Available online at www.sciencedirect.com

SCIENCE DIRECT

Talanta 67 (2005) 992–996

Talanta

www.elsevier.com/locate/talanta

Determination of lead in water samples by graphite furnace atomic absorption spectrometry after cloud point extraction

Jianrong Chen[a,*], Shanmei Xiao[b,c], Xiaohua Wu[a], Keming Fang[a], Wenhan Liu[c]

[a] *College of Chemistry and Life Science, Zhejiang Normal University, Jinhua, Zhejiang 321004, China*
[b] *Jinhua College of Profession and Technology, Jinhua, Zhejinag 321017, China*
[c] *College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou, Zhejiang 310032, China*

Received 28 November 2004; received in revised form 18 April 2005; accepted 18 April 2005
Available online 12 May 2005

Abstract

Cloud point extraction (CPE) has been used for the pre-concentration of lead, after the formation of a complex with 2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol (5-Br-PADAP), and later analysis by graphite furnace atomic absorption spectrometry (GFAAS) using octylphenoxypolyethoxyethanol (TritonX-114) as surfactant. The chemical variables affecting the separation phase were optimized. Separation of the two phases was accomplished by centrifugation for 15 min at 4000 rpm. Under the optimum conditions i.e., pH 8.0, cloud point temperature 40 °C, [5-Br-PADAP] = 2.5×10^{-5} mol l^{-1}, [Triton X-114] = 0.05%, added methanol volume = 0.15 ml, pre-concentration of only 10 ml sample permitted an enhancement factor of 50-fold. The lower limit of detection (LOD) obtained under the optimal conditions was 0.08 $\mu g\,l^{-1}$. The precision for 10 replicate determinations at 5 $\mu g\,l^{-1}$ Pb was 2.8% relative standard deviation (R.S.D.). The calibration graph using the pre-concentration system for lead was linear with a correlation coefficient of 0.9984 at levels near the detection limits up to at least 30 $\mu g\,l^{-1}$. The method was successfully applied to the determination of lead in water samples.

Keywords: Cloud point extraction; GFAAS; Lead

1. Introduction

Heavy metal pollution is and will be a public health problem. Lead, which produces several diseases, is one of the most important and widely distributed pollutants in the environment [1]. Lead is one of the most toxic elements and has accumulative effect. It is called environmental priority pollutants. It is therefore important to monitor the levels of lead in environments.

Several analytical techniques such as atomic absorption spectrometry (AAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma-optical emission spectrometry (ICP-OES), polarographic analysis and inductively coupled plasma mass spectrometry (ICP-MS) are available for the determination of lead with sufficient sensitivity for most of applications [2]. However, the determination of trace metal elements in aqueous samples is difficult due to various factors, particularly their low concentrations and matrix effects. Pre-concentration and separation techniques, such as liquid–liquid extraction [3,4], ion exchange [5,6], co-precipitation [7,8], especially on-line liquid–liquid extraction [9,10], and on-line solid phase extraction [11–13], etc. can solve these problems and lead to a higher confidence level and easy determination of the trace elements.

In recent years, a methodology of separation and pre-concentration based on cloud point extractions are becoming an important and practical application of the use of surfactants in analytical chemistry [14]. Aqueous solutions of many non-ionic surfactant micellar systems become turbid when the temperature has been changed. This temperature is named ‘cloud point’. Above the cloud point, the solution separates into two phases: the surfactant-rich phase with very small volume, and the bulk aqueous solution, containing surfactant

---

[*] Corresponding author. Fax: +86 579 2282489.
E-mail address: cjr@zjnu.cn (J. Chen).

0039-9140/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2005.04.029

monomers. The use of micellar systems as an alternative to other techniques of separation offers several advantages including low cost, safety and high capacity to concentrate a wide variety of analytes of widely varying nature with high recoveries and very high concentration factors [15–18].

