



Evaluation of DMIT [4,5-Dimercapto-1,3-Dithiol-2-Thionate] as chelating agent in a cloud point extraction procedure for Pb²⁺ determination in water samples

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ABSTRACT. The present study proposes a new method for cloud point preconcentration of Pb²⁺ ions based on complex formed with [4,5-dimercapto-1,3-dithiol-2-thionate] and posterior determination by flame atomic absorption spectrometry (FAAS). The preconcentration of Pb²⁺ was carried at pH 5.0 under following conditions: time and temperature of batch at 15 min. and 70°C, respectively, 0.1% (v/v) Triton X-114, 0.003 mol L⁻¹ acetate/acetic acid buffer solution, 1.0 x 10⁻⁵ mol L⁻¹ DMIT and 0.5% (m/v) NaCl. Under the best analytical conditions the method provided a limit of detection of 2.85 µg L⁻¹ by preconcentrating 10.0 mL of sample and calibration curve ranging from 0 up to 650 µg L⁻¹ (r = 0.99945). The applicability of proposed method for Pb²⁺ determination in natural waters without interferences was checked through addition/recovery tests.

Keywords: DMIT [4,5-dimercapto-1,3-dithiol-2-thionate], cloud point, lead, FAAS.

Avaliação do DMIT [4,5-Dimercapto-1,3-Ditiol-2-Tionato] como agente complexante em um procedimento de extração por ponto nuvem para determinação de Pb²⁺ em amostras de água

RESUMO. O presente estudo propõe um novo método para pré-concentração por ponto nuvem de Pb²⁺ baseado no complexo formado com [4,5-dimercapto-1,3-ditiol-2-tionato] e posterior determinação por espectrometria de absorção atômica em chama (FAAS). A pré-concentração de Pb²⁺ foi realizada em pH 5,0 nas seguintes condições: tempo e temperatura do banho de 15 min. e 70°C, respectivamente, Triton X-114 0.1% (v/v), solução tampão acetato/ácido acético 0,003 mol L⁻¹, DMIT 1.0 x 10⁻⁵ mol L⁻¹ e NaCl 0,5% (m/v). Nas condições otimizadas, o método forneceu um limite de detecção de 2,85 µg L⁻¹ pré-concentrando 10,0 mL de amostra e curva de calibração variando de 0 até 650 µg L⁻¹ (r = 0,99945). A aplicabilidade do método proposto para determinação de Pb²⁺ em águas naturais sem interferências foi confirmada por meio de testes de adição e recuperação.

Palavras-chave: DMIT [4,5-dimercapto-1,3-ditiol-2-tionato], ponto nuvem, chumbo, FAAS.

Introduction

Cloud point extraction (CPE) is an alternative suitable separation technique, which is based on the phenomenon of turbidity of the solution where the surfactants monomers aggregate and scattering visible light (PALEOLOGOS et al., 2005). This phenomenon occurs above a threshold concentration, known as critical micellar concentration (cmc), that is promoted by an alteration on the solution conditions, such as pressure and temperature, or the addition of a salting-out agent. The insolubility of the surfactant causes the turbidity of the solution, promoting the separation of surfactant-rich phase from the poor phase, which must be discarded since the metal is preconcentrated in the surfactant-rich phase (AMAS; TARLEY, 2008;

BEZERRA; FERREIRA, 2006; SOUZA; TARLEY, 2008). The cloud point extraction presents inherent advantage when compared with conventional liquid-liquid extraction, once the surfactants used on CPE are biodegradable, cost effective and the amounts required to have an effective extraction is minimal when compared with the solvents organics used in conventional extraction. Besides, after the dilution of the surfactant-rich phase in ethanol solution containing nitric acid, the surfactant is easily introduced into FAAS nebulizer by manual injection and the micellar system has the ability to concentrate analytes with high preconcentration factors (KOLACHI et al., 2011; LEMOS et al., 2007; PALEOLOGOS et al., 2005). The high sensibility and selectiveness of the

