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## Effect of nitric and hydrochloric acids on rare earth element (REE) intensities in inductively coupled plasma emission spectrometry\*

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**Abstract**—Atypical depressive effects on rare earth element (REE) intensities, reproducible within experimental error, generated by high concentrations of nitric and hydrochloric acids in an Ar inductively coupled plasma–atomic emission spectrometer (ICP–AES) are reported. It was observed that in the presence of nitric acid, the REEs did not respond as a coherent group, the intensity of each REE line responding differently to increasing acid concentrations. However, in the presence of hydrochloric acid, the response of all REE spectral lines were comparable. These effects were generally similar regardless of the mode of aerosol generated (conventional pneumatic nebulization using concentric and ultrasonic nebulizers (USNs) with aerosol desolvation). However, in the USN the effect was reduced due to removal of nitric acid in desolvation. In the argon ICP, using a conventional pneumatic nebulizer, the excitation temperature ( $T_{\text{exc}}$ ) decreased with increasing nitric acid concentration from about 7500 K in an aqueous solution to 7000 K in 7 N  $\text{HNO}_3$ . Temperatures did not vary significantly for variations in concentration of hydrochloric acid up to 10 N. Consequently, in the case of HCl, the similar reduction in intensities for all REEs may be due to a physical effect in the aerosol transport system.  $T_{\text{exc}}$ , however, for the ultrasonic nebulizer was generally lower by about 500 K. The depressive effects of the REE spectral intensities due to  $\text{HNO}_3$  were not directly correlative with the thermal (heat of evaporation, heat of fusion, melting and boiling points) and spectroscopic characteristics (ionization and excitation potentials) of the REE spectral lines employed and are not attributable to physical transport effects in the sample introduction system.

### 1. INTRODUCTION

In analytical atomic spectrochemistry, the effects of high concentrations of acids are attributed to physical effects in the aerosol generation process or due to plasma perturbations as a result of temperature changes. Because solution aspiration is still the most common method of sample introduction in the inductively coupled plasma (ICP), the prerequisite for quantitative multielement analysis depends on the quality of solid sample decomposition. In most dissolution schemes samples are decomposed using single or mixtures of concentrated mineral acids, namely HCl,  $\text{HNO}_3$ , and  $\text{HClO}_4$  [1]. In preconcentration procedures using chelating resins, the analytes of interest are usually eluted using concentrated  $\text{HNO}_3$  or HCl [2]. When REEs are separated using ion-exchange resins, they are eluted using 6–7 N nitric or hydrochloric

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acids [3, 4]. Therefore the effect of high and variable concentrations of mineral acids on the REE signals is an important analytical consideration in selecting calibration schemes and internal standards. REEs, frequently occur in very low concentrations which may be too low to be determined with a conventional pneumatic nebulizer and an ultrasonic nebulizer (USN) has to be used. Consequently there is a need to understand the possible effects caused by high acid concentrations.

Acid effects in ICP–AES have been identified by numerous workers. Many investigators concluded that they were related to transport mechanisms. One of the first reports on the effect of mineral acids was by GREENFIELD *et al.* [5] who attributed the observed effects to reductions in the sample uptake rate due to the change of surface tension. FARINO *et al.* [6], studied the effect of sulfuric and phosphoric acids and also concluded that the observed intensity suppressions were due to the decrease in the analyte mass transport to the ICP due to viscosity differences which influence the quality of the aerosol and particle dimensions. Recently, Garden *et al.* [7] made a study of mineral acid interferences by ICP–AES and observed up to 40% signal depressions under normal operating conditions. They compared the influence of HCl and HNO<sub>3</sub> and found that in the range of 0–20% (v/v) acid concentrations, the effects were similar. Both recoveries and short-term precision were improved substantially using real-time internal standardization using Sc [8, 9]. BOTTO [10] used the intensity of the H<sub>β</sub> emission line to monitor changes in analyte intensities due to varying concentrations of acid. It was observed that H<sub>β</sub> emission was proportional to the rate of sample introduction in the presence of nitric acid even up to 55% (v/v). In contrast, in an extensive examination of acid effects, DAHLQUIST and KNOLL [11] demonstrated that various spectral lines of various elements responded differently to different acids and different concentrations. On the basis of their data one could conclude that a single internal standard would not compensate for these variations. YOSHIMURA *et al.* [12] and CHUDINOV *et al.* [13] studied the effects of low concentrations of mineral acids in ICP–AES. YOSHIMURA *et al.* [12] demonstrated that there were two mechanisms that resulted in the lowering of spectral line intensities: lowering of excitation temperatures, and reduction in aspiration rates. Their data indicated that the former process is more predominant at lower acid concentrations, whereas physical effects in the solution transport system were more influential at high acid concentrations. In all these studies the behavior of the REEs was not evaluated. MARICHY *et al.* [14], and FERNANDEZ *et al.* [15] also evaluated the effects of low acid concentrations using V as the test element. In the former study, no effect was observed for nitric acid below 1%. In the latter investigation a significant depressive effect for the ionic lines was attributed to a change in excitation conditions. The behavior of the REEs was not studied.

