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PAPER

An on-line separation and preconcentration system coupled with flame atomic absorption spectrometry for the determination of lead

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A simple on-line separation/preconcentration procedure is described for the determination of trace levels of Pb(II) by flame atomic absorption spectrometry (FAAS). A mini-column packed with Dowex Marathon C (DMC) ion-exchange resin was used for the on-line preconcentration of Pb(II) at pH 3.5. Pb(II) was sorbed on the resin, from which it could be eluted with 3 mol L^{-1} HCl and then introduced directly to the nebulizer–burner system of FAAS. The parameters influential on the determination of Pb(II) ions such as the pH of sample solution, eluent type, interfering ions and flow variables were studied. Under the optimum conditions, the calibration graph obtained was linear over the concentration range of 0.01–0.1 mg L^{-1}. The detection limit of the method was 1.3 μg L^{-1} while precision was 1.1% ($n = 15$) at a 0.05 mg L^{-1} Pb(II) level. The accuracy of the method was proven using standard reference materials. The developed method has been applied successfully to the determination of lead in water and various environmental samples with satisfactory results.

1 Introduction

The determination of heavy metals, particularly some toxic metals which play important roles in biological mechanisms, has been receiving much attention. Even very low concentrations of some toxic metals can cause serious biological disorders that can lead to some serious diseases.[1]

Lead is a toxic metal, which accumulates in the vital organs of humans and animals. It is well known that lead is a very 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. Its cumulative poisoning effects are serious hematological damage, brain damage, anemia and kidney malfunctioning.[2,3]

The quality control of the drinking water is a world concern and many procedures using different methodologies have been performed for analysis of these samples.[4–8] The health effects of lead are most severe, and for infants and children exposure to high levels of lead in drinking water can result in retardation in physical or mental development. For adults, it can result in high blood pressure. Although the main sources of exposure to lead

are ingesting paint chips and inhaling dust, the Environmental Protection Agency (EPA) estimates that 10% to 20% of human exposure to lead may come from lead in drinking water.[9] Infants who consume mostly mixed formula can receive 40% to 60% of their exposure to lead from drinking water. Considering it, the maximum permissible level for lead in drinking water has been established for several national and international health organizations. The EPA fixed as being 15 and 10 μg L^{-1}.[10] In natural water its typical concentration lies between 2 and 10 μg L^{-1}, whereas the upper limit recommended by World Health Organization (WHO) is less than 10 μg mL^{-1}.[3]

Among various analytical techniques devoted to metal determination, the most attractive one is obviously the atomic absorption spectrometry. However, the main problem with this technique is its low sensitivity for trace metals at a μg L^{-1} level. The combination of flow injection on-line separation and preconcentration techniques using solid-phase reagents with FIA-FAAS has proved to be of considerable interest in the last few years on account of its high potentials for enhancing the relative sensitivity and selectivity of FAAS. The most important aspect of an on-line solid phase extraction (SPE) and preconcentration method is the nature and properties of the sorbent materials.[11] Various sorbents have recently been used for the on-line solid phase preconcentration and determination of lead by FAAS in different samples. Some of these sorbents are activated carbon loaded with xylenol orange,[12] polytetrafluoroethylene,[13] polyurethane foam,[10,14] synthetic zeolite,[15] impregnated hollow fibre,[16] silica gel functionalized with methylthiosalicylate,[17] and multiwall carbon nanotubes.[18]

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In this paper, an automatic on-line preconcentration procedure for the determination of lead using a flow-injection (FI) approach with flame atomic absorption spectrometry (FAAS) as the detection method is described. For this reason, the optimum experimental conditions of the method have been established using the on-line preconcentration system with a home-made time controller having five independent channels. The system combining FAAS with on-line preconcentration is very effective in enhancing the sensitivity. To the best of our knowledge, an on-line preconcentration system combined with the Dowex Marathon C (DMC) resin has not been used before in the determination of Pb(II) by FAAS.

