DETERMINATION OF LEAD IN THE PARANA RIVER BY SOLID PHASE SPECTROPHOTOMETRY

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Abstract

The paper proposes a procedure for determination of lead in water samples by solid phase spectrophotometry (SPS). It is based on the reaction of Pb(II) ion with 2-(5-Bromo-2-pyridylazo)-5-(diethylamino)phenol (5-Br-PADAP) immobilized on an anion-exchange resin, that gives rise to a coloured complex, whose absorbance is measured directly in the solid phase. The method provides a detection limit of 2.4 µg L^{-1} and a sample throughput of 2 h^{-1}. The relative standard deviation (R.S.D.) was 1.7% for a Pb(II) concentration of 10.0 µg L^{-1}. The calibration graph obtained was linear with a correlation coefficient of 0.9995, in the range from the detection limit up to at least 100 µg L^{-1}. This method was successfully applied to the determination of Pb(II) in natural superficial waters from the Parana River in Argentina.

Resumen

Este trabajo propone un procedimiento para la determinación de plomo en muestras de agua mediante espectrofotometría de fase sólida (SPS). Está basado en la reacción de Pb(II) con 2-(5-Bromo-2-piridilazo)-5-(dietilamino)fenol(5-Br-PADAP) inmovilizado sobre una resina de intercambio iónico, lo que origina un complejo coloreado. La absorbancia del compuesto coloreado se mide directamente en la fase sólida. El método provee un límite de detección de 2,4 µg L^{-1} y una velocidad de ciclado de 2 h^{-1}. La desviación estándar relativa (R.S.D.) fue 1,7% para una concentracion de Pb(II) de 10,0 µg L^{-1}. El gráfico de calibración resultó lineal con un coeficiente de correlación de 0,9995, en el rango desde el límite de detección hasta al menos 100 µg L^{-1}. Este método resultó adecuado par la determinación de Pb(II) en aguas superficiales del Río Paraná en Argentina.

Introduction

It is well known that lead is an abundant heavy metal; it represents a potential problem not only because of its widespread distribution throughout the environment, but also because of its toxicity. Lead enters the organism primarily via the alimentary and/or respiratory tract. The main sources of this metal intake are food, air and drinking water [1].

Pb(II) determination in natural waters is of considerable interest in the environmental sciences, so the development of quick, simple and cheap spectrophotometric methods is of great interest for analytical practices [2].

Solid Phase Spectrophotometry (SPS) [3,4] is a technique based on analyte preconcentration on a solid substratum, and the subsequent absorbance measuring of a coloured compound directly at the solid phase. In this work Pb(II) reacts with 2-(5-Bromo-2-pyridylazo)-5-(diethylamino)phenol (5-Br-PADAP) immobilized on an anionic resin, providing a simple, sensitive, selective, fast and inexpensive method.

There are several instrumental techniques available, including, GFAAS, ICP-AES and ICP-MS for Pb(II) determination. All of them have very low limits of determination, but the cost of the required instrumentation may be prohibitive to many laboratories.

The SPS advantage over the traditional molecular absorption spectrophotometry lies in sensibility increasing, higher sample volumes, increase sensibility in batch procedures, being able to quantify smaller levels of concentration down to 0.10 ng. mL^{-1}. Trace elements determinations can be carried out without the preconcentration stage [5].

In fact, this paper describes a method for Pb(II) traces determinations based on Solid-Phase Spectrophotometry (SPS), whith 5-BrPADAP as complexing reagent.

Experimental

Reagents

Analytical reagents grade chemicals and distilled, deionised water were used throughout.

Stock solutions with a 1000 μg mL^{-1} solution of Pb(II) were prepared by dissolution of the appropriate amount of Pb(NO$_3$)$_2$ (Merck®) in water and by dilution to the required volume.

A stock solution of 2-(5-Bromo-2-pyridylazo)-5-(diethylamino)phenol (5-Br-PADAP) (Aldrich®) 2 x 10^{-3} mol L^{-1} solution was prepared by dissolution in ethanol 96 %.

A octylphenol poly(ethyleneglycol) ether (Triton X-100, Merck®) 5% (v/v) non ionic surfactant solution in water was prepared.

A buffer solution was prepared by diluting a 3.0 mol L^{-1} ammonium hydroxide solution adjusted to pH 9.2 with hydrochloric acid solution.

The anion-exchanger was Dowex 1-X8® (200 – 400 mesh); used in its chloride form. The resin was washed several times with water, treated with 2.0 mol L^{-1} HCl for 4 h and finally washed with water until the washing was neutral, air-dried and stored in polyethylene containers.

