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Preconcentration of trace multi-elements in water samples using Dowex 50W-x8 and Chelex-100 resins prior to their determination using inductively coupled plasma atomic emission spectrometry (ICP-OES)

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A B S T R A C T

This work presents a solid phase extraction (SPE) method for simultaneous preconcentration of trace elements in water samples prior to their ICP-OES determination. Dowex 50W-x8 and Chelex-100 resins were used as SPE sorbent materials for preconcentration of trace Cd, Co, Cr, Cu, Fe, Ni, Pb and Zn. The optimum sample pH, eluent concentration and sample flow rates were found to 6, 3.0 mol L^{-1} and 3.0 mL min^{-1}, respectively. In terms of multi-element preconcentration capabilities, Dowex 50W-x8 appeared to be a better sorbent. The recoveries for all the tested analytes were >95%. However, Chelex-100 showed a better performance in terms of recovery (>95%) towards Cu, Fe and Zn. Under optimized conditions using Dowex 50W-x8, the relative standard deviations for different metals were <3%. The limits of detection and limits of quantification ranged from 0.01–0.39 μg L^{-1} and 0.05–0.1.3 μg L^{-1}, respectively. The accuracy of the preconcentration method was confirmed by spike recovery test and the analysis of certified reference materials. The SPE method was applied for preconcentration of the analyte ions in tap water, bottled water and wastewater samples.

1. Introduction

Monitoring of trace metals in environmental samples is crucial since most of these metals have negative or positive effects on human health even at very low concentrations not easily detectable with standard techniques (Tufekci et al., 2012; Kazi et al., 2009). Even though some of the metals such as Co, Cr, Cu, Fe, Ni and Zn have a range of biochemical functions in living organisms, they still can be toxic when taken in excess (Tufekci et al., 2012). In contrast, the presence of non-essential metals such as lead and cadmium, even in trace levels, damages central nervous functions, lowers energy levels, damages the blood composition, lung, kidneys, liver, and other vital organs (Tufekci et al., 2012; Afridi et al., 2006). Therefore, monitoring of trace elements in the environment is extremely important because it helps to control exposure of humans and animals to these substances (dos Santos Silva et al., 2012).

Due to the high toxicity of heavy metals, it is crucial to detect ultra-low levels especially in drinking water. The determination of metal ions in water samples has been successfully carried out with different analytical techniques (Soylak, 2004; Tuzen et al., 2005). These include flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS) (Soylak, 2004; Komjarova and Blust, 2006; Bezerra et al., 2007). Among the above mentioned analytical techniques, ICP-OES is extensively used for the determination of metal ions. This is because ICP-OES displays attractive features such as multi-element detection capacity, wide linear range, low limits of detection and high sample throughput (Xiong et al., 2010). However, ICP-OES is not suitable for direct analysis of extremely low metal levels. In addition, it suffers from matrix interferences. Therefore, prior to detection with ICP-OES an effective pre-concentration step such as solid phase extraction (SPE) is required. The latter is a widely applied and powerful pre-treatment approach prior to analysis (Hennion, 1999). Among other advantages, SPE is commonly used because a variety of extraction materials (sorbents) are available, and the extraction can be tuned depending on how these sorbents interact with the analytes. As a result, various adsorbents such as Amberlite XAD resins (Ramesh et al., 2002; Elci et al., 2000; Narin et al., 2003; Malla et al., 2002), Chelex-100 (Soylak, 2004), Chemisorb 108 (Tuzen et al., 2005) and Dowex 50W-x4 (Pohl and Prusisz, 2004), among others, have been used for the separation/pre-concentration of trace elements in various complex samples.

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The present study seeks to determine the most suitable cation exchange resin that will have high metal retention efficiency over a wide operating pH range. Therefore, performance of Chelex-100 and Dowex 50W-x8 sorbents for simultaneous pre-concentration of cadmium, cobalt, chromium, copper, iron, nickel, lead and zinc in aqueous solutions was investigated. Various factors affecting the cation exchange process, such as sample volume, concentration of the eluent, sample and eluent flow rates as well as the accuracy of the method, were investigated.

2. Experimental

2.1. Instrumentation

Analyte metal ions were determined using Spetro Arcos ICP-OES equipped with Cetac ASX-520 autosampler. Solid phase extraction was carried out in a VacMaster-24 sample SPE station (Supelco, PA, USA). The latter was used to control the sample loading and elution flow rate to 3.0 mL min^{-1}.

