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ORIGINAL ARTICLE

Development of an in situ solvent formation microextraction and preconcentration method based on ionic liquids for the determination of trace cobalt (II) in water samples by flame atomic absorption spectrometry

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Abstract A simple in situ solvent formation microextraction (ISFME) methodology based on the application of ionic liquid (IL) as an extractant solvent and sodium hexafluorophosphate ($NaPF_6$) as an ion-pairing agent was proposed for the preconcentration of the trace levels of cobalt ions. In this method cobalt was complexed with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) and extracted into an ionic liquid phase. After phase separation, the enriched analyte in the final solution is determined by flame atomic absorption spectrometry (FAAS). Some effective factors that influence the microextraction efficiency were investigated and optimized. Under the optimum experimental conditions, the limit of detection and the enrichment factor were 0.97 $\mu g\ L^{-1}$ and 50, respectively. The relative standard deviation (R.S.D.) was obtained as 2.4%. The proposed method was assessed through the analysis of certified reference water and recovery experiments.

1. Introduction

Cobalt is an important element, not only for industry but also for biological systems. The toxicity of cobalt is low and it is considered as an essential element, which is required in the normal human diet in the form of vitamin B_{12} (cyanocobalamin). For this reason, cobalt has been used in the treatment of anemia (Underwood, 1971). However, the ingestion or inhalation of large doses of this analyte may lead to toxic effects (Bratter and Schramel, 1980; Tsalev and Zaprianov, 1983). Since one of the routes of incorporation of cobalt into the human body is by ingestion (Seiler et al., 1994), its determination in drinking water becomes important. Cobalt concentration levels are very low in water samples, and therefore sensitive analytical techniques are required to carry out its detection.

In spite of great improvements in the sensitivity and selectivity of modern instrumental analyses such as ICP-MS, ICP-OES and electrothermal atomic absorption spectrometry

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(ETAAS), difficulties still lie in the analysis of trace heavy metals because of both their low abundance levels in the samples and the high complexity of the sample matrices (Abulhassani et al., 2010).

Separation and preconcentration procedures are of great importance in the elemental analysis as they eliminate or minimize matrix effects and concomitants, lowering the detection limit and enhancing the sensitivity of detection techniques toward metals and their species. Solvent extraction of metal cations is a very important technique for their mutual separation and preconcentration (Alegret, 1998; Rydberg et al., 2004). In solvent extraction, generally, various hydrophobic solvents are used as extraction phase solvents. However, most of the solvents are toxic, flammable and volatile, and it has been recommended that their use should be avoided. The demand to reduce solvent volumes and to avoid using toxic organic solvents in liquid–liquid extraction (LLE) has led to substantial efforts in adapting existing sample-preparation methods to the development of new approaches. Within these approaches, an important effort has been shifted to the development of microextraction procedures, mainly characterized for eliminating or minimizing the consumption of organic solvents commonly employed in conventional extraction methods. For this purpose, several microextraction methods, such as liquid-phase microextraction (LPME) (Pena-Pereira et al., 2010), dispersive liquid–liquid microextraction (DLLME) (Zgola-Grzeskowiak and Grzeskowiak, 2011), etc., have been developed to miniaturize the LLE procedure and to reduce the amount of organic solvent. In these procedures, however, the use of toxic solvents, such as benzene, toluene or chloroform, as the extraction phase is a common practice.