Apparatus

A single beam, microprocessor-controlled Metrolab® 1700 UV/Vis spectrophotometer attached to a personal computer with specific software (Metrolab® v. 2) and equipped with Hellma® cells of 1.0 mm light path.

Other apparatus were an Altronix® pH-meter fitted with a saturated calomel electrode, a home made rotating bottle agitator and a Rolco® desk centrifuge.

Absorbance measurements

The absorbance of the complex sorbed on the solid phase was measured with a quartz cell (1-mm) at two wavelengths, 550 nm (absorption maximum) and 800 nm (wavelength at which

the analyte does not absorb). The net absorbance for Pb(II) complex A_{net} in solid phase was obtained from:

$A_{net} = A_{complex} - A_{blank}$ where $A_{complex} = A_{550} - A_{800}$ for the sample and

$A_{blank} = A_{550} - A_{800}$ for the blank solution [6].

Preparation of the loaded resin: reagent immobilization

4 g exchanger was added to 40 mL of an ethanol (10 % v/v) solution of 4×10^{-5} mol L^{-1} 5-Br-PADAP. The value for the 5-Br-PADAP concentration was established as optimum from previous assays realized for this work. The mixture was stirred for 20 min, centrifuged and washed several times with water. It was then air dried and stored in a plastic container.

General procedure

5-Br-PADAP reacts with Pb(II) in solution to form a stable red complex, in the presence of a tensioactive as Triton X-100, between the pH-values of 9 and 11, exhibiting a single sharp peak with maximum absorbance at 550 nm [7]. This complex sorbed on the anionic resin Dowex 1X8 shows an absorption peak at the same wavelength.

An appropriate volume of aqueous solution containing 0.2 µg to 2 µg of Pb(II) was transferred into a 50 mL plastic tube with stopper plus 0.5 mL 5% Triton X-100 solution and 1 mL of a 0.01 mol L^{-1} NH_4^+/NH_4Cl buffer solution. The total volume of the solution was adjusted to 50 ml with water (the final concentration of Pb(II) was $10 - 100$ µg L^{-1}), 70 mg of Dowex 1X8 – 5-Br-PADAP resin was added to the solution and the mixture was stirred for 20 min. The solution was centrifuged and the resin beads were collected with a small volume of solution and transferred into a 1-mm quartz cell with the aid of a pipette. A blank solution without Pb(II) was prepared in the same way as described for the sample. The net absorbance was obtained from the difference between those of sample and blank, measured as described above.

Sampling and Handling

The Parana River is located in South America, with a length of 4,880 km, draining an area of roughly 2.8 million km^2. Its width and depth are variable depending on the geological composition of its bed. It is formed at the junction of the Paranaiba and Grande rivers in south central Brazil, it follows Paraguay's borders with Brazil and then in Argentina. The river flows into the Río de la Plata estuary. Water samples were collected at the right bank of the Parana River at Corrientes (27º 46' S, 58º 83' W) Argentina [8]. The measuring station was chosen based on the local availability of facilities.

Samples were filtered through a 0.45 µm membrane filter and collected in a polyethylene container carefully cleaned with nitric acid. The samples were stored at 4 ºC until analysis. Analyses were performed with the least possible delay. Usual general precautions were taken to avoid contaminations [9].

Finally, to eliminate organic matter, the samples (50 mL) were digested with a 1.0 mL of a mixture (1+1) nitric acid (65 %) and hydrogen peroxide 10 mol L^{-1} (100 vol), carefully heated on a hot plate and finally allowed to stand until became transparent.

        After that the digested solutions were neutralized with a concentrate ammonia solution and dilute to volume in a 50 mL standard flask.

Results and discussion

Reagent immobilization

        Both the baseline and the analytical signal increase with the concentration of 5-Br-PADAP in the solution used for immobilization as consequence of the increase of the amount of 5-Br-PADAP fixed on the resin. It was necessary to select a suitable solution that provided not only a large response but also an acceptable range within which to perform the absorption measurements (4×10^{-5} mol L^{-1}). In order to avoid the precipitation of 5-Br-PADAP in the aqueous medium, the solution of the reagent was prepared in the presence or ethanol. Finally the solution was shaken 40 min.