2 Experimental

2.1 Instrument

A PerkinElmer (Norwalk, CT, USA) model AAnalyst 800 flame atomic absorption spectrometer equipped with a deuterium background correction system and an air–acetylene burner was used for the determination of lead. The wavelength used for lead was 283.3 nm. A spectral bandwidth of 0.7 nm, acetylene flow rate of 1.4 L min^{-1}, and nebulizer flow rate of 10.0 mL min^{-1} were conventional working parameters. For measuring pH values in the aqueous phase, a Consort model C533 pH meter combined with a glass-electrode and also a magnetic stirrer (Chiltern) was used.

The flow system comprises a peristaltic pump with variable speed (Watson-Marlow Inc., Wilmington, MA, USA), a multi-channel peristaltic pump (Ismatec SA, Glattbrugg, Switzerland) furnished with silicone tubes to deliver all solutions, and two three-way valves (Cole-Parmer Inc. Co., Illinois, USA) to select solution ways. The peristaltic pumps (PP) and the valves (V) were controlled by the five-channel time controller and each channel can be set for 36 different timing periods with thumble switches. This unit was constructed in our instrumentation laboratory (at low cost).[19] The flow system was made using fittings, unions and tees made of plastic and high density polyethylene (HDPE) materials. The DMC resin packed into a home-made minicolumn (glass, 3.5 cm length and 0.3 cm i.d.) was used for the on-line preconcentration of the Pb(II) ions.

2.2 Reagents and standard solutions

All reagents used were of the highest available purity and at least of analytical reagent grade (Merck, Darmstadt, Germany). Deionized ultra pure water was used for the preparation of the solutions. A 100 mg L^{-1} stock Pb(II) solution was prepared by dissolution of 50 mg lead nitrate (Merck) in 2% HNO$_3$. Standard solutions of lead were prepared by appropriate dilution of the stock solution with 0.1 mol L^{-1} HNO$_3$ just before use. Hydrochloric acid was also used as eluent throughout the experiments.

DMC resin with the sulfonic acid group was used (Fluka, Buchs, Switzerland) as the solid phase extractant. In order to remove organic and inorganic contaminants, the resin was washed with distilled water, 1 mol L^{-1} HNO$_3$ in acetone and distilled water, respectively. The glassware used was cleaned by

soaking overnight in dilute HNO$_3$ (1 : 5, v/v), and then rinsed with distilled water several times.

The following buffer solutions were used for the presented preconcentration procedure: HCl/KCl buffer for pH 1.0–2.0; CH$_3$COONa/CH$_3$COOH buffer for pH 3.0–5.0; and CH$_3$COONH$_4$/CH$_3$COOH buffer for pH 6.0–7.0.

2.3 Column preparation

An amount of 90 mg of the sorbent was packed in a mini-column. A slurry of the polymer beads was injected into the minicolumn with a syringe. The ends of the minicolumn were fitted with glass wool to retain the packing material. Before use, ethanol, 3 mol L^{-1} nitric acid solution and deionized water were passed through the minicolumn at a flow rate of 2.5 mL min^{-1} in order to clean it. Washing with nitric acid and ethanol was necessary in order to prevent any metal and/or organic contamination. All the minicolumns prepared in this way showed good reproducibility. The resin bed was approximately 1.0 cm length. The packed column was washed with blank solutions to condition the DMC resin. After each elution cycle, it was automatically treated with deionized water and the buffer solution, respectively. The resin is very stable and used without any loss of its capacity throughout all the experiments.

