STUDYING THE INTERFERENCE EFFECTS OCCURRING IN THE COURSE OF ANALYSIS OF ENVIRONMENTAL SAMPLES IN ICP-AES SPECTROMETRY USING A SPECTROMETER WITH AXIAL VIEW

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Abstract
The analysis of overwhelming part of environmental samples is usually performed by application of ICP-AES spectrometry. So that the possible most accurate analytical results could be obtained, the study of different interference effects has a key importance in the course of developing and validating analytical methods aiming at the analysis of environmental samples using ICP-AES spectrometry.

1. Introduction

ICP-AES spectrometry has been a wide-spread, favorable analytical method for decades, and therefore it has been used extensively for the elementary analysis of different kind of environmental samples. The reason for this fact is that ICP-AES spectrometry has some very important advantages, comparing with other instrumental analytical methods. It makes possible the determination of almost 75–80 elements, with favorable detection power in most cases. Another important feature of the method is that the calibration function, i.e. the relationship between the concentration of an element to be analyzed in the solution and that of the measured line intensity is linear, or at least close to that through several magnitudes. It is also well-known that relatively few interference effects exist in ICP-EAS, but it does not mean that this method is free from interferences. Therefore in the course of developing new analytical methods applying ICP-AES or in the course of analysis of samples having no information about the type of matrices, care must be taken of the possible interferences [1, 2].

According to the literature two types of interferences can be encountered; the first type of these effects is related to the plasma and the other one is related to the samples introduction [3]. The most frequent effects in the first group are the so-called spectral interferences, which include the spectra overlapping and the effect of different molecular bands. Most of them are well-known and thoroughly studied. In most cases they can be relatively easily eliminated, a suitable other analyte line must be selected. Most of the modern ICP spectrometers are equipped with some kind of CCD detector, which makes the line-selection simple.

The other type of interferences is related to the sample introduction and therefore it has an influence usually on all the analytical lines and frequently causes changes in the background too. Its presence is reflected in the deterioration of the performance characteristics such as the detection power, accuracy, and it may produce sudden changes in the signal either. Basically the chemical composition of the sample and the chemicals used in the course of the sample preparation are responsible for its occurrence, because they have a strong effect on the physical characteristics of the solution, such as surface tension, viscosity etc. These parameters influence the phenomena of forming and evaporation of liquid droplets and, as a consequence of that, the efficiency of the sample introduction and
long-time behavior of the sample introduction device. Although, the general laws and rules of these phenomena are well-known because of their thoroughful investigation, the real environmental samples have such a diverse chemical composition, and their sample preparation procedure may demand such different methods, that there are no uniform, general rules for predicting the occurrence of such effects. So each different new sample and sample preparation procedure needs a careful study before the routinely application, so that the possible most confident analytical results could be achieved.

The aim of this work is to study the effect of some frequent matrices and chemicals used in the sample preparation procedure on the some performance characteristics.

2. The matrices and chemicals studied

Matrices. Though the environmental samples have diverse chemical composition, there are certain components that frequently can be found at a high concentration in these kinds of samples, therefore it may be useful to know their influence on the ICP analysis. Two metallic elements were chosen, aluminium and calcium. It was because they may be present at a higher concentration in different minerals, soils, rocks. Both of them were applied at a concentration of 1,000 mg/dm$^3$. The Ca was in the solution in the form of Ca(NO$_3$)$_2$ and the solution contained besides the salt, nitric acid at a concentration of 10 g/dm$^3$. The Al solution had a rather high Na level, as it contained 4000 mg/dm$^3$ NaNO$_3$ and nitric acid at a concentration of 40 g/dm$^3$.

Chemicals used in the sample preparation procedure. There are numerous methods to dissolve samples. Besides methods that totally dissolve the samples, there are ones that only partly dissolve them. The latter are the so-called extraction methods, which are also standardized. One of the most frequently used extraction agents is the ammonium-acetate with pH of 4.5. We applied it at a concentration of 0.1 mol/dm$^3$, which can be obtained by dilution from the standardized 1 mol/dm$^3$ solution. Most rocks and minerals contain silicon in some form. If silicon is to be determined, the sample preparation procedure should include the addition of hydro-fluoric acid, so that the silicon could be dissolved. On the other hand, the hydrofluoric acid is dangerous for the torch, spray chamber and that of the torch, as they are made of glass and silica. So that these parts could not be damaged, boric acid should be added to the solution before the analysis in such cases. Boric acid forms fluoroboric acid (HBF$_4$) with the free HF, therefore, it is also interesting to know, what matrix effect may be expected in the presence of HBF$_4$. That is why HBF$_4$ at a concentration of 10 g/dm$^3$ was chosen for a second chemical to be studied.

