Flagging and correcting non-spectral matrix interferences with spatial emission profiles and gradient dilution in inductively coupled plasma–atomic emission spectrometry

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Abstract

Matrix interference remains one of the most daunting challenges commonly encountered in inductively coupled plasma-atomic emission spectrometry (ICP-AES). In the present study, a method is described that enables identification and correction of matrix interferences in axial-viewed ICP-AES through a combination of spatial mapping and on-line gradient dilution. Cross sectional emission maps of the plasma are used to indicate the presence of non-spectral (plasma-related and sample-introduction-related) matrix interferences. In particular, apparent concentrations of an analyte species determined at various radial locations in the plasma differ in the presence of a matrix interference, which allows the interference to be flagged. To correct for the interference, progressive, on-line dilution of the sample, performed by a gradient high-performance liquid-chromatograph pump, is utilized. The spatially dependent intensities of analyte emission are monitored at different levels of sample dilution. As the dilution proceeds, the matrix-induced signal variation is reduced. At a dilution where the determined concentrations become independent of location in the plasma, the matrix interference is minimized.

Keywords: Inductively Coupled Plasma Atomic Emission Spectrometry; Organic solvents; Gradient dilution; Matrix effects; Axial viewing; Plasma spatial profile

1. Introduction

The existence of matrix interference in Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) remains a difficult problem. Clearly, it would be desirable to have available a detection method to alert the analyst to the presence of an interference. Once the analyst is aware of the interference, a correction method could be applied to obtain accurate analytical results. Our research group has been developing indicators to flag the presence of matrix interferences [1]. Among the indicators investigated, the use of spatial profiles was found to be most sensitive [2]. This interference indicator functions on the principle that in the absence of matrix interference, the shapes of spatial emission maps of the reference and the sample should be the same, which in turn leads to constant ratios (relative intensities) of the two spatial intensity profiles. In contrast, if the sample suffers from a matrix interference, the relative-intensity profile will change with spatial location as a result of signal enhancement or depression caused by the matrix and by the inhomogeneity of the plasma. This relative-intensity profile then serves as an indicator for the presence of a matrix interference.

One drawback of this method is its inability to correct an interference when the plasma is in axial-viewing mode. In the radial-viewing mode [3, 4], a crossover point (the location in the plasma where the enhancement effect is balanced by a depression effect) exists and can be located by making multiple dilutions of the sample, based on the fact that the crossover point location remains the same for a given emission line in the same matrix. Unfortunately, when the plasma is viewed axially, only a few emission lines exhibit crossover points. This absence of

crossover points for some emission lines is observed in both aqueous- and organic-solvent-based axial viewing ICP-AES analysis [5, 6]. For lines that do exhibit crossover points, those points are often in a region of the plasma with a relatively weak emission signal. Therefore, it is not feasible to use the crossover-point method to correct interferences in axial-viewing mode.

As a result, alternative methods (e.g. matrix stripping, matrix matching, internal standardization [7-9], and standard additions [10-13]) must be used to correct for matrix interference, among which dilution is one the most common [14-16]. A previous study [17] by our research group showed that the intensity ratio of two emission lines (from the same or different elements) can be used as a matrix-effect indicator when the sample is progressively diluted by means of a gradient high-performance liquid chromatography (HPLC) pump. Due to a disparity in the upper-state energies of two emission lines, the effect of the progressively diluted matrix on these emission lines is different. As a result, the intensity ratio of the two lines changes with dilution for a sample that suffers from an interference. In contrast, a constant ratio is observed for samples free of matrix interference. Conveniently, the dilution factor needed to reduce a matrix effect to an acceptable level can be identified as the point where the signal ratio becomes virtually constant (i.e. comparable to that of a matrix-free reference sample). A drawback of this method is that the intensity-ratio profile is less sensitive to changes in plasma conditions (and therefore to the presence of a matrix interference) than is the spatial emission profile. We have shown [17] that a 10% change in solvent composition can cause significant matrix effects. Unfortunately, the intensity-ratio method was not able to flag this error.

