SPECTROPHOTOMETRIC DETERMINATION OF Pb (II) WITH *o*–HYDROXY-THIOBENZMORPHOLIDE

I. Badea *, Luminita Vladescu and Cornelia Cercasov

A new and selective spectrophotometric method for the determination of trace amounts of Pb(II) in aqueous environmental samples is reported. The interaction in solution between Pb(II) and o-hydroxy-thiobenzmorpholide was studied. In the presence of o-hydroxy-thiobenzmorpholide Pb(II) forms a stable complex. The method was used to determine the content of Pb(II) in synthetic and real samples.

Introduction

Lead is a cumulative poison that enters the body from lead water pipes, lead-based paints and leaded petrol [1]. The determination of trace amount of lead is very important in the context of environmental monitoring. Atomic absorption and atomic emission spectrometry are used for routine trace analysis of lead, however a large number of spectrometric methods are reported. Therefore, there is a continued interest in the synthesis of new organic reagents that could be able to be used for direct and rapid spectrophotometric determination of trace level of lead, especially in aqueous solutions. Thioamides are organic reagents used recently for the determination of trace level of elements in biological and environmental samples [2,3÷5]. Based on these observations this paper reports a new spectrophotometric method for the determination of trace level of Pb(II) with a new reagent without preconcentration. This method offers the advantage of simplicity, rapidity, high sensitivity and direct determination of Pb(II) without separation. Synthesis and characterisation of the reagents are described in the previous papers [6,7,8]. The formula of the o – hydroxy – thiobenzmorpholide is shown in Fig. 1. This organic reagent is noted in this paper by **R**.
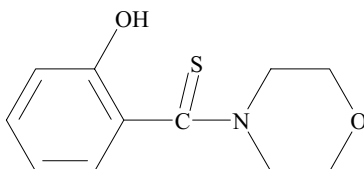

Fig. 1: *Formula of the reagent.*

*   Department of Analytical Chemistry, Faculty of Chemistry, University of Bucharest,
    2-14 Bv. Regina Elisabeta, 70346 Bucharest, Romania

Experimental

Reagents

All chemicals used were analytical reagent grade. Water was purified and distilled. All reagents, other than organic reagents were purchased from Merck. Stock aqueous solution of Pb(II) 0.001 mol.L^{-1} was obtained by dissolving the required quantity of $Pb(NO_3)_2$ in a small volume of nitric acid followed by dilution with distilled water prepared using Pb(NO3)$_2$. The working solutions (5.10^{-4} mol.L^{-1}) were prepared by dilution just before use. Aqueous solution 0.001 mol.L^{-1} of **R** in HCl 0.1 mol.L^{-1} was obtained from pure organic reagent. Acetate buffer solution of pH 4.05 was used. Aqueous solutions of different cations 0.010 mol.L^{-1} were obtained by dissolving the appropriate substance in distilled water.

Apparatus

The absorption spectra were recorded on a Jasco V 530 spectrometer, with $1,00$ cm quartz cells. An IBM compatible computer was employed also for the statistical analysis.

Procedure

The solutions to be studied were prepared in 25 mL volumetric flask. Exactly measured volumes of Pb(II) and organic reagent solutions were introduced in the flasks and they were filled up to the mark with acetate buffer solution ($pH = 4.05$). Absorbance of each solution was measured against a corresponding blank similarly prepared.

Results and discussion

The influence of wavelength, amount of organic reagent and concentration of Pb(II) on the absorbance was studied in order to establish the optimal working conditions for the quantitative determination of Pb(II). The stoichiometry of complex was predicted and the stability constant determined.

Influence of the wavelength

The spectrum recorded for a solution containing Pb(II) and organic reagent are presented in Fig. 2. A chemical interaction between Pb(II) and organic reagent has occurred. Due to the fact that the organic reagent absorbs little at the maximum complex wavelength ($\lambda_{max} = 242$ nm), all further measurements have been performed versus a corresponding blank.

