Schiff base immobilized silica gel framework as an efficient sorbent for preconcentration of Pb and Zn ions in aqueous media

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Abstract: A novel preconcentration method for Pb and Zn ions using a column packed with Schiff base modified silica gel is described. The method was based on the sorption of analytes on N,N'-bis(4-methoxysalicylidene)-1,3-propanediamine modified silica gel and elution with HNO_3 prior to flame atomic absorption analysis. The parameters pH, flow rate, sample volume, eluent volume, and concentration were optimized using a central composite design. The detection limits were 10.0 μg L^{-1} for Pb and 1.1 μg L^{-1} for Zn. The suggested procedure was validated with Lake Ontario water as a certified reference material and recovery percentages were 101.8% for Pb and 98.2% for Zn. The application of the method was performed on snow, tap, bottled, mineral, and lake water samples and recovery percentages were in the range of 96.7%–101.6% and 96.4%–98.4% for Pb(II) and Zn(II), respectively.

Key words: Solid phase extraction, N,N'-bis(4-methoxysalicylidene)-1,3-propanediamine, modified silica gel, lead, zinc, FAAS

1. Introduction

Trace levels of some elements have important roles in many living bodies. Thus, small amounts of these elements are essential. This necessity is acceptable for small quantities of elements. However, in large amounts, they become toxic and lead to metabolic disorders. Because of the vital importance of these elements, monitoring of trace element levels has gained notable attention and various detection instruments including spectroscopic, electroanalytical, and hyphenated techniques have been employed for this purpose.[1−5]

Flame atomic absorption spectrometry (FAAS)[2,6] is frequently employed as an analytical technique due to its simplicity and low cost. Additionally, it is fast, accurate, and precise. On the other hand, insufficient sensitivity or matrix interferences limit the applications of FAAS. These difficulties have been eliminated by various separation and preconcentration techniques. Solvent extraction,[7] precipitation/coprecipitation,[6,8] cloud point extraction,[9] solid phase extraction (SPE),[10,11] and electroanalytical techniques[12] have been widely used to preconcentrate extremely low concentrations of analytes and to overcome complex matrix problems prior to analysis.

SPE has been widely used as a sample preparation technique among the mentioned applications. Several advantages of SPE over the other techniques such as higher enrichment factor, enable to online/offline automated analysis, stability, and reusability of the solid phase make it a powerful tool in laboratories. It

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has been reported that commercially available or lab-made solid phase materials including activated carbon,[13] silica gel,[3] carbon nanotubes,[14] alumina,[15] magnetic nanoparticles,[16] polyurethane foam,[17] octadecyl silica membrane,[18] amberlite XAD,[10] sea sponge,[19] and natural adsorbents[20] were successfully employed in the separation/preconcentration of metal ions or organic analytes at trace levels. Chelating agent modified silica gel has been popular and attractive around the world in preconcentration studies when compared to other organic and inorganic solid supports due to its cheapness, stability, and easy modification.[3,21]

In this paper, we introduce a simple, low-cost, sensitive, effective, and optimized preconcentration method for routine FAAS analysis of trace amounts of Pb and Zn ions in aqueous samples. Silica gel was used as a solid support and modified using a Schiff base N,N'-bis(4-methoxysalicylidene)-1,3-propanediamine (MSPA) (Figure 1). The new synthesized and characterized sorbent (Si-MSPA) was employed in separate preconcentration of Pb and Zn. The effects of various analytical parameters such as pH, sample volume, concentration and volume of eluent, and flow rate of eluent and sample solution were investigated with preliminary tests. Considering these results, each parameter was optimized with a central composite design (CCD). Additionally, the effects of some interfering ions were investigated. The suggested method was applied to various water samples and the concentrations of Pb(II) and Zn(II) were determined by FAAS.
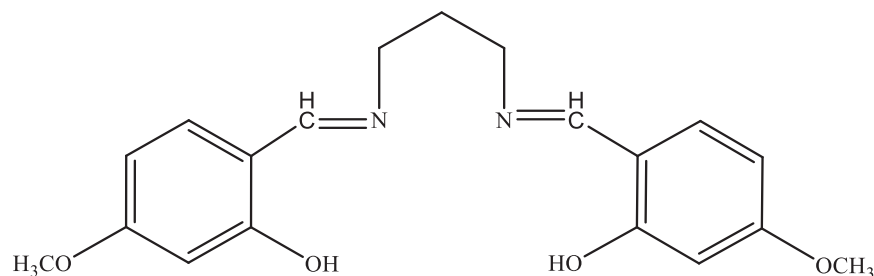

Figure 1. Scheme of N,N'-bis(4-methoxysalicylidene)-1,3-propanediamine.

