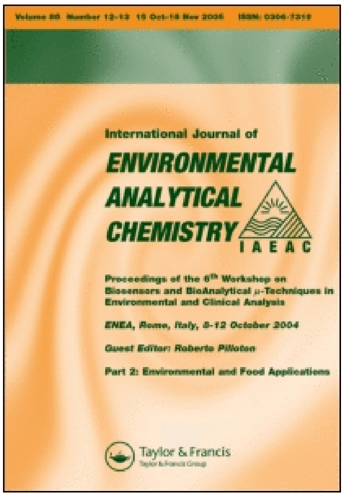
This article was downloaded by:
On: *19 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Microdetermination of Lead in Water Samples, Preconcentration by Coprecipitation Followed by its Atomic Absorption Spectrophotometric Determination

Anil K. Shrivastava[a]; S. G. Tandon[a]
[a] Department of Chemistry, Ravishankar University, RAIPUR, India

To cite this Article Shrivastava, Anil K. and Tandon, S. G.(1982) 'Microdetermination of Lead in Water Samples, Preconcentration by Coprecipitation Followed by its Atomic Absorption Spectrophotometric Determination', International Journal of Environmental Analytical Chemistry, 12: 3, 169 — 176

To link to this Article: DOI: 10.1080/03067318208078325

URL: http://dx.doi.org/10.1080/03067318208078325

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Intern. J. Environ. Anal. Chem., 1982, Vol. 12, pp. 169–176
0306-7319/82/1204-0169 $06.50/0
© Gordon and Breach Science Publishers Inc., 1982
Printed in Great Britain

Microdetermination of Lead in Water Samples, Preconcentration by Coprecipitation Followed by its Atomic Absorption Spectrophotometric Determination

ANIL K. SHRIVASTAVA and S. G. TANDON
Department of Chemistry, Ravishankar University, RAIPUR, 492.010, India

Downloaded At: 08:50 19 January 2011

(*Received January 5, 1982*)

The method incorporates coprecipitation of lead on zirconium hydroxide and its quantitative spectrophotometric determination in natural, polluted and synthetic water samples. The method incorporates coprecipitation of lead on zirconium hydroxide and its quantitative determination by AAS using 283.3 nm wavelength.

INTRODUCTION

There has been a widespread interest in the pollution problems associated with lead. Water pollution by lead has been described as an important ecological problem.[1] The MAC value (maximum allowed concentration) for lead in drinking water fixed by the Ministry of Health, the Government of India[2] and W.H.O.[3] is 0.1 ppm whereas both the Environmental Protection Agency (EPA)[4] and the U.S. Public Health Service (USPHS)[5] have fixed the value 0.05 ppm. Lead pollution in water is generally from motor vehicle exhaust fumes and industrial fall out.[6]

The traditional spectrophotometric method for determining lead with dithizone is complicated in the submicrogram range and requires critical control of experimental conditions. In recent years atomic absorption spectrophotometric methods have been widely suggested for the microdetermination of lead. However, direct atomic absorption spectrophotometry is subject to serious matrix interferences and requires preconcentration steps.

The present paper reports a novel method for microdetermination of lead in synthetic, polluted and river water samples. It incorporates preconcentration of lead by its micro (co)precipitation on zirconium hydroxide at pH 8.2–9.5 which is redissolved in nitric acid and followed by its atomic absorption spectrophotometric determination. The method is simple, reliable and precise and recommended to the laboratories where large number of samples are to be analysed. The proposed method is demonstrated to be equal or superior to the currently used methods.

EXPERIMENTAL

Apparatus

A Pye Unicam SP 2900 atomic absorption spectrophotometer equipped with a lead hollow cathode lamp was employed for atomic absorption measurements. A Systronics pH meter 325 was employed for pH measurements.

Graduated apparatus of standard calibration were used for measurements. Contamination from glassware, stoppers and pipette tips was scrupulously prevented. All glassware was washed with nitric acid (5% v/v); new glassware was allowed to stand for several hours in acid. After three rinses with deionized water and three rinses with further purified water, the glassware was stored under dust free conditions.

