



Study of the fundamental plasma parameters by HG ICP-OES with a dual hydride generation system

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Resumen:

En este trabajo se realizó un estudio del efecto del hidrógeno producido en la generación de hidruros sobre las características del plasma en espectroscopia de emisión óptica con plasma inductivamente acoplado con un sistema dual-generador de hidruros. Las condiciones de excitación mejoran en comparación con la nebulización estándar. La temperatura de excitación, la densidad electrónica y la relación Mg (II)/Mg (I) se incrementaron significativamente cuando el sistema fue operado en el modo dual, incluso a muy bajos flujos de reductor. Las magnitudes de estos parámetros aumentaron con el incremento del flujo del reductor y la concentración ácida.

Palabras clave: plasma inductivamente acoplado; generación de hidruros; generador dual; diagnóstico de plasmas

Abstract

The effect of hydrogen from hydrides generation in a radially-viewed inductively coupled plasma optical emission spectroscopy with a dual hydride-generator system on plasma excitation characteristic was studied. The effects of the acid concentration and reductant solution flow rate on the fundamental parameters were evaluated. Results showed an improvement on the plasma excitation conditions compared to standard nebulization. The excitation temperature, the electron number density and the ionic-to-atomic lines Mg(II)/Mg(I) ratio increased significantly when the system was operated in the dual mode, even at very low reductant flow. These parameters increased in magnitude when increased reductant flow rate and acid concentration

Keywords: Inductively coupled plasma; Hydride generation; Dual generator, Plasma diagnostic

Introduction

The hydride generation (HG) technique is an excellent procedure for analytes separation of gaseous hydride from the matrix. This sample-introduction procedure in inductively coupled plasma optical emission spectroscopy (ICP-OES) provides a better sensitivity in one or two orders of magnitude compared to sample solution nebulization techniques. This is mainly due to the high efficiency of both the analyte transport to plasma and the atomization and excitation process of the volatile hydrides in the plasma discharge¹. At the same time the mutual interferences from hydrides are absent². Thompson *et al.*³ were the first in using HG as a procedure for introduction of the sample into an ICP. They found limits of detection 500 times lower with respect to pneumatic nebulization. HG has been developed as a routine method for volatile hydride-forming elements (As, Se, Te, Bi, Sb, Ge, Pb and Sn). The chemical reaction in the hydride generator, the separation of volatile products from liquid phase and the transport of the gaseous species to the excitation source can be performed for liquids in different

devices using a continuous flow system or flow injection (FI). Several works reported hydride-generator systems that combine hydride production and gas-liquid separation in one unit, obviating the use of a separate mixing/reaction coil and gas-liquid separator. These systems provide convenient way of determining hydride and non-hydride forming elements, either by aerosol or vapour generation, or simultaneously in the same device (dual mode)⁴⁻¹⁴. The HG reaction and the gas phase separation can occur inside the spray chamber. Reactants, sample solutions and NaBH₄ are nebulised into the spray chamber via concentric^{5,6} and V-groove modified nebulizers having two^{7,8} or three⁹ solution channels. Systems with two tandem⁴, or opposed¹⁰ nebulizers were also developed. Other devices included modified chamber¹¹⁻¹⁴, Huang *et al.*¹¹ developed a nebulizer hydride generator system in which large droplets of the acid sample aerosol from the pneumatic nebulizer were trapped by the impact wall of a smoking-pipe shaped hydride generator, and reacted with reductant. The gas-aerosol mixture passed into an ICP for simultaneous determination of hydride and non-hydride forming elements. The LODs for the hydride-forming

elements could be improved over 20 times those obtained with the conventional nebulizer. The LODs of other elements remained unaffected. McLaughlin¹² and Wiltscche¹³ reported a multimode sample introduction system (MSIS[®]) in which a cyclonic spray chamber was modified by addition of two conical tubes located vertically in the centre of the spray chamber for introduction of the sample and sodium borohydride solutions. The MSIS[®] can be operated either as a vapour generator or conventional spray chamber, separately or simultaneously, while retaining the sensitivity and LODs of both modes of sample introduction. Finally, Maldonado *et al.*¹⁴ reported a dual nebulizer sample introduction system in which two micronebulizers were coupled to a modified a cyclonic spray chamber.

