Effective application of ultrasonic nebulizer to ICP-AES analysis of REE, Y and Sc in geochemical samples

Iwao KAWABE, Takahiro TORIUMI, Atsuyuki OHTA
and Satoshi KANDA

*Department of Earth and Planetary Sciences, School of Science,
Nagoya University, Chikusa, Nagoya 464-01, Japan*

ABSTRACT

An ultrasonic nebulizer used in ICP-AES analyses of REE, Y, and Sc improves analytical sensitivities for the elements by one order of magnitude relative to the conventional pneumatic nebulizer. The detection limits (the concentrations corresponding to 3σ-background variations) by ICP-AES with the ultrasonic nebulizer range between 0.05 ppb and 0.5 ppb for Eu, Tm, Yb, Lu, Y, and Sc, and between 0.5 ppb and 5 ppb for La, Ce, Nd, Sm, Gd, Tb, Dy, Ho, and Er. Only for Pr, the detection limit is 10 ppb. The detection limits correspond to about 2% of the chondritic abundances or less, except for Pr and Tb. No significant memory effects have been found in the ultrasonic nebulizer. It takes 50 to 60 sec to clean out a sample solution after its measurements. The clean-out time is only about twice that of the conventional pneumatic nebulizer. Intermittent injections of dilute HF solution (0.5%) are so effective to maintain a quartz transducer clean. This makes its nebulization efficiency approximately constant. The ultrasonic nebulizer can be applied to routine ICP-AES analysis of REE, Y, and Sc in a wide spectrum of geochemical samples in couple with adequate wet chemical techniques for their group separation. Ar gas and sample solutions consumed by the ultrasonic nebulizer in each run are about twice as much as those by the pneumatic one. To save running cost and sample solutions, it is better to use the ultrasonic nebulizer as a complement to the conventional pneumatic one only for a limited number of REE which are relatively insensitive and less abundant like Pr, Tb, Ho, and Tm. Some examples of our application are presented.

INTRODUCTION

For enhancement of analytical sensitivities in ICP-AES, ultrasonic nebulizers have been proposed by Boumans and de Boer (1975) and Olson et al. (1977). This nebulization method indeed improved analytical sensitivities up to ten times as high as conventional pneumatic nebulizers. However, it has been pointed out that ultrasonic nebulizers have the following drawbacks: (1) significant memory effects, namely, sample solutions once injected into the nebulizer are not readily cleaned out, unlike the case of pneumatic nebulizers. (2) the nebulization efficiency is rather unstable because of changing surface condition of quartz transducer during repeated use of it (Potts, 1987; Hara-

guchi, 1986). Because of the drawbacks, the application of ultrasonic nebulizers to routine ICP-AES analysis has not been recommended by Potts (1987) and Haraguchi (1986).

In the course of our geochemical studies of REE with ICP-AES (Kawabe et al., 1994; Kawabe, 1995), we have tested the performance of a ultrasonic nebulizer system (CETAC UT-5000AT) attached to a scanning type ICP-AES spectrometer (SEIKO SPS-1500R). As a result, we have confirmed that the ultrasonic nebulizer system can be effectively applied to routine ICP-AES analysis of REE, Y, and Sc. Our conclusion is contrary to previous ones. The purpose of this paper is to present our evaluation for the ultrasonic nebulizer system used in ICP-AES analysis of REE, Y, and Sc.

EXPERIMENTAL

The ultrasonic nebulizer system used in this study consists of a ultrasonic nebulizer (CETAC UT-5000AT), a carrier gas controller unit (SEIKO Instruments), and a peristaltic pump (TOKYO RIKA Corp.) for injecting sample solutions (Fig. 1). The flow rate of Ar carrier gas was 1.0 l/min. The heating and desolvation units of the nebulizer system were kept at 140°C and 2°C, respectively. The nebulizer system was attached to a SEIKO SPS-1500R, which has a computer-controlled sequential Czerny-Turner scanning monochromator with the focal length of 1.0 m and the holographic grating of 3,600 grooves/mm. Aerosols of sample solutions are transferred into the ICP torch via the 1 m-long Tygon tubing with inner diameter of 3/16 inches. For all emission measurements, the plasma power and the measurement position
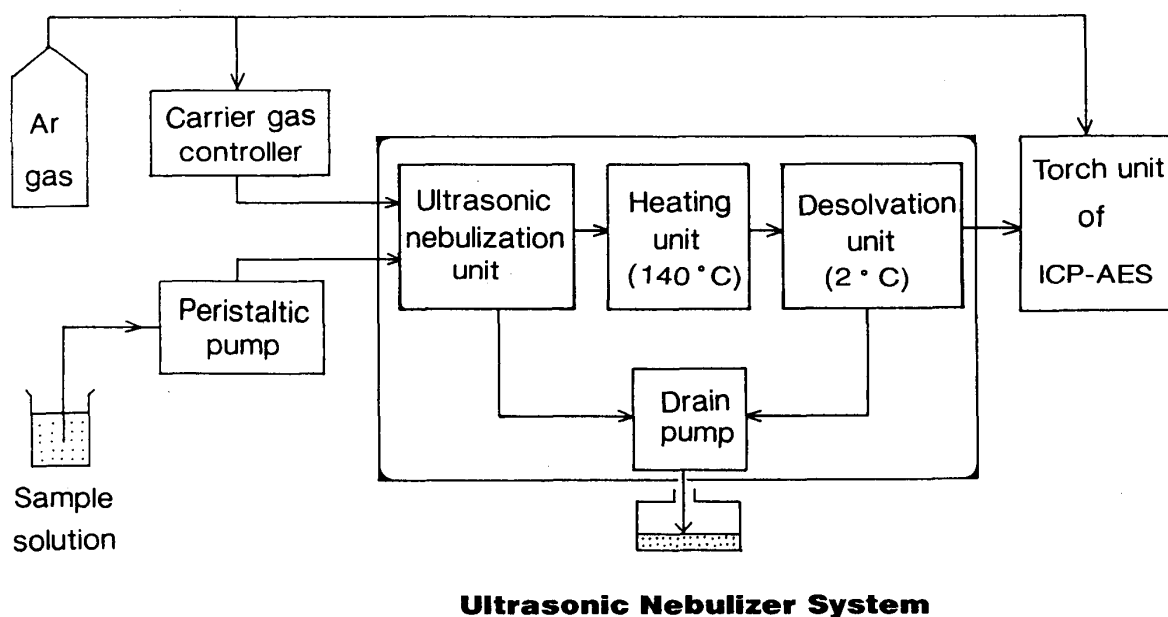