In a previous investigation [16] we indicated that about ten-fold enhancement of the REE limits of detection can be obtained when using a USN. However the effect of desolvated aerosols produced from high acid concentrations was not studied. In the present investigation, we have evaluated several unusual interference effects due to high acid concentrations. REE intensity responses obtained with a USN were compared to those obtained with a conventional pneumatic concentric nebulizer. In a companion paper [17] the depressive effects were attributed to a decrease in the energy transfer from the plasma to the REE analytes. Using principal component analysis (PCA), the role of oxide bond strength and ionization energy was elucidated. It was observed that the effect could be simulated by varying the sheathing gas flow rate.

## 2. EXPERIMENTAL

### 2.1. Instrumentation and operating conditions

A 1 m Jobin Yvon (Longjumeau, France) JY 38 sequential spectrometer was employed for the measurement evaluation of all REE spectral line emissions. The use of this monochromator produced interference-free spectra due to its superior resolution of 6 pm in the 190–490 nm range. A Jobin Yvon JY 48, 48 channel vacuum polychromator was employed for the validation

Table 1. Instrumentation

Monochromator	Jobin Yvon JY 38
Grating	3600 gr/mm, range 180–490 nm
Dispersion	0.27 nm/mm, 6 pm in the first order (25 $\mu$ m slit widths)
Polychromator	Jobin Yvon JY 48 1 m
Grating	2550 gr/mm, spectral range 170–450 nm
Dispersion	0.35 nm/mm
RF generator	Plasma therm 2.5 kW, <10 W reflected
Torch	Jobin Yvon, Rytan demountable

Table 2. ICP and USN operating conditions

Pneumatic nebulizer	Meinhard TR-C-20, 45 psi
Ultrasonic nebulizer	Cetac U 5000AT
Desolvation	Cooling temperature, $-5^{\circ}\text{C}$ ; heating $140^{\circ}\text{C}$
Cooling gas	14 l/min
Auxiliary	0.2–0.4 l/min
Sheath gas	Trassy-Mermet pneumatic nebulizer, 0.3 l/min; USN, 0.3 l/min
Aerosol carrier	0.7 l/min for pneumatic nebulizer and 0.9 l/min for USN
Washout period	Meinhard nebulizer, 30 s; USN, 50 s
Integration period	Polychromator 10 s, monochromator 1 s

of the behavior of Y, La, Ce, Yb, and Eu. A Cetac (Omaha, Nebraska) USN with a desolvation system was employed. The instrumental configuration and operating conditions are listed in Tables 1 and 2. Additional experimental details are included in previous studies [16, 18].

## 2.2 REE calibration

A graded set of multielement REE calibration standards in aqueous solution was prepared by stepwise dilution of stock solutions prepared from Specpure REE oxides (Johnson Matthey, UK). The acid effects were studied by analyzing solutions containing 1 mg/l REEs in nitric and hydrochloric acid varying in concentration up to 7.2 N and 10 N, respectively. The REE spectral lines used, their limits of detection ( $2\sigma$ ), and excitation and ionization potentials are listed in Table 3.

Table 3. REE spectral lines and their ICP-AES-MSN and ICP-AES limits of detection ( $2\sigma$ ) in mg/l

Wavelength	Meinhard	USN	EP*	IP†
Lu II 261.542	0.08	0.008	4.74	5.42
Yb II 328.937	0.4	0.03	3.77	6.25
Tm II 328.220	0.01	0.3	3.58	6.18
Gd II 342.246	0.3	0.09	3.53	6.14
Ho II 345.600	0.2	0.05	3.87	6.02
Tb II 350.917	2.3	0.3	3.53	5.85
Dy II 353.171	0.1	0.04	3.5	5.93
Sm II 359.260	0.9	0.3	3.83	5.63
Er II 369.265	0.6	0.15	3.41	6.10
Y II 371.030	0.4	0.30	3.52	6.38
La II 379.478	1	0.35	3.51	5.58
Eu II 381.967	0.5	0.06	3.24	5.67
Ce II 413.765	5.9	1.2	3.52	5.47
Pr II 422.535	1.6	0.8	3.17	5.42
Nd II 430.358	2.1	0.5	2.88	5.49

\*Excitation potential (eV).