Several studies have been reported that plasma characteristics of the argon ICP were affected by both water and hydrogen introduction¹⁵⁻²⁶. Alder *et al.*¹⁵ and Caughlin and Blades¹⁶ reported a significant reduction in electron number density (*ne*) when water from the aerosol gas was removed. Tang and Trassy¹⁷ demonstrated that the hydrogen from water has a predominant influence in the thermal exchange processes between the plasma and the sample. Long and Browner¹⁸ found that water loading have a major influence on *ne* and ionization temperature (*Te*). Novotny *et al.*¹⁹ and Grotti *et al.*²⁰ reported that in robust conditions, an improvement of electron number density and excitation temperature were obtained by the effect of water loading. In contrast, under non-robust conditions, the plasma was highly sensitive to water loading and a degradation of plasma characteristics was observed. Under these conditions, desolvation led to an improvement in the plasma conditions. These results were confirmed by Mason *et al.*²¹ who reported that the same behaviour.

Several studies²²⁻²⁶ on liquids sample introduction have demonstrated that plasma excitation characteristics can be affected by the presence of hydrogen, even small amounts produce an increase on excitation temperatures and electron number density²²⁻²⁵. The enhancement was attributed to the higher thermal conductivities of hydrogen as compared with argon, since the higher thermal conductivity leads to an improvement on the energy transfer from the ring plasma towards the injected aerosol²³. Moreover, hydrogen generated improved signal-to-background ratio and LODs of several elements due to the increased in signal intensity and plasma stability²⁶. Walters and Barnardt²² reported that controlled desolvation and careful addition of hydrogen may increase the electron density and ionization temperature in the ICP source.

In dual-mode sample introduction systems, volatile hydride and other gaseous products from the NaBH₄ reaction (hydrogen, carbon dioxide and water vapour) as well as the sample aerosol are introduced simultaneously into the ICP source. Hydrogen gas from the HG reaction pass through the

central channel of the plasma and can have a similar effect when added as mixing gas. After reviewing the literature, few papers were found reporting an exhaustive diagnostic of the plasma characteristics with volatile hydride injection^{13,20,27,28}. Batistoni *et al.*²⁷ evaluated the intensity of the line as the background as well as electron number density by HG-ICPOES. They reported an enhancement of 52% on electron number density in the ICP discharge when NaBH₄ is used as reductant agent in the traditional hydride generation for the As analysis. Grotti *et al.*²⁰ reported that the hydrogen formed during the hydride generation process significantly improved the plasma excitation properties. They also reported that these ones were affected by the reductant concentration and the carrier gas flow rate. Wiltscche *et al.*¹³ concluded that the presence of hydrogen formed in the hydride generation process has a positive effect. It increases plasma energy, slightly increases plasma temperature and therefore increases ionization efficiency of hydride and nonhydride forming elements. In a recent paper, Pohl *et al.*²⁸ reported that the excitation temperature and electron number density values were found to be similar for both hydride generation only or simultaneous hydride generation and pneumatic nebulization.

Normally, the efficiency of energy transfer in the plasma is measured by plasma robustness in ICP-OES^{29,30}. Under robust conditions, no significant variation in the analyte signal intensities is observed when the matrix or reagent composition change. The intensity of the Mg II 280.270/Mg I 285.213 nm ratio is commonly used to estimate plasma robustness, where high ratios indicate a more robust plasma³¹. Rojas *et al.*⁸ using a dual direct hydride generation nebulizer (DHGN) system, which consisted of a modified V-groove type nebulizer with two solution channels coupled with conventional double-pass Scott spray chamber, reported that Mg II 280.270/Mg I ratio values were about 8 (robust conditions) at borohydride solution uptake rates between 0 to 1.3 mL min⁻¹. They demonstrated that hydrogen from reductant reaction did not significantly affect the plasma robustness. Zoltan *et al.*⁹ using a similar DHGN with three solution channels, reported similar Mg II 280.270/Mg I ratio values at optimized conditions. Gómez *et al.*¹⁰ using a dual sample introduction system consisting of two pneumatic nebulizers connected to the conventional spray chamber also reported that gases generated in the hydride reaction did not significantly affect the plasma discharge.