All these four solutions were used as a kind of blank solutions and each of them was spiked with a known quantities of a multi-element certified reference material solution (Merck Ltd., CertiPUR IV multielement solution, with 23 elements, each of them at a concentration of 1,000 mg/dm$^3$), so that the analyte concentration was 5 mg/dm$^3$ for each element studied. Distilled water containing 10 g/dm$^3$ nitric acid was used as reference blank solution, and an aqueous spiked standard, at an analyze concentration of 5 mg/dm$^3$ was used as reference standard solution.

3. The spectrometer and the measuring conditions

In the course of the measurements 720 OE ICP spectrometer, manufactured by the Varian Inc. (at present belongs to Agilent) was used. Its main features can be found in Table 1.
Table 1

Features of the ICP spectrometer used in the course of experiments

<table>
<thead>
<tr>
<th>Feature</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of viewing the plasma</td>
<td>Axial</td>
</tr>
<tr>
<td>The frequency of the generator</td>
<td>40 MHz</td>
</tr>
<tr>
<td>The RF performance applied on the torch</td>
<td>900–1500 W, adjustable by the software</td>
</tr>
<tr>
<td>Type of the optical system</td>
<td>Double monochromatic with Echelle gratings</td>
</tr>
<tr>
<td>Type of detector</td>
<td>Two-dimension CCD</td>
</tr>
<tr>
<td>Wavelength range</td>
<td>160–780 nm</td>
</tr>
<tr>
<td>Primary sample introduction system</td>
<td>Pneumatic (K-type) nebulizer</td>
</tr>
<tr>
<td>Secondary sample introduction system</td>
<td>Ultrasonic nebulizer</td>
</tr>
<tr>
<td>Controlling software</td>
<td>ICP Expert II (under Microsoft Windows XP OS)</td>
</tr>
</tbody>
</table>

Though the CRM solution used to spike the solutions contained 23 elements, only three of them were studied here: Ba, Cd and Pb. As the optical system makes possible the simultaneous multi elemental analysis, i.e. any of the lines in the range of 160–780 nm can be chosen and more than 100 than lines can be measured at the same time, three lines were selected for each element to be studied. During the line selection care was taken that both atomic and ionic lines should be chosen and they should be suitable for trace analysis, i.e. they should be among the most sensitive lines of the chosen element. Ba was an exception as it does not have a sensitive atomic line because of its low ionisation energy. The spectral characteristics of the selected lines are presented in Table 2.

Table 2

The characteristics of the selected spectral lines

<table>
<thead>
<tr>
<th>Element</th>
<th>Ionization energy [eV]</th>
<th>Type of the line</th>
<th>Wavelength [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>5.21</td>
<td>Ionic</td>
<td>233.527</td>
</tr>
<tr>
<td>Ba</td>
<td></td>
<td>Ionic</td>
<td>455.404</td>
</tr>
<tr>
<td>Ba</td>
<td></td>
<td>Ionic</td>
<td>493.407</td>
</tr>
<tr>
<td>Cd</td>
<td>8.99</td>
<td>Ionic</td>
<td>214.440</td>
</tr>
<tr>
<td>Cd</td>
<td></td>
<td>Ionic</td>
<td>226.502</td>
</tr>
<tr>
<td>Cd</td>
<td></td>
<td>Atomic</td>
<td>228.802</td>
</tr>
<tr>
<td>Pb</td>
<td>7.42</td>
<td>Ionic</td>
<td>182.143</td>
</tr>
<tr>
<td>Pb</td>
<td></td>
<td>Atomic</td>
<td>217.000</td>
</tr>
<tr>
<td>Pb</td>
<td></td>
<td>Ionic</td>
<td>220.353</td>
</tr>
</tbody>
</table>
4. Results and their discussion

The reference blank and the reference standard solutions were also used as calibration samples. Ten replicates were measured and then averaged for each measured line in case of each solution. The length of the integration time was 5 s. In case of each matrix the blank solution was measured, and then it was followed by the (spiked) standard. After each pair of solutions the reference blank solution was re-measured, so that all the traces of the previous pair of solutions could be washed out. From the measured intensities the standard deviation of the blank solution, the net peak intensity of the spiked samples and finally the detection limit values have been calculated.

