

Development of an Ultrasonic Nebulizer Using a Domestic Humidifier

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An inexpensive ultrasonic nebulizer (USN) was developed utilizing a home humidifier. The ultrasonic transducer was taken from a commercial USN and the power supply was from a humidifier. Sample was continuously fed into the nebulizer and the detection limit was improved 3-20 times over a pneumatic nebulizer. Undesirably, noise in signal was also increased several times. 0.5 ppm of Mn was used as an internal reference and the "long-term" drift could be successfully corrected. Since the noise contained high and low frequency components, both could be effectively removed only by the real-time correction method such as the Myer-Tracy method, where the reference line was simultaneously monitored with the analytical lines. The performance of USN was tested with NIST SRMs and showed good agreement with the certified values.

Introduction

Ultrasonic nebulizer (USN) have begun to be widely used in recent studies¹⁻⁷ of atomic spectrometry because of its higher efficiency over pneumatic nebulizer (PN).⁸⁻⁹ The nebulization efficiency ranges from 10-20%, which is about 10 times as high as that of PN. Narrow droplet size distribution and small mean diameter of droplets were attributed to enhancement of signals.¹⁰⁻¹² Improvements of 5-50 times in detection limits have been common with the use of USN.

The other important characteristics of USN, which is inherently different from PN, is its relative independency of carrier gas flow^{13,14} to nebulization efficiency. This can provide a greater freedom in adapting the nebulizer to a system of which gas flow rate does not match with that of pneumatic nebulizer. For example, if Microwave Induced Plasma (MIP) which uses a low gas consumption is to be used, USN can be employed at such a low gas flow rate that is required. Also, it is relatively independent of sample uptake rate thus providing a greater flexibility in use with a chromatographic system such as HPLC-MS (High Performance Liquid Chromatography-Mass Spectrometry). Additional merits of USN can be found in other literatures.^{10, 15-16}

Commercial USN have gained wider acceptance in these days and have been used in the areas of ICP (Inductively Coupled Plasma),¹⁷⁻¹⁹ MIP,⁹ and ICP-MS.^{8,4,20,21} However, a commercial USN is not an inexpensive system and its performances are sometimes not so reliable as PN. Several early studies^{16,22} reported some drifts in USN. Thus, there are needs to develop an inexpensive system and a correction method to ensure the precise measurement with the use of USN.

There have been several attempts^{9,23,24} to utilize a commercial humidifier as an USN in atomic spectroscopic area. However, they are a "batch nebulizer" where the sample solution is contained in a sample cell of which base is transparent to ultrasonic waves. Sample solutions are held in a container thus can not be easily changed. Sample throughput is severely limited and practical usage is discouraged. Another type of USN, which is now being used in a commercial neb-

ulizer, is a continuous-flow type. The sample solution is constantly fed into a chemically resistant plate which is bonded onto the ultrasonic transducer.

Thus, in this research, a continuous-flow USN has been developed and characterized utilizing an inexpensive home humidifier. The sensitivity and detection limits have been found to be improved over PN more than 3-20 times. Another important quality of a nebulizer is signal stability. The signal of USN developed in this study shows a large drift and noise due to the unstability of the ultrasonic power generator. To make it more reliable, one has to find a method to compensate for the drift. One of the most effective method to correct for the sample drift is employing the internal standard method, which has been successfully applied in this study. Myer-Tracy signal compensation method²⁵ has been applied and found to be very effective in increasing the precision greatly. In this method, Sc is used as an internal standard and its line is constantly monitored as the reference by a photodiode designated. Since both reference and analytical lines are monitored simultaneously, any changes in sample nebulization and transport efficiencies as well as plasma fluctuations can be corrected.

Experimental Section

The system was consisted with ultrasonic transducer, spray chamber, heater, and condenser. This design was the same as a commercial one. The ultrasonic transducer was taken from a commercial USN (Model SP5125, CETAC Technologies, Omaha, NE, USA) and the spray chamber was constructed locally. The total volume of the spray chamber was about 50 cm³. A heating tape was wrapped around the quartz transport tube and the temperature was set around 160 °C. The condenser temperature was controlled by a cooling bath (Jeio Tech. Co, model RBC-10) at -5 °C. The ultrasonic power generator was taken from a home humidifier (LG Co., model H-473) and the power was set at the maximum of the instrument setting during the normal operation.

