Talanta 127 (2014) 244–249

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Sequential determination of lead and cobalt in tap water and foods samples by fluorescence ☆

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ARTICLE INFO

Article history:
Received 14 March 2014
Received in revised form
7 April 2014
Accepted 16 April 2014
Available online 24 April 2014

Keywords:
Lead
Cobalt
8-Hydroxyquinoline
Luminescence
Tap water
Foods

ABSTRACT

In this work, a new procedure was developed for the separation and preconcentration of lead(II) and cobalt(II) in several water and foods samples. Complexes of metal ions with 8-hydroxyquinolein (8-HQ) were formed in aqueous solution. The proposed methodology is based on the preconcentration/separation of Pb(II) by solid-phase extraction using paper filter, followed by spectrofluorimetric determination of both metals, on the solid support and the filtered aqueous solution, respectively. The solid surface fluorescence determination was carried out at λ_{em}=455 nm (λ_{ex}=385 nm) for Pb(II)-8-HQ complex and the fluorescence of Co(II)-8-HQ was determined in aqueous solution using λ_{em}=355 nm (λ_{ex}=225 nm). The calibration graphs are linear in the range 0.14–8.03 × 10^4 μg L^{-1} and 7.3 × 10^{-2}–4.12 × 10^3 μg L^{-1}, for Pb(II) and Co(II), respectively, with a detection limit of 4.3 × 10^{-2} and 2.19 × 10^{-2} μg L^{-1} (S/N=3). The developed methodology showed good sensitivity and adequate selectivity and it was successfully applied to the determination of trace amounts of lead and cobalt in tap waters belonging of different regions of Argentina and foods samples (milk powder, express coffee, cocoa powder) with satisfactory results. The new methodology was validated by electrothermal atomic absorption spectroscopy with adequate agreement. The proposed methodology represents a novel application of fluorescence to Pb(II) and Co(II) quantification with sensitivity and accuracy similar to atomic spectroscopies.

1. Introduction

Today it is well known that many diseases have an environmental origin, considering environmental everything about life: air, water, food, habits, solar radiation and pharmaceuticals, among others [1]. The knowledge of the harmful compounds to human health present in water and foods is of interest to scientists, environmentalist, governments and general public. The scientific community has the responsibility to provide reliable data with the aim of informing people.

Metals are widespread non-biodegradable chemical contaminant found in the environment because of the anthropogenic activities such as industrial production, fertilizer use and sludge fertilization. Heavy metal contamination is a known causative of various disorders such as genomic instability, endocrine disruption, neurotoxicity, carcinogenicity, immunological problems and also impaired psycho-social behavior [2,3].

Lead has a high toxicity, product of exposure in the workplace, environmental and household pollution. The main routes of incorporation into the body are the respiratory and digestive, through consumption of contaminated food and water. Chronic poisoning with this metal leads to a condition known as *saturnism*, which is characterized by severe anemia, digestive, cardiovascular, renal and nervous disorders [4,5]. Cobalt, meanwhile, is an essential element for humans. Cobalt deficiency can cause megaloblastic anemia, affects the development of the nervous system and the immune response. On the other hand, high intakes can cause polycythemia, hypothyroidism, thyroid and heart failure [6,7].

The determination of traces of both metals is of interest in the fields of environmental analysis, process control and clinical toxicological analysis. Also, the development of analytical methodologies with high sensitivity and accuracy is necessary for their quantification.

The determination of metals in foods and tap water is usually associated with a step of preconcentration of the analyte before

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☆ "In memoriam" of Dr. Adriana Masi, prominent researcher, dear colleague and a friend, who passed away prematurely as a consequence of public insecurity, killed by a shot in the head at the door of her house.

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http://dx.doi.org/10.1016/j.talanta.2014.04.020
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detection, due to low concentrations present in these matrices [8,9]. A variety of procedures for preconcentration of metals, such as solid phase extraction (SPE), liquid–liquid extraction (LLE), coprecipitation and cloud point extraction (CPE) have been developed [10–12].

