

Dispersive Solid Phase Extraction of trace Pb(II) in water samples by New Fabricated Multi walled carbon nanotubes carboxylate

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ABSTRACT: A novel, simple, sensitive and effective method has been developed for preconcentration of the trace Pb (II) ions in aqueous Samples by CNT carboxyl which in order to improve the performance of extraction and preconcentration was used. Amounting of the ions density in solution was performed by the method of flame atomic absorption spectrometry. The effective parameters on extraction such as: effect of pH, the amount and eluent solvent, time of extraction and effect of other cation were optimized. Concentrate factor was found 30 and LOD method of limit of detection was found to 0.17 $\mu\text{g.L}^{-1}$. The relative standard deviation is 1.70% (RSD%).

Keywords: Multi walled carbon nanotubes carboxylate (MWCNTs-COOH), Pb(II), Preconcentration, Solid phase extraction.

INTRODUCTION

The design of highly selective reagents for binding of metal ions is of vital importance to broad areas of analytical chemistry and separation science. Due to the specific metal ion complexing abilities of macrocyclic crown ethers, extensive studies of these ligands and their metal ion complexes have been carried out (Leyden, *et al.*, 1976; Narin, *et al.*, 2000; Akama, *et al.*, 2000; Ohta, *et al.*, 2001). Pb, at trace concentrations, acts as both a micronutrient and a toxicant in marine and fresh water systems (Cuculic, *et al.*, 1997; Moghimi, *et al.*, 2012; Moghimi, *et al.*, 2019). The direct determination of trace metals especially toxic metal ions

such as Pb, Tin, Arsenic, Lead, Antimony and Selenium from various samples requires mostly an initial and efficient pre-concentration step (Leyden, *et al.*, 1976). This pre-concentration is required to meet the detection limits as well as to determine the lower concentration levels of the analyte of interest (Jones, *et al.*, 1983). This can be performed simply in many ways including liquid and solid phase extraction techniques (Nambiar, *et al.*, 1998; Caroli, *et al.*, 1991). The application of solid phase extraction technique for preconcentration of trace metals from different samples results in several advantages such as the minimal waste generation, reduction of sample matrix effects as well as sorption of the target species on the solid surface in a more

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stable chemical form (Alexandrova, *et al.*, 1993). The normal and selective solid phase extractors are those derived from the immobilization of the organic compounds on the surface of solid supports which are mainly polyurethane foams (Arpadjan, *et al.*, 1997), filter paper (Leyden, *et al.*, 1975), cellulose (Gennaro, *et al.*, 1983) and ion exchange resins (Grote, *et al.*, 1985). Silica gel, alumina, magnesia and zirconia are the major inorganic solid matrices used to immobilize the target organic modifiers on their surfaces (Unger, 1979) of which silica gel is the most widely used solid support due to the well documented thermal, chemical and mechanical stability properties compared to other organic and inorganic solid supports (Boudreau, *et al.*, 1989). The surface of silica gel is characterized by the presence of silanol groups, which are known as weak ion exchangers, causing low interaction, binding and extraction of the target analytes (Kvitek, *et al.*, 1982). For this reason, modification of the silica gel surface with certain functional groups has successfully been employed to produce the solid phase with certain selectivity characters (Bruening, *et al.*, 1991). Two approaches are known for loading the surface of solid phases with certain organic compounds and these are defined as the chemical immobilization which is based on chemical bond formation between the silica gel surface groups and those of the organic modifier, and the other approach is known as the physical adsorption in which direct adsorption of the organic modifier with the active silanol groups takes place (Unger, 1979). Selective solid phase extractors and pre-concentrators are mainly based on impregnation of the solid surface with certain donor atoms such as oxygen, nitrogen and sulfur containing compounds (Mahmoud, 1997; Mahmoud, *et al.*, 1997; Tong, *et al.*, 1990; Dadler, *et al.*, 1987). The most successful selective solid phases for soft metal ions are sulfur-containing compounds, which are widely used in different analytical fields. Amongst these sulfur-containing compounds are dithiocarbamate derivatives for selective extraction of Pb(II) (Mahmoud, 1998; Mahmoud, 1999) and pre-concentration of various cations (Leyden, *et al.*, 1976; Narin, *et al.*, 2000; Akama, *et al.*, 2000; Ohta, *et al.*, 2001; Cuculic, *et al.*, 1997; Moghimi, *et al.*, 2009; Thurman, 1998; Pawliszyn, 1997; Izatt, *et al.*, 1996; Hagen, *et al.*, 1990; Krueger, 1995; Yamini, *et al.*,

