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Study of the depressive effects of nitric acid on the line intensities of rare earth elements in inductively coupled plasma atomic emission spectrometry*

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Abstract—Depressive effects of nitric acid on the line intensities of rare earth elements in ICP–AES have been attributed to a decrease in the energy transfer from the plasma to the analyte. Principal component analysis was used to differentiate the behaviour of rare earth elements and to emphasize the influence of the oxide bond strength and the ionization energy on the acid effect. A similar behaviour was obtained by substituting the acid effect for that of a sheathing gas.

1. INTRODUCTION

DEPRESSIVE effects resulting from the addition of acids have been reported in inductively coupled plasma atomic emission spectrometry [1–26]. The depression in the line intensities has been attributed to a change (i) in the aerosol formation and transport [2, 11, 13]; (ii) in the aerosol composition [22, 25]; and (iii) in the plasma characteristics [24]. It has been shown that a careful selection of the ICP operating conditions allows the ICP user to separate the acid effects originating from the sample introduction system from those originating in the plasma [24, 25]. In particular, some acid effects can be partly explained by a decrease in the efficiency of energy transfer from the surrounding plasma to the central channel where the analyte is located [25]. A companion paper [26] has indicated that depressive effects could be observed for rare earth elements (REE) for increasing concentrations of hydrochloric and nitric acids. The study of REEs is an interesting example as these elements exhibit similar physical and chemical properties. It could be expected that a change in acid concentration would lead to an identical behaviour of the REEs. However, slightly different behaviours were observed for a set of REE analytical lines. The acid effects were observed regardless of the sample introduction system, i.e. a pneumatic nebulizer or an ultrasonic nebulizer associated with a desolvation system. Different conclusions were obtained for hydrochloric acid and nitric acids. Increasing the nitric acid concentration caused a 400 K decrease in the excitation temperature in contrast to hydrochloric acid where no significant change was observed. Depressive effects due to HCl were attributed to a physical effect in the aerosol transport. The effects of HNO_3 were found to be more complex. Attempts to correlate the effects to a single property of REEs such as the heat of evaporation, the ionization energy, the melting

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Table 1. Line selection, ionization energy, E_{ion}, excitation energy, E_{exc}, sum of the ionization energy and the excitation energy, E_{sum}, oxide bond strength, E_{X-O}, and addition of the sum of energy and the oxide bond strength for the rare earth elements used in this work

Line	E_{ion}	E_{exc}	E_{sum}	E_{X-O}	$E_{sum} + E_{X-O}$
La II 333.75	5.58	4.12	9.7	8.28	17.98
Ce II 413.76	5.47	3.52	8.99	8.26	17.25
Pr II 417.94	5.42	3.17	8.59	7.79	16.38
Nd II 430.35	5.49	2.88	8.37	7.27	15.64
Sm II 359.26	5.63	3.83	9.46	5.84	15.30
Eu II 381.97	5.67	3.24	8.91	4.97	13.88
Gd II 342.25	6.14	3.53	9.67	7.46	17.13
Tb II 350.92	5.85	3.53	9.38	7.38	16.76
Dy II 353.17	5.93	3.50	9.43	6.27	15.70
Ho II 345.60	6.02	3.87	9.89	6.34	16.23
Er II 369.27	6.10	3.41	9.51	6.34	15.85
Tm II 346.20	6.18	3.58	9.76	5.20	14.96
Yb II 371.03	6.38	3.52	9.90	7.47	17.37
Lu II 261.54	5.43	4.74	10.17	7.03	17.20

Energies are expressed in eV.

point were not successful. The purpose of this work is to suggest some explanations for the HNO_3 effect on the REE line intensities, under the operating conditions used for the experiment.

