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STUDY OF THE INTERFERENCE EFFECTS OF ALUMINIUM ON THE ATOM- AND ION-LINES OF ALKALINE EARTH METALS IN AQUEOUS SOLUTIONS USING AN ICP SPECTROMETER WITH AXIALLY VIEWED PLASMA

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The main advantage of inductively coupled plasma spectrometers with axially viewed plasma relative to the radially viewed plasma is the better detection power. The detection limits of the former are about 5–10 times lower than the latter. On the other hand, the axially viewed plasma has disadvantages. The most notable is the increased number of interference effects. In this paper, the study of the interference effects of aluminium on the atom- and ion-lines of alkaline earth metals are presented by examining different types of sample-introduction devices, such as a simple Meinhart-type concentric nebuliser, a V-groove nebuliser using a Sturman-Masters spray chamber, and an ultrasonic nebuliser.

Keywords: aluminium interference effects, ICP atom- and ion-lines, alkaline earth metals, sample-introduction device, axially viewed plasma

1. Introduction

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) is a widely used method for the elementary analysis of different types of material due to its advantageous features. The axial plasma view offers an increased detection power, which is important when the element of interest is present in trace levels. On the other hand, the emitted light is subjected to strong interferences as it reaches the entrance slit of the optical system of the spectrometer. Therefore, it is an important task to understand the origin and nature of the interference effects [1–3].

The interference may affect both the sample-introduction and excitation processes taking place in the plasma. In the first case, they may have different effects on the different types of sample-introduction devices, while they might affect the atom- and ion-lines of a given element in different ways [4].

ICP is commonly used for the analysis of liquid samples, where different types of nebulisers are the most frequently applied devices for sample-introduction. During nebulisation, the liquids to be analysed are dispersed into small droplets. The difference regarding the different nebulisers lies partially in different processes resulting in small liquid droplets and the nebulisation efficiency. These kinds of effects may be different when different nebulisers are applied, while they appear in the case of both radially and axially viewed plasma.

The spectral interferences are stronger and more frequent when an axially viewed ICP source is used. This is due to the light being emitted from the hot internal part of the plasma that has to travel a long way to reach the entrance slit of the optical system. On its way, the emitted light goes through layers of plasma at a lower temperature. This process may be subjected to strong self-absorption effects. Consequently, the intensity of the ion- and atom-lines of a given element may change. This change affects the relationship between the emitted line intensity and analyte concentration in the sample, and thus the calibration procedure.

The alkaline earth metals may be present from trace up to high concentration levels in different materials, such as surface and groundwater, different types of rocks and minerals, metal alloys, etc. In many cases, these materials may contain aluminium in high concentrations that contributes to the observation of interferences [2,3]. In the present work, we studied the effect of aluminium on the spectral lines of alkaline earth metals present in low-concentrations in aqueous solutions, as well as the influence of different sample-introduction devices.

2. Experimental

2.1. ICP Spectrometer

For the presented experiments, a Varian 720 ES spectrometer was used, which is an axially viewed, instrument with key parameters summarised in *Table 1.*

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Table 1. Characteristics of the ICP spectrometer used in the given study.

Plasma-view:	axial
The frequency and power of the RF generator:	40 MHz, 900–1500 W adjustable via software
The optical system employed:	Echelle build-up with a double monochromator
Detector used:	Two-dimension CCD
Wavelength range:	160 – 780 nm
Available sample-introduction systems:	Concentric (K-type) nebuliser, V-groove nebuliser, Ultrasonic nebuliser
Controlling software:	ICP Expert II (Microsoft Win XP OS)

Due to the layout of the optical system, many (even several hundred) spectral lines can be measured simultaneously, which makes the study of the interferences on several atom- and ion-lines of a given element possible. In the course of line selection, care was taken in choosing both more and less sensitive lines, where enough lines were available. The spectral lines examined in this study are summarised in *Table 2*.

2.2. The Sample-Introduction Devices

Three types of sample-introduction device were used in the given set of experiments: a concentric nebuliser, a V-groove nebuliser, and an ultrasonic nebuliser. The concentric nebuliser is the one that is used most commonly for the ICP-AES analysis of liquid samples. Its nebulisation efficiency is rather low, but it can be operated easily, and its maintenance demand is low. Generally, it is used in combination with a cyclone-type glass spray chamber.

