Activated carbons modified as a tool for separation and pre-concentration in heavy metals analysis

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ABSTRACT

A sensitive, simple and relatively fast methods has been developed to selectively separate and concentrate trace amounts of heavy metal ions from aqueous samples for the measurement by flame atomic absorption spectrometry. The method is based on the adsorption of Pb²⁺, Cu²⁺, Zn²⁺, Fe³⁺, Ni²⁺ and Cd²⁺ on 2-amino-5-mercapto-1,3,4-thiadiazole (AMTD) loaded on activated carbon. The metals content on the complexes are eluted using 6 ml 4M HNO₃. The detection limits by three sigma for analyte ions were 1.6µg l⁻¹, 1.8µg l⁻¹, 1.3µg l⁻¹, 1.7µg l⁻¹, 1.6µg l⁻¹ and 1.7µg l⁻¹ using AMTD for Pb²⁺, Cu²⁺, Zn²⁺, Fe³⁺, Ni²⁺ and Cd²⁺, respectively. The presented procedure was applied to the determination of analytes in vegetable samples and different water samples with successfully results (recoveries greater than 97%, R.S.D.’s lower than 1.8 % for n=3).

INTRODUCTION

Important positive and negative roles of trace heavy metal ions in human health are known[11]. Considering biological research, the role of some trace and ultra-trace elements in the body is very rich and varied. Since these heavy elements are taken in mostly by human diet, the determination of their concentration in food and waters is very important. Considering biological research, the role of some trace and ultra-trace elements in our body is very rich and varied. Some of them are essential to life while others are toxic even at very low concentrations.

For the determination of low contents of trace elements in geological and technological samples, pre-concentration procedure is required. Of all pre-concentration and separation procedures sorption possesses several advantages: large pre-concentration factors that can be obtained in a short time, simplicity of phase separation and suitability for automation[2-6]. Solid phase extraction combines the benefits of solvent extraction and solid phase pre-concentration, eliminating some of their drawbacks. It consists of the recovery of hydrophobicmetal species on solid support of hydrophobic functionality. Desorption of metals is simply achieved by the change in solvent polarity. It does not require the use of concentrated acids or other aggressive reagents, and provides the opportunities of online combination of pre-concentration and determination steps.

Various solid phase extraction materials including Diaion HP-20[7], cellulose[8], activated carbon[9], Lewatit S 100[10], SDS coated alumina[11] polyurethane foam[12], Chelex 100[13], microcrystalline naphthalene[14], modified silica[15] and diaion HP-2MG[16].
Among which activated carbon has been widely applied. The reasons for widespread application of the activated carbon as a trace collector for metal ion pre-concentration are strong interaction and quantitative adsorption of molecules with π electrons on activated carbon. Because activated carbon is a type of hydrophobic adsorbent which adsorbs non-polar or little polar substances in aqueous solutions, metal ions to be pre-concentrate need to be transformed corresponding metal chelates. Metal chelates could provide higher selectivity and high enrichment factor for such a separation and pre-concentration techniques.

It was assumed that the sorption is quantitative when the chelate contains systems of π-electrons in the molecule and when the centers for binding on carbon and those for the metal ions are spatially separated so that their orbital do not have a substantial influence. The major advantage of these models is their simplicity; however, the models fail to describe accurately the adsorption equilibrium under varying conditions, such as pH and ionic strength. The adsorption equilibrium studies have revealed that pH is the dominant parameter controlling the adsorption.

The purpose of this work is pre-concentration-separation of Pb²⁺, Cu²⁺, Zn²⁺, Fe³⁺, Ni²⁺ and Cd²⁺ on activated carbon modified 2-amino-5-mercapto-1,3,4-thiadiazole (AMTD). The influences of the some analytical parameters including pH and sample volume on the quantitative recoveries of the analytes were investigated.

EXPERIMENTAL

Instruments

The measurements of metal ions were performed with a 680 AA shimadzu spectrometer equipped with a hollow cathode lamp and a deuterium background corrector, at respective wavelengths (resonance line) using an air-acetylene flame. The instrumental parameters were those recommended by the manufacturer. A Metrohm 691pH/Ion meter with a combined glass-calomel electrode was used for adjustment of test solution pH.

