

Determination of Lead(II) in Milk by Flame Atomic Absorption Spectrometry after Solid Phase Extraction

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A simple and selective solid phase extraction method for determination of lead in milk and aroarous solutions has been reported. The method is based on the adsorption of lead on octadecyl bonded silica cartridges (C₁₈) modified by sodium dodecyl sulfate and 1-(2-pyridylazo)-2-naphthol. The influence of acidity, eluting agents, stability of the column, sample volume and interfering ions has been investigated. The adsorbed complex could be eluted using environmentally benign 5 mL of 1 mol L⁻¹ HNO₃ and the concentration of lead(II) was determined by flame atomic absorption spectrometry. A detection limit of 0.050 µg L⁻¹ could be achieved and the developed procedure was successfully applied for the determination of lead(II) in tap water and milk samples. Precision at 1 mg L⁻¹ was 1.44 % (n = 5).

Key Words: Lead(II), Preconcentration, Octadecyl bonded silica cartridges, 1-(2-Pyridylazo)-2-naphthol.

INTRODUCTION

Lead is one of the most ubiquitous elements in the environment and recognized as a major health risk to humans and animals^{1,2}. Flame atomic absorption spectrometry is a simple technique, commonly used for determination of lead in water³, soil^{4,5} and plant samples⁶. However, the determination of traces of lead by flame atomic absorption spectrometry in such complex matrices is difficult due to its low sensitivity (0.01 µg cm⁻³) and the interfering effects of matrix components. Hence, separation step is frequently necessary to improve the detection limit and sensitivity⁷ which is nowadays preferably done by solid phase extraction due to the several advantages it offers⁸.

Solid phase extraction procedures for lead have been reported using various solid supports such as active carbon⁹, silica gel¹⁰, cellulose¹¹, amberlite XAD series resins¹²⁻¹⁷, chromosorb resin¹⁸, Amborsorb resin¹⁹ and polyurethane foam²⁰. Two methodologies were commonly practiced for solid phase extraction of lead. One was based on chemical reactions either for synthesis of a selective ligand¹⁴ or its covalent coupling to support material^{12,15,16} and other for functionalization of the solid support itself^{10-13,17}. These methods were somewhat lengthy and time-consuming.

A relatively simple alternative for preparation of the solid phase is based upon the impregnation of reagents on solid supports. Interesting studies using acidic organophosphorous extractant such as [di-(2-ethylhexyl) phosphoric acid] (DEHPA),

Cyanex 272 (*bis*-(2,4,4-trimethyl pentyl)phosphinic acid), Cyanex 302 (*bis*-(2,4,4-trimethyl pentyl)monothio phosphinic acid), Cyanex 301 (*bis*-(2,4,4-trimethyl pentyl)dithio phosphinic acid) and PC-88A or IONOQUEST 801 (2-ethylhexyl hydrogen 2-ethylhexyl phosphonate) impregnated on a solid support have been reported²¹⁻²⁹. Mechanism and kinetics of the sorption of cadmium(II) with Cyanex 302²³ and Cyanex 301²⁴ was undertaken. The extent of impregnation of Cyanex 302²⁵ and PC-88A²⁶ on different Amberlite XAD series resins was found to influence the extractability of cadmium(II) and lead(II)²⁵ and ytterbium(III), terbium(III), samarium(III) and lanthanum(III)²⁶. Selective separation of iron(III), cadmium(II) and nickel(II) was achieved using Cyanex 272 and Cyanex 302 impregnated on Amberlite XAD-2 by controlling aqueous phase pH²⁷. While the decontamination of ground water for some heavy metals was possible due to the high sorption capacity of Cyanex 302 impregnated on Amberlite IRA-96²⁸. Extraction of lead with DEHPA, Cyanex 272 and IONOQUEST 801 impregnated on Amberlite XAD-7 was influenced by the pH of aqueous phase and type of extractant²⁹. No attempts have been made for selective separation and concentration of lead to facilitate its determination from complex matrices using 1-nitroso-2-naphthol-3,6-disulfonic acid impregnated on C₁₈ disk.