The cloud point extraction has been first used to separate and pre-concentrate organic compounds [19]. The cloud point extraction has also been used to pre-concentrate trace metals based on the formation of chelates in the surfactant aggregate. U [20], Er [21], and Gd [22] were determined by spectrophotometry, Pd [23] by room temperature phosphorescence, Cu [24], Cd [25], Mn [26,27], Co [28], Ni and Co [29], Cd and Ni [30], Ag and Au [31], Cr(III) and Cr(VI) [32] by FAAS, Fe(III) by GF-AAS [33], As(III) and As(V) by ET-AAS [34] after CPE using complexing agents. Au [35] and Pb [36] were extracted efficiently without a complexing agent, using PONPE7.5 as a non-ionic surfactant. Cd, Cu, Pb, and Zn [37] were simultaneous pre-concentration after the formation of a complex with 1-(2-thiazolylazo)-2-naphthol (TAN), and later analysis by FAAS, using TritonX-114 as surfactant. Stalikas [38] reviewed the CPE as a tool for separation and pre-concentration in metal analysis. Burguera and Burguera [39] reviewed analytical applications of organized assemblies for on-line spectrometric determination.

In the present work, we report the results obtained in a study of the cloud point pre-concentration of Pb, after the formation of a complex with 2-(5-Bromo-2-pyridylazo)-5-(diethylamino)-phenol (5-Br-PADAP), and later analysis by graphite furnace atomic absorption spectrometry using octylphenoxypolyethoxyethanol (TritonX-114) as surfactant. The proposed method is also applied to the determination of Pb in water samples.

2. Experimental

2.1. Apparatus

A Perkin-Elmer Analyst 800 atomic absorption spectrometer including the AS-800 Autosampler equipped with Zeeman-effect background correction, and lead hollow-cathode lamp radiation source, were used. The operating conditions of lead hollow-cathode were those recommended by the manufacturer (wavelength 283.3 nm, slit width 0.7 nm, current 10 mA). The furnace program was tested. The results were shown in the Table 1. The pressure of argon was adjusted to 3.5–4.0 MPa. A volume of 20 μl of the final solution was injected into the graphite tube by the autosampler. A centrifuge was used to accelerate the phase separation process.

2.2. Reagents and solutions

The non-ionic surfactant TritonX-114 was obtained from ACROS ORGANICS (New Jersey, USA) and was used without further purification. A solution of (0.5×10^{-3} mol l^{-1}) 5-Br-PADAP was prepared from the Merck product. Stock standard solution of lead at a concentration of 1000 μg ml^{-1} was prepared from pure lead powder (Shanghai Reagent Factory, Shanghai, China). Working standard solutions were obtained by appropriate dilution of the stock standard solution. Stock buffer solution, 0.1 mol l^{-1}, was prepared by dissolving appropriate amounts of $Na_2B_4O_7 \cdot 10H_2O$ (AR, Shanghai Reagent Factory, Shanghai, China) in water. Nitric acid (AR, Shanghai Reagent Factory, Shanghai, China) and methanol (AR, Shanghai Reagent Factory, Shanghai, China) were used. All solutions were prepared in ultra-high-quality water obtained from water purification system (Millipore, Bedford, MA, USA). Standard Reference Material (SRM) 1640 was obtained from National Institute of Standards and Technology (NIST), USA.

The materials and vessels used for trace analysis were kept in 10% nitric acid for at least 24 h and subsequently washed four times with ultra-high-quality water before use.

2.3. Procedures

For the cloud point extraction, aliquots of the cold solution containing the analyte, TritonX-114 and 5-Br-PADAP, buffered at a suitable pH, were kept for 15 min in the thermostatic bath at 40 °C. Separation of the two phases was accomplished by centrifugation for 15 min at 4000 rpm. On cooling in an ice-bath, the surfactant-rich phase become viscous and was retained at the bottom of the tubes. The aqueous phases can readily be discarded simply by inverting the tubes. Later, 0.15 ml of a solution of methanol containing 0.1 mol l^{-1} HNO_3 was added to the surfactant-rich phase. The acidified methanolic aqueous samples were introduced into the graphite furnace by autosampler.