2. Results and discussion

2.1. Characterization of Si-MSPA

FT-IR and XRD analysis were utilized for confirmation of Si-MSPA. The FT-IR spectrum of silica gel and Si-MSPA given in Figure 2 corresponds to modification. The broad feature between 3100 and 3600 cm^{-1} shows O–H stretch and proves attachment of Schiff base to the silica gel. Moreover, specific –C=N– stretch of Schiff bases was observed at 1636 cm^{-1} on modified silica gel. XRD patterns of bare and modified silica gel are given in Figure 3 and an amorphous diffraction peak was observed at 24° as expected. It was previously reported that the intensity of the Schiff base modified silica gel decreases.[22] As seen in Figure 3, the pattern is consistent with the literature. Briefly, FT-IR and XRD analysis have proven the modification of silica gel with MSPA Schiff base successfully. In the modification period, the absorbance change versus time (Figure 4) showed that 2 h of mechanical shaking of silica gel and Schiff base solution is adequate for modification.

2.2. Preliminary tests for effective enrichment parameters

2.2.1. Influence of pH

The pH of the solution is one of the most important parameters in the sorption of trace metals. Considering the decomposition of Schiff bases in strong acid media, precipitation of metal ions as hydroxides, and dissolution of solid support in an alkaline environment, the pH studies were carried out between 3.00 and 7.00. The pH of

a 5.0-mL portion of standard solutions including 10.0 μg of Pb and 2.5 μg of Zn was adjusted to the required pH using diluted HNO_3 or NaOH individually for each element. According to the batch equilibrium technique, 0.5 g of Si-MSPA was treated with analyte solutions for 1 h; then metal amounts in the supernatant were determined using FAAS. Figure 5 represents the relation between extraction yield and sample pH. It can be seen that sorption percentages of Pb(II) and Zn(II) increased with increasing pH values. At low pH values, metal ions were in competition with hydrogen ions to bind on Si-MSPA and extraction yields of the metal ions were decreased. Accordingly, pH 5.00 and 7.00 were selected as center values for the optimization procedure for Pb and Zn ions, respectively.
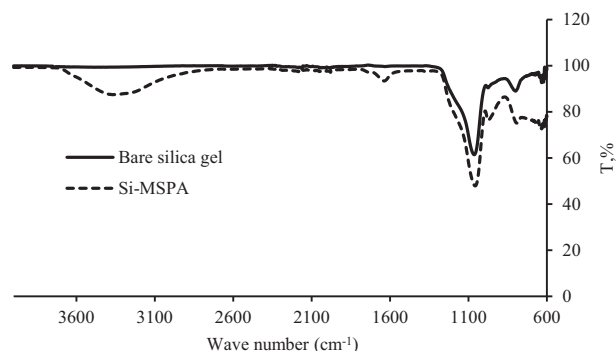

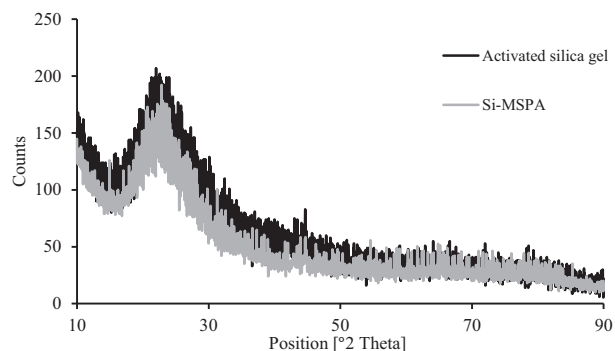**Figure 2.** FT-IR spectra of bare and modified silica gel.