2.4 On-line preconcentration system

The performance of the on-line preconcentration method was tested with model solutions before its application to real samples. The schematic diagram of the flow injection (FI) manifold and operational sequence for the on-line separation and preconcentration system coupled with FAAS has been described in a previous paper.[19] In the sample loading step, PP1 and V1 are active while PP2 and V2 are inactive, and the sample solutions adjusted to pH 3.5 with CH$_3$COONa/CH$_3$COOH buffer were passed through the minicolumn (MC) for 3.4 min at a flow rate of 5 mL min^{-1}. The lead retained on the minicolumn while the effluent was collected as waste. Afterwards, the minicolumn was washed with water in order to remove matrix ions. At this period, PP1 and V2 are active while PP2 and V1 are inactive. Finally, in the elution step, the eluent (E), 3 mol L^{-1} HCl, was aspirated by PP2 at a flow rate of 2.4 mL min^{-1}. During the elution, PP1 is inactive. The released metal ions are directly transported into the nebulizer of the spectrometer. The signals were measured in the peak area mode using the instrument software. In the following step, the minicolumn was washed with water (PP1 and V2 are active, PP2 and V1 are inactive) to clean the resin. Afterwards, the buffer solution was pumped to the column to condition it before a new preconcentration cycle. During this period, PP1 was active while PP2, V1 and V2 were inactive. The calibration curve was linear for Pb(II) concentrations in the range of 0.01–0.1 mg L^{-1}, with a regression coefficient of 0.9966. Real sample solutions were similarly subjected to the on-line preconcentration procedure as described above.

2.5 Application of the proposed method

The proposed on-line method was successfully applied to the various water samples for the determination of Pb(II). Tap water

samples were collected from two locations in Turkey, Yeşilhisar (a field of mine) in Kayseri and Yozgat provinces. Pre-washed polyethylene bottles were used to store the water samples until analysis. 2 mL of concentrated HNO_3 (65%, w/w) were added to 100 mL of the water samples and the proposed procedure was applied to these samples. Preparations of blank solutions were carried out in the same way. Then the on-line preconcentration procedure given above was applied to the samples. The determination of Pb(II) ions in the final solutions was performed by FAAS.

The proposed method was successfully applied to the on-line determination of Pb(II) in various plant samples. A 1.0 g crushed and ground portion of the plant sample was weighed into a beaker. In order to decompose, 10 mL of aqua regia was added to the beaker and the mixture was heated until to almost dryness. Then, 10 mL of aqua regia was added again to the residue and the mixture was evaporated to dryness. The insoluble part of the sample was filtered through a blue ribbon filter paper using 0.1 mol L^{-1} of HNO_3. The volume of filtrate was diluted to 25 mL with deionized water. After the pH of the solution was adjusted to 3.5 by adding 2 mL of CH_3COONa/CH_3COOH buffer, the solution was completed to 50 mL with deionized water. Blank solutions were run in the same way. Then the on-line preconcentration procedure given above was applied to the samples. The determination of Pb(II) ions in the final measurement solutions was performed by FAAS.

In order to ascertain the validation of the proposed procedure, the method was applied for the analysis of Pb(II) ions in the certified reference materials (TMDA-64 lake water, SPS-WW2 Batch 108 waste water, and SRM 1547 peach leaves). 10 mL portions of TMDA-64 lake water and SPS-WW2 Batch 108 waste water were previously treated with 1 mL of concentrated HNO_3. Then the on-line preconcentration procedure was applied to the samples.

A 0.1 g portion of NIST-1547 Peach leaves samples was digested with a mixture of 4 mL of HNO_3 (65%, w/v) and 2 mL of H_2O_2 (30%, w/v). Preparation of blank solutions was carried out in the same way without sample. Then the on-line preconcentration procedure was applied to the samples.

3   Results and discussion

The chemical and hydrodynamic conditions in the flow injection on-line separation/preconcentration system were optimised by applying the proposed procedure to model solutions involving 0.05 mg L^{-1} lead in which the following important analytical parameters were tested individually and precisely.