†Ionization potential (eV).

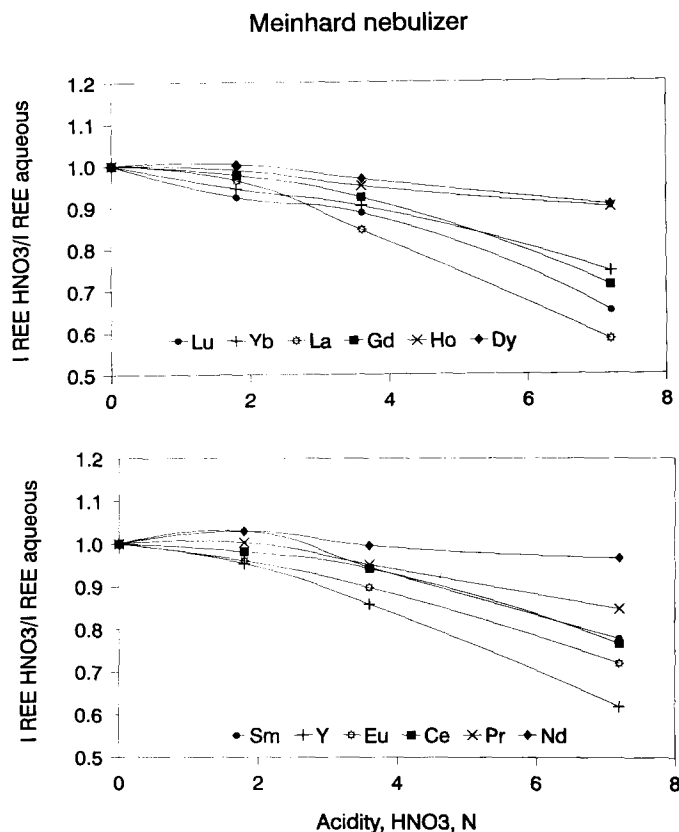


Fig. 1. Effect of nitric acid on REE spectral line intensity. Conventional nebulization using a Meinhard pneumatic nebulizer. REE concentrations, 1 mg/l. Observation height above load coil (ALC), 14 mm.

### 3. RESULTS

#### 3.1. *Effect of nitric acid*

When high nitric acid concentrations containing REEs were aspirated into the ICP using a conventional pneumatic nebulizer and a USN, it was observed that the REE spectral lines investigated did not respond as a coherent group, each REE line decreasing at a consistent rate with increasing acid concentration. However, the extent to which the intensities decreased differed for the various REEs, and the deviations increased with increasing acid concentrations (Figs. 1 and 2). It is noteworthy that the effects noted for several of the REEs using the pneumatic nebulizer (Fig. 1) were larger than those obtained with the USN (Fig. 2). The smaller depressive effect obtained with the USN could be due to the removal of HNO<sub>3</sub> in the desolvation process.

#### 3.2. *Effect of hydrochloric acid*

In the case of HCl, the REE intensity responses were similar, intensities decreasing at a similar rate with increasing acid concentration (Figs. 3 and 4). Contrary to that observed with nitric acid, the variations observed with the concentric nebulizer were smaller than those obtained with the USN and desolvation. In the latter sample introduction system, a sharp decrease was observed for all REEs for less than 1 N HCl.

