

Automatic on-line pre-concentration system using a knotted reactor for the FAAS determination of lead in drinking water

Anderson S. Souza^{a,b}, Geovani C. Brandão^a, Walter N.L. dos Santos^b, Valfredo A. Lemos^c,
Edgard M. Ganzarolli^{d,1}, Roy E. Bruns^e, Sérgio L.C. Ferreira^{a,*}

^a Universidade Federal da Bahia, Instituto de Química, Núcleo de Excelência em Química Analítica da Bahia,
Campus Universitário de Ondina, Salvador, Bahia 40170-290, Brazil

^b Universidade Estadual de Santa Cruz, Ilhéus, Bahia, Brazil

^c Universidade Estadual do Sudoeste da Bahia, Campus de Jequié, Jequié, Bahia 45206-190, Brazil

^d Universidade Estadual do Centro-Oeste, Departamento de Química, Rua Presidente Zacarias, 875, CP 33010, 85010-990 Guarapuava, PR, Brazil

^e Universidade Estadual de Campinas, Instituto de Química, CP 6154, 13083-970 Campinas, SP, Brazil

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Abstract

An automatic on-line pre-concentration system is proposed for lead determination in drinking water using flame atomic absorption spectrometry (FAAS). Lead(II) ions are retained as the 1-(2-pyridylazo)-2-naphthol (PAN) complex in the walls of a knotted reactor, followed by an elution step using 0.50 mol L⁻¹ hydrochloric acid solution.

Optimisation involving the sampling flow rate, pH and buffer concentration factors was performed using a Box–Behnken design. Other factors were established considering results of previous experiments.

The procedure allows the determination of lead with a 0.43 µg L⁻¹ detection limit ($3\sigma/S$) and precisions (expressed as relative standard deviation) of 4.84% ($N=7$) and 2.9% ($N=7$) for lead concentrations of 5 and 25 µg L⁻¹, respectively. The accuracy was confirmed by the determination of lead in the NIST SRM 1643d trace elements in natural water standard reference material. The pre-concentration factor obtained is 26.5 and the sampling frequency is 48 h⁻¹. The recovery achieved for lead determination in the presence of several ions demonstrated that this procedure could be applied to the analysis of drinking water samples. The method was applied for lead determination in drinking water samples collected in Jequié City, Brazil. The lead concentration found in 25 samples were always lower than the permissible maximum levels stipulated by World Health Organization.

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1. Introduction

Cadmium, lead, nickel, and mercury are heavy metals of unquestionable toxicity [1–3]. These metals are main sources of contamination for humans being found in foods and drinking water. As such, the World Health Organization (WHO) has established maximum allowable limits of 3, 10, 20 and 1 µg L⁻¹ for cadmium, lead, nickel and mercury, respectively [4] in drinking water. Therefore content control of these metals in drinking water should be carefully done.

The determination of mercury in drinking water is relatively simple considering the low detection limit obtained with cold vapour atomic absorption spectrometry (CV AAS). However, the determinations of cadmium, nickel and lead are more complicated since conventional spectroanalytical techniques such as flame atomic absorption spectrometry (FAAS) and inductively coupled plasma optical emission spectrometry (ICP OES) do not have detection limits for direct determination comparable to those allowed in drinking water samples. Considering this, several pre-concentration procedures have been performed in order to allow the determination of these metals in drinking water samples with FAAS and ICP OES, using separation techniques like liquid–liquid extraction, solid phase extraction, coprecipitation and cloud point extraction [1,5–8].

* Corresponding author. Fax: +55 71 32355166.

E-mail address: slcf@ufba.br (S.L.C. Ferreira).

¹ Tel.: +55 42 2691444x224.

The knotted reactor constitutes a good alternative for construction of on-line pre-concentration systems. The enrichment process is based on the adsorption of hydrophobic complexes of metal ions on the walls of knotted reactors, followed by an elution step using acidic solutions [6,9] and/or organic solvents such as methanol or ethanol, among others [10–12].

Several automatic pre-concentration systems have been proposed using solenoids valves. These require less handling and allow higher precision methods. Pre-concentration procedures were performed using solid phase extraction as the separation technique [13–15].

