

A sensitive spectrophotometric method for lead determination by flow injection analysis with on-line preconcentration

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Abstract

A new flow injection (FI) system for the determination of Pb(II) at trace level with a preconcentration step and spectrophotometric detection is proposed. It is based on preconcentration of lead ions on chitosan and dithizone–lead complex formation in aqueous medium (pH 9). The chemicals and FIA variables influencing the performance of the system were optimized and applied to the determination of lead in natural, well, and drinking water samples. It is a simple, highly sensitive, and low cost alternative methodology. The method provided a linear range between 25 and 250 $\mu\text{g l}^{-1}$, a detection limit of 5.0 ng ml^{-1} and a sample throughput of 15 h^{-1} . The obtained results of spiked samples are in good agreement between the proposed method and ICP-AES.

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1. Introduction

The determination of ultra traces of lead in environmental samples plays an important role in the environmental pollution monitoring, owing to its cumulative toxicity. Lead is used in storage batteries, cable sheath, solders, and radiating shielding and it is widely distributed in the nature. The environmental and health problems come fundamentally from the use of gasoline antiknock products and paint pigments [1]. It is confirmed that most of the lead contamination in humans is from foods and drinks consumed. A regular absorption of small quantities of lead may cause serious injuries to health such as encephalopathy, kidney damage and damage to the body in several other ways [2].

Electrothermal atomic absorption spectrometry (ETAAS) is the most frequently used technique for lead and others toxic trace elements determination [3–5]. Other detectors are also used such inductively coupled plasma mass spectrometry (ICP-MS) [6], hydride generation-inductively coupled plasma-atomic emission spectrometry (HG-ICP-AES) [7], with smaller frequency.

The spectrophotometry detection is widely used as detection technique in FI analysis due to the low cost of the instrument, the simplicity of procedures, as well as their speed, precision, and accuracy. In literature, many chromogenic reagents have been reported for lead determination by spectrophotometric methods [8–11]. The method reported in this paper presents several advantages such as an acceptable linear range and sample throughput, a comparable sensitivity to the most sensitive methods, lower consumption time for the analysis, a lower sample volume consumption, and that the analytical process from sample treatment is implemented on-line.

Dithizone is an old and known reagent which was widely used for heavy metal determination [12,13]. As this reagent is soluble in organic solvents, the spectrophotometric method always needed solvent-extraction techniques. Paradkar and Williams [14] proposed an aqueous/surfactant medium to prepare dithizone solution. However, there is no evidence in literature about the use of dithizone prepared through this method, probably due to the instability of the solution upon light exposure.

The aim of this paper was to develop an automatized spectrophotometric method for lead determination. The analytical method was based on dithizone–lead complex formation at pH 9, working in an aqueous medium. The FIA

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system was implemented in such a way that the dithizone reagent was prepared on-line, also the pretreatment of the sample for lead preconcentration and the regeneration of the mini-column was connected on-line.

2. Experimental

2.1. Apparatus

The flow assembly (Fig. 1) was provided with two Rheodyne 5041 and 5011 injection valves, two peristaltic pumps, Gilson model Minipuls 3, and an UV-V Hewlett Packard 8452A diode array spectrophotometer as detector with a Hellma 178-010-QS flow cell (inner volume, 18 μl). The reaction coils were made of PTFE tubing (i.d., 0.5 mm) and the SBSR reactor (length, 6.5 cm; i.d., 1.1 mm) was made with PTFE tubing (i.d., 0.8 mm) packed with glass beads (425–600 μm).

2.2. Preconcentration column

The preconcentration column was prepared by packing a Tygon tube (i.d., 6.0 cm \times 5.0 mm) with chitosan [poly(D-glucosamine)]. The ends of the tube were fitted with a piece of cigarette filter to keep the adsorbent material inside the tube.

2.3. Reagent and solutions

All the reagents used were of analytical grade and the solutions were prepared in distilled, deionised water.

The Triton X-100 solution (5% v/v) was prepared by diluting 50 ml of surfactant in 100 ml of 1 M hydrochloric acid, and then making up the volume to 1000 ml with water.

Boric acid (0.4 M) was prepared dissolving 24.74 g of H_3BO_3 in 1000 ml of water.

A 2.070 g l^{-1} lead stock solution was prepared dissolving $\text{Pb}(\text{NO}_3)_2$ (Riedel-de-Haën) in water. From these, working solutions were prepared as required.