#### 3.3. *Temperature variation*

Excitation temperatures obtained from Boltzmann plots were used as a criterion for evaluating the possible dependence of the REE intensity variations and with

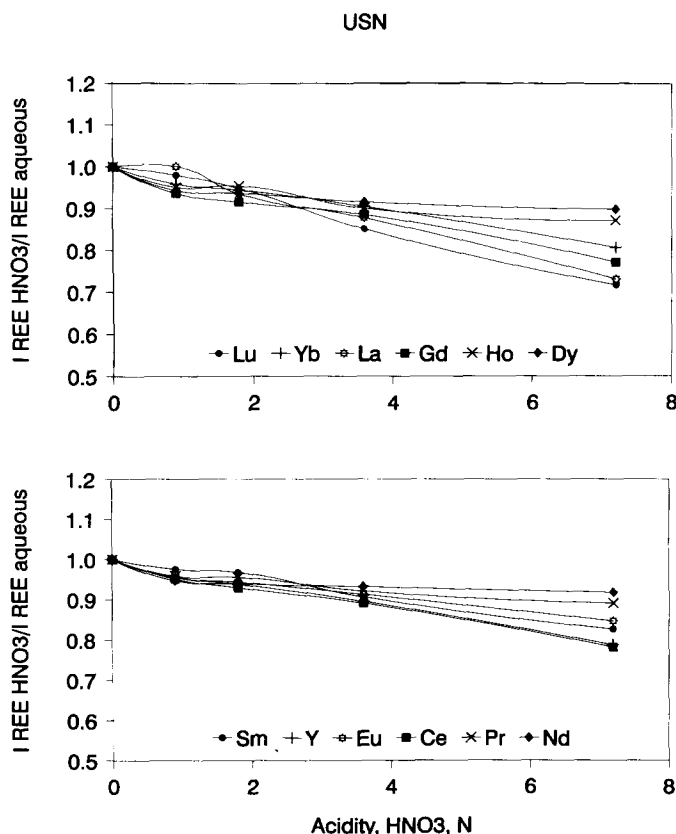


Fig. 2. Effect of nitric acid on REE spectral line intensity. USN with desolvation. REE concentration, 1 mg/l. Observation height ALC, 14 mm.

temperature.  $T_{\text{exc}}$  was measured according to BLADES *et al.* [19] using solutions containing 100 mg/l Fe. Temperatures were calculated by regressing  $\ln(I\lambda/gA)$  with  $E_p$ , where  $I$  is the net line intensity,  $\lambda$  is the wavelength of the Fe transition,  $g$  is the statistical weight,  $A$  is the transition probability, and  $E_p$  is the excitation energy. The temperatures measured for HNO<sub>3</sub> and HCl using a conventional pneumatic concentric nebulizer and a USN with desolvation are illustrated in Fig. 5. The maximum error in each measurement was about 2%. In an argon ICP the temperature decreased with increasing nitric acid concentration, from about 7500 K in an aqueous solution, to about 7000 K in 7 N HNO<sub>3</sub> using a concentric Meinhard nebulizer. In the presence of HCl, the temperatures did not vary significantly. Indeed a slight  $T_{\text{exc}}$  increase was observed with increasing HCl concentration.

The temperature was significantly lower when the aerosol was generated with a USN and desolvated at 140°C (cooled at -5°C). It is clearly evident, however, that the pattern of behavior was similar to that observed with the pneumatic nebulizer.

### 3.4. Relation with excitation potentials

Several Ce spectral wavelengths, having different excitation potentials (EP) varying from 3 to 5 eV, were selected in order to evaluate the relation between these signal depressions and EPs. A single REE was selected in order to eliminate the possible effects related to various REE thermochemical properties. The relation of Ce intensities and HNO<sub>3</sub> and HCl concentrations are illustrated in Fig. 6. In both experiments, the intensities of all the Ce lines decreased sharply at 1 N concentration. The decrease in intensities was moderate but similar for both acids at concentrations above 1 N. In the case of these Ce lines it appears that excitation potentials did not play a major