SPE has become a preferred method for concentrating the analyte prior to its analysis by instrumental techniques. SPE has come to the forefront compared to other preconcentration and/or separation techniques, as it offers several advantages such as flexibility, higher enrichment factors, absence of emulsion, low cost, high speed and simplicity, safety with respect to hazardous samples and more importantly environment friendly [13–15]. Nowadays, investigators are interested in improving the selectivity of the sorbents used in SPE. This objective is particularly important when analyzing complex matrices. Several solid materials as silica gel, exchange resins, aluminum oxide, poly(vinylalcohol), C18 membranes, cyclodextrines, filter papers, Nylon membranes, among others have been successfully employed as supports for SPE [16,17].

SPE followed by ETAAS, ICP-OES or ICP-mass spectrometry are shown to be suitable for analysis of metal traces [18,19]. The application of molecular fluorescence in the determination of traces of lead and cobalt has shown several analytical advantages such as high sensitivity, proper selectivity and wide dynamic range when it is associated to separation/preconcentration step [20].

The aim of present work is to propose an alternative methodology to traditional atomic spectroscopies for both metals monitoring in real samples of tap waters belonging different regions of Argentina and foods using an instrument accessible in control laboratories. Considering economic aspects and operating simplicity, in this opportunity filters papers ribbon blue are proposed as support for Pb(II) and Co(II) complexes retention for their posterior determination by fluorescence.

2. Experimental

2.1. Reagents

Stock solutions of Pb(II) and Co(II) 1×10^{-4} mol L^{-1} were prepared by dilution of 100 μg mL^{-1} standard solution plasmapure (Leeman Labs, Inc.).

A 1×10^{-2} mol L^{-1} sodium tetraborate (Mallinckrodt Chemical Works, New York, Los Angeles, St. Louis, USA) solution was prepared, obtaining the desired pH by addition of dilute HClO4 (Merck) or NaOH (Mallinckrodt Chemical Works) solutions.

Acetic/acetate (Mallinckrodt Chemical Works, New York, Los Angeles, St. Louis, USA) buffer solution 1×10^{-2} mol L^{-1} was prepared by dissolution of the appropriate amount of each, in ultrapure water. The pH was adjusted to the desired value, by adding NaOH (Mallinckrodt Chemical Works) solutions using a pHmeter (Orion Expandable Ion Analyzer, Orion Research, Cambridge, MA, USA) Model EA 940.

Stock solution of 8-hydroxyquinoleine (8-HQ, H.E – Daniel Ltd., England) 1×10^{-6} mol L^{-1} was weekly prepared by dissolving the appropriate amount of reagent in ultrapure water. The stability of solutions was checked by spectrophotometric measurements.

All used glass materials were previously washed with a 10% v/v HNO_3 solution and then with Milli-Q ultrapure water. All used reagent were analytical grade.

Nylon membranes (Millipore, Sao Paulo, Brazil) 0.45 μm pore size and 47 mm diameter, cellulose acetate (Whatman, England) 0.45 μm pore size and 47 mm, mixed esters (Schleicher & Schuell, Germany) 0.45 μm pore size and 47 mm, Immobilon (+) (Millipore, Sao Paulo, Brazil), Filter papers Blue Ribbon (FP, Whatman, England) 2–5 μm pore size and 12.5 cm diameter were used in sorption studies.

2.2. Apparatus

Spectrofluorimetric measurements were made using a Shimadzu RF-5301 PC spectrofluorometer equipped with a 150 W Xenon lamp and 1.00 cm quartz cells. For solid surface fluorescence measurements a solid sample holder was used. A combined glass electrode and a pHmeter (Orion Expandable Ion Analyzer, Orion Research, Cambridge, MA, USA) Model EA 940 were used for pH adjustments.

Measurements were performed with a Shimadzu Model AA-6800 Atomic Absorption Spectrometer (Tokyo, Japan) equipped with a deuterium background corrector, an EX7-GFA electrothermal atomizer and an ASC-6100 autosampler. L'vov graphite tubes (Shimadzu, Tokyo, Japan) were used in all experiments. Lead and cobalt hollow-cathode lamps (Hamamatsu, Photonics K., Japan) was employed as the radiation sources. Wavelengths used were 240.7 (Slit Width: 0.2 nm) for lead and 283.3 nm (Slit Width: 1 nm) for cobalt using a pyrolysis times of 13 and 10 s at 400 and 800 °C and atomization times of 3 s at 2500 °C and 2 s at 2400 °C, respectively.