Reagents

Acids and bases were of the highest purity available from Merck and were used as received. Doubly distilled deionized water was used throughout. Nitrate lead, cadmium, mercury, iron, cobalt, nickel, copper, zinc, magnesium, calcium, strontium, barium, silver, sodium and potassium (all from Merck) were of the highest purity available and used without any further purification. The pH adjustment was done by addition of dilute nitric acid or sodium hydroxide to phosphate solution for preparing the desired pH buffer solution. Activated Carbon (AC) (gas chromatographic grade, 40-60 mesh from Merck), were soaked in hydrochloric acid for 1 d, it was then washed with deionized water and dried at 110°C for 1d. The ligand 2-amino-5-mercapto-1,3,4-thiadiazole (AMTD) was purchased from Merck Company and used as received.

Preparation of AMTD coated activated carbon

Ligand loaded activated carbon was prepared by dissolving a weighed amount of AMTD in water to the required amount of activated carbon. After 48 h, the solutions were filtered through the filter paper and activated carbons were washed with distilled water until the filter out was no longer alkaline. Finally, the mixtures were dried at 70°C overnight. The solid phase columns were initially preconditioned with solution with desired pH. For the final optimum experiments the solid phase was prepared as follow: 25mg AMTD per 800mg of AC.

Preconcentration procedure

The pH of model solutions containing 0.05μg/mL of ions metal was adjusted to the desired pH value by adding nitric acid and NaOH solution. Before each operational cycle the solid phase was preconditioned with the buffer solution. The samples were passed through the column of modified activated carbon with the aid of a suction pump at a flow rate 3mL/min⁻¹, to effect the deposition of analyte. The adsorbed ions by adding 6mL of 4.0M nitric acid at column for 5min then were passed through the column with a flow rate of 2.0mL/min⁻¹. The analyte ions in the eluent were determined by flame atomic absorption spectrometer.

Analysis of the real samples

Spinach (mixture of 4 food vegetable) was purchased from Gachsaran Iran. A 40g of spinach was heated in silica crucible for 3h on a hot plate and the
charred material was transferred to furnace for overnight heating at 650°C. The residue was cooled, treated with 10.0mL concentrated nitric acid and 3mL 30% H₂O₂, again kept in furnace for 2h. The final residue was treated with 3mL concentrated hydrochloric acid and 2-4 mL 70% perchloric acid and evaporated to fumes. The solid residue was dissolved in water, filtered and by keeping the pH at 5.5 by adding nitric acid and NaOH solution. The pre-concentration procedure given above was applied to these solutions.

River and waste water samples were collected from rivers in Iran. Before the analysis, the samples were filtered through a cellulose membrane filter (Millipore) of pore size 0.45mm. The organic content of the water samples were oxidized in the presence of 1% H₂O₂ and addition of concentrated nitric acid. The water samples were filtered through a filter paper. After acidification to 1% with concentrated nitric acid, they were stored in polyethylene bottles.

For the pre-concentration procedure, pH of the 250mL of water samples was adjusted to 5.5 using phosphate buffer and the sample passed through the column at flow rate of 3mL/min⁻¹. The analyte ions retained on column were eluted with 6mL of 4mol L⁻¹ HNO₃. The eluent was sent to flame atomic absorption spectrometry for evaluation of their metal content evaluation

**RESULTS AND DISCUSSION**

The purpose of this work is to investigate the feasibility of absorption of these ions on activated carbon modified with AMTD. For obtaining maximum signal for evaluation of these ion contents, the effective parameters viz. pH of sample, amount of ligand and solid phase, type and concentration of eluting agent and flow rate must be optimized.

**Effect of pH on recovery**

In the solid phase extraction studies for heavy metal ions based on chelation, the influence of pH of the aqueous solution one of the main factor for quantitative recoveries of the analytes. Due to this important point, the influences of pH were investigated at the pH ranges 2-8 for both sorbents with model solutions, keeping the other parameters constant. Analyte deposition depended on the sample pH, and as shown in figure 1, high deposition efficiency was achieved at a pH of 2.0-8.0. The progressive decrease in the retention of lead at a low pH is due to the competition of the hydrogen ion with the lead for reaction with AMTD. The decrease in absorption at pH>5.5 is probably due to the precipitation of lead as lead hydroxide and formation of a negative charge on the activated carbon, which results in the reduction of AC adsorption. To achieve high efficiency and good selectivity, a pH of ~5.5 was selected for subsequent work.

