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Comparison of matrix effects in inductively coupled plasma using laser ablation and solution nebulization for dry and wet plasma conditions

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Abstract

Matrix effects of calcium in inductively coupled plasma-atomic emission spectrometry were investigated. Matrix effects were studied by monitoring the excitation conditions of the plasma using Zn ionic to atomic spectral line intensity ratios. Dry and wet inductively coupled plasmas with robust and non-robust conditions were compared. Laser ablation and solution nebulization sample introduction were used to produce the dry and wet plasma conditions, respectively. Low (0.6 L/min) and high (1.0 L/min) carrier gas flow rates were used to produce the robust and non-robust conditions, respectively. No differences in the trend of matrix effects for dry and wet plasmas were observed at vertical positions above normal observation height (> 8 mm height above load coil) for low and high carrier gas flow rates. However, matrix effects in the lower part of the plasma (< 8 mm height above load coil) were significantly different between dry and wet plasmas when a high carrier gas flow was used. The differences are likely due to the desolvation process.

Keywords:

Matrix effects; ICP; water loading; laser ablation; plasma diagnostics.

1. Introduction

Plasma-related non-spectroscopic matrix effects from easily ionizable elements (such as K, Na) and other matrices (such as HNO₃, H₂SO₄) cause analyte signal suppression or enhancement in inductively coupled plasma-atomic emission spectrometry (ICP-AES) [1-12]. Matrix effects remain an important yet not fully understood phenomenon in plasma emission spectrometry [12-15]. Different mechanisms have been proposed for the plasma-related non-spectroscopic matrix interferences in ICP-AES including increased collisional excitation [1-5], ambipolar diffusion [1], shift in analyte-ionization equilibrium [1-3], ion-electron recombination [5-7], lateral diffusion [2-3, 8-9], change in energy distribution of species that collide with and excite the analyte [10] and change in excitation conditions of the plasma [11]. So far there is no agreement on the dominant mechanism [12-15]. A possible reason for the lack of a general theory on matrix effects is that most of the reports on matrix effects in ICP-AES used direct solution nebulization or solution nebulization followed by desolvation [1-11]. The aerosol is not completely dry even with desolvation, and water remains a major component among the injected species [16]. Matrix interference may be partially influenced by the processes of water vaporization, dissociation, and ionization. Matrix effects may be more easily observed and studied if a solid sample introduction technique is used [16].

In a recent paper, we reported matrix effects in ICP-AES using laser ablation sampling [17]. Calcium, strontium, lithium, sodium, potassium, magnesium and aluminum matrices were investigated as to their effect on plasma conditions (temperature and electron number density). The effects on plasma conditions were found to be matrix-element specific instead of a mass-

loading effect. Calcium, strontium and magnesium were found to have a more pronounced matrix effect than the easily ionizable elements. The same matrix effects were observed over the entire vertical profile, from 0 to 20 mm height above the load coil (HALC) [17] in contrast to reports in the literature. Blades and Horlick [1] studied ICP excitation conditions by measuring the ionic to atomic line intensity ratios of Ca, Mg and Cd using solution nebulization with and without a Na matrix. For these three elements, an enhancement in the ionic to atomic line intensity ratio by the Na matrix was found at low vertical positions in the plasma; a depression in the intensity ratio was measured at higher positions in the plasma. A cross over point (i.e., at a particular position, there was “no matrix effect”) in the vertical profile from enhancement to depression was reported for these and other easily ionizable elements (EIE) [3, 5, 18-20].

The absence of a cross over point in the vertical profile in our previous study using laser ablation sampling does not necessarily indicate a different matrix effect for laser ablation sampling versus solution nebulization. Most of the matrix effects studies in the literature were based on solution sample introduction [1-11, 18-20], in which the central channel gas flow rate was typically 1 L/min. The flow rate used in our previous study using laser ablation sampling was 0.4 L/min. Therefore, it is possible that with a low central-channel gas flow rate, the vertical emission profile shifts downward and the cross over point (if any) shifts to a position below the measurement region [2]. On the other hand, it is possible that the differences arise from operating a dry plasma versus a wet plasma. Water can have a drastic effect on ICP excitation conditions [16, 21-28]. Mermet *et. al.* studied the plasma conditions for sample introduction using solution nebulization, solution nebulization followed by desolvation, and laser ablation. They found different plasma conditions for the three cases [16]. In addition, they found that

tolerance to water loading was highly dependent on the ICP operating conditions, in particular the carrier gas flow rate [16].