The current study introduces a new method to overcome the shortcomings of both procedures described above. Spatial emission maps are used to detect the presence of a matrix interference, and gradient dilution is employed to determine the optimal dilution to minimize the

interference. As in the earlier technique, the reference and sample solutions are diluted by a gradient high-performance liquid chromatography (HPLC) pump. However, the relative-intensity spatial profiles (ratio of the spatial intensity profiles of the reference and sample solutions) of the sample are monitored at each gradient step. In a sample that suffers from matrix interference, a curved relative-intensity profile is observed at the beginning of the gradient dilution. As dilution proceeds, this curved profile becomes flatter, finally reaching a point where its flatness is comparable to that of a matrix-free reference sample. The optimal dilution factor is then the point on the gradient dilution where the relative-intensity profile becomes statistically flat. With this method, a calibration curve can be constructed from a single gradient-dilution run. This enables one to determine both the correct concentration of the analyte as well as the optimal dilution factor to minimize matrix interference in samples with a similar matrix.

The foregoing problems are even more acute when organic solvents are used in ICP-AES. Organic solvents are often used in the petroleum, pharmaceutical, and food industries for the determination of trace metals. The presence of certain metals in petroleum and petroleum products can deactivate expensive catalysts [18, 19]. Direct injection (with dilution) of petroleum products into ICP-AES for metal analysis is a rapid and convenient method for the determination of these contaminants [20-24]. However, matrix interference is a major concern; since the sample matrices can range from crudes, heavy oils to diesels and gasoline [25, 26]. Samples dissolved in *o*-xylene (one of the most commonly used solvents in the petroleum industry) are one focus of the present study.

2. Experimental

2.1 Instrumentation

The experimental setup used here is identical to that employed in previous studies by our group to flag and correct matrix interferences [6]; accordingly, only a brief descriptions is given below. A commercial ICP–AES Czerny–Turner spectrometer (Horiba Jobin-Yvon ACTIVA ICP–AES spectrometer, Longjumeau, France) is used. With a vertical entrance slit and with the plasma mounted axially, analyte emission from a plasma cross section is collected onto a two-dimensional charge coupled device (CCD), which enables both wavelength and cross-sectional emission intensity information to be collected simultaneously on the x and y axes of the detector, respectively. As a result, spatially resolved analyte emission from the entire plasma cross-section and multiple emission lines within a selected spectral window (4 nm to 8 nm for Grating one 4343 groove/mm and 4 nm to 14 nm for Grating two 2400 groove/mm) are monitored at once. The width of the spectral window for each grating is dependent on the wavelength of interest.

A gradient HPLC pump (Hitachi Ltd. Model L-7100 pump) is used in place of a peristaltic pump to perform both on-line mixing of sample and diluent solutions and to introduce the resulting solution into the nebulizer. Solutions exiting the flow restrictor are directed into a Meinhard concentric nebulizer, and the resulting aerosol passed through a chilled (5° C), water-jacketed Scott-type double-pass spray chamber prior to introduction into the ICP. A Thermo Finnigan Element ICP torch with a 1.5 mm (I.D.) injector tube is used in all experiments.

Unless otherwise specified, the ICP operating parameters used in all experiments are as listed in Table 1. These parameters were tailored to accommodate the use of organic solvents (*o*-xylene, *p*-xylene, and toluene in the current study). Such solvents have high volatility and carbon content, and consume appreciable plasma energy and cause solvent loading of the plasma [27, 28]. As a result, a chilled (5° C), water-jacketed spray chamber was used to lower solvent vapor pressure. Also, the nebulizer flow was reduced to 0.35 L/min and plasma power was raised to 1300 W. To prevent

carbon buildup on the torch injector [29, 30], oxygen was added to the central-gas flow at a rate of 12 mL/min and auxiliary gas flow was increased to 1.2 L/min.

2.2 Reagents

In order to demonstrate the viability of this interference-reduction method for practical use, *o*-xylene, one of the most commonly used solvents in the petroleum industry, was used in the current study. All solutions were prepared by dissolving certified standards (Conostan custom blend, division of SCP Science, Baie D'Urfe, Canada) in *o*-xylene. Reference solutions contained only the analytes in 100% *o*-xylene. For plasma-related matrix-effect experiments, a few hundred ppm of selected matrix elements (K and Ca) were added to the *o*-xylene solutions, which also contained the same analyte concentrations as the reference solutions. For sample-introduction-related matrix-effect experiments, samples contained the same concentration of analytes as the reference solutions but were instead dissolved in 20%/80% v/v toluene/*o*-xylene or 40%/60% v/v *p*-xylene/*o*-xylene.

2.3 Experimental procedures

First the matrix-free reference solution was diluted in a linear gradient while spatial emission profiles of the chosen analytical lines were collected, followed by the collection of spatial emission profiles of the same analytical lines in an “unknown” sample solution (one prepared to exhibit either a sample-introduction-related or plasma-related matrix interference). The spatial profile of relative intensity was expressed as the ratio of the emission intensities collected from the reference and sample. For a sample that is free from matrix interference, a flat relative-intensity spatial profile is obtained; this flat pattern indicates that at each observed spatial location in the plasma, the signal response is the same for the calibration standards and the unknown sample. In contrast, for a sample that suffers from a matrix interference, the magnitude of the interference varies from one location to another, due to the heterogeneity of the plasma.