Figure 3. XRD patterns of bare and modified silica gel.
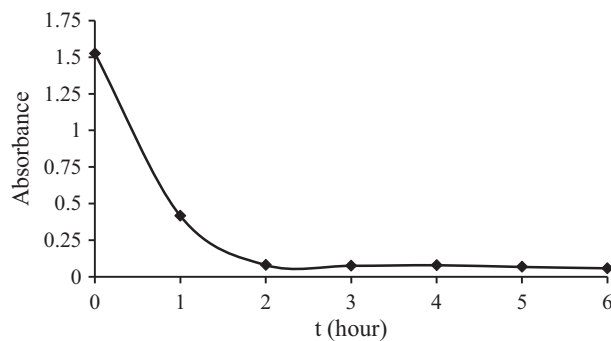
Figure 4. Time-dependent change in MSPA absorbance ($\lambda = 328$ nm).
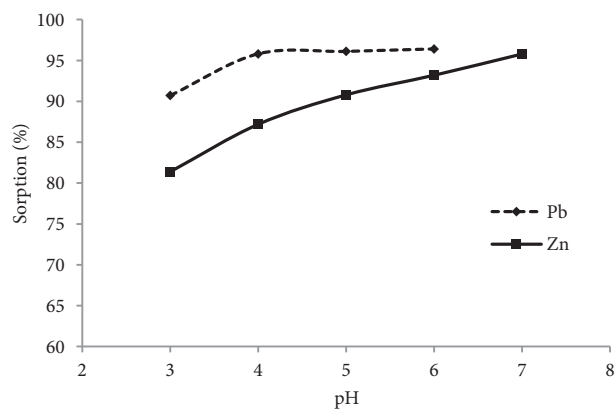
Figure 5. Effect of pH on sorption of Pb and Zn.

2.3. Effect of eluting agents

It is known that elution of metal ions from sorbent surfaces may be achieved with acid solutions, organic solvents, or a mixture of them.[23,24] In this study, the preliminary tests for the elution of retained Pb(II) and Zn(II) were tested with 5 mL of 0.5 mol L^{-1} of HNO_3, H_2O_2, H_2SO_4, HCl, and CH_3COOH. The results are summarized in Table 1 and HNO_3 was the most effective eluent. In the optimization step, center values were considered as 5 mL and 0.5 M for volume and concentration of HNO_3, respectively.

Table 1. Selection of desorption reagent (N = 3).

| Desorption reagent*	Elution, %	
	Pb	Zn
HNO$_3$	100.0 ± 1.3	96.2 ± 0.1
H$_2$O$_2$	5.2 ± 0.8	2.8 ± 0.1
H$_2$SO$_4$	16.4 ± 2.5	80.8 ± 0.1
HCl	79.8 ± 0.1	87.3 ± 0.1
CH$_3$COOH	83.1 ± 4.9	15.20 ± 0.03

*0.5 M aqueous solution

2.3.1. Effect of flow rate

Flow rate is an effective parameter in sorption and desorption of analytes on chelating resins. Accordingly, 50 mL of solution including 10 μg of Pb or 2.5 μg of Zn individually was passed from the column in the range of 4–20 mL min^{-1} for sorption. Similarly, 5 mL of eluent was passed through the column in the range of 3–10 mL min^{-1} for elution studies. According to Figure 6a, recoveries were quantitative up to 6 mL min^{-1} for Pb and 10 mL min^{-1} for Zn in the sorption test. Additionally, eluting recoveries were satisfactory (>95%) below 6 and 5 mL min^{-1} for Zn and Pb, respectively (Figure 6b). The recovery values decreased with increasing flow rate due to insufficient contact time between sorbent and analyte ion. It is clearly seen that quantitative enrichment was highly dependent on flow rate. In order to avoid a possible abrupt change in enrichment, 5 mL min^{-1} flow rate was chosen for the sorption and elution of each element as the center value for further optimization studies.
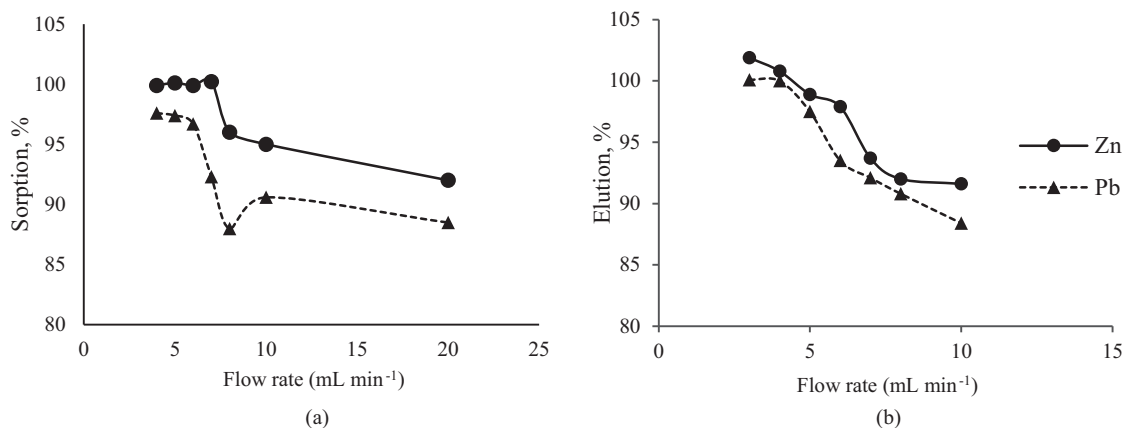
Figure 6. The influences of flow rate on sorption (a) and elution (b) of Pb and Zn.

