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Influence of the sample introduction system on acid effects in inductively coupled plasma atomic emission spectrometry*

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Abstract—Influence of the aerosol formation and transport on acid effects has been studied in inductively coupled plasma atomic emission spectrometry in order to elucidate the decrease in the analyte intensity. To separate the role of the ionization and excitation conditions from that of the sample introduction, operating conditions have been set-up to obtain a constant ratio of the ionic line to atomic line intensity of magnesium. A 27 MHz crystal-controlled generator and a 40 MHz tuned-line generator were used to verify the possible influence of the generator type. Once the ionization and excitation conditions were kept constant, the influence of the sample introduction system could be assessed by using the Mg I 285 nm line. Perchloric acid up to a concentration of 50% (v/v) has been used as the test acid. The ClI 725.662 nm line was also used to assess the amount of chlorine reaching the plasma. Several pneumatic nebulizers were used: Meinhard concentric nebulizers, a Perkin Elmer cross-flow nebulizer, and a Perkin Elmer cone-spray nebulizer. Depressive effects resulting from the perchloric acid depended on the nebulizer type, the carrier gas flow rate and the spray chamber design. Droplet size of the primary and tertiary aerosol were measured. At perchloric acid concentrations higher than 1% (v/v), results suggested that the depressive effect on the Mg line intensity cannot only be explained by a change in the aerosol density but also by a variation in the analyte concentration in the fraction of aerosol that reached the plasma. A careful selection of the sample introduction system components and parameters could minimize the acid effects. Results were compared with those obtained with an ultrasonic nebulizer associated with a desolvation system. Acid effects were more important for the ultrasonic nebulizer than for the pneumatic nebulizers and were explained by a reduction in the production of aerosol.

1. INTRODUCTION

ALTHOUGH acidic media are widely used for solid digestion and solution storage, little has been discussed [1–25] regarding their influence in inductively coupled plasma (ICP), atomic emission spectrometry (AES) and mass spectrometry (MS). At concentrations below 1% (v/v), an increase in the net line intensity can be observed [22], but usually a decrease in the signal is observed at high acid concentrations, i.e. above 1%. The depression in intensity has been attributed to the following causes: (i) a change in the uptake rate due to a variation in the viscosity; (ii) a change in nebulizer efficiency [2, 11] and droplet size distribution; (iii) a variation in the aerosol transport efficiency [18] due to a change in the aerosol density [25] and the spray chamber configuration [2]; and (iv) a change in the ICP atomization and excitation conditions.

The viscosity effect has been reported for H_2SO_4 [1–3, 7, 12, 15] and H_3PO_4 [1, 9, 12, 14, 18]. The use of a peristaltic pump ensures a constant uptake rate but a decrease in the signal is still observed [7, 8, 14]. Although recent work [26] indicates that a disagreement is observed between the empirical relationship of NUKIYAMA and TANASAWA and experimental droplet diameter measurements, the role of both the viscosity and the surface tension in droplet formation is large enough to explain the

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signal reduction obtained with H_2SO_4 and H_3PO_4. However, the change in the viscosity and the surface tension is almost negligible for HCl, $HClO_4$ and HNO_3, which cannot explain the effects that were observed. The only physical change is the solution density.

The variation in the excitation and ionization conditions has been reported to depend on the design and the tuning of the HF generator. Therefore, the type of generator can modify the acid effect [19]. However, different nebulizers were used for the experiments and, therefore, the effects of the nebulizers and the generators could not be clearly separated [19]. Excitation of ionic lines is also dependent on the acid concentration [19, 21] and seems to be related to the energy sum of the line (ionization energy plus excitation energy) [19, 24]. YOSHIMURA *et al.* [21] have also described the relation between the decrease in the signal and the excitation energy. However, it does not seem that a similar agreement is observed between the variation in the atomic line intensities and the acid concentration.

Clearly, there are two types of acids. The first family includes H_2SO_4 and H_3PO_4 and their effects can be partly explained by a change in the viscosity. The second family includes HCl, $HClO_4$ and HNO_3 and their effects can originate in a change in the aerosol formation and transport and the excitation conditions. The depressive effect due to the change in the aerosol formation and transport can be explained by: (i) a variation in the amount of aerosol introduced into the plasma; and/or (ii) a decrease in the concentration of the test element in the fraction of aerosol reaching the plasma.

It has been demonstrated [24] that the acid effects originating from the ionization and excitation conditions can be separated from those originating from the sample introduction system by selecting operating conditions that lead to a constant ratio of ionic to atomic line intensity. Under these conditions, ionization and excitation conditions are kept constant, and the acid effects that can be observed are attributed mainly to the sample introduction system, i.e. to the aerosol formation and transport. These conditions are usually obtained by using a high incident power (greater than 1 kW) and a long residence time, which is obtained for a large inner diameter of the injector and a low carrier gas flow rate, e.g. less than 0.7 l min^{-1} [24].

Therefore, a series of experiments were performed under conditions where the acid effects resulting from the sample introduction system were predominant in order to study the parameters influencing these effects and to provide information on the origin of the depressive effect. The main parameters were the nebulizer type, the carrier gas flow rate and the design of the spray chamber for pneumatic nebulizers and the carrier gas flow rate for an ultrasonic nebulizer associated with a desolvation device.