Ultrasonic Nebulizer System

Fig. 1.   A schematic illustration of an ultrasonic nebulizer system for ICP-AES spectrometer used in this study.

were set to be 1.4 kW and 10 mm above the work coil, respectively. The plasma gas flow rate and the auxiliary gas flow rate were 16 l/min and 0.4 l/min, respectively. The wave-length used for each element was the same as in our previous works (Kawabe et al., 1994; Kawabe, 1995). Each wave-length is selected to minimize spectroscopic interferences due to the other elements of this group (REE, Y, and Sc).

RESULTS AND DISCUSSIONS

1. Detection limits by ICP-AES with ultrasonic nebulizer

Detection limits (DL) and background equivalent concentrations (CBE) for REE, Y, and Sc in ICP-AES analysis with the ultrasonic nebulizer have been evaluated by the following method: After setting the monochromator at each wave-length, the emission intensity of a 0.6 ppm standard solution was integrated for 2.0 sec. This was repeated five times. Similarly, the background emission intensity was measured twenty times by introducing distilled water. From the emission intensity data, the mean for twenty background values and its 3-σ variation are converted into the background equivalent concentration (CBE) and the detection limit (DL), respectively.

Table 1 lists the results of DL and CBE for REE, Y, and Sc, along with respective wave-lengths used. According to DL-values, we can classify the elements into three groups. The first group consists of Eu, Tm, Yb, Lu, Y, and Sc. Their DL-values are the lowest ranging between 0.05 ppb and 0.5 ppb. The second group includes La, Ce, Nd, Sm, Gd, Tb, Dy, Ho, and Er. Their DL-values are within 0.5 ppb to 5 ppb. The third group includes only Pr, the DL value of which is 10 ppb. This is the highest DL-value in the sixteen elements. The obtained DL-values positively correlate with the CBE-values as shown in Fig. 2. This correlation is consistent with the fact that all the emission intensity data have been measured with rather constant relative standard deviations of 1 to 2%. Hence, the DL-values are mainly determined by the signal/background emission ratios at selected wave-lengths for respective elements.

In Table 1, we added the set of abundance values of this group of elements in the C1 chondrite (Anders and Grevesse, 1989). We have calculated the ratios of respective DL-values to C1 chondrite abundances. The DL/C1 ratio for each element can be a measure for actual sensitivity in the analysis of geochemical samples by this method. All the DL/C1 ratios for the elements except Pr and Tb are less than 0.02. Such ratios even for Pr and Tb are 0.11 and 0.055, respectively. Hence, in view of analytical sensitivities alone, ICP-AES with the ultrasonic nebulizer system can be applied to REE, Y, and Sc analyses of natural materials with chondritic abundances or less.

Table 1.   Detection limits (DL) and background equivalent concentrations (CBE) of ICP-AES analysis of REE, Y, and Sc by the ultrasonic nebulizers.

Element	Wave-length (nm)	DL(3σ)* (ppb)	CBE* (ppb)	C1 Chondrite (ppb)	DL/C1† (%)
La	398.852	1.7	30	234.7	0.72
Ce	413.38	3.9	75	603.2	0.65
Pr	417.939	10	170	89.1	11
Nd	430.358	2.5	80	452.4	0.55
Sm	442.434	3.0	79	147.1	2.0
Eu	381.967	0.31	4.9	56.0	0.55
Gd	342.247	1.0	15	196.6	0.51
Tb	350.917	2.0	49	36.3	5.5
Dy	353.170	0.64	12	242.7	0.26
Ho	345.600	1.1	24	55.6	2.0
Er	369.265	0.9	21	158.9	0.57
Tm	313.126	0.45	8.4	24.2	1.9
Yb	328.937	0.05	1.3	162.5	0.031
Lu	261.542	0.11	1.3	24.3	0.45
Y	371.030	0.13	2.0	1560	0.0083
Sc	361.384	0.056	1.6	5820	0.0010

*   The 3σ-standard deviations of background emission intensities at the respective wave-lengths are converted into DL-values in the concentration unit by one-point calibrations of standards of 0.6 ppm. The background emission intensities themselves are also converted into the concentration unit as background equivalent concentrations (CBE).

