

Field-amplified sample injection and in-capillary derivatization for capillary electrophoretic analysis of metal ions in local wines

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Abstract

In-capillary derivatization and field-amplified sample injection (FASI) coupled to capillary zone electrophoresis (CZE) was evaluated for the analysis of metals (Co(II), Cu(II), Ni(II), and Fe(II)) using 2-(5-Nitro-2-Pyridylazo)-5-(*N*-Propyl-*N*-Sulfopropylamino)Phenol (Nitro-PAPS) as the derivatizing agent. For FASI, the optimum conditions were water as sample solvent, 1 s hydrodynamic injection (0.1 psi) of a water plug, 5 s of electrokinetic introduction (10 kV) of the sample. The in-capillary derivatization was successfully achieved with zone-passing strategy in order tandem injection of Nitro-PAPS reagent (0.5 psi, 7 s), a small water plug (0.1 psi, 1 s), and metal ion introduction (10 kV, 5 s). The solution of 45 mmol L⁻¹ borate pH 9.7 and 1.0 × 10⁻⁵ mol L⁻¹ Nitro-PAPS containing 20% acetonitrile was used as the running buffer. The limit of detection obtained by the proposed method was lower than those from pre-capillary derivatization about 3–28 times. The recovery of the method was comparable to pre-capillary derivatization method. In-capillary derivatization-FASI-CZE was applied to analysis of metals in wine samples. The results were compared with those obtained by CZE with pre-capillary derivatization method and atomic absorption spectrometry (AAS).

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1. Introduction

The analysis of heavy metals in a range of substances is of considerable interest due to potential human toxicities. There is increasing demand for simple and reliable methods for the simultaneous detection of several metal ions with low detection limits and low sample/reagent consumption. Atomic absorption spectrometry (AAS) is the most widely used method for metal analysis but simultaneous multi-element analysis is not possible. Inductively coupled plasma atomic emission spectrometry (ICP-AES) is capable of multi-element analysis, but the instrumentation is relatively expensive. The simultaneous determination of metal ions with conventional high performance liquid chromatography (HPLC) and ion chromatography (IC) have several disadvantages, such as long analysis times and consumption of large volumes of reagents. Recently, capillary

electrophoresis (CE) has been shown to be a powerful separation technique for the analysis of metals in a wide variety of sample matrices [1–8] because of the significant advantages of resolution, speed, simplicity and lower sample/reagent consumption. The electrophoretic determination of metals can be easily achieved by indirect detection through the addition of appropriate species to the background electrolyte to produce UV-absorbing species [9,10], but the number of appropriate compounds for this environment is limited. The pyridylazo reagent, 2-(5-Nitro-2-Pyridylazo)-5-(*N*-Propyl-*N*-Sulfopropylamino) Phenol (Nitro-PAPS) is a synthesized chromogenic reagent which forms water-soluble chelates with giving high molar absorptivities of ca. 10⁴–10⁵ L mol⁻¹ cm⁻¹ [11–13]. Nitro-PAPS has been used as a chromogenic reagent in various analytical techniques for the determination of various metal ions. Flow-injection spectrophotometry for the determination of Fe(II) in purified salts [13] and the trace analysis of V(V) in river water [14] using Nitro-PAPS have been demonstrated. The HPLC-based determination of Cu(II), Co(II), Ni(II) and Fe(II) in rain and river waters using Nitro-PAPS has

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been reported [11]. The use of Nitro-PAPS chelates incorporating pre-capillary derivatization in CE for the determination of trace metal impurities in nickel and iron salts has been described [15].

In CE, derivatization has been accomplished by either pre-capillary [16,17], post-capillary [18] and in-capillary [1,2,19–21] methods. Pre-capillary derivatization requires large amounts of derivatization ligand, whereas post-capillary derivatization requires significant post-capillary hardware modification, and loss of efficiency during separation and peak broadening has been noted [18,22,23]. The increased popularity of in-capillary derivatization takes advantage of the fact that there is minimal sample dilution compared to pre-capillary and post-capillary derivatization. In-capillary derivatization can be performed by three modes: zone-passing, at-inlet and throughout-capillary [24–26]. Among these strategies, zone-passing is appropriate for the Nitro-PAPS derivatization since the formation of the metal complex occurs within seconds.