2. RESULTS

Results have been reported in Ref. [26] using a 1-m JY 38 sequential ICP system. A 27-MHz Plasmatherm generator was used with a power of 1.2 kW. A conventional Meinhard TR-C-20 concentric nebulizer was operated at a flow rate of 0.75 l min^{-1}. The i.d. of the injector was 3 mm. Unless otherwise stated, a 0.2 l min^{-1} sheathing gas flow rate was added at the exit of the spray chamber. An alternative to the pneumatic nebulizer was the use of a CETAC 5000 AT ultrasonic nebulizer with a desolvation system, which was operated at a flow rate of 0.75 l min^{-1}. When used, hydrogen was mixed with the outer gas at a flow rate of 0.1 l min^{-1}. Effect of HNO_3 was studied up to a concentration of 7.2 N. Ionic lines were used for each REE. Line selection is given in Table 1.

The change in the line intensity to the addition of HNO_3 7.2 N is shown in Fig. 1.
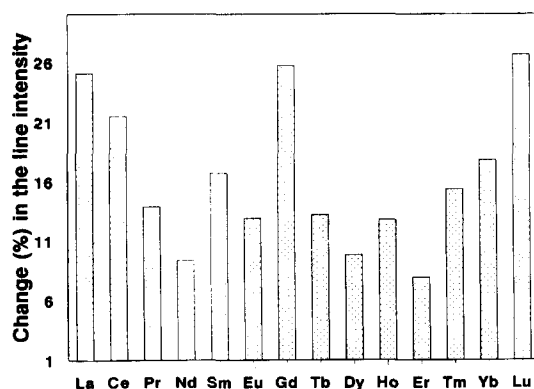

Fig. 1. Effect of 7.2 N nitric acid concentration on the line intensities of rare earth elements. Lines are given in Table 1. The change is expressed as the percentage of (signal at 0 N − signal at 7.2 N/signal at 0 N). REEs are classified according to their atomic number.
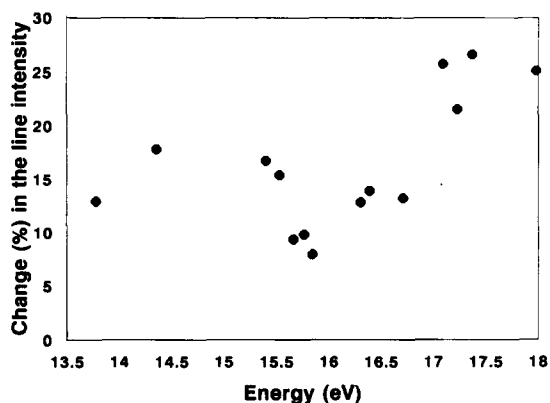
Fig. 2. Change (%) in line intensity of rare earth elements as a function of the sum of oxide dissociation energy, ionization energy and excitation energy as listed in Table 1 for a 7.2 N nitric acid concentration.

The change is expressed as the percentage of (signal at 0 N − signal at 7.2 N/signal at 0 N). REEs are classified according to their atomic number. Clearly, it may be seen in Fig. 1 that there is a significant periodic variation as a function of the atomic number, with a maximum depressive effect for elements such as La, Ce, Gd and Lu.

3. DISCUSSION

3.1. Correlation of the line behaviour with the REE properties

Any attempt to correlate the percentage change given in Fig. 1 with a single REE property such as the ionization energy, the excitation energy, the oxide bond strength, the melting and boiling points was unsuccessful. In any instance, data were scattered. This suggests that, instead of considering a single energy or property, the total energy to bring a REE from the molecule to the excited state of an ion should be taken into account. Not only the sum of ionization energy and excitation energy should be included, but the REE oxide bond strength should also be considered as the presence of REE oxides in the ICP has been reported [27, 28] because of the oxygen originating from water dissociation and the high REE oxide bond strength. Evidence has been given in ICP mass spectrometry [29] that a high LaO^+ concentration is observed when ICP operating conditions result in a poor energy transfer. The percentage change given in Fig. 1 was, therefore, plotted as a function of the sum of the oxide bond strength, the ionization energy and the excitation energy (Table 1). Results are given in Fig. 2. Although no obvious correlation is obtained, the presence of groups of elements which exhibit similar behaviour may be observed.