†   Each DL-value is divided by the C1 chondrite abundance (Anders and Grevesse, 1989) in the left column.
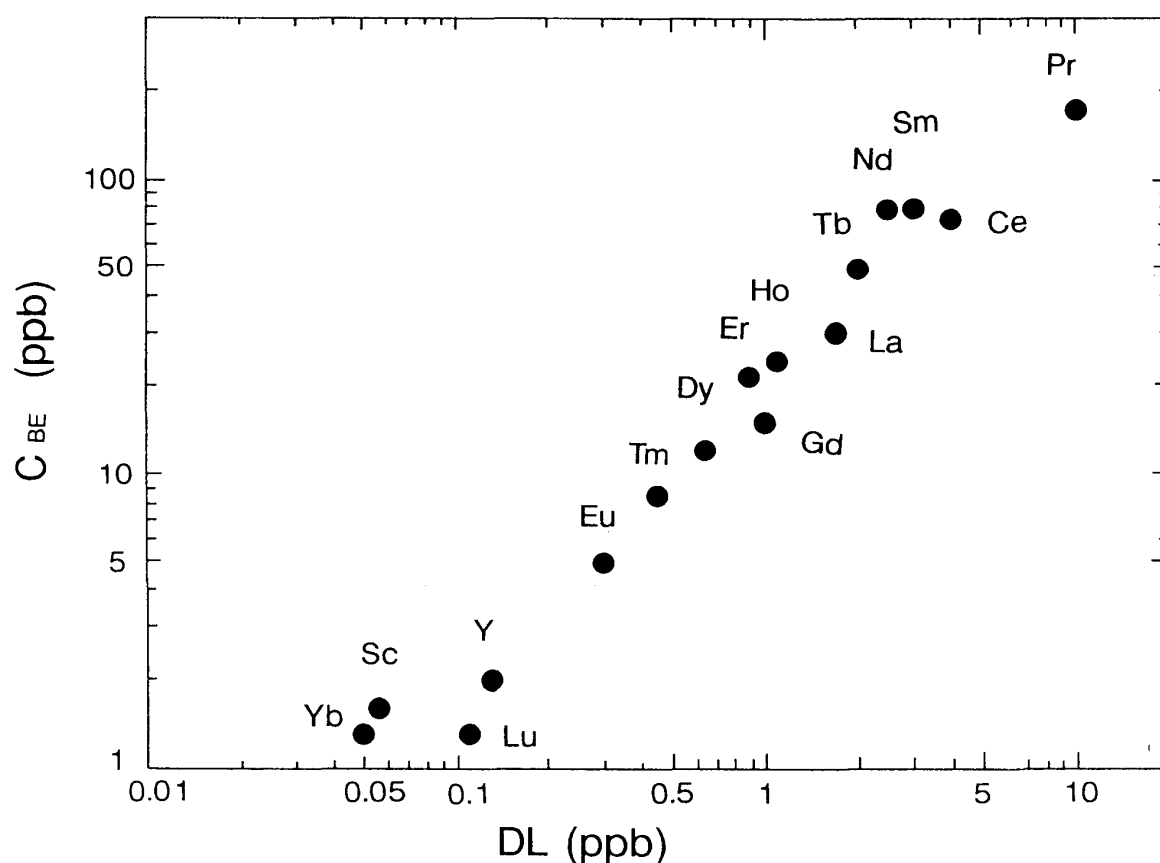
Fig. 2.   A correlation between the detection limits (DL) and background equivalent concentrations (CBE) in ICP-AES analysis of REE, Y, and Sc with the ultrasonic nebulizer.

2. Sensitivity increases by the use of ultrasonic nebulizer

In order to evaluate enhancements of analytical sensitivities by the ultrasonic nebulizer relative to a pneumatic one, we made calibration curves for each element by using both types of nebulizers. The slope values of calibration curves by the two nebulizers have been compared. A pneumatic nebulizer of concentric type was used. The sample uptake rates were set to be approximately the same (1.4 ± 0.2 ml/min) between measurements by the two nebulizers. Standard solutions of 0.012, 0.036, 0.06, and 0.10 ppm of respective elements were used to make the calibration curves by the ultrasonic nebulizer. For the calibration curves by the pneumatic nebulizer, standard solutions of 0.1, 0.2, and 0.6 ppm of respective elements were used. Only for the calibration curve of Pr by the pneumatic one, the four standard solutions of 0.1, 0.2, 0.6, and 1.0 ppm were used.

