Flame atomic absorption spectrometric determination of trace amounts of Pb (II) after soild phase extraction using multiwalled carbon nanotube

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Abstract: In this paper, the multiwalled carbon nanotubes (MWCNTs) have been used as sorbent for preconcentration traces amount of lead (II), by solid phase extraction Prior to determination by flame atomic absorption spectroscopy (FAAS). Dithizon was added after complexing with lead ion on absorbing walls of carbon nanotube, then eluted quantitatively with 5 ml nitric acid (1M in acetone). The effective practical Parameters in system including pH, the amount of MWCNTs, dithizon and elution solvent were optimized. The linear dynamic range, detection limit and the relative standard deviation are 40-180 µg L^{-1}, 3.3 µg L^{-1}, and 1.1 % (for 100 µg L^{-1} of Pb^{2+}) respectively. The proposed method was used for determination of lead in the some real samples of interior and exterior rice, which gave satisfactory results.
Keywords: Solid Phase Extraction, Lead, Multiwalled Carbons Nanotubes, Dithizon.

1. Introduction

The determination of metal ions at trace level by flame atomic absorption spectrometry (FAAS) has a number of advantages which include high selectivity, speed and fairly low operational cost. Direct determination of trace elements at extremely low concentration is often very difficult due to the insufficient sensitivity of the methods and the matrix interferences [1,2]. Solid-phase extraction (SPE) is the most common technique used for preconcentration of analytes because of high concentration factor, simple operation, the ability to handle large volume samples in a closed system free from contamination, rapid phase separation, and the possibility of combination with different analytical techniques [3,4].

Nowadays, carbon nanotubes (CNTs) have been proposed as a novel solid phase extractant for various inorganic and organic compounds/elements at trace levels [5,6].These tubes are classified as multiwalled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) according to the carbon atom layers in the wall of the nanotubes [7]. MWCNTs and oxidized-MWCNTs they have been widely used to remove many kinds of pollutants such as triethylphosphorothioate [8], atrazine [9], chlorbenzuron [10], thifensulfuron-methyl [11], Sulfonamides family [12], 1,2-Dichlorobenzene [13], linear alkylbenzene sulfonat [14] and metal ions from different matrices.

In the presented paper, a preconcentration-separation procedure for traces lead ions as their dithizon chelates on multiwalled carbon nanotubes was described. The conditions for quantitative and reproducible preconcentration, elution and subsequent flame atomic absorption spectrometric determination of lead were established.

2.Experimental

2.1. Reagents and solutions

All chemicals used in this work, were of analytical reagent grade and were used without further purification. Deionized water (Milli-Q Millipore 18.2 M¸ cm^{-1} conductivity) was used for all dilutions. All the plastic and glassware were cleaned by soaking in dilute HNO_3(1+9) and were rinsed with distilled water prior to use. The element standard solutions used for calibration were produced by diluting a stock solution of 1000 mg l^{-1} of the given element supplied by Sigma and Aldrich. Stock solutions of diverse elements were prepared from high purity compounds.

Multiwalled carbon nanotube (Aldrich no.: 636630) was purchased from Aldrich, Milwaukee, WI, USA. The BET surface area and density of nanotubes were 600 m^2 g^{-1} and 2.1 g ml^{-1} , respectively. It has high purity.

An 1,5 diphenyl thiocarbazon (DZ) solution (0.1%,w/v) was prepared by dissolving the requisite amounts of DZ in water/ethanol (75/25%, v/v). The solution was discharged one day.

Acetate buffer solutions (CH_3COO^-/CH_3COOH) were prepared by mixing of appropriate volumes of 0.1 mol l^{-1} acetic acid and 0.1 mol l^{-1} sodium acetate solutions (pH 6). For pH 7, a 250 ml of borate buffer was prepared by use of 2.5 ml of 1 mol l^{-1} HCl and 0.4450 g $NaBO_2$. Ammonium buffer solution (NH_4/NH_3) was prepared by mixing of appropriate amounts of 0.1 mol l^{-1} ammonia and 0.1 mol l^{-1} ammonium chloride solutions for pH 8-11.

2.2. Instruments

A Perkin-Elmer AAnalyst 300 atomic absorption spectrometer with deuterium background corrector was used. All measurements were carried out in an air/acetylene flame. A 10 cm long slot-burner head, a lamp and air-acetylene flame were used. The operating parameters for working elements were set as recommended by the manufacturer.

A pH meter, Jenway 3510 model glass-electrode was employed for measuring pH values in the aqueous phase. Milestone Ethos D closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300 C) was used for digestion of sample.

