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.

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

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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.

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