY RATIOS

Element	Wavelength nm	Concentration μg ml^{-1}	RSD (%) Intensity	RSD (%) Intensity ratio[a]
B I	249.77	5	6.6	1.8
Cd II	214.44	5	7.1	0.6
Co II	238.89	10	2.9	0.9
Cr II	205.55	10	6.0	1.1
Mn II	257.61	1	11.8	1.0
Ni II	232.00	10	10.6	1.6
P I	213.62	100	5.3	0.5
Zn I	213.86	10	12.2	1.5
Cu I	324.75	10	11.8	0.8
Ti II	334.94	10	9.2	1.3
Zr II	343.82	10	9.2	1.3

a) Internal standard: 10 μgY ml^{-1}, Y II 371.03 nm for Cu, Ti and Zr, and Y II 224.31 nm for other elements.

TABLE 2. RELATIVE STANDARD DEVIATION OF INTENSITY RATIOS AT DIFFERENT TITANIUM CONCENTRATIONS

Ti (μg ml^{-1})	RSD (%) Intensity[a]	RSD (%) Intensity ratio[b]
0	2.22	14.0
0.01	1.89	13.9
0.1	2.16	6.98
1	9.04	1.59
10	11.8	0.19

a) Line + background. b) Internal standard: 10 μg Y ml^{-1}, Y II 371.03 nm.

Accuracy was tested by analyses of standard reference materials. Titanium (certified values 0.066, 0.098%) and chromium (certified values 0.011, 0.036%) in low alloy steels (Japan Standards of Iron and Steel, JSS 168-2 and 170-2) were determined by preparing solutions containing 10 mg of the sample and 10 μg of yttrium per ml with satisfactory results (0.065 and 0.098%Ti, and 0.012 and 0.038%Cr).

Although the proposed ultrasonic nebulizer is less stable and more susceptible to acid concentrations than the conventional pneumatic nebulizer, it may be quite useful for analyses of samples of limited volumes, *i.e.*, microliter samples.

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