



Determination of Trace Lead with Cloud Point Extraction Precipitation Method

YAN ZHAO, XIAOXIA ZHANG*, YUQIN MA and SHAOHU OUYANG

College of Chemistry and Environmental Engineering, Changchun University of Science and Technology, Changchun 130022, P.R. China

*Corresponding author: E-mail: zxx581219@aliyun.com

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This work presented the determination of lead with Na_2S as precipitant and with the cloud point phenomenon of Triton X-114 to separate the precipitate and then determine the trace amount of lead by atomic adsorption spectrometry. This method has remarkable advantages compared with the traditional method. This test optimized the determination condition and the selectivity of this method was studied. The regression equation is found: $A = 0.0623 C (\mu\text{g}/25 \text{ mL}) + 0.003$, the correlation coefficient is $r = 0.9998$, the linear range is 1-320 $\mu\text{g}/\text{L}$, the lead detection limit is $C_L = 1 \mu\text{g}/\text{L}$ ($n = 11$). The method is applied for concentration determination of trace amount of lead in samples of water, tea and pollen. The relative standard deviations is 1.19-5.60 % and the standard recovery is 92-106 %.

Keywords: Lead, Cloud point, Flame atomic absorption spectrophotometer.

INTRODUCTION

The lead content in environmental samples is usually at trace level. When it is determined by flame atomic absorption spectrometry, the performance is insensitive due to its sensitive line locating at far ultraviolet region. Therefore the preconcentration step has to be adopted before determination. In recent years, the cloud point extraction method for enrichment was studied to replace the toxic, hazard and volatile organic extractants¹⁻⁸. But this method requires using chelating agent to form chelate with metal ions before extraction. In this paper, a new method was established to separate and concentrate the lead through Triton X-114 cloud point phenomenon without the using of chelator, the determination sensitivity was improved.

EXPERIMENTAL

TAS-990 AFG atomic spectrophotometer (Beijing Purkinjie General Instrument Limited Liability Company), digital thermostat water bath (Beijing Medical Equipment Factory) and PHS-3B precision acidity meter (Shanghai Precision Scientific Instruments Limited Company) were used.

Standard Pb^{2+} stock solution: 1.00 mg/mL (study of production units: National steel materials testing center), which was diluted step by step for preparing the working solution; Na_2S solution: 10 mg/mL; nonionic surfactant Triton X-114 solution: 5 % (v/v); 95 % ethanol and concentrated hydrochloric acid.

All the reagents used above are guarantee reagent. De-ionized water was used throughout the experiment.

Procedure: Initially, 2 mL of 10 $\mu\text{g}/\text{mL}$ Pb^{2+} solution, 1 $\mu\text{g}/\text{mL}$ of 10 mg/mL Na_2S solution and 4 mL of 5 % Triton X-114 surfactant were added into the 25 mL colorimetric tube in turn. The resulting solution was diluted to the mark with water and shaken up (At this $\text{pH} = 4$), then it was heated in 38 °C water bath for 40 min and taken out after complete separation. The upper aqueous phase was abandoned and then 0.2 mL of concentrated hydrochloric acid was added to make the precipitation disappear (about 4 drops), then it was heated for 2 min in 38 °C water bath with the cover open to ensure complete reaction, then 0.5 mL ethanol was added. The solution was diluted to 3 mL with water and mixed well, finally, the absorbance of Pb is determined at 283.3 nm wavelength with atomic absorption spectrophotometer after cooling.

Operating parameters of the atomic absorption spectrophotometer were shown as follow: Wavelength: 283.3 nm; lamp current: 2 mA; spectral bandwidth: 0.4 nm; negative voltage: 300 V; gas flow rate: 1500 mL/min; acetylene outlet pressure: 0.05 MPa; compressed air outlet pressure: 0.25 MPa; burner height: 5 mm.

RESULTS AND DISCUSSION

Influence of pH: As the method depends on the formation of PbS precipitation from Na_2S reacted with trace Pb in the solution and then the enrichment of the precipitate, the influence of pH is obvious. The test result indicated that when the $\text{pH} < 3$, the PbS precipitation was incomplete; when the pH is from 3 to 9.5, the PbS precipitation was complete; when the $\text{pH} > 9.5$, the absorbance decreased. May be the incomplete

PbS precipitation was due to the formation of a small amount of amphoteric $\text{Pb}(\text{OH})_2$ precipitation. So the optimal pH was set between 4-9.