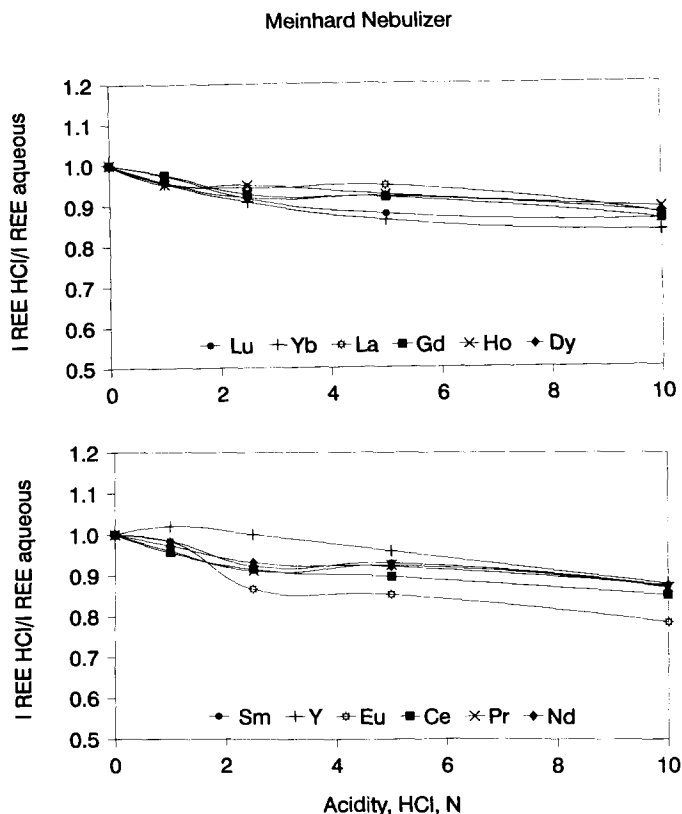


Fig. 3. Effect of hydrochloric acid on REE spectral line intensity. Conventional nebulization using a Meinhard pneumatic nebulizer. REE concentrations, 1 mg/l. Observation height ALC, 14 mm.

role in the depression process of the REE emission even though the range of EPs is not large.

### 3.5. Role of the observation height

Fig. 7 illustrates that the depression effects varied as a function of height in the plasma column. In the case of nitric acid (Fig. 7(A)) it is evident that REE intensities did not vary coherently. The depressive effects were large in the lower part of the plasma and they decreased with increasing height, equality with an aqueous solution being attained for some of the REEs but not for others. In the case of HCl (Fig. 7(B)), the REE spectral lines behaved as a coherent group and the overall variation was approximately 20%. The depressive effect of HCl was also prominent in the lower part of the plasma and the matrix effect decreased with increase in height of observation. Equality of the HCl with the aqueous solution was not attained in the range of observation used.

## 4. DISCUSSION

The diverse amounts of depression at high  $\text{HNO}_3$  concentrations, are not directly correlative with excitation potentials of a single REE line, nor with the thermal constants of the REE compounds. Nevertheless, the height dependent matrix effect due to  $\text{HNO}_3$ , implies that there may be an element dependent particle-plasma interaction, which recedes higher up in the plasma column, possibly suggesting a delay in particle atomization as described by OLESIK and FISTER [20]. This height dependent effect may explain the diverse REE intensity behavior in nitric acid. In the companion

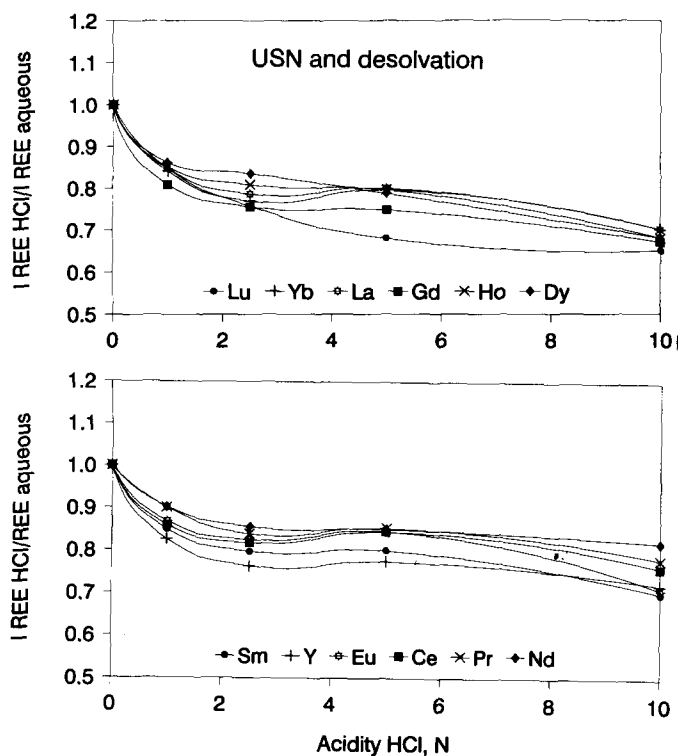


Fig. 4. Effect of hydrochloric acid on REE spectral line intensity. USN with desolvation. REE concentration, 1 mg/l. Observation height ALC, 14 mm.

