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Studies on transport phenomena in electrothermal vaporization sample introduction applied to inductively coupled plasma for optical emission and mass spectrometry

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Abstract

In the present work electrothermal vaporization (ETV) was used in both inductively coupled plasma mass spectrometry (ICP-MS) and optical emission spectrometry (OES) for sample introduction of solution samples. The effect of (Pd+Mg)-nitrate modifier and $CaCl_2$ matrix/modifier of variable amounts were studied on ETV-ICP-MS signals of Cr, Cu, Fe, Mn and Pb and on ETV-ICP-OES signals of Ag, Cd, Co, Cu, Fe, Ga, Mn and Zn. With the use of matrix-free standard solutions the analytical curves were bent to the signal axes (as expected from earlier studies), which was observed in the 20–800 pg mass range by ICP-MS and in the 1–50 ng mass range by ICP-OES detection. The degree of curvature was, however, different with the use of single element and multi-element standards. When applying the noted chemical modifiers (aerosol carriers) in microgram amounts, linear analytical curves were found in the nearly two orders of magnitude mass ranges. Changes of the $CaCl_2$ matrix concentration (loaded amount of 2–10 μg Ca) resulted in less than 5% changes in MS signals of 5 elements (each below 1 ng) and OES signals of 22 analytes (each below 15 ng). Exceptions were Pb (ICP-MS) and Cd (ICP-OES), where the sensitivity increase by Pd+Mg modifier was much larger compared to other elements studied. The general conclusions suggest that quantitative analysis with the use of ETV sample introduction requires matrix matching or matrix replacement by appropriate chemical modifier to the specific concentration ranges of analytes. This is a similar requirement to that claimed also by the most commonly used pneumatic nebulization of solutions, if samples with high matrix concentration are concerned.

Keywords: Electrothermal vaporization; Inductively coupled plasma-mass spectrometry; Inductively coupled plasma-optical emission spectrometry; Sensitivity; Calibration

1. Introduction

Electrothermal vaporization (ETV) is employed as a sample introduction method in inductively coupled plasma mass spectrometry (ICP-MS) [1,2] and optical emission spectrometry (OES) [3]. The sample is disposed on a graphite surface, which is heated until it is vaporized and the aerosol formed by the nucleation–condensation of the vapor is transferred into the plasma excitation–ionization source. Sturgeon and Lam have summarized the benefits and drawbacks of using ETV sample introduction in ICP-MS [4]. Accordingly, the benefits include: (i) a large versatility, as it allows the analysis of liquid and slurry samples, as well as, powdered solids; (ii) small amount of sample is required; and (iii) possibility of in situ sample pretreatment before its introduction into the plasma, which helps in the reduction of spectral and non-spectral matrix interferences. On the other hand, the most characteristic drawback is the changing efficiency of sample introduction for the different analytes

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in the absence of a matrix or a chemical modifier of constant concentration [5,6].

The transport efficiency enhances with increasing amount of the vaporized substance up to a certain limit that results in non-linear calibration curves with matrix-free standard solutions [6–8]. The non-linearity is the most severe for MS signals in the available lowest concentration ranges [7], but it is also significant in higher concentration ranges covered by flame atomic absorption spectrometry (AAS) and ICP-OES methods [6]. A general mechanism has been proposed [9] for the aerosol generation and transport based on nucleation and condensation processes. Transport efficiency studies employing different methods have been published [10–15], and analyte losses have been determined in the sample transporting interface and tubing [16,17]. The role of the ETV design [14,17–19] and the influence of the graphite tube conditions [19–22], with respect of transport efficiency have also been studied. The size distribution of the particles exiting the furnace has been determined [23] and characterized [24]. Several tools have been used for instrument diagnostics and to improve the performance of the ETV in ICP-MS [25,26]. Finally, the use of chemical modifiers has been the subject of several studies in ETV-ICP-MS [7,8,27].

Chemical modification in ETV can involve the improvement in the separation of the analyte and the matrix by selective vaporization [28], thus achieving in-situ enrichment [29,30] or separation of the different chemical forms of the same element for speciation analysis [31,32]. On the other hand, if co-vaporization of the analyte and the modifier takes place in a smaller or larger extent, the effect of the modifier is manifested in the increase of transport efficiency for the analyte(s), i.e., the modifier is applied for yielding a carrier effect.

In the mechanism suggested in connection with nucleation-condensation theory [6–9], the carrier effect is explained by considering that the vapor of the modifier nucleates to a higher extent than the analyte vapor and the latter can physically condense onto the modifier nuclei. Ediger and Beres [7] called this phenomenon a *physical carrier effect*. However, “chemical condensation” can often be the case with complex matrices, when a less volatile compound is formed by a chemical reaction in the vapor phase [6,9]. Therefore, the term *aerosol carrier effect* might be a more general expression [6]. It follows from the above considerations that the way in which the aerosol is transferred from the furnace into the plasma is a rather complex process, which should be considered in explaining the change of analytical signals together with the elimination of the curvature of the calibration graphs.

Literature review shows that several compounds of metals such as Pd, Mg, Ni and Ir and mixtures of them have been used as modifiers [27,32–35], and also the effects of NaCl [7,36,37] and seawater [38] have been investigated. However, no compound has been recommended for universal use as aerosol carrier. On the other hand, spectral interference effects have been considered [39] to a priori preclude the use of certain compounds for this purpose in specific analytical tasks.

The aim of this study is the coupling of the same ETV system alternatively to ICP-MS and ICP-OES instruments in order to cover broad concentration ranges of analytes. The effect of variable amounts of modifier in different analyte mass ranges is studied and the use of multi-element standard solutions versus single-element standard solutions is investigated and discussed.

2. Experimental

2.1. ICP-MS equipment

An Elan 5000 Perkin-Elmer ICP-MS instrument (Perkin-Elmer Sciex, Concord, Ontario, Canada) was used. The data acquisition was made by means of the ICP-MS software, version 2.2. The experimental parameters are shown in Table 1. The ion optics lens settings where adjusted by following the manufacturer’s instructions to provide the optimum signal for ^{103}Rh, with CeO^+/Ce and Ba^{2+}/Ba^+ ratios below 3%. A cross-flow nebulizer coupled to a Ryton double pass spray chamber was employed for the set-up procedure prior to the use of ETV sample introduction.

In ICP-MS, the isotopes measured were those employed according to the manufacturer’s recommendation to check the ETV-ICP-MS system performance. For this purpose, the most abundant Fe isotope, the ^{56}Fe, is selected, although it is interfered by ArO^+ signal if pneumatic nebulization of aqueous solutions is applied for sample introduction. As known, oxygen is produced by the thermal dissociation of water in the ICP. However, this isobaric interference is not relevant to ETV sample introduction method, provided drying of the disposed solutions is performed and the transport line of dry aerosol is free from air penetration. Consequently, by monitoring the ^{56}Fe signal, the operation of the ETV unit can be checked. A background level of 20,000 cps for ^{56}Fe is considered as a maximum for having an acceptable performance of the ETV device, which could easily be accomplished.

Regarding the possibility of polyatomic interference effects, it is also noted that the most abundant isotopes of oxygen and calcium, ^{16}O and ^{40}Ca, can combine to m/z 56 and interfere the detection of the ^{56}Fe isotope when aqueous solution is introduced by pneumatic nebulizer (PN) sample introduction. Also this spectral interference effect can be eliminated with the use of the ETV method, so that the detection of ^{56}Fe in the presence of calcium matrix is feasible (see Section 3.1.3).

2.2. ICP-OES equipment

In the ICP-OES experiments the intensities were obtained with an Optima 3000 DV instrument (Perkin-