Box–Behnken [16–18] is a multivariate technique of experimental design, which has found fewer applications in analytical chemistry than the central composite and Doehlert matrix designs [19]. However, in recent years several analytical methods have been optimised using this tool [20–25]. It requires the same number of experiments as the Doehlert matrix and sometimes even a few than less than the central composite one [16,18]. Its main advantages are that it can be performed in statistical blocks and that experiments with all factors at their maximum or minimum levels are avoided [18].

In this paper, an automatic on-line pre-concentration system using a knotted reactor was performed for lead determination in drinking water by FAAS, using (1-(2-pyridylazo)-2-naphthol) PAN as complexing reagent. Optimum experimental conditions of the system were established using a Box–Behnken design.

2. Experimental

2.1. Apparatus

The determination of lead was performed on a Varian Model SpectrAA 220 (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer equipped with deuterium lamp background correction and an air–acetylene burner. The lead hollow cathode lamp was used according to the manufacturer's recommendations (10.0 mA, 283.3 nm). Spectral bandwidth (0.5 nm), burner height (13.5 mm) and nebulizer flow rate (6.0 ml min^{-1}) had also conventional values.

The flow system consisted of an eight-channel peristaltic pump (Alitea model C-6 XV, Stockholm, Sweden) equipped with silicone tubes to deliver reagent, eluent and sample solutions, and four 12 V, 1/4 inch three-way solenoid valves from Cole Parmer (Vernon Hills, USA) to select elution and pre-concentration steps. Capillary tubes of PTFE (0.5 mm i.d.) were also used in the manifold.

The knotted reactor (KR) was made by tying interlaced knots in 0.5 mm i.d., 1.5 mm o.d. and 2.0 m length PTFE tubing as in a previously published paper [26]. The knots were made with about 5 mm diameter loops. They overlapped each other and care was taken to prevent constrictions in the conduit, which would impede the flow through the reactor.

A laboratory-made interface [27], based on an integrated circuit ULN2003 from SGS Thomson Microelectronics (Agrate Brianza, MI, Italy) was used to activate the valves from the printer exit of a PC IBM/XT compatible microcomputer. The

control program was written in Turbo Pascal 4.0 from Borland Co. (Scotts Valley, CA, USA).

2.2. Reagents

All inorganic chemicals were of analytical-reagent grade or better. High purity water of $18 \text{ M}\Omega \text{ cm}^{-1}$ resistivity was obtained from EASYpure RF (Barnstedt, Dubuque, IA, USA). The acids used were of Suprapur grade (Merck, Darmstadt, Germany). Laboratory glassware was kept overnight in 10% nitric acid solution. Before use the glassware was rinsed with deionised water and dried in a dust free environment.

A stock lead standard solution ($1000 \mu\text{g mL}^{-1}$) was obtained from Merck and Pb working standard solutions were prepared by appropriate stepwise dilution with a 1% hydrochloric acid solution.

PAN solution ($10^{-2} \text{ mol L}^{-1}$) was prepared by dissolving 0.25 g of 1-(2-pyridylazo) 2-naphthol (PAN) in 100 mL of ethanol (Merck).

Tris buffer solution (pH 8.8) was prepared by dissolving 12.10 g of Tris-(hydroxymethyl) aminomethane (Merck) in 1000 mL of deionised water. The pH was adjusted with hydrochloric acid.

2.3. Sample preparation

The samples were filtered through 0.45 mm membrane immediately after sampling, and were acidified to pH 2.0 with nitric acid and stored at 6°C . The bottles were previously washed with a 10% (v/v) nitric acid–water solution and afterwards with ultrapure water.

2.4. Effect of other ions in the pre-concentration system

This experiment was carried out using multielemental ICP OES solution Quality Control Standards (QCS-19), which contained arsenic, antimony, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, molybdenum, nickel, thallium, titanium, vanadium, zinc, lead, magnesium, manganese and selenium.

2.5. Pre-concentration step

The flow manifold is shown schematically in Fig. 1 and was made up of a peristaltic pump fitted with tygon tubes, four three-way solenoid valves and a knotted reactor. The manifold was coupled to a flame atomic absorption spectrometer.

In the sample loading step (Fig. 1A), the V_1 and V_2 valves are initially activated and the others turned off, so the sample or standard solution (at a 9.0 mL min^{-1} flow rate) and the reagent solution (at a 2.7 mL min^{-1} flow rate) flow together to form the metal complex that is loaded into the KR for 60 s. The effluent flows towards waste (W).