According to the above pre-concentration procedure, all the water samples were filtered to remove suspended particulate matter and were stored at 6 °C in the dark. To 10 ml of water sample, 0.5 ml of 1% TritonX-114, 0.5 ml of 2.5×10^{-5} mol l^{-1} 5-Br-PADAP and 1 ml of

Table 1
Furnace program

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Internal flow (ml min^{-1})	Gas type
1	110	1	30	250	Normal
2	130	15	30	250	Normal
3	420	10	20	250	Normal
4	1400	0	5	0	Normal
5	2450	1	3	250	Normal

$Na_2B_4O_7 \cdot 10H_2O$ buffer (pH 8.0) were added. After phase separation, the above steps were followed.

Five milliliters of SRM 1640 was adjusted with 0.5 mol l^{-1} NaOH to pH about 8.0 and diluted with Milli-Q water to 10 ml. The samples were assayed as described in the previous section on the procedures.

3. Results and discussion

3.1. Effect of pyrolysis and atomization temperatures on absorbance

The purpose of the pyrolysis step is to remove as much of the matrix as possible prior to atomization. This decreases the possibility of chemical interference and reduces the magnitude of the background signal. However, lead compounds are more volatile when the temperature is higher than 500 °C. In order to avoid losing the lead during the pyrolysis step, the optimal pyrolysis temperature is necessary. Fig. 1 shows the effect of the pyrolysis temperature on the integrated absorbance. 420 °C was selected as the optimized pyrolysis temperature for lead.

The optimal temperature depends upon the properties of the compound in which the element resides. It may be necessary to determine the optimal temperature from a plot of integrated absorbance versus atomization temperature. Fig. 2 shows that the optimal atomization temperature of lead is 1400 °C.

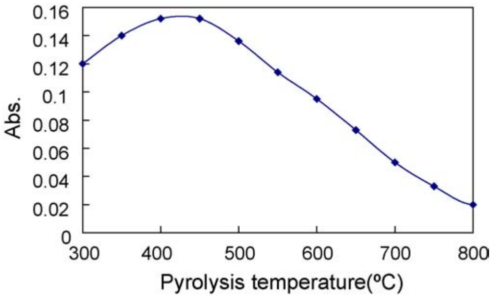

Fig. 1. Optimization of the pyrolysis temperature for lead.

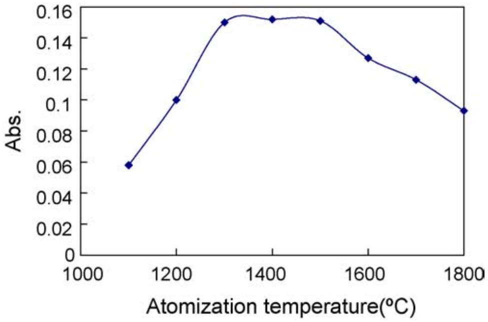

Fig. 2. Optimization of the atomization temperature for lead.

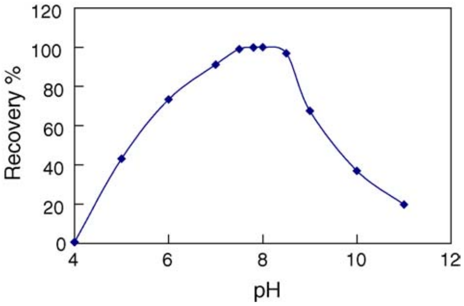

Fig. 3. Effect of pH on the extraction of lead Pb^{2+} 5 μg l^{-1}, 5-Br-PADAP: 2.5×10^{-5} mol l^{-1}, TritonX-114: 0.05%.

3.2. Effect of pH

Cloud point extraction of lead was performed in different pH buffer solutions, The separation of metal ions by the cloud point method involves prior formation of a complex with sufficient hydrophobicity to be extracted into the small volume of surfactant-rich phase, thus obtaining the desired preconcentration. Extraction yield depends on the pH at which complex formation is carried out.

Fig. 3 shows the effect of pH on extraction of lead complexes. It can be seen that the yield is almost constant and near quantitative recovery in the range pH 7.5–8.5. Hence, the optimum pH value at 8.0 was chosen for the analytes.

