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Technical Note

Micro-electrodeposition in the presence of ionic liquid for the preconcentration of trace amounts of Fe, Co, Ni and Zn from aqueous samples

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ABSTRACT

The paper presents the preconcentration of trace elements via electrodeposition onto a (micro)aluminum cathode in the presence of ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆] as a supporting electrolyte. The advantages of the proposed method include very simple instrumentation for the preconcentration of trace elements and low-cost reagents. The experiment showed that the use of ionic liquid in the electrodeposition process significantly improves sensitivity, recovery and detection limits for the determination of trace amounts of iron, cobalt, nickel and zinc. The preconcentrated metals were determined using X-ray fluorescence spectrometry. The optimum parameters for electrodeposition such as pH, the volume of the analyzed solution, the voltage and the deposition time were studied. Under the optimized conditions, the detection limits were 5, 2, 3 and 6 μg L⁻¹ for iron, cobalt, nickel and zinc, respectively. The precision and recovery of the method were in the range of 3–5.5%, and 92–103%, respectively. The calibration was performed using aqueous standards of Fe(III), Co(II), Ni(II) and Zn(II) in the range 0.01–0.25 mg L⁻¹. The method was applied successfully in water analysis.

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1. Introduction

Some of the convenient techniques for the determination of trace elements include inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry, atomic absorption spectrometry (AAS) and total reflection X-ray fluorescence spectrometry (TXRF). However, the use of these techniques is restricted, not only by inadequate sensitivity in the determination of ultratrace elements, but also by matrix interferences. The preconcentration and separation of trace analytes from the interfering matrices could solve these problems. Commonly used preconcentration methods include liquid–liquid extraction [1] and solid phase extraction [2,3]. A lot of papers are now devoted to preconcentration methods on a microscale such as liquid–liquid and solid-phase microextractions [4,5]. These methods are usually combined with electrothermal atomic absorption spectrometry (ETAAS), but papers devoted to combination with TXRF [6] and micro-XRF [7] have also been published recently. Electrodeposition (ED) is an alternative sample preparation method for many techniques. Knápek et al. [8] showed that laser evaporation/ablation of heavy metals preconcentrated on the surface of an electrode provides applicable and reliable analytical results. Using electrodeposition high saline matrix samples (e.g. seawater) can be analyzed,

where as direct nebulization of a sample in ICP-AES is difficult or impossible. Najafi et al. [9] developed the combination of electrodeposition with arc atomic emission spectrometry (ED–arc AES). The results showed that the sensitivity and detection limits were improved 1000–2000-fold over those of conventional arc AES in the determination of Ni, Cr and Pb. They also showed that the combined ED–arc AES had progressed substantially toward the ultimate goal of the direct interference-free determination of trace elements in complex samples. Komarek et al. [10] proposed electrodeposition on a graphite ridge probe as a preconcentration and matrix separation procedure prior to ETAAS determination. The method was used for the determination of trace metals in seawater. Optimum conditions for the electrodeposition of Cu, Cd, Pb, Ni, Cr and Cr were examined. Chen et al. [11,12] described the electrodeposition enrichment method useful for sensitive determination of toxic heavy metals in natural water by laser induced breakdown spectroscopy (LIBS). Trace heavy metals were electrodeposited on the surface of a polished high purity aluminum plate and then quantitatively analyzed by LIBS. It was demonstrated that the electrodeposition method significantly enhanced the sensitivity for Cr, Mn, Cu, Zn, Cd and Pb by preconcentration and elimination of water matrix interference. The limits of detection improved by 5–6 orders of magnitude compared to when aqueous solutions were directly analyzed by LIBS. The electrodeposition is a useful tool for the determination of elements by XRF and particularly by TXRF. The deposited elements may be directly measured by XRF and TXRF without any further sample preparation step. Moreover, the homogeneous thin layer of the

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analytes is an ideal sample form for TXRF, because scattered radiation from the sample itself is significantly minimized. Ritschel et al. [13] proposed the electrodeposition of mercury onto a solid, polished disk of pure niobium which was also used as sample carrier for the TXRF measurement. Griesel et al. [14] constructed a special electrode tip as a holder for the TXRF sample carrier, which consisted of polished glassy carbon. In this way, several elements such as Cr, Mn, Fe, Co, Ni, Cu, Zn, Ag, Cd, Pb, As and U were preconcentrated and then determined simultaneously in saline matrix. A special holder for a copper electrode was also constructed to perform the determination of Te, Bi, Ni, Sb, and Au in anode slime [15]. After the electrolysis, the copper electrode was easily removed from the holder and analyzed by wavelength-dispersive XRF. The proposed trace elements preconcentration method provided suitable samples which were devoid of the negative and undesirable effects of the XRF analysis, such as particle size and matrix effects. Some papers are devoted to electrodeposition performed at microscale combined with ETAAS [16,17].

Ionic liquids are known as “green alternatives” to conventional solvents in a variety of applications. Fascinating properties including low volatility, tunable viscosity and miscibility, as well as electrolytic conductivity make ionic liquids unique and useful for many applications. Ionic liquids are frequently used as solvents in synthetic applications, catalysis, electrochemistry, and analytical chemistry [18]. In the area of analytical chemistry ionic liquids have been applied in liquid–liquid extraction of various compounds, such as metal ions [19], small organic molecules [20] and biological compounds [21]. Nevertheless, using ionic liquid liquids in the microextraction techniques i.e., liquid phase microextraction [22], single-drop microextraction [23], dispersive liquid–liquid microextraction [24] and solid-phase microextraction has been considered as a breakthrough in analytical application.

