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Review

Recent advances in on-line coupling of capillary electrophoresis to atomic absorption and fluorescence spectrometry for speciation analysis and studies of metal–biomolecule interactions

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ABSTRACT

Speciation information is vital for the understanding of the toxicity, mobility and bioavailability of elements in environmental or biological samples. Hyphenating high resolving power of separation techniques and element-selective detectors provides powerful tools for studying speciation of trace elements in environmental and biological systems. During the last five years several novel hybrid techniques based on capillary electrophoresis (CE) and atomic spectrometry have been developed for speciation analysis and metal–biomolecule interaction study in our laboratory. These techniques include CE on-line coupled with atomic fluorescence spectrometry (AFS), chip-CE on-line coupled with AFS, CE on-line coupled with flame heated quartz furnace atomic absorption spectrometry (FHF-AAS), and CE on-line coupled with electrothermal atomic absorption spectrometry (ETAAS). The necessity for the development of these techniques, their interface design, and applications in speciation analysis and metal–biomolecule interaction study are reviewed. The advantages and limitations of the developed hybrid techniques are critically discussed, and further development is also prospected.

Contents

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1. Introduction

Speciation analysis of metal and metalloid elements has become increasingly important due to the fact that the environmental and biological behavior of a given element critically depends on its actual chemical form [1]. In numerous methodologies developed to date for speciation analysis, hybrid approaches are currently preferred for real-sample speciation analysis [1]. The combination of gas chromatography (GC) or high-performance liquid chromatography (HPLC) with atomic spectrometry has been extensively studied and demonstrated to be powerful for speciation analysis [1–3].

The application of capillary electrophoresis (CE) for speciation analysis has been growing rapidly in the past decade [4–6]. Compared with GC or HPLC, CE offers several unique characteristics that make it particularly attractive for elemental speciation analysis, such as high resolving power, minimal reagent consumption, rapid and low cost analyses, and the possibility of separations with only minor disturbances of the existing equilibrium between the different species [4–9]. However, on-column detection in CE with commercially available UV or fluorescence detector for speciation analysis possesses inherent drawbacks, such as poor detection limits and interference of coexisting species with the same mobility. Since most metal species are UV transparent and have no native fluorescence, a precolumn derivatization step is required before direct UV or fluorescence detection.

When CE is coupled with an element-selective detector, only different forms of a particular element of interest need to be separated from each other. Since Olesik et al. [10] first proposed the idea of interfacing CE with inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) for elemental speciation analysis, many reports on the hyphenation of CE with ICP-AES and ICP-MS for elemental speciation analysis have been published [8–23]. The combination of CE with ICP-MS becomes of growing importance in the field as it promises substantial improvements in sensitivity and in the identification and quantification of multi-species systems.However, the high instrumental and operational costs of these ICP-based techniques and their requirement for well-trained analysts certainly limit their wide applications for speciation analysis in routine laboratory. Thus, it is imperative to develop simple, cost-effective and sensitive methodologies using easily available/constructed instruments for studies of metal speciation and metal–biomolecule interactions.

During the last five years several simple, cost-effective and sensitive hybrid techniques have been developed in our laboratory by coupling CE to volatile species generation–atomic fluorescence spectrometry (VSG–AFS), flame heated quartz furnace atomic absorption spectrometry (FHF-AAS) and electrothermal atomic absorption spectrometry (ETAAS) for speciation analysis and metal–biomolecule interaction study [24–33]. In this paper we attempt to give an overview on these hybrid techniques in respect of interface design, analytical performance and applications in speciation analysis and metal–biomolecule interaction study.

2. On-line coupling of CE or chip-CE with AFS via volatile species generation (VSG)

VSG–AFS alone or in combination with HPLC and GC has been extensively explored for sensitive and selective determination and speciation analysis of hydride-forming elements and mercury due to its low instrument setup and operational costs, short warm-up time, good precision, easy operation and robustness. In principle, the marriage of VSG–AFS to CE should be promising for element speciation analysis due to the combined advantages of these two techniques. However, the combination of VSG–AFS with relatively new separation technique CE had been ignored for a long time until we reported their hyphenation for speciation analysis of arsenic in 2002 [24].