In the elution step (Fig. 1B), after sample loading the V_1 and V_2 valves are turned off and the V_3 and V_4 valves are activated, so a 0.5 mol L^{-1} hydrochloric acid solution (at a 5.0 mL min^{-1} flow rate) liberates the retained metal complex from the inner

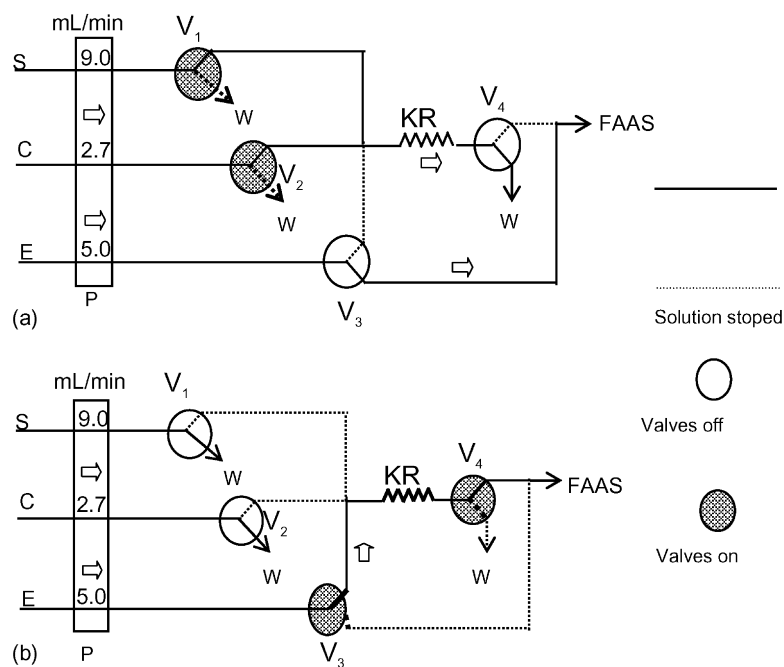


Fig. 1. Diagram of the pre-concentration system.

surface of the knotted reactor and the eluate is driven directly to the nebulizer–burner system of the flame atomic absorption spectrometer.

2.6. Optimisation strategy

The optimisation process was carried out using a Box–Behnken design involving the pH, sampling flow rate (SFR) and buffer concentration (BC) variables, considering the absorbance (AS) as the response. The experimental data were processed using the STATISTICA program. All the experiments were performed using 10.0 mL of 25.0 $\mu\text{g L}^{-1}$ lead solution.

3. Results and discussion

3.1. Optimisation of the experimental conditions of the on-line system

On-line pre-concentration systems using a knotted reactor have many variables to optimise. In this system the knotted reactor length, eluent concentration (hydrochloric acid solution), eluent flow rate and reagent concentration (PAN) factors were fixed as being 200 cm, 0.5 mol L^{-1} , 5.0 mL min^{-1} and 3.0 $\cdot 10^{-5}$ mol L^{-1} , respectively. These factors were optimised using univariate methodology, considering the results included of our previous paper performed for cadmium determination [28]. The variables: pH, buffer concentration and sampling flow rate were optimised using a Box–Behnken design. The experiments executed for this design and their results are presented in Table 1.

A quadratic model in the three factor variables was found to adequately describe the data in Table 1. An analysis of variance

(ANOVA) showed that the model does not suffer from lack of fit since the $\text{MS}_{\text{lof}}/\text{MS}_{\text{pe}}$ (lof = lack of fit and pe = pure error) calculated value of 1.98 is less than the 95% confidence critical value of 19.25. Furthermore, the ANOVA indicated that both the linear and quadratic terms for pH and buffer concentration (BC) were significant at the 95% confidence level whereas all the terms involving the sampling flow rate (SFR) were not. This explains why the results for the (5,7), (6,8), (9,11) and (10,12) pairs of experiments have analytical signals that are almost the same since each pair has common pH and BC levels.