The obtained pairs of calibration curves were regressed by linear lines, and shown in Figs. 3a to 3e. Good calibration lines even for the concentration range between 12 ppb and 60 ppb have been obtained by the use of the ultrasonic nebulizer system. The results of Figs. 3a to 3e indicate that each DL-value in Table 1 evaluated by using a single standard solution of 0.6 ppm is a
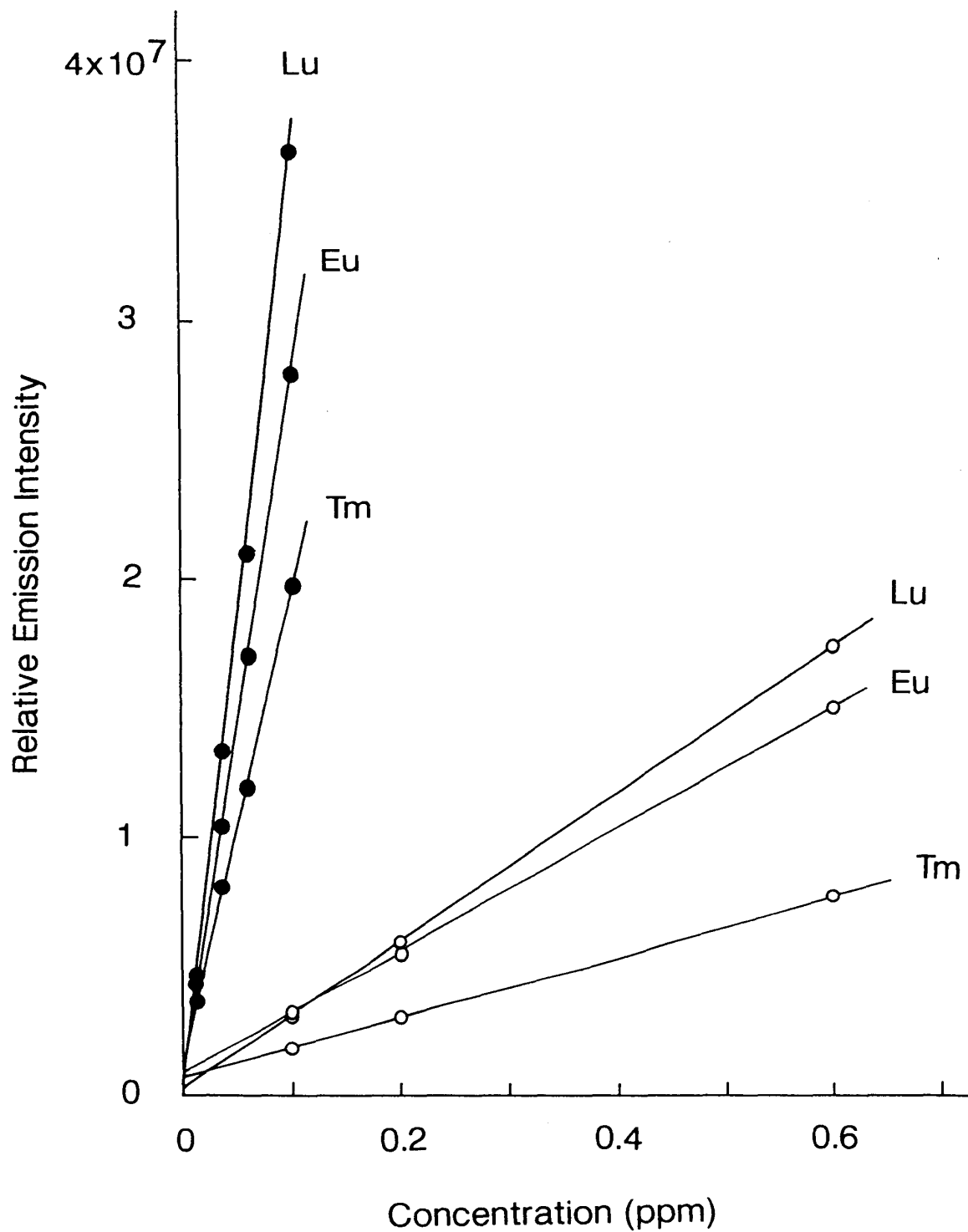
Fig. 3a. Calibration curves for Lu, Eu, and Tm by the ultrasonic nebulizer (filled circles) compared with those by the pneumatic nebulizer (open circles).