The V-groove nebuliser eventually becomes a modified Babington-type nebuliser. It is used with a Sturman-Masters type spray chamber, which has a special plastic surface and is resistant to almost all chemicals including hydrogen fluoride. Its detection power is slightly less than that of the concentric nebuliser, but it has an excellent salt-enduring ability.

The CETAC 5000 type ultrasonic nebuliser boasts a detection power 10 times better than the former two devices. On the other hand, its operation is more difficult and it may be sensitive to higher matrix concentration levels.

2.3. Samples Used

The solution samples contained some acid, the alkaline earth analyte elements and aluminium as a matrix component. The matrix element was diluted from a Spectrascan (Teknolab) stock solution containing aluminium at a concentration of 10 g dm^{-3}. The aluminium concentration in the sample solutions was 0, 200, 500, 1000, and 5000 mg dm^{-3}. The analyte elements were diluted from a multi-element Spectrascan solution of 0.1 g dm^{-3}. The concentrations of the elements studied were in the range of 0.1 and 10 mg dm^{-3}. The solutions contained hydrochloric acid in a concentration of 0.5 mol dm^{-3}.

Table 2. The spectral lines (wavelength λ in nm and excitation energy *E* in eV) studied.

Element	Type of the line	λ	*E*
Be	Be I	234.861	5.30
Be	Be I	249.473	5.01
Be	Be II	313.042	3.99
Be	Be II	313.107	3.99
Mg	Mg I	285.213	4.38
Mg	Mg I	383.829	3.23
Mg	Mg II	279.553	4.47
Mg	Mg II	280.270	4.59
Ca	Ca I	422.673	2.96
Ca	Ca II	317.933	3.93
Ca	Ca II	393.366	3.18
Ca	Ca II	396.847	3.15
Sr	Sr I	460.780	2.71
Sr	Sr II	216.596	5.76
Sr	Sr II	407.771	3.07
Sr	Sr II	421.552	2.96
Ba	Ba I	705.994	1.77
Ba	Ba II	233.527	5.36
Ba	Ba II	455.403	2.75
Ba	Ba II	493.408	2.53

2.4. Measurements

Each of the solutions was measured at a 1050 W output of high frequency power. The recorded signal intensity was averaged from 3–10 s long replicates. The raw intensities were corrected applying the so-called two-side off-peak background correction method.

In order to easily evaluate the effects, the net intensities measured using sample solutions containing no aluminium were used as reference values, and the net intensity values measured in the presence of aluminium were divided by these reference values. In other words, the evaluation presented here is based upon the relative intensities.

3. Results

In the experiments, we studied the intensity changes of several atom- and ion-lines of the alkaline earth metals as a function of aluminium concentration, analyte concentration and that of the device used for sample-introduction. The results measured using a concentric nebuliser are presented in *Figs.1–10*. The net intensities obtained using a V-groove nebuliser (*Figs.11* and *12*) and an ultrasonic nebuliser (*Figs.13* and *14*) are also presented for the case of calcium ions.

4. Discussion

Figs.1–10 show that by using the concentric nebuliser both atomic- and ionic-lines of all alkaline earth metals are affected by aluminium. Nevertheless, substantial differences can be seen depending on the element, type

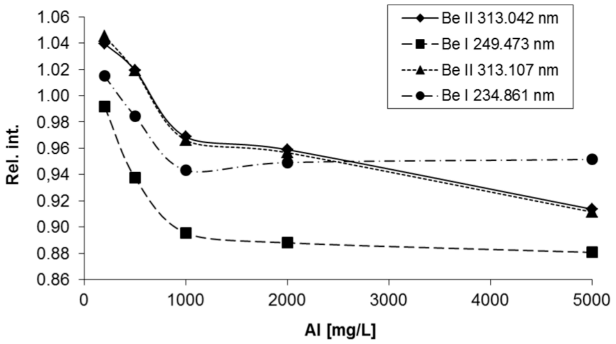

Figure 1. The relative intesities of 0.1 mg dm^{-3} Be as a function of Al concentration, using a concentric nebuliser.

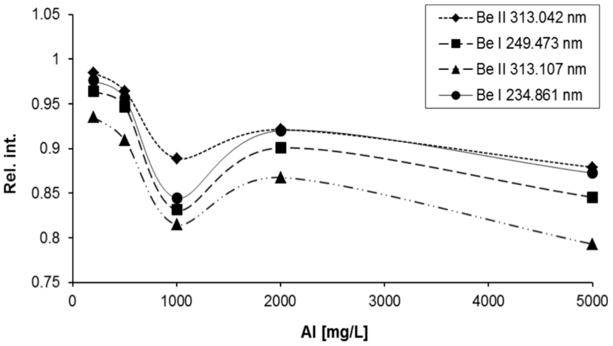

Figure 2. The relative intesities of 10 mg dm^{-3} Be as a function of Al concentration, using a concentric nebuliser.

