

Influence of Operating Conditions on the Effects of Acids in Inductively Coupled Plasma Atomic Emission Spectrometry*

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The influence of the operating conditions on interferences from HCl, HNO₃ and H₂SO₄ in inductively coupled plasma atomic emission spectrometry was studied. The acid concentration was in the 0–2 mol l⁻¹ range. It was found that the acid interferences were strongly dependent on the operating conditions. Several different plasma excitation conditions were obtained by modifying the aerosol carrier gas and the intermediate gas flow rates. The test element was vanadium. Plasma diagnostics were performed by measuring the excitation temperature, the electron number density and the ionic-to-atomic line intensity ratio. In each instance, it was found that the excitation temperature was not modified as a function of the acid concentration. For long residence time and efficient energy transfer, the electron number density and the ionic-to-atomic line intensity ratio were not modified. Only a minor depressing effect was observed for ionic lines, which was attributed to the aerosol formation and transport. In contrast, for short residence time and inefficient energy transfer, both the electron number density and the ionic-to-atomic line intensity ratio were depressed. The significant depressing effect for ionic lines was attributed to a change in the excitation conditions. It is, therefore, possible to separate the acid effects originating from the sample introduction system from those originating in the plasma by carefully selecting the operating conditions of the plasma.

Keywords: *Inductively coupled plasma; atomic emission spectrometry; mineral acid interference*

The acidic medium is one of the most commonly used matrices in inductively coupled plasma atomic emission spectrometry (ICP-AES). However, use of mineral acids generally leads to interferences. Few investigations on acid effects have been reported so far.^{1–10} In general, increasing the mineral acid concentration causes a significant decrease in the emission signal observed in ICP-AES. The depression of intensity has been attributed to: (i) a decrease in the sample aspiration rate as a result of increased viscosity;^{1,2} (ii) a change in nebulizer efficiency and droplet size distribution;^{4,6,7} (iii) a variation in the aerosol transport efficiency; and (iv) a change in plasma excitation conditions.^{3,8,9}

Chudinov *et al.*⁸ and Yoshimura *et al.*⁹ have reported that the magnitude of the interference due to the acids differs from one line to another. In the instance of ionic lines, the change in line intensity is correlated with the excitation energy. Chudinov *et al.*⁸ have indicated that the acid effect depends on the type of acid and this effect increases in the following order: HCl < HNO₃ < HClO₄ < H₃PO₄ < H₂SO₄. They found a decrease in excitation temperature (≤ 300 K) with increasing concentration of mineral acid in the range of 0–2 mol l⁻¹. They concluded that, for a low-power plasma and a low acid concentration range (≤ 1 mol l⁻¹), the depressing effect results from a decrease in excitation temperature rather than a reduction in sample uptake rate. However, no explanation was provided to elucidate the mechanisms involved in change in excitation temperature.

Marichy *et al.*¹⁰ reported the effect of mineral acid at concentrations below 1% v/v. They found an increase in analyte emission signals when HCl was used with a maximum effect at a concentration of 0.001%, in contrast to the depression observed with HClO₄. No significant effect was reported with HNO₃ in this concentration range. This enhancement or depressive effect could not be explained by a change in aerosol characteristic or changes in nebulizer and transport

efficiency. It was, rather, a change in the chemical composition of the aerosol, with a 50% decrease in acid concentration compared with that of the solution.

In the present work, the effect of HCl, HNO₃ and H₂SO₄ was investigated using vanadium as the test element. Both the ionic and atomic line intensities were studied as a function of the operating conditions of the ICP. The acid concentration was varied in the range 0–2 mol l⁻¹. In order to evaluate the influence of the operating parameters on the effect of acid, a full two-level and three-factor factorial study was designed. Three sets of operating conditions were selected by adjusting the carrier gas flow rate, the intermediate gas flow rate and the power. The corresponding plasma excitation conditions were assessed by measuring the excitation temperature, the electron number density and the ionic-to-atomic line intensity ratio.