2.3.2. Effect of sample volume

A high enrichment factor could be obtained with the application of large sample volume without loss of analyte(s). Nature of the sorbent, analyte concentration, and amount of solid phase could affect the applicable maximum sample volume. A fixed amount of Zn (2.5 μg) or Pb (10 μg) was passed through the Si-MSPA column in different volumes (25–1000 mL) to investigate the sample volume effect. Recovery percentages were satisfactory up to 1000 mL for Pb and 250 mL for Zn and the recovery percentage results were 96.9%–103.1% and 90.5%–104.1%, respectively. Regarding the sample and eluent volumes, preconcentration factors were calculated as 200 for Pb and 50 for Zn. Considering the time in the whole procedure, the center value of sample volume was selected as 50 mL.

2.4. Optimization of the enrichment parameters

The proposed procedure is based on enrichment of Pb(II) and Zn(II) on a Si-MSPA column and pH, sample flow rate (F_S), sample volume (V_S), eluent flow rate (F_E), eluent volume (V_E), and eluent concentration (C_E) parameters were optimized using CCD. The selected parameters, which were established according to preliminary tests, were investigated at five levels and are summarized in Table 2. The experimental CCD matrix of 20 runs and the response values obtained from sorption/elution recoveries of Pb(II) and Zn(II) are given in Table 3. The obtained data were evaluated according to the CCD procedure and quadratic equations illustrate the relationship between the investigated variables for sorption (Eq. (1)) and elution (Eq. (2)) of Pb.

Table 2. Factors and levels for CCD optimization.

	Factors	Symbol		Levels				
				$-\alpha$	$-$	0	$+$	$+\alpha$
Sorption	pH	pH	Zn(II)	5.32	6.00	7.00	8.00	8.68
			Pb(II)	3.32	4.00	5.00	6.00	6.68
	Flow rate (mL min^{-1})	F_S		3.3	4.0	5.0	6.0	6.7
	Sample volume (mL)	V_S		8.0	25.0	50.0	75.0	92.0
Elution	Flow rate (mL min^{-1})	F_E		3.3	4.0	5.0	6.0	6.7
	Eluent volume (mL)	C_E		3.3	4.0	5.0	6.0	6.7
	Eluent concentration (M)	V_E		0.08	0.25	0.50	0.75	0.92

F_S: sorption flow rate (mL min^{-1}), V_S: sample volume (mL)
F_E: elution flow rate (mL min^{-1}), V_E: eluent volume (mL), C_E: eluent concentration (M)

Table 3. Experimental CCD matrix and response values.