Solid phase extraction methods using columns with a narrow internal diameter limit the usable flow rates to a range of 1-10 cm³ min⁻¹ resulting in long time for enrichment from large sample volumes. While C₁₈ disks enable much higher flow rates^{5,30-48}.

This work preconcentration of Pb^{2+} based on the adsorption of its 1-(2-pyridyl azo)-2-naphthol (Fig. 1) complex on an octadecyl bonded silica cartridges. The adsorbed complex could be eluted using environmentally and the concentration of Pb^{2+} was determined by flame atomic absorption spectrometry. 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 milk samples.

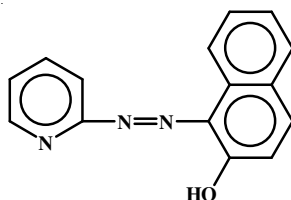


Fig. 1. Molecular structure of 1-(2-pyridylazo)-2-naphthol

EXPERIMENTAL

Determination of Pb^{2+} 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 recommendations of the manufacturers. These characteristics are tabulated in (Table-1). The pH measurements were carried out by an pH meter (sartorius model PB-11).

TABLE-1
OPERATIONAL CONDITIONS OF FLAME FOR
DETERMINATION OF LEAD

Slit width	0.7 nm
Operation current of HI-HCL	5.0 mA
Resonance fine	283.3 nm
Type of background correction	Deuterium lamp
Type of flame	Air/acetylene
Air flow	7.0 mL min ⁻¹
Acetylene flow	1.7 mL min ⁻¹

1-(2-Pyridylazo)-2-naphthol (PAN) and sodium dodecyl sulfate was of analytical grade from E. Merck, D-6100 Darmstadt, Germany. The solutions were prepared using analytical grade reagents. Triple distilled and deionized water was used for the preparation of solutions. A stock solution of 1000 $\mu\text{g mL}^{-1}$ $Pb(\text{II})$ was prepared by dissolving 0.160 g of lead(II) nitrate (Qualigens Fine Chemicals, Mumbai, India) in 100 mL water. A working solution of 10 $\mu\text{g mL}^{-1}$ was prepared by suitable dilution. About 0.01 g of 1-(2-pyridylazo)-2-naphthol (PAN) was dissolved in minimum amount of HNO_3 1 M of deionized water. Neutral octadecyl bonded silica cartridges (Himedia Research Laboratories, Mumbai, India) of particle size 150 mesh was used as the adsorbent. Sulfuric acid (Qualigens Fine Chemicals, Mumbai, India) of concentration 1 mol L⁻¹ was prepared by diluting 55.5 mL of conc. sulfuric acid with 1 L of deionized water. Water samples (Pilani, India) were collected, acidified and stored in polythene bottles.

Octadecyl bonded silica cartridge: A glass column 1.5 cm in diameter and 15 cm in length was used for the preconcentration of lead(II). About 5 g of octadecyl bonded silica cartridge was mixed with 25 mL of 1 M HCl to form slurry

and then loaded on to the column. Cotton was placed at the bottom for allowing octadecyl bonded silica cartridge to settle properly. The column was packed up to a height of 3 cm.

Procedure for preconcentration: A 50 mg sodium dodecyl sulfate and 30 mg 1-(2-pyridylazo)-2-naphthol of 50 mL was loaded on to the column of neutral octadecyl bonded silica cartridge maintaining a flow rate of 2 mL min⁻¹. Then 250 mL volume of 10 $\mu\text{g mL}^{-1}$ $Pb(\text{II})$ solution was loaded on to the column. The sample solution was loaded on to the column of neutral octadecyl bonded silica cartridge maintaining a flow rate of 2 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 HNO_3 1 M at a flow rate of 0.5 mL min⁻¹ and the concentration of lead (II) was determined by flame atomic absorption spectrometry.