The objective of this study was to compare calcium matrix effects in “dry” and “wet” plasmas. Calcium was chosen because it showed significant matrix effects for both laser ablation sampling [17] and solution nebulization [11, 29-31]. Dry plasma is referred to the conditions when laser ablation sampling is used (i.e., no water introduced to the plasma). Wet plasma is referred to the conditions when a pneumatic nebulizer is used to introduce water aerosols. The matrix and monitor elements were introduced to the plasma by laser ablation, regardless of whether dry or wet plasma conditions were under study. The function of the nebulizer was only to introduce water aerosol to establish wet plasma conditions. Matrix effects in a wet plasma with different water loading were also studied by varying the carrier gas flow rates, and keeping a constant water aerosol introduction rate into the ICP.

Temperature and electron number density are two important characteristics of the plasma [32], which can be influenced by the matrix. Temperature and electron number density changes can be measured from changes in the ionic to atomic spectral emission intensity ratio of an element [33]. In this work, Zn was chosen as a monitor element of the plasma condition due to its high first ionization potential. The spectroscopic data (wavelength, energy levels, statistical weight, and Einstein transition probability) for the Zn emission lines used in this study are listed in Table 1 [34-35].

2. Experimental

2.1 *Experimental set-up*

The matrix and the monitor elements were both introduced into the ICP by laser ablation. The experimental system previously used [17] was modified to include a concentric nebulizer and spray chamber for water introduction. The exit port of the spray chamber was connected to the exit port of two ablation chambers (connected in series) via a T-joint, before entering the central channel of the ICP torch. A schematic diagram of the system is shown in Fig. 1. Wet plasma conditions were achieved by nebulizing deionized water. To obtain dry plasma conditions, the nebulizer inlet was not dipped into a solution, but sealed with Paraffin™ film to avoid air from entering the nebulizer. The function of the nebulizer was only to introduce water aerosol when wet plasma conditions were needed. Direct comparison of matrix effects is possible using this set-up.

For a particular total central channel flow rate, the flow rate through the three chambers was constant for both wet and dry plasmas. The identical flow rate ensures similar transport efficiency for the laser ablated matrix. The mass flux of material introduced is approximately constant and the degree of matrix effects obtained under wet and dry plasma condition can be compared directly. Secondly, the particle size distribution is kept constant for the dry and wet plasma experiments because the matrix and the monitor element were introduced using laser ablation in both cases. The particle size distribution for laser ablation sampling and solution nebulization may be different. For nebulization, the analyte dries from liquid droplets to form small particles in the plasma; for laser ablation sampling, larger dry particles are directly

introduced into the ICP [36-38]. Even if the water content in the carrier gas stream is kept constant, the atomization and excitation characteristics can be different for the nebulized solution sample versus laser ablated particles [38] due to size differences in dried aerosol versus laser-ablated particles [39]. Using the ablation chambers - nebulizer/spray chamber system of Fig. 1, differences in matrix effects for dry and wet plasmas arising from different particle sizes should be eliminated.

2.2 *Inductively coupled plasma*

The ICP was a Plasma Therm 20P operated with a forward power of 1250 W (reflected power \approx 0-2 W). All gas flow rates were regulated using Matheson mass flow controllers (Model 8274). The argon outer and intermediate gas flow rates were 14 and 1 L/min, respectively. Argon flowed through the ablation chambers at 0.2 to 0.6 L/min and through the nebulizer at 0.4 L/min. The total carrier gas flow was 0.6 to 1.0 L/min. The nebulizer gas flow was fixed to obtain a constant uptake and nebulization rate of water. Due to the relatively short distance from the T-joint to the bottom of the ICP torch (\sim 15 cm), it is assumed that the transport efficiency and the water mass flux into the ICP are constant for different total carrier gas flow rate. Different gas flow rates through the ablation chambers will affect the amount of monitor element and matrix introduced into the plasma. However, the trend of matrix effects should be the same [17].

2.3 *Laser ablation*

Two lasers were used for ablation: a Nd:YAG laser (New Wave Research, MiniLase II-30) with a pulse duration of 6 ns was used at a low irradiance (~ 1.7 mJ/pulse, laser power density $\sim 10^8$ Wcm $^{-2}$) to ablate the monitor element (Zn). Another Nd:YAG laser (Infinity, Model 40-100) was used to ablate the matrix at a higher irradiance ($\sim 10^{11}$ Wcm $^{-2}$). Both lasers were operated at 266 nm wavelength and 10 Hz laser repetition rate. Pellets of calcium carbonate powder (analytical reagent, Aldich) were formed under high pressure (about 9 ton/cm 2) and were used as the matrix target. Zinc metal (Goodfellow Corporation, 99.95%) was used as the monitor element target. Iron metal (Goodfellow Corporation, 99.999%) was ablated to measure the excitation temperature of the plasma.