2.3. Column preparation

150 mg of multiwalled carbon nanotubes was loaded after washing acetone, 1mol l^{-1} HNO_3 solution and water, respectively, into a 10 mm × 100 mm glass column with a glass frit resin support. The resin bed was approximately 1.5 cm. The column was preconditioned by the blank solution prior to each use. After the elution, the column was washed with a 10-15 ml of the eluting solution and of water, subsequently.

2.4. Test procedure

Test solutions containing 40-180 µg of analyte were adjusted to desired pH. Then dithizon was added to form the metal-dithizon chelates. After 10 min, the solution was loaded to the column. The flow of sample solution through the column was gravitationally performed. After passage of the solution finshed, the column was washed with 2 ml dithizon solution adjusted to the working pH. The metals were recovered with the aid of 5 ml of 1 mol l^{-1} HNO_3 in acetone at 5.0 ml min^{-1} of flow rate. The analyte concentrations in the final solution were determined by flame atomic absorption spectrometry. Digestion conditions microwave system for samples were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min [15].

3. Results and discussion

In order to obtain quantitative recoveries of the metal ions on multiwalled carbon nanotubes, the enrichment/separation procedure was optimized for various analytical parameters such as pH, sample volume, amounts of multiwalled carbon nanotubes, matrix effects etc. The percent of metal adsorbed on nanotubes was calculated from the amounts of metal in the starting sample and the amounts of metal in the final solution.

3.1. Influences of pH

Because the pH of the aqueous samples is the very important factor for the quantitative recoveries of the metal ions in the solid phase extraction studies [16], the influences of pH of the analyte solutions on the recoveries of Pb(II), as dithizon chelates on multiwalled carbon nanotubes were investigated in the pH range 6.0-11. The quantitative recoveries (>95%) for lead was achived at pH 8 (Fig. 1). The recovery values were decreased after pH 8. At the basic pH values, the recoveries were not quantitative. This value is supported to our quantitative recovery values at the acidic pHs. All subsequent studies were carried out at pH 8.0 by using a ammonia buffer solution. The volume of buffer solution had no effect in the range of 2-10 ml.
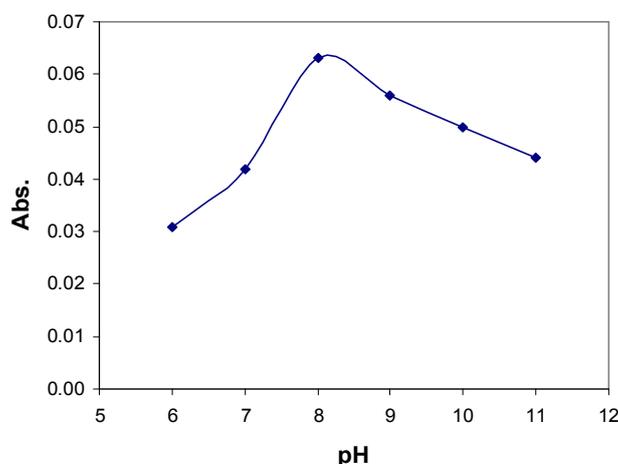
Fig. 1. Effect of pH on thw perposed method

3.2. Effects of amounts of Dithizon

The amounts of the ligand are also an important factor for the quantitative retentions of metal ions in solid phase extraction techniques. In order to investigate the optimum amounts of dithizone (1,5 diphynil thiocarbazon) on the quantitative recoveries of the analyte ions on multiwalled carbon nanotubes, the study was examined by varying the amounts of dithizon from 0.2 to 2.0 mg. The results are given in Table 1. The recoveries of analyte ions increased with increasing amounts of dithizon added and reached a constant value over 95 % with at least 0.7 mg. The recovery values of analytes were quantitative at the amounts of ligand range of 0.70-2.0 mg. On this basis, all the studies were carried out at an dithizon amount of 0.70 mg.

3.3. Eluent type and volume

Various eluent solutions were used for desorption of metal dithizon chelates from multiwalled carbon nanotubes. The results were given in Table 2. Quantitative recoveries for analyte ions were obtained only with 1 mol l^{-1} HNO_3 in acetone. Recoveries were not generally quantitative other eluents used present study with some exceptions shown in Table 2.

The effect of eluent volume on the recoveries of the analytes was also studied by using 1 mol l^{-1} HNO_3 in acetone; it was found that quantitative recoveries could be obtained with 2.0-6.0 ml of 1 mol l^{-1} HNO_3 in acetone. Therefore, the volume of 5.0 ml of 1 mol l^{-1} HNO_3 in acetone was used in the following experiments.