RESULTS AND DISCUSSION

Effect of acidity: The effect of acidity plays a significant role in the preconcentration studies. The volume of 0.5 mol L⁻¹ sulfuric acid was varied from 1 to 6 mL in 100 mL sample volume. Quantitative recovery (> 97 %) was obtained in the range 3.5-6.0 mL of 0.5 mol L⁻¹ sulfuric acid. Beyond 6 mL, there was no change in the recovery of lead(II).

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 of lead(II), methanol, ethanol, acetone, 1 M HCl, 3 M HCl, 1 M H_3PO_4 and acidified methanol (acidified solvents obtained by addition of 1 M HNO_3), were studied. The adsorption studies were carried out maintaining an overall $Pb(\text{II})$ concentration of 10 μg in 100 mL sample volume. The recovery of lead(II) was found to be quantitative with ethanol and 1 M HNO_3 as eluting agents. However, 1 M HNO_3 was preferred owing to its non-inflammability and less toxicity^{16,17}. It was observed that when the ratio of 1 M HNO_3 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 1 M. The results are presented in. As can be seen from the figure, it is evident that the recovery of lead(II) is quantitative (> 97 %) up to 250 mL sample volume. A preconcentration factor of 170 could be attained for quantitative recovery (>97 %) of $Pb(\text{II})$ when the sample volume was 250 mL.

Effect of flow rate: The flow rate of 1-7 mL min⁻¹ was found to be suitable for optimum loading of $Pb(\text{II})$ 1-(2-pyridyl azo)-2-naphthol complex on the octadecyl bonded silica cartridge. At higher flow rates, there was a reduction in the percentage adsorption of lead(II). This could be probably due to the insufficient contact time between the sample solution and octadecyl bonded silica cartridge. A flow rate of 2 mL min⁻¹ was maintained for the elution of lead(II) (Fig. 2).

Effect of the amount of octadecyl bonded silica cartridge: The amount of octadecyl bonded silica cartridge loaded was varied from 0.25 to 2.0 g and the preconcentration studies were carried as before. Quantitative recovery of $Pb(\text{II})$ could be attained in the range 0.75-2.0 g of octadecyl bonded silica

cartridge. For amounts less than 0.75 g there was a significant reduction in the recovery beyond a sample volume of 100 mL.

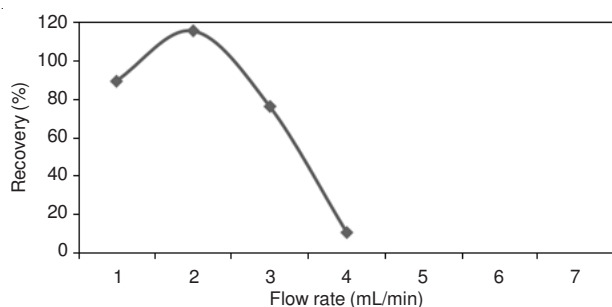


Fig. 2. Effect of flow rates of the sample solutions on recovery percentage of lead(II)

Precision studies and limit of detection: The precision studies were carried out at 10 μg level of lead(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 1.44 %. 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 Octadecyl bonded silica cartridge is not perceptibly seen. The limit of detection was found to be 0.78 $\mu\text{g L}^{-1}$.

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) 1-(2-pyridylazo)-2-naphthol (PAN) complex on sodium dodecyl sulfate was eluted using 6 mL of HNO_3 1 M. 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 lead(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 10 μg Pb(II) maintaining a sample volume of 100 mL. The studies indicated that Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cd^{2+} , Cl^- , Br^- , Fe^{3+} , NO_3^- , Zn^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} did not cause any significant reduction in the recovery of lead(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 concentration 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 lead(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 lead(II) to tap water (Tehran, taken after 10 min operation of the tap) and rain water (Tehran, 31 January, 2011) samples and milk sample. The water samples were filtered and stored in polythene bottles. The recovery of lead(II) was found to be satisfactory with a relative standard deviation of 1.44 % 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 as compared to conventional procedures to determine lead⁴⁹⁻⁵¹. As can be seen from the references, it is evident that the preconcentration factor obtained with octadecyl bonded silica cartridge is comparable to or even better than most of the other chelating matrices. The other significant feature of the proposed method is the use of environmentally benign HNO_3 1 M for the elution of the complex.