preconcentration method depends on adequate choice of the ligand and surfactant, because in aqueous solution the metal ions are commonly extracted as a hydrophobic metallic complex that will interact with the hydrocarbon tail of the micelles and, consequently, it can be extracted by cloud point (GHAEDI et al., 2009). The determination of metals, such as lead, cobalt and chromium, in environmental and biological samples are usually reported in literature employing preconcentration by cloud point extraction associated with flame atomic absorption spectroscopy (CITAK; TUZEN, 2010; KIRAN et al., 2008). An application example is the determination of lead in blood sample of children by cloud point extraction after the complexation of the lead with ammonium pyrrolidinedithiocarbamate (APDC) and diethyldithiocarbamate (DDTC) separately with further determination by FAAS (SHAH et al., 2011). There are many ligands used on the cloud point extraction/preconcentration of lead reported in the literature, such as methyl-2-pyridylketone oxime (MPKO) (GHAEDI et al., 2008), dimethylglyoxime (DMG) (BAKIRCIOGLU, 2012), 1-(2-thiazolylazo)-2-naphthol (TAN) (CHEN; TEO, 2001; SILVA; ROLDAN, 2009), bis((1H-benzo [d] imidazol-2yl)ethyl) sulfane (BIES) (GHAEDI et al., 2009), dithizone (WEN et al., 2012), O,O-diethyldithiophosphate (DDTP) (BORGES et al., 2003; MANZOORI; BAVILI-TABRIZI, 2002) and 2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol (5-Br-PADAP) (CHEN et al., 2005). As observed, studies focusing on new ligands aiming at to get methods with higher sensibility, selectivity, high preconcentration factor and low sample consumption, have been intensively evaluated. In the present paper, we have used the ligand [4,5-dimercapto-1,3-dithiol-2-thionate] (DMIT) to determine Pb(II) by FAAS, which has high toxicity and long residence time in the environmental (NAGASHIMA et al., 2009). The ligand DMIT is a sulfur-based heterocycle that belongs to dithiolenes class and it is stabilized as metallic complexes mainly with Ni^{2+} and Zn^{2+} , which are soluble in organic solvents (BARRETO et al., 1992; PULLEN; OLK, 1999). This ligand has a π donor-acceptor system that is highly delocalized that promotes physical proprieties such as conductivity, optics and magnetism and can be used in transistors, chemical sensors and analytical methods (DIAS et al., 2007). An example of analytical method, is the determination of Hg^{2+} , Pb^{2+} and Cu^{2+} by liquid-liquid extraction with the organic solvents dimethyl sulfoxide and methyl isobutyl ketone with posterior analysis by spectrophotometric in visible region (BARRETO et al.,

1999, 2005). Since the ligand DMIT possesses sulfur donor atoms, which are considered soft-base, it can establish soft-soft interactions with lead receptor atoms that is borderline soft-acid (SHRIVER; ATKINS, 2003). Thus, in the substitution reaction, the Pb^{2+} replaces the Zn^{2+} in the complex $[\text{Zn}(\text{DMIT})_2]^{2-}$, as shown in the Equation (1) (BARRETO et al., 2005).



According to aforementioned, this paper demonstrates the analytical performance of ligand DMIT on the complexation of lead(II) ion in micellar systems with posterior preconcentration by cloud point extraction.

Material and methods

Reagents and instruments

A Shimadzu model AA-7000 atomic absorption spectrometer equipped with deuterium background correction and hollow cathode lamp for lead was used for absorbance measurements at a wavelength of 217.0 nm and lamp current of 10 mA. The air-acetylene flow rate was used at 2.0 L min⁻¹ of acetylene and 10.0 min. L⁻¹ of air and the nebulizer flow at 5.0 L min⁻¹. A pHmeter Metrohm 826 mobile (Netherlands) was used for pH adjustments, a thermostatic bath (Marconi, modelo MA 127 – Piracicaba, São Paulo State, Brazil) was operated for controlling the temperature, a Fanem[®] model 206 (São Paulo, Brazil) was used to accelerate the phase-separation process and a hot plate (EVLAB, modelo EV:017 – Londrina, Paraná State, Brazil) was used for the sample decomposition. All chemicals were of analytical-reagent grade and were used without previous purification. The laboratory glassware was kept in 10% (v/v) for 24 hours and washed with distilled/deionized water and dried. Standard stock solutions of Pb^{2+} ions was prepared by appropriate dilution of stock solution at a concentration of 1,000 mg L⁻¹ (Merck, Germany). Stock solutions of 2.4×10^{-3} mol L⁻¹ DMIT [4,5-dimercapto-1,3-dithiol-2-thionate] was prepared by the dissolution of 0.1099 g of the compound $[\text{Zn}(4,5\text{-dimercapto-1,3-dithiol-2-thionato})_2]$, or $[\text{Zn}(\text{dmit})_2]^{2-}$, in 100 mL of dimethyl sulfoxide (Acros, Belgium). The synthesis of the compound was carried out in according to previous work (BARRETO et al., 1992) and a solution of 2.4% (v/v) of Triton X-114 (Acros, Belgium) was prepared with deionized water of Milli-Q purification system (Millipore, Brazil). Buffer solution was prepared from sodium acetate (Merck) for pH 5.0 and the NaCl (Biotec) solution was prepared in concentration of 6.0% (w/v). Nitric acid 65% (Sigma-Aldrich) was used for sample decomposition.