Use of principal components analysis (PCA) was thus applied [30] to the data given in Fig. 2. PCA results are shown in Fig. 3. There are clearly three different groups of REEs: a first group that consists of Gd, Ce, Lu and La, a second group of Er, Nd, Dy, Ho, Pr and Tb, a third one of Eu, Yb, Tm and Sm.

3.2. Groups of REEs

A so-called small periodic system of the REE group has been reported in 1929 [31]. Although the properties of REEs seem to be closely similar, a detailed inspection of the electronic configuration, the oxide bond strength and the ionization energy will allow us to distinguish several groups of REEs. A first difference between REEs exists when the electronic configuration is considered. Table 2 indicates the $4f$, $5d$ and $6s$ electronic configuration. La, Ce, Gd and Lu are the only REEs with a $5d^1$ electronic configuration, instead of an empty $5d$ orbital [32]. Ionization for most REEs corresponds to a change in the electronic configuration from $f^q d^0 s^2$ to $f^q d^0 s^1$, with the exception
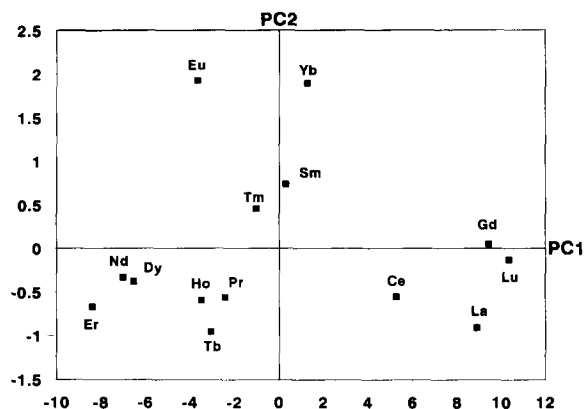
Fig. 3. Principal components analysis of the data shown in Fig. 2.

Table 2. Electronic configuration of the 4 f,
5 d and 6 s orbitals of the REEs

Element	4 f	5 d	6 s
La	0	1	2
Ce	1	1	2
Pr	3	0	2
Nd	4	0	2
Pm	5	0	2
Sm	6	0	2
Eu	7	0	2
Gd	7	1	2
Tb	9	0	2
Dy	10	0	2
Ho	11	0	2
Er	12	0	2
Tm	13	0	2
Yb	14	0	2
Lu	14	1	2

of La ($\rightarrow d^2 s^0$), Ce ($\rightarrow d^2 s^0$), Gd ($\rightarrow d^1 s^1$) and Lu ($\rightarrow d^0 s^2$). This exception corresponds to an abnormal ionization energy for La, Ce, Gd and Lu. Table 1 and Fig. 4 show that there is a constant increase in the ionization energy as a function of the atomic number, except for La, Ce, Gd and Lu. When considering the ionization energy of REEs [33, 34], these four elements have, therefore, a behaviour different
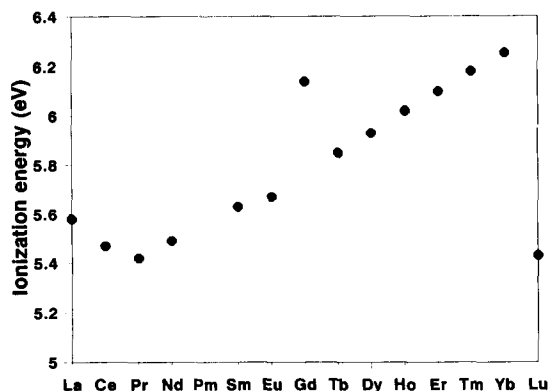

Fig. 4. Ionization energy (eV) for the rare earth elements listed according to their atomic number.
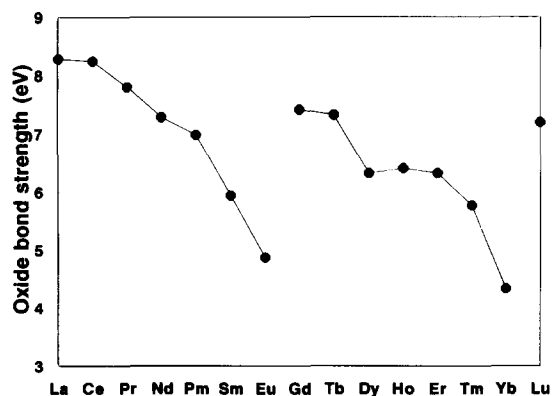
Fig. 5. Oxide dissociation energy (eV) for the rare earth elements listed according to their atomic number.

from the other REEs. Clearly, La, Gd, Lu and, to a less extent, Ce, belong to a separate group.