Recently, considerable interest has been raised by the use of ionic liquids (ILs) as attractive green solvents in microextraction methods, because of their unique chemical and physical properties. Ionic liquids (ILs) are salts with melting points below 100 °C, typically consisting of nitrogen-containing organic cations such as 1-alkyl-3-methylimidazolium or *N*-alkylpyridinium together with an inorganic or organic anion commonly containing fluorine, for example, BF_4^-, PF_6^-, CF_3COO^-, SbF_6^-, or $(CF_3SO_2)_2N^-$ (Wasserscheid and Welton, 2003). ILs are being recently considered as replacement solvents in sample preparations, because of their unique chemical and physical properties such as negligible vapor pressure, non-flammability, good extractability for various organic compounds and metal ions as neutral or charged complexes, as well as tunable viscosity and miscibility with water and organic solvents which make their use very attractive in separation processes (Dadfarnia et al., 2010; Greaves and Drummond 2008; Liu et al., 2009; Marsh et al., 2004; Pandey, 2006; Soylak and Yilmaz, 2011; Sun et al., 2010). Furthermore, the high interest is also due to the capability of ILs to form a wider range of intermolecular interactions than typical volatile organic solvents. This includes interactions of the following type: strong and weak ionic, hydrogen bonding, van der waals, dispersive, n–π and π–π interactions (Luczak et al., 2008).

In 2009, Baghdadi and Shemirani developed a novel microextraction technique as a high performance and powerful preconcentration method termed in situ solvent formation microextraction (ISFME) (Baghdadi and Shemirani, 2009). The approach is based on the dissolution of a hydrophilic IL in an aqueous solution containing the analytes of interest, followed by the addition of an ion-exchange reagent which undergoes an in situ metathesis reaction forming an insoluble IL. Thus, analytes are extracted and preconcentrated once the IL is insolubilized. There is no interface between the aqueous media and the extraction phase. Thus, mass transfer from aqueous media into IL has no significant effect on the performance of the extraction method. ISFME is a simple and efficient method for the separation and preconcentration of metal ions from aqueous solutions with high ionic strength. The approach has been applied to the determination of metals (Baghdadi and Shemirani, 2009; Mahpishanian and Shemirani, 2010; Vaezzadeh et al., 2010; Zeeb et al., 2011).

In the present work, we have developed a simple, rapid, sensitive and highly selective in situ solvent formation microextraction method for the trace determination of cobalt in various water samples using 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) as the complexing agent by FAAS.

2. Experimental

2.1. Instrumentation

A PG-990 (PG instrument Ltd., United Kingdom) atomic absorption spectrometer equipped with deuterium background correction and cobalt hollow cathode lamp was used for the determination of cobalt at a wavelength of 240.7 nm. The instrumental parameters were adjusted according to the manufacturer's recommendations and the absorbance signal was measured according to the peak height in continuous aspiration mode. A Hettich centrifuge (Model Universal 320R, Germany) was used for centrifuging. The pH values were measured with a Metrohm pH-meter (model: 827) supplied with a glass-combination electrode.

2.2. Reagents and solutions

All reagents used were of analytical reagent grade. Doubly distilled water was used throughout the experiment. A 1000.0 mg L^{-1} stock standard solution of Co (II) was prepared from pure Co $(NO_3)_2$. 6 H_2O (Merck, Darmstadt, Germany). Before the investigations, working standard solutions were obtained by appropriate stepwise dilution of the stock standard solutions. The all standard solution for calibration FAAS instrument was prepared in ethanol.

A 0.010 mol L^{-1} solution of 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) (Sigma–Aldrich, USA) was prepared in pure ethanol. 1-Hexyl-3-methylimidazolium tetrafluoroborate ([Hmim][BF_4]), ethanol and sodium chloride were purchased from Merck (Darmstadt, Germany). Sodium hexafluorophosphate ($NaPF_6$) was purchased from ACROS (Geel, Belgium).

Pipettes and vessels used for trace analysis were stored in 10% nitric acid for at least 24 h and washed four times with doubly distilled water before use.

2.3. ISFME procedure

50 mL sample or standard solution containing Co^{2+} in the concentration range of 5–100 μg L^{-1} and 2.0×10^{-4} mol L^{-1} 5-Br-PADAP was adjusted to pH 3.0 (±0.2) and was poured in a screw cap conical-bottom glass centrifuge tube. 150.0 μL

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