Table 1. Effect of amounts of dithizon on recovery %

DZ (mg)	0.20	0.50	0.70	1.00	1.50	2.00
Recovery%	41	79	99	95	94	96

Table 2. Effect of type and concentration of eluent

type and concentration of acid	HCl (0.5 M)	HCl (1.0 M)	HNO_3 (0.5 M)	HNO_3 (1.0 M)	HNO_3 (1.0 M in acetone)
Recovery %	30	35	75	85	96

3.4.Effects of amounts of multiwalled carbon nanotubes (MWNTs)

The effects of the amounts of multiwalled carbon nanotubes on the adsorption of analytes were investigated at 5.0 ml min^{-1} flow rates of sample and eluent solutions. The recovery values for analyte ions were found quantitative in the resin amounts of 30-250 mg. In all further studies, the short glass column was filled with 100 mg of MWNTs (Fig. 2).

3.5. Effect of the sample volume

In order to obtain high preconcentration factor, the effect of sample volume on the sorption behavior of analytes on MWNTs was investigated by passing 50-1000 ml of solutions. Amount of lead in supernatant solution determined by flame atomic absorption spectrometry The sorption of lead ions were quantitatively recovered at the range of 50-600 ml. At

the higher volumes then 600 ml, the recoveries for analytes were not quantitative. The preconcentration factor was 30.

3.7. Effect of divers ions

The influences of possible matrix ions in the environmental samples and some transition metals on the recoveries of analytes on multiwalled carbon nanotubes were also examined. A 5 ml portion of sample solution containing analytes and a given amounts of foreign ions were concentrated. The experimental results are shown in Table 3. The ions normally present in some real samples do not interfere under the experimental conditions used. Some of the transition metals at mg l^{-1} levels were not interfered on the recoveries of the analyte ions on MWNTs. This results show that the proposed preconcentration /separation method could be applied to the highly saline samples that contains some transition metals at mg l^{-1} levels.
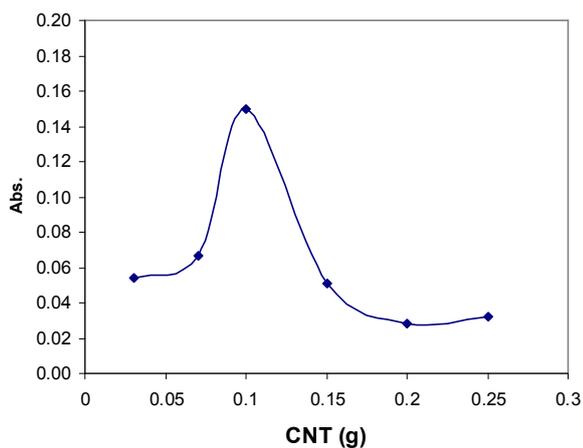

Fig. 2. Effect of MWNTs on the perposed method

Table 3. Effect of divers ions on the absorption of the analyte

Ion	Foreign ions Analyte
Na^+، Cu^{2+}،Al^{3+} ، Fe^{3+}، Ag^+،Mg^{2+}، Zn^{2+} K^+،	1000
Cl^-، F^-، HCO_3^-، PO_3^- ، NO_3^-	1000
Hg^{2+}, Mn^{2+}، Cd^{2+}, V (V)	500

3.8. Adsorption capacity

In order to study the adsorption capacity of multiwalled carbon nanotubes, 20 mg MWNTs was added to 25 ml of solution containing 0.2 mg of metal ion at pH 8.0. After shaking for 30 min, the mixture was filtered. Ten milliliters of the supernatant solution was diluted to 50 ml and determined by flame atomic absorption spectrometry. This procedure was repeated for each analyte ions separately. The capacity of MWNTs for analytes was found as 2.06 mg g^{-1}. The stability of multiwalled carbon nanotubes was excellent. The adsorption of metal-dithizon chelates is related with the physical interaction of the surface of the nanotubes and the metal-dithizon chelates.

3.9. Limit of detections

The detection limit (LOD) of the presented solid phase extraction study was calculated under optimal experimental conditions after application of the preconcentration procedure to blank solutions. The detection limits, defined as the concentration equivalent to three the standard deviation (N=10) of the reagent blank were found as 3.30 µg l^{-1}. Calibration curve was linear in the range of 40-180 µg l^{-1} in optimum conditions.

3.10. Applications of the presented procedure

The procedure presented was also applied to the determination of analytes in rice samples. The results were given in Table 4. A good agreement was obtained between the added and measured analyte amounts. These results confirm the validity of the proposed method. The presented method could be applied successfully for the separation, preconcentration and determination of trace amounts of lead ions in rice samples.
Also the application of the proposed solid phase extraction procedure for the determination of analyte ions was performed to the microwave digested environmental samples.

4. Conclusion

Multiwalled carbon nanotubes were used as solid phase extractor for heavy metal ions at trace levels in the presented paper. The conditions for quantitative and reproducible preconcentration, elution and FAAS determinations were studied.

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