Run	The levels of factors			Zn(II)		Pb(II)	
	pH^1	F_S^1	V_S^1				
	F_E^2	V_E^2	C_E^2	$y_{sorption}$	$y_{elution}$	$y_{sorption}$	$y_{elution}$
1	$-$	$-$	$-$	0.1646	0.0215	0.0814	0.1271
2	$+$	$-$	$-$	0.0197	0.0249	0.0225	0.0250
3	$-$	$+$	$-$	0.0846	0.0689	0.0900	0.1765
4	$+$	$+$	$-$	0.0194	0.5242	0.0205	0.0209
5	$-$	$-$	$+$	0.1269	0.0341	0.0524	15.0000
6	$+$	$-$	$+$	0.0192	0.0371	0.0346	0.0364
7	$-$	$+$	$+$	0.1965	5.5560	0.0531	0.0735
8	$+$	$+$	$+$	0.1171	0.0636	0.0290	0.0302
9	0	0	0	6.0900	0.0136	1.3909	0.7895
10	$-\alpha^*$	0	0	0.2538	0.0134	0.0164	0.0166
11	$+\alpha^*$	0	0	0.0247	0.0137	0.0154	0.0156
12	0	$-\alpha^*$	0	3.0450	0.0204	0.5667	5.0000
13	0	$+\alpha^*$	0	0.8700	0.0590	0.0994	0.1210
14	0	0	$-\alpha^*$	0.0591	0.1403	0.2250	0.1531
15	0	0	$+\alpha^*$	0.1965	0.1362	2.1857	0.1485
16	0	0	0	0.3806	0.4209	2.5500	0.6250
17	0	0	0	0.4350	0.0965	3.8250	0.4412
18	0	0	0	0.2900	0.2724	1.0200	0.3333
19	0	0	0	0.6767	0.2105	0.5100	10.0000
20	0	0	0	1.0150	2.3150	0.4371	3.0000

$^*\alpha = 1.685$

$$
\begin{aligned}
y \;=\; & 2.495315 - 1.11773\,(pH) - 1.69085\,(F_S) + 1.082344\,(V_S) - 0.65179(pH)^2 + 0.24757(F_S)^2 \\
& -0.60418(V_S)^2 + 1.858346(pH)(F_S) - 1.84366(pH)(V_S) - 1.87224(F_S)(V_S)
\end{aligned} \tag{1}
$$

$$
\begin{aligned}
y \;=\; & 1.156794 + 0.0671\,(F_E) + 0.00479\,(V_E) + 0.047539\,(C_E) - 0.26635(F_E)^2 - 0.4619(V_E)^2 \\
& -0.25538(C_E)^2 + 0.005717(F_E)(V_E) + 0.000341(F_E)(C_E) - 0.00687(V_E)(C_E)
\end{aligned} \tag{2}
$$

Similarly, results obtained from the preconcentration experiments for Zn were evaluated and fitted as the following second order equations for sorption (Eq. (3)) and elution (Eq. (4)), respectively.

$$
\begin{aligned}
y \;=\; & 1.500618 - 0.05729\,(pH) - 0.26147\,(F_S) + 0.029458\,(V_S) - 0.60162(pH)^2 + 0.041085(F_S)^2 \\
& -0.60566(V_S)^2 + 0.013505(pH)(F_S) + 0.002883(pH)x_3 + 0.030977(F_S)(V_S)
\end{aligned} \tag{3}
$$

$$
\begin{aligned}
y \;=\; & 0.530444 - 0.36829\,(F_E) - 0.451011\,(V_E) + 0.369328\,(C_E) - 0.0316(F_E)^2 - 0.02238(V_E)^2 \\
& -0.012467(C_E)^2 - 0.63046(F_E)(V_E) - 0.74351(F_E)(C_E) + 0.625206(V_E)(C_E)
\end{aligned} \tag{4}
$$

In these y equations, linear terms $(pH, F_S, V_S, F_E, V_E, C_E)$ show first order effects, while quadratic terms $(pH^2, F_S^2, V_S^2, F_E^2, V_E^2, C_E^2)$ show second order effects. Additionally, $(pH)(F_S)$, $(pH)(V_S)$, $(F_S)(V_S)$, $(F_E)(V_E)$, $(F_E)(C_E)$, and $(V_E)(C_E)$ indicate interactions between factors. The derivatives of these equations in terms of each variable were equalized to zero and the optimum values of the factors were obtained. The real values of optimum preconcentration conditions are given in Table 4 and used in further experiments.