TABLE-2
EFFECT OF DIVERSE IONS ON THE RECOVERY OF
10 μg Pb(II) IN A SAMPLE VOLUME OF 100 mL

Ions	Amount (mg)	Recovery of found ion (%)	Recovery of lead (%)
Na^+	10.00	1.12(1.2)	99.6(0.5)
K^+	10.00	0.23(2.5)	99.0(1.3)
Ca^{2+}	10.00	1.14(1.1)	98.4(1.3)
Mg^{2+}	10.00	0.25(1.6)	99.0(0.2)
Fe^{3+}	0.80	2.15(2.3)	98.1(1.7)
Cd^{2+}	0.80	1.88(1.5)	98.1(1.4)
Cr^{3+}	0.80	1.95(2.3)	98.9(0.7)
Co^{2+}	0.50	1.56(0.5)	97.9(1.3)
Ni^{2+}	0.50	0.55(2.3)	99.0(1.0)
NO_3^-	0.50	0.16(1.8)	98.9(1.2)
Cl^-	0.50	0.11(0.5)	99.5(1.3)
Br^-	0.05	0.49(2.3)	98.6(1.4)
F^-	0.05	1.95(0.5)	101.7(0.8)
Mn^{2+}	0.05	0.29(0.2)	7.99(0.9)
Zn^{2+}	0.05	0.76(1.7)	103(1.9)

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	N.D	N.D
	30.00	30.06(0.4)	29.86(1.8)
Ground water	0.00	35.09(1.3)	38.17(2.0)
	30.00	52.3(1.3)	51.58(2.5)
Milk sample	2.00	2.172(1.0)	2.163(1.3)
	30.00	64.09(1.5)	64.18(2.1)
Synthesis sample	0.00	N.D	N.D
0.2mg of Co^{2+} , Cd^{2+} , Na^+ , Al^{3+} , Ba^{2+} , Ca^{2+}	30.00	30.47(1.1)	30.47(1.5)

Calibration curve: The calibration curve of lead(II) solutions is represented in Fig. 3 and the related regression is $A = 0.0245C - 0.00060$ providing a correlation coefficient of $R^2 = 0.9989$.

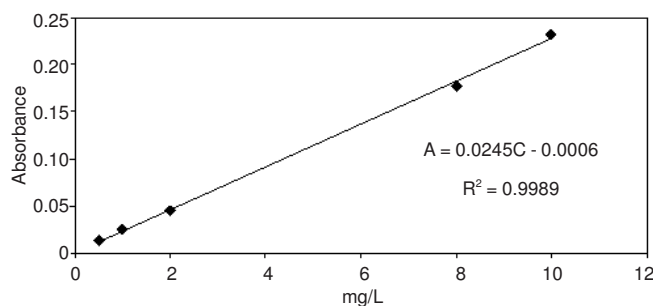


Fig. 3. Calibration curve of lead(II) measured by SPE-AAS

Conclusion

The proposed spectrophotometric method for lead(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 1 M HNO₃ 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 36 for a 250 mL sample volume. The method showed minimum interferences with commonly found ions in water sample and the recovery of lead(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 lead(II) with a low relative standard deviation of 1.48 % reflects the validity and accuracy of the proposed method when applied to real samples. The method developed was simple, reliable and precise for determining lead in water. Also, the proposed method was free of interference compared to conventional procedures to determine lead^{46,50,51}.

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