The spectrometric system used in this study was a sequen-

Table 1. Experimental apparatus and operating conditions used in the experiment

Conditions of spectrometer	
Monochromater	
Focal length	: 1 m
Grating	: 2400 grooves/mm
Operating condition	
Observation height	: 6-12 mm for USN 10-15 mm for PN
Argon gas flow rate	
Outer	: 15 L/min
Auxiliary	: 1.0 L/min
Nebulizer	
Ultrasonic nebulizer	: 0.7-0.8 L/min
Pneumatic nebulizer	: 1.0 L/min
Sample flow rate	
Ultrasonic nebulizer	: 2.0-2.5 mL/min
Pneumatic nebulizer	: 1.0 mL/min
RF power	: 1.0 kW
Heating temperature	: 160 °C
Condenser temperature	: -5.0 °C
Ultrasonic nebulizer Power	: Maximum setting

tial ICP 1000 (Perkin-Elmer, CT., U.S.A). Experimental apparatus and their operating conditions are summarized in Table 1. Optimum operating condition was set to give the best signal-to-noise ratio with 5.0 ppm Cd solution. Observation height was optimized for each element studied.

Experiments were proceeded with the optimization of sample gas flow rate and liquid sample flow rate. Nebulizer gas flow rate was changed from 0.4 L min⁻¹ to 1.0 L min⁻¹ with a fixed sample flow rate. With the optimized sample gas flow rate, liquid sample uptake rate was varied from 1.0 L min⁻¹ to 3.5 L min⁻¹. The position of sample delivery tube was also found very important¹² in producing fine aerosols. 1.0 mm gap between the sample delivery tube and the transducer surface was found to be the best.

Result and Discussion

Detection Limit (DL). Detection limit in this study was defined as the concentration of which signal is three times larger than the standard deviation of the background or the signal-to-noise ratio, S/N, is 3. Using doubly deionized water as a blank, background and noise in background were determined at various wavelengths (Cd 214.438 nm, Be 234.861 nm, Ni 221.647 nm, Bi 223.061 nm, Pb 220.353 nm, Zn 213.856 nm, Sn 235.484 nm, Tb 350.917 nm, Cr 205.552 nm). Standard solutions of 0.5 ppm to 100.0 ppm (Cd 10.0 ppm, Be 0.5 ppm, Ni 10.0 ppm, Bi 50.0 ppm, Pb 50.0 ppm, Zn 5.0 ppm, Sn 100.0 ppm, Tb 10.0 ppm, Cr 10.0 ppm) were aspirated and measured 30 times for each element as signals. DLs were calculated and shown in Table 2 with the improved factor. Currently, the USN used in this research showed significant improvement of sensitivity from

Table 2. Improvement of Detection limits of USN over PN for several elements

Element	Concentration (ppm)	Wavelength (nm)	Detection Limit		Improved Detection Limit Factor
			USN (ppb)	PN (ppb)	
Cd	10.0	214.438	0.594	12.0	20.2
Be	0.50	234.861	0.0440	0.440	9.9
Ni	10.0	221.647	1.888	21.4	11.3
Bi	50.0	223.061	4.466	60.5	13.5
Pb	50.0	220.353	7.735	104.1	13.5
Zn	5.0	213.856	0.446	6.67	15.0
Sn	100.0	235.484	16.08	102.7	6.4
Tb	10.0	350.917	2.275	7.38	3.2
Cr	10.0	205.552	3.105	35.7	11.5

3 to 20 times over PN. The reasons for the improvement are thought to be a large generation of secondary aerosols and removal of solvent water.¹⁸

Though the USN made with a home humidifier showed excellent sensitivity, precision was still needed to be improved. A drift in signal was checked at every 5 seconds for 2.5 minutes (30 times) and was defined as a "short-term" noise. The comparison between PN and USN showed that USN was worse about 4.5 times than PN (Table 3). In a "long-term" drift, where the signals were measured for 7 hours period, the noise in signal was 11.2%. It was measured for every hour and each measurement was taken for 3 minutes, 30 times of reading and 5 seconds for each reading. The fact that "long-term" drift was more significant than "short-term" drift suggested a slow drift was dominant in USN system. It has been reported¹⁶ that USN suffer from the contamination on the transducer disc in a long use, thus "long-term" precision deteriorated. However, the "long-term" noise characteristics observed in this study were not an one-directional drift but random in nature. Thus, the origin of low frequency noise was suspected as the unstability of ultrasonic generator than the contamination of disc.