The response surface model for the FAAS analytical signal (AS) for lead as a function of pH, BC and SFR is

Table 1
Absorbance results for the Box–Behnken design with real and coded values

Experiments	pH	BC (mol L^{-1})	SFR (mL min^{-1})	Response (absorbance)
1	7.0 (−1)	0.01 (−1)	8.0 (0)	0.0068
2	9.0 (+1)	0.01 (−1)	8.0 (0)	0.0222
3	7.0 (−1)	0.03 (+1)	8.0 (0)	0.0118
4	9.0 (+1)	0.03 (+1)	8.0 (0)	0.0306
5	7.0 (−1)	0.02 (0)	6.0 (−1)	0.0140
6	9.0 (+1)	0.02 (0)	6.0 (−1)	0.0286
7	7.0 (−1)	0.02 (0)	10.0 (+1)	0.0110
8	9.0 (+1)	0.02 (0)	10.0 (+1)	0.0344
9	8.0 (0)	0.01 (−1)	6.0 (−1)	0.0220
10	8.0 (0)	0.03 (+1)	6.0 (−1)	0.0280
11	8.0 (0)	0.01 (−1)	10.0 (+1)	0.0187
12	8.0 (0)	0.03 (+1)	10.0 (+1)	0.0245
13	8.0 (0)	0.02 (0)	8.0 (0)	0.0278
14	8.0 (0)	0.02 (0)	8.0 (0)	0.0307
15	8.0 (0)	0.02 (0)	8.0 (0)	0.0300

given by

$$\begin{aligned} AS = & 0.0295 + 0.00903 (\text{pH}) + 0.00315 (\text{BC}) \\ & (\pm 0.0009) \quad (\pm 0.00054) \quad (\pm 0.00054) \\ & - 0.00050 (\text{SFR}) - 0.00648 (\text{pH})^2 - 0.00518 (\text{BC})^2 \\ & (\pm 0.00054) \quad (\pm 0.00079) \quad (\pm 0.00079) \\ & - 0.00103 (\text{SFR})^2 + 0.00085 (\text{pH})(\text{BC}) \\ & (\pm 0.00079) \quad (\pm 0.00076) \\ & + 0.00220 (\text{pH})(\text{SFR}) - 0.00005 (\text{BC})(\text{SFR}) \\ & (\pm 0.00076) \quad (\pm 0.00076) \end{aligned}$$

where standard errors are in parentheses below their corresponding model coefficients.

Taking derivatives with respect to pH, BC and SFR results in three equations that can be used to determine the maximum AS value and the corresponding factor variable levels:

$$\begin{aligned} \frac{\partial(AS)}{\partial(\text{pH})} = & 0.00903 - 0.01296 (\text{pH}) + 0.00085 (\text{BC}) \\ & + 0.00220 (\text{SFR}) = 0, \end{aligned}$$

$$\begin{aligned} \frac{\partial(AS)}{\partial(\text{BC})} = & 0.00315 + 0.00085 (\text{pH}) - 0.01036(\text{BC}) \\ & - 0.00005 (\text{SFR}) = 0, \end{aligned}$$

$$\begin{aligned} \frac{\partial(AS)}{\partial(\text{SFR})} = & -0.00050 + 0.00220 (\text{pH}) - 0.00005 (\text{BC}) \\ & - 0.00206 (\text{SFR}) = 0 \end{aligned}$$

This equation predicts a maximum of 0.0336 absorbance for the codified factor levels of 0.829 for pH, 0.369 for BC and 0.637 for SFR. In laboratory units this corresponds to a pH of 8.83, a buffer concentration of 0.024 mol L⁻¹ and a 9.27 mL min⁻¹ sampling flow rate. Of all the results in Table 1 run number 8 has experimental conditions closest to this predicted maximum with an absorbance of 0.0344. Fig. 2 shows the response surface for the lead AS as a function of pH and BC. Besides number 8, experiment number 4 is also close to the predicted maximum.