2. EXPERIMENTAL

The following pneumatic nebulizers were tested: Meinhard type C concentric nebulizers (TR-50-C1, TR-50-C0.5 and TR-30-K3), a Perkin-Elmer cone-spray nebulizer and a Perkin-Elmer cross-flow nebulizer (with ruby tips). For the cone-spray design, instead of using a V-groove for the solution feeding [27], a cone was used as an expansion nozzle [28, 29] and was designed to have a divergence angle greater than the Prandtl–Meyer angle. The cone was made of machined ruby. The nebulizers were associated with a double pass, Scott-type spray chamber and fed via a peristaltic pump (2 ml min^{-1}). The spray chamber was made of Ryton. To provide a different means of aerosol production, a Cetac 1.4 MHz ultrasonic nebulizer (USN) was also used associated with a desolvation system. The oven was set up at 140°C and the water–ethylene glycol cooling mixture at 0°C.

Two types of HF generator were used to study their possible influence: a 27 MHz crystal-controlled generator (Perkin-Elmer Plasma 2000 ICP system) and a 40 MHz tuned-line generator (Jobin-Yvon JY 38 Plus ICP system). Unless otherwise stated, the power was 1 kW. In both systems, the carrier gas flow rate was adjusted via a mass flow controller. The inner diameters (i.d.) of the injectors were 2 and 3 mm for the Perkin-Elmer and the Jobin-Yvon systems, respectively. Addition of a sheathing gas at the exit of the spray chamber (0.36 l min^{-1}) was possible with the JY 38 Plus ICP system.

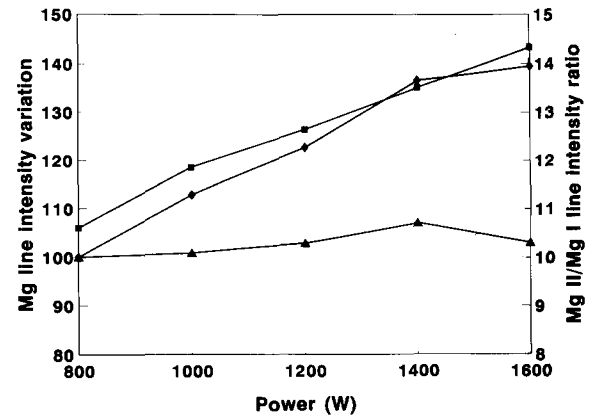

Fig. 1. Effect of the power on the Mg I 285 nm (▲) and Mg II 280 nm (◆) line intensities (arbitrary units) and on the Mg II 280 nm/Mg I 285 nm line intensity ratio (■) for a concentric nebulizer and using the Perkin-Elmer PE 2000 ICP system.

Perchloric acid was selected as the test acid as CHUDINOV *et al.* [19] have indicated that the effect of $HClO_4$ was usually the strongest among HCl, $HClO_4$ and HNO_3. This will be verified later. Acidic solutions were diluted (v/v) from perchloric acid (Prolabo Normapur, 70% m/v). Therefore, a 1% (v/v) $HClO_4$ solution contained 0.116 mol l^{-1}. Experiments were conducted with increasing concentrations of acid and using an equilibrium time of several minutes between successive concentrations. Droplet sizes were measured with a Malvern 2600 system, using a 63-mm focal length lens and a beam diameter of 9 mm. The probing zone was centred 5 mm from the tip of the nebulizer of the exit of the spray chamber.

Magnesium was selected as the test element. Solutions of 1 mg l^{-1} of Mg were prepared from $Mg(CH_3COOH)_2 \cdot 4H_2O$ (Prolabo Normapur). The ionic to atomic line intensity ratio is a classic way [30] to measure the atomization and ionization efficiency in an ICP. From the concept of soft and hard lines [31, 32], the ionic line intensity is highly sensitive to a change in excitation and ionization conditions in contrast to the atomic line intensity (Fig. 1).Variation in the atomic line intensity will reflect mostly the change in the aerosol formation and transport efficiency. The Mg II 280.270 nm and Mg I 285.213 nm line pair is commonly used [30]. On the millisecond scale [33, 34], the ratio is a measure of the pertubation caused by the introduction of large droplets. In the vicinity of large droplets still present in the plasma, a local pertubation occurs, which corresponds to a decrease in the Mg II line intensity in contrast to an increase in the Mg I line intensity. When time-averaging is used, i.e. an integration time longer than 0.1 s, values of the ratio close to the local thermodynamic equilibrium (LTE), i.e. between 10 and 13, can be observed for a high power and a long residence time [30]. As mentioned above, this long residence time is obtained by combining a low carrier gas flow rate (<0.7 l min^{-1}) and a large i.d. of the injector (>1.8 mm). Under these conditions the plasma is robust to matrix effects. In particular, change in acid concentrations do not modify significantly the ionization and excitation conditions of the ICP [24]. In this instance, acid effects are mainly related to the sample introduction system and will be evaluated based on the use of the Mg I 285 nm line intensity.