3.1   Effect of pH

To find the optimal conditions for the on-line separation/preconcentration of trace lead, a careful examination of the effect of pH on the analytical signals of Pb(II) ions was carried out. The pH values, from 1.0 to 7.0, of the model solutions including 0.05 mg L^{-1} Pb(II) were individually adjusted for each pH by using the proper (appropriate) buffer solutions (see Section 2.2). The retention conditions of the analyte were optimized by

evaluating the analytical signals monitored during the measurement with FAAS while changing the pH of the solutions that pass through the minicolumn on the flow system. The solutions were pumped through the minicolumn packed with the resin at a loading time of 3.4 min. As illustrated in Fig. 1, the absorbance of the analyte increased sharply with increasing the pH of the sample solution from 1.0 to 3.0 and then a significant decrease observed beyond pH 4.0. For the pHs lower than 3, a competition between protons and the analyte ions for the adsorption sites may be responsible from the low analytical signals. Probably the concomitant ions may compete with the analyte ions for the binding sites of the resin. In the light of these results, the optimum pH of the flow injection system for the online determination of Pb(II) was chosen as 3.5.

3.2   Flow rates of samples and elution solutions

The flow rate of the sample solution establishes the contact time between the analyte and the sorbent. At high sample flow rates, Pb(II) ions could probably not equilibrate properly with the resin due to the increase in velocity of the ions, which reduces the contact time between the two phases. In contrast, low flow rates decrease the sample throughput, resulting in long analysis times. For this reason, the effect of flow rates of the sample solution on the adsorption of Pb(II) ions was considered by varying the flow rate from 2 to 10 mL min^{-1} while keeping constant the amount of the analyte. The analyte signals increased gradually from 2 to 4 mL min^{-1}, while they were nearly constant between 4 and 6, and then again decreased from 6 to 10 mL min^{-1} for the flow rates of the sample solutions. The
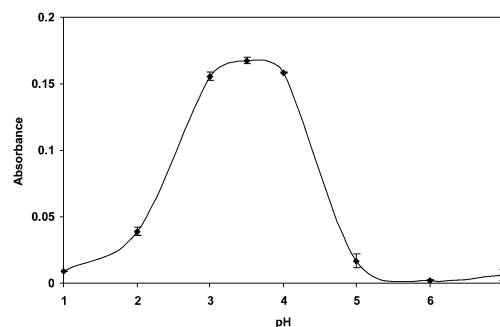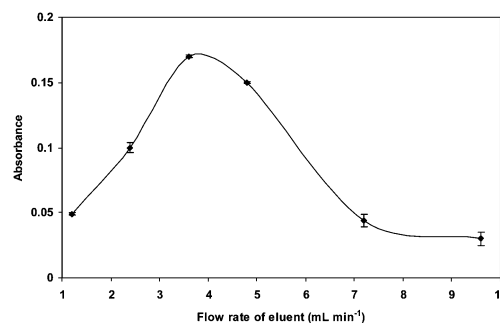
Fig. 1 Effect of pH on the recovery of Pb(II) signals.

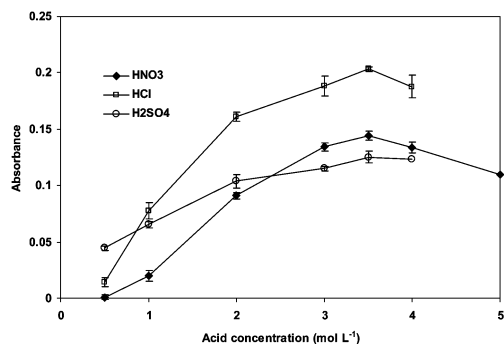**Fig. 2** Effect of flow rate of the eluent on Pb(II) signals.

Fig. 3 Effect of acid concentration on Pb(II) signals.

sample flow rate was maximum around 5 mL min^{-1}. For all subsequent experiments, 17.0 mL of the sample volume at the sample flow rate of 5.0 mL min^{-1} for 3.4 min of loading time was chosen as a compromise between sensitivity and the sample consumption.

