



NOVEL METHOD FOR MICRO DETERMINATION OF LEAD IN WATER SAMPLES

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ABSTRACT

A simple, rapid, precise and reliable analytical method for the micro determination of lead in water samples has been developed. The method incorporates co-precipitation of lead on zirconium hydroxide followed by its determination employing atomic absorption spectrophotometer (AAS) using 283.3 nm wavelength. The reliability of the method was established by analyses of water samples. The newly developed method has been successfully validated with spiked river, bore well and rain water samples. The method is superior to currently used methods for the determination of lead in water samples.

Key words: Co-precipitation, Zirconium hydroxide, Lead, Water Pollution, Flame atomic absorption spectrometry.

INTRODUCTION

Lead has been known to have toxic effects on human health at very low concentration¹. Lead is a toxic heavy metal and is of great concern to the public as it has been widely used in batteries, cable sheath, and addition of lead based antiknock compounds, in petrol. Other sources include lead plumbing, glazed pottery, solder used in tin cans and lead based paints². The principal problems of lead in water is associated with mining and ore processing, industrial effluents, lead plumbing and urban road or motor ways run off³. Lead pollution is one of the most serious environmental problems because of their stability in contaminated sites and the complexity of mechanism for biological toxicity⁴. Lead is easily adsorbed through gastrointestinal tract. Around 70-90 % of lead assimilated goes into the bones, liver and kidney⁵. It leads to the renal tumors. It interferes in metabolism of calcium and vitamin-D and adversely affects hemoglobin formation and causes anemia. It also adversely affects nervous system and causes behavioral abnormalities, retarding intelligence and mental development⁶. The World Health organization (WHO) had established provisional tolerable weekly intakes of lead of 0.025 mg Kg⁻¹ body weight for all human groups^{7,8}. In 1991, the United States Environmental Protection Agency (USEPA), published a regulation to control lead in drinking water, which included an action level of 0.015 mgL⁻¹.⁹ WHO has released the guidelines for drinking water quality containing the guideline value of 0.01 mgL⁻¹ for lead. There is a great demanding need to develop a simple, selective and inexpensive method for the continuous monitoring of lead in water samples^{10,11}.

Graphite furnace atomic absorption spectrometry (GFAAS) is a very attractive option for the determination of trace amounts of lead in various samples. However, the direct determination of trace amounts of lead in real samples with GFAAS is usually difficult due to its low levels in samples. In addition the samples are generally not compatible with the detection limit and major constituents such as organic compounds and inorganic salts, cause matrix effects. Consequently, separation and preconcentration procedures are often needed before GFAAS application. The most widely used techniques for the separation and preconcentration of trace lead in GFAAS include solid phase extraction (SPE)¹² and cloud point extraction (CPE)^{11,13,14}. However, these techniques have certain disadvantages, such as, time consuming, unsatisfactory enrichment factors, requirements of large organic solvents and secondary wastes etc., which make them of limited applications.

In recent years, liquid phase micro extraction (LPME) has been developed as a solvent-minimised samples pretreatment procedure since it is inexpensive and has minimal exposure to the operator to toxic organic solvents¹⁵. The combination of LPME with inductive coupled plasma-atomic absorption spectrometry (ICP-AES) or GFAAS has been established as an effective method for determination of trace elements¹⁶ and applied for the determination of trace lead in water samples^{17,18}. However, these methods suffer from certain limitations such as the fast stirring rate, which would tend to the formation of air bubbles¹⁹, time consuming extraction and equilibrium could not be attained after a long time in most cases²⁰.

EXPERIMENTAL

Apparatus

Graduated apparatus of standard calibration were used for measurements. All glasswares were washed with nitric acid (5% v/v), new glasswares were allowed to stand for several hours in nitric acid. After three rinses with distilled water, the glasswares were stored under dust free conditions.

Atomic absorption spectrophotometer

Electronics Corporation of India Ltd. (ECIL), Model No. AAS 4139 was employed for end determinations of lead. For determination of lead 283.3 nm wavelength; 5.0 mA lamp current; 0.5 nm slit width were utilized.