1994; Brunner, *et al.*, 2003; Zelder, *et al.*, 2004; Boll, *et al.*, 2005; Nayebi, *et al.*, 2006; Moghimi, *et al.*, 2007; Moghimi, 2007) and 2- mercaptobenzothiazol-modified silica gel for on-line pre-concentration and separation of silver for atomic absorption spectrometric determinations (Qiaosheng, *et al.*, 1998). Ammonium hexa-hydroazepin-1-dithiocarboxylate (HMDC)-loaded on silica gel as solid phase pre-concentration column for atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) was reported (Alexandrova, *et al.*, 1993). Mercapto-modified silica gel phase was used in pre-concentration of some trace metals from seawater (Moghimi, *et al.*, 2010). Sorption of Pb(II) by some sulfur containing complexing agents loaded on various solid supports (Tajodini, *et al.*, 2010; Abniki, *et al.*, 2020) was also reported. 2-Amino-1-cyclopentene-1-dithiocarboxylic acid (ACDA) for the extraction of silver(I), Pb(II) and palladium(II) (Moghimi, *et al.*, 2009), 2-[2-triethoxysilyl-ethylthio] aniline for the selective extraction and separation of palladium from other interfering metal ions (Narin, *et al.*, 2000) as well as thiosemicarbazide for sorption of different metal ions (Campderros, *et al.*, 1998) and thioanilide loaded on silica gel for pre-concentration of palladium(II) from water (Narin, *et al.*, 2000) are also sulfur containing silica gel phases.

This work preconcert of Pb²⁺ based on the adsorption of its complex on Multi walled carbon nanotubes carboxylate (MWCNTs-COOH). The adsorbed complex could be eluted using environmentally and the concentration of Pb²⁺ was determined by FAAS. The influence of various experimental parameters such as acidity, sample volume, flow rate, diverse ions, etc. was examined in detail. The validity of the proposed method was tested in tap water samples and waste water.

EXPERIMENTAL

Instrumentation

Determination of Pb²⁺ contents in working samples were carried out by a PG-990 flame atomic absorption spectrometer equipped with a high intensity hollow cathode lamp (HI-HCl) according to the recommen-

Table 1. The operational conditions of flame for determination of Pb

Slit width	0.7 nm
Operation current of HI-HCL	5.0 mA
Resonance fine	395.2 nm
Type of background correction	Deuterium lamp
Type of flame	Air/acetylene
Air flow	9.0 mL.min ⁻¹
Acetylene flow	2.7 mL.min ⁻¹

dations of the manufacturers. These characteristics are tabulated in (Table 1). The pH measurements were carried out by a pH meter (Sartorius model PB-11).

Chemicals and reagents

Multi walled carbon nanotubes carboxylate (MWCNTs-COOH) were prepared from Merck (Darmstadt, Germany). Method and dried for a week over phosphorus pentoxide in a vacuum desiccators before use. 4-Isocyanatobenzenesulfonyl azide was prepared from 4-carboxybenzenesulfonyl azide via a published procedure (Graf, *et al.*, 2007). All solutions were prepared with doubly distilled deionized water from Merck (Darmstadt, Germany). C₁₈ powder for chromatography with diameter of about 50 μm obtained from Katayama Chemicals from supelco. It was conditioned before use by suspending in 4 M nitric acid for 20 min, and then washed two times with water.