3. Results for the Pneumatic Nebulizers

3.1. *Ionic to atomic line intensity ratio*

Optimization of the signal to background ratio using Mg I and Mg II lines led to carrier gas flow rates between 0.7 and 0.8 l min^{-1} on both ICP systems. The ratio of the Mg II to the Mg I line intensity was measured for a carrier gas flow rate of 0.75 l min^{-1} (Fig. 2) as a function of the concentration of perchloric acid up to a 50% (v/v) and for an observation height above the load coil of 4 mm. Even when adding a sheathing gas flow rate of 0.36 l min^{-1}, which degrades the efficiency of energy transfer between the plasma and the sample [35], only a minor change in the ratio was observed between 30% (v/v) and 50% (v/v). Therefore, it was considered that

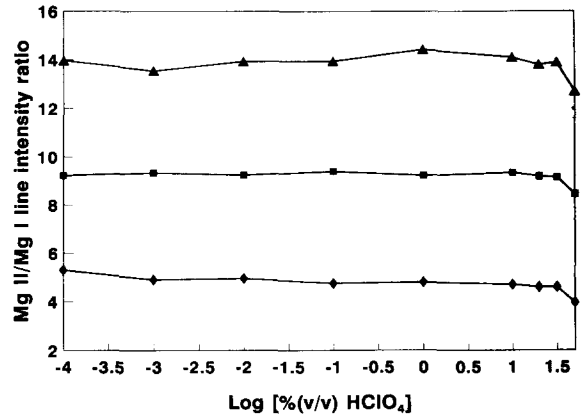

Fig. 2. Effect of the $HClO_4$ concentration on the Mg II 280 mn/Mg I 285 nm line intensity ratio for several operating conditions: (▲) JY 38 Plus ICP system, 1 kW and 0.75 l .min^{-1}; (■) PE 2000 ICP system, 1 kW and 0.75 l min^{-1}; (◆) JY 38 Plus ICP system, 1 kW, 0.75 l min^{-1} + 0.36 I min^{-1} sheathing gas.

the addition of perchloric acid did not modify significantly the ionization and excitation conditions of both ICP systems.

This was confirmed for carrier gas flow rates between 0.6 and 1.0 l min^{-1}, which is the range normally used with the two ICP systems. Figure 3 shows the effect of the carrier gas flow rate on the ionic to atomic line ratio for two incident powers and two perchloric acid concentrations (0.01% and 50%). The Perkin-Elmer ICP system was used. The only significant change resulted from the different values of the incident power. This means that, under our operating conditions, an increase in the acid concentration did not significantly modify the plasma characteristics, even for a relatively low Mg II/Mg I ratio. Consequently, it was assumed that the acid effect was mainly resulting from the aerosol formation and transport.

3.2. *Possible influence of the generators*

The same pneumatic nebulizer (concentric type, C1), spray chamber and carrier gas flow rate (0.75 l min^{-1}) were used on both ICP systems. In both experiments, the

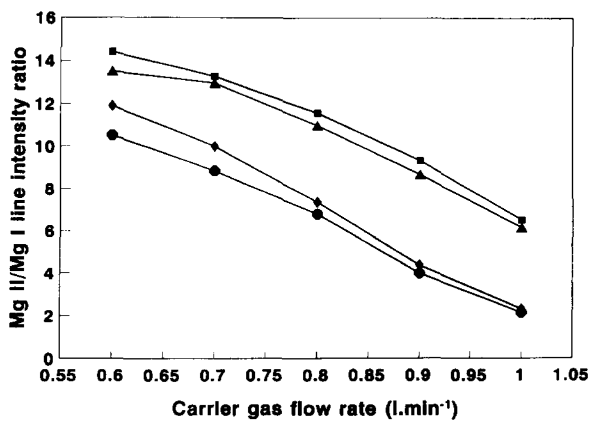

Fig. 3. Effect of the carrier gas flow rate on the Mg II 280.270 nm to the Mg I 285.213 nm line intensity ratio, using a cone-spray nebulizer and the PE 2000 ICP system. Two powers and two $HClO_4$ concentrations (% v/v) were used: (■) 1.8 kW, 0.01%; (▲) 1.8 kW, 50%; (●) 1 kW, 0.01%; (◆) 1 kW, 50%.

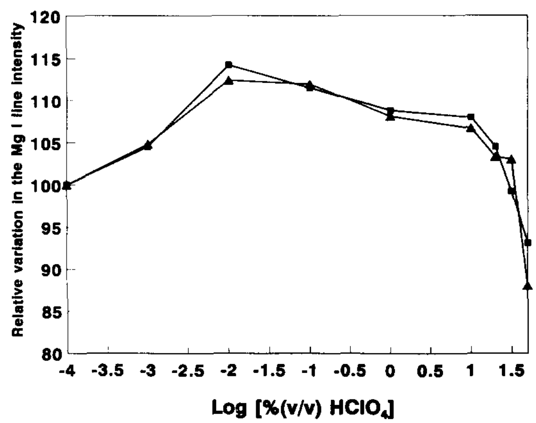

Fig. 4. Effect of the $HClO_4$ concentration (% v/v) on the relative variation in the Mg I 285 nm line (normalized to 0.0001%) using the same concentric nebulizer, double-pass spray chamber and carrier gas flow rate (0.75 l min^{-1}) for two different ICP systems: (■) PE 2000 ICP system; (▲) JY 38 Plus ICP system.

spray chamber was kept at room temperature. Figure 4 shows the influence of the $HClO_4$ concentration on the Mg I 285 nm line intensity for the two generators. The concentration was in the range of 0.0001% to 50% (v/v). It can be seen that a maximum was observed near 0.01%, as reported previously for nitric acid in the same concentration range [22] and that a depressive effect was obtained at a concentration of 50%. However, the behaviour of the line intensity was the same for the two ICP systems although these two generators had different ionization and excitation conditions (Fig. 2). At least for the two ICP systems used in this work and under our operating conditions, it appears that the type of generator did not play a significant role in the acid effect as this effect was similar in both instances. This confirms that the acid effect was related to the sample introduction system.