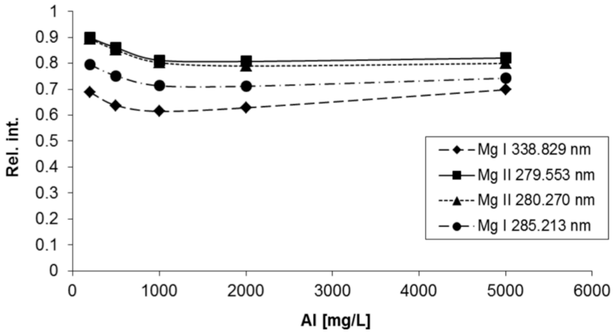

Figure 3. The relative intesities of 0.1 mg dm^{-3} Mg as a function of Al concentration, using a concentric nebuliser.

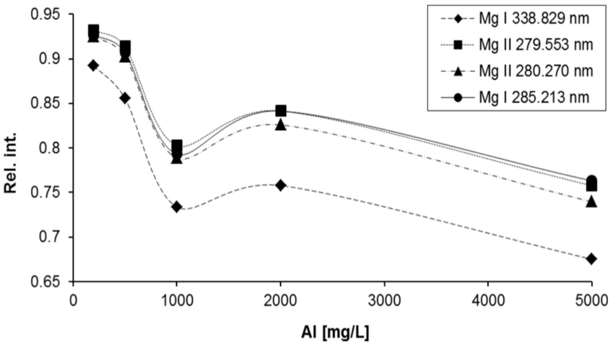

Figure 4. The relative intesities of 10 mg dm^{-3} Mg as a function of Al concentration, using a concentric nebuliser.

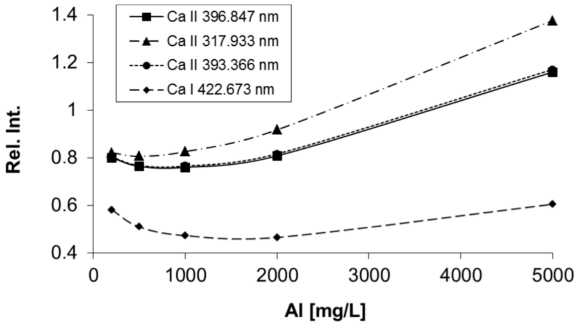

Figure 5. The relative intesities of 0.1 mg dm^{-3} Ca as a function of Al concentration, using a concentric nebuliser.

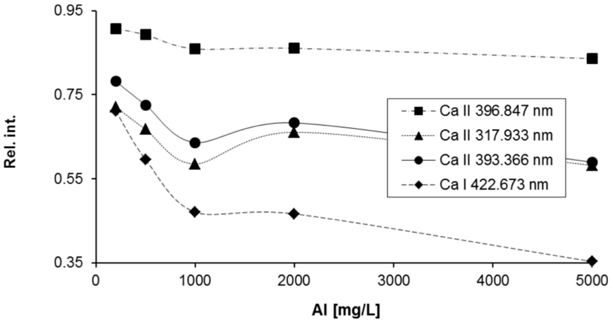

Figure 6. The relative intesities of 10 mg dm^{-3} Ca as a function of Al concentration, using a concentric nebuliser.

of spectral line studied, concentration of aluminium, and that of the analyte. At low beryllium concentrations (0.1 mg dm^{-3}) the intensities on all lines are heavily affected even at relatively low aluminium concentration (1 g dm^{-3}) levels. Higher aluminium concentrations cause only a moderate reduction in the signal. Similar behaviour can be observed in the case of magnesium, strontium, and barium. As for calcium, the greatest decrease was observed also at an aluminium concentration of 1 g dm^{-3}, but higher aluminium concentrations cause a smaller decrease, even some increase can be observed in the ion-lines. It can also be observed that atom-lines are usually more strongly affected than ion-lines.

At higher analyte concentrations, the effect of aluminium is greater on all the lines examined and increases with increasing aluminium concentration. The only exception is the intensities measured at an aluminium concentration of 1 g dm^{-3}, where in the case of each analyte the relative intensities are significantly lower than both the values gained at aluminium concentrations of 0.5 and 2 g dm^{-3} concentration, though the extent of the effect is different. This effect is larger or even larger in the case of beryllium, magnesium, and barium, and it is less profound for calcium and strontium.