Downloaded At: 08:50 19 January 2011

Reagents

All reagents used were of analytical grade of B.D.H. or S.M. Triple glass distilled water was used for solution preparation and other purposes.

Stock lead solution—1000 mg l^{-1}; 1.6000 g $Pb(NO_3)_2$ was dissolved in 5 ml of 5 M nitric acid and made up to 1 litre. Working standards were prepared by diluting this solution and kept for minimum time before use.

Zirconium solution—2 mg ml^{-1}; 3.53 g $ZrOCl_2 . 8H_2O$ was dissolved in 10 ml of 6 M hydrochloric acid and made up to 500 cm^3.

Ammonia solution—(20% v/v).

SAMPLING

Seawater samples

Seawater samples of Arabian Sea (71.2° longitude and 21.5° latitude) were procured from the Salt and Marine Research Institute, Bhavnagar, India. Samples were transferred into polyethylene sample bottles, with the addition of 1 ml of nitric acid (AnalaR). The polyethylene bottles were cleaned by soaking them in nitric acid (5% v/v) overnight, followed by thorough washing with de-ionised water and glass-distilled water. Artificial seawater samples were also prepared by dissolving 28.0 g sodium chloride, 0.8 g potassium chloride, 5.33 g magnesium sulphate and 1.33 g calcium chloride in one litre triple glass-distilled water.

River water samples

Water samples of the Kharun river, Kumhari, India and Chhipra river, Ujjain, India were collected by standard techniques. All samples were filtered through a 0.045 μM filter.

ANALYTICAL PROCEDURE

The pH of water sample (200–250 ml) was adjusted to 8.2–9.5 by the addition of ammonia solution (20% v/v) and then 5 ml zirconyloxychloride solution (2 mg ml^{-1}) was added. The solution was boiled for about 2 min, and allowed to stand (precipitation) for about 10 min. The supernated water was siphoned off, the precipitate transferred to a centrifuge tube, centrifuged and dissolved in 2–3 ml of nitric acid (50% v/v). The solution was transferred to a 5, 10 or 25 ml measuring flask depending upon the lead level being determined. A final volume of 10 ml is generally satisfactory.

Final measurements were done by atomic absorption spectrophotometry. Instrumental settings used were those recommended in the manufacturer's manuals, i.e. 283.3 nm wavelength, 0.4 nm slit width and air-acetylene as fuel. After extraction by the recommended procedure the total blank was subtracted from sample concentration. It is recommended that a special blank determination should be carried out so as to check the lead content of each batch of nitric acid and zirconyloxychloride. Normal precautions for trace analysis were taken throughout.

RESULT AND DISCUSSION

Seawater analysis

The direct determination of lead in seawater was found to be impossible[7] because the aspiration of seawater into a flame results in scatter of radiation and clogging of the burner by the high salt concentration.[8] Attempts for direct analysis of seawater were made but the sensitivity was

Downloaded At: 08:50 19 January 2011

poor.[10] Boyle and Edmond[9] reported cobalt pyrrolidine dithiocarbamate as a coprecipitant. Riley[7] reviewed analytical methods for the analysis of trace metals in seawater. An excellent study of the problems caused by heavy matrix effects has been made by Cruze and Vanloon.[11]

Method development

The aim of the present work was to develop a method for the microdetermination of lead in water samples with very high sensitivity. Zirconium (IV) hydroxide as a collector gave promising results for the microdetermination of lead in various water samples. The siphon and centrifugation techniques were employed to make the method rapid and to check the loss of lead by washing, dissolution, evaporation, etc. stages. For dissolution purpose nitric acid was preferred to hydrochloric acid which helped to get rid of chloride interferences.[12] Preconcentration by coprecipitation seems advisable as it is advantageous in comparison with the solvent extraction methods by making it possible to determine the total content of the trace element regardless of the species in which it occurs in water. The precision of the method for the lower level of determination was evaluated by the analysis of synthetic water samples. Replicate analysis of each concentration level was done and the results were statistically evaluated (Table 1).