2.4. Procedure

The FIA system is depicted in Fig. 1. The dithizone solution was obtained on-line by using a solid reagent column (SRC). This solution merged with a stream of Triton X-100 (5% v/v) in the R_1 reactor in order to obtain an adequate dilution of the reagent for the forward complex formation.

The preconcentration column was incorporated in the FIA system between V_1 (six-way valve) and V_2 (selection valve). The chitosan inside the column was regenerated by passing an HCl solution (pH 4) in order to reach the optimum pH for the forward lead adsorption (pH 7). The sample was loaded by passing through it for 2.5 min, after this time a water stream (pH 7) was passed to remove the sample still present in the line and in the column. Then, V_1 valve was switched again to allow the NaOH (0.2 M) solution that went through the column to eluate the analyte. At the same time, V_2 valve was switched and the eluate merged with dithizone solution inside the reactor R_2 . This stream merged with a boric acid stream in the R_3 reactor in order to attain the optimum medium (pH 9) for dithizone–lead complex

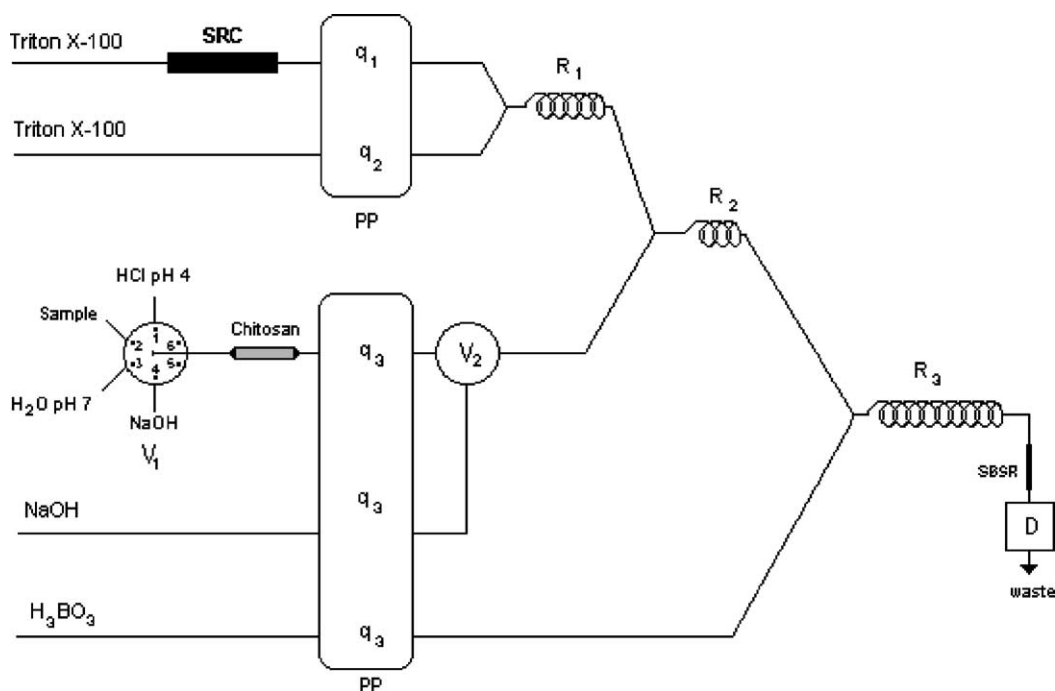


Fig. 1. PP, peristaltic pump; V_1 , six way valve; V_2 , selection valve; q_1 , Triton X-100 flow rate; q_2 , diluent flow rate; q_3 , HCl (pH 4); sample, water (pH 7) and NaOH flow rates; SRC, solid reagent column; R_1 , R_2 , and R_3 , reactors; D, detector; SBSR, single bead string reactor.

formation. A SBSR reactor was placed after R₃ reactor to get a good base line. The complex was detected at 536 nm.

3. Results and discussion

3.1. Optimization of chemical and FIA variables

The operational conditions of the FIA system and chemical variables were optimized in a univariant way in order to obtain the high signal and the best reproducibility. A 200 µg l⁻¹ Pb standard solution was used for the optimization.