2.4 *Experimental procedures*

The ICP emission intensity of Zn was measured after 600 pre-ablation laser pulses without any matrix ablation. The initial value of the Zn ionic to atomic line intensity ratio in the absence of matrix was calculated. Ablation of Zn continued while the matrix sample (CaCO $_3$) was then ablated. According to a previous study, the mole ratio of Ca to Zn ranged approximately from 10^3 to 10^4 times [17]. The ICP emission intensity of Zn was measured continuously. The Zn ionic to atomic line intensity ratio during the ablation of matrix was compared to the initial value and represents any change in plasma conditions by the matrix. Finally, matrix ablation was stopped while the monitor element ablation continued. The Zn line intensity ratio continued to be measured to check for drift in plasma conditions during the course of the experiment.

The possibility of self-absorption on the spectral lines and the influence of different amounts of ablated monitor element during repetitive laser ablation sampling were checked using a method described previously [17]. The Zn ionic to atomic line intensity ratio was constant and independent of the ablated mass for the experimental conditions used in this study. Changes in intensity ratios in subsequent experiments are due to changes in plasma conditions by the matrix.

3. Results and Discussion

3.1 Excitation temperature and electron number density under dry and wet plasma conditions

The tolerance of the ICP to water loading is strongly dependent on the ICP operating conditions, in particular the carrier gas flow rate [16]. The carrier gas flow rates for relatively high and low tolerance to water loading was first determined, and then matrix effects in wet plasmas with different water tolerance was studied.

When the plasma is highly tolerant to water loading, the temperature and electron number density between dry and wet plasmas should be similar. Excitation temperature and electron number density of the plasma were measured using the line pair intensity ratio of Fe and ionic to atomic line intensity ratio of Zn (Saha method), respectively. FeI 381.584nm and FeI 385.991nm were chosen for the line pair intensity ratio method because of the large difference in the upper energy levels (Table 1).

Fig. 2 and 3 show the excitation temperature and electron number density, respectively, for dry and wet plasmas at different central channel gas flow rates. The ranges of temperature and electron number density agree with those reported in the literature using similar measurement techniques [32]. However, the measured electron number density (Fig. 3) is significantly lower than those reported in the literature using the Stark width of the H_{β} line [40]. The disagreement between the Saha method and the Stark width of H_{β} line for electron number density measurements has been reported in the literature [32, 40]. The disagreement may be due to the questionable LTE assumption when the Saha method is used [32], especially for wet plasma conditions with high carrier gas flow rates. Nevertheless, the objective of measuring the temperature and electron number density in this study is to understand whether the plasma is strongly tolerant to water loading. Therefore, a relative indication of the temperature and electron number density is sufficient.

The temperature and electron number density are similar for dry and wet plasmas only at a flow rate of 0.6 L/min; they are also the largest at this flow rate. The temperature and electron number density decreased when the gas flow rate increased from 0.6 to 1.0 L/min, for both dry and wet plasmas. At flow rates > 0.6 L/min, the temperature and electron number density were greater for the dry versus the wet plasma. The plasma appears to have a strong tolerance to solvent loading at carrier gas flow of 0.6 L/min, and the tolerance decreased at higher carrier gas flows. This measurement is consistent with that of Mermet and co-workers who reported that temperature and $MgII/MgI$ intensity ratio decreased at all vertical positions when the central channel flow rate increased, for both high (1600W) and low (800W) ICP forward power [16]. They also reported that under robust plasma conditions (high power and low carrier gas flow rate), the

plasma had a high tolerance to water loading, and desolvation had almost no effect on the plasma conditions [16]. Because the plasma conditions are similar for dry and wet plasmas at the carrier gas flow rate of 0.6 L/min but significantly different at 1.0 L/min, these two flow rates will be studied separately for matrix effects.