The eluent flow rate is another important parameter for stripping the analyte off the column. In order to get an analytical signal as high as possible, the eluent flow rates were scanned. The scanning was carried out from 1.2 to 9.6 mL min^{-1} for 90 mg of the resin at pH 3.5. The peak area response is nearly maximum at a flow rate of 3.6 mL min^{-1}. The optimum flow rate was selected to be 3.6 mL min^{-1} for subsequent studies in order to match the elution and the nebulization flow rates. The low response obtained at the lower flow rates was consistent

Table 1 Effect of foreign ions on the determination of 0.05 mg L^{-1} Pb(II) using the on-line preconcentration system ($n = 3$)

Ions	Added as	Concentration (mg L^{-1})	Recovery (%)
Na$^+$	NaNO$_3$	750	97 ± 1^a
K$^+$	KNO$_3$	500	100 ± 1
Ca^{2+}	Ca(NO$_3$)$_2$·4H$_2$O	100	96 ± 1
Mg^{2+}	Mg(NO$_3$)$_2$·6H$_2$O	100	98 ± 1
Zn^{2+}	Zn(NO$_3$)$_2$	10	98 ± 1
Fe^{3+}	Fe(NO$_3$)$_3$·6H$_2$O	10	98 ± 1
Cu^{2+}	Cu(NO$_3$)$_2$·4H$_2$O	10	100 ± 1
Mn^{2+}	Mn(NO$_3$)$_2$	10	95 ± 1
Ni^{2+}	Ni(NO$_3$)$_2$·6H$_2$O	10	95 ± 1
Cl$^-$	NaCl	1000	99 ± 1
SO$_4$$^{2-}$	Na$_2$SO$_4$	1000	98 ± 1
H$_2$PO$_4$$^-$	NaH$_2$PO$_4$·2H$_2$O	1000	100 ± 2

^{a} Average of three measurements $\pm$ standard deviation.

Table 2 The determination of lead in various environmental samples after the application of the presented procedure ($n = 3$)

Sample (mg L^{-1})	Added	Found	Recovery (%)
Deep water 1	—	0.27 ± 0.04^a	—
	0.5	0.76 ± 0.01	99 ± 2
Dereköy Ayraklı Place	—	0.40 ± 0.03	—
	0.5	0.91 ± 0.04	101 ± 1
Dereköy 1682	—	0.11 ± 0.02	—
	0.5	0.60 ± 0.06	98 ± 1
Waste water (H$_2$SO$_4$)	—	2.00 ± 0.03	—
	0.5	2.51 ± 0.04	100 ± 1
Waste water (Boric acid)	—	—^{b}	—
	0.5	0.48 ± 0.06	96 ± 1
Alacadağlar Çoban Fountain	—	—	—
	0.5	0.52 ± 0.03	104 ± 2
Akdağ Pit	—	—	—
	0.5	0.49 ± 0.01	98 ± 2
Sorgun Pit	—	—	—
	0.5	0.52 ± 0.04	104 ± 2
Gelingüllü Dam water	—	—	—
	0.5	0.48 ± 0.02	96 ± 1
Dereköy 1679	—	—	—
	0.5	0.49 ± 0.02	98 ± 1
Deep water 3	—	—	—
	0.5	0.51 ± 0.04	102 ± 2

Sample (µg g^{-1})	Added	Found	Recovery (%)
Vine leaf	—	—	—
	0.5	0.49 ± 0.01	98 ± 2
Vine branch	—	—	—
	0.5	0.48 ± 0.01	96 ± 1
Rose leaf	—	—	—
	0.5	0.50 ± 0.01	100 ± 1
Rose branch	—	—	—
	0.5	0.49 ± 0.01	98 ± 2
Tree leaf	—	10.10 ± 0.10	—
	5	14.80 ± 0.02	98 ± 2
Tree branch	—	—	—
	0.5	0.49 ± 0.01	98 ± 2
Grass	—	8.00 ± 0.10	—
	5	12.98 ± 0.10	100 ± 1