The viability of simultaneous determination of both hydride and non-hydride-forming elements using one same introduction system has been reported and applied at different sample matrices⁴⁻¹⁴. However, the effect of reduction reaction conditions on the plasma excitation characteristics has not been sufficiently studied. In this sense, this work is aimed to study the influence of parameters associated with the hydrogen generation reaction and the water loading, which

affect directly the plasma excitation characteristic. Optimization of a dual direct hydride generation nebulizer (DHGN) system was previously reported^{7,8}. Basically, the DHGN is a modified V-groove Babington-type nebulizer with two solution-input channels. These channels were used for delivering the reductant and sample solution. The hydride generation reaction is performed by contact between the aerosol from the sample and reductant solution therefore, the HG reaction occurs. In this study, the effect of the acid concentration and the reductant flow rate on the excitation temperature, electron number density and magnesium ionic to atomic line intensity ratio were evaluated and discussed.

Experimental

Instrumentation and operating conditions

Measurements were carried out using a radially-viewed Ar ICP-OES instrument Jobin-Yvon (Longjumeau, France) JY-24 operating at 40 MHz and 1.3 kW. Injector's id was 2.5 mm. A Brooks (USA) 5850E Mass flow controllers replaced the original gas flow meter for the aerosol carrier. The sample introduction system was a laboratory-built continuous direct hydride generator nebulizer (DHGN), described earlier,^{7,8} coupled with a conventional double pass Scott-type spray chamber. It consists of a V-groove Babington-type nebulizer with a 70 mm gas orifice and two solution input channels with 0.25 mm orifices. A 70 μm gas orifice nebulizer exhibits a better detection limit than the 120 μm nebulizer.⁷ The input channels were used for the delivery of the borohydride solution and sample solution, respectively. The acidified samples and the reductant solution were simultaneously pumped into the hydride-generation system. In the region of convergence of the two solutions and the carrier gas, the aerosol of both sample and sodium borohydride react to produce the hydride. The sample and sodium borohydride solution were delivered to the DHGN using a Gilson (France)

Minuplus 3 peristaltic pump. The H_{β} 486.133 nm line profile was performed using the EZChrom Chromatography Data System version 6.8 Scientific Software, Inc. (USA). The instrument characteristic and operating conditions are listed in Table 1.

Measurement of Fundamental Parameters

Temperature measurements: The linear Boltzmann plot method was used to measure the excitation temperature³² with a set of nine Fe I lines (table 2). For this, a Fe solution containing 50 $\mu\text{g mL}^{-1}$ was used. The error of the slope of the Boltzmann plot was in the range from 200 to 300 K.

Electron number density: The electron number density was determined from Stark broadening of the 486.133 nm (H_{β} line) using Griem's approximation describe in ref. 32.

Ionic-to- atomic line intensity ratio: The intensity of the Mg II 280.270 nm line to the Mg I 285.213 nm line was measured verify the plasma conditions³¹

Results and Discussion

Volatile hydrides and other gaseous products from the NaBH_4 reaction (hydrogen, carbon dioxide and water vapour) as well as sample aerosol were introduced simultaneously into the plasma source using the dual direct hydride generation nebulizer (DHGN) system, previously reported^{7,8}.

Several studies¹⁶⁻²⁶ on liquid samples introduction have demonstrated that excitation characteristics of the plasma can be affected by the introduction of low amounts of hydrogen. In this regard, the plasma characteristics using the dual mode sample introduction system, was studied. The influence of the reductant solution flow rate and sample acid concentration on the plasma excitation conditions, such as excitation temperature, electron number density and MgII/MgI line intensity ratio were studied.

Table 1: Optimal working conditions for ICP-OES system

ICP-OES parameters	
Generator	40.68 MHz, free-running
Optical mount	Czerny – Turner
Grating line number / mm^{-1}	3600
Focal length / m	0.64
Detector	PMT IP28 type
Plasma gas flow rate / L min^{-1}	18
Carrier gas flow rate / L min^{-1}	0.5
Observation height / mm (above load coil)	15
Hydride Generator	
Sample uptake rate / mL min^{-1}	0.75
Sample solution acidity / mol L^{-1}	Variable
NaBH_4 concentration (in 0.05% m/v NaOH) / % m/v	0.3
NaBH_4 solution flow rate / mL min^{-1}	variable
Working wavelengths / nm	Mg (I) 285.213, Mg (II) 280.270, As (I) 196.03

Table 2: Emission line data employed for evaluation of excitation temperature via the linear Boltzmann plot method³².