3.2 *Comparison of matrix effect for dry and wet plasma at 1.0 L/min carrier gas flow rate*

Fig. 4 shows the ZnII/ZnI intensity ratio for dry and wet plasmas with and without the ablation of calcium carbonate, using a total carrier gas flow of 1.0 L/min. The flow rates through the ablation chambers and the nebulizer were 0.6 and 0.4 L/min., respectively. The plasma conditions were different for the dry and wet plasmas, even in the absence of matrix. The ZnII/ZnI intensity ratio decreased with increasing height in the plasma for both plasma conditions; the ratio for the dry plasma was always higher than the wet plasma, indicating the dry plasma was more robust.

Fig. 5 shows the change in the ZnII/ZnI intensity ratio in the presence of a calcium matrix; the effect of Ca matrix is different for the dry and wet plasmas. For the dry plasma, the ZnII/ZnI intensity ratio was decreased over the entire vertical profile. For the wet plasma, the change in ZnII/ZnI intensity ratio was more complex; the ratio at the lower part of the plasma (from 1 to 4 mm HALC) increased in the presence of Ca matrix, while the ratio decreased for vertical positions above 6 mm HALC. At 5 to 6 mm HALC, there was no change in ZnII/ZnI intensity ratio and a cross-over point was observed. The cross over point was only observed for the wet plasma.

Fig. 6a and 6b show the normalized intensity profiles (normalized to the peak intensity) of ZnI 213.857nm and ZnII 206.200nm, respectively. In the absence of a matrix, the difference between the normalized emission profiles for the dry and wet plasmas is large; the normalized Zn intensity has a maximum closer to the load coil and drops faster versus HALC for the dry plasma. The earlier peak maximum position in the vertical profile of the dry plasma indicates that vaporization and/or excitation of Zn (and possibly the matrix) starts earlier in the dry plasma. It must be emphasized that the difference in vertical profile of the Zn emission is not due to differences in particle size distribution of the Zn aerosol, because both studies used laser ablation to generate the aerosol. The earlier appearance of the Zn peak is probably because desolvation was not required for the dry plasma. By comparing the vertical profiles of various atomic and ionic emission lines using electrothermal vaporization and solution nebulization, Long and Browner concluded that when the sample was introduced as a wet aerosol, the onset of excitation was delayed and the position for peak emission was shifted upward [23]. In addition, incompletely desolvated droplets can extensively cool a region of the plasma [41]. Incompletely desolvated water aerosol may locally cool the plasma and consume some energy that would otherwise be available for the vaporization and/or excitation of the matrix, leading to the earlier appearance of the peak Zn emission.

The presence of Ca matrix changes the normalized vertical profiles for the dry and wet plasmas. The matrix depressed the normalized intensity at vertical positions beyond the peak intensity for both dry and wet plasmas. The matrix slightly enhanced the normalized intensity for positions below the peak for the dry plasma; the enhancement at positions below the peak for the wet

plasma was more dramatic, especially for the ZnII line. An enhancement at positions low in the plasma by Ca matrix is widely reported in the literature using solution nebulization [1, 2, 5]. The same matrix effect was observed in this work for the wet plasma regardless of whether the monitor element and matrix were introduced as solution aerosols or dried particles.

3.3 *Comparison of matrix effect for dry and wet plasmas at 0.6 L/min carrier gas flow rate*

Fig. 7 shows the ZnII/ZnI intensity ratio at different vertical positions in the dry and wet plasmas, with and without the ablation of calcium carbonate matrix, for a total carrier gas flow rate of 0.6 L/min. The flow rate was decreased from 1.0 L/min to 0.6 L/min by decreasing the ablation chamber gas flow from 0.6 L/min to 0.2 L/min, while the nebulizer gas flow was maintained at 0.4 L/min (i.e., constant injection rate of water into the ICP).

In the absence of matrix, the ZnII/ZnI intensity ratio decreased monotonically with increasing height in the plasma, for both plasma conditions. Only at very low positions (2mm to 5mm), was the ZnII/ZnI intensity ratio of the wet plasma significantly different from the dry plasma. From 5mm to 20mm HALC, the ZnII/ZnI intensity ratio was the same within experimental error for both plasmas. The nearly identical vertical profiles indicate that the plasma is strongly tolerant to water at this flow rate. With the ablation of calcium carbonate matrix, the ZnII/ZnI intensity ratio showed a decrease in the entire vertical profile for both plasmas. Clearly, no cross-over point was observed for both cases.

Fig. 8a and 8b show the normalized intensity profile (normalized to the peak intensity) of ZnI 213.857nm and ZnII 206.200nm, respectively. Although the difference between the normalized emission profiles for the dry and wet plasmas is small, the normalized Zn intensity has a maximum closer to the load coil and drops faster versus HALC for the dry plasma. In addition, the matrix effect from Ca did not alter the vertical profiles of Zn emission in both dry and wet cases.