Preparation of Multi walled carbon nanotubes carboxylate (MWCNTs-COOH) cartridge

A glass column 1.5 cm in diameter and 15 cm in length was used for the preconcentration of Pb(II). About 5 g of Multi walled carbon nanotubes carboxylate (MWCNTs-COOH) cartridge was mixed with 25 mL of HCl 1M to form slurry and then loaded on to the column. Cotton was placed at the bottom for allowing Multi walled carbon nanotubes carboxylate (MWCNTs-COOH) cartridge to settle properly. The column was packed up to a height of 3 cm.

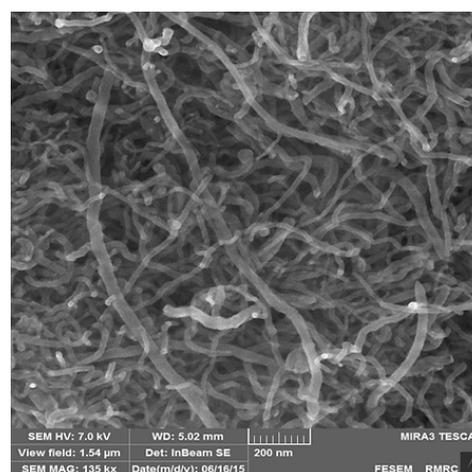
Procedure for preconcentration

A 50mg SDS of 50mL was loaded on to the column of neutral Multi walled carbon nanotubes carboxylate (MWCNTs-COOH) cartridge maintaining a flow rate of 5mL min⁻¹. Then 250 mL volume of 10 μgm Pb(II)

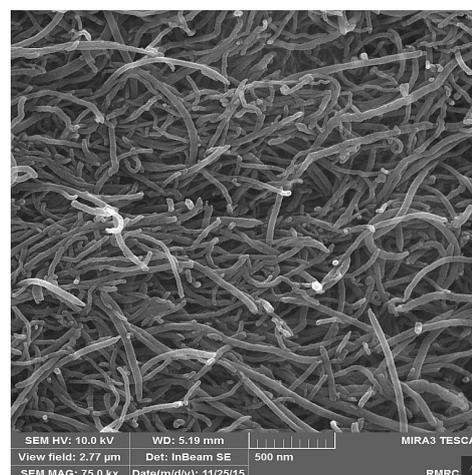
solution was loaded on to the column. The sample solution was loaded on to the column of neutral Multi walled carbon nanotubes carboxylate (MWCNTs-COOH) cartridge maintaining a flow rate of 0.5 mL min⁻¹. The complex was adsorbed as a narrow band on the top of the column. The adsorbed complex was eluted using 10 mL of HNO₃ 4M at a flow rate of 0.5mL min⁻¹ and the concentration of Pb(II) was determined by FAAS.

RESULTS AND DISCUSSION

The treatment of Multi walled carbon nanotubes carboxylate (MWCNTs-COOH) functional groups via adsorption (Hummers and Offeman, 1958) (Fig. 1). The formation of SWCNTs was followed by Raman



(a)



(b)

Fig. 1. SEM image of Multi walled carbon nanotubes carboxylate (MWCNTs-COOH)

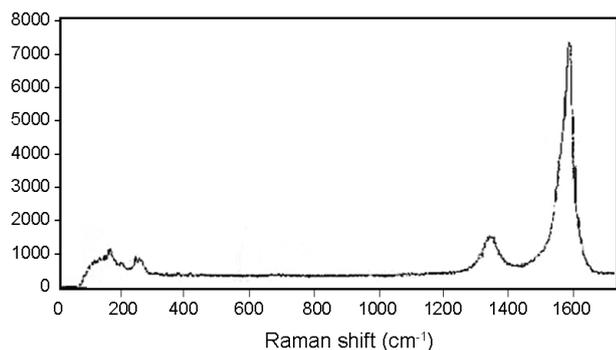


Fig. 2. Raman Spectroscopy image Multi walled carbon nanotubes carboxylate (MWCNTs-COOH)

Spectroscopy. Initially, in the spectrum of GO, the carbonyl vibration appears at 1580 cm^{-1} , while there are fingerprints at 160 cm^{-1} and 230 cm^{-1} due to the presence of hydroxyl species at the carbon nanotubes (Leyden, *et al.*, 1976) (Fig. 2).