A similar study can be carried out as a function of the oxide bond strength. A double periodic variation in the oxide bond strength has been reported by Ames et al. [35]. Oxide dissociation energies for the d^1s^2 REEs, i.e. La, Ce, Gd and Lu form a baseline for the series [36, 37]. Other d^0s^2 REEs fall below this baseline. It can be seen (Table 1 and Fig. 5) that five elements exhibit an abnormal behaviour: Sm, Eu, Tm, Yb and Lu. Actually, the number of f electrons is the same for the element and for the oxide for each REE, except for Eu and Yb.

This is why the properties mentioned above allow a periodic arrangement of the REEs (Fig. 6). This figure permits us to recognize the three groups obtained by PCA. Although REEs seem to have similar properties, the slight difference in their ionization energy and oxide bond strength is sufficient to differentiate their behaviour to a change in nitric acid concentration. It should be noted that, although the excitation energy has to be taken into account, this parameter did not play a role in the acid effect as lines of Ce with different excitation energies provided similar results [26].

As both the oxide bond strength and the ionization energy are involved in the nitric acid effect, data suggest that the presence of a high nitric acid concentration results in a change in the dissociation and atomization efficiency. Presence of nitric acid corresponds to an increase of the energy consumption and, therefore, to a degradation of the energy transfer to the analyte.

3.3. Change in the efficiency of energy transfer

In order to confirm this assumption, an experiment was conducted to degrade the efficiency of energy transfer with a method that does not involve the action of an acid. In a previously published work [38], it has been reported that the use of a sheathing gas flow rate added at the exit of the spray chamber results in a degradation of the energy transfer. This is explained by the fact that the sheathing effect still exists in the plasma and hampers the transfer of energy by adding an intermediate layer at the edge of the central channel. Sheathing gas has already been used [24] to enhance the acid effect due to a change in the plasma characteristics. A $0.6 \ 1 \ min^{-1}$ sheathing
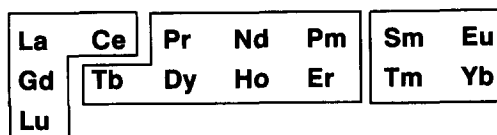

Fig. 6. Periodic arrangement and groups of the rare earth elements according to their electronic configuration and their properties.
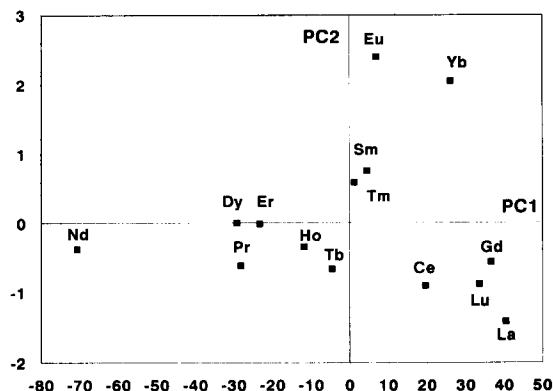
Fig. 7. Principal components analysis of the data obtained by adding a 0.6 l min⁻¹ sheathing gas at the exit of the spray chamber in order to degrade the energy transfer to the analyte. There was no addition of nitric acid. The same line selection was used as in Fig. 3.

gas was, therefore, added and results were compared to those obtained without sheathing gas. Obviously, no nitric acid was added for this experiment. It has been reported that the Mg II 280.270 nm to Mg I 285.213 nm line intensity ratio is a useful indicator of the efficiency of energy transfer to the analyte [39]. The value of the ratio was decreased from 12.6 to 3.2 when the sheathing gas flow rate was increased from 0 to 0.6 l min⁻¹, which corresponded to a large degradation of the energy transfer. As in Fig. 3, PCA was performed and results are given in Fig. 7. It can be seen that there is a marked similarity between Figs 3 and 7. PCA leads to the same REE groups as those in Fig. 3. This is clear evidence that the presence of high nitric acid concentration results in a significant absorption of energy and a consequent decrease in energy transfer from the plasma to the analyte.