Experimental

Instrumentation

A Jobin-Yvon JY-24 ICP emission spectrometer was used. The original gas flow meters for the aerosol carrier and intermediate gas were replaced by mass flow controllers (Brooks 5850E). Solutions were introduced into the plasma by means of a Meinhard nebulizer (TR-20-C2) with a Scott-type spray chamber working at room temperature.

Temperature Measurements

The Boltzmann plot method was used to measure the excitation temperature. Sixteen vanadium ionic lines were selected. Their wavelength, energy level and oscillator strength values were taken from refs. 11 and 12.

Electron Number Density

The electron number density was determined from the Stark broadening of the 486.12 nm (H β -line) using Griem's approximation described in ref. 13.

* Presented at the XXVIII Colloquium Spectroscopicum Internationale (CSI), York, UK, June 29–July 4, 1993.

Ionic-to-atomic Line Intensity Ratio

The intensity ratio of the Mg II 280.270 nm line to the Mg I 285.213 nm line was measured as this is a simple test to verify the plasma conditions.¹⁴ It has been found that values of the ratio of above eight generally lead to robust conditions, *i.e.*, a plasma not sensitive to matrix effects, in contrast to values at less than four, where the plasma is significantly sensitive to matrix effects.

Chemicals and Emission Lines

Vanadium was also selected as the test element to study the effect of acid because stable aqueous solutions of vanadium can be obtained without the addition of acid and it presents well known atomic and ionic emission lines. Wavelengths and excitation potentials are listed in Table 1. Each net intensity line was obtained by subtracting the background from the gross intensity. Relative line intensities (I_r) were normalized to the intensity measured in the absence of any acid.

Solutions of vanadium were prepared at a concentration of 20 mg ml⁻¹ by dilution from a concentrate prepared from NH₄VO₂ (Merck, *pro analysi* grade). Hydrochloric acid (37% v/v), HNO₃ (65% v/v) and H₂SO₄ (32% v/v) from Riedel-de Haën were used. Measurements were taken after each increase in acid concentration. An equilibrium time of approximately 5–10 min was found to be necessary between measurements at different acid concentrations.^{3,10,15} At least five replicates with an integration time of 0.3 s were used for each concentration.

Full Two-level and Three-factor Factorial Study

In order to evaluate the influence of the operating parameters on the effect of acid concentration for atomic and ionic emission intensities, a full two-level and three-factor (2³) factorial study was designed. The three factors considered were power (P), aerosol carrier gas flow rate (C) and intermediate (or sheathing) gas flow rate (S). The response used was the I_r of vanadium at a 2.0 mol l⁻¹ acid concentration normalized to that obtained without acid. This part of the work was conducted for HNO₃ as the interferent and the results were extrapolated to HCl and H₂SO₄. The V II 294.602 nm and V I 437.924 nm lines were selected for this study. The three factors and their levels are listed in Table 2.

Results and Discussion

Factorial Study

The experimental values of the relative signal of the vanadium lines for each combination of operating parameters are listed

Table 1 Wavelengths and excitation potentials of vanadium emission lines examined

Spectral species	Wavelength/nm	Excitation potential/eV
V II	292.402	4.63
V II	292.464	4.61
V II	309.311	4.40
V I	437.924	3.13
V I	446.029	4.64

Table 2 Factor levels for the two-level and three-factors factorial study

Factor	Level	
Power/kW	0.91	1.08
Intermediate gas flow rate/l min ⁻¹	0	0.38
Aerosol gas flow rate/l min ⁻¹	0.70	1.00

in Tables 3 and 4 for the ionic and atomic lines, respectively. From the complete analysis of variance for the factorial design, conclusions can be drawn for ionic and atomic lines. For the ionic line, the F -test showed that the intermediate (or sheathing) gas flow rate (S) and the aerosol carrier gas flow rate (C) and their interactions were statistically significant at 1%. However, the effect and the interaction of the power (P), $P \times S$ and $P \times C$, were not statistically significant at 10%. The effects calculated from the factorial analysis are listed in Table 5. A comparison of the estimates with their standard errors suggested that C and S and their interactions were significant, whereas the remaining effect (P) and their interaction could be generated by noise. The effect of C and S cannot be interpreted separately because of the large interaction. For the atomic line, the F -test shows that all effects and their interactions were not statistically significant. A comparison of the estimate with their standard errors (as listed in Table 5) suggested that all the effects could be generated by noise. The results obtained show that the magnitude of the acid interference for ionic lines is strongly affected by the aerosol carrier and intermediate gas flow rates. However, the magnitude of the effect of the acid for atomic lines is independent of both flow rates.