With respect to the different types of lines, in the case of beryllium, where all the lines studied are sensitive, one of the atom-lines (234.861 nm) is less, while the other (249.473 nm) is more affected than the ion-lines. One of the atom-lines (383.829 nm) of magnesium is a weak line, while the other one (285.213

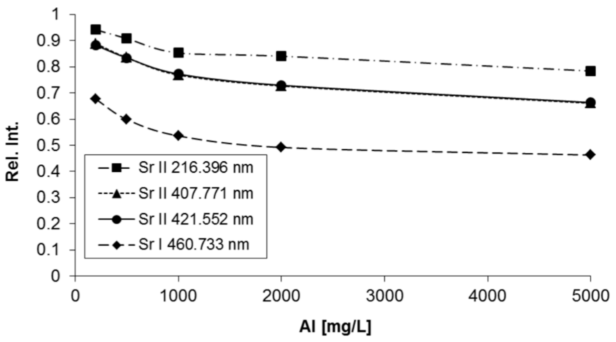

Figure 7. The relative intesities of 0.1 mg dm^{-3} Sr as a function of Al concentration, using a concentric nebuliser.

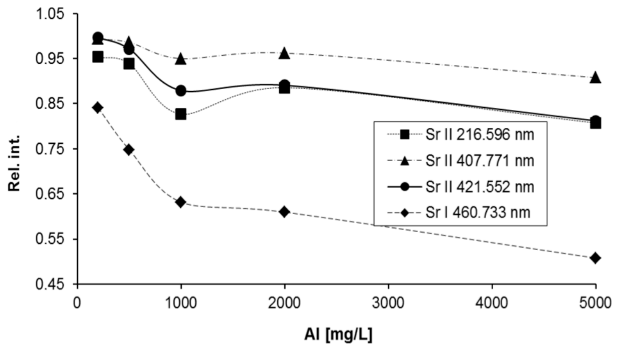

Figure 8. The relative intesities of 10 mg dm^{-3} Sr as a function of Al concentration, using a concentric nebuliser.

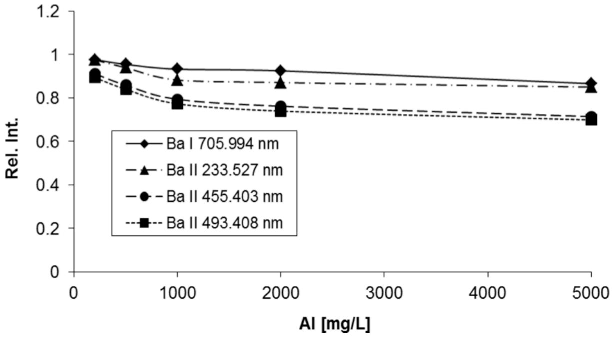

Figure 9. The relative intesities of 0.1 mg dm^{-3} Ba as a function of Al concentration, using a concentric nebuliser.

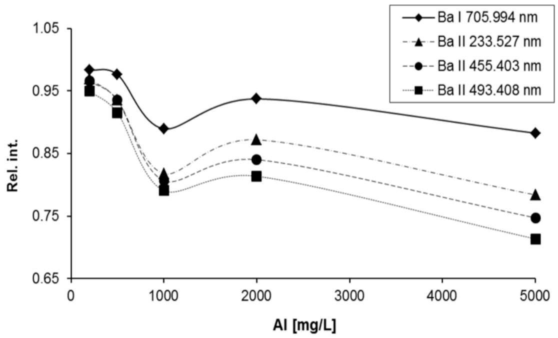

Figure 10. The relative intesities of 10 mg dm^{-3} Ba as a function of Al concentration, using a concentric nebuliser.

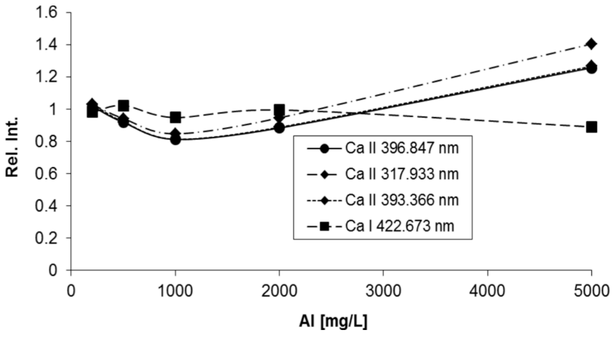

Figure 11. The relative intesities of 0.1 mg dm^{-3} Ca as a function of Al concentration, using a V-groove nebuliser.