Reagents

All reagents used were of analytical grade. Double distilled water was used for solution preparation.

Lead stock solution

A stock solution of lead was prepared by dissolving 1.5986 g of pure lead nitrate in distilled water and diluted to 1 Liter with distilled water. Working solutions for trace analysis were prepared daily by appropriate dilutions.

Zirconium oxy chloride solution: Zirconium oxy chloride solution was prepared by dissolving 8.8316 g of zirconium oxy chloride (Riedel- De Haen Ag Seelze, Hannover) in 500 mL of distilled water.

Ammonia solution: 20 % (v/v) Sampling.

Seawater samples: Seawater samples of Arabian Sea (18°57'N longitude and 72°50'E latitude) were collected from "South Break water", Pier harbour; Mumbai, India. Samples were transferred into polyethylene sample bottles (1 Litre volume) with the addition of 1 mL of nitric acid (A.R). The

polyethylene bottles were cleaned by immersing them in nitric acid (5% v/v) overnight followed by thorough washing with deionized water and distilled water.

River water samples: Water samples of Ulhas River, Thane, India were collected following the standard techniques. All samples were filtered through 0.45 μm filter.

Rain water samples: Rainwater samples were randomly collected from Ambernath locality, Thane, India.

Bore well water samples: Bore well water samples were randomly collected from Ambernath locality, Thane, India.

Analytical procedure

5 mL of zirconium oxy chloride (4.926 mg/mL) was added to the water samples. The pH of water sample (volume between 25 and 5000 mL) was adjusted between 8.5 and 10.0 by addition of ammonia solution (20% v/v); the solution was heated to $60 \pm 5^\circ\text{C}$ for about 10 minutes. The superannuated water was siphoned off; the precipitate was transferred to centrifuge tube, centrifuged and dissolved in 2-3 mL of nitric acid (50% v/v). The solution was transferred to a 10 mL measuring flask. Final determinations were done by atomic absorption spectrophotometry. Normal precautions for trace analysis were taken throughout.

RESULTS AND DISCUSSION

Method development

Co-precipitation is one of the most efficient enrichment techniques for trace metal ions. The most important requirement for this technique necessitate that the collector should be easily separated from the matrix solution. This can be achieved by filtering, centrifuging and washing of the precipitate. Also, it is desirable that the collector should be pure and readily available material. The advantages of this technique are its simplicity and simultaneous separation and preconcentration of various analyte ions. Inorganic hydroxides of indium²¹, aluminium²², terbium²³ and iron²⁴ and organic co-precipitants generally dithiocarbamates of bismuth²⁵, copper^{26,27}, nickel²⁸ and cobalt²⁹ have been employed as efficient collectors of trace elements. Tokahogulu et al.⁵ have utilized the combination of 2-mercaptobenzo-thiazole as a chelating reagent and copper as a co-precipitate carrier for the determination of lead in water samples by flame atomic absorption spectrometry.

The aim of present work was to develop an analytical method for the micro determination of lead in water samples with very high sensitivity. Zirconium hydroxide seems to be a valuable co-precipitant for the separation and preconcentration of lead in water samples. This technique might be applicable to variety of determination techniques because zirconium is an excellent carrier. The siphon and centrifugation technique were employed. This had offered a simple and rapid preconcentration technique. For dissolution purpose, nitric acid was preferred to hydrochloric acid, which helped to prevent interference due to chloride. The combination of preconcentration and utilization of flame atomic absorption spectrophotometry technique not only provided improvement in the detection limits but also significantly reduced the interferences caused by matrix. The co-precipitation technique has several advantages such as, higher pre concentration factor, simple operation, lower cost and rapidity. The precision of newly developed method for the determination of lead was evaluated by analyses of water samples using standard addition technique. The precision and accuracy of the newly developed method was also established. Replicate analysis of each concentration level was done and the results were evaluated statistically (Table 1).