Table 4. Optimum values of sorption and elution parameters.

| Element | Parameters | | | | | |
| | Sorption | | | Elution | | |
	pH	F_S	V_S	F_E	V_E	C_E
Pb	5.40	5.5	39.9	5.1	5.0	0.5
Zn	7.00	5.3	50.8	5.3	4.8	0.4

F_S: sorption flow rate (mL min^{-1}), V_S: sample volume (mL)
F_E: elution flow rate (mL min^{-1}), V_E: eluent volume (mL), C_E: eluent concentration (M)

2.5. Concomitants effects
Experiments were carried out in optimized conditions in order to assess the possible interfering effects of some anions and cations on preconcentration of Pb(II) and Zn(II). The interfering ions Fe^{+3}, Cu^{+2}, Cr^{+3}, Cd^{+2}, Mn^{+2}, Co^{+2}, Ni^{+2}, Ca^{+2}, Mg^{+2}, K^+, Cl^-, SO_4^2, NO_3^-, and Na^+ were added as nitrate or potassium salts to 10 μg of Pb or 2.5 μg of Zn individually. The tolerance limits were defined as the largest amount of the concomitant ion causing $< \pm 5\%$ in preconcentration of analytes. The tolerable amounts of the concomitant ions are summarized in Table 5. These suggest that the new solid phase resin has good selectivity and the proposed method is free from interferences.

2.6. Reproducibility and reusability
Reproducibility of the suggested procedure was tested with ten repeated analyses. Accordingly, model solutions including 10.0 μg of Pb and 2.5 μg of Zn metal ions were analyzed under optimum conditions. Mean recoveries

were 99.0 $\pm$ 2.6% for Pb and 98.4 $\pm$ 2.7% for Zn with 2.6% and 2.8% relative standard deviation (RSD), respectively. Additionally, bias was calculated as –1.4% for Pb and –1.6% for Zn.

Table 5. Effect of concomitant ions on preconcentration of Pb and Zn.

Concomitant ion	Concomitant ion/analyte (w/w)	
	Zn	Pb
K^+, Cl^-	200	1000
SO_4^{2-}, Na^+	1000	1000
NO_3^-	2000	1000
Ca^{2+}, Mg^{2+}	1000	750
Fe^{3+}	200	100
Cd^{2+}	200	500
Mn^{2+}, Co^{2+}, Ni^{2+}	500	500
Pb^{2+}	1000	250
Cu^{2+}, Cr^{3+}	200	250

Regarding usage of HNO_3 in elution and degradation of Schiff bases in acidic media, modified Si-MSPA was only used in one cycle of the sorption–elution process. On the other hand, silica gel may be reused several times and be easily modified with MSPA.

2.7. Analytical figures of merit

External calibration was employed in the determination of analytes. The calibration curves were linear at 0.5–20.0 mg L^{-1} for Pb and 0.01–5.0 mg L^{-1} for Zn with 0.999 regression coefficients. The method was validated with certified reference material and the results were satisfactory. According to experiments (N = 3), recoveries were 101.8% for Pb and 98.2% for Zn. Additionally, experimental t values were calculated as 0.35 and 0.60 for Pb(II) and Zn(II), respectively. Considering the critical t value (4.30), the experimental results were not significantly different from certified values at 95% confidence level. The detection (LOD) and quantification (LOQ) limits were determined by the analysis of blank solutions (N = 10) in optimized conditions. The LODs ($3s_b/m$) were found to be 10.0 μg L^{-1} for Pb and 1.1 μg L^{-1} for Zn. Moreover, LOQ ($10s_b/m$) values were 33.4 and 3.6 μg L^{-1} for Pb(II) and Zn(II), respectively. Considering maximum applicable sample volume, preconcentration factors were calculated as 200 and 50 for Pb(II) and Zn(II), respectively.

2.8. Analysis of natural samples

The suggested procedure has been applied for the determination of Pb(II) and Zn(II) in natural water samples. The results indicate the applicability of the enrichment technique for the determination of Pb(II) and Zn(II) in natural samples. Therefore, snow, tap, bottled, mineral, and lake water samples were analyzed within this scope. Moreover, addition–recovery tests were performed on Pb(II) and Zn(II) spiked real samples. As seen in Table 6, the obtained results were satisfactory and the recovery values were 96.7%–101.6% for Pb and 96.4%–98.4% for Zn. The results showed that the proposed method is suitable for the preconcentration of Pb(II) and Zn(II) from natural water samples.

Table 6. Natural sample analysis (N = 3).