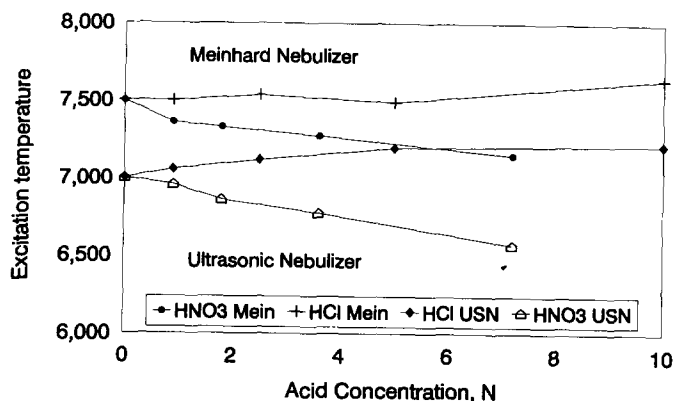


Fig. 5. Variation of excitation temperatures for nitric and hydrochloric acids using conventional pneumatic and ultrasonic nebulization. Observation height ALC, 14 mm.

to this paper [17], the effect appears to be due to a complex inter-relationship with bond strength, oxide dissociation, and ionization energy.

The depressive effects also appear to be influenced by the sheath gas flow, which affects the residence time and the extent of energy transfer. Noteworthy is the reduced depressive effect when USN was used. This is ascribed to the partial removal of nitric acid during desolvation.

In distinguishing these effects from those observed with HCl, we have adopted the rationale that in the case of physical interference effects in the transport system, all the REE intensities should have been affected equally. It is unlikely that the refractory REE elements could be discriminated in the USN and in a conventional pneumatic nebulizer-Scott type spray chamber. However, it can be noted that in the case of

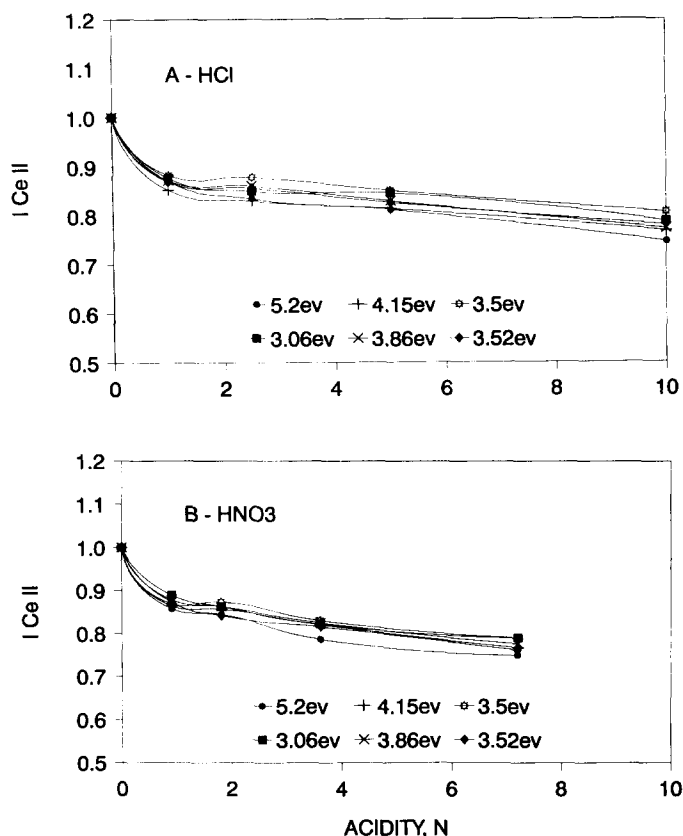


Fig. 6. Effect of concentrated HCl (A) and HNO<sub>3</sub> (B) on various Ce lines differing in excitation potential. Ultrasonic nebulization. Observation height, 14 mm ALC.

HCl, intensity variations are not entirely due to a physical transport effect, but are also due to this plasma interaction.

The elucidation of this behavior has avoided analytical bias in the REE determinations in high acid concentration media. A single element internal standard cannot compensate for the variations caused by nitric acid, although Sc adequately corrects for variations due to HCl. Therefore, a matrix-match calibration procedure was used for the routine determination of REEs in concentrated nitric acid media [18].