Table 1: Determination of lead in spiked water samples

Volume of sample = 250 mL		pH for co-precipitation = 9.0 ± 0.5	
Lead concentration (µg)	No. of samples analysed (n)	Relative standard deviation (%)	
50	6	4.61	
100	5	2.28	
200	6	1.82	
300	6	1.00	

Sea, river, bore well and rain water analysis

The direct determination of lead in seawater by AAS was found to be impossible because the aspiration of seawater into a flame results in scatter of radiation and clogging of the burner by the high salt concentration. Attempts for direct analysis of seawater were made but the sensitivity was found to be very poor. The utility of the proposed method was evaluated by investigating the recovery of lead from sea, river, bore well and rain water samples spiked with lead and following the recommended procedure. The samples were filtered through a membrane filter (Millipore, pore size 0.45 µm) immediately after sampling. The proposed method was successfully employed for micro determination of lead in sea, river, bore well and rain water samples (Table 2).

Table 2: Determination of lead in sea, river, bore well and rain water samples

Sample volume = 250 mL		pH: 9.0 ± 0.5		
Source of sample	Pb added (µg)	Pb Obtained (µg)	Recovery (%)*	
Sea water sample collected from South break water, Mumbai India	25	24.8	99.2	
River water samples collected from Ulhas river, Thane, India	25	25.2	100.8	
Rain water samples collected from Ambernath, Thane, India	25	24.6	98.4	
	25	25.2	100.8	
Bore well water samples collected from Ambernath, Thane, India	25	24.4	97.6	
	25	24.8	99.2	
Bore well water samples collected from Ambernath, Thane, India	25	25.4	101.6	
	25	24.8	99.2	

*Mean of three analyses

Analytical parameters for co-precipitation of lead

The influence of various analytical parameters including the effect of pH, temperature, co-precipitant concentration, time for co-precipitation was investigated and after finding the optimum ranges of analysis, the method was applied.

Effect of pH: Since the pH is one of the main parameters for co-precipitation, it was the first variable optimized in co-precipitation procedure for that purpose, the influence of pH on co-precipitation was studied in the range of 7.5 to 11. The effect of pH on the recovery of lead is presented in Fig. 1. Quantitative recovery of lead was found optimum at pH between 8.5 and 10.0.

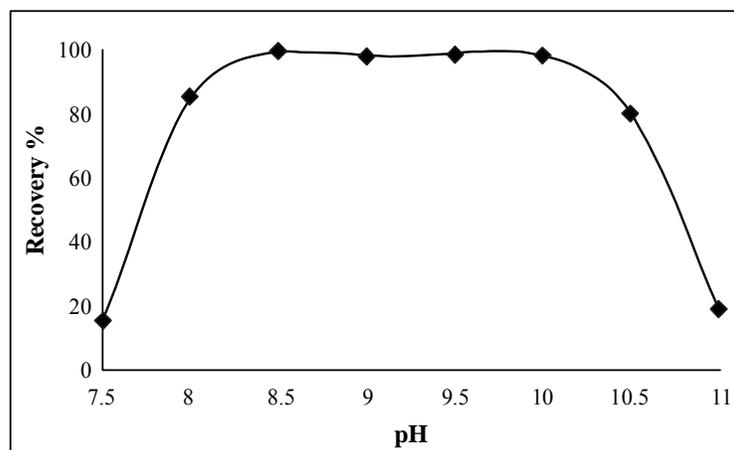


Fig. 1: Effect of pH on co-precipitation

Effect of temperature: It is desirable to have the lowest possible temperature for co-precipitation. Therefore the effect of temperature was investigated from 40-80°C. Studies on the effect of temperature during co-precipitation had revealed that recoveries of lead were between 97 and 100% at $55 \pm 5^\circ\text{C}$ temperature (Fig. 2).