3.3. Effect of buffer concentration

The influence of buffer amount was carried out in which the other experimental variables remained constant. The results have shown that above 0.2 ml of buffer solution (0.1 mol l^{-1} $Na_2B_4O_7$) added in 10 ml of solution, no obvious variation took place in the extraction yield. A 1.0-ml aliquot of buffer solution was added in all subsequent experiments.

3.4. Effect of 5-Br-PADAP concentration

The effect of 5-Br-PADAP concentration on the extraction yield of Pb was studied. For 10 ml of a solution containing 5 μg l^{-1} lead in 0.05% TritonX-114 and medium buffered at pH 8.0 containing various amounts of 5-Br-PADAP were subjected to the cloud point extraction process. The yield increases up to a 0.2-ml volume of 5.0×10^{-4} mol l^{-1} 5-Br-PADAP and reaches 100% extraction efficiency. A 0.5-ml volume of 5.0×10^{-4} mol l^{-1} 5-Br-PADAP was chosen to account for other extractable species.

3.5. Effect of TritonX-114 concentration

The variations in the analytical signal as a function of the concentration of TritonX-114 in the range of 0.01–0.1% (m/v) were investigated. The results have shown that quantitative extraction was observed when the TritonX-114 concentration was above 0.03%. An amount of 0.05% TritonX-114 was chosen in order to achieve quantitative extraction and thereby the highest extraction efficiency.

3.6. *Effects of equilibration temperature and time*

It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, which compromise completion of reaction and efficient separation of phases. It was found that a temperature of 40 °C is adequate for lead analysis. The dependence of extraction efficiency upon equilibration time was studied within a range of 5–30 min. An equilibration time of 15 min was chosen as the best to obtain quantitative extraction.

3.7. *Effect of ionic strength and centrifugation time*

Ionic strength had no considerable effect upon the magnitude of extraction and sensitivity effect up to 0.5 mol l^{-1}.

The effect of centrifugation time upon extraction efficiency was studied for the range: 5–20 min. The complete phase separation was achieved for times longer than 10 min. A centrifugal time of 15 min was chosen as the best condition.

3.8. *Interferences*

In the view of the high selectivity provided by GFAAS, the only interferences studied were those related to the preconcentration step. The effects of representative potential interfering species were tested. Commonly encountered alkali and alkaline earth elements generally do not form stable complexes and are not CPE-extracted. The results were shown in Table 2 and proved that lead recoveries were almost quantitative in the presence of excessive amount of possible interfering cations.

Table 2
Effect of foreign ions on the preconcentration and determination of lead (5 μg l^{-1})

Ions	Ion/Pb ratio (w/w)	Recovery (%)
K^+	4000	99.8
Na^+	4000	98.3
Ca^{2+}	2000	99.2
Mg^{2+}	2000	101.0
Ba^{2+}	4000	102.0
Al^{3+}	2000	99.0
Cd^{2+}	80	99.5
Fe^{3+}	80	98.1
Co^{2+}	80	102.0
Ni^{2+}	80	98.8
Cu^{2+}	80	97.6
Zn^{2+}	80	96.9

3.9. *Calibration, precision and detection limit*

Calibration graphs were obtained by pre-concentrating 10 ml of the sample in presence of 0.05% TritonX-114 in a medium buffered at pH 8.0. A volume of 20 μl of the final solution was introduced into the graphite furnace by autosampler. In this case, the calibration graph using the preconcentration system for lead was linear with a correlation coefficient of 0.9984 at levels near the detection limits up to at least 30 μg l^{-1}. Regression equation was $A = 2.63 \times 10^{-2} C$ (μg l^{-1}) + 5.77×10^{-3}. The precision for 10 replicate determinations at 5 μg l^{-1} Pb was 2.8% relative standard deviation (R.S.D.). The lower limit of detection (LOD) obtained under the optimal conditions was 0.08 μg l^{-1} (3σ). The enhancement factor, calculated as the ratio of absorbance of preconcentration samples to that obtained without preconcentration, was 50 times.

There are some publications on cloud point extraction of lead for atomic spectrometric determination. The enrichment factors and the LOD of the methods and the proposed method were summarized in Table 3. It shows a good enrichment factor and sensitivity of the proposed method.