There could be other sources of noise in this system in addition to the ones from ICP spectrometry and the nebu-

Table 3. Comparison of short-term noise (%RSD) for USN and PN

Element	Ultrasonic Nebulizer (%)	Pneumatic Nebulizer (%)	Ratio of Precision*
Cd	2.53	0.79	3.2
Be	3.52	0.51	6.9
Ni	3.05	0.74	4.1
Bi	2.35	0.53	4.4
Pb	4.24	0.87	4.9
Zn	3.60	0.64	5.6
Sn	2.37	0.76	3.1
Tb	2.24	1.35	1.7
Cr	8.12	1.35	6.0
AVERAGE	3.56	0.84	4.2

*Ratio was calculated by RSD of USN/RSD of PN.

Table 4. Change of precision using the Internal Standardization Method

	Short-term stability*		Long-term stability*		
	Without internal standard	With internal standard	Without internal standard	With internal standard	Improved Factor
Cd (214.438 nm)	7.2%	8.2%	13.7%	4.4%	3.1
Co (238.892 nm)	5.8%	6.7%	15.1%	1.8%	8.4
Zn (213.856 nm)	4.7%	6.9%	14.3%	0.80%	18

*Stability is % RSD in signal for 1 minute (short-term) or 3 hour (long-term)

lizer. One of them could be from the transport lines between USN and the plasma. For examples, aerosols can be evaporated and condensates at the wall. Dried salt also can be lost in the way or dissolved into liquid in condenser. Noises were monitored for PN with the same desolvator. It showed little degradation when the condenser was attached or not, which suggests that the noises were mainly from the USN itself.

One of the technique to compensate for noise, still not using an expensive ultrasonic power generator, is to use the internal standard method. Mn was put into sample to be 0.5 ppm. The sample intensity (10.0 ppm Cd, 10.0 ppm of Co, and 5.0 ppm of Zn) was normalized by the internal standard Mn intensity. After analytical lines are measured, the reference line of Mn is checked and the process be repeated for several times. The software in this P 1,000 ICP allows the process to be automatic. The "long-term" drift was improved about 3, 8, and 18 times for Cd, Co, and Zn, respectively as shown in Table 4. However, the "short-term" precision was not improved at all. Since the ICP instrument used in this study is a sequential spectrometer, it takes time (from a fraction of a second to few seconds) to change from a wavelength to another. While the spectrometer changes from a wavelength of sample to that of the internal standard, signals can be changed during the transition and correction can not improve or even becomes worse, as is observed in Table 4. Any noise of which time scale is shorter than the wavelength transition period can not be corrected.

Since this time window for wavelength transition was only few seconds at most, a "long-term" drift of several hours, 3 hours in this case, should not be affected at all and the result shows dramatic improvement. In a simultaneous spectrometer, the internal standard method should be working for both "long and short-term" noises. The spectrometer used in this research have a "real-time" correction method, Myer-Tracy method, by which Sc is constantly monitored with a phototube. Part of the beam from ICP is sent to the phototube through a filter, always. Any fluctuations in the reference Sc signal, whether it be due to the sample aerosol fluctuation or

plasma flickering, is monitored and cancels out the noise in signal simultaneously. 50 ppm of Sc solution was used in the Myer-Tracy method and the result in Table 5 shows good improvement both in "long and short-term" noises. This result could sometimes be better than that of PN because it corrects even for the noise in the plasma. When compared to a commercial USN, of which precision is about 1.0%, this system showed very larger fluctuations in signal and could be analytically used only after the compensation.