Influence of adding amount of Na_2S : Different volume of Na_2S solution was added in the reaction system, respectively. When the Na_2S concentration was in the range of 0.004-0.5 mg/mL, the system absorption was basically unchanged and at maximum. Therefore 1 mL of 10 mg/mL Na_2S solution was selected as the adding amount in this system, in which the concentration of the Na_2S solution was 0.4 mg/mL.

Influence of adding amount of TritonX-114: When adding 1-2 mL of 5 % Triton X-114 solution, the absorbance showed rising tendency; when adding 2-4.5 mL, the absorbance kept unchanged; when adding 4.5-7 mL; the absorbance decreased slowly. Therefore 4 mL of 5 % Triton X-114 solution was selected as the best volume.

Influence of heating temperature and time: In the same experimental conditions, the tubes were heated for 45 min at different temperature respectively: 25, 30, 35, 40, 45 and 50 °C. When the temperature was lower than 35 °C, the absorbance increased with the increasing temperature; but when the temperature was higher than 40 °C, the absorbance began to decline. The results showed that the effect of phase separation came to the best when the temperature was in the range of 35-40 °C.

Under the optimal condition, different time of 10, 20, 25, 30, 35, 40, 45 and 50 min were tested to find its influence on phase separation. The results indicated that, when the heating time was up to 40-50 min, the separation effect is best. The optimal heating time was 40 min.

Influence of solution viscosity: The lifting capacity and efficiency of the atomizer will reduce if the solution viscosity and surface tension are great, so that the amount of atomic ground state which enters the flame will reduce and the measuring sensitivity will decline. Therefore 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.5 mL of 95 % ethanol was added to test the influence on determination signal. The addition of ethanol makes the absorbance values increased significantly, The absorbance came to the best when the adding amount was 0.4-0.6 mL. So 0.5 mL of 95 % ethanol was selected in this experiment.

Influence of coexisting ions: Under the optimal condition, the coexisting ions interference experiment was performed in the system of 25 mL with 20 µg content of Pb (acceptable relative error $\pm 5\%$). It was found that large amount of Ca^{2+} , Mg^{2+} , Ba^{2+} , Sr^{2+} , Fe^{3+} , Cl^- , Br^- , SiO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$, CO_3^{2-} , BrO_3^- , IO_3^- , PO_3^{3-} , Cr^{3+} , K^+ , Na^+ , Ni^{2+} , As^{3+} , As^{5+} , Al^{3+} , did not affect the determination of Pb. The maximum allowable multiples of the coexisting ions forming sulfide precipitation were showed as following: Fe^{2+} (1000), Mn^{2+} (650), Zn^{2+} (500), Cu^{2+} (250), Ag^+ (100), Co^{2+} , Cd^{2+} (50), Hg^{2+} (1.25). If the interference ion concentration in the samples is higher than the above multiples, the influence can be eliminated by increasing the adding amount of Na_2S solution.

Analytical characteristics of method: Determination was carried out under the optimal conditions, obtained the results in Table-1.

The sensitivity of this method is nearly 10 times higher than no extraction system.

Analytical parameters	Pb without pre-concentration	Pb with pre-concentration
Linear range (µg/L)	700-12000	1-320
Intercept	0.003	0.003
¹ Slope	0.16	1.56
Correlation coefficient	0.9971	0.9998
² Detection limit (µg/L)	700	1.00

¹The slope of the calibration graph is the calibration sensitivity according to IUPAC definition. $K = dA/dC$ (C: µg/mL); ²Detection limit calculated according to the IUPAC definition: $3S/K$, where K is the slope of the calibration graph

Sample analysis and methods precision: Taking water samples from water tap after letting out the water for 3 min. According to the experimental methods, five parallel determinations of standard adding sample and no standard adding sample were performed respectively and the results were shown in Table-2.