Over the $HClO_4$ concentration range shown in Fig. 4, it can be seen that the maximum variation in the Mg I line intensity was between 0.01% and 50%. Acid effect will be therefore described as the percentage decrease in the Mg I line intensity and expressed as: 100 × (signal at 50%/signal at 0.01%).

3.3. *Comparison of acid effects*

As mentioned above, CHUDINOV *et al.* [19] have indicated that the effect of $HClO_4$ is usually stronger than those of HCl and HNO_3. This was verified by comparing the $HClO_4$ and HNO_3 effects under our operating conditions (Fig. 5) for the Perkin-Elmer and the cone-spray nebulizer. It should be noted that 50% (v/v) HNO_3 and 50% (v/v) $HClO_4$ correspond to 7.2 mol l^{-1} and 5.8 mol l^{-1}, respectively, which is a rather similar molar concentration. It can be seen that the $HClO_4$ effect was significantly larger than that of HNO_3. Similar results were obtained for the other pneumatic nebulizers.

3.4. *Effect of the carrier gas flow rate and the nebulizer type*

Under conditions used in Fig. 2, the effect of the carrier gas flow rate on the acid effect was studied. Results obtained for the Perkin-Elmer and the cone-spray nebulizer are given in Fig. 6. Two powers were used to confirm the absence of influence of power. Figure 6 confirms that power did not play a role in the acid effect, at least at carrier gas flow rates less than 0.9 l min^{-1}. From Fig. 6, it can also be seen that the percentage decrease in the Mg I line intensity was depending on the carrier gas flow rate and was larger at low flow rates than at high flow rates. This was a trend that had been found for the pneumatic nebulizers (concentric or cross-flow type) tested in this work, although the magnitude of the effect can vary. In any instance, the effect

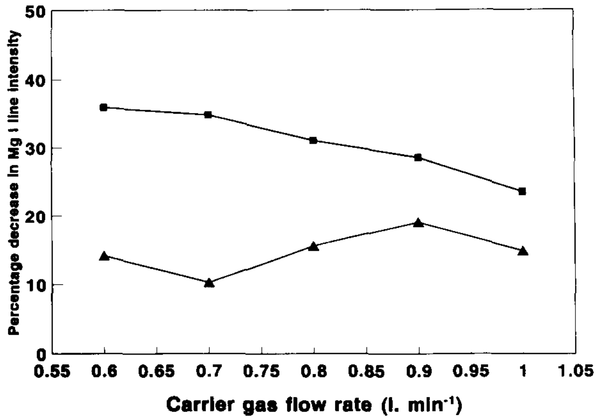

Fig. 5. Comparison of the effect of the carrier gas flow rate on the percentage decrease in the Mg I 285 nm line for $HClO_4$ and HNO_3 for an acid concentration variation between 0.01% (v/v) and 50% (v/v). The PE 2000 ICP system and a cone-spray nebulizer were used with a power of 1.8 kW. (■) $HClO_4$; (▲) HNO_3.

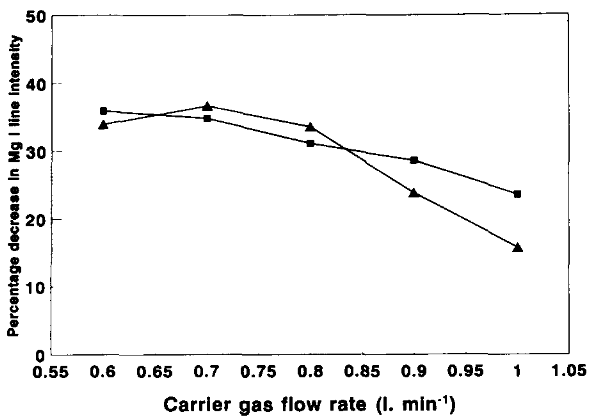

Fig. 6. Effect of the carrier gas flow rate on the percentage decrease in the Mg I 285 nm line for a $HClO_4$ concentration variation between 0.01% (v/v) and 50% (v/v). The PE 2000 ICP system and a cone-spray nebulizer were used with two powers. (■) 1.8 kW; (▲) 1 kW.

could be minimized by using carrier gas flow rates near 1 l min^{-1}. This could be in favor of the role played by the aerosol density. Results are summarized in Fig. 7 in the 0.6–1.0 l min^{-1} range. Interesting results were obtained for the Perkin-Elmer cross-flow nebulizer as enhancement effects were observed at high carrier gas flow rates instead of a depressive effect (Fig. 7).

The amount of aerosol at the exit of the spray chamber can be estimated by using a silica gel trapping. However, this method was not accurate enough to give significant evidence of a change of a few per cent in the aerosol production. In contrast, change in the droplet size distribution can be accurately measured.