Effect of pH in does not occur

The effect of pH of the aqueous solution on the extraction of 100 ng of each of the cations Pb(II) was studied in the pH range of 1-10. The pH of the solution was adjusted by means of either 0.01 M HNO_3 or 0.01 M NaOH . The results indicate that complete chelation and recovery of Pb(II) occurs in pH range of 6-8 and that of in 2-9 and are shown in Fig. 3. It is probable that at higher pH values, the cations might be hydrolyzed and complete desorption occur. Hence, in order to prevent hydrolysis of the cations and also keeping on the cartridge C_{18} , pH=7.0 was chosen for further studies.

Choice of the eluent

A variety of reagents were tested in order to elute the adsorbed complex from the column. In order to choose the most effective eluent for the quantitative recovery

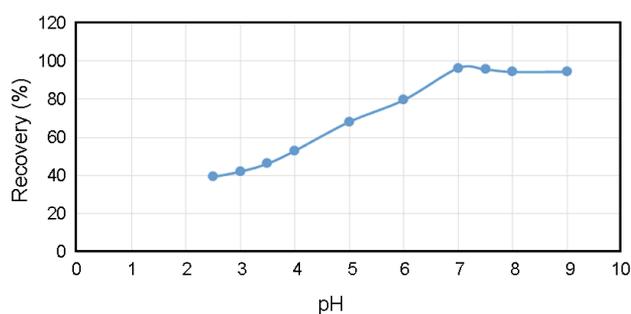


Fig. 3. Extraction percentage of Pb(II) against pH.

of Pb(II), methanol, ethanol, acetone, HCl 1M, HCl 3M, H_3PO_4 1M, and Acidified methanol (Acidified solvents obtained by addition of HNO_3 4M), were studied. The adsorption studies were carried out maintaining an overall Pb(II) concentration of $10\text{ }\mu\text{g}$ in 100mL sample volume. The recovery of Pb(II) was found to be quantitative with ethanol and HNO_3 4M as eluting agents. However, HNO_3 4M was preferred owing to its non-inflammability and less toxicity (Gennaro, *et al.*, 1983; Graf, *et al.*, 2007). It was observed that when the ratio of HNO_3 4M a recovery of 99.7% could be attained.

Effect of sample volume

The effect of sample volume on the recovery of the analyte was investigated in the range 100–1500 mL maintaining an overall concentration of 0.025 mol L^{-1} sulfuric acid. The resulting complex was eluted using 10 mL of HNO_3 4M. The results are presented in. As can be seen from the figure, it is evident that the recovery of Pb(II) is quantitative ($>97\%$) up to 250 mL sample volume. A preconcentration factor of 30 could be attained for quantitative recovery ($>97\%$) of Pb(II) when the sample volume was 250 mL.

Effect of flow rate

The flow rate of $1\text{--}7\text{ mL min}^{-1}$ was found to be suitable for optimum loading of Pb(II) complex on the Multi walled carbon nanotubes carboxylate (MWCNTs-COOH) cartridge. At higher flow rates, there was a reduction in the percentage adsorption of Pb(II). This could be probably due to the insufficient contact time between the sample solution and Multi walled carbon nanotubes carboxylate (MWCNTs-COOH) cartridge. A flow rate of 5 mL min^{-1} was maintained for the elution of Pb(II) Fig. 4.

