



Use of gradient dilution to flag and overcome matrix interferences in axial-viewing inductively coupled plasma-atomic emission spectrometry[☆]



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ABSTRACT

Despite the undisputed power of inductively coupled plasma-atomic emission spectrometry (ICP-AES), its users still face serious challenges in obtaining accurate analytical results. Matrix interference is perhaps the most important challenge. Dilution of a matrix-containing sample is a common practice to reduce matrix interference. However, determining the optimal dilution factor requires tedious and time-consuming offline sample preparation, since emission lines and the effect of matrix interferences are affected differently by the dilution. The current study exploits this difference by employing a high-performance liquid chromatography gradient pump prior to the nebulizer to perform on-line mixing of a sample solution and diluent. Linear gradient dilution is performed on both the calibration standard and the matrix-containing sample. By ratioing the signals from two emission lines (from the same or different elements) as a function of dilution factor, the analyst can not only identify the presence of a matrix interference, but also determine the optimal dilution factor needed to overcome the interference. A ratio that does not change with dilution signals the absence of a matrix interference, whereas a changing ratio indicates the presence of an interference. The point on the dilution profile where the ratio stabilizes indicates the optimal dilution factor to correct the interference. The current study was performed on axial-viewing ICP-AES with *o*-xylene as the solvent.

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1. Introduction

Identification and remediation of non-spectral interferences remains a critical challenge in inductively coupled plasma-atomic emission spectrometry (ICP-AES) [1]. Without knowledge of the composition of a sample solution, which itself is the subject of the analysis, matrix interferences are difficult to detect or correct. Since awareness of the existence of a problem is the first step towards its correction, it is desirable to have indicators that can alert an operator of the presence of matrix effects in an on-line fashion. Potential indicators were previously examined by our research group [2]. Among the possible methods, we concluded that monitoring argon emission and spatially resolved analyte emission was attractive for flagging plasma-related matrix effects. Both indicators exploited changes in emission signals to flag effects caused by a sample matrix. A similar principle is employed in the present study to flag and correct matrix interferences.

Of similar importance to the recognition of matrix effects is their correction. Four of the most commonly used methods to control matrix effects are matrix stripping, matrix matching, internal standardization, and standard additions [3–6]. Unfortunately, each of these methods carries inherent limitations. Matrix stripping is often not fully effective and can result in loss of analyte. Similarly, matrix matching requires prior knowledge or analysis of the sample composition in order to provide an accurate match to the sample matrix. Apart from matrix-manipulation methods, internal standardization requires that added standards be carefully chosen to ensure similar signal response between the standards and analytes. In addition, more than one internal standard might be needed for a multi-element analysis, which increases complexity and can itself result in additional inter-element effects. The same holds true for the standard-addition method. The number of added standards must at least equal the number of analytes. The concentrations of the standard-addition solutions also play an important role. Inaccurate results can arise if the standard-addition concentrations are too high or too low compared to the analyte. Studies [7] have shown that the concentration ratio of an added standard and sample should be at least two to ensure adequate precision and accuracy. Pre-analysis of the sample is therefore needed to obtain a rough estimate of the analyte concentration. In addition, too high of an added concentration can significantly alter the matrix composition of the sample, especially when

[☆] This paper is dedicated to Nicoló Omenetto, on the occasion of his 75th birthday, in recognition of his outstanding contributions to the field of laser spectrochemistry and as an editor of Spectrochimica Acta Part B.

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multi-additions are needed. Last of all, these four methods all require the addition of foreign reagents to the sample solution, which increases the likelihood of contamination.

Considerable work has been done to alleviate the drawbacks of traditional methods. To shorten sample preparation and analysis time, and to reduce human error and chemical impurities, high-performance liquid chromatography (HPLC) pumps, multi-peristaltic-pump systems, and flow injections have been used to mix standards and analyte solutions on-line. These approaches were used with atomic absorption [8–10], atomic emission [11], and mass spectrometry [12–14]. However, a major limitation of these methods was the time lag between successive gradient steps and the limited gradient resolution of HPLC pumps. To avoid the addition of foreign reagents, Al-Ammar and Barnes [6] developed an internal standardization method to correct matrix interference by relating the ratios of two spectral-line intensities of the same analyte and matrix concentration. Despite the effectiveness of this method, pre-determination of the matrix concentration and the correction factors are still required. Dilution of the matrix is also commonly used to reduce the magnitude of a matrix effect [5], since the matrix concentration is often directly proportional to the magnitude of the matrix effect [4,15]. Unfortunately, analysis of discrete dilutions is required to obtain a suitable dilution factor where the matrix effects are reduced to an acceptable level. Such analyses are tedious and time-consuming, given the offline sample preparation that is required.