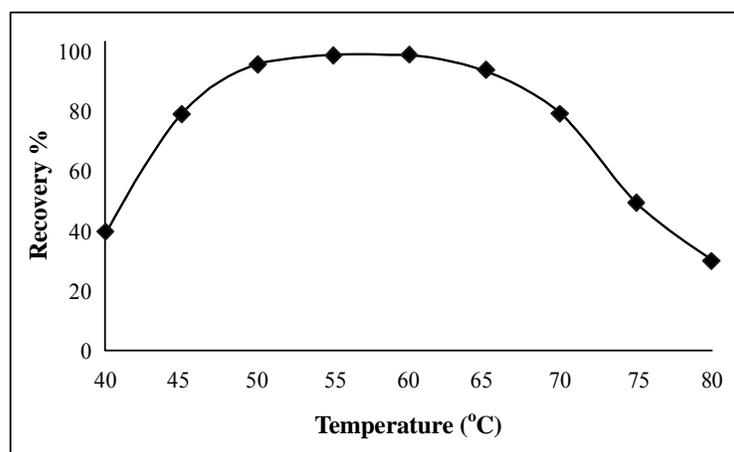


Fig. 2: Effect of temperature on co-precipitation

Effect of concentration of zirconium: The concentration of co-precipitant is a critical phenomenon. Therefore, a study on effect of concentration of co-precipitant on the recovery of lead was carried out, which showed that about 25 mg of zirconium must be precipitated to obtain 25 μg of lead. However, excess amount of co-precipitant did not interfere in the determination of lead. This adds to simplicity of the newly developed method. In addition, it makes the method adoptable particularly when the levels of lead are not known (Table 3).

Effect of sample volume

In order to obtain high preconcentration factor, the sample volume is one of the most important analytical factors for preconcentration with a view to explore the possibility of enriching low concentration of lead from large volume of samples, the influence of sample volumes on recoveries of lead were examined. The recoveries of lead from different volumes of aqueous solution containing the same amount of lead were tested. The recoveries were found to be stable. The proposed method was successfully employed for micro

determination of lead varying the volume of samples ranging from 25 mL to 2500 mL (Table 4). On the basis of these results the preconcentration factor was calculated by the ratio of the highest sample volume (2500 mL) and the lowest final volume (10 mL) thus the preconcentration factor for lead was calculated as 250. This establishes the applicability of the proposed method for the analysis of polluted water samples.

Table 3: Effect of concentration of co-precipitant

Zr concentration = 4.296 mg/mL pH 9.0 ± 0.5
 Volume of sample = 250 mL

Zirconium added (mL)	Recovery of lead (%) [*]
1	10.8
2	60.5
3	80.8
4	97.2
5	98.8
6	99.8
7	99.3
8	98.2
9	99.3
10	98.2

^{*}Mean of three analysis

Table 4: Effect of sample volume

Zr concentration = 4.926 mg/mL pH = 9.0 ± 0.5

Sample volume (mL)	Recovery of lead (%) [*]
25	99.4
50	101.2
100	98.7
250	98.2
100	99.3
500	98.4
1000	98.3
2000	97.1
2500	96.4

^{*}Mean of three analyses

Effect of time: It is desirable to have shortest incubation time. Therefore, the effect of time on co-precipitation study was conducted which revealed that the time between 5 and 20 minutes is sufficient for complete co-precipitation of lead. However, the co-precipitated lead should not be left over for a long duration as lead may redissolve in solution leading to poor recoveries of lead. This established the rapidity of the proposed method (Fig. 3).