λ (nm)	E (cm ⁻¹)	G	A (10 ⁸ s ⁻¹)
371,9930	26875	11	0,1620
372,2560	27560	5	0,0497
372,7620	34547	5	0,2250
373,3320	27666	3	0,0620
373,8470	33695	11	0,9020
373,7190	27167	9	0,1420
374,8270	27560	5	0,0915
374,9490	34040	9	0,7640
375,8230	34329	7	0,6340

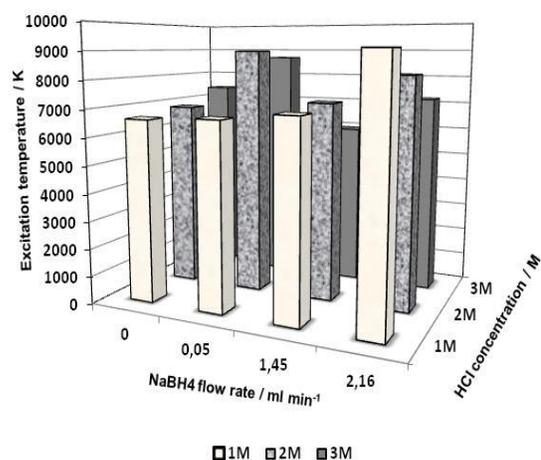
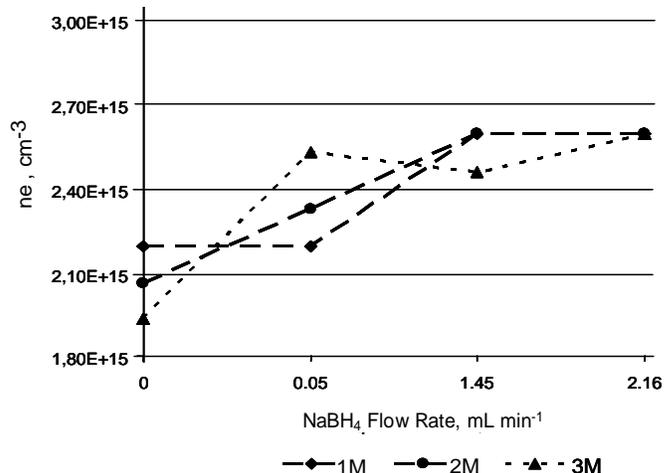
Excitation Temperature

It has been reported^{19,22-25} that the effect of hydrogen, even in small amount, led to an improvement in plasma excitation characteristics, as well as a temperature increase. Figure 1 shows the combined effect of NaBH₄ flow rate and acid concentration on the excitation temperature. It can be observed that the excitation temperature increased significantly when the system was operated in the dual mode, even at very low reductant flow rate (0.05 mL min⁻¹). It is evident, that the increase in the excitation temperature is associated to the hydrogen produced during the chemical vapour generation. These results agree with those reported by several researchers for conventional nebulization^{19,22-25}, which state that the presence of hydrogen results in a temperature increase along the central channel when hydrogen is introduced as a premixed or a sheathing gas in the nebulizer. In general, temperature enhancements found are about 1000K and 2000K (Figure 1). It is observed from this figure that excitation temperature values are affected by NaBH₄ flow rate and HCl concentration. At low NaBH₄ flow rate (0.05 mL min⁻¹) excitation temperatures increased when increased HCl concentration. In contrast, at 2.16 mL min⁻¹, excitation temperature decreased when increased HCl concentration. This result can be explained by the excessive amount of hydrogen produced. Important variations in the excitation temperatures were not found when changed sample acid concentrations (at the nebulization mode (without NaBH₄)). These results are in agreement with those results reported by Fernández *et al.*³³, and Brenner *et al.*³⁴, and differ from those obtained by others like Chudinov³⁵ and Yoshimura.³⁶

Electron number density

Figure 2 shows the combined effect of the NaBH₄ flow rate and acid concentration on the electron number density. It can be seen that the electron number density decreases slightly with HCl concentration in the nebulization mode (without NaBH₄). By other hand, Fernández *et al.*³³ (Meinhard

nebulizer) reported that under robust plasma conditions, the electron number density remains unchanged with the acid concentration, whereas under non-robust plasma conditions, it significantly decreased at 1M HCl, by then, no variation was observed at 2M HCl.