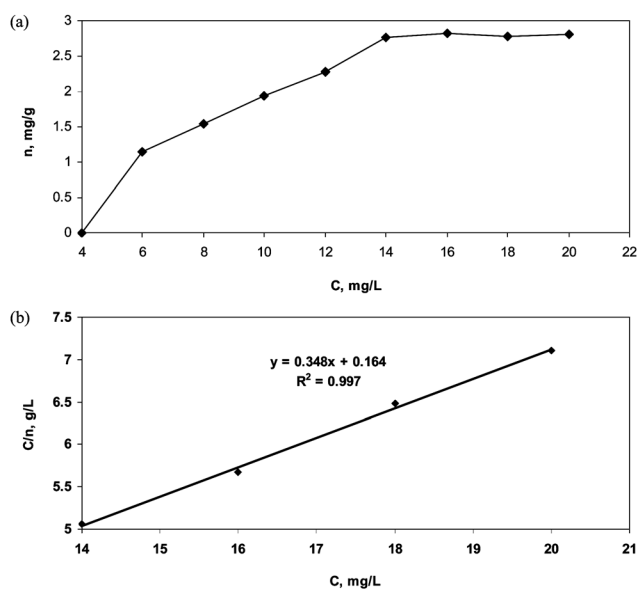^{a} Average of three measurements $\pm$ standard deviation. ^{b} Below detection limit.

Fig. 4 (a) Breakthrough curve by plotting Pb(II) concentrations (mg L^{-1}) vs. the milligrams of Pb(II) adsorbed per gram of the resin and (b) the regression plot obtained by the least squares method for the adsorption capacity ($nm = 2.87$ mg g^{-1}) and the binding equilibrium constant (K) obtained from the slope and the intercept of the straight line.

Table 3 The determination of lead in the standard reference materials by using the presented on-line preconcentration procedure ($n = 3$)

Sample	Certified value	Found	Recovery (%)
SPS-WW2 Batch 108 (waste water, mg L^{-1})	0.500 ± 0.003	0.502 ± 0.005^a	100 ± 1
TMDA-64 (lake water, mg L^{-1})	0.297 ± 0.028	0.294 ± 0.006	99 ± 1
SRM 1547 (peach leaves, µg g^{-1})	0.87 ± 0.03	0.864 ± 0.010	99 ± 4

^{a} Average of three measurements $\pm$ standard deviation.

with nebulizer starvation, whereby the carrier stream flow rate was less than the natural uptake rate of the nebulizer (≤ 2.4 mL min^{-1}), whereas the decrease in response at the high flow rates (≥ 3.6 mL min^{-1}) is due to an insufficient contact time between the solid phase and the eluent (see Fig. 2).

3.3 Effects of eluent type

The desorption of the retained lead ions from the minicolumn was tested using HCl, HNO$_3$, and H$_2$SO$_4$ solutions (0.5–5 mol L^{-1}). The results obtained are shown in Fig. 3, from which it is clear that 3 mol L^{-1} HCl solution is the best eluent. The increase of HCl concentration from 3 to 4 mol L^{-1} did not give any improvement in the lead signals. Therefore, 3 mol L^{-1} HCl was chosen as eluent for stripping off Pb(II) from the column in subsequent experiments.

3.4 Effect of foreign ions

The effect of interferences on the determination of lead was investigated using the optimized on-line preconcentration system. Metal ions were added individually to model solutions containing 0.05 mg L^{-1} Pb(II) and then the proposed procedure was applied. The effect of each species was considered as interference when the analytical signal in the presence of the species resulted in an absorbance deviation of more than $\pm 5\%$. The results are shown in Table 1. The results indicate that various substances commonly present in water samples do not

interfere in the analysis of lead(II) under the experimental conditions.