Water samples	Pb			Zn		
	Added (μg L^{-1})	Found (μg L^{-1})	Recovery (%)	Added (μg L^{-1})	Found (μg L^{-1})	Recovery (%)
Snow	-	28.8 ± 2.8	-	-	28.0 ± 1.4	-
	125.3	152.6 ± 8.8	98.8	98.4	124.0 ± 4.5	97.6
Bottled	-	< LOD	-	-	10.0 ± 0.6	-
	125.3	127.3 ± 6.3	101.6	98.4	104.9 ± 1.6	96.4
Tap	-	< LOD	-	-	147.0 ± 1.0	-
	125.3	123.3 ± 4.0	98.4	98.4	243.3 ± 2.2	97.9
Selimiye Lake	-	< LOD	-	-	15.9±1.8	-
	125.3	125.6 ± 5.5	100.2	98.4	112.4 ± 0.8	98.1
Mineral	-	< LOD	-	-	13.2 ± 1.4	-
	125.3	121.0 ± 5.8	96.7	98.4	110.0 ± 0.8	98.4

LOD values: 10.0 μg L^{-1} for Pb and 1.1 μg L^{-1} for Zn
Optimum sample volume: 39.9 mL for Pb and 50.8 mL for Zn

2.9. Comparison with reported enrichment studies

The proposed methodology was compared with various preconcentration techniques that were suggested for the determination of Pb(II) and Zn(II). Some parameters such as preconcentration factor, LOD, and detection technique were found to be comparable and are summarized in Table 7. Considering coprecipitation,[25] ion exchange,[26] dispersive liquid–liquid microextraction,[27] cloud point extraction,[28] solid phase extraction,[29,30] and liquid–liquid extraction[31] enrichment techniques for Pb and/or Zn, the maximum preconcentration factor has been found as 100. Additionally, the obtained LOD values were lower than those.[29,31] On the other hand, detection limits of some reported[28,30,31] enrichment procedures were better, but in these methodologies high cost instruments such as ICP-MS, ICP-OES, and GFAAS were employed for detection. Consequently, application of this method for preconcentration of Pb(II) and Zn(II) is simple, sensitive, and low cost for routine laboratory analysis.

In conclusion, the present study suggests an effective and selective optimized enrichment procedure for Pb(II) and Zn(II) prior to FAAS detection. Easy preparation of the sorbent, sorption of the elements with high preconcentration factor, fast desorption, and low cost detection of each element with good accuracy and precision offer a desirable alternative enrichment procedure. Additionally, the comparable method is feasible for the trace analysis of Pb(II) and Zn(II) in aqueous samples with satisfactory results. Further work should be carried out to promote an on-line preconcentration and detection procedure.

3. Materials and methods

3.1. Instrumentation

Characterization of the synthesized Si-MSPA was achieved using a Philips X Pert-Pro X-ray diffractometer (XRD) (Cu K$\alpha\lambda$ = 1.54060 Å, 30 mA, 40 kV), and a PerkinElmer Spectrum 65 Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectrometer. A PG Instrument T80+ UV-Vis spectrometer with 1 cm matched quartz cells was utilized to monitor the time needed for modification. Determination of Pb(II) and Zn(II) was performed with a PerkinElmer AAnalyst200 FAAS. The operating parameters for the elements were set as recommended by the manufacturer and are given in Table 8. A Thermo Orion 5 Star model pH

Table 7. Comparison of the preconcentration techniques for Pb and Zn.

Preconcentration technique	Analyte	Sample	Detection technique	LOD† (μg/L, ^{a} μg/mL)	PF*	Ref.
Coprecipitation	Pb	Water	FAAS	0.022^a	20	25
Solid phase	Zn, Pb	Water	FAAS	nd	100	26
Liquid–liquid extraction	Pb	Water	FAAS	0.54	265	27
Cloud point extraction	Zn, Pb	Water	ICP-OES	Zn 0.05 Pb 0.34	Zn 18.85 Pb 10.54	28
Solid phase extraction	Pb	Plant	ICP-OES	70.8	100	29
Solid phase extraction	Zn, Pb	Water, plant	ICP-MS	Zn 0.007 Pb 0.021	33.3	30
Liquid–liquid extraction	Pb	Food	GFAAS	0.05	50	31
Solid phase extraction	Zn, Pb	Water	FAAS	Zn 1.1 Pb 10.0	Zn 50 Pb 200	This work

† LOD: limit of detection; * PF: preconcentration factor; nd: not defined

meter with a combined glass electrode was used for pH measurements. Additionally, a GFL 3005 orbital shaker, Sartorius TE214S electronic balance, and Heidolph MR 3001 K model magnetic stirrer were employed in the experiments. Flow control of the aqueous solutions through the Si-MSPA column was achieved with a Velp Scientifica SP311 peristaltic pump.