For the ionic line, the effect of the intermediate gas flow rate is very important and the effect of the carrier gas is strongly dependent on the former. As can be seen in Table 3, for the runs with intermediate gas flow rate at a high level, the effect of the aerosol carrier gas flow rate is positive, increasing the interference from the acid. However, in the runs with the

Table 3 Experimental values obtained for the relative signal (I_r) for the V II line at 292.402 nm; all values correspond to the average of three replicate runs

Power/kW	Aerosol carrier gas flow rate/l min ⁻¹			
	0.70*	1.00*	0.70†	1.00†
1.08	0.8753	0.9440	0.8734	0.7050
0.91	0.8983	0.9549	0.8464	0.7018

*Intermediate gas flow rate, 0.1 min⁻¹.

†Intermediate gas flow rate, 0.38 l min⁻¹.

Table 4 Experimental values obtained for the relative signal (I_r) for the V I line at 437.924 nm, all values correspond to the average of three replicates runs

Power/kW	Aerosol carrier gas flow rate/l min ⁻¹			
	0.70*	1.00*	0.70†	1.00†
1.08	0.960	0.9490	0.9649	0.9502
0.91	0.956	0.946	0.943	0.9588

*Intermediate gas flow rate, 0.1 min⁻¹.

†Intermediate gas flow rate, 0.38 l min⁻¹.

Table 5 Calculated effects and standard errors for 2³ factorial design, for V lines

Effect	Estimate ± standard error	
	V II 292.402 nm	V I 437.924 nm
Average	0.850	0.953
<i>Main effects—</i>		
C	-0.047 ± 0.004	-0.005 ± 0.005
S	-0.136 ± 0.004	0.001 ± 0.005
P	0.000 ± 0.004	0.005 ± 0.005
<i>Two-factor interactions—</i>		
$C \times S$	-0.110 ± 0.004	0.005 ± 0.005
$C \times P$	-0.003 ± 0.004	0.005 ± 0.005
$S \times P$	0.016 ± 0.004	0.002 ± 0.005
<i>Three-factor interaction—</i>		
$C \times S \times P$	0.000 ± 0.004	0.007 ± 0.005

Table 6 Operating instrumental conditions and plasma excitation conditions

Condition	Power/ kW	Aerosol carrier gas flow rate/ l min ⁻¹	Intermediate gas flow rate/l min ⁻¹	Excitation temperature/K	Electronic density/cm ⁻³	Mg II/Mg I
1	1.08	0.75	0	5100	205 ± 10 ⁻¹³	8.5
2	0.91	0.95	0.25	4765	95 ± 10 ⁻¹³	4.9
3	0.91	1.00	0.38	4200	62 ± 10 ⁻¹³	2.0

intermediate gas flow rate at a low level, the effect of the aerosol carrier gas is negative.

Influence of Plasma Conditions on the Acid Effects

To relate the influence of plasma excitation conditions to the effect of acid concentration, three different sets of operating conditions were selected in order to cover a large range of temperatures, electron number densities and ionic-to-atomic line intensity ratios. The operating parameters are listed in Table 6, along with the corresponding excitation temperatures, electron number densities and Mg II to Mg I ratios, which were measured without acid. Conditions 1 lead to a high Mg II to Mg I line intensity ratio, whereas conditions 3 lead to a low ratio. It could be anticipated that the influence of HNO₃, HCl and H₂SO₄ on vanadium atomic and ionic line intensities would be different for each set of conditions.