2.3. Sampling procedure

Tap water samples were allowed to run for 10 min, and approximately 1000 mL of each were collected. Tap water samples were processed once they arrived in the laboratory, without previous treatment.

Food samples were acquired in local shops, choosing products manufactured in Argentine. In order to guarantee representative samples, a randomize strategy sampling was used; a total of three recipients of the same brand for each product were acquired. The whole of the contents of each product was homogenized and reserved for sample preparation.

About 0.5 g of each solid sample (milk powder, express coffee, cocoa powder) were digested using a microwave furnace. Then resulting solutions were transferred to 100 mL volumetric flasks and made to the top with bidistilled water. Portions of 100 μL of each sample were put into 100 mL volumetric flasks and diluted with bidistilled water. These solutions were reserved to Pb(II) and Co(II) determinations by general procedure.

2.4. General procedure

Adequate volumes of sample/standard solutions containing Pb(II) and Co(II) ($0.14–8.03 \times 10^4$ μg L^{-1} and $7.3 \times 10^{-2}–4.12 \times 10^3$ μg L^{-1}, respectively), 500 μL 8-HQ 1×10^{-6} mol L^{-1}, 200 μL buffer sodium tetraborate solution 1×10^{-3} mol L^{-1} (pH=10.0) were placed into a 10 mL volumetric flask. The whole mixture was made to 10 mL with ultrapure water. Systems were filtered across the membranes of filters paper (FPs), using a vacuum pump and dried at room temperature. The filtrated solution containing Co(II)-8-HQ complex was collected and pH was reconditioned by adding 1 mL acetic acid/acetate buffer1 $\times 10^{-2}$ mol L^{-1} (pH=4.0). Pb(II) concentration was determined on FP by solid surface fluorescence (SSF) at λ_{em}=455 nm (λ_{exc}=385 nm), using a solid sample holder; cobalt concentration was determined in the filtrated solution by fluorescent emission at λ_{em}=355 nm (λ_{exc}=225 nm) using the conventional quartz cell (see Fig. 1).

2.5. Interferences study

Different amounts of ions which may be present in water samples (1/1, 1/10, 1/100 and 1/1000 Pb(II) or Co(II)/interferent

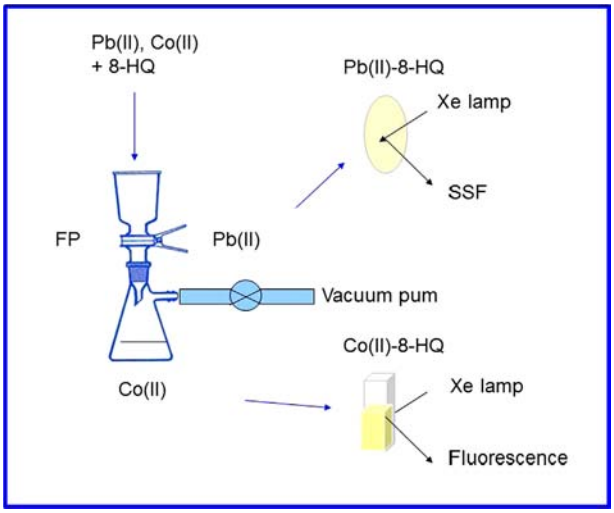

Fig. 1. Schematic representation of general procedure of developed methodology.

ratio) were added to the test solution containing 4.15 μg L^{-1} Pb(II) and 1.2 μg L^{-1} Co(II), respectively, and general procedure was applied.

2.6. Precision study

The repeatability (within-day precision) of the methodology was tested for replicate of samples ($n=4$) spiked with 4.15 μg L^{-1} Pb(II) and 1.2 μg L^{-1} Co(II), respectively, and the contents were determined by proposed methodology.

2.7. Validation

Pb(II) and Co(II) contents in waters and foods samples were determined by ETAAS, using operational conditions previously consigned in apparatus item.

3. Results and discussion

In general, 8-HQ can react with metal ions to form neutral chelates. In order to study the luminiscent spectral behaviors, systems containing Pb(II) and Co(II) were separately prepared adding 8-HQ and buffer sodium tetraborate aqueous solutions. Also, a reagent blank solution was prepared. Optimal excitation and emission wavelengths were selected and respective spectra of emission of Pb(II) and Co(II) quelates were scanned. The fluorescent emission of organic dye was increased by the presence of Pb (II) and the Co(II). In these experimental conditions, both metallic chelates showed an important spectral interference with overlaping of the maximum emission wavelength (365 nm). This fact makes it impossible for the quantification of both metals in samples where they are together by molecular fluorescence.