Table 8. Experimental conditions for FAAS.

Instrumental parameters	Element	
	Zn	Pb
Wavelength (nm)	213.86	261.42
Bandwidth (mm)	2.7/1.8	1.8/0.6
Lamp current (mA)	15	12
Oxidant gas flow rate (L min^{-1})	10	10
Fuel gas flow rate (L min^{-1})	2.5	2.5

3.2. Chemicals

All reagents were of analytical grade and used without any further purification. The solid support silica gel (70–230 mesh) was purchased from Merck. Stock solutions of lead and zinc were prepared from their high purity nitrate salts (Merck) as 1000 mg L^{-1} and daily dilutions were carried out to prepare working solutions. The required pH adjustments of the metal solutions were achieved by dropwise addition of diluted HNO_3 and NaOH. MSPA was synthesized by a usual condensation of 4-methoxysalicylidene and 1,3-propanediamine in 2:1 molar ratio in ethanol.[32] The water standard reference material (Lake Ontario water, TMDA-53.3) was obtained from the National Water Research Institute of Canada and used to check the validity of the suggested procedure. All glassware and vessels were cleaned by soaking in 10% HNO_3 and rinsed with purified water. The purification of water was achieved by reverse osmosis.

3.3. Sample preparation

Snow and tap water samples were collected in polyethylene bottles from Balıkesir University, Balıkesir, and analyzed without pretreatment. Bottled and mineral water samples were commercially purchased and transferred to polyethylene bottles. The lake water sample was collected from Selimiye Lake, Balıkesir, filtered, and acidified with 1 mL of concentrated acid per liter of the sample. All water samples were kept at +4 °C until analysis.

3.4. Immobilization of MSPA on silica gel and column preparation

Silica gel was activated with 0.5 M HNO_3 under reflux, filtered off, and washed with purified water until it was acid-free. A 10.0-g portion of activated silica gel was refluxed with 50.0 mg of MSPA in 50 mL of acetone for 2 h. Then the resulting modified silica gel was washed with water to remove unadsorbed reagent, filtered, and dried at room temperature.

The modification period of the Si-MSPA was monitored according to the literature.[22] Accordingly, 1 mL of Schiff base solution was pipetted from the liquid phase and the absorbance was monitored at 328 nm for 6 h with 1-h intervals.

Next 500 mg of Si-MSPA was loaded in a 10 × 100 mm glass column with a glass frit resin support and combined with a peristaltic pump. The height of resin bed was approximately 1.0 cm in the column.

3.5. Optimization of the experimental conditions

The sorption and elution conditions for preconcentration of Pb(II) and Zn(II) were optimized using the standard CCD procedure.[33] The variables pH, flow rate, and sample volume were considered as factors in the sorption step. Additionally, flow rate, volume, and concentration of eluent were the factors for the elution step. The center values of the selected factors were decided according to preliminary tests. Preconcentration studies were performed separately for each analyte. Certain volumes of standard solutions including 10 and 2.5 μg of Pb(II) and Zn(II), respectively, were loaded on a Si-MSPA column. After this, HNO_3 solution was used for the elution; then the concentrations of analytes were measured by FAAS. In order to optimize the conditions, 20 runs were carried out according to Table 3 for sorption and elution separately. Determination of the element contents in solutions was achieved by FAAS and the experimental data were evaluated using Microsoft Excel.

3.6. Application of the optimized procedure

In analysis of aqueous samples, preconcentration of Pb(II) and Zn(II) was achieved separately under optimized conditions obtained using CCD. Accordingly, 50.8 mL of sample solution at pH 7.00 was passed through the Si-MSPA column at 5.3 mL min^{-1} in preconcentration of Zn from aqueous samples. The retained zinc ions were eluted with 4.8 mL of 0.4 M HNO_3 at 5.3 mL min^{-1}. Similarly, the lead ions were enriched in the following conditions: sorption was achieved with 39.9 mL of sample solution at pH 5.40 with 5.5 mL min^{-1} flow rate and elution was carried out with 5.0 mL of 0.5 M HNO_3 at 5.1 mL min^{-1} flow rate. The eluent solutions were aspirated into an air–acetylene flame and the concentrations of Pb(II) and Zn(II) were determined by AAS.

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