

# Preconcentration And Determination Of Trace Amounts Of $\text{Ag}^+$ And $\text{Pb}^{2+}$ Using Multiwalled Carbon Nanotubes By Solid Phase Extraction-Flame Atomic Absorption Spectrometry

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**Abstract:** Multiwalled carbon nanotubes (MWNTs) were used as absorbent for extraction of  $\text{Ag}^+$  and  $\text{Pb}^{2+}$  in the presence of 4,2 pyridylazo resorsinol (PAR) as a chelate by solid phase extraction method. The complexes were eluted with  $1 \text{ mol L}^{-1} \text{ HNO}_3$  in methanol and determined the analytes by flame atomic absorption spectrometry. The influences of the experimental parameters including pH of the solutions, amounts of MWNTs, amounts of PAR, eluent type and volume and sample volume on the quantitative recoveries of analytes ion were investigated. Calibration curve was linear in the ranges of 10- 120 and 15-150  $\mu\text{g L}^{-1}$  for  $\text{Ag}^+$  and  $\text{Pb}^{2+}$ , respectively. The presented method has been applied to the determination of analytes in some real sample which gave satisfactory results.

**Keywords:** Solid Phase Extraction, Multiwalled Carbon Nanotubes, PAR.

## 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 sulfonate [14] and metal ions from different matrices.

In the presented paper, a preconcentration-separation procedure for traces silver and lead ions as their PAR chelates on multiwalled carbon nanotubes was described. The conditions for quantitative and reproducible preconcentration, elution and subsequent flame atomic absorption spectrometric determination of analytes 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 $\Omega$  cm<sup>-1</sup> conductivity) was used for all dilutions. All the plastic and glassware were cleaned by soaking in dilute HNO<sub>3</sub> (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<sup>-1</sup> of the given element supplied by Merck. Stock solutions of diverse elements were prepared from high purity compounds. The calibration standards were not submitted to the preconcentration procedure.

Multiwalled carbon nanotube (Plasma Chem GmbH) was purchased from Plasma, Rudower Chaussee 29, and D- 12489 Berlin. The Purity of nanotubes was more than 95%. An PAR solution (0.1%, w/v) was prepared by dissolving the requisite amounts of PAR in water/ethanol (75/25%, v/v). The solution was discharged one day.

### 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, Sartorius pp-15 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.

### 2.3. Column preparation

150 mg of multiwalled carbon nanotubes was loaded after washing acetone, 1mol l<sup>-1</sup> HNO<sub>3</sub> solution and water, respectively, into a 10 mm × 100 mm glass column with a glass frit resin support. The resin bed was approximately 1 cm. The column was preconditioned by the blank solution prior to each use. After the elution, the resin in the column was washed with a 10-15 mL of the eluting solution and of water, subsequently.

### 2.4. Test procedure

Test solutions containing 5-120 μg of each analytes were adjusted to desired pH. Then PAR was added to form the metal-PAR 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 finished, the column was washed with 2 ml

PAR solution adjusted to the working pH. The metals were recovered with the aid of 3 ml of 1 mol l<sup>-1</sup> HNO<sub>3</sub> in methanol. The analyte concentrations in the final solution were determined by flame atomic absorption spectrometry.

## 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. 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. The quantitative recoveries were found at the pH 7. The recovery values were decreased after pH 7. All subsequent studies were carried out at pH 7. Effects of pH on the absorption of the analyte were given in Fig. 1.

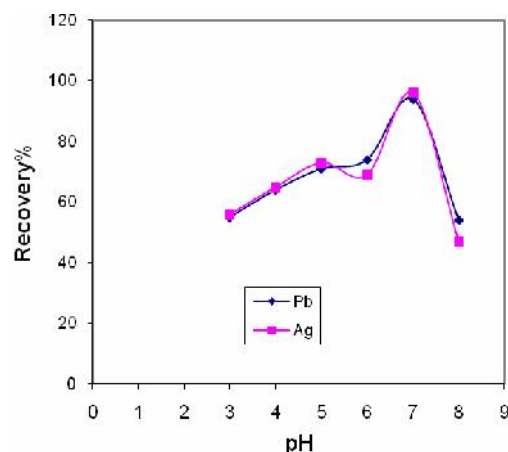


Fig.1. Effects of pH on the absorption of Ag<sup>+</sup> and Pb<sup>2+</sup> on multiwalled carbon nanotubes

### 3.2. Effects of amounts of PAR

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 PAN on the quantitative recoveries of the analyte ions on multiwalled carbon nanotubes, the study was examined by varying the amounts of PAR from 0.5 to 2.5 mg. The results are given in Fig. 2. The recoveries of analyte ions increased with increasing amounts of PAN added and reached a constant value

over 95 % with at least 1.5 mg. The recovery values of analytes were quantitative at the amounts of ligand of 1.5 mg. On this basis, all the studies were carried out at a PAR amount of 1.5 mg.

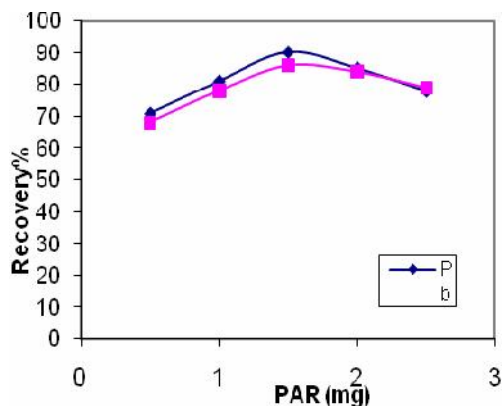


Fig.2. Effects of amount of PAR

### 3.3. Effects of amounts of multiwalled carbon nanotubes (MWNTs)

The effects of the amounts of multiwalled carbon nanotubes on the adsorption of analyte were investigated. The recovery values for analyte ions were found quantitative in the resin amounts of 150-250 mg. In all further studies, the short glass column was filled with 150 mg of MWNTs.