3.5. *Acid effect and droplet size distribution*

Use of a different carrier gas flow rate and type of nebulizer can have consequences for the droplet size distribution. Droplet size measurements were performed mostly with acid concentration below 0.01% (v/v). However, there was no significant difference in the primary and tertiary aerosol droplet size when adding $HClO_4$: The droplet size of the primary aerosol depended slightly on the carrier gas flow rate. Figure 8 shows the effect of the carrier gas flow rate on the droplet size distribution for a concentric

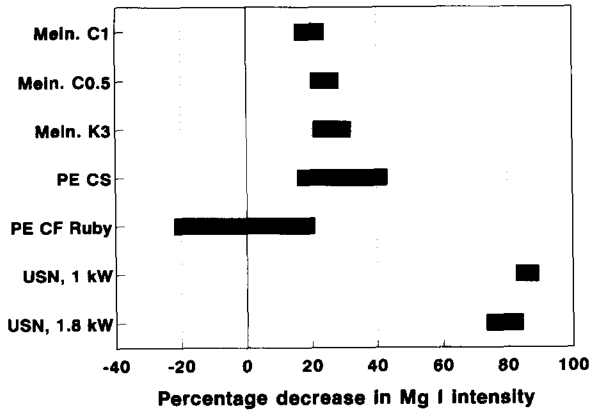

Fig. 7. Overall percentage decrease in the Mg I line intensity for different pneumatic nebulizers and the ultrasonic nebulizer with desolvation measured with the Perkin-Elmer Plasma 2000 ICP system. The $HClO_4$ concentration variation was between 0.01% (v/v) and 50% (v/v). The power was 1.0 kW except for the USN where two powers were used, 1 kW and 1.8 kW. The carrier gas flow rate ranged from 0.6 to 1.0 l min^{-1}, except for the ultrasonic nebulizer (0.5 to 1.0 l min^{-1}) and the Meinhard type K3 concentric nebulizer (0.6 to 0.7 l min^{-1}). USN is the Cetac ultrasonic nebulizer; Mein. C 0.5 is a Meinhard type C concentric nebulizer optimized for low flow rates; Mein. K3 is a Meinhard type K concentric nebulizer; CS is the Perkin-Elmer cone-spray nebulizer; CF Ruby is the Perkin-Elmer cross-flow nebulizer with ruby tips.

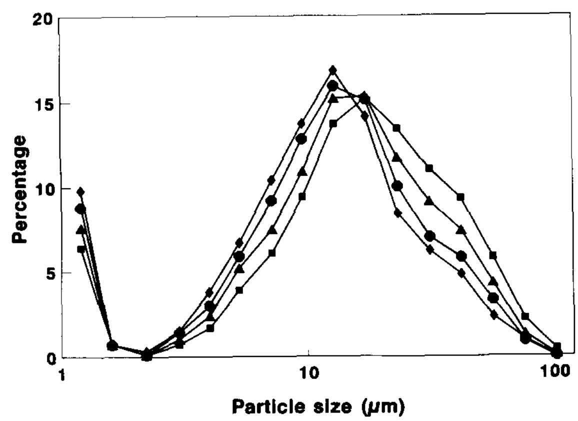

Fig. 8. Relative volume frequency (%) of the droplet size distribution of the primary aerosol produced by a concentric nebulizer (C1) for different carrier gas flow rates. This was measured with a Malvern 2600 system. (■) 0.7 l min^{-1}; (▲) 0.8 l min^{-1}; (●) 0.9 l min^{-1}; (◆) 1.0 l min^{-1}.

nebulizer (C1). The lower the carrier gas flow rate, the higher the diameter of the droplet size. However, there was no significant difference for the tertiary aerosol at the exit of the spray chamber (Fig. 9) for the results provided with the various carrier gas flow rates.

The influence of the nebulizer type is shown in Fig. 10 for the concentric (C1) and the cross-flow nebulizers for which the acid effect was significantly different. Figure 10 indicates that the droplet size of the primary aerosol obtained with a concentric nebulizer differed from that of the cross-flow nebulizer. The corresponding Sauter diameters were 5.6 μm and 10 μm. Similarly to the effect of the carrier gas flow rate, use of the spray chamber led to the same droplet size distribution (Fig. 11), irrespective of the nebulizer. In each instance, the Sauter diameter was about 2.3 μm. As the droplet size of the tertiary aerosol was similar irrespective of the nebulizer type and the carrier gas flow rate, this means that the filtering effect of the spray chamber was different. Therefore, the proportion of large droplets (or small droplets) that were

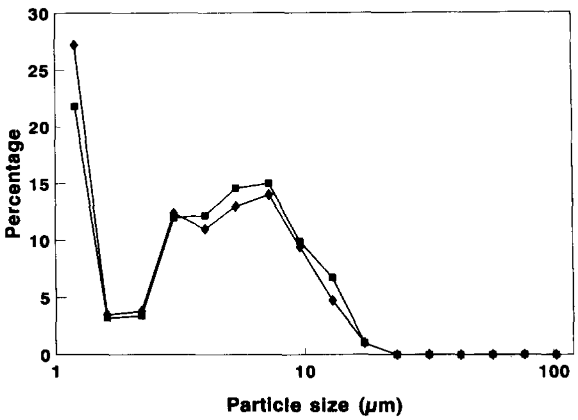

Fig. 9. Relative volume frequency (%) of the droplet size distribution of the tertiary aerosol produced by a concentric nebulizer (C1) and a double-pass spray chamber for different carrier gas flow rates. (■) 0.7 l min^{-1}; (◆) 1.0 l min^{-1}.