Table 3
Summary of cloud point extraction of lead for atomic spectrometric determination

Enrichment factors	LOD (μg l^{-1})	Atomic spectrometry	References
72	0.4	FAAS	[40]
>300	0.077	ICP-OES	[41]
55.6	1.1	FAAS	[37]
67	53[a]	FAAS	[36]
34	0.08	TE-AAS	[42]
43	2.86	FAAS	[43]
50	0.08	GF-AAS	This paper

[a] Sensitivity.

3.10. *Determination of lead in water samples*

In order to test the reliability of the proposed methodology suitable for the assaying of lead, it was applied to determine the concentration of lead in tap water, underground water, river water and SRM 1640 for verification of the proposed method and procedures.

Table 4
Determination of lead in water samples ($n = 3$)

Samples	Added (μg l^{-1})	Measured (μg l^{-1})	Recovery (%)
Tap water	0	0.20 ± 0.01	
	10	10.21 ± 0.22	100.1
	20	21.1 ± 0.42	104.5
Underground water	0	8.02 ± 0.18	
	10	17.8 ± 0.33	97.8
	20	27.9 ± 0.36	99.4
River water	0	10.6 ± 0.29	
	10	20.7 ± 0.49	101.0
	20	30.5 ± 0.68	99.5

	Assayed values	Certified values
SRM 1640	27.46 ± 0.48	27.89 ± 0.14

Mean ± S.D. ($n = 3$).

For this purpose, 10 ml of each of the samples were pre-concentration with 0.05% TritonX-114 and 2.5×10^{-5} mol l^{-1} 5-Br-PADAP following the proposed method. The results were shown in Table 4. For calibration purpose, the working standard solutions were subjected to the same pre-concentration procedure as applied to the analyte solutions.

In addition, the recovery experiments of different amounts of Pb were carried out. The results shown in Table 4 have confirmed the validity of the proposed method. It was noted that the assayed value of Pb of the SRM 1640 are in close agreement with the certified value.

4. Conclusions

In this work, the use of micellar systems as an alternative to other techniques of separation and pre-concentration offers several advantages including low cost, safety and high capacity to pre-concentration various elements with high recoveries and very good extraction efficiency. The results for this work demonstrate the possibility of using the 5-Br-PADAP-TritonX-114 system for the pre-concentration of lead. The surfactant-rich phase can be easy introduced into the graphite furnace by autosampler after dilution with methanol and directly detected by GFAAS. The proposed method can be applied to the determination of trace metals in various water samples.

Acknowledgement

This material is based upon work funded by Zhejiang Provincial Natural Science Foundation of China under Grant No. 202127.