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## REFERENCES

- [1] R. I. Botto, *Spectrochim. Acta Rev.* **14**, 141 (1991).
- [2] Z. Horvath, A. Lasztity and R. M. Barnes, *Spectrochim. Acta Rev.* **14**, 45 (1991).
- [3] I. Roelandts and G. Michel, *Geostand. Newslett.* **10**, 135 (1986).
- [4] I. B. Brenner, E. A. Jones, A. E. Watson and T. W. Steels, *Chem. Geol.* **45**, 135 (1984).
- [5] S. Greenfield, H. McD. McGeachin and P. B. Smith, *Anal. Chim. Acta* **84**, 67 (1976).
- [6] J. Farino, J. R. Miller, D. D. Smith and R. Browner, *Anal. Chem.* **59**, 2303 (1987).
- [7] L. M. Garden, J. Marshall and D. Littlejohn, *J. Anal. At. Spectrom.* **6**, 159 (1991).
- [8] I. B. Brenner, H. Eldad, S. Erlich and N. Dalman, *Anal. Chim. Acta* **66**, 51 (1984).
- [9] G. J. Schmidt and W. Slavin, *Anal. Chem.* **54**, 2491 (1982).
- [10] R. I. Botto, *Spectrochim. Acta* **40B**, 397 (1985).
- [11] R. L. Dahlquist and J. W. Knoll, *An interim discussion of "acid effects"*, Hasler Research Center, Applied Research Laboratories Report, California, 1 September (1976).



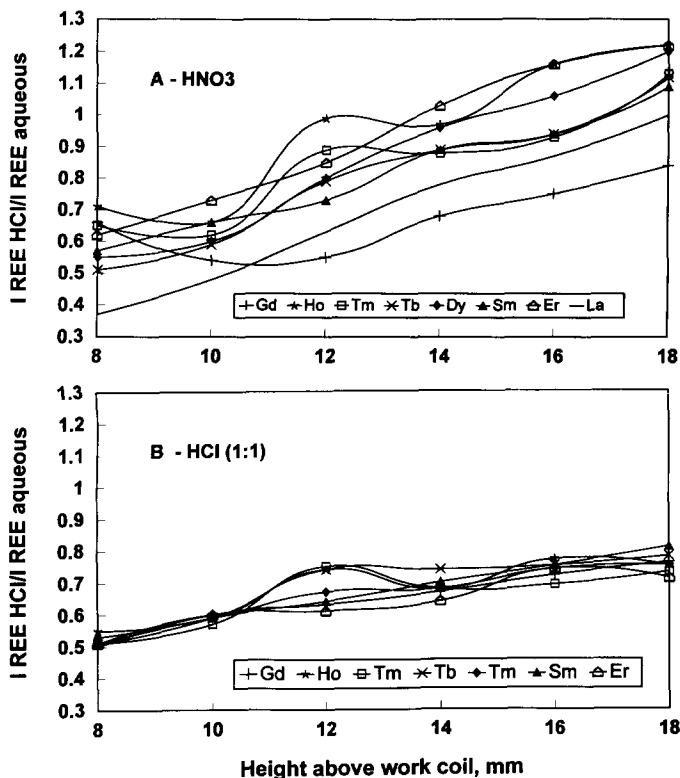


Fig. 7. Distribution of REE intensity depression effects for HNO<sub>3</sub> (A) and HCl (B) as a function of observation height in the argon ICP following ultrasonic nebulization.

- [12] E. Yoshimura, H. Suzuki, S. Yamazaki and S. Toda, *Analyst*. **115**, 167 (1990).
- [13] E. G. Chudinov, I. I. Ostroukhova, and G. V., Varvanina, *Fresenius' Z. Anal. Chem.* **335**, 25 (1989).
- [14] M. Marichy, M. Mermet and J. M. Mermet, *Spectrochim. Acta* **45B**, 1195 (1990).
- [15] A. Fernandez, M. Murillo and N. Carrion, *J. Anal. At. Spectrom.* **9**, 217 (1994).
- [16] I. B. Brenner, R. Binstock, E. Dorfman and L. Halicz, *ICP Newsletter* **18/8**, 473 (1992).
- [17] I. B. Brenner, I. Segal, M. Mermet and J. M. Mermet, *Spectrochim Acta* **50B**, 333 (1995).
- [18] I. B. Brenner and E. Dorfman, *J. Anal. Atom. Spectrom.* **8**, 833 (1993).
- [19] M. W. Blades, B. L. Caughlin, Z. H. Walker and L. L. Burton, *Prog. Anal. Spectrosc.* **10**, 57 (1987).
- [20] J. W. Olesik and J. C. Fister, *Spectrochim. Acta* **46B**, 851 (1991).