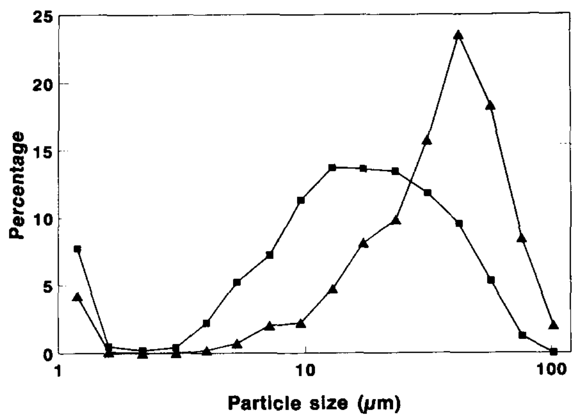

Fig. 10. Comparison of the relative volume frequency (%) of the droplet size distribution of the primary aerosol produced by a C1 concentric nebulizer (■) and a close-flow nebulizer (▲). The carrier gas flow rate was 0.7 l min^{-1}.

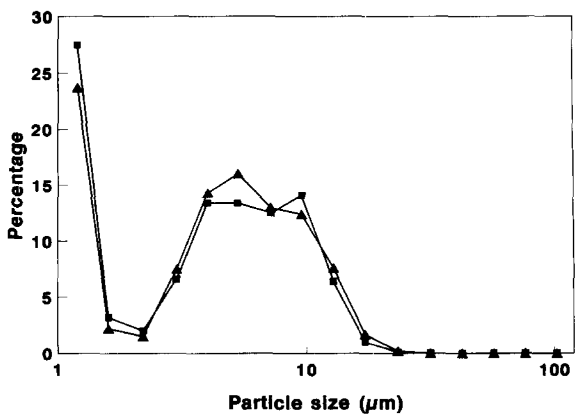

Fig. 11. Comparison of the relative volume frequency (%) of the droplet size distribution of the tertiary aerosol produced by a C1 concentric nebulizer (■) and a cross-flow nebulizer (▲) associated with a double-pass spray chamber. The carrier gas flow rate was 1.0 l min^{-1}.

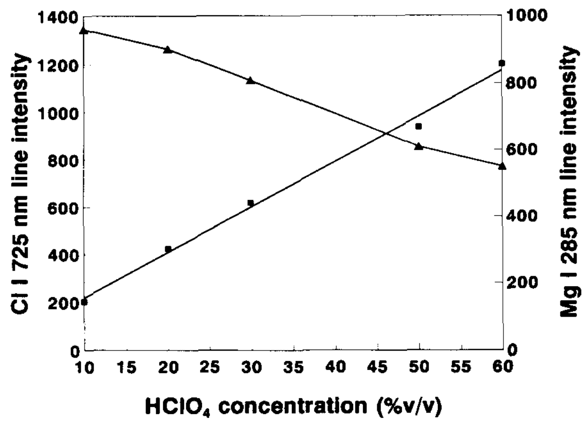

Fig. 12. Effect of the $HClO_4$ concentration on the Cl I 725.662 nm (■) line intensity (left scale), using the JY 38 Plus ICP system and the cone-spray nebulizer. The corresponding Mg I 285.213 nm (▲) line intensity (for a constant concentration of 1 mg l^{-1}) is plotted (right scale) for the same range of $HClO_4$ concentration.

trapped was not the same. Regardless of the acid effect, i.e. aerosol ionic redistribution or variation in the aerosol density, a change in the design of the spray chamber should lead to different effects.

3.6. *Influence of the spray chamber*

The influence of the spray chamber design on the acid effects has already been reported [2]. Instead of using the conventional double-pass spray chamber, we have used a reduced-size spray chamber [36] to study the influence of the spray chamber configuration. The main characteristics were a single-pass design and a reduced volume (25 cm^3 instead of 100 cm^3). Droplet size separation was mainly achieved through an impact process. This spray chamber was set up on the JY 38 Plus ICP system. Using the cone-spray nebulizer, a large set of experiments gave the average value of 16% for the percentage decrease in the Mg I line intensity for the single-pass design, whereas an average value of 37% was obtained for the double-pass design. Using the concentric nebulizer, results were 0% and 19% for the single- and double-pass design, respectively. It can therefore be deduced that the influence of the spray chamber was significant on the acid effect. However, it must be noted that not only the two nebulizers produced different droplet size distribution but also a different shape of the spray. The divergence of the spray formed by the cone-spray nebulizer was larger than that formed by the concentric one. The role of the spray chamber was certainly different for these two nebulizers, in particular if aerosol density was concerned, which explained the different percentage decreases in the Mg I line.

Besides the decrease in the Mg I line intensity, it was thought useful to verify whether the amount of $HClO_4$ reaching the plasma was proportional to the concentration of $HClO_4$ in the solution to be nebulized. This was measured through the emission of chlorine.