Taking into account the similar spectral responses of both metals in aqueous solution, the retention of chelates on solid supports was explored. The above prepared systems were filtered through FPs using a vacuum pump. The filtered solutions were received in clean separated vessels and FPs were dried at room temperature. FPs were put in the solid samples holder and SSF were registered for Pb(II) and Co(II) chelates. Likewise, filtrated solutions were explored by molecular fluorescence. The results showed that Pb(II)-8-HQ was selectively retained for the FP, while Co(II)-8-HQ remained in the filtered solution (Fig. 2).

On these results, the main variables affecting the separation and determination processes, such as pH, nature and concentration of buffer, concentration of chelating agent and nature of solid support were studied and optimized for Pb(II) and Co(II) traces quantification.

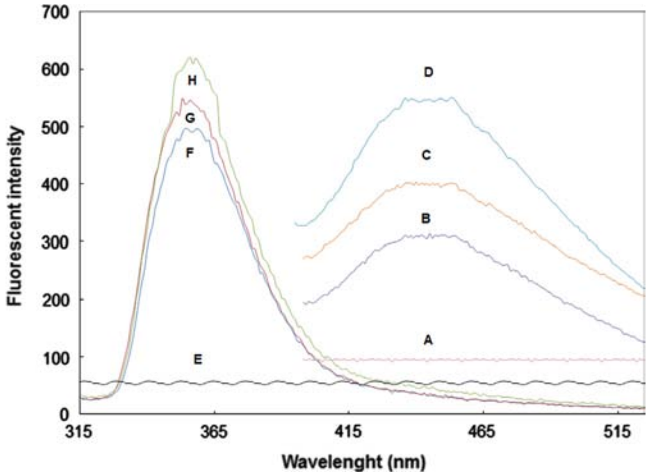

Fig. 2. Emission spectra for Co(II) and Pb(II)-8-HQ complexes. (A) Filter paper, (B) filter paper with 8-HQ ($C_{8\text{-HQ}}=5\times10^{-7}$ mol L^{-1}), (C) idem B with Pb(II) 4.15 μg L^{-1}, (D) idem B with Pb(II) 8.5 μg L^{-1}, (E) blank filtrated solution, (F) idem E with Co(II) 1.20 μg L^{-1}, (G) idem E with Co(II) 2.50 μg L^{-1}, and (H) idem E with Co(II) 5.00 μg L^{-1}. Conditions: SSF: $\lambda_{exc}=385$ nm; $\lambda_{em}=455$ nm (slits 3/3); $C_{\text{buffer borax}}=2\times10^{-4}$ mol L^{-1}, pH 10. Filtrated solution: $\lambda_{exc}=225$ nm; $\lambda_{em}=355$ nm (slits 3/3); $C_{\text{buffer acetic/acetate}}=1\times10^{-4}$ mol L^{-1}, pH 4.00. Other experimental conditions are described under procedure.