Such variations result in a curved relative-intensity profile, and enable the presence of matrix interference to be flagged.

To quantitatively assess the curvature of each relative-intensity profile, a relative range (the range of all data points divided by the average value of the data set) is calculated and expressed as a percentage [1]. For this calculation, only those data points in the range from 5% to 95% of the maximum and minimum of the data set are used, which prevents distortion of the relative range by outliers. The relative range of the reference solution, which is free from any matrix interference, is then used as a threshold for determination of whether a matrix interference exists in a sample. This comparison helps compensate for differences in noise level from one spectral line to another. Any relative-intensity profile with a relative range that exceeds the predetermined threshold of the reference is said to suffer from a matrix interference.

To determine the optimal dilution factor to practically eliminate a matrix interference but to minimize losses in analyte signal, the spatial profile of the target analytical line was continuously monitored as gradient dilution progressed. When the relative ranges of the two relative-intensity profiles (sample and reference) are comparable (within 1%) to each other, it can be said that matrix interference is minimized and the corresponding dilution factor is optimal.

3. Results and Discussion

3.1 Flagging matrix interference with relative-intensity profiles

Relative-intensity profiles of the Ti II 323.45 nm line in the presence of four different matrices are shown in Figure 1. The reference solution was prepared in 100% *o*-xylene. A plasma-related matrix interference was induced by adding high concentrations of K and Ca to the sample solution, since easily ionized elements such as K [4], and elements with low second ionization

energies, like Ca [31, 32], are known to induce the most severe plasma-related matrix interference. Toluene and *p*-xylene were added to the sample solution to induce a sample-introduction related matrix interference, due to the different physical properties among toluene, *p*-xylene, and *o*-xylene that affect nebulization and desolvation. Adding these matrices separately is intended to demonstrate the effectiveness of the spatial profiles to flag both of these interference types; however, plasma-related and sample-introduction related matrix interferences are not easily examined separately. The stock oil standards containing K and Ca (used in preparing interferent-containing sample solutions) have higher viscosity than the stock oil standards used in preparing reference solutions. Therefore, the surface tension, density, and viscosity of the sample solution might be different from those of the reference solution, inducing sample-introduction-related matrix interference in the samples intended to experience only a plasma-related interference. Similarly, the introduction of toluene and *p*-xylene might change the ionization and excitation conditions in the plasma due to differences in volatility, which could induce a plasma-related matrix interference. Therefore, it is best to assume that the matrix interference observed in the current study is a combination of both plasma-related and sample-introduction-related effects.

From Figure 1, curved relative-intensity profiles are observed for the Ti II 323.45 nm line in the presence of all four matrices. The relative range of the reference solution (drift test) is calculated to be 1.0%, while the relative ranges for sample solutions in the presence of K, Ca, *p*-xylene and toluene matrices are 4.0%, 3.5%, 2.7%, and 3.0%, respectively, strongly indicating a matrix effect. Interestingly, in the presence of the K and Ca matrix, the enhancement in Ti ionic emission is stronger in the surrounding plasma than in the central channel, while in the presence of *p*-xylene and toluene, the largest enhancement is observed in the central channel. It is difficult to reconcile the possible causes of these different relative intensity profiles with the combinations of

plasma and sample-introduction related effects discussed earlier. The overall enhanced Ti emission in the four matrices might indicate the formation of smaller aerosol droplets [25, 33]. In addition, K and Ca matrices are known to suppress analyte emission due to the fact that they are easily ionized and have low secondary-ionization potentials [34, 35]. With the aerosol concentrated in the central channel, the overall enhancement could be more pronounced in *p*-xylene and toluene matrices while less pronounced in K and Ca matrices.

Figure 2 shows relative-intensity profiles for five emission lines with upper-state energies ranging from 4.02 eV to 12.67 eV. All these emission lines exhibit curved relative-intensity profiles in the presence of the K matrix. The relative range threshold in this experiment is determined from the drift test to be 1.0%, while the relative ranges for Al I 308.22 nm, Si I 212.41 nm, Ti II 323.66 nm, Ba II 233.53 nm, and Fe II 259.94 nm are 10.5%, 4.40%, 21.0%, 9.55%, and 12.4%, respectively. With significantly larger relative ranges than the reference solution, it can be safely concluded that the relative-intensity profiles of emission lines with a wide range of upper-state energies can be used to flag the existence of both plasma-related and sample-introduction-related matrix interferences.