In order to increase the sensitivity of detection in CE, the on-line preconcentration methods have been developed with different strategies, such as large volume sample stacking [27], sweeping [28], dynamic pH junction-sweeping [29], and field-amplified sample injection (FASI) [8,30–35]. FASI is very popular since it is quite simple, requiring only the electrokinetic injection of the sample after the introduction of a small plug of high-resistivity solvent (mainly water). In FASI, samples are normally prepared in a low conductivity buffer and injected electrokinetically into a capillary containing a high-conductivity running buffer.

In this work, the feasibility of combining FASI with in-capillary derivatization of metal ions (Co(II), Cu(II), Ni(II), and Fe(II)) with Nitro-PAPS before their analysis by capillary zone electrophoresis (CZE) is demonstrated. The combination of electrokinetic injection and water or organic solvent field-amplified sample stacking is investigated. Studies of effects of diluents (aqueous versus organic) on the stacking by the electroinjection under FASI are performed. Finally, in-capillary derivatization-FASI-CZE is applied to the analysis of these metal ions in local wine samples.

2. Materials and methods

2.1. Chemicals and reagents

All the reagents used in this work were of analytical reagent grade. Nitro-PAPS was obtained from Dojindo (Japan). A 1×10^{-3} mol L⁻¹ stock solution of Nitro-PAPS was prepared in deionized water. The 1000 mg L⁻¹ stock atomic absorption standard solutions of metal ions including Co(II), Cu(II), Ni(II) and Fe(II), was purchased from Ajax Finechem (Australia). The working solutions of each metal were daily prepared in deionized water except for Fe(II) was prepared in acidic medium of HCl (1% v/v). Sodium tetraborate was purchased from Univar-Ajak (Australia). Water for preparation of samples and buffer solution was the deionized water obtained from a RiO_sTM Type I Simplicity 185 (Millipore-Waters, U.S.A.) with the resistivity of 18.2 MΩ cm.

2.2. Instrumentation

Experiments were performed on a Beckman P/ACE MDQ capillary electrophoresis instrument (Fullerton, CA, U.S.A.) equipped with a photodiode array detection system. The 32 Karat software version 5.0 (Beckman) was used for instrument control, data acquisition and data analyses. Electrophoretic separations were carried out using uncoated fused-silica capillaries (Beckman) with a total length of 60.2 cm (50.0 cm effective length) and 75 μm I.D. On-capillary detections were performed at either selected wavelengths (200, 214, 250 and 570 nm) or in the scanning mode (190–600 nm). All CZE experiments were thermostated at 25 °C.

A Perkin-Elmer Instruments AAnalyst 100 atomic absorption spectrometer (U.S.A.) equipped with Perkin-Elmer single element hollow cathode lamps and an air-acetylene flame with air and acetylene flow rates of 10 and 3 mL min⁻¹ was used for the determination of metals. The wavelengths (nm) selected for the determination of the analytes were as follows: Co 240.7, Cu 324.8, Ni 232.0, and Fe 248.3.

2.3. Pre-capillary derivatization (as a reference method)

The working solutions of metal ions were mixed with Nitro-PAPS solution (1×10^{-3} mol L⁻¹) in the mole ratio of ligand: metal of 2:1 at pH 6.0 at room temperature. The sample solution was introduced into the electrophoretic system by hydrodynamic injection at 0.5 psi (1 psi=6895 Pa) for 5 s before separation. The absorbance was detected at 250 nm.

2.4. In-capillary derivatization and FASI

In-capillary derivatization of metals and Nitro-PAPS was performed by zone-passing option in the tandem mode. Briefly, the capillary was first filled with the carrier electrolyte and then a plug of Nitro-PAPS solution was introduced at 0.5 psi for 7 s. After that, FASI was performed by an introduction of a small water plug (0.5 psi, 1 s) and then the sample was introduced into the capillary with electrokinetic injection at 10 kV for 5 s. Subsequently, the separation voltage of 20 kV was applied through the capillary and the on-line reaction occurred inside the capillary when the metals mixed with the Nitro-PAPS. The complexing reaction occurs during the separation to obtain the corresponding metal-Nitro-PAPS chelates and subjected to spectrometric detection.

2.5. Electrophoretic separation

Prior to use, all new capillaries were initially pretreated with the following cycles: methanol, 0.1 mol L⁻¹ HCl and 0.1 mol L⁻¹ NaOH for 10 min each and deionized water for 5 min between each rinse and finally equilibrated with the buffer solution for 10 min before applying voltage of 10 kV across the capillary for 5 min. To maintain reproducible migration times, the capillary was pre-conditioned with the running buffer for 3 min before each run. After completing the separation session, the capillary was flushed with 0.1 mol L⁻¹

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