In this study ionic liquid has been applied to improve the efficiency of the electrodeposition technique. This novel modification has been used in order to preconcentrate trace amounts of Fe(III), Co(II), Ni(II) and Zn(II) before the analysis by energy-dispersive X-ray fluorescence spectrometry (EDXRF).

2. Experimental

2.1. Instrumentation

A laboratory-constructed EDXRF spectrometer has been used. An air-cooled side-window Rh target X-ray tube of ca. 100 μm nominal focal spot size (XTF 5011/75, Oxford Instruments, USA) supplied by an XLG high-voltage generator (Spellman, USA) was used as the excitation source. The X-ray tube was operated at 45 kV and 1200 μA . The X-ray spectra emitted by the sample were collected using a thermoelectrically cooled Si-PIN detector (XR-100CR Amptek, Bedford, MA, USA) with a 145 eV resolution at 5.9 keV that was coupled to a multichannel analyzer (PX4 Amptek, Bedford, MA, USA). The spectrometer is described in detail in Ref. [25]

An atomic emission spectrometer, ICP model M (Spectro Analytical Instruments, Germany) with sequential spectrometer was used with the following parameters: frequency – 27.12 MHz, RF output power – 1.1 kW, coolant gas – Ar, 14 L/min, auxiliary gas – Ar, 0.5 L/min, nebulizer gas – Ar, 1 L/min, observation height – 11 mm, nebulizer – concentric type Meinhard, monochromator with 2400 lines/mm, grating, sample uptake rate – 1 mL/min, wavelength – Fe 259.94 nm, Co 228.62 nm, Ni 221.65 nm, and Zn 213.86 nm.

2.2. Reagents and materials

Stock solutions (1 g L⁻¹ of Fe(III), Co(II), Ni(II) and Zn(II) (as nitrates)), nitric acid (65%, Suprapur®), sodium hydroxide solution

and ionic liquid: 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆] were purchased from Merck (Darmstadt, Germany), aluminum foil was purchased from Aldrich (St. Louis, USA). The pH of the analyzed solutions was adjusted with 0.1 mol L⁻¹ HNO₃ and 0.1 mol L⁻¹ NaOH. A standard solution (100 mg L⁻¹ of Fe(III), Co(II), Ni(II) and Zn(II)) was prepared from the stock solutions (1 g L⁻¹) by diluting with high purity water obtained from the Milli-Q system.

2.3. Sample preparation

The analytical procedure consisted of four steps:

The preparation of electrodes. A platinum wire and aluminum foil of 20 μm thickness were used as anode and cathode, respectively. The aluminum foil was placed between two pieces of adhesive tape as shown in Fig. 1. A circular hole had been punched in one piece of the adhesive tape, so the electrodeposition took place only on the round-shaped area of the aluminum cathode revealed by the opening. A circular cathode of a 5 mm diameter was used in our research. When direct XRF analysis of the cathode is possible and electrodeposition of analytes is quantitative, the combination of these two techniques seems a particularly convenient tool for multielement trace analysis. The advantages of the proposed preparation of cathode include the following: the proposed construction is easy and quick to make; the used tape is durable, stable, water and acid-proof; cutting out an opening in the tape is easy so any expected size and shape of the cathode can be easily achieved; a lot of different materials e.g. copper and silver foils, can be used as cathode material.

The preparation of analyte solutions. 1 mL of 10 mg L⁻¹ multi-elemental solution of Fe(III), Co(II), Ni(II) and Zn(II), and 50 μL of [BMIM][PF₆] were introduced into 50 mL of distilled water. pH of sample solution was adjusted at 7 by 0.1 mol L⁻¹ HNO₃ and 0.1 mol L⁻¹ NaOH.

The electrolysis process. The electrodes were immersed in the analyte solution. The distance between the anode and the cathode was 20 mm. During the electrolysis the solution was stirred with a magnetic stirrer. The electrodeposition was performed at 6 V during 15 min.

The XRF determination. The cathode with electrodeposited elements was rinsed with water in order to remove the residue of the electrolyte. Then, the dried electrode with the deposit was measured by XRF. The aluminum electrode is suitable for XRF measurements because of the lack of overlapping of K α and K β lines with analyte lines.

2.4. The preparation of water samples

The water samples were collected from an industrial district of Poland. The samples were filtered through a membrane filter (0.45 μm pore size, Millipore) and acidified with nitric acid. Fe(III), Co(II), Ni(II) and Zn(II) were electrodeposited in the presence of [BMIM][PF₆] from 100 mL of water of pH adjusted to 7.

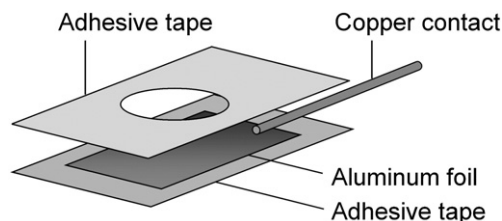


Fig. 1. The scheme of cathode construction.

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