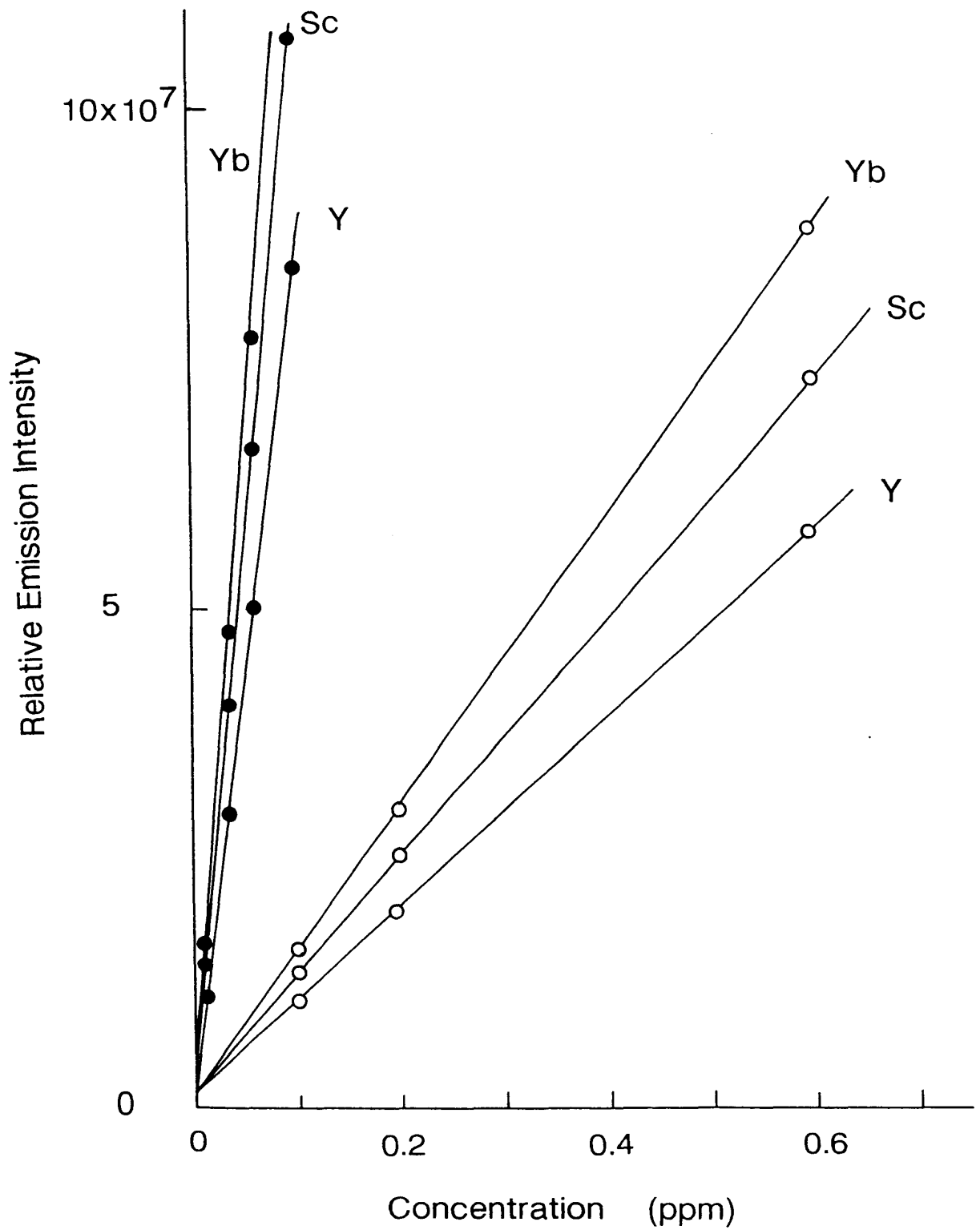
Fig. 3b.   Calibration curves for Yb, Sc, and Y by the ultrasonic nebulizer (filled circles) compared with those by the pneumatic nebulizer (open circles).
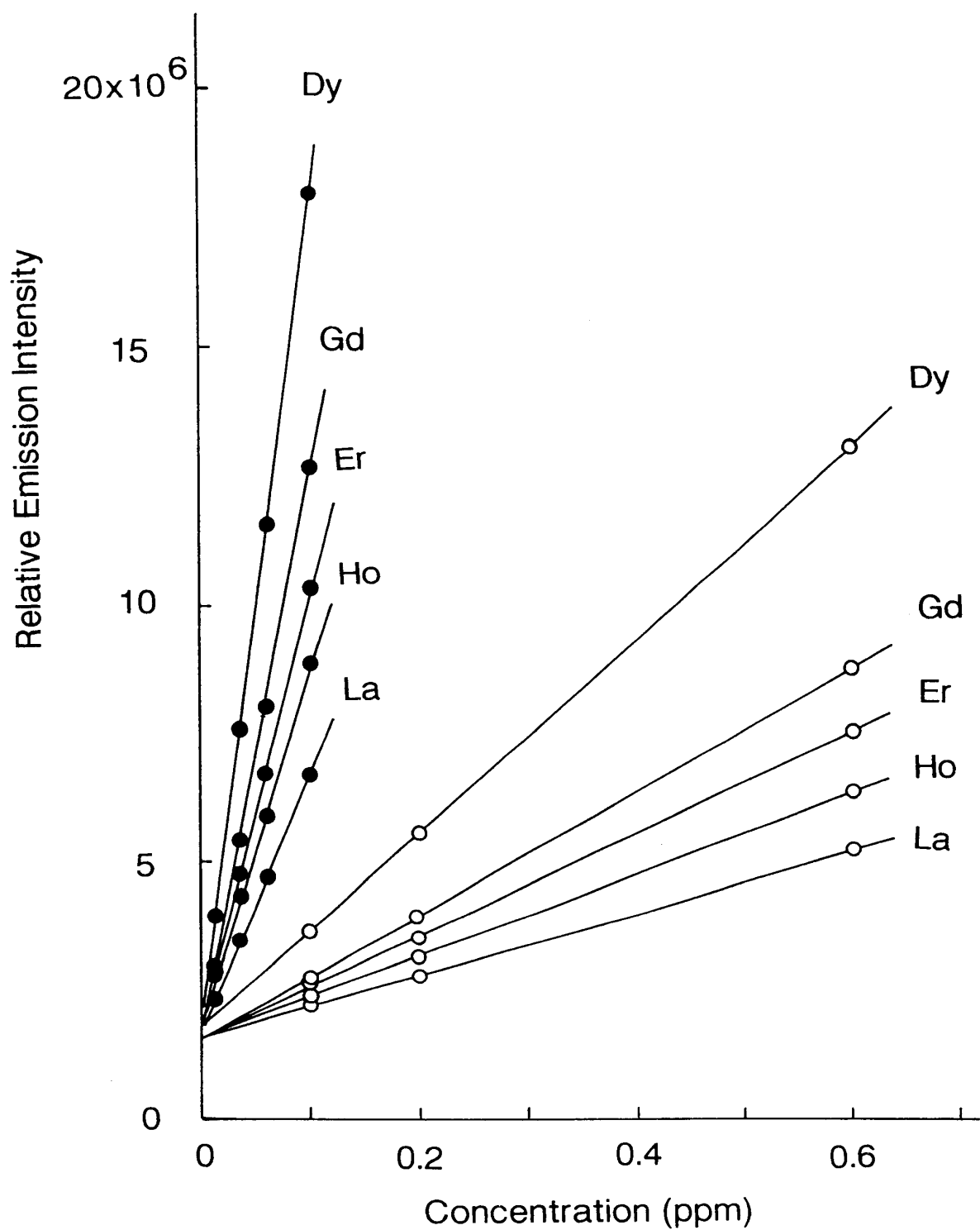
Fig. 3c.   Calibration curves for Dy, Gd, Er, Ho, and La by the ultrasonic nebulizer (filled
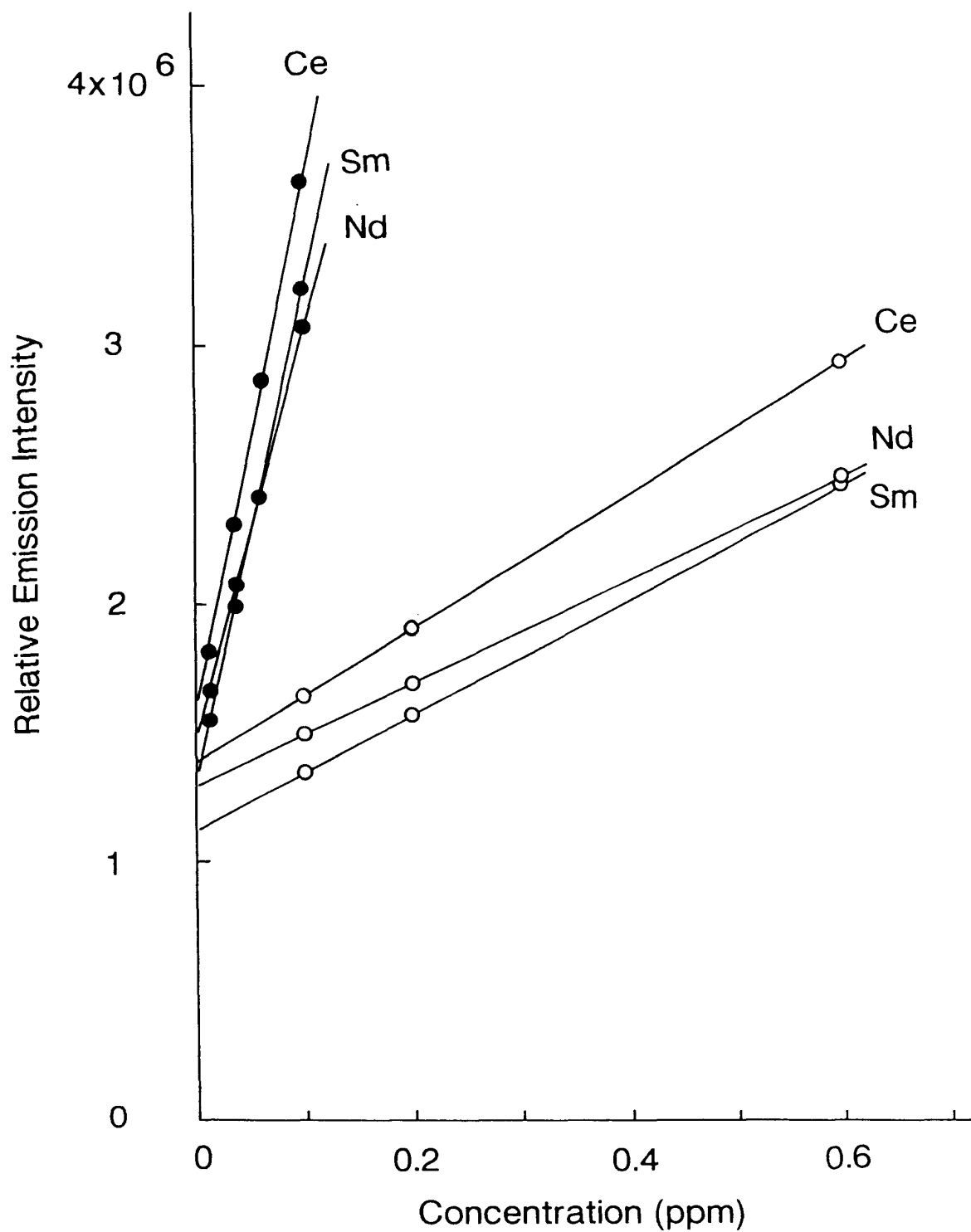circles) compared with those by the pneumatic nebulizer (open circles).