Memory Effect. Memory effect is expressed as the wash-out time measured with a standard solution. In this research, a Cd 10.0 ppm solution was aspirated into ICP until a plateau in signal was reached. A blank was aspirated and the time taken for the signal to be reduced to 5% or 1% of the original signal was recorded as the wash-out time. In Table 6, memory effect was compared for PN and USN and it is about 5 times larger for USN than PN. A commercial USN typically has 2-3 times larger wash-out time than PN. One of the main reason why USN has a long wash-out time is that sample tends to be remained around the non-active transducer much longer than PN. By adding an additional fast pumping step,⁵ wash-out time could be greatly reduced. However, some of the aerosols absorbed in a condenser or transport wall can slowly be leaked out. By reducing the volume of spray chamber and the length of transport tube between the USN and plasma, absorbed sample aerosol can be minimized.

Analysis of NIST SRMs. To check the performance of USN, NIST SRM 1571 (Orchard leaves) and SRM 1566 (Oyster tissue) were analyzed for Cr, Pb, and Zn. For SRM 1571, 1.000 g of sample was digested in nitric acid and diluted to 100 mL. Sc was added as an internal standard so

Table 6. Comparison of wash-out times for USN and PN

	USN	PN
Wash-out times (5%)	51 sec	9 sec
Wash-out times (1%)	68 sec	13 sec

Table 5. Improvement of precision using the Myer-Tracy Signal Compensation Method

	Short-term stability*			Long-term stability*		
	Without Internal Standard	With Myer-Tracy	Improvement Factor	Without Internal Standard	With Myer-Tracy	Improvement Factor
Cd (214.438 nm)	8.3%	2.40%	3.5	15.9%	4.5%	3.5
Co (238.892 nm)	6.3%	0.70%	9.0	13.1%	1.3%	10
Zn (213.856 nm)	7.0%	0.50%	14	11.7%	0.8%	15

*Stability is % RSD in signal for 1 minute(short-term) or 3 hours(long-term)

Table 7. Determination of Cr, Pb, and Zn in biological NIST SRMs unit: $\mu\text{g}/\text{kg}$

	SRM 1571		SRM 1566		DL of USN
	certified ^a	measured	certified ^a	measured	
Cr	10.4±1.2	8.2±0.8	3.4±1.3	-	3.1
Pb	182±21	167±1.6	2.3±0.2	-	7.7
Zn	101±12	96.2±3.8	4160±68	4119±76	0.4

*Uncertainty is expressed in two standard deviation (σ). ^aThe concentrations shown here are the final values in solution after dissolution and dilution of solid samples.

that the final concentration to be 50 ppm. SRM 1566 was treated in the same manner. The results obtained are shown in Table 7 and agree well with the certified values. The concentration of Cr in the sample after the dilution was even below the detection limit of ICP using PN. However, with the use of USN, the signal was enhanced and could be successfully measured. The uncertainty level in Cr is high because of the low concentration close to the DL. For SRM 1566, the concentrations of Cr and Pb were even below the detection limits and were not detected.

Conclusion

Sensitivity was greatly enhanced by using an USN made from a home humidifier in ICP spectrometry. With optimized experimental conditions, detection limits were improved 3-20 times over pneumatic nebulizer. However, the signal was not as stable as that of PN. Unstable power generator was considered as the largest source of drift. Internal standard method has been successfully applied for the compensation of drift. Because of the nature of the instrument, only the "long-term" noise could be improved with the internal standard method. A "real-time" internal standard method could resolve for the "long and short-term" noises. Myer-Tracy internal standard method where Sc line is constantly monitored simultaneously with sample wavelengths has been applied and the result has shown good agreement with NIST standard reference materials. Wash-out time was longer than that of PN. To be more practical, USN needs an improved design of washing cycle and smaller spray chamber.

As the noises were characterized and compensated, this inexpensive USN made from a home humidifier could provide good sensitivity and precision. To be able to use this USN to any kind of system even where simultaneous correction is not possible, a different compensation method is needed. For example, if the amount of aerosol generation can be monitored, signal drift can be corrected and it can be

applied in wider areas. For this purpose, a laser scattering method is under investigation in our laboratory.

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