The effect of HNO₃ concentration on the atomic and ionic vanadium lines is shown in Fig. 1 for the three conditions. For conditions 1 [Fig. 1(a)], the decrease in the line intensities was less than 5% with increasing HNO₃ concentration. This behav-

our was observed for both atomic and ionic lines. For conditions 2 and 3 [Fig. 1(b and c), respectively] a strong decrease in the ionic lines was observed in contrast to atomic lines where the effect was less marked. The behaviour of atomic lines was similar to that observed under conditions 1. The effect of acid on the ionic lines was sensitive to the plasma conditions, whereas the depressive effects on atomic lines were independent of these conditions.

The effect of HCl concentration on the vanadium line intensities is shown in Fig. 2. The effect of HCl was found to be similar to that obtained for HNO₃. The results obtained for H₂SO₄ are shown in Fig. 3. Under conditions 1 [Fig. 3(a)], the magnitude of the H₂SO₄ effect was approximately the same for atomic and ionic lines and more important than that observed with HNO₃ and HCl under the same operating instrumental conditions. This behaviour can easily be explained by the significant change in viscosity of the solution caused by the increase in H₂SO₄ concentration. However, when working under conditions 2 and 3 [Fig. 3(b and c), respectively], a further depressing effect was observed for ionic lines compared with atomic lines. This means that, besides the viscosity effect,

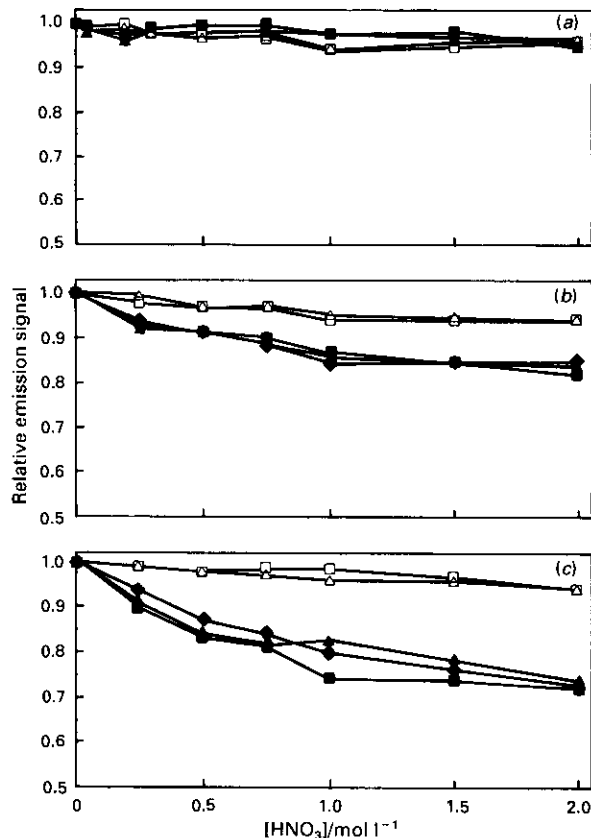


Fig. 1 Effect of HNO₃ concentration on the relative emission intensities of vanadium atomic and ionic lines under the three different instrumental operating conditions: (a) 1; (b) 2; and (c) 3 (see text for details of 1, 2 and 3). ■, V II 292.402 nm; ▲, V II 292.464 nm; ◆, V II 309.311 nm; △, V I 437.924 nm; and □, V I 446.029 nm