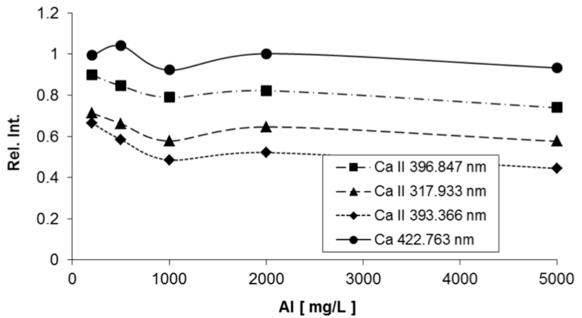

Figure 12. The relative intesities of 10 mg dm^{-3} Ca as a function of Al concentration, using a V-groove nebuliser.

nm) is sensitive. The first is heavily affected by aluminium, while the other lines manifest smaller effects. In the case of calcium and strontium, the atom-line is much more affected than the ion-lines, while the reverse can be observed for barium. Its atom-line is much less affected than its sensitive ion-lines.

The effect of the sample-introduction devices in *Figs.11–14* in the case of calcium manifests that at low analyte concentrations (0.1 mg dm^{-3}) almost the same type of curve is observed with the help of an ultrasonic nebuliser. Using a V-groove type device, only slight effects were detected. At higher analyte concentrations, all the lines are affected using the V-groove nebuliser; while in the case of the ultrasonic device the sensitive ion-lines (393.366 nm and 396.847 nm) are only slightly affected.

5. Conclusion

Using the axially viewed plasma, the light emitted from the high-temperature inner part of the plasma has to pass through the flame to reach the entrance slit of the optical system. As the photons travel, they pass through plasma layers of lower and lower temperatures. In the cooler environment, self-absorption, secondary excitation, and scattering processes can take place. These processes depend on the local temperature, which is also influenced by the high/higher concentration of elements in the sample than the analyte. All these processes make the relationship between line-intensities emitted and analyte concentration rather complicated.

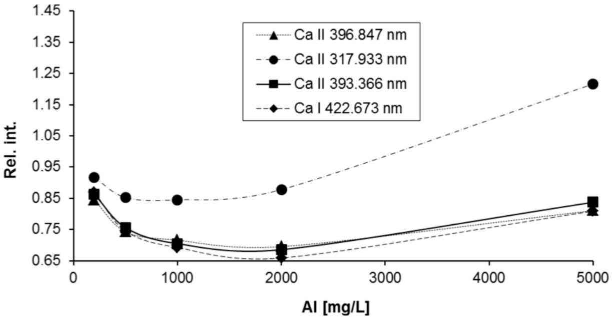

Figure 13. The relative intesities of 0.1 mg dm^{-3} Ca as a function of Al concentration, using an ultrasonic nebuliser.

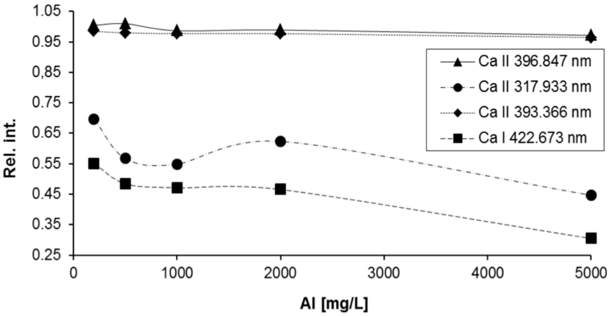

Figure 14. The relative intesities of 10 mg dm^{-3} calcium as a function of Al concentration, using an ultrasonic nebuliser.

It can be concluded that aluminium exhibits a strong interference effect on the emitted spectral line intensities of all alkaline earth elements studied. It can also be seen that atom-lines are usually more affected than ion-lines.

Although the relationship between the interferences and line intensities is complicated, in practice it can be eliminated by careful matrix-matching, i.e. the calibration solutions must contain the interfering element (Al) possibly at the same concentration level as the analyte in the samples. In addition, calibration curves can be extended, only with care in the presence of Al, as it could be observed that the extent of the interference is different at low and high analyte concentrations.

Acknowledgement

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