**Figure 1:** Effect of the reductant flow rate and sample acid concentration on excitation temperature**Figure 2:** Effect of NaBH₄ flow rate and sample acid concentration on electron number density

The electron number density increased significantly with NaBH_4 flow rate in the dual mode (with NaBH_4), and the same maximum value was observed at each acid concentration studied. From these results, it stands out that the hydrogen generated during the HG reaction compensates the depressing effect of acid concentration on the electron number density when the nebulizer operates without NaBH_4 . Murillo *et al.*²⁵ reported similar results, when hydrogen gas was introduced as a sheathing gas at the exit of the spray chamber by using conventional nebulization. Batistoni²⁷ and Grotti²⁰ have also reported an increase in the electron number density when working with conventional hydride generation techniques (“dry” plasma) with respect to standard nebulization.

The ne values found are in the same order of magnitude reported by Batistoni²⁷ ($1.57 \pm 0.22 \times 10^{15} \text{ cm}^{-3}$), and Grotti²⁰ (63, 159 and $225 \times 10^{19} \text{ m}^{-3}$, under non-robust, intermediate and robust conditions, respectively). When the sample is introduced via hydride generation, the hydrogen formed in situ, during the vapour generation reaction, produces the same effect on the plasma characteristics, as the hydrogen addition via nebulizer gas²²⁻²⁵.

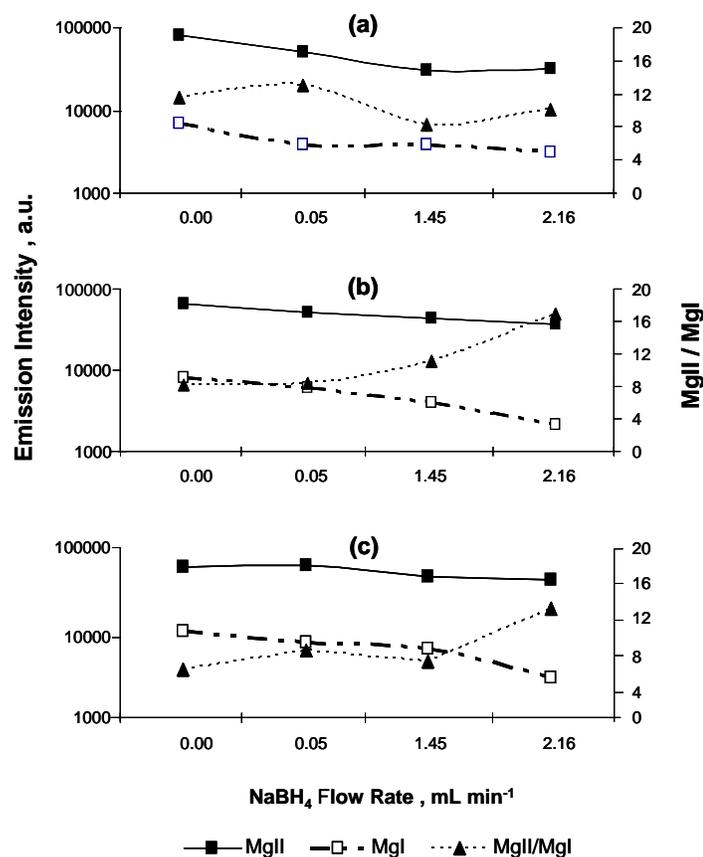


Figure 3: Effect of the NaBH_4 solution flow rate and acid concentration sample on the MgII/MgI ratio. a) 1M HCl b) 2M HCl c) 3M HCl

Ionic to atomic line intensity ratio

The MgII(280.270 nm)/MgI(285.213 nm) ionic to atomic line intensity ratio is usually used to monitor plasma robustness^{29,31-33}. Figures 3(a)-(c) show the effect of the NaBH_4 solution flow rate and acid concentrations on Mg (II) 280.270 nm, Mg (I) 285.213 nm line signal intensities and MgII/MgI line intensity ratio. In general, it was observed that the intensity of both lines, II and I, decreases when increased the NaBH_4 flow rate. However, line I is the more affected than line II, probably due to the fact that hydrogen improves energy transfer, and hence favors as well the excitation-ionization of line II²³.