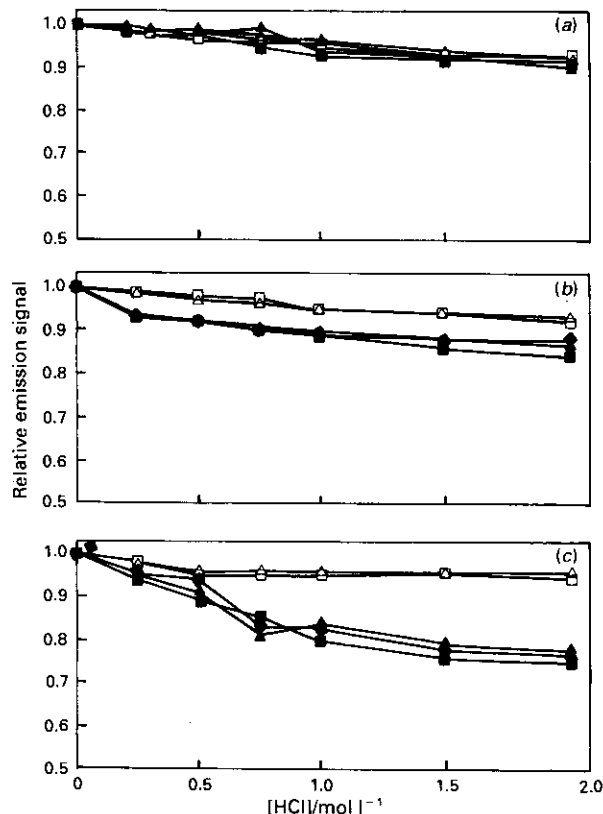


Fig. 2 Effect of HCl concentration on the relative emission intensities of vanadium atomic and ionic lines. Under the three different instrumental operating conditions: (a) 1; (b) 2; and (c) 3 (see text for details of 1, 2 and 3). ■, V II 292.402 nm; ▲, V II 292.464 nm; ◆, V II 309.311 nm; △, V I 437.924 nm; and □, V I 446.029 nm

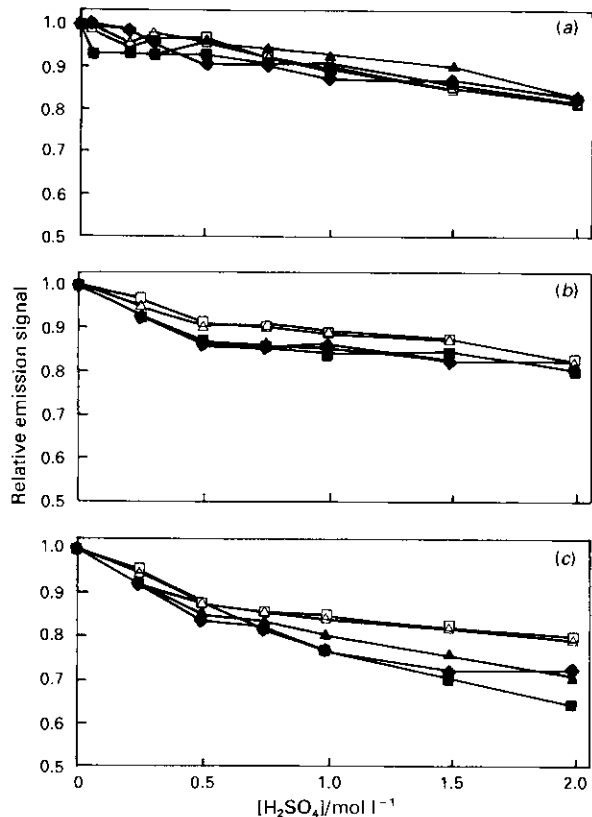


Fig. 3 Effect of H_2SO_4 concentration on the relative emission intensities of vanadium atomic and ionic lines. Under the three different instrumental operating conditions: (a) 1; (b) 2; and (c) 3 (see text for details of 1, 2 and 3). ■, V II 292.402 nm; ▲, V II 292.464 nm; ◆, V II 309.311 nm; △, V I 437.924 nm; and □, V I 446.029 nm

a change similar to that obtained for HCl and HNO_3 was observed. It is, therefore, important to verify the possible effect of change in acid concentration on the plasma conditions.

Effect of Acid on Plasma Excitation Conditions

The effect of HCl concentration in the 0–2 mol l^{-1} range on the excitation temperature, the electron number density and the Mg II 280.270 nm to Mg I 285.213 nm ratio under conditions 1 and 3 is summarized in Figs. 4, 5 and 6, respectively. Although conditions 1 and 3 lead to significantly different temperatures, it is shown in Fig. 4 that the HCl concentration has no effect on the excitation temperature, even under conditions 3. The same results were obtained with HNO_3 and H_2SO_4 . Several independent measurements were repeated to