Cloud point extraction/preconcentration

The cloud point extraction was carried out according to the following procedure. An aliquot of 10 mL of aqueous solution containing Pb^{2+} and 0.6% (m/v) NaCl was added to centrifuge tube, followed by addition of 1 mL of 0.036 mol L^{-1} acetate buffer, 500 μL of 2.4% (v/v) Triton X-114 and 500 μL of 2.4×10^{-4} mol L^{-1} [Zn(4,5-dimercapto-1,3-dithiol-2-tionato)₂] (DMIT) were sequentially added. Under this conditions, the final concentrations of sodium chloride, acetate buffer, Triton X-114 and DMIT were, respectively, 0.5% (w/v), 0.003 mol L^{-1} , 0.1% (v/v) and 1×10^{-5} mol L^{-1} . The mixture was manually shaken and heated in a thermostatic water bath at 70°C for 15 min. (incubation time). Separation of the phases was accomplished by centrifuging at 3600 rpm for 10 min. The supernatant (poor phase) was removed with a Pasteur pipette and 500 μL 1.0 mol L^{-1} HNO_3 in ethanol was added in the surfactant rich phase to reduce its viscosity. The final solution was then analyzed by FAAS.

Analysis of real samples

Tap water, mineral water and lake water were collected at State University of Londrina, local supermarket and Igapó Lake, respectively, Londrina, Paraná State, Brazil. These samples were filtered through a 0.45 μm cellulose acetate membrane and had the pH adjusted (pH 5.0) with acetate/acetic acid and immediately analyzed by proposed method. The seawater sample was collected from Itapoá beach, Santa Catarina State, Brazil, and also filtered through a 0.45 μm cellulose acetate membrane. In order to decompose some organic compounds, this sample (70 mL) was heated on a hot plate (100°C) with 30 mL of concentrated nitric acid to near dryness and then cooled to room temperature. Then, the pH was adjusted (pH 5.0) with acetate/acetic acid buffer and immediately analyzed.

Results and discussion

Effect of pH

The effect of pH play an important role on the metal-ligand complex formation and its chemical stability, hence, it can affect the extraction yield (SHOKROLLAHI et al., 2008). Thus, aqueous solution of Pb^{2+} at 200 $\mu\text{g L}^{-1}$ concentration were preconcentrated by cloud point procedure under different pH values (1.0 to 8.0). The solutions were buffered with KCl/HCl (pH 1.0), acetate/acetic acid (pH 3.0 and 5.0) and tris-HCl (pH 7.0 and 8.0). As shown in Figure 1, a considerably increase on the absorbance was observed with increasing pH up to 3.0, and after this value the absorbance remains

constant. The low efficiency on extraction at lower pH values can be related to the protonation of sulfur atoms from DMIT ligand avoiding an effective complex formation with Pb^{2+} ions. According to the results, pH 5.0 buffered with acetate/acetic acid was chosen for further experiments due to better buffering capacity in comparison to pH 3.0.

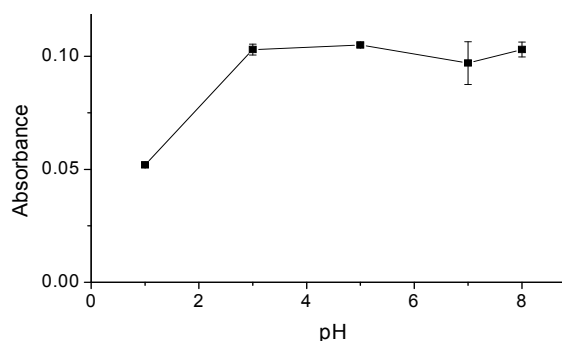


Figure 1. Effect of pH on the cloud point extraction of Pb^{2+} ions on the conditions of 1×10^{-5} mol L^{-1} DMIT, 0.1% (v/v) Triton X-114, 0.05 mol L^{-1} buffer and bath time of 25 minutes and temperature of 70°C.0