Figure 4 exhibits the combined effect of reductant flow rate and acid concentration, on the MgII/MgI ratio. It is observed that the MgII/MgI ratio increases as the reductant flow rate increases at high HCl concentration (2 and 3 M HCl). However, at low acid concentration, the robustness decreases as the reductant flow rate increases. These results disagree with those results obtained by Grotti *et al.*²⁰, who observed no relevant changes in plasma excitation conditions with the systematic variation of HCl concentration from 0.1 to 6 M, in conventional hydride generation techniques (“dry” plasma). Also, in our previous work with a 27 MHz Ar ICP instrument operated with a similar dual system having 120 μm gas orifice⁸, it was found that MgII/MgI ratio remains practically constant between 0 to 1.3 mL min⁻¹ NaBH_4 flow rate.

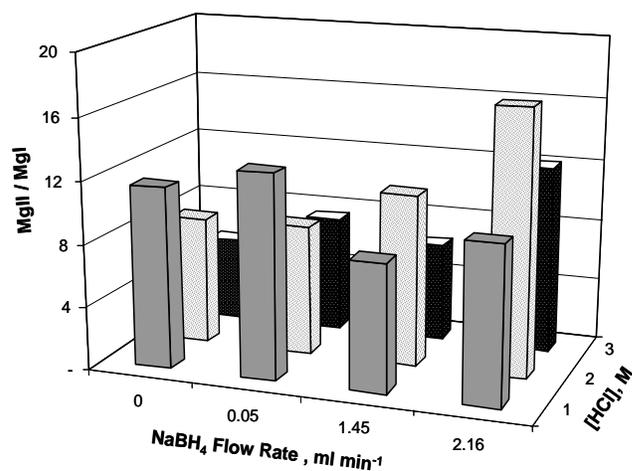


Figure 4: Combined effect of NaBH_4 flow rate and HCl concentration on MgII/MgI ratio

The majority of MgII/MgI ratio values are higher than 8 (Figure 4), indicating that it worked under robust condition. However, it was observed significant changes in plasma excitation conditions that revealed a complex effect of hydrogen and water vapor on ICP properties combined with the effect of aerosol generation and transport to the plasma.

Also, it can be observed in figure 4 a depressive acid effect on the MgII/MgI ratio in nebulization mode (without NaBH_4), passing from robust conditions (Mg ratio 12 at 1M HCl) to