3.7. *Measurement of chlorine concentration*

Chlorine is not a sensitive element in ICP–AES as its most sensitive lines are located below 150 nm and cannot be observed with a commercial ICP system. However, for concentrations of $HClO_4$ higher than 1% (v/v), use of the Cl I 725.662 nm line made possible the measurement of the Cl concentration with sufficient accuracy. Therefore, the Cl concentration was measured in the 10–60% (v/v) range. Figure 12 shows the effect of the $HClO_4$ concentration on both the Cl I and Mg I line intensities for the cone-spray nebulizer. Clearly, the chlorine emission is proportional to the $HClO_4$ concentration in contrast to the Mg emission which is acid dependent instead

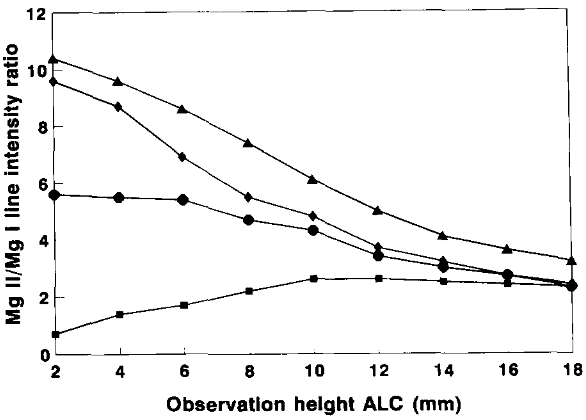

Fig. 13. Effect of the observation height above the load coil (ALC) on the Mg II/Mg I line intensity ratio for different nebulizers and carrier gas flow rates. The PE 2000 ICP system was used with a power of 800 W. (■) Concentric nebulizer, 1.0 l min^{-1}; (●) USN, 1.0 l min^{-1}; (◆) USN, 0.7 l min^{-1}; (▲) concentric nebulizer, 0.7 l min^{-1}.

of being constant. The experiment was repeated under various conditions, nebulizer type, spray chamber design and temperature, carrier gas flow rates. Similar behaviour of the chlorine line was obtained in each instance. If $HClO_4$ is still present in the droplets, this means that there is no loss of the aerosol and that the acid effect can be partly explained by a concentration change in the fraction of the aerosol reaching the plasma. In contrast, if $HClO_4$ is in a gaseous form, the acid effect can be explained by both a change in the aerosol density and an increase in the volatility of the aerosol.

This could be confirmed by measuring the Mg concentration either in the aerosol or in the drain. Currently, both experiments suffer from limitations. Solving this problem would require to bring improvements in the collection of the material at the exit of the spray chamber so as to collect it quantitatively, regardless of its physical form. Even if an efficient trapping of both the aerosol and the gaseous phase could be performed, measurement of the Mg concentration should be carried out with an analytical method not using a nebulization, which excludes the ICP and flame atomic absorption spectrometry. The measurement of the Mg concentration in the drain solution cannot also be used: as the amount of aerosol is small compared with that of the drain solution, even a large change in the Mg concentration in the aerosol will not modify significantly the Mg concentration in the drain.

4. Results for the Ultrasonic Nebulizer with Desolvation

In the configuration of the USN, the solution is fed by means of a peristaltic pump onto the surface of a transducer. This configuration was described by Olson *et al.* [37] where the transducer was water-cooled. Compared to this design, the only important modification of the CETAC USN is the cooling of the transducer, which is air-cooled instead of water-cooled, resulting in a better coupling efficiency between the transducer and the solution. Even if little has been described concerning the influence of acids [38], it is basic knowledge that the use of acids leads to a drastic decrease in the aerosol production. This can be verified by the visual inspection of the decrease in aerosol formation at high acid concentrations.

As a dry aerosol is injected into the plasma, ionization and excitation conditions can differ from those obtained with a pneumatic nebulizer. This can be verified by measuring the ionic to atomic line intensity of magnesium (Fig. 13). The experiment was performed at a power of 800 W for the Perkin-Elmer ICP system as a function of the observation height above the load coil. This low power was selected to enhance any difference between a dry and a wet aerosol [30]. For a carrier gas flow rate of

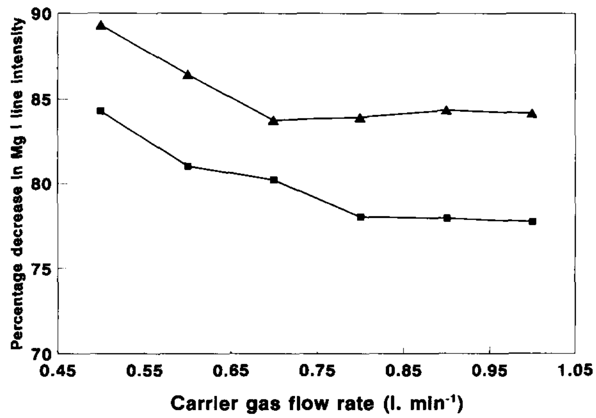

Fig. 14. Effect of the $HClO_4$ concentration on the Mg II 280.270 nm to the Mg I 285.213 nm line intensity ratio for the ultrasonic nebulizer and two operating conditions. The PE 2000 ICP system was used. (■) 1.0 kW, 0.7 l min^{-1}; (▲) 1.6 kW, 0.5 l min^{-1}.