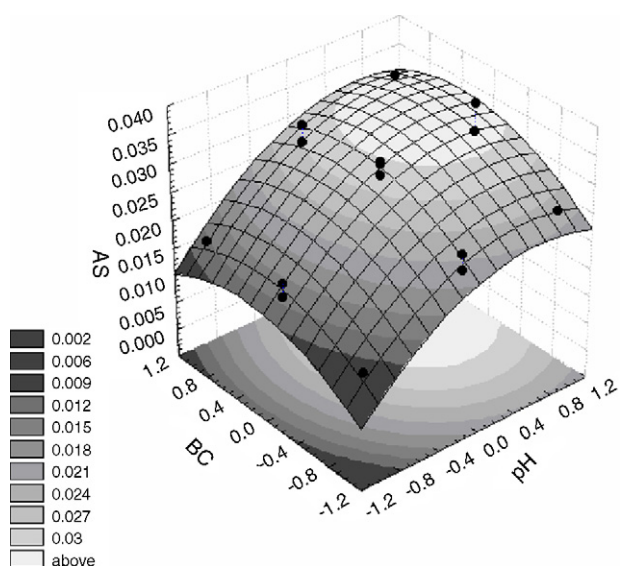


Fig. 2. Response surface plot of the lead analytical signal as a function of pH and buffer concentration at a sampling flow rate of 8.0 mL min⁻¹.

Table 2

Factorial design for robustness evaluation

Experiments	pH	BC (mol L ⁻¹)	Response (absorbance)
1	8.3	0.02	0.0314
2	9.3	0.02	0.0318
3	8.3	0.028	0.0323
4	9.3	0.028	0.0353
5	8.8	0.024	0.0297
6	8.8	0.024	0.0340
7	8.8	0.024	0.0335

3.1.1. The effect of other ions on the pre-concentration system

In order to check the effect of other ions on lead determination, a standard solution containing lead and 18 other metallic ions (each one at 10.00 μg L⁻¹) was prepared and lead was determined using the proposed on-line pre-concentration system. The results showed that at this concentration, the other ions do not interfere in the lead determination. This result demonstrates that the proposed method can be applied perfectly for lead determination in water samples.

3.2. Validation process

3.2.1. Robustness

The model obtained with the Box–Behnken design demonstrated that all the terms involving the factor sampling flow rate are not significant. This means that this factor is robust for the interval from 6.0 to 10.0 mL min⁻¹. So a robustness study was performed only for the pH and buffer concentration factors using a full factorial design. This evaluation was done for a variation of ±0.5 units of pH and ±20% in buffer concentration. Experimental data for this design are summarized in Table 2. There was no lack of fit for the model containing the principal and interaction factors and the Pareto chart (Fig. 3) obtained demonstrates clearly that the pH and buffer concentration variables are robust for intervals of 8.8 ± 0.5 and 0.024 ± 0.004 mol L⁻¹, respectively.

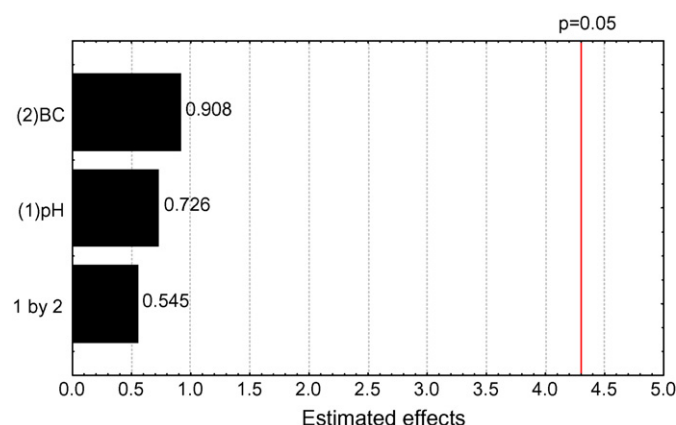


Fig. 3. Pareto chart for the main and interaction effects of the 2² factorial design for robustness.

3.2.2. Calibration

The equation for the calibration curve using the on-line pre-concentration system was given as $Abs = 0.0049 + 0.00103 [Pb^{2+}, \mu g L^{-1}]$, with $R^2 = 0.9978$, with three replicates performed at each concentration ($N=6$). By using direct aspiration in FAAS without the pre-concentration step in the $5\text{--}25 \mu g mL^{-1}$ interval $Abs = 0.00537 + 3.89 \cdot 10^{-5} [Pb^{2+}, \mu g mL^{-1}]$ with $R^2 = 0.9999$ was obtained ($N=6$). The experimental enrichment factor, calculated as the ratio of the slopes of the calibration graphs with and without pre-concentration, was 26.5 [9]. The concentration efficiency defined as the “pre-concentration factor of an analyte achieved by the system per minute” is 21.2 [9].