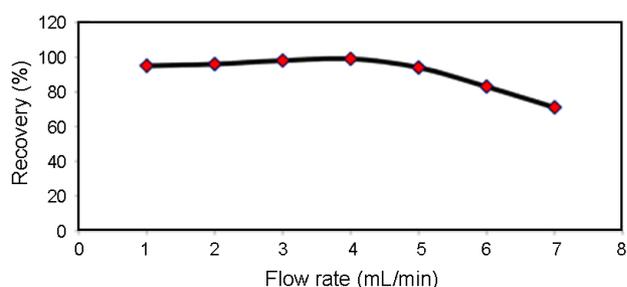


Fig. 4. Effect of flow rates of the sample solutions on the recovery percentage of Pb(II).

Effect of the amount of Multi walled carbon nanotubes carboxylate (MWCNTs-COOH) silica cartridge. The amount of Multi walled carbon nanotubes carboxylate (MWCNTs-COOH) cartridge loaded was varied from 0.25 to 2.0 g and the preconcentration studies were carried as before. Quantitative recovery of Pb(II) could be attained in the range 0.75–2.0 g of Multi walled carbon nanotubes carboxylate (MWCNTs-COOH) cartridge. For amounts less than 0.75 g there was a significant reduction in the recovery beyond a sample volume of 100 mL.

Precision studies and limit of detection

The precision studies were carried out at 10 µg level of Pb(II) by carrying out 10 separate determinations using the above-mentioned procedure. The sample volume was maintained at 100 mL. The relative standard deviation of the method was found to be 0.76%. The sensitivity of the developed method is reflected by the limit of detection studies, defined as the lowest concentration of Pb(II) below which quantitative recovery of the metal ion by Multi walled carbon nanotubes carboxylate (MWCNTs-COOH) cartridge is not perceptibly seen. The limit of detection was found to be 0.07 µg.mL⁻¹.

Stability of the column

The stability of the column was tested using 10 µg Pb(II) maintaining a sample volume of 50 mL. The adsorbed Pb(II) complex on SDS was eluted using 6 mL of HNO₃ 4M. The column could be used with good precision and quantitative recovery (>97%) for at least 10 cycles. Beyond 10 cycles, there was a significant reduction in the recovery of Pb(II).

Effect of other ions

The interfering effect of diverse ions was studied at varying concentrations. The preconcentration studies were carried out as mentioned above using 10µg Pb(II) maintaining a sample volume of 100 mL. The studies indicated that Na⁺, K⁺, Ca²⁺, Mg²⁺, Pb²⁺, Cl⁻, Br⁻, Fe³⁺, NO₃⁻, Zn²⁺, Co²⁺, Ni²⁺, Mn²⁺ did not cause any significant reduction in the recovery of Pb(II). The results are presented in Table 2 showing the recovery of Pb(II) with varying concentrations of metal ions. The recovery was found to be quantitative in the concen-

Table 2. Effect of diverse ions on the recovery of 10 µg Pb(II) in a sample volume of 100 mL.

Ions	added (mg)	Recovery of Pb(II) (%)
K ⁺	0.11	91.3(1.3)
Ca ⁺	0.02	91.6(1.2)
Mg ⁺	1.05	92.3(1.3)
Na ⁺	0.11	92.4(2.2)
Zn ⁺	1.0	93.3(2.2)
Cl ⁻	0.09	90.2(1.8)
NO ₃ ⁻	0.50	91.3(2.3)
SO ₄ ²⁻	0.16	92.8(2.2)
CH ₃ COO ⁻	0.1	92.2(2.2)
Cr ₂ O ₇ ²⁻	0.15	91.1(1.5)

^a: Values in parenthesis are CVs based on three individual replicate measurements

tration range of the metal ions that was investigated. Since, the ions that are commonly present in water samples did not interfere significantly, the method was applied to study the recovery of Pb(II) in water samples.