2.2. Reagents and solutions

All reagents were of analytical reagent grade unless otherwise stated and Millipore water was used throughout the experiments. Spectrascan stock solutions (1000 mg L^{-1}) of Cd, Co, Cr, Cu, Fe, Ni, Pb and Zn (Teknolab A/S, Dröbak, Norway) were used to prepare the working solutions for SPE at concentrations of 6 μg L^{-1} (Cr, Co, Ni), 10 μg L^{-1} (Cd), 12 μg L^{-1} (Pb), 30 μg L^{-1} (Cu, Fe and Zn). Working solutions, as per the experimental requirements, were freshly prepared from the stock solution for each experimental run. A Spectrascan multi-element standard solution at concentration of 100 mg L^{-1} was used to prepare working standard solutions at concentrations of 10–70 μg L^{-1} for Cd, Co, Cr, Fe, Ni and Pb; and 30–180 μg L^{-1} for Cu and Zn in measurements of concentrations of analytes in all model and sample solutions. Solutions of nitric acid at concentrations of 0.5, 1.0, 2.0, 3.0 and 4.0 mol L^{-1} used for the elution of the analytes from the column were prepared from ultrapure concentrated acid (65%, Sigma–Aldrich, St. Loius, MO, USA). The pH adjustments were performed with 1.0 M HNO_3 and NaOH solutions. The cation exchangers used in this study as packing materials were Chelex-100 and Dowex 50W-x8 (sodium forms) purchased from Sigma Aldrich (St. Loius, MO, USA).

2.3. Water samples and preparation

Tap water samples were obtained from University of Johannesburg (Doornfotein and Kingsway campuses). Effluent wastewater samples were collected from Johannesburg Water. The wastewater samples were filtered through a 0.45 μm pore-size Millipore cellulose nitrate membrane to remove any fine particulate matter present. Bottled water samples were obtained from a local supermarket.

2.4. Column preparation

Supelco polyethylene columns (1.35 cm in diameter and 6.5 cm in length) with frits were employed for SPE. The columns were soaked in 5% HNO_3 solution and then rinsed successively with Millipore water. Afterwards, slurries of 1.5 g of Chelex-100 or Dowex 50W-x8 resin in Millipore water were loaded into the columns. A porous frit was placed at the bottom of the column and at the top of the packing material to hold and confine the adsorbent within the designated capacity/volume. The resin columns were washed using triple distilled water followed by conditioning with 10 mL ammonium acetate buffer (1.0 mol L^{-1}, pH 9.0). After each use, the resin in the column was washed with 20 mL of water followed by 10 mL of 1.0 mol L^{-1} NaOH. This was done in order to keep the resin in sodium form.

2.5. Preconcentration procedure

The pH values of the model solutions of Cd, Co, Cr, Cu, Fe, Ni, Pb and Zn were adjusted to 6. The solutions were then each passed through a SPE column packed with either Chelex-100 or Dowex 50W-x8 at a flow rate of 2.0 and 3.0 mL min^{-1}, respectively. Metal ions retained on the resins were eluted with 5.0 mL of HNO_3 at a flow rate of 3.0 mL min^{-1}. The metal concentrations in the final solution were determined using ICP-OES. The same procedure was applied to the blank solutions. After each run, the columns were conditioned as per Section 2.3.

2.6. Optimization of preconcentration parameters

The SPE system was optimized in order to determine the best retention/ elution conditions for trace metal ion determination with good sensitivity and precision (Soylak, 2004). Several experimental variables affecting the pre-concentration system such as eluent concentrations, sample and eluent flow rates, among other parameters, were evaluated and optimized. To obtain these conditions, preliminary tests were performed to investigate factors that exert significant influence on the retention of the analytes by cation exchange resin. The factors selected include eluent concentration, sample volume as well as sample flow rate. In previous study (Soylak, 2004), the maximum retention of the analytes onto the cation exchange resin was observed at pH 6. We decided to use the same pH value at 6 in the present study, for all the experiments.

The optimization of the sample flow rate was carried out to ensure the quantitative retention of the analytes of interest. The effect of flow rate of the sample solution on the retention of the studied metal ions on the Chelex-100 and Dowex 50W-x8 resins was carried out with a column packed with 1.5 g of resin. Sample solutions were passed through the column at various flow rates (1.0–5.0 mL min^{-1}). The flow rates less than 1.0 mL min^{-1} were not studied to avoid long analysis time.

3. Results and discussion

The SPE system was optimized in order to determine the best retention/elution conditions for trace metal ion determination with good sensitivity and precision (Soylak, 2004). Several experimental variables affecting the pre-concentration system, such as eluent concentrations, sample and eluent flow rates, among other parameters, were evaluated and optimized. The percentage recoveries were calculated by relating the final obtained concentration (C_f) of the analyte to the original concentration (C_i) of the metal ion in the model solution.

3.1. Effect of pH

The sample pH for quantitative preconcentration of Cd, Co, Cr, Cu, Fe, Ni, Pb and Zn in the Dowex 50W-x8 and Chelex 100 columns is one of the most important factors (Jiménez et al., 2002). This is because, highly acidic solutions may lead to protonation of resin's functional group while highly alkaline solution may result in the precipitation of metal ions as hydroxides. This may results in the underestimation of metal ion concentrations in drinking water samples. Therefore, the effect of sample pH on the retention of the analytes onto Dowex 50W-x8 and Chelex 100 resins was carried out between pH 4 and 10. The influence of the sample pH on the pre-concentration of Cd, Co, Cr, Cu, Fe, Ni, Pb and Zn is presented in Fig. 1. It was observed that for both resins, lower recoveries