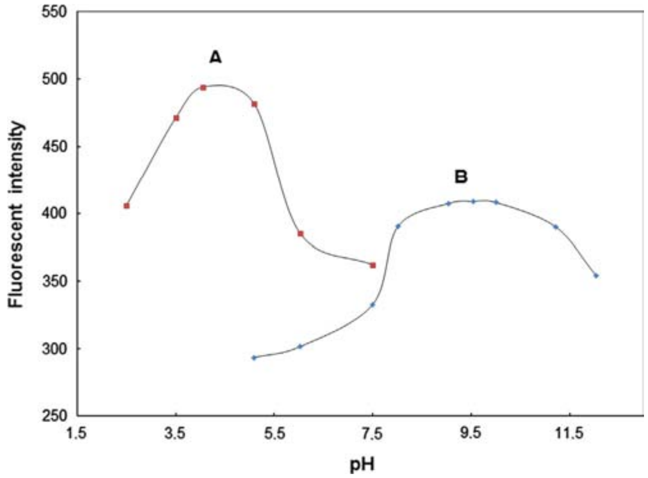

Fig. 3. Influence of pH on Co(II) and Pb(II)-8-HQ complexes emission. Conditions: (A) $C_{\text{Co(II)}}=1.20$ μg L^{-1}; $C_{8\text{-HQ}}=5\times10^{-7}$ mol L^{-1}; $C_{\text{buffer acetic/acetate}}=1\times10^{-2}$ mol L^{-1}, pH 4.00; $\lambda_{exc}=225$ nm; $\lambda_{em}=355$ nm and (B) $C_{\text{Pb(II)}}=4.15$ μg L^{-1}; $C_{8\text{-HQ}}=5\times10^{-7}$ mol L^{-1}; $C_{\text{buffer borax}}=2\times10^{-4}$ mol L^{-1}, pH 10; $\lambda_{exc}=385$ nm; $\lambda_{em}=455$ nm. Other experimental conditions are described under procedure.

In order to assure the quantitative formation of both metallic chelates, the effect of the 8-HQ concentrations on the analytical responses was optimized in the range from 1×10^{-9} to 1×10^{-6} mol L^{-1}. The emission of 8-HQ is enhanced remarkably in the presence of analytes. The signal reached maximum when the concentration of 8-HQ was 5×10^{-7} mol L^{-1}. When the concentration continues to increase until 1×10^{-6} mol L^{-1}, the emission slightly decreased. A 8-HQ concentration of 5×10^{-7} mol L^{-1} was chosen as optimal for the following assays.

The effect of pH was studied in order to achieve selective retention of Pb(II) and the sensitive detection to Co(II). The optimum Pb(II) recoveries were found when the pH was adjusted between 5.0 and 12.0 and maximum recovery was established at the pH value of 10.0. Between the assayed buffers, sodium tetraborate (2×10^{-4} mol L^{-1}) resulted the more adequate to obtain the maximum SSF for Pb(II)-8-HQ. Furthermore, the emission for Co(II)-8-HQ was poor at pH 10.0. Then, filtrated solution was reconditioned by the addition of acetic acid (1×10^{-2} mol L^{-1}) bringing the pH at a final value of 4.0, obtaining so the best emission signal (Fig. 3).

Other important experimental condition was the nature of solid support for Pb(II)-8-HQ retention. Different membranes (cellulose acetate, Nylon, Teflon, FPs) were assayed in filtration step without previous treatment, being satisfactory Nylon membrane and FP blue ribbon for the selective and quantitative retention of Pb(II) complex, showing a maximal signal. FP was chosen taking into account that reduces substantially the cost for assay and its easy acquisition in the trade.

4. Analytical figures of merit

The limits of detection (LOD) of the proposed method for the determination of investigated elements were studied under optimal experimental conditions by applying the procedure for blank solutions. The detection limits of the investigated elements based on three times the standard deviations of the blank ($N = 15$) were 4.3×10^{-2} and 2.19×10^{-2} µg L^{-1}, respectively.

The calibration graphs are linear in the range 0.14–8.03×10^4 µg L^{-1} for Pb(II) and 7.3×10^{-2} to 4.12×10^3 µg L^{-1} for Co(II). Tables 1 and 2 summarize the main characteristics of calibration plot and optimized experimental conditions, which sustain the proposed procedure for quantification of Pb(II) and Co (II) traces.

4.1. Interferences study

The effect of foreign ions on the recoveries of Pb(II) and Co(II) were tested. Different amounts of ions commonly present in water and food samples were added to the test solution containing 4.15 µg L^{-1} of Pb(II) and 1.20 µg L^{-1} of Co(II), and the developed procedure was applied. An ion was considered as interferent, when it caused a variation in the fluorescent signal of the test system greater than ±5%. The tolerance limits of various foreign ions are given in Fig. 4. These results demonstrate that large excess amounts of some common cations and anions do not interfere on the determinations of both analytes, putting in evidence the adequate selectivity of the developed methodology.

Table 1
Experimental conditions and analytical parameters for lead determination by SSF.