Chemical variables

        Solutions were prepared with a known amount of Pb(II) and 70 mg of 5-Br-PADAP-Resin, to form the metal complex. The pH was varied by adding diluted HCl or NaOH solutions, so that the net absorbance of each solution was obtained at the corresponding pH and containing 50 µg L^{-1} of Pb(II). The optimum pH for the formation and fixation of the species was in the range 8.5 to 10.0. At pH values below 8.0 or above 10.0 the absorbance decreased significantly. Hence, we chose pH 9.2 as the working pH. This pH-value was adjusted with NH_4^+/NH_4Cl buffer solution. Figure 1 shows the response at different pH values.

        The effect of the surfactant concentration in the medium was studied by following the batch procedure above described, preparing solutions under the same conditions at pH 9.2 and containing different Triton X-100 percentages. Figure 2 shows the effect of surfactant percentage upon the complex retention on the resin.

        The optimum stirring time was 20 min for a 50 mL sample volume. The fixed complex was stable for at least 120 min after equilibration. The order of addition of reagents did not affect the results. Sample + Tr X-100 + Buffer + 5-Br-PADAP-Resin was used.

        As large amounts of resin lowered the absorbance values [10], the minimum amount of dry resin required to fill the cell and facilitate handling, i.e. 70 mg, was used for all the measurements.

Analytical parameters

        Analytical parameters are summarized in Table 1. Reproducibility was evaluated for a 50 mL of standard solution of Pb(II) (10.0 µg L^{-1}) repeating the procedure ten times. The relative standard deviation (R.S.D.) was 1.7 %, with centrifugation of cell packed for 1 min at 3500 rpm.

        The calibration graph was obtained over the concentration range 5.0 - 100.0 µg L^{-1}, it was linear with a correlation coefficient of 0.998 between the detection limit up to at least 100 µg L^{-1}. The detection limit (DL) was calculated as the amount of Pb(II) required to yield a net signal equal to three times the standard deviation of the blank signal (3σ). The value of DL obtained in aqueous solutions of Pb(II) was 2.4 µg L^{-1}.
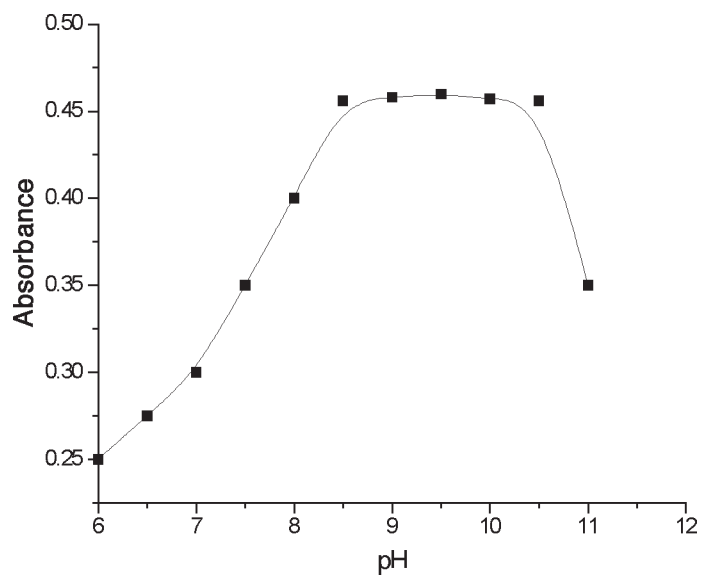
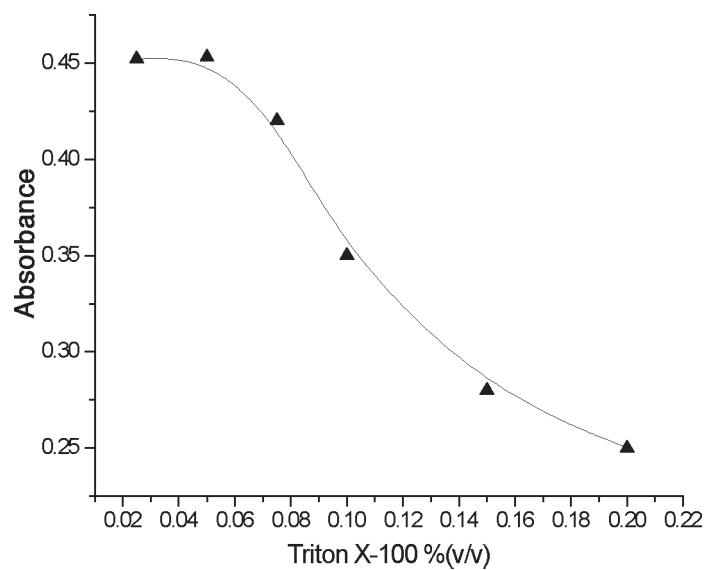**Figure 1.** *pH dependence – [Pb(II)] = 50 μg L⁻¹; amount of 5-Br-PADAP-resin = 70 mg*