The small difference in the relative-intensity profiles of the Ti II lines in Figs. 1 and 2 probably results from two sources. First, the two experiments were performed on different days, so instrumental drift is a factor. In addition, the experiments were performed with two different sets of solutions; even though the concentrations were nominally the same, it is likely that small differences exist. Regardless, from the similar shapes of these profiles, we can conclude that the effect of the K matrix on Ti emission was confirmed.

3.2 Determining the optimal dilution factor

Once a matrix interference is detected, the next important step is to determine the optimal dilution where these interferences are brought to an acceptable level while minimizing the loss in

sensitivity due to dilution. In this study, an on-line gradient dilution is performed by replacement of a portion of the flow from a sample solution with a diluent (*o*-xylene). Figure 3 shows a typical gradient-dilution curve (time vs. intensity) for the Mg I 285.21 nm line. This spectral line was selected, rather than the more sensitive ion line, because of the rather high Mg concentration in our multielement oil standards. In the plot of Figure 3, only the emission from the central channel of the plasma was viewed. As would be expected, the signal is greatest at time zero before any dilution has taken place, and linearly decreases with time as the dilution proceeds. The x-axis of Figure 3 can be converted to dilution factor by means of Equation (1).

$$\frac{I_{\text{Mg}}}{I_{\text{Mg}} + I_{\text{MgO}}} = \frac{I_{\text{Mg}}}{I_{\text{Mg}} + I_{\text{MgO}}} \left(\frac{I_{\text{Mg}}}{I_{\text{Mg}} + I_{\text{MgO}}} \right)^{-1} \quad (1)$$

At each data point in Figure 3, a corresponding relative-intensity profile for Mg I 285.20 nm was determined. Four data points were selected at dilutions shown as blue hollow symbols in Figure 3 along with their corresponding dilution factors. Their corresponding relative-intensity profiles are shown in Figure 4 a-d.

Figure 4a compares the relative-intensity profile of the reference solution to that of the sample solution in the toluene matrix. A significant curvature is observed before dilution, which indicates the presence of a matrix interference from toluene. A quantitative evaluation reveals that the relative range for the reference solution is 1.2%, while that of the undiluted interferent-containing sample solution is 7.6%. As dilution of the sample solution increases, the relative range of its relative-intensity profile declines, as shown in Figures 4b, 4c and 4d. Over the course of the dilution, from a factor of 1 (no dilution) to 1.8, the relative range of the sample dropped from 7.6% to 3.9%.

As was discussed above, the relative range is affected by the noise in the system. At the lowest analyte concentration explored here (dilution factor of 1.8), a larger relative range was observed for the reference solution, (3.8% compared to 1.2% before any dilution). Regardless of this rise in the threshold of the relative range, it is apparent both qualitatively from the profile in Figure 4 (d) and quantitatively from the relative range of the reference and sample (3.8% and 3.9%, respectively), that the matrix interference has been greatly reduced. Therefore, it can be concluded that the optimal dilution factor to bring the toluene matrix interference under control in the current experiment is 1.8.

Ideally, the relative range of a sample solution should be compared with that of a reference solution with a similar signal level, so the dominant noise sources and levels are comparable [36]. At a high emission intensity (high concentration), the dominant noise source is likely analyte flicker noise, which scales linearly with the signal. In contrast, at a low emission intensity (low concentration), analyte shot noise becomes more significant, and its magnitude scales as the square root of the signal. In order to examine how the relative range was affected by signal level, spatial profiles of the signal from the Mg I 285.2 nm spectral line in a 100% *o*-xylene matrix were monitored throughout the course of a gradient dilution, and the relative range at each point recorded. From these data, a plot of relative range vs. signal was constructed (Figure 5) and used to determine where the drop in signal produced a change in relative range that was larger than 1%, the same criterion used to flag the presence of a matrix effect in Section 2.3. The difference in dominant noise is reflected in the increasing relative range of the reference solution as dilution proceeds (cf. Figure 5). As dilution progresses (from left to right in Figure 5), the analyte signal drops and the relative range goes up. As a result, if the concentrations of the reference and sample solutions are greatly different, a comparison of their

relative ranges can be inaccurate due to differences in the dominant noise source. From Figure 5, for the Mg I 285.2 nm spectral line, the signal between the sample and the reference solutions should be within a factor of two (the ratio of two red data points) of each other to produce relative ranges that are within 1%. This treatment assumes that the signal is high enough that analyte flicker is the dominant source of noise. At lower signal levels where shot noise is dominant (the right side of the curve in Figure 5), even more similar intensities would be required as the relative range is more strongly affected by signal strength in this region.