Parameters	Studied range	Optimal conditions
Support	Cellulose acetate, nylon, teflon, filter paper	Filter paper (blue ribbon)
pH	5.0–12.0	10.0
Buffer sodium Tetraborate	1×10^{-5}–0.5 mol L^{-1}	2×10^{-4} mol L^{-1}
8-HQ concentration	1×10^{-9}–1×10^{-5} mol L^{-1}	5×10^{-7} mol L^{-1}
LOD	–	4.3×10^{-2} µg L^{-1}
LOQ	–	0.14 µg L^{-1}
LOL	–	0.14–8.03×10^4 µg L^{-1}
r^2	–	0.999

Table 2
Experimental conditions and analytical parameters for cobalt determination.

Parameters	Studied range	Optimal conditions
pH	2.0–7.5	4.0
Buffer acetic/acetate	1×10^{-5}–0.1 mol L^{-1}	1×10^{-2} mol L^{-1}
8-HQ concentration	1×10^{-9}–1×10^{-6} mol L^{-1}	5×10^{-7} mol L^{-1}
LOD	–	2.19×10^{-2} µg L^{-1}
LOQ	–	7.3×10^{-2} µg L^{-1}
LOL	–	7.3×10^{-2}–4.12×10^3 µg L^{-1}
r^2	–	0.999

5. Applications and validation

The usefulness of the proposed method was evaluated for the determination of analytes in tap water belonging different regions of Argentine and foods (milk powder, express coffee and cocoa

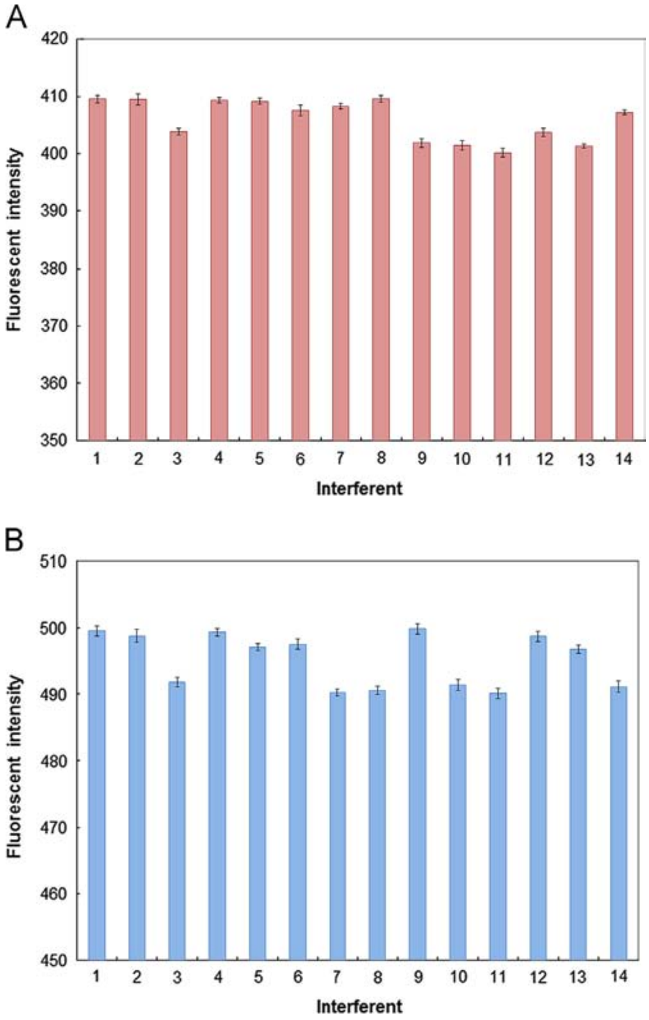

Fig. 4. (A) Tolerances of cations of Pb(II) quantification by solid surface fluorescence. %SDs (I–I) have been included for each interferent. (B) Tolerances of cations of Co(II) quantification in filtrated solution. %SDs (I–I) have been included for each interferent. Fluorescent intensity ± SD. (A) 1: Pb (II) 4.15 µg L^{-1}; 2: Pb (II) in presence of Co(II); 3: Pb (II) in presence of K(I); 4: Pb (II) in presence of Na(I); 5: Pb (II) in presence of Cd(II); 6: Pb (II) in presence of Ca(II); 7: Pb (II) in presence of Zn(II); 8: Pb (II) in presence of Mn(II); 9: Pb (II) in presence of Sr(II); 10: Pb (II) in presence of Ba(II); 11: Pb (II) in presence of Cr (III); 12: Pb (II) in presence of Fe(III); 13: Pb (II) in presence of Cu(II); and 14: Pb (II) in presence of Al(III). (B) 1: Co (II) 1.20 µg L^{-1}; 2: Co (II) in presence of Pb(II); 3: Co (II) in presence of K(I); 4: Co (II) in presence of Na(I); 5: Co (II) in presence of Cd(II); 6: Co (II) in presence of Ca(II); 7: Co (II) in presence of Zn(II); 8: Co (II) in presence of Mn(II); 9: Co (II) in presence of Sr(II); 10: Co (II) in presence of Ba(II); 11: Co (II) in presence of Cr (III); 12: Co (II) in presence of Fe(III); 13: Co (II) in presence of Cu(II); and 14: Co (II) in presence of Al(III).