Fig. 3d.   Calibration curves for Ce, Sm, and Nd by the ultrasonic nebulizer (filled circles) compared with those by the pneumatic nebulizer (open circles).
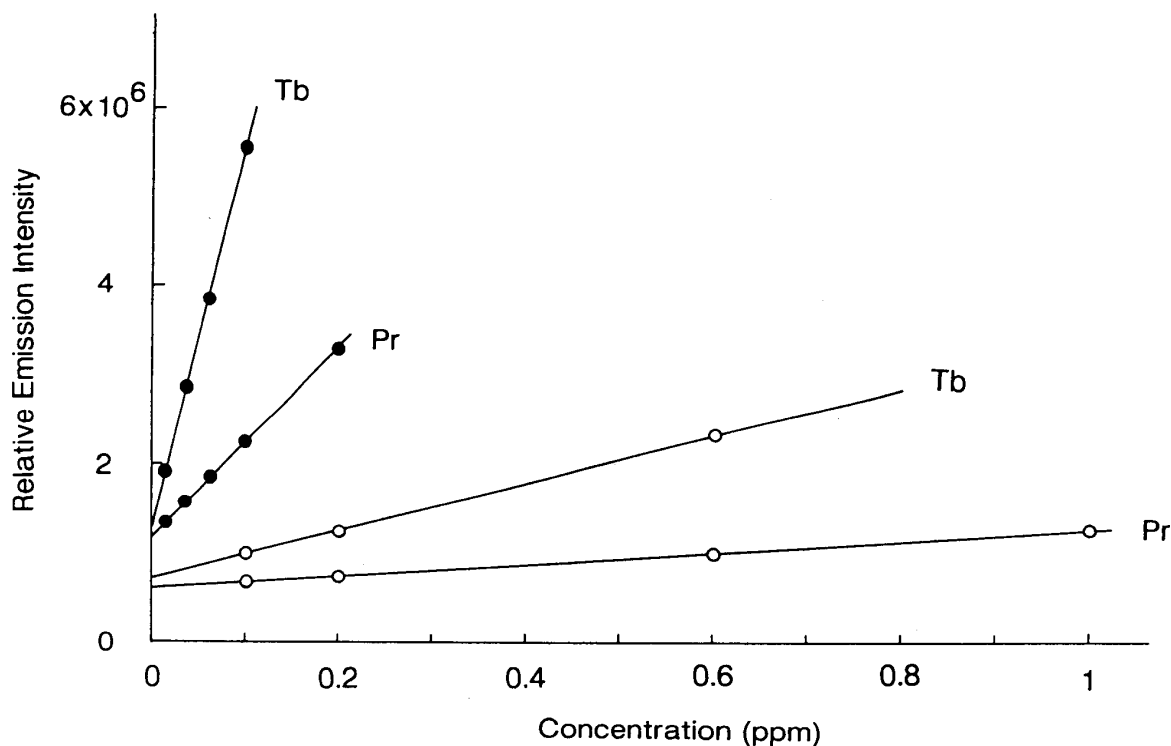
Fig. 3e.   Calibration curves for Tb and Pr by the ultrasonic nebulizer (filled circles)
compared with those by the pneumatic nebulizer (open circles).