The present study explores an improved sample introduction system that overcomes the drawbacks associated with typical dilution analysis and offers higher accuracy. This method enables both on-line identification and remediation of non-spectral matrix interferences. The method employs a gradient high-performance liquid chromatography (HPLC) pump to perform on-line dilution of a sample solution. Small gradient steps were performed during the analysis and no time lag between steps was observed. Furthermore, the accuracy of the gradient pump was found to be better than 1% with organic-solvent-based ICP analysis, which agrees with the results of a recent study [16] that employed the same pump to perform standard-addition experiments.

Measurement of the intensity ratio of two emission lines (from the same or different elements) as a function of dilution enables detection of the presence of matrix interferences. A constant emission-intensity ratio is observed for samples free of matrix interference. In contrast, for a sample that suffers from interferences, the intensity ratio will change with dilution, as a result of concentration-dependent differences in the effect of the matrix on emission lines with different upper-state energies. A suitable dilution factor to overcome the interference can then be identified as the point on the dilution-dependent intensity-ratio profile where the ratio reaches a constant value. Conveniently, use of a linear gradient dilution enables the time dependence of the ratio to be used directly. The sample can then be diluted on-line and analyzed at a concentration where it is free of the matrix interferences.

Axial-viewing ICP-AES is employed in the current study with *o*-xylene as solvent. The axial-viewing mode offers better detection limits than conventional radial viewing, but is known to be even more prone to matrix effects [17,18]. Organic-solvent based analysis is widely used in the petroleum, pharmaceutical, food and other industries since the wide variety of chemical and physical properties of organic solvents enable dissolution of compounds and liquids beyond those offered with aqueous matrices. Unfortunately, the different chemical and physical properties of organic solvents make these analyses more susceptible to sample-introduction-related matrix interference. Further, plasma-related matrix interferences have been reported in organic-solvent-based ICP analyses and are still not well understood [19]. Accordingly, it is particularly attractive to explore methods to flag and overcome matrix interference in such analytical settings.

2. Experimental

2.1. Instrumentation

The gradient-dilution system is similar to one described earlier [16]. A gradient HPLC pump (Hitachi Ltd. Model L-7100 pump) was used both to perform on-line mixing of samples and to introduce the resulting solutions into the nebulizer. This pump offers a range of mixing ratios from 0–100% in increments of 1%. Both discrete and gradient mixing can be performed, although the present study employed only linear gradients. A flow restrictor (PEEK polymer capillary tubing of 0.08 mm I.D.) was installed at the outlet of the gradient pump to increase pump backpressure and thereby to improve flow stability. Solutions exiting the flow restrictor were directed into a Meinhard nebulizer, and the resultant spray 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 was used in all experiments.

Unless otherwise specified, the ICP operating parameters used in all experiments were as listed in Table 1. A commercial ICP-AES Czerny-Turner spectrometer (Horiba Jobin-Yvon ACTIVA ICP-AES spectrometer, Longjumeau, France) was used. This spectrometer employs a two-dimensional CCD detector that can simultaneously collect spatially resolved emission signals across the entire cross section of the plasma in the axial-viewing mode [20,21], as well as multiple emission lines within a selected spectral window (4 nm to 8 nm, depending upon the grating being used).

2.2. Reagents and solvents

Multielement solutions were prepared by diluting 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, the *o*-xylene solutions contained the same analyte concentrations as the reference solutions, but also contained a few hundred ppm of selected matrix elements. For sample-introduction-related matrix-effect experiments, solutions contained the same concentration of analytes as reference solutions but were dissolved in a 10% toluene, 90% *o*-xylene solvent.

2.3. Experimental procedures

Signals from emission lines of two analytes (or of the same analyte) were collected simultaneously while the matrix-free solution was diluted in a linear gradient. The same exercise was repeated with the matrix-containing sample solution. The intensity ratios of the two lines for both the matrix-free and matrix-containing conditions were then plotted against time. Because linear dilution gradients were used, time on these plots is proportional to dilution factor, in accordance with Eq. (1).

$$\text{Dilution Factor (DF)} = \frac{\text{Total analysis time } (\tau)}{\text{Total analysis time } (\tau) - \text{Time of data collection } (t)} \quad (1)$$

In the absence of a matrix interference, the intensity ratio of the two emission lines will be consistent throughout the gradient dilution, as long as the analyte itself does not appreciably alter the ICP conditions. However, if a matrix interference is present, the signal of one emission line will often differ from that of other emission lines as dilution proceeds, because of the concentration-dependent effect of the matrix on the ICP. In this case, the intensity ratio will vary with dilution. One reason for this behavior is the difference in the matrix effect on lines of different upper-state energies. The dilution-dependent change in intensity ratio can then be used as an indicator for the presence of a matrix interference.

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