Effect of incubation time

It is well known that incubation time exerts influence on the efficiency of cloud point formation as well as on complex formation. Therefore, the incubation time was investigated in the range 5 to 35 min. by setting the batch temperature at 70°C. Within this experimental domain, an improvement at ca. 8% on the analytical signal was observed by changing the time from 5 up to 15 min. On the other hand, no significant difference was observed by increasing of incubation time from 15 up to 35 min. This finding is in agreement with work previously published (BARRETO et al., 2005), where the complex formation between Pb^{2+} ions and DMIT in dimethyl sulfoxide medium takes place in 20 min. Thus, 15 min. as incubation time was fixed for the subsequent studies in order to maintain a satisfactory analytical frequency of proposed method.

Effect of Triton X-114 concentration

The cloud point extraction efficiency also was evaluated by the study of the Triton X-114 concentration, which was studied in the range of 0.01 to 1% (v/v). As one can see from Figure 2, the best analytical signals were obtained in the range 0.1-0.3% (v/v). Concentrations above 0.3% (v/v) promoted decrease on analytical signal due to increase of the surfactant-rich phase volume and, as consequence, a decrease of the enrichment factor. In addition, the viscosity of surfactant-rich phase becomes higher with the increase of the surfactant concentration and, consequently, the

analytical signal is deteriorated due to the poor efficiency of nebulization (GHAEDI et al., 2009; PALEOLOGOS et al., 2005). Bearing in mind that there is no difference on analytical signal in the range of 0.1-0.3% (v/v), the concentration of 0.1% (v/v) of Triton X-114 was chosen as the best value in order to minimize consumption of reagents.

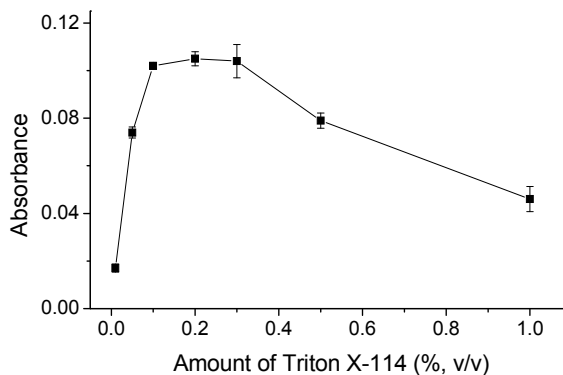


Figure 2. Effect of Triton X-114 concentration on the cloud point extraction of Pb^{2+} ions on the conditions of 1×10^{-5} mol L^{-1} DMIT, pH 5.0, 0.05 mol L^{-1} buffer and bath time of 15 minutes and temperature of 70°C.

Effect of kind and buffer concentration

The acetate buffer concentration was investigated in the range of 0.003 to 0.12 mol L^{-1} by fixing the pH at 5.0. Higher efficiency of method was verified by using lower concentration of buffer solution, possibly due to competitive interaction of acetate anions and DMIT towards Pb^{2+} ions. The preconcentration of Pb^{2+} ions using different buffers (tartrate acetate and citrate) at pH 5.0 and concentration of 0.003 mol L^{-1} was performed. This study pointed out to acetate as the best buffer. This result was somewhat expected, once tartrate and citrate buffers are considered chelating agents capable to form complex with Pb^{2+} ions. (ANDRADE et al., 2009; BOTTARI; VICEDOMINI, 1972a and b). Thus, the subsequent experiments were carried out using acetate buffer, in which the signal was considerably higher.

Effect of ligand concentration

The DMIT concentration was studied in the range of 1.0×10^{-6} to 1.0×10^{-4} mol L^{-1} (Figure 3). The absorbance increases up to the concentration of 1.0×10^{-5} mol L^{-1} which is enough to obtain complete complexation of the metal considering that the molar ratio Pb^{2+} and DMIT on the procedure is approximately 1:10 and, as can be seen from Equation 1, the stoichiometry of

reaction between Pb^{2+} and DMIT is 1:2. However, above 1.0×10^{-5} mol L^{-1} , the lower preconcentration rate is observed, indicating that the excess of DMIT promotes a competitive effect on the preconcentration of $[Pb(DMIT)_2]^{2-}$ within interior of micelles.