realistic value as a detection limit. The relative increase in analytical sensitiv-
ity of ICP-AES for each element by the ultrasonic nebulizer can be expressed
by the ratio of slope value of calibration line by the ultrasonic nebulizer to
that by the pneumatic one. The resultant ratios of slope values are shown
graphically in Fig. 4. The ultrasonic nebulizer increases the slope values of
calibration curves for REE, Y, and Sc by factors of 8 to 16 in comparison with
the conventional pneumatic nebulizer. The relative enhancement factor is 10
± 3 on the average for the sixteen elements.

3. Memory effect and stability of ultrasonic nebulizer

We have checked memory effects of the ultrasonic nebulizer system in the
course of our measurements described as above. Under the condition of the
carrier Ar gas flow rate of 1.0 l/min and the sample uptake rate of 1.4 ± 0.2
ml/min as well as the experimental setting described above, it takes 25 to 30
sec that aerosols of each sample solution introduced by the peristaltic pump
reach the ICP torch. Emission signals become constant within 1—2% in the
next 20 to 25 sec. Therefore, it takes 45 to 55 sec until measurements for a
new sample are ready after starting its nebulization. This waiting time is
about twice as long as that of the pneumatic nebulizer. To clear out a sample
solution having been measured already, it needs to inject distilled water for 50
to 60 sec. This clear-out time is about twice that of the pneumatic nebulizer.
Hence, the clear-out time of the ultrasonic nebulizer is not too long to be
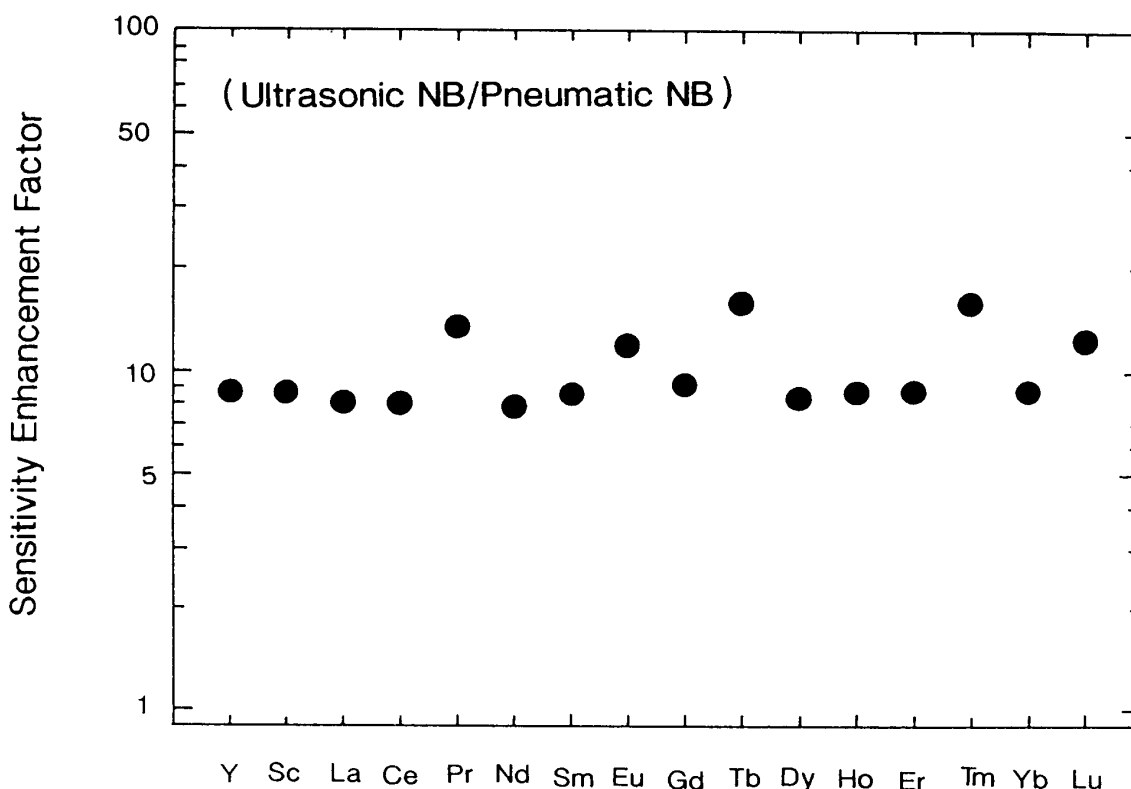
Fig. 4.   Sensitivity enhancement factor in ICP-AES analysis of REE, Y, and Sc with the ultrasonic nebulizer in reference to those by the conventional pneumatic nebulizer. The enhancement factors are the ratios of the slope values of calibration curves by the ultrasonic nebulizer to the respective slope values by the pneumatic one shown in Figs. 3 a — 3e. The average of sensitivity enhancement factors for the sixteen elements is 10 ± 3.

applied even in routine analyses. We conclude that no significant memory effect is associated with our ultrasonic nebulizer system. Ar gas and sample solutions consumed by the ultrasonic nebulizer in each run, in fact, are about twice as much as those by the pneumatic nebulizer. We believe that the use of ultrasonic nebulizer in the routine analysis has the merit as far as the improved sensitivities compensate the demerits of increases in running cost and consumed volumes of sample solutions.

Another important problem is instability of quartz transducer due to the change in its surface condition during repeated use. The constancy of nebulization efficiency depends significantly on the constant surface condition of quartz transducer. The installation manual by SEIKO Instruments recommends to wash the quartz transducer with diluted HF solution (0.5%) for 20 to 30 sec in order to keep the quartz transducer surface clean. This cleaning procedure was found so effective. We washed the ultrasonic nebulizer before and after every run: The HF solution of 0.5% was injected into the nebulizer for 30 sec, and then the HF solution was exchanged with distilled water for next 60 sec. This was repeated three times before and after every run. By this cleaning procedure, we have experienced no trouble originated from

instability of the quartz transducer for last one and half years.

4. Application of ultrasonic nebulizer to routine ICP-AES analysis of relatively insensitive and less abundant REE

We are continuing to analyze REE and Y in geochemical samples by ICP-AES with a preconcentration technique (Kawabe et al., 1994; Kawabe, 1995). Using aliquots of such sample solutions in our routine analysis by a pneumatic nebulizer, we have applied the ultrasonic nebulizer to ICP-AES analysis of some REE, in particular, relatively insensitive and less abundant elements including Pr, Tb, Ho, and Tm.

Tables 2 lists our routine analysis of Tb and Ho in several sample solutions of Pacific deep-sea manganese nodules. Tb and Ho in the respective sample solutions have been determined by both pneumatic and ultrasonic nebulizers. Although the pairs of analyses are in good agreements, analytical errors by the ultrasonic nebulizer are significantly smaller than those by the pneumatic one. Table 3 shows our ICP-AES analyses of all REE, Y, and Sc in two aliquots of JDo-1 (a reference dolomite by Geological Survey of Japan). Pr, Tb, and Tm have been determined by the ultrasonic nebulizer, but the others by the pneumatic nebulizer. The results for the two aliquots (5.8 g and 9.3 g) are in excellent agreement. The average differences between analytical results for the elements on the two aliquots are all within a range between 1 and 4%, and their grand mean is 1.6%. When ICP-AES spectrometers are used for determining REE in geochemical samples (Walsh et al., 1981; Jarvis and Jarvis, 1985; Roelandt, 1988; Sholkovitz, 1990), some REE of Pr, Tb, Ho, and Tm

Table 2.   ICP-AES analyses of Tb and Ho in sample solutions from Pacific ferromanganese nodules both by the pneumatic and ultrasonic nebulizers (concentration unit: ppb)*.