Downloaded At: 08:50 19 January 2011

TABLE I

Determination of lead in synthetic water samples: Preconcentration by coprecipitation

Lead concentration[a] (μg)	n	Standard deviation ($\times 10^{-2}$)	Relative standard deviation (%)
0.50	6	4.6	9.2
1.00	9	8.7	8.7
1.20	10	9.0	7.5
1.50	10	10.1	6.7
2.00	10	10.0	5.0
2.50	6	11.5	4.6
3.00	8	12.0	4.0
3.50	7	11.2	3.2
5.00	7	10.5	2.1

[a] Volume of sample = 250 ml.

Recovery of lead from sea and river water samples

In order to check the efficiency of the proposed method standard lead solution was added to artificial seawater samples and its determination by the method described earlier was done. The results are summarised in Table 2. The excellent agreement between the amount of lead added and found establishes the reliability of the proposed method. The method was successfully employed for the determination of lead in polluted sea and river water samples. Results are illustrated in Table III.

TABLE II

Determination of lead in artificial seawater samples[a] by proposed method

Lead added (μg)	Lead found (μg)	Relative error (%)
1.00	0.92	−8.0
1.50	1.52	+1.3
2.00	2.06	+3.0
2.50	2.45	−2.0
3.00	3.06	+2.0
3.50	3.40	−2.9
5.00	4.90	−2.0

[a] Volume of sample = 200 ml.

TABLE III

Determination of lead in polluted water samples: Preconcentration by coprecipitation

Sample	Concentration of lead		Standard deviation	C.V.	
	(μg ml^{-1})	Av. value (μg ml^{-1}	($\times 10^{-2}$)	(%)	n
Sea water (Bhavnagar, India)	0.67, 0.67 0.57, 0.50 0.61, 0.57 0.58, 0.59	0.59	5.63	0.54	8
Chhipra river water (Ujjain, India)	0.074, 0.071 0.084, 0.085 0.088, 0.088 0.084, 0.077	0.081	0.65	8.03	8
Kharun river water (Kumhari, India)	0.026, 0.027 0.028, 0.026 0.029, 0.030 0.024, 0.027 0.031	0.027	0.23	8.37	9

Downloaded At: 08:50 19 January 2011

Analytical conditions for coprecipitation of lead

Effect of pH The data in Table 4 indicate that the optimum pH value for coprecipitation is between 8.2 and 9.5.

Effect of zirconium(IV) A study of the effect of the coprecipitant on the recovery of lead shows that about 8 mg of zirconium must be precipitated to obtain complete recovery of 10 μg of lead (Table 4).

Effect of sample volume The proposed method was sucessfully employed for the microdetermination of lead varying the volume of sample ranging from 10 ml to 1 litre. This establishes the applicability of the proposed method especially for the analysis of polluted water samples (Table 5).

TABLE IV

Analytical conditions for coprecipitation of lead

(A) Effect of pH on recovery of lead:

pH	% Recovery[a]
7.2	78.2
7.5	86.8
8.0	94.7
8.2	99.0
8.5	100.6
9.0	100.0
9.5	100.4
9.8	96.1

(B) Effect of coprecipitant on recovery of lead:

Volume of zirconium solution (ml)	Zirconium (IV) (mg)	% Recovery[a]
0.5	1	8.2
1.0	2	22.6
1.5	3	32.4
2.0	4	48.8
3.0	6	80.7
3.5	7	92.6
4.0	8	98.8
4.5	9	100.9
5.0	10	100.2
6.0	12	100.0
8.0	16	100.5

Volume of sample, 250 ml; Lead added, 10 μg

[a] Average of 3 analyses.

Downloaded At: 08:50 19 January 2011

TABLE V

Effect of volume of sample

Volume of sample (ml)	Lead found (μg)[a]	Concentration of lead (ppb)	Relative error (%)
10	0.103	10.0	+3.0
25	0.098	4.0	−2.0
50	0.097	2.0	−3.0
100	0.104	1.0	+4.0
200	0.103	0.5	+3.0
250	0.100	0.4	0.0
500	0.097	0.2	−3.0
1,000	0.095	0.1	−5.0

Amount of lead added = 0.10 μg.