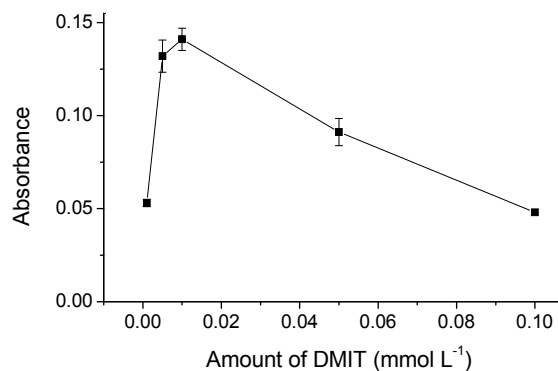


Figure 3. Effect of DMIT concentration on the cloud point extraction of Pb^{2+} ions on the conditions of 0.1% (v/v) Triton X-114, pH 5.0, 0.003 mol L^{-1} buffer and bath time of 15 minutes and temperature of 70°C.

Effect of incubation temperature

In similar way as other parameters, the incubation temperature seems to play an important role in improving preconcentration efficiency. This parameter was studied in the range 30 to 80°C. Figure 4 shows that when the temperature increases occurs dehydration of micelles and results in decreasing the volume of the surfactant-rich phase with consequent increase in preconcentration factor (GHAEDI et al., 2009; MUKHERJEE et al., 2011; PALEOLOGOS et al., 2005). Therefore, an incubation temperature of 70°C was further used in all experiments.

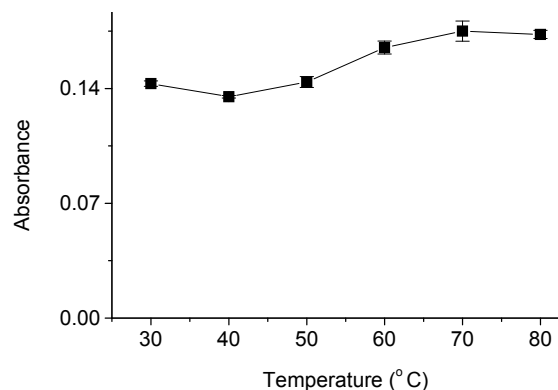


Figure 4. Effect of temperature concentration on the cloud point extraction of Pb^{2+} ions on the conditions of 0.1% (v/v) Triton X-114, 1×10^{-5} mol L^{-1} DMIT, pH 5.0, 0.003 mol L^{-1} buffer and bath time of 15 minutes.

Effect of salting-out

Previous works report that the presence of electrolytes promotes higher efficiency on the CPE due to the decrease of cloud point temperature. This phenomenon is known as “salting-out”, where the electrolytes promotes the dehydration of poly(oxyethylene) chains (MUKHERJEE et al., 2011). The dehydration of micelles occurs due to the preferential interactions of water molecules with the salt (intermolecular force of the ion-dipole type) which results on the dissociation of the salt, where the ions of the salt are solvated by the water, moving this molecules and, consequently, the micelles can approximated each other by means of hydrogen bonds of the poly(oxyethylene) chains and form “clusters”, which precipitate. The effect of NaCl on the cloud point extraction was studied in the range of 0.01 to 5.0% (m/v). The Figure 5 shows that the higher analytical signal was obtained with the concentration of 0.5% (m/v). Concentrations above 0.5% promoted decrease on the preconcentration efficiency because the high concentrations of NaCl promote an additional charge on the surface of micelles, preventing the micelle formation process (SHOKROLLAHI et al, 2008).

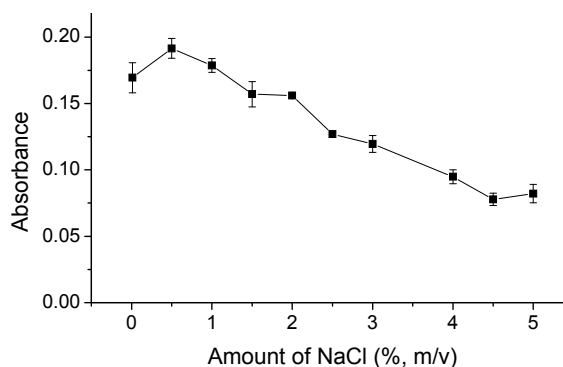


Figure 5. Effect of NaCl concentration on the cloud point extraction of Pb^{2+} ions on the conditions of 0.1% (v/v) Triton X-114, 1×10^{-5} mol L^{-1} DMIT, pH 5.0, 0.003 mol L^{-1} buffer and bath time of 15 minutes and temperature of 70°C.