### 3.4. 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 analyte and a given amounts of foreign ions were concentrated. The

experimental results are shown in Table 1. The ions normally present in natural waters do not interfere under the experimental conditions used until the proportion of foreign ions to analyte is equal 1000 and for transition metals be equal 500. The results show that the proposed preconcentration /separation method could be applied to the highly saline samples that contains some transition metals at  $\text{mg l}^{-1}$  Levels.

**Table 1** Effect of divers ions on the absorption of the analyte

Foreign ions Analyte	Ion
1000	$\text{Cu}^{2+}$ $\text{Na}^+$ $\text{K}^+$ $\text{Mg}^{2+}$ $\text{Fe}^{3+}$ $\text{Al}^{3+}$
1000	$\text{NO}_3^-$ $\text{PO}_4^{3-}$ $\text{HCO}_3^-$ $\text{F}^-$ $\text{Cl}^-$
500	$\text{Zn}^{2+}$ $\text{Mn}^{2+}$

### 3.5. Figures of merit

A calibration curve was constructed by preconcentrating 10 ml of sample standard solutions with Triton X-114. Under the optimum experimental conditions, Calibration curve was linear in the ranges of 10- 120 and 15-150  $\mu\text{g L}^{-1}$  for  $\text{Ag}^+$  and  $\text{Pb}^{2+}$ , respectively. The limit of detection was sufficiently low (6  $\mu\text{g L}^{-1}$ ). Further improvement is also feasible, either by preconcentrating larger amounts of the sample solution or diluting the surfactant rich phase to a smaller volume of the methanol solution.

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### References:

- [1] R. Thomas, A. Dulski, Trace Elemental Analysis of Metals: Methods and Techniques, Marcel Dekker Inc., New York, 1999.
- [2] T. Shamspur, M.H. Mashhadizadeh, I. Sheikshoae, Flame atomic absorption spectrometric determination of silver ion after preconcentration on octadecylsilica membrane disk modified with bis[5-((4- nitrophenyl) azosalicylaldehyde)] as a new Schiff base ligand, J. Anal. At. Spectrom. 2003, 18, 1407–1410.
- [3] V.A. Lemos, L.S.G. Teixeira, M.A. Bezerra, A.C.S. Costa, J.T. Castro, L.A.M. Cardoso, D.S. de Jesus, E.S. Santos, P.X. Baliza, L.N. Santos, New materials for solid-phase extraction of trace elements, Appl. Spectrosc. Rev. 2008, 43, 303–334.
- [4] V. Camel, Solid phase extraction of trace elements, Spectrochim. Acta Part B 2003, 58, 1177–1233.
- [5] M. Tuzen, K.O. Saygi, M. Soylak, Solid phase extraction of heavy metal ions in environmental samples on multiwalled carbon nanotubes, J. Hazard. Mat. 2008, 152, 632.
- [6] R.A. Gil, S.N. Goyanes, G. Polla, P. Smichowski, R.A. Olsina, L.D. Martinez, Application of multi-walled carbon nanotubes as substrate for the on-line preconcentration,

- speciation and determination of vanadium by ETAAS, *J. Anal. At. Spectrom.* 2007, 22, 1290.
- [7] S. Iijima, Helical microtubules of graphitic carbon, *Nature* 1991,354, 56–58.
- [8] C. Basheer, A.A. Alnedhary, B.S.M. Rao, S. Valliyaveetil, H.K. Lee, Development and Application of Porous Membrane-Protected Carbon Nanotube Micro-Solid-Phase Extraction Combined with Gas Chromatography/Mass Spectrometry, *Anal. Chem.* 2006, 78, 2853.
- [9] Q. Zhou, J. Xiao, W. Wang, G. Liu, Q. Shi, J. Wang, Determination of atrazine and simazine in environmental water samples using multiwalled carbon nanotubes as the adsorbents for preconcentration prior to high performance liquid chromatography with diode array detector, *Talanta* 2006, 68, 1309.
- [10] Q. Zhou, Y. Ding, J. Xiao, Simultaneous determination of cyanazine, chlorotoluron and chlorbenzuron in environmental water samples with SPE multiwalled carbon nanotubes and LC, *Chromatographia* 2007, 65, 25.
- [11] Q. Zhou, W. Wang, J. Xiao, Preconcentration and determination of nicosulfuron, thifensulfuron-methyl and metsulfuron-methyl in water samples using carbon nanotubes packed cartridge in combination with high performance liquid chromatography, *Anal. Chim. Acta* 2006, 559, 200.
- [12] G.Z. Fang, J.X. He, S. Wang, Multiwalled carbon nanotubes as sorbent for on-line coupling of solid-phase extraction to high-performance liquid chromatography for simultaneous determination of 10 sulfonamides in eggs and pork. *J. Chromatogr. A* 2006, 1127, 12.
- [13] G. Liu, J. Wang, Y. Zhu, X. Zhang, Application of Multiwalled Carbon Nanotubes as a Solid-Phase Extraction Sorbent for Chlorobenzenes, *Anal. Lett.* 2004, 37, 3085.
- [14] Z. Guan, Y. Huang, W. Wang, Carboxyl modified multi-walled carbon nanotubes as solid-phase extraction adsorbents combined with high-performance liquid chromatography for analysis of linear alkylbenzene sulfonates. *Anal. Chim. Acta*, 2008, 627, 225.

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