3.4. Use of an ultrasonic nebulizer with a desolvation system and addition of hydrogen

Other evidence of the different behaviour of some REEs can be given by using an ultrasonic nebulizer with a desolvation system and an addition of hydrogen. Use of desolvation permits the removal of a large amount of water. Solvent loading is, therefore, lower than for a conventional pneumatic nebulizer. A further addition of 0.1 l min⁻¹ hydrogen in the outer gas facilitates the atomization processes because of a high thermal conductivity [40]. Compared with the use of a pneumatic nebulizer, this system should lead to a significantly different influence of nitric acid [26]. In Fig. 8 the percentage change is shown expressed as % (signal at 0.9 N − signal at 7.2 N/ signal at 0.9 N). Three elements exhibit an enhancement effect, namely La, Gd and Lu. We recognize the elements in the first row in Fig. 6. Although the use of an ultrasonic nebulizer results in different acid effects [26], influence of the REE properties is still significant.

4. CONCLUSION

Study of the effect of nitric acid on the REE line intensities confirms the complexity of the acid effect. Presence of a high concentration of non-viscous acid can result in a variation in the aerosol formation, transport and composition, and a change in the plasma characteristics. The contribution of each process will depend on the plasma parameters, either fixed, i.e. the nebulizer type, the spray chamber design and the injector i.d., or adjustable, i.e. the carrier gas flow rate and the power. Moreover, use of different acids such as nitric acid, hydrochloric acid, and perchloric acid does not necessarily provide similar results. This explains the difficulty of obtaining general
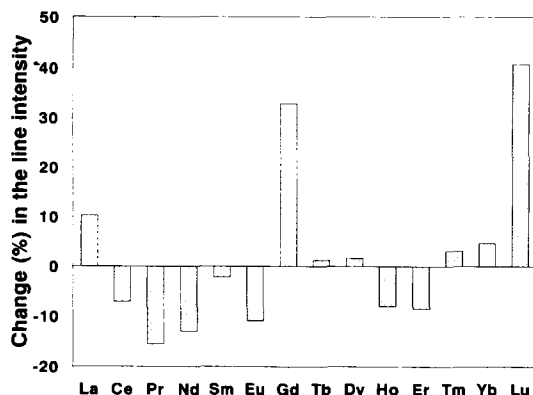
Fig. 8. Effect of a 7.2 N nitric acid concentration on the line intensities of rare earth elements. Lines are given in Table 1. The change is expressed as the percentage of (signal at 0.9 N − signal at 7.2 N/signal at 0.9 N). REEs are classified according to their atomic number. An ultrasonic nebulizer was used with a desolvation system and an addition of 0.1 l min^{-1} hydrogen in the outer gas in order to obtain different atomization conditions.

conclusions on acid effects from previously published work, as these effects can differ with respect to the ICP system and the working conditions used for the experiment.

This complexity has been illustrated for the influence of nitric acid on REEs. Although no direct correlation was found with the ionization energy and the oxide dissociation energy, evidence has shown that a slight difference in oxide bond strength and ionization energy was sufficient to observe a different behaviour with change in acid concentration. Although other REE properties should be considered, both oxide dissociation energy and ionization energy are crucial parameters for the acid effects.

It could be thought that REEs exhibit sufficiently similar properties so that internal standardization can be ideally applied to compensate for acid change. However, under the operating conditions used for this experiment, use of one of the REEs as an internal standard could have led to misleading results for some REEs, depending on the internal standard selection. Whenever it is possible, matching of the standard and unknown solutions in terms of acid concentration would avoid a systematic bias in the accuracy.

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