Figure 2. *Effect of surfactant Triton X-100 – [Pb(II)] = 50 μg L⁻¹; amount of 5-Br-PADAP-resin = 70 mg, pH 9.2*

Table 1. *Analytical parameters for the SPS Pb(II) determination*

Parameter	
Intercept	-0.104
Slope (μg^{-1} L)	0.012
Linear range ($\mu g\ L^{-1}$)	5 – 100
Correlation coefficient	0.995
% R. S. D. (n = 10)[a]	1.7
Detection limit ($\mu g\ L^{-1}$)[b]	2.4
Determination limit ($\mu g\ L^{-1}$)[c]	2.7

[a] *R. S. D. was established at 10 $\mu g\ L^{-1}$ Pb(II).*
[b] *3σ criterion.*
[c] *10σ criterion [16]*

Interferences

The effect of potential interfering species in the determination of 10 $\mu g\ L^{-1}$ of Pb(II) was studied. Tolerance is defined as the foreign ion concentration causing an error smaller than ± 5% in the determination of the analyte.

The cations Cu(II), Co(II), Hg(II), Ni(II) and Zn(II) produce a large degree of interference due to their reaction with 5-Br-PADAP. The aggregate of 0.2 mL KCN 0.1 mol L^{-1} to a 50 mL sample, reduces the interferences by complexation of this cations. Tolerance limits are showed in Table 2.

It can be concluded that, there is no obvious interference to be expected from normal concomitant levels of metals found in natural waters. Then we can affirm that the proposed method is acceptably selective.

Analytical applications

Finally, the results of the method applied to Pb(II) determination in natural waters was applied to samples from the Parana River, extracted at Corrientes (Argentina) in different seasons, see Table 3. The concentrations were in the range of 8.4–58.0 $\mu g\ L^{-1}$. The values found for concentrations of Pb(II) in the Parana River are in agreement with historic reference values quoted in the National Guidelines for Environmental Water Quality of Argentina [11].

In order to check the accuracy of the proposed method, the results obtained were compared with those found by inductively coupled plasma [12] (ICP-OES), always with an excellent agreement.

This method was applied to drinking water in Corrientes (Argentina), the Pb(II) content was found to be lower than the detection limit. Then, a recovery study was performed by spiking different amounts of Pb(II) (Table 3). The average percentage of recovery was acceptable. The method of standard addition is considered as a validation procedure [13].

Table 2. *Tolerance limits of interfering ions. Pb(II) concentration: 10 µg L⁻¹*

	Tolerance Level ($\mu g\ L^{-1}$)	
Interferent		with KCN
Cl^-, NO_3^-	10000	
K(I)	10000	
Ca(II)	5000	
Mg(II)	1000	
Al(III)	1000	
Ba(II)	1000	
Fe(III), SO_4^{2-}	500	
PO_4^{3-}	250	
As(III)	50	
Zn(II)	2	10
Cu(II)	2	10
Ni(II)	2	10
Hg(II)	2	10

Table 3. *Analytical applications*

Simple	Season	Date	Pb(II) content found[a] ($\mu g\ L^{-1}$)	Pb(II) content found by ICP-AES ($\mu g\ L^{-1}$)
Parana River	Autumn	14-May-2005	52.6 ± 0.4	51.5 ± 0.2
	Winter	25-Aug-2005	10.5 ± 0.4	10.6 ± 0.1
	Spring	29-Set-2005	8.4 ± 0.3	8.2 ± 0.1
	Summer	21-Dec-2005	58.2 ± 0.5	58.0 ± 0.3
		Amount added ($\mu g\ .\ L^{-1}$)	Pb(II) content found[a] ($\mu g\ L^{-1}$)	Recovery (%)
Drinking water		—	N/D	—
	5	5.2	104.0	
	10	9.8	98.0	
	20	20.0	100.0	

[a] Average of three determinations

Conclusions

The concentration range in which the proposed method was applied is in the order of traces. It has been shown that adequate sensitivity and accuracy can be attained by using solid phase spectrophotometry for assessment of lead in natural waters. The results are in all cases strongly related to the values obtained with the reference method. The conducted recovery studies indicate the determination shows good reproducibility and accuracy. Finally, the technique showed the advantages of simplicity and low economical cost of installation and operation, when compared with other instrumental methods.

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