By comparison of Fig. 6 and 8, the normalized intensity profile for the dry plasma is similar while the profile for the wet plasma is significantly different. In both cases, the emission intensity was highest low in the dry plasma. The peak emission intensity was strongly flow rate dependent for the wet plasma; the vertical profile for the dry plasma was insensitive to change in gas flow rate whereas the profile for the wet plasma was highly sensitive to change in gas flow. Similar behavior was previously reported [28] when vertical emission profiles for spark-generated and solution nebulized sample introduction techniques were compared. Also, the Ca matrix effect did not change the vertical profile for either plasma at the low flow rate (0.6 L/min.) whereas the vertical profile was changed significantly by the Ca matrix when a higher flow rate was use (1.0 L/min.). A possible reason may be related to the robustness of the plasma; the robustness decreased and the plasma became less tolerant to matrix when a high gas flow was used.

3.4 Discussion on possible mechanisms for the existence of cross over point

For the wet plasma at 1.0 L/min carrier gas flow rate, a cross over point exists between the curves of the Zn ionic to atomic line intensity ratio obtained in the absence and presence of

calcium carbonate matrix. However, no cross over point was observed for the wet plasma at 0.6 L/min or the dry plasma at both high and low flow rates. The existence and position of the cross over point implies that two different interference mechanisms with opposing effects are operative in the ICP at different vertical positions.

The enhancement of ionic to atomic line intensity ratio below the cross over point is believed to be related to increased collision excitation efficiency due to additional electrons from ionization of the matrix [1, 3, 5]. The absence of a cross over point in the dry plasma implies that the desolvation process may be a significant factor in defining matrix effects. The position of the cross-over point may be related to the tolerance of the ICP to water loading. It has been shown that the decrease in ZnII/ZnI ratio due to Ca matrix high in the plasma is relatively independent of plasma temperature [17], as shown by the constant decrease in ZnII/ZnI ratio along the vertical profile for the dry plasmas. If the negative effect is assumed to be constant along the vertical profile of the ICP, the position where the measured matrix effect became constant can be regarded as the position where the effect from increased collisional excitation efficiency ceased. From Fig. 5, it was found that the ZnII/ZnI ratio decreased to a constant value when the HALC was > 9mm. This position showed some correlation with the temperature and electron number density of the ICP (Fig. 2 and 3); both temperature and electron number density start to increase above 9mm HALC for the wet plasma with 1.0 L/min flow. The enhancement effect was only observed when the temperature and electron number density were relatively low.

There are two possible mechanisms in which the desolvation process can determine the extent of opposing matrix effects. Firstly, the electrons from Ca ions have significant contribution to the

total electron number density at lower temperature. The first ionization potential of Ca is low (6.113eV [42]). Based on an LTE model [43], over 99% of the Ca exists as Ca^+ for plasma temperature from 3000K to 6500K. The number of electrons produced by the Ca matrix is roughly similar to that from ionization of Ar if the temperature of the plasma is low. For this study, the estimated mass removal rate of CaCO_3 ranged from $1\mu\text{g}$ to $100\mu\text{g}$ per laser pulse [44]. Assuming 10% transport efficiency [44], the estimated mass introduction rate of the Ca matrix ranged from $1\mu\text{g}$ to $100\mu\text{g}$ (i.e., 10 to 1000 nano-moles) per second. Therefore, the electrons generated from the matrix should range from 10^{15} to 10^{17} electrons per second. With the carrier gas flow rate at 1 L/min and 4500 K gas temperature in the ICP, the volume of Ar gas is 250 cm^3 per second. Therefore, the electrons generated from the Ca matrix would contribute 10^{13} to 10^{15} electrons/ cm^3 to the electron number density in the plasma. In this estimation, it is assumed that all the Ca was atomized and remained in the central channel (such an assumption probably leads to an overestimation of the electron concentration from Ca ionization) [43]. Olesik found that the analyte number density was an order of magnitude lower than those measured in the literature [43]. Holclajter-Antunović and co-workers also calculated the number density of different species in the ICP using minimization of the Gibbs-free energy function [7]. Their calculation showed that in a plasma containing 1.5×10^{-6} relative concentration of Ca, the dominant ion was Ca^+ and was in comparison or even exceeded Ar^+ by orders of magnitude when the plasma temperature was below 4000K. Also, when $T > 7000\text{K}$, the ionization of argon was the exclusive process providing the overall electrons. Both calculations (LTE model and minimization of Gibbs free energy) showed that the contribution of electron number density from Ca matrix ionization was similar to that from ionization of Ar if the temperature of the plasma was low (i.e., low position in the plasma when high carrier gas flow and a wet plasma were used). The