powder). The accuracy of the methodology was performed using the standard addition method and validated by ETAAS. Different sample aliquots (0.250 mL) were spiked with increasing amounts of Pb(II) (4.15 and 8.30 $\mu g\ L^{-1}$) and Co(II) (1.20 and 2.50 $\mu g\ L^{-1}$). Obtained results showed satisfactory agreement with adequate precision. The reproducibility of the method was evaluated repeating the proposed methodology, 4 times for each sample. Tables 3 and 4 show the recovery results achieved for each sample. Obtained results indicate that the proposed method is suitable for determination of both analytes in such studied samples.

6. Conclusions

This novel procedure provides a simple, economical, rapid, and precise method for the preconcentration and determination of lead and cobalt in water and foods samples using 8-hydroxyquinolein as chelating agent. The solid phase extraction method was used for selective retention/preconcentration of Pb(II) on filter paper being a powerful tool for sensitive determination of analyte in studied samples. Also, Co(II) was determined in filtrated solution with adequate sensitivity. The good tolerance at high

Table 3
Recuperation and validation studies by lead determination in water and foods samples.

Sample	Pb(II) added ($\mu g\ L^{-1}$)	Proposed methodology		ETAAS
		Pb(II) found ± CV ($\mu g\ L^{-1}$)	Recovery (%, $n=4$)	Pb(II) found ± CV ($\mu g\ L^{-1}$)
1	–	2.47 ± 0.02	–	2.45 ± 0.07
	2.05	4.50 ± 0.03	99.20	
	4.15	6.63 ± 0.04	100.40	
	8.30	10.75 ± 0.05	99.20	
2	–	1.75 ± 0.08	–	–
	2.05	3.77 ± 0.06	98.30	
	4.15	5.92 ± 0.01	101.15	
	8.30	10.03 ± 0.03	98.86	
3	–	1.82 ± 0.06	–	1.85 ± 0.008
	2.05	3.85 ± 0.08	98.90	
	4.15	5.98 ± 0.04	100.55	
	8.30	10.15 ± 0.05	101.65	
4	–	1.93 ± 0.05	–	1.97 ± 0.009
	2.05	4.00 ± 0.05	101.03	
	4.15	6.08 ± 0.03	100.00	
	8.30	10.22 ± 0.04	99.50	
5	–	2.04 ± 0.02	–	2.00 ± 0.007
	2.05	4.10 ± 0.03	101.00	
	4.15	6.20 ± 0.02	100.50	
	8.30	10.35 ± 0.04	100.50	
6	–	2.17 ± 0.01	–	2.15 ± 0.008
	2.05	4.25 ± 0.08	101.38	
	4.15	6.33 ± 0.09	100.45	
	8.30	10.45 ± 0.04	99.10	
7	–	2.89 ± 0.03	–	2.85 ± 0.01
	2.05	4.97 ± 0.07	101.03	
	4.15	7.05 ± 0.08	100.35	
	8.30	11.23 ± 0.04	101.40	
8	–	0.32 ± 0.01	–	–
	0.50	0.81 ± 0.05	96.90	
	1.05	1.37 ± 0.04	100.00	
	2.25	2.56 ± 0.07	96.90	
9	–	0.93 ± 0.02	–	–
	0.50	1.45 ± 0.04	102.15	
	1.05	1.98 ± 0.08	100.00	
	2.25	3.17 ± 0.01	98.93	
10	–	0.87 ± 0.05	–	–
	0.50	1.35 ± 0.03	97.70	
	1.05	1.91 ± 0.06	98.85	
	2.25	3.13 ± 0.08	101.15	

1- Tap water (San Luis city, Argentina).
2- Tap water (Potrero de los Funes, San Luis, Argentina).
3- Tap water (Campus UNSL, San Luis, Argentina).
4- Tap water (Córdoba city, Argentina).
5- Tap water (Huinca Renancó, Córdoba, Argentina).
6- Tap water (Rio Cuarto, Córdoba, Argentina).
7- Tap water (Mendoza city, Argentina).
8- Cocoa powder.
9- Milk power.
10- Express coffee.