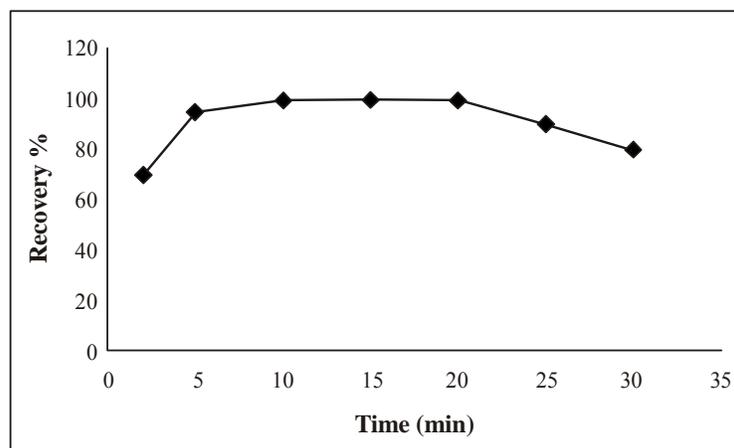


Fig. 3: Effect of time on co-precipitation

Interference effect

One of the challenging problems in preconcentration method is the elimination of interfering ions. The matrix related problems in river water analysis are the alkali and alkaline earth metals, generally in the form of chlorides, whereas, seawater has a complex matrix of interfering ions sodium, potassium, magnesium, calcium etc. In order to detect the potential interferences on the co-precipitation of lead, the effect of diverse ions on the recoveries of lead was examined by adding a known volume of ions in question to a solution containing 25 μg of lead and preceded as per recommended analytical procedure. The method proposed offered rejection of interfering ions. The results are summarized in Table 5. The freedom from interferences of several ions is a definite advantage of the proposed method.

Table 5: Effect of diverse ions

Lead concentration = 25 μg

Volume of sample = 250 mL

pH: 9.0 ± 0.5

Ion	Added as	Amount added (μg)	Lead obtained (μg)
Fe^{3+}	FeCl_3	500	24.2
		250	24.5
Ni^{2+}	NiCl_2	500	23.9
		250	24.6
Zn^{2+}	ZnCl_2	500	23.7
		250	24.2
Cd^{2+}	CdCl_2	500	24.1
		250	24.8
Al^{3+}	AlCl_3	500	23.8
		250	24.1
Ba^{2+}	BaCl_2	500	24.7
		250	23.8

Table 6: Comparative study from some recent studies on pre-concentration-separation of heavy metal ions

Sr. No.	Technique employed	Analyte (s)	System	PF	Detection limit (μgL^{-1})	References
1	FAAS	Pb, Cd	-----	150	1.08	[5]
2	SPE	Cd, Cr, Cu, Pb, Zn	Sorbent (Rice bran)	100	0.56-1.85	[30]
3	SPE	Cu, Fe, Mn, Ni	Chelating resin	21.3-44.1	0.5-1.1	[31]
4	SPE	Fe (III), Pb (II), Ni (II)	<i>Aspergillus niger</i>	50	1.7-5.6	[32]
5	Co-precipitation	Cd (II), Cr (II), Pb (II), Mn (II)	Magnesium hydroxide		0.08-1.5	[33]
6	Co-precipitation	Ni (II), Cd (II), Pb (II)	Copper hydroxide	100	2.0-7.0	[36]
7	CPE	Cu, Ni, Co	MPKO (Triton X-114)	58-67	1.6-2.1	[34]
8	CPE	Zn, Ni, Co, Pb	2GBI (Triton X-114)	13-29.6	4.9-11	[35]
9	CPE	Cu, Pb, Co	1-PTSC (Triton X 114)	25	0.61-1	[3]
10	Co-precipitation	Pb	Zirconium hydroxide	250	0.24	Present work

FAAS : Flame atomic absorption spectrometry, SPE : Solid phase extraction,

CPE : Cloud point extraction, MPKO- Methyl – 2 pyridylketone oxime,

GBI : 2 – Guanidinobenzimidazole, PTSC : Phenylthiosemicarbazide,

AAS : Atomic absorption spectrophotometer, PF : Preconcentration factor

Blank: The blank consist of lead in the reagents introduced during sampling and other stages. In most cases, the lead content in the reagent was below detection limit. However, the end determination was carried out employing a blank sample to set the zero line.

CONCLUSION

The co-precipitation method with zirconium hydroxide was successfully employed for determination of lead in water samples with acceptable accuracy and precision. The proposed method is reliable, simple, economical, fairly rapid and precise and hence recommended to the laboratories where a large number of samples are to be analysed. The comparison of the results found in the present study and some recent works as reported in literature has been compared (Table 6). The proposed method is superior to the currently used methods for having lower detection limits and high preconcentration factor.

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