3.1.1. Preconcentration system

The presence of amino group in the chitosan chain does it selective for metal ions. Therefore, it confers high capacity to retain transition metals [15]. Thus, chitosan was chosen as the adsorbent material. Their characteristics were: flakes form, 3.64% moisture content, 0.71% ash, and 78.10% deacetylation degree.

The mini-column was home-made with a glass tube packed with chitosan. The column length was optimized over the range of 2.5–6.5 cm and the optimum results were obtained with 6 cm. The inner diameter was tested (2–5 mm) and 5 mm was the optimum.

NaOH was selected for the elution of adsorbed Pb(II) ions, which has been reported by Lista and Fernández Band [16] and the concentration was varied between 0.15 and 0.25 M. A 0.2 M solution was used.

A hydrochloric acid solution (pH 4) was selected for chitosan regeneration [17] which give a suitable pH for the Pb(II) adsorption (pH 7).

The sample and eluent flow rates, loading time and regeneration time of the column were optimized and their optimum values are shown in Table 1.

In order to evaluate the preconcentration system, the enrichment factor (EF) was calculated as the ratio of the slopes of the calibration curves, before and after the preconcentration treatment [18]. The obtained value was 8.2.

Table 1
Optimization of FIA variables

Variable	Studied range	Optimum value
Reactor length R ₁ (mm)	300–900	600
Reactor length R ₂ (mm)	100–400	300
Reactor length R ₃ (mm)	600–2900	1900
Dithizone flow rate (ml min ⁻¹)	0.40–0.76	0.54
Triton X-100 flow rate (ml min ⁻¹)	0.40–1.10	0.76
Sample flow rate (ml min ⁻¹)	0.40–1.50	1.10
Eluent flow rate (ml min ⁻¹)	1.00–3.80	1.00
Loading time (min)	1.5–3.0	2.5
Regeneration time (s)	60–120	100
SBSR length (cm)	5.0–7.5	6.5
SBSR inner diameter (mm)	0.80–1.10	0.80

3.1.2. FIA system

Dithizone is soluble in Triton X-100 aqueous solution in acidic medium, but it is unstable to light exposure. Therefore, the dithizone solution was prepared on-line by using a mini-column (SRC) filled with solid dithizone and a Triton X-100 solution passing through it. The SRC was prepared by using a dark Tygon[®] tube (length, 5 cm; i.d., 3 mm). Different percentages of Triton X-100 solution were tested (1–10%) in order to obtain a suitable concentration of dithizone. The optimum value was 5%.

The adequate pH for dithizone–Pb(II) complex formation was 9. In order to obtain this pH and considering that NaOH 0.2 M solution was used as an eluent, a boric acid solution stream was introduced in the system. The concentration of this solution was tested between 0.2 and 0.8 M and the best results were obtained when 0.4 M was used.

All other FIA variables and their optimum values are listed in Table 1.

3.2. Interferences

The effect of potential interfering species in the determination of 50 µg l⁻¹ of lead was studied. The levels of tolerated concentration of foreign ions was considered as maximum concentration found to cause a change in signal, less than 5%, compared with the signal for lead alone. The tolerance limits are shown in Table 2. Some masking agents were used to remove the interference caused for metals. Thus, sodium tartrate solution (0.16 M) to remove up 0.1 mg l⁻¹ of cadmium, tiourea solution (1.89 × 10⁻² M) to eliminate the interference of mercury (0.5 mg l⁻¹), and sodium thio-sulphate solution (0.096 M) to eliminate copper (1 mg l⁻¹) were used.

Table 2
Tolerance limits of interfering ions

Tested ion	Tolerance limit (mg l ⁻¹)
Cu ²⁺	0.05 (interfere)
Hg ²⁺	1.0 (interfere)
Cd ²⁺	0.05 (interfere)
Zn ²⁺	2
Mg ²⁺	150
Ca ²⁺	200
Ni ²⁺	2
Fe ³⁺	0.2 (interfere)
Na ⁺	>250
K ⁺	>500
F ⁻	>100
Br ⁻	>100
Cl ⁻	>900
NO ₃ ⁻	>800
NO ₂ ⁻	>60
S ²⁻	1.5
SO ₄ ²⁻	600
PO ₄ ³⁻	>150
C ₂ O ₄ ²⁻	>100
Humic acid	>12