1 l min^{-1}, i.e. a short residence time, the amount of water was too high with the wet aerosol to ensure a complete volatilization and an efficient transfer of energy to the sample. Use of a dry aerosol facilitated the atomization of the sample, resulting in a better ionic to atomic line intensity ratio (Fig. 13), in particular for low observation heights. In contrast, for a low carrier gas flow rate of 0.7 l min^{-1}, i.e. a long residence time, a complete atomization and an efficient ionization is obtained for the wet aerosol. In this instance, dissociation of water produced hydrogen, which, in turn, improved the energy transfer [39]. Use of a dry aerosol did not result in an improvement in the ionic to atomic line intensity ratio, as no hydrogen was available. For high incident powers (greater than 1.2 kW), values of the ionic to atomic line intensities observed for the dry and the wet aerosol were quite similar. Therefore, change in the atomization, ionization and excitation conditions between a dry aerosol and a wet aerosol depends mainly on the operating conditions of the ICP, i.e. the efficiency of energy transfer and the residence time. Because of the use of a desolvation system, it was interesting to compare the behaviour of the USN with those of the pneumatic nebulizers as a function of the $HClO_4$ concentration.

Effect of the $HClO_4$ concentration on the Mg II/Mg I line intensity ratio is given in Fig. 14 for two extreme operating conditions of the USN: (i) a power of 1 kW and a carrier gas flow rate of 0.7 l min^{-1}, i.e. a rather low Mg II/Mg I line intensity ratio; and (ii) a power of 1.6 kW, and a carrier gas flow rate of 0.5 l min^{-1}, i.e. a higher Mg II/Mg I line intensity ratio. The two curves in Fig. 14 exhibit similar shapes with a maximum of the ratio near a concentration of 20%. This means that, in contrast to the results obtained with the pneumatic nebulizers, the acid had some effects on the ionization and excitation conditions, even at high power. This is explained by the use of a desolvation system. The effect of the $HClO_4$ concentration on the percentage decrease in Mg I line intensity is given in Fig. 15 for two powers, 1 kW and 1.8 kW. Similar to the trend observed for the pneumatic nebulizers (Fig. 6), the effect of $HClO_4$ was stronger for the lowest carrier gas flow rates. However, the percentage decreases were: (i) significantly depending on the power in contrast to those observed for the pneumatic nebulizers; and (ii) far more important than those obtained with the pneumatic nebulizers (Fig. 7). Although the perchloric acid had an effect on the ionization and excitation conditions, its major effect was related to a drastic reduction in the aerosol production.

5. Conclusions

Acid effects in ICP–AES are complex because they can be related to a change in the ionization and excitation conditions of the plasma and to a change in the aerosol

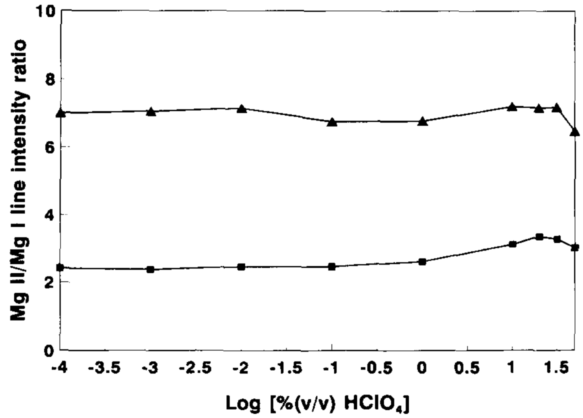

Fig. 15. Effect of the carrier gas flow rate on the percentage decrease in the Mg I 285 nm line for $HClO_4$. The PE 2000 ICP system and the USN were used with two powers. (■) 1.8 kW; (▲) 1 kW.

formation and transport. Under conditions where the variations in the plasma characteristics can be neglected, acid effects for pneumatic nebulizers are related to the nebulizer type, the carrier gas flow rate and the spray chamber design. The major change in the aerosol properties due to addition of non-viscous acids is an increase in the density [25]. Most of the results described in this work can be explained by this change, in particular the effect of the carrier gas flow rate and the role of the spray chamber. However, in some instances, an adequate combination of a pneumatic nebulizer and a spray chamber can result in the absence of acid effects. This means that additional effects have to be considered such as aerosol ionic redistribution and partial evaporation of the smallest droplets of the aerosol. Aerosol ionic redistribution has been already reported in ICP–AES [40]. However, aerosol ionic redistribution for real world samples has not yet been studied, in particular for the influence of the acids. At low acid concentrations (<1%), we found previously [22] that a change was observed in the acid concentration of the aerosol compared to the acid concentration in the solution to be nebulized. However, a different effect is observed at high acid concentrations (>1%), as the acid concentration reaching the plasma remains proportional to the acid concentration in the solution. Two different processes seem to occur, over the range of carrier gas flow rates currently used in ICP–AES, with the transition point near an acid concentration of 0.01% (v/v). For a better understanding of the acid effects, it remains (i) to use more test elements in the same solution; (ii) to improve the aerosol collection methods and to determine the concentration of analytes in the aerosol by independent methods; and (iii) to measure the amount of aerosol by a method not involving the collection of the droplets (e.g. light scattering if the droplet size of the tertiary aerosol is constant).

The current trend of working at low carrier gas flow rates in order to improve the residence time is contrary to what is required to obtain a low acid effect. So far, spray chambers were only designed to reject large droplets. It seems that an optimization of the design of a spray chamber should also take into account acid effects. Moreover, the spray chamber must be matched with a given pneumatic nebulizer.

Use of an ultrasonic nebulizer provides an improvement in the limits of detection for "pure" solutions. Unfortunately, this type of nebulizer is very sensitive to the acid concentration. Acid effect is mainly related to a drastic decrease in the aerosol production in contrast to the effect observed for pneumatic nebulizers.

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