The detection limit values were calculated by the following formula:

\[
DL = \frac{3 \times SD_{IBL}}{I_{Std}} \times C_{Std}
\]

where:
- \(DL\) the detection limit [mg/dm\(^3\)]
- \(SD_{IBL}\) standard deviation of the intensity of the blank solution [a.u.]
- \(I_{Std}\) background corrected net intensity of the standard [a.u.]
- \(C_{Std}\) the concentration of the analyte in the standard solution [mg/dm\(^3\)].

No spectral interferences could be noticed on any of the studied spectral lines, as it can be seen in Figure 1, 2 and 3, where the studied lines and their spectral environment can be seen.

\[\text{Figure 1: The spectral environment of the selected Ba lines}\]
In these figures the data obtained by measuring the spiked solution containing fluoroboric acid matrix are presented.

So that the data could be evaluated more easily, the peak values of standards were divided by the peak values and of the reference standard, which did not contain any matrix. Similarly the calculated detection limits were divided by the detection limit measured with the reference standard solution, which was eventually an aqueous solution without any specific matrices. The results are presented in Table 3 and Table 4.
Reduction of the peak signal. Looking at Table 3, it can be noticed that each of the matrices decreased the net peak signal compared with that of measured in the matrix-free solution. It also can be seen that there are no substantial differences in the decrease, they are more or less uniform at all the lines studied.

Obviously, it does not mean that there are no differences among the effects of the different matrices. The data presented in the table suggest that it is the ammonium-acetate that has the lowest effect on the signal. The highest reduction occurred is about 15%, and there are only 2 lines where the decrease exceeds 10%. On the other hand it can be stated that it is the fluoroboric acid that has the highest impact on the signal, the smallest value it caused is approximately 12% and the largest one is about 34%.

Changes of the detection power. As the aim of the analysis in case of environmental samples to determine elements, whose concentration may be very low, the detection power of the analytical methods applied to this field is a parameter of key-importance. The detection power is characterised by the detection limit values. That’s why the possible effects of matrices on their value are also very important. According to the formula used to calculate the detection limits, the result depends on both the net peak intensity and that of the standard deviation of the background. With the same net peak intensity value the higher is the standard deviation, the higher is the calculated detection limit, and consequently, the poorer is the detection power.

Looking at Table 4 it can be stated that there are no huge changes in most cases and in some cases where the ratio is smaller than 1, i.e. the detection limit in that matrix is somewhat better than that of measured in the matrix-free solution. Nevertheless, it should be mentioned that in the analytical practice there are often cases where a much higher matrix concentration has to be encountered, and in these conditions poorer detection power...
can be expected by all means. Regarding the different matrices it can be stated that fluoroboric acid has the highest impact on the detection limit values, it has a great influence on all of the studied lead lines, producing the largest increase of the values. From the solutions studied, the one containing Ca has perhaps the lowest effect on the results. Looking at the effects on a specific spectral line, there are two cases worth mentioning. The first thing is, that both aluminium and fluoroboric acid cause a strong decrease in the detection power at all of the lead lines. It seems to be a specific effect, though no such influence could be expected based upon the data presented in Table 1. Probably some kind of chemical interference might be responsible for that.

The other interesting case is the 493.407 nm Ba line. Each of the studied matrices decreased the detection power at about 50%. As only one Ba line is affected among the three lines, it suggests that this is not a physical effect but it must be some kind of spectroscopic effect, which influences the transition probability and by that the emission intensity, which may be the real reason.

There is one question left concerning these interferences, how they could be eliminated, or what is to be done if such effects may be encountered.

Normally, it is not possible to eliminate these effects, because the matrices themselves cannot be removed from the solution. It means that the analyst should take into account their effect in the course of method-development and during the analysis.

The reduced peak intensities may lead to false results if the calibration is based upon matrix-free calibration standards, therefore – in agreement with the literature data [4, 5] – it is inevitable to use matrix-matched calibration standards if any serious matrix effect may be encountered.

The poorer detection ability usually increases the lowest quantity of the determination, in other words, in such cases the limit of the quantitative analysis becomes higher, and the method is less sensitive in the presence of the matrix producing the interference.

5. Summary

In this paper the physical interference effects of 4 matrices on 9 spectral lines of three elements important from view of environment, such as Ba, Pb and Sr, were studied in the course of ICP-AES analysis. Because of the influence of the matrices both signal depression and deterioration of the detection power could be obtained. Regarding the signal depression it can be stated that the fluoroboric acid has the largest effect on the signal, while no substantial differences could be obtained among the lines studied.

As for as the detection power, again the fluoroboric acid produces the greatest influence. Among the spectral lines all the lead lines are sensitive both fluoroboric acid and aluminium and the 493.407 nm Ba line is almost uniformly influenced by each of the matrices.
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REFERENCES