Table 3
Determination of Pb(II) in real samples

Sample	Pb(II) added ($\mu\text{g ml}^{-1}$)	Pb(II) found ($\mu\text{g ml}^{-1}$) ^a		Recovery \pm s (%) ^a	
		Proposed method	Reference method (ICP-AES)	Proposed method	Reference method (ICP-AES)
1–6	0	No signal	No signal	–	–
1	a	0.049	0.005	98.5 \pm 0.1	102.0 \pm 0.2
	b	0.199	0.197	99.8 \pm 0.2	98.5 \pm 0.3
2	a	0.050	0.048	100.4 \pm 0.2	96.0 \pm 0.3
	b	0.200	0.202	100.0 \pm 0.5	101.0 \pm 0.1
3	a	0.053	0.055	107.1 \pm 0.4	110.0 \pm 0.4
	b	0.199	0.203	99.8 \pm 0.2	101.0 \pm 0.2
4	a	0.053	0.051	106.1 \pm 0.4	102.0 \pm 0.2
	b	0.190	0.205	95.3 \pm 0.2	102.5 \pm 0.1
5	a	0.054	0.055	108.6 \pm 0.2	110.0 \pm 0.4
	b	0.196	0.198	98.0 \pm 0.1	99.0 \pm 0.1
6	a	0.052	0.048	105.2 \pm 0.4	96.0 \pm 0.4
	b	0.199	0.202	99.7 \pm 0.2	101.0 \pm 0.1

1: Sample of Colorado River (Paso Alsina, Río Negro State, Argentine) 2: Sample of Paso Piedras Dike, Grunbein, (Bahía Blanca, Bs. As. state, Argentine) 3: Drinking water of Bahía Blanca (Bs. As. State, Argentine) 4: Sample of Negro River (C de Patagones, Río Negro State, Argentine) 5: Sample of well water from San Cayetano (Bs. As. state, Argentine) 6: Sample of Paso Piedras Dike, B. Patagonia, (Bahía Blanca, Bs. As. State, Argentine).

^a Average of three replicate determinations (a) 0.05, (b) 0.20.

3.3. Analytical performance

The calibration graph for the determination of Pb(II) was obtained under the experimental conditions above described. The results showed that a good linear relationship was observed over the range 25–250 $\mu\text{g l}^{-1}$. The calibration curve was $A = (0.0048 \pm 0.00036) + (0.2135 \pm 0.0026) \cdot [\text{Pb(II)} \mu\text{g ml}^{-1}]$, $r^2 = 0.9996$. The detection limit estimated (S/N = 3) was 5.0 ng ml^{-1} Pb(II). The repeatability of the method was calculated as the relative standard deviation (RSD) of the maximum peak heights calculated from 10 replicates containing 0.1 mg l^{-1} Pb(II) injected by duplicate and the obtained result was 4.5%. The sample throughput was 15 h^{-1} .

3.4. Determination of lead in natural waters

The FIA method for lead determination was validated against the ICP-AES method. As the water samples showed that lead was not present in them, they were spiked with different levels of concentrations of lead standard solution.

Sodium tartrate solution, sodium thiosulphate solution, and thiourea were added to the spiked samples, to remove the possible metals interference. Then, lead determination was carried out with the proposed method and with the alternative method. Results and recovery values are shown in Table 3.

The statistical t -test was used to compare the recoveries (%) from both methods. The results revealed no significant differences between the percentages obtained and 100%. Then, as both variances are equal ($F_{\text{calculated}} = 1.18$ and $F_{\text{critic}(95\%,11)} = 2.82$), a comparison between recovery percentages of the proposed method and the reference method was done. The calculated t is less than t from the table, which

shows that they were not significantly different ($t_{\text{calculated}} = 0.057$ and $t_{\text{critic}(95\%,22)} = 2.07$) between them.

4. Conclusions

A new simple, highly sensitive and low cost FIA method is proposed for the determination of lead in natural, well and drinking waters. It presents good reproducibility and sample throughput. By using suitable masking agents, the method is selective.

The on-line preparation of the reagent avoids the tedious procedure of freshly preparing solution, which is unstable at light exposure. Moreover, the use of toxic organic solvents that may bring secondary pollution is not necessary, unlike the other extractive determination methods of lead [12,13,19].

The preconcentration procedure is totally automatized and it is necessary low volume of sample (less than 3 ml) to determine lead in low levels. The detection limit is better than other previously reported [20–23].

The method was applied successfully to the analysis of different water samples. The results obtained with the proposed method are comparables with that obtained by reference method.

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