Table 4
Recuperation and validation studies by cobalt determination in water and food samples.

Sample	Co(II) added ($\mu g\ L^{-1}$)	Proposed methodology		ETAAS
		Co(II) found ± CV ($\mu g\ L^{-1}$)	Recovery (%, $n=4$)	Co(II) found ± CV ($\mu g\ L^{-1}$)
1	–	5.12 ± 0.04	–	5.00 ± 0.003
	1.20	6.33 ± 0.03	100.20	
	2.50	7.60 ± 0.02	99.60	
	3.70	8.85 ± 0.05	100.60	
2	–	4.30 ± 0.01	–	4.40 ± 0.004
	1.20	5.51 ± 0.01	100.23	
	2.50	6.78 ± 0.03	99.55	
	3.70	7.87 ± 0.07	97.00	
3	–	4.55 ± 0.04	–	4.50 ± 0.001
	1.20	5.77 ± 0.05	100.45	
	2.50	7.06 ± 0.05	100.20	
	3.70	8.20 ± 0.03	98.90	
4	–	5.24 ± 0.03	–	5.25 ± 0.004
	1.20	6.45 ± 0.03	100.20	
	2.50	7.75 ± 0.04	100.20	
	3.70	8.98 ± 0.06	100.75	
5	–	4.63 ± 0.07	–	4.60 ± 0.001
	1.20	5.85 ± 0.02	100.50	
	2.50	7.12 ± 0.04	99.80	
	3.70	8.30 ± 0.01	99.35	
6	–	6.92 ± 0.03	–	7.00 ± 0.002
	1.20	8.13 ± 0.03	100.15	
	2.50	9.41 ± 0.04	99.85	
	3.70	10.65 ± 0.08	100.45	
7	–	5.42 ± 0.05	–	–
	1.20	6.63 ± 0.02	100.20	
	2.50	7.90 ± 0.04	99.63	
	3.70	9.10 ± 0.07	99.60	
8	–	2.07 ± 0.03	–	2.00 ± 0.004
	1.20	3.25 ± 0.03	99.05	
	2.50	4.58 ± 0.02	100.50	
	3.70	5.80 ± 0.03	101.45	
9	–	5.26 ± 0.07	–	5.30 ± 0.007
	1.20	6.48 ± 0.01	100.40	
	2.50	7.77 ± 0.03	100.20	
	3.70	8.93 ± 0.06	99.40	
10	–	8.32 ± 0.04	–	8.50 ± 0.009
	1.20	9.55 ± 0.05	100.40	
	2.50	10.80 ± 0.05	99.75	
	3.70	12.00 ± 0.02	99.75	

1- Tap water (San Luis city, Argentina).
2- Tap water (Potrero de los Funes, San Luis, Argentina).
3- Tap water (Campus UNSL, San Luis, Argentina).
4- Tap water (Córdoba city, Argentina).
5- Tap water (Huinca Renancó, Córdoba, Argentina).
6- Tap water (Rio Cuarto, Córdoba, Argentina).
7- Tap water (Mendoza city, Argentina).
8- Cocoa powder.
9- Milk power.
10- Express coffee.

levels of regular foreign constituents put in evidence the high selectivity and versatility of the new methodology. Precision and accuracy were tested and validated by ETAAS with good agreement. The developed methodology was successfully applied to both analytes quantification to tap waters belonging of different sites of Argentine and foods samples. The reached sensitivity was comparable at those arrived with atomic spectroscopies employing a simple and inexpensive instrumental.

Acknowledgments

Authors wish to thank the Instituto de Química San Luis – Consejo Nacional de Investigaciones Científicas y Tecnológicas (INQUISAL–CONICET), National University of San Luis (Project 22/Q228) for the financial support.

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