1 g pre-dried and grinded samples were weighted and put into the 100 mL beakers, respectively, then the samples was wet with little water and added 10 mL 4:1 mixed acid of HNO_3 and HClO_4 , placed for 24 h with plastic membrane covered. Then the digestion reaction in low temperature continued until the substance became yellowish and transparent. 2 mol/L sodium hydroxide solutions was added to make the substance pH 4 and then the solution was settled to the volume of 25 mL for use. The reagent blank test was done at the same time. Determined the standard adding sample and no standard adding sample for 5 times, the results were shown in Table-3.

Conclusions

The advantages of this method lies in (1) Comparing with other cloud point extraction system, the chelating extractants are no longer required, the pollution of colored and toxic waste water to the environment was avoided. The centrifugal separation method no longer be applied, so the determination cost is reduced. (2) Comparing with traditional liquid-liquid chelating extraction, no toxic and volatile organic reagents are required in this method. The extractant dosage for each sample is only 0.2 mL, which can be easily recycled and can meet the needs of green analysis development. (3) It is easier to remove completely the supernatant than centrifugal separation method because the viscosity of surfactant is bigger. It is more simpler than filtration method to separate precipitate and without precipitate loss. Because the K_{sp} of PbS is extremely small and no precipitate distribution in two phases, so the precipitate can

TABLE-2
ANALYTICAL RESULTS OF THE TAP WATER SAMPLES

Sample	Measured (ng/mL)	Average (ng /mL)	RSD (%)	Standard added (ng/mL)	Recovered (ng/mL)	Recovery (%)
Tap water	2.83, 2.90, 2.88, 2.83, 2.83	2.85	1.19	8.00	8.48	106

TABLE-3
ANALYTICAL RESULTS OF THE TEA AND POLLEN SAMPLES

Sample	Measured ($\mu\text{g/g}$)	Average ($\mu\text{g/g}$)	RSD (%)	Standard added (μg)	Recovered (μg)	Recovery (%)
Tea	0.112, 0.105, 0.112, 0.112, 0.109	0.110	5.60	0.30	0.276	92
Pollen	0.105, 0.101, 0.103, 0.106, 0.100	0.103	2.48	0.30	0.282	94

TABLE-4
COMPARISON OF LEAD DETERMINATION METHODS USING CLOUD POINT
EXTRACTION-FLAME ATOMIC ABSORPTION SPECTROMET

Surface active agent	Chelating agent	Detection limit ($\mu\text{g/L}$)	*Sensitivity K = dA/dC	RSD (%)	Recovery (%)	Linear range	Ref.
PONPE-7.5	—	53	0.11	0.58	98-99	0.6-4.1 mg/L	[1]
Triton X-114	5-Br-PADAP	50	—	—	93-99	0.15-35 mg/L	[2]
Triton X-114	TAN	4.5	—	1.6-3.2	95-107	—	[3]
Triton X-114	PAN	0.82	2.0	3.5	98-102	0.82-120 $\mu\text{g/L}$	[4]
Triton X-114	PMBP	1.49	1.2	2.43	96-102	5-200 $\mu\text{g/L}$	[5]
Triton X-114	Pyrogallol	0.4	5.4	2.5	99-103	0.4-185 $\mu\text{g/L}$	[6]
Triton X-100	PMBP	3.70	—	4.25	86-93	—	[7]
OP-7	8-Hydroxyquinoline	58.7	0.07	4.52	75.6-95	200-400 $\mu\text{g/L}$	[8]

5-Br-PADAP: 2-(5-Olfactory-2-pyridylazo)-5-two diethylamino phenol; TAN: 1-(2-Thiazolylazo)-2-naphthol; PAN: 1-(2-Pyridylazo)-2-naphthol; PMBP: 1-Phenyl-3-methyl-4-benzoyl pyrazolone quinoline ketone-5; *The slope of the calibration graph is the calibration sensitivity according to IUPAC definition

be separated completely and the extractive efficiency is improved. (4) The detection limit of this method is 1 $\mu\text{g/L}$, the sensitivity is 1.56, RSD is 1.19-5.6 %, the linear range is 1-320 $\mu\text{g/L}$, the recovery rate, in the 92-106 %, the coefficient of correlation is 0.9998. Comparing these analytical characteristics with those of other cloud point extraction system in Table-4, it is suggested that this method is better than most of the other systems. Though the analytical characteristics with pyrogallol is better than the said method, but the pyrogallol is a toxic reagent, it should be applied only in a necessary situation.

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