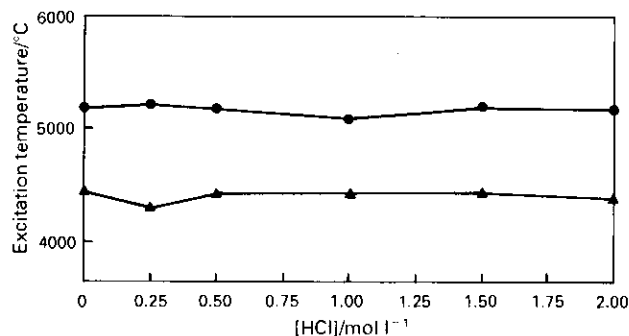


Fig. 4 Effect of the concentration of HCl acid on the excitation temperature, under different instrumental operating conditions: ●, 1; and ▲, 3

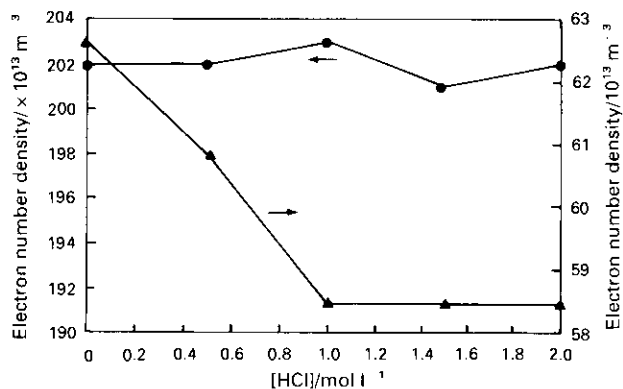


Fig. 5 Effect of the concentration of HCl on the plasma electron density, under different instrumental operating conditions: ●, 1; and ▲, 3

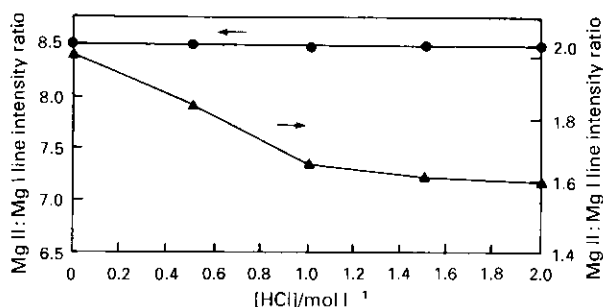


Fig. 6 Effect of the concentration of HCl on the Mg II/Mg I line intensity ratio, under different instrumental operating conditions: ●, 1; ▲, 3

confirm these results. These results differ from those obtained by other workers.^{8,9}

However, a different conclusion is obtained for the electron number density. The density remains the same under conditions 1, whereas it is significantly decreased under conditions 3. The decrease was most significant over the 0–1 mol l^{-1} concentration range, which corresponded to the large decrease in ionic line intensities, as shown Fig. 5 for HCl. Although no change in the excitation temperature was observed, there is a variation in the ion-to-atom equilibrium resulting from the change in the electron number density. This is confirmed by the measurement of the Mg II to Mg I line intensity ratio. It is shown in Fig. 6 that the ratio is not modified under conditions 1 whereas it is significantly changed under conditions 3.

The same experiment based on the use of several elements, vanadium, manganese, lanthanum, barium and magnesium, which were selected because of the possibility of having a stable solution without acid (see Fig. 7). Two acid concentrations are plotted, 0.5 and 2 mol l^{-1} , respectively. Conditions 3 were used. Lines and energies are listed in Table 7. Results were normalized to those obtained without acid and plotted as a function of the sum of ionization and excitation energy. The higher the energy sum, the stronger the effect of acid. This confirms that there is a change in the excitation conditions under conditions 3. It is interesting to note that the manganese lines exhibited a different behaviour. This is because their sum of energies is close to the ionization energy of argon. A charge transfer process is involved in the ionization and excitation of the manganese lines.¹⁶ A behaviour similar to that of manganese has also been reported near 16 eV for copper ionic lines with HNO_3 .⁹

Clearly, at least two effects can be attributed to the presence of acids such as HCl and HNO_3 . These effects can be summarized by plotting the behaviour of the V II 292.402 nm line