Effect of foreign ions

The effect of the potential interfering species was tested in order to evaluate the applicability of the preconcentration of lead by cloud point. On the study, binary solutions containing 200 $\mu g L^{-1}$ Pb^{2+} were preconcentrated on the presence of each metallic ion Mg^{2+} , Ca^{2+} , Ba^{2+} , Fe^{3+} , As^{3+} , Cu^{2+} , Cd^{2+} , Sb^{3+} or Se^{4+} . The tolerable level of each concomitant was taken as the concentration which caused less than 15% error in comparison with measures of Pb^{2+} ions alone. The Table 1 shows the results of the study and as observed, different

anlyte:foreign ion ratios (1:1, 1:5, 1:10, 1:50 and 1:100 m/m) were evaluated and no interference was observed on the Pb^{2+} determination.

Table 1. Effects of foreign ions on the recovery analytical signal of Pb^{2+} with the concentration of 200 $\mu g L^{-1}$ ($n = 3$).

Foreign ions	Concentration (mg L^{-1})	Recovery of analytical signal of Pb^{2+} (%)
Mg^{2+}	10	113.84
	20	86.74
Ca^{2+}	10	102.61
	20	99.24
Ba^{2+}	10	96.49
	20	94.20
Fe^{3+}	0.2	103.81
	1.0	87.91
As^{3+}	0.2	100.78
	2.0	95.40
Cu^{2+}	0.2	90.66
Cd^{2+}	0.2	99.71
Sb^{3+}	0.2	99.61
Se^{4+}	0.2	90.60

Characteristics of the method and application in water samples

The proposed method provided a calibration curve from 0 up to 650 $\mu g L^{-1}$, with linear equation of $Abs = 0.00462 + 0.000793[Pb^{2+}, \mu g L^{-1}]$ ($r = 0.99945$). The limits of detection and quantification obtained as three and ten folds the standard deviations of the blank were found to be 2.58 and 11.63 $\mu g L^{-1}$, respectively (LONG; WINEFORDNER, 1983). The precision of the method evaluated in terms of repeatability and standard relative deviations (RSD) for ten determinations were found to be 3.39 and 1.07%, for the respective concentrations 50.0 and 200.0 $\mu g L^{-1}$. The method provided an enrichment factor of 16, which was calculated by the ratio between the slopes of the calibration curve with and without preconcentration method, and consumption rate of 0.63 mL. The accuracy of the proposed method was evaluated by analysis of different kind of water samples. As can be observed from Table 2, the recovery values, ranging from 99.4 to 102.2%, confirm the accuracy of the method for the determination of Pb^{2+} in water samples without any interference.

Table 2. Determination of Pb^{2+} in water samples using the proposed method.

Sample	Added ($\mu g L^{-1}$)	Found* ($\mu g L^{-1}$)	Recovery (%)
Tap water	0	ND	-
	100.0	102.24 $\pm$ 2.47	102.2
Mineral water	0	ND	-
	41.67	41.42 $\pm$ 2.50	99.4
Seawater	0	19.72 $\pm$ 2.47	-
	100.0	122.29 $\pm$ 8.90	102.2
Lake water (Igapó)	0	ND	-
	100.0	100.67 $\pm$ 7.07	100.7

ND = Not detected (below of limit of detection). * Results are expressed as mean value $\pm$ standard deviation based on three replicates ($n = 3$).

Conclusion

The use of DMIT as chelating agent of Pb^{2+} ions in micellar medium associated to cloud point extraction procedure was described. As analytical features, the proposed method provided low sample consumption and satisfactory limit of detection for the Pb^{2+} ions monitoring in natural water samples in according to guidelines natural water samples established by CONAMA (BRASIL, 2005). In addition, the developed method shows robustness for the Pb^{2+} ion extraction in a wide pH range, as well as efficiency to separate the target analyte with relative selectivity.

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