electron number density from ionization of Ar can change by two orders of magnitude from low position in the plasma (~3 mm HALC) to its maximum point (Fig. 3). It is possible that at a certain position in the plasma, the increase in electron number density from ionization of argon become so significant that electrons from ionization of Ca matrix are negligible to the overall electron number density. As a result, the enhancement effect in the ZnII/ZnI ratio ceased.

Another possible reason for the cross-over point is that injecting water aerosol at high carrier gas flow decreases the temperature of the plasma (Fig. 2). When the injected water aerosol significantly cools the plasma, the matrix needs to travel a longer distance before it can be fully vaporized, atomized, and ionized to produce the electrons needed for an increased collisional-excitation mechanism. However, when the plasma is dry or the plasma is highly tolerant to water loading, atomization and ionization of the matrix may occur at a low position in the plasma (lower than the top of the load coil). As a result, the entire emission profile is shifted down and the cross over point may be below the observation region of the plasma.

The effects of calcium matrix at observation heights above the cross over point are more complicated. In addition to the interference mechanisms discussed in the literatures [1-9], interference from double-charged calcium ions may occur. The interference mechanism may involve interactions between double-charged calcium ions and argon species and is discussed elsewhere [45].

4. Conclusion

ICP conditions in the absence of matrix for dry and wet plasma were similar when the carrier gas flow rate was low (i.e., at 0.6 L/min). When the carrier gas flow rate was increased, differences between dry and wet plasma conditions became significant. For a wet plasma at 1.0 L/min carrier gas flow, Ca matrix increased the ionic to atomic spectral line intensity ratio of the monitor element (Zn) at low position in the plasma, but decreased the intensity ratio at higher HALC (i.e., a crossover point was observed). However, for dry plasmas with the same flow rate, there was a decrease in the ionic to atomic line intensity ratio for the entire vertical profile of the plasma. The crossover point may be related to the desolvation process or solvent loading in the plasma. Similar trends in matrix effects were observed above the normal observation height (> 8 mm HALC) for dry and wet plasmas. Therefore, it is possible to use laser ablation to study matrix interference mechanism in ICPs. The advantage of using laser ablation in studying matrix effects in the plasma is its feasibility to directly introduce the desired matrix into the plasma.

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Table 1. Spectral lines and spectroscopic data used in this study.

Element	λ (nm)	E_p (cm^{-1})	E_q (cm^{-1})	g_q	A_{pq} (s^{-1})	Ref
ZnII	206.200	0	48482	2	3.290×10^8	[34]
ZnI	213.857	0	46748	3	7.039×10^8	[34]
FeI	381.584	11976	38175	7	1.3×10^8	[35]
FeI	385.991	0	25900	9	9.7×10^6	[35]

Figure Captions

- Figure 1. Experimental set-up for studying matrix effects studies in dry and wet plasmas using laser ablation sample introduction technique.
- Figure 2. Excitation temperature of the plasma under dry and wet plasma conditions and different carrier gas flow rates.
- Figure 3. Electron number density of the plasma under dry and wet plasma conditions and different carrier gas flow rates.
- Figure 4. Emission line intensity ratio of ZnII 206.200nm to ZnI 213.857nm under dry and wet plasma conditions, in the absence and presence of CaCO₃ matrix. Carrier gas flow was 1.0 L/min.
- Figure 5. Change in ZnII/ZnI intensity ratio for dry and wet plasma conditions in the presence of CaCO₃ matrix. Carrier gas flow was 1.0 L/min.
- Figure 6. Normalized intensity of (a) ZnI 213.857nm and (b) ZnII 206.200nm in the absence and presence of CaCO₃ for dry and wet plasmas. Carrier gas flow was 1.0 L/min.
- Figure 7. Emission line intensity ratio of ZnII 206.200nm to ZnI 213.857nm under dry and wet plasma conditions, in the absence and presence of CaCO₃ matrix. Carrier gas flow was 0.6 L/min.
- Figure 8. Normalized intensity of (a) ZnI 213.857nm and (b) ZnII 206.200nm in the absence and presence of CaCO₃ for dry and wet plasmas. Carrier gas flow was 0.6 L/min.