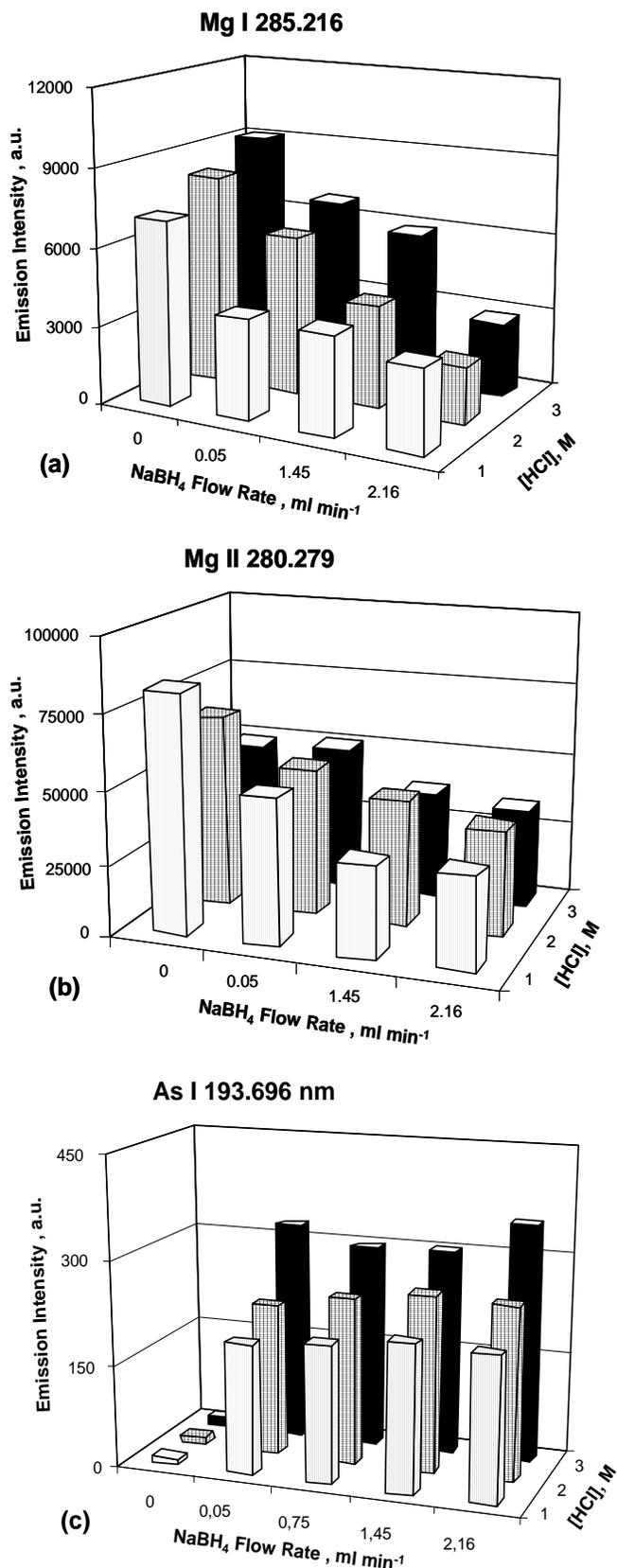


Figure 5: Combined effect of NaBH₄ flow rate and HCl concentration on a) MgI, b) MgII and c) AsI intensity emission signal

non-robust (Mg ratio 5 at 3M HCl). These findings disagree with those results obtained by Fernández *et al.*³³, working at similar experimental conditions, except the type of nebulizer used (Meinhard versus V-groove Babington-type nebulizers). Significant differences between Meinhard and V-groove nebulizers have been reported by Borkowska-Burnecka *et al.*³⁹ A decrease in analytical signals, solvent transport rates (38 to 19 a.u. respectively) and transport efficiencies (3.5 to 1.7 % respectively) have been reported. On the other hand, differences in the MgII/MgI ratio obtained in this work, using nebulization mode, compared to those reported by other authors could be the result of aerosol quality⁴⁰.

Effects of the reaction conditions on the emission intensity

Figure 5 a to c show the effect of the NaBH₄ flow rate and sample acid concentration on the MgI, MgII and AsI signal intensities, respectively. A different behaviour between both atomic lines can be recognized. Significant changes in emission intensity of the MgI (Figure 5a) and MgII (Figure 5b) lines were observed and they are associated with the NaBH₄ flow rate and the acid concentration, Nevertheless, the emission intensity of AsI increased with acid concentration and remained practically invariant within the NaBH₄ flow rate range studied (Figure 5c).

During the nebulization mode (absence of NaBH₄), the signal intensity of MgI (Figure 5a) decreases, while MgII signal increases (Figure 5b) as the HCl concentration increases.

During the dual mode operation, the emission intensities of MgI line and MgII line decrease with the NaBH₄ flow rate. The atomic line intensities increase (Figure 5a) as the HCl concentration increases while ionic line signal (Figure 5b) remains practically invariant within the acid concentration range studied.

On the other hand, the increase of the arsenic emission intensity as the acid concentration increases, observed in this work (Figure 5c) was also reported for other authors, working with conventional hydride generation techniques^{41,42}.

Conclusions

The hydrogen generated during the NaBH₄ hydrolysis reaction has an important role on excitation conditions of the plasma. Results indicate that the plasma excitation conditions when using the dual-mode are better than those obtained when using standard nebulization or conventional hydride generation techniques. Similarly, excitation temperature and electron number density in the plasma increased significantly when the system is operated in the dual mode, even at very low NaBH₄ flow rate.

The improvement on the plasma excitation characteristics could benefit both atomisation-excitation processes when non-forming hydride elements are determined. For the

hydride-forming elements such as arsenic, the higher signal emission intensity was obtained at the highest acid concentration.

In summary, that the plasma operating parameters should be carefully optimized to get obtain good sensitivity and precision when simultaneous determination of hydride and non-hydride forming elements is performed in the Ar radially viewed ICP OES.

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