References

[1] M.O. Luconi, M.F. Silva, R.A. Olsina, L.P. Fernández, Talanta 51 (2000) 123.
[2] W. Qi, Z. Sun, R. Li, Shanghai Environ. Sci. 21 (2002) 32.
[3] P.L. Malvankar, V.M. Shinde, Analyst 116 (1991) 1081.
[4] P.S. More, A.D. Sawant, Anal. Lett. 27 (1994) 1737.
[5] S.Y. Bae, X. Zeng, G.M. Murray, J. Anal. At. Spectrom. 13 (1998) 1177.
[6] N. Prakashi, G. Csanady, R.A. Michaelis, G. Knapp, Mikrochim. Acta III (1989) 257.
[7] M. Vircaus, V. Rone, A. Palne, D. Vircava, Anal. Chim. Acta 299 (1994) 291.
[8] L. Elci, U. Sahin, S. Öztas, Talanta 44 (1997) 1017.
[9] J. Wang, E.H. Hansen, J. Anal. At. Spectrom. 17 (2002) 1284.
[10] J. Wang, E.H. Hansen, Anal. Chim. Acta 456 (2002) 283.
[11] J. Wang, E.H. Hansen, J. Anal. At. Spectrom. 17 (2002) 1278.
[12] J. Wang, E.H. Hansen, J. Anal. At. Spectrom. 17 (2002) 248.
[13] Y. Li, Y. Jiang, X.-P. Yan, Talanta 64 (2004) 758.
[14] K. Goto, S. Taguchi, Y. Fukue, H. Watanabe, Talanta 24 (1977) 752.
[15] W.L. Hinze, D.W. Armstrong (Eds.), Ordered Media in Chemical Separations, American Chemical Society, Washington, DC, 1987.
[16] W.L. Hinze, E. Pramauro, Crit. Rev. Anal. Chem. 24 (1993) 133.
[17] E. Pramauro, E. Pelezetti, Surfactants in Analytical Chemistry. Applications of Organized Amphiphilic Media, vol. XXXI, Elsevier, Wilson & Wilson's, The Netherlands, 1996.
[18] F.H. Quina, W.L. Hinze, Ind. Eng. Chem. Res. 38 (1999) 4150.
[19] Y. Ma, Z. Yan, J. Huang, Progress Chem. 13 (2001) 25.
[20] M.E. Fernandez Laespada, J.L. Perez Pavón, B. Moreno Cordero, Analyst 118 (1993) 209.
[21] M.F. Silva, L. Fernández, R. Olsina, D. Stacchiola, Anal. Chim. Acta 342 (1997) 229.
[22] M.F. Silva, L. Fernández, R. Olsina, Analyst 123 (1998) 1803.
[23] S. Igarashi, K. Endo, Anal. Chim. Acta 320 (1996) 133.
[24] S.A. Kulichenko, V.O. Doroschuk, S.O. Lelyushok, Talanta 59 (2003) 767.
[25] C. García Pinto, J.L. Pérez Pavón, B. Moreno Cordero, E. Romero Beato, S. García Sánchez, J. Anal. Spectrom. 11 (1996) 37.
[26] K.C. Teo, J. Chen, Analyst 126 (2001) 534.
[27] V.O. Doroschuk, S.O. Lelyushok, V.B. Ishchenko, S.A. Kulichenko, Talanta 64 (2004) 853.
[28] C.C. Nascentes, M.A.Z. Arruda, Talanta 61 (2003) 759.
[29] J. Chen, K.C. Teo, Anal. Chim. Acta 434 (2001) 325.
[30] J.L. Manzoori, G. Karim-Nezhad, Anal. Chim. Acta 521 (2004) 173.
[31] M.A. Mesguita da Silva, V.L. Azzolin Frescura, F.J. Nome Aguilera, A.J. Curtius, J. Anal. At. Spectrom. 13 (1998) 1369.
[32] E.K. Paleologos, C.D. Stalikas, S.M. Tzouwara-Karayanni, G.A. Pilidis, M.I. Karayannis, J. Anal. At. Spectrom. 15 (2000) 287.
[33] A. Ohashi, H. Ito, C. Kanai, H. Imura, K. Ohashi, Talanta 62 (2005) 525.
[34] F. Shemirani, M. Baghdadi, M. Ramezani, Talanta 65 (2005) 882.
[35] S. Akita, M. Rovira, A.M. Sastre, H. Takeuchi, Sep. Sci. Technol. 33 (1998) 2159.
[36] M.O. Luconi, M.F. Silva, R.A. Olsina, L.P. Fernández, Talanta 51 (2000) 123.
[37] J. Chen, K.C. Teo, Anal. Chim. Acta 450 (2001) 215.
[38] C.D. Stalikas, Trends Anal. Chem. 21 (2002) 343.
[39] J.L. Burguera, M. Burguera, Talanta 64 (2004) 1099.
[40] F. Shemirani, S.D. Abkenar, A. Khatouni, Bull. Korean Chem. Soc. 25 (2004) 1133.
[41] M.O. Luconi, L.L. Sombra, M.F. Silva, L.D. Martinez, R.A. Olsina, L.P. Fernandez, Chemia Analityczna 48 (2003) 749.
[42] D.L.G. Borges, M.A.M. Silva da Veiga, V.L.A. Frescura, B. Welz, A.J. Curtius, J. Anal. At. Spectrom. 18 (2003) 501.
[43] J.L. Manzoori, A. Bavili-Tabrizi, Anal. Chim. Acta 470 (2002) 215.