3.3 Verification of optimal dilution factor

In order to validate the determined optimal dilution factor, the Mg concentration in the sample solution was calculated at a dilution factor of 1.8 and compared with the theoretical value. A calibration curve was obtained from linear dilution of the reference standard (cf. Figure 3) by conversion of the x-axis from time to concentration ($r^2 = 0.9998$). With this calibration equation, the concentration of Mg in the toluene-containing sample solution was determined at the optimal dilution level. The resulting Mg concentration (1.65 ppm) was then corrected by multiplying it by 1.8 to obtain its true concentration (2.96 ppm) in the undiluted sample solution. The discrepancy between the theoretical concentration (3.00 ppm) and the one determined by this method (2.96 ppm) is only 1.22%, which indicates that the matrix interference is minimal.

4. Conclusions

Relative-intensity spatial profiles were used to successfully flag the presence of non-spectral matrix interferences in *o*-xylene-based, end-on viewed ICP-OES analysis. In addition, a method was tested to determine the optimal dilution factor to minimize the detected matrix interference

while maintaining strong analyte signals. With the new method, non-spectral matrix interferences can be detected and corrected in a single analysis, to ensure accurate analytical results in a fast turnaround time.

Like any other analytical method, drawbacks to this approach exist. Currently, each gradient dilution run requires approximately 30 minutes. It would not be desirable to perform such a time-consuming experiment on every sample. To shorten analysis time, the speed of the gradient run could be increased substantially, with fewer spatial profiles collected along the concentration gradient. An optimal dilution factor could still be determined with this approach, although the reduced sampling of the spatial profiles would lessen its accuracy. The drawback to faster gradients could be remedied by faster spectrometers and detectors. Ultimately, even in the case of a very fast spectrometer and detector, the time required for this method would be constrained by the wash-out time of the spray chamber, which limits the speed at which concentration changes in a gradient can be observed. Modification of the sample-introduction pathway would be needed to address this problem. Also, for the new method to be fully effective, the concentration ratio of the matrix and analyte must be considered. The maximum dilution that the present gradient pump (Hitachi L-7100 model) can accurately provide is 1:100, which might be insufficient to eliminate matrix interferences in a sample in which the matrix concentration is very high. In such a situation, pre-dilution of the sample might be required prior to the on-line gradient dilution.

Acknowledgement

This work was supported in part by the U.S. Department of Energy through grant DE-FG02-98ER14890. We are grateful to Horiba Jobin-Yvon for the loan of the ACTIVA instrument and

to Precision Glassblowing for providing a modified wear-metal one-piece torch for ICP organic-solvent analysis.

Table 1. Instrument operating parameters

ICP spectrometer	Horiba Jobin-Yvon ACTIVA	Sample uptake rate	0.35 mL/min
Forward power	1300 W	Plasma axial cutoff gas flow (nitrogen)	25 L/min
Outer gas flow (argon)	14 L/min	Central channel oxygen flow	10 mL/min
Intermediate gas flow (argon)	1.2 L/min	Sheath gas flow (argon)	0.1 L/min
Nebulizer gas flow (argon)	0.35 L/min	Spray chamber temperature	5 °C

Figure 1. Relative-intensity profiles for the Ti II 323.45 nm line in the presence of four different matrices. The drift test is obtained from the ratio of patterns from a matrix-free standard taken before and after the other measurements.

Figure 2. Relative-intensity profiles for five emission lines with different upper-state energies in a 300 ppm K matrix.

Figure 3. Concentration-dependent signal profile for the Mg I 285.21 nm spectral line in a reference solution (contains only Mg and *o*-xylene) over a 30-min gradient run. Relative-intensity profiles were measured at four dilution factors (open squares) to determine the optimal dilution factor needed to bring the matrix interference to an acceptable level yet minimize signal loss.

(a)

(b)

(c)

(d)

Figure 4. Relative intensity profiles for the Mg I 285.21 nm line in sample and reference solutions at dilution factors of (a) 1 (no dilution) (b) 1.4, (c) 1.6, and (d) 1.8

Figure 5. Comparison of relative ranges at different analyte signal levels in the reference solution.

Reference

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