**Effect of amounts of activated carbon on recovery**

The AMTD-AC can retain all of the mention metal ions while the untreated AC cannot quantitatively retain Pb²⁺, Cu²⁺, Zn²⁺, Fe³⁺, Ni²⁺ and Cd²⁺. Evidently, the pre-concentration of the metals with the untreated AC is not suitable for Pb²⁺, Cu²⁺, Zn²⁺, Fe³⁺, Ni²⁺ and Cd²⁺. Therefore, AMTD-AC seems to be a better sorbent in simultaneous sorption of the studied elements. The ef-
fecteds of the amount of activated carbon at fix value of AMTD on the sorption of metal ions at pH =5.5 were examined in the range of 0.2-1.5g. The results demonstrated that, quantitative recoveries (>95%) of the working elements were observed in the range of 0.8 g. Above 800mg, the recoveries were below 95% with 6mL of the eluent. In the proposed procedure, 800mg of activated carbon is recommended (Figure 2). In preparing the ligand-impregnated adsorbents, some properties are required for ligand: they should be chemically stable, their solubility in aqueous solutions should be sufficiently low and they should be strongly adsorbed onto the substrates. In addition, we preferred ligands capable to form complexes with as many metals as possible at the natural pH of the sample solution.

**Effect of ligand amount on recovery**

The effects of the ligand amount on the retention of the analyte ions on AMTD were also examined and are depicted in figure 3. The recoveries of analytes were quantitative till by the addition of 25mg ligand. After that, the recovery values decreased, probably due to the formation of charged complex which could not be completely retained on solid phase.

**Sample flow rate**

Two important factors for the quantitative recoveries and desorption of metal chelates on the solid-phase extraction studies are flow rates of the sample and eluent solutions. The influences of the flow rates of the sample and eluent solution for the recoveries of analytes were investigated in the flow rate ranges of 1-12mL/min. The recovery values for analyte ions were quantitative in all the working range of sample flow rates. The quantitative recovery values for eluent solution were obtained at the flow rate range of 2-4mL/min. All further studies were performed at the sample and eluent flow rates of 2.0mL/min.

**Type and volume of the eluent**

The nature and concentration of eluent were found to have a significant effect on the desorption process of lead from the column. Different eluents, such as HCl, HNO₃, H₂SO₄ and H₃PO₄ at various concentrations, were examined and results are shown in figure 4 and TABLE 1. From result of figure 4 and TABLE1, it is obvious that 6mL of nitric acid with a concentration of 4.0 M were sufficient for quantitative recovery of absorbed lead.

**Calibration graphs and precisions**

The calibration curve were obtained by using 250mL 0.02-2.0μg/mL ions solutions at pH=5.5 at the optimum condition. The eluting solution was sent to AAS for evaluating ion content and results are shown in TABLE 2. The results indicate that calibration curve was linear for Lead, copper, zinc, iron, nikel and cad-
Interferences that may be concomitant with this ion were investigated. The interference effect of calcium, magnesium and other alkali and alkaline earth ions were presented in TABLE 3 display that these ions up to 1000 fold are negligible and this high selectivity able the method for accurate and precise determination Pb²⁺, Cu²⁺, Zn²⁺, Fe³⁺, Ni²⁺ and Cd²⁺ ion content in real samples.

**Analytical performance of the method**

The correctness of results was verified by analyzing the concentration after the addition of known amounts of analytes into a river, waste water samples and vegetable sample. The results were summarized in TABLES 4.5. Satisfactory recoveries were obtained for spiked analyte ions. The recoveries were higher than 97%, thus confirming the accuracy of the presented procedure.

**CONCLUSION**

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The ligands loaded on activated carbon are sensitive and accurate method for determination of trace amounts of copper and lead ions in low concentrations. The results presented in this paper have confirmed the applicability of the separation and preconcentration of metals. This method is simple and there is no necessity for elaborate cleanup procedure. Each column can be used for at least 10 successive analyses without considerable change in metal ions recovery. After the use by passing simple solution of ligand the column could be used for at least 100 times.

REFERENCES

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