3.2.3. Precision and accuracy

The precision was expressed as the relative standard deviation (R.S.D.), calculated using lead solutions with concentrations of 5 and $25 \mu g L^{-1}$ and were 4.51 and 2.02%, respectively (7 replicates). The detection and quantification limits calculated according to IUPAC recommendations [29] were $0.43 \mu g L^{-1}$ (3σ) and $1.42 \mu g L^{-1}$ (10σ). The accuracy was checked by lead determination in the trace elements in natural water standard reference material, NIST SRM 1643d, which has a certified lead value of $18.15 \pm 0.64 \mu g L^{-1}$. Using the proposed method the lead concentration obtained in this SRM was $18.6 \pm 3.4 \mu g L^{-1}$. The statistical comparison *t*-test showed no significant difference between the lead values obtained from the proposed method and the certified values. This standard reference material has a typical drinking water matrix with the presence of calcium (31.0), magnesium (8.0), potassium (2.4) and sodium (22.1) at

Table 3
Lead determination in drinking water ($N=3$)

Sampling station	Quarter	Concentration ($\mu g L^{-1}$)
1	Algaroba	5.6 ± 2.1
2	Bairro Preto	6.1 ± 1.3
3	Brasil Novo	4.0 ± 0.8
4	Cachoeirinha	4.7 ± 0.7
5	Campo do América	2.8 ± 0.8
6	Centro	3.6 ± 0.4
7	Cidade Nova	4.8 ± 2.0
8	Curral Novo	4.1 ± 0.6
9	Fazenda Velha	4.3 ± 0.4
10	Inocop	3.5 ± 1.0
11	Itaigara	4.9 ± 1.3
12	Jequiezinho	5.5 ± 1.5
13	Joaquim Romão	4.0 ± 1.4
14	Km 3	4.7 ± 0.9
15	Km 4	2.1 ± 0.5
16	Lot. Água Branca	3.6 ± 0.6
17	Lot. Jardim Nazaré	3.5 ± 0.5
18	Lot. Parque da colina	6.1 ± 2.2
19	Lot. São Judas	2.6 ± 0.9
20	Mandacaru	5.1 ± 2.0
21	São José	2.7 ± 0.2
22	São Luís	3.5 ± 0.9
23	Sol Nascente	6.3 ± 0.3
24	Urbis IV	5.4 ± 2.2
25	Vila Rodoviária	5.2 ± 2.1

N = determination number.

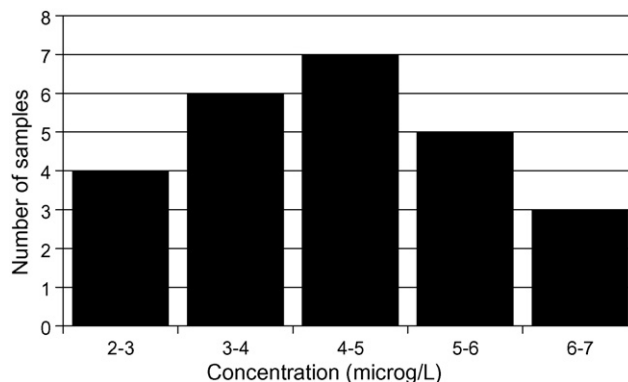


Fig. 4. Histogram of lead concentration in drinking water samples.

the milligram per litre level and common trace elements at the microgram per litre level demonstrating that it is adequate for this kind of application.

3.2.4. Application—lead determination in drinking water samples

The method was applied to the determination of lead in 25 drinking water samples consumed in different quarters of Jequié city. The results are described in Table 3. The lead concentrations found were in the $2.1\text{--}6.3 \mu g L^{-1}$ range. All these results are lower than the permissible maximum level stipulated by the World Health Organization and also by Health Ministry of Brazilian government [30], which established $10 \mu g L^{-1}$ as the maximum limit. Fig. 4 shows a histogram of the results that resembles a normal distribution with a mean value of $4.4 \mu g L^{-1}$.

4. Conclusions

The proposed pre-concentration system using a knotted reactor allows lead determination in drinking water samples. The method is simple, inexpensive, precise and accurate.

The lead contents of drinking water samples collected in Jequié City, Brazil were lower than the permissible maximum World Health Organization level ($5.0 \mu g L^{-1}$).

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