Stoichiometry of the complex

The effect of reagent concentration was examined by measuring the absorbance of the solution containing a known concentration of Pb(II) and different amounts of organic reagent. The spectrophotometric titration using a constant amount of organic reagent and variable concentration of Pb(II) as well as Job's method were also employed in order to establish the stoichiometry of the complex. The results obtained in the study of chemical interaction between Pb(II) and **R** indicate the formation of a complexes Pb(II) : **R** = 1 : 2.
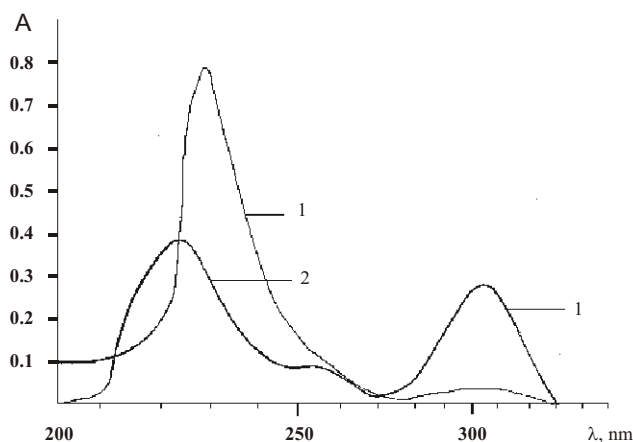
Fig. 2: *Variation A = f(λ); 1 – Pb(II) + **R** vs. **R**; 2 – **R** vs. solvent.*

The stability constant

The apparent stability constant of the complex was calculated from the data obtained using the mole ratio method. The value of the stability constant is: 1.35×10^5 for **R**. The value of stability constant obtained at $20 \pm 2°C$ show a very stable complex for the corresponding stoichiometry.

Calibration curve

Beer Lambert law is followed for Pb(II) concentration in the 0.20÷10 ppm (r = 0.9997). The molar absorptivity coefficient is $16.000 \; L.mol^{-1}.cm^{-1}$.

Interferences

No interference of Ag(I), Hg(II), Cu(II), Cd(II) Co(II) Zn(II) ions was observed in sample in which the concentration of such ions are the same or little reported at the lead concentration. The Fe(III) and Ni(II) interfere only at the same or greater concentration reported at the lead concentration.

Determination of Pb(II) in synthetic and real samples. The spectrophotometric method was tested on synthetic solution containing known amounts of Pb(II). The results obtained are presented in Table 1 and show a good agreement between the amounts present in the sample and those determined. The method was applied to the determination of Pb(II) in water. The results presented in Table 2 show a good agreement between the values determined by the proposed method and the consecrated spectrometric method with 4-(2-pyridylazo) resorcinol (PAR) [9].

Table 1. Results of the Pb(II) content determination in synthetic samples

	Content of Pb(II), ppm		
	in sample	proposed method	reference method [9]
sample 1	0.25	0.24 ± 0.01	0.26 ± 0.01
sample 2	0.50	0.51 ± 0.01	0.48 ± 0.01
sample 3	0.75	0.74 ± 0.01	0.75 ± 0.01
sample 4	1.00	1.03 ± 0.02	0.98 ± 0.01
sample 5	1.50	1.52 ± 0.02	1.52 ± 0.02

Note: Each value is the mean of five determinations.

Table 2. Results of the Pb(II) content determination in real samples

	Content of Pb(II), ppm	
	proposed method	reference method [9]
sample 1	1.21 ± 0.02	1.27 ± 0.02
sample 2	3.84 ± 0.01	3.85 ± 0.01
sample 3	10.52 ± 0.02	10.53 ± 0.01

Note: Each value is the mean of five determinations.

Conclusion

The reagent forms with Pb(II) a 1 : 2 stable complex soluble in water. The value of the stability constant is 1.35×10^5 at $20 \pm 2°C$. On this basis a spectrophotometric method for quantitative determination of traces of Pb(II) was elaborated. This method has a sensibility comparable with the consecrated extractive spectrophotometric method and it has the great advantage that permits the direct determination of Pb(II) in aqueous sample without separation. The method was applied to the Pb(II) determination in water samples.

REFERENCES

1. Renner,. R. (1995) *Environ. Sci. Technol.* **29**, 256.

2. Paudey, J. and Pitre, K.S. (1987) *J. Indian Chem. Soc.* **15**, 259.

3. Kamal, A.D., Hahn, F. E. and Raymond, K. N. (1990) *J. Am. Chem. Soc.* **112**, 1519.

4. Ambhore, D.M. and Joshi, A.P. (1991) *J. Indian Chem. Soc.* **68**, 825..

5. Badea, I., Vladescu, L. and Cercasov, C. (1992) *Rev. Roumaine Chim.* **37**, 467.

6. Leopardi, C. P., Fabre, O., Zimmermann, D., Reise, J., Cornea, F. and Fulea, C. (1977) *Canad. J. Chem.* **55** 2649.

7. Cornea, F., Cercasov, C. and Ciureanu, M. (1980) *Spectrochim. Acta*, **36A**, 775.

8. Cercasov, C., Cornea, F., Ciureanu, M., Hilebrand, M., Sahini, V.E. and Volanschi, E. (1982) *Org. Mag. Resonanace* **20** 217.

9. *** Merck (1977), Organic Reagent for trace analysis, 220.