[a] Average of 3 measurements.

Downloaded At: 08:50 19 January 2011

Interference effects The effect of diverse ions on the lead determination was studied by adding a known amount of the ion in question to a solution containing 10 μg of lead and proceeding as in the recommended analytical procedure. The results are summarised in Table 6. The freedom from interference of several ions is a definite advantage of the proposed method.

Blank The blank consists of lead in the reagents and introduced during sampling and other stages. In most cases, the lead content in the reagent was below the detection limit. The maximum blank in the sample was between 0.044 and 0.052 $\mu g\,l^{-1}$ with a standard deviation of 1.0×10^{-3} and a relative standard deviation of 8.33% ($n = 7$). It is noteworthy that all experiments were done at an ordinary laboratory bench and the somewhat high lead value in the total blank was probably due to contamination from the laboratory air.

Acknowledgement

The authors are greatly indebted to the Director, Salt and Marine Research Institute, Bhavnagar, India, for providing them with sea water samples. One of the authors (A.K.S.) is grateful to the University Grants Commission, New Delhi, India for the award of a Research Fellowship.

TABLE VI

Effect of diverse ions on the recovery of lead by the proposed method
Lead concentration = 10 μg/250 ml.

Ion	Added as	Amount of ion added (μg)	% Recovery[a]
Al^{3+}	$Al(NO_3)_3.9H_2O$	10,000	98.2
Ca^{2+}	$Ca(NO_3)_2.4H_2O$	1,000	97.8
Cd^{2+}	$3CdSO_4.8H_2O$	10,000	98.6
Co^{2+}	$Co(NO_3)_2.6H_2O$	10,000	101.8
Cu^{2+}	$Cu(NO_3)_2.3H_2O$	10,000	100.7
Fe^{3+}	$Fe(NO_3)_3.6H_2O$	10,000	98.6
Mn^{2+}	$Mn(NO_3)_2.6H_2O$	10,000	96.8
Ni^{2+}	$Ni(NO_3)_2.6H_2O$	10,000	98.9
NH_4^+	NH_4NO_3	1,000	98.9
Acetate	CH_3COONa	1,000	102.6
Carbonate	Na_2CO_3	10,000	101.8
Chloride	NaCl	5,000	99.6
Fluoride	NaF	1,000	98.2
Nitrate	$NaNO_3$	10,000	102.5

[a] Mean of 3 repetitive analyses of the same sample.

Downloaded At: 08:50 19 January 2011

References

1. K. H. Mancy, *Water Pollution Control*, in Anal. Chem. Key to Progress in National Problems, *Nat. Bur. Stand.* (U.S.A.), Special Publ. No. 351 (1972).
2. Drinking Water Standards, Ministry of Health, Government of India (1971).
3. International Standards for Drinking Water, World Health Organization, Geneva, Switzerland (1971).
4. National Secondary Drinking Water Regulations, E.P.A., Federal Register US Govt. Printing Office, Washington, D.C. (1977).
5. Public Health Service Drinking Water Standards—1962, USPHS Publication 956, US Govt. Printing Office, Washington, D.C. (1962).
6. E. G. Zook, F. E. Greene and E. R. Morris, *Cereal Chem.* **47,** 720 (1970).
7. J. P. Riley, in *Chemical Oceanography*, J. P. Riley and G. Skirrow (eds.) London, Vol. 3, p. 193 (1975).
8. D. C. Burrell, *Atomic Spectrometric Analysis of Heavy Metal Pollutants in Water*, Ann Arbor Science Publ., Michigan (1974).
9. E. A. Boyle, J. M. Edmond, *Anal. Chim. Acta* **91,** 189 (1977).
10. W. C. Campbell, J. M. Ottaway, *Analyst* **102,** 495 (1977).
11. R. B. Cruz, J. C. Vanloon, *Anal. Chim. Acta* **72,** 231 (1974).
12. D. C. Manning, W. Slavin, *Anal. Chem.* **50,** 1234 (1978).