Table 7 Wavelength, excitation and ionization potential of different elements studied

Spectral species	Wavelength/nm	Excitation potential/eV	Ionization potential/eV
V II	292.402	4.63	6.74
V II	292.464	4.61	6.74
V II	309.311	4.40	6.74
Mn II	259.373	4.77	7.432
Mn II	261.020	8.16	7.432
Mn II	263.984	8.75	7.432
Mn II	343.987	4.78	7.432
Mn II	344.198	5.37	7.432
La II	394.910	3.54	5.61
La II	408.672	3.03	5.61
La II	412.323	3.32	5.61
Ba II	455.403	2.72	5.21
Ba II	493.406	2.51	5.21
Mg	280.270	4.42	7.644

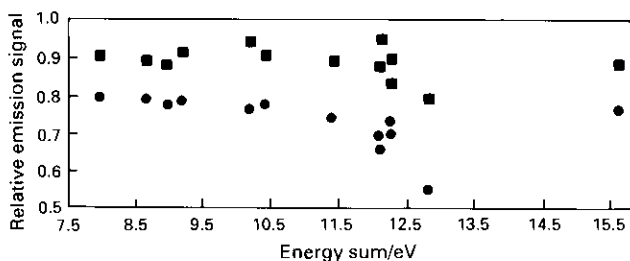


Fig. 7 Relative emission intensity for different elements under instrumental operating conditions 3. HCl concentration: ■, 0.5; and ●, 2 mol l⁻¹

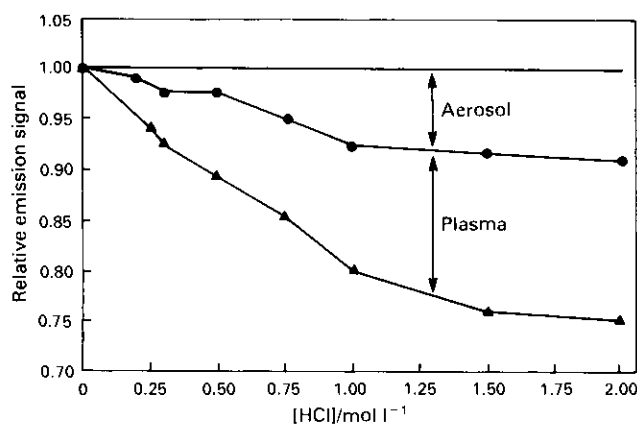


Fig. 8 Effect of the HCl concentration on the relative emission intensity for the V II 292.402 nm line, under instrumental operating conditions ●, 1 and ▲, 3 (see text for details of 1 and 3)

intensity against the HCl concentration under conditions 1 and 3 (Fig. 8). The ideal behaviour would be no influence of the acid, which is represented by a straight line in Fig. 8. Under conditions 1, as there is no change in the excitation temperature and the electron number density, the slight decrease in the line intensity can be attributed to a change in

the aerosol formation and transport. Under conditions 3, the significant decrease can be mainly attributed to the change in the plasma conditions.

Conclusions

A study of mineral acid influence in ICP-AES is complex due to the combination of several possible causes leading to the depressing effect. Study of a given cause can be made possible by careful selection of the appropriate ICP operating conditions. For instance, the influence of the sample introduction system can only be easily studied under operating conditions that lead to a high ionic-to-atomic line intensity ratio, e.g., above eight when the Mg II 280 nm to Mg I 285 nm line intensity ratio is used for the experiment. In contrast, the influence of the excitation conditions can be enhanced when working with operating conditions resulting in a low ionic-to-atomic line intensity ratio, e.g., less than four. The influence of the generator remains to be verified as different conclusions have been reported.⁸ More importantly, an understanding of why a change in the electron number density was observed without a similar change in the temperature is required.

The authors acknowledge the support of the Consejo de Desarrollo Científico y Humanístico de la Universidad Central de Venezuela for this research, Grant No. 03.12.2620/91.

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Paper 3/04703B
 Received August 4, 1993
 Accepted September 3, 1993