3.5 Analytical figures of merit

The characteristic data for the performance of the FI on-line preconcentration system under the optimum conditions were studied. The flow injection system shows a linear response within the concentration range from 0.01 to 0.1 mg L^{-1} for a sample loading time of 3.4 min and a sample flow rate of 5 mL min^{-1}. The calibration curve under the optimum flow conditions was obtained by using the least squares method, i.e., $A = 0.0008 + 0.05531 \times C_{Pb}$, where A is the absorbance and C_{Pb} is the Pb(II) concentration of the standard solutions. The enrichment factor was achieved to be 50. The detection limit as the concentration that gives a response equivalent to three times the standard deviation of the blank solutions ($n = 21$) was 1.25 µg L^{-1}. The precision for ($n = 15$) replicate measurements was 1.1% (as relative standard deviation, RSD) at a 0.05 mg L^{-1} Pb(II) level. The adsorption capacity of the resin for Pb(II) was found to be 2.87 mg g^{-1} and the binding equilibrium constant was calculated to be 2.12 L mg^{-1} (see Fig. 4).[20]

3.6 Accuracy and applications of the method

In order to investigate the accuracy of the proposed procedure, the first work made was the recovery study. For this reason, the known amounts of the analyte ion were added to various tap water samples and then the proposed method has been applied. The results are shown in Table 2. A good agreement was obtained between the added and the measured amounts of the metal. The recovery values calculated were always higher than 95%, thus confirming the accuracy of the proposed procedure and its independence from the matrix effects. These results confirm the accuracy of the proposed on-line separation/preconcentration method.

To verify the accuracy of the on-line solid phase extraction procedure, the second work made was to analyze the certified reference materials, TMDA-64 lake water, SPS-WW2 Batch 108 waste water and SRM 1547 peach leaves. The results are given in Table 3. The obtained values of the analyte from the analyses of the certified reference materials were in good agreement with their certified values.

Table 4 Comparative data from some recent studies on separation/preconcentration of lead ions

Method	System	DL (µg L^{-1})	RSD (%)	PF^b	pH	SC^c (mL)	F^d (h^{-1})	Reference
SPE	FI-USN-ICP-OES^a	40	3	225	9.0	—	50	2
SPE	FI-ICP-AES	15.3	0.9	41	9.2	24	—	17
Direct	FI-Vis	8	0.35	2.5	1 M HNO$_3$	0.45	14	18
CPE	FI-FAAS	4.5 (for Pb)	1.6	15.1	8.4	2.4	12	21
SPE	FI-FAAS	2.6	7.7–1.4	44.2	4.7	—	36.5	22
SPE	FI-FAAS	0.9 (for Pb)	2.6	180	0.03 M HNO$_3$	12	24	23
SPE	FI-FAAS	0.8	2.6	330	2	13	15	24
SPE	FI-FAAS	2.48	<2.76	56.5	4	—	—	25
SPE	FI-FAAS	1.3	1.1	124	3.5	17	13	This work

^{a} (FI-USN-ICP-OES): flow injection-ultrasonic nebulization associated with inductively coupled plasma optical emission spectrometry. ^{b} Preconcentration factor. ^{c} SC: sample consumption. ^{d} F: sampling frequency.

The method was also used for on-line separation and pre-concentration of trace lead in the various tap water and environmental samples. The results are shown in Table 2.

4   Conclusions

The DMC resin was successfully applied to the on-line pre-concentration and determination of lead by FAAS. To achieve good sensitivity and precision, the chemical and flow conditions were optimized for the FI on-line preconcentration system for FAAS determination of lead. A comparison of the proposed procedure with other on-line preconcentration systems which use various adsorbents for the determination of lead can be seen in Table 4. All these results are lower than the permissible maximum level stipulated by the World Health Organization. Analytical features such as enrichment factor, detection limits, and precision are comparable to the methods presented in the literature.[21–25] The developed method shows a considerable chemical selectivity and allows very high sensitivity enhancements even from small sample volumes and all processes are made automatically by the system itself. On-line procedures have also the advantage of working in closed systems, thereby reducing contamination of the samples due to the laboratory environment. Also, the obtained detection limits and pre-concentration factors are among the best known values in the literature for lead with respect to the very small sample volume. The resin is commercially available, stable, efficient, and free from matrix effects.

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