Recovery studies in tap water and rain water samples. The validity of the proposed method was tested by spiking known concentrations of Pb(II) to tap water (Tehran, taken after 10 min operation of the tap), and rain water (Tehran, 31 January, 2020) samples. The water samples were filtered and stored in polythene bottles. The recovery of Pb(II) was found to be satisfactory with a relative standard deviation of 2% for five replicate measurements and the results are shown in Table 3.

Comparison with other solid phase adsorbents

The proposed methodology was compared to a variety of solid adsorbents reported recently in the literature. Also, the proposed method was free of interference compared to conventional procedures to determine Pb. 46,51,52 As can be seen from the references, it is evident that the preconcentration factor obtained with Multi walled carbon nanotubes carboxylate (MWCNTs-COOH) cartridge is comparable to or even better than most of the other chelating matrices. The other significant feature of the proposed method is the

Table 3. Analytical results for the recovery of Pb(II) in water samples

Sample	Pb(II) added (μg)	Found of Pb(II) with FAAS (μg)	GF-AAS (μg)
Tap Water	0.00	0.002(1.4)	0.003(1.7)
	15.00	17.27(1.7)	17.14(1.9)
	20.00	23.16(1.3)	(1.6)22.94
Ground water	0.00	1.24(1.2)	1.41(1.3)
	10.00	21.74(1.1)	21.93(1.2)
	20.00	29.83(1.8)	29.78(0.7)
Waste water	0.00	3.94(1.8)	3.85(1.7)
	5.00	9.63(1.9)	9.74(0.8)
	15.00	17.85(1.6)	17.23(1.2)
Synthesis sample 0.2 mg of Co^{2+} , Ni^{2+} , Na^+	0.00	N.D ^b	N.D
	10.00	15.84(1.8)	15.73(0.9)
Al^{3+} , Ba^{2+} , Ca^{2+}	20.00	26.57(1.2)	26.46(0.6)

^a: Values in parenthesis are CVs based on three individual replicate measurements

^b: Not Detection

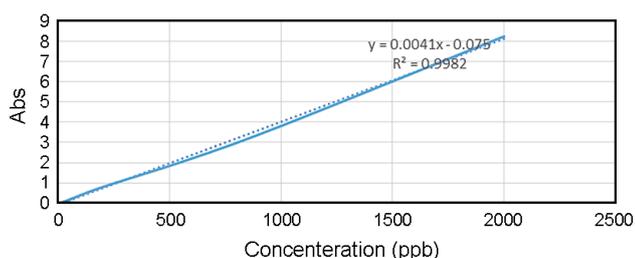


Fig. 5. Calibration curve of Pb(II) measured by SPE-AAS.

use of environmentally benign HNO_3 4 M for the elution of the complex.

Calibration curve

The calibration curve of Pb(II) solutions is represented in Fig. 5 and the related regression is $Y=0.0041X+0.075$ providing a correlation coefficient of $R^2=0.9982$.

CONCLUSIONS

The proposed spectrophotometric method for Pb(II) is simple, sensitive and exhibits good selectivity. The elution of the complex does not involve strong acids or toxic organic solvents. The advantage of using HNO_3 4 M as the eluent lies in the fact that it is non-inflammable, inexpensive and non-toxic. The conventional solvent extraction procedure associated

with metal dithizonates is avoided in this methodology. The highest preconcentration factor attainable was 57 for a 250 mL sample volume. The method showed minimum interferences with commonly found ions in water sample and the recovery of Pb(II) was quantitative. The important features of the proposed method are its higher adsorption capacity with good preconcentration factor. The developed method is sensitive in detecting Pb(II) at ppb levels. The column could be used with good precision and quantitative recovery for at least 10 cycles. The quantitative recovery of Pb(II) with a low relative standard deviation of 0.79% reflects the validity and accuracy of the proposed method when applied to real samples. The method developed was simple, reliable, and precise for determining Pb in water. Also, the proposed method was free of interference compared to conventional procedures to determine Pb(II) (Moghimi, *et al.*, 2012; Moghimi, *et al.*, 2019; Narin, *et al.*, 2000).

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