Sample Name		HW-1	HW-2	HW-3	HW-4	HW-5
Tb	Pneumatic N.	68.5	68.8	72.8	76.2	58.2
		±1.0	±1.9	±1.6	±3.0	±1.7
	Ultrasonic N.	65.6	69.8	69.7	74.5	56.4
		±0.9	±1.1	±1.0	±0.9	±1.1
Ho	Pneumatic N.	63.6	69.2	70.2	73.4	53.9
		±0.6	±1.5	±0.5	±2.2	±1.0
	Ultrasonic N.	64.1	70.5	70.8	76.3	55.7
		±0.6	±0.3	±0.3	±0.5	±0.6

* The errors are one-sigma standard deviations of three emission intensity measurements. Each sample solution (20.0 ml) was prepared from an aliquot of 0.25 g of each deep-sea ferromanganese nodule by a preconcentration technique similar to that in Kawabe (1995).

Table 3.   ICP-AES analyses of all REE, Y, and Sc for two aliquots (A and B) of
JDo-1, a reference dolomite by Geological Survey of Japan*.

	A (5.781 g) (ppm)		B (9.364 g) (ppm)		Av. Diff. (%)
La	7.97	± 0.09	7.71	± 0.08	1.7
Ce	2.26	± 0.03	2.23	± 0.02	0.67
Pr†	0.98	± 0.02	0.91	± 0.02	3.7
Nd	4.35	± 0.03	4.20	± 0.03	1.8
Sm	0.691	± 0.006	0.694	± 0.005	0.22
Eu	0.163	± 0.002	0.160	± 0.001	0.93
Gd	0.900	± 0.003	0.876	± 0.001	1.4
Tb†	0.123	± 0.002	0.115	± 0.004	3.4
Dy	0.776	± 0.002	0.757	± 0.005	1.2
Ho	0.173	± 0.003	0.170	± 0.002	0.87
Er	0.477	± 0.006	0.465	± 0.002	1.3
Tm†	0.0612	± 0.0008	0.0589	± 0.0007	1.9
Yb	0.312	± 0.002	0.304	± 0.001	1.3
Lu	0.0436	± 0.0005	0.0421	± 0.0004	1.8
Y	10.51	± 0.06	10.15	± 0.06	1.7
Sc	0.133	± 0.001	0.127	± 0.001	2.3
			Grand mean and S.D. for Av. Diff. (n=16) 1.6 ± 0.9 (%)		

* The sample solutions (20.0 ml) for ICP-AES were prepared by the
preconcentration technique by Kawabe et al. (1994). The errors are
one-sigma standard deviations of three emission intensity measure-
ments.
† The elements with this symbol have been measured by the ultrasonic
nebulizer, and those without it by the pneumatic nebulizer.

or all of them are not analyzed usually because of their lower abundances and
insufficient sensitivities. The use of ultrasonic nebulizer, however, makes it
easier to determine all the REE in geochemical samples than in our previous
ICP-AES method (Kawabe et al., 1994; Kawabe, 1995).

In our present routine analysis, the pneumatic nebulizer is used as far as
possible in order to save both Ar gas and the limited volumes (15—20 ml) of
sample solutions given by our preconcentration method. The ultrasonic

nebulizer is used only for a complementary purpose to make the analyses of relatively insensitive and less abundant REE more reliable. Such a use of the ultrasonic nebulizer complementary to the pneumatic one is an example of its effective application to the routine ICP-AES analysis.

CONCLUSIONS

We have tested an ultrasonic nebulizer system (CETAC UT-5000AT) connected with a scanning type ICP-AES spectrometer (SEIKO SPS-1500R) in hoping improvements in our ICP-AES analyses of REE, Y, and Sc in geochemical samples. Its performance was found satisfactory for our purpose. The results are summarized as follows:

(1) In comparison with the ICP-AES method with a conventional pneumatic nebulizer, the ultrasonic nebulizer system can enhance analytical sensitivities for REE, Y, and Sc by factors of 10 ± 3.

(2) The detection limits (DL-values) corresponding to 3σ-background variations for Eu, Tm, Yb, Y, and Sc are as low as 0.05 ppb to 0.5 ppb by the use of the ultrasonic nebulizer. The DL-values for the other REE except Pr are ranging between 0.5 ppb to 5 ppb. Only the detection limit of Pr (10 ppb) is not so low as those for the other elements. Most of the DL-values, however, are only 2% of the chondritic abundances or less.

(3) The memory effect of the ultrasonic nebulizer system is not so significant. It takes 50 to 60 sec to clean out a sample solution having been measured already by injecting distilled water. This clean-out time is only twice that of a concentric pneumatic nebulizer.

(4) The nebulization efficiency of the ultrasonic nebulizer decreases as it is used repeatedly because the surface state of quartz transducer is changed. This problem, however, can be overcome by washing the transducer surface with a dilute HF solution between runs.

(5) Overall performance of the ultrasonic nebulizer system is good. This can be applied to routine ICP-AES analysis of REE, Y, and Sc in a wide spectrum of geochemical samples in couple with adequate wet chemical techniques for their group separation.

(6) Ar gas and sample solutions consumed by the ultrasonic nebulizer in each run are about twice as much as those by the pneumatic nebulizer. When saving running cost and sample solutions is important, we had better use the ultrasonic nebulizer as a complement to the conventional pneumatic one only for analyzing relatively insensitive and less abundant REE like Pr, Tb, Ho, and Tm.

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