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Solid-phase extraction of Mn(II), Co(II), Ni(II), Cu(II), Cd(II) and Pb(II) ions from environmental samples by flame atomic absorption spectrometry (FAAS)

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Abstract

A new method using a column packed with Amberlite XAD-2010 resin as a solid-phase extractant has been developed for the multi-element preconcentration of Mn(II), Co(II), Ni(II), Cu(II), Cd(II), and Pb(II) ions based on their complex formation with the sodium diethyldithiocarbamate (Na-DDTC) prior to flame atomic absorption spectrometric (FAAS) determinations. Metal complexes sorbed on the resin were eluted by $1 \, mol \, L^{-1}$ HNO_3 in acetone. Effects of the analytical conditions over the preconcentration yields of the metal ions, such as pH, quantity of Na-DDTC, eluent type, sample volume and flow rate, foreign ions etc. have been investigated. The limits of detection (LOD) of the analytes were found in the range $0.08–0.26 \, \mu g \, L^{-1}$. The method was validated by analyzing three certified reference materials. The method has been applied for the determination of trace elements in some environmental samples.
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1. Introduction

Determination of trace metal ions is very important in the context of environmental protection, food and agricultural chemistry and high purity materials, and also for monitoring environmental pollution. Several sensitive methods have been developed for the determination of metal ions. Flame atomic absorption spectrometry (FAAS) has been widely used for the determination of trace metal ions because of the relatively simple and inexpensive equipment required. However, direct determination of metal ions at trace levels by FAAS is limited due to their low concentrations and matrix interferences. Preconcentration and separation methods have been routinely used to eliminate matrix effects and cope with low metal levels [1].

Currently, the widely used techniques for preconcentration and separation of trace metals include liquid–liquid extraction [2,3], ion-exchange [4,5], coprecipitation [6–8], solid-phase extraction [9–14], flotation [15], electrochemical deposition [16,17], and cloud point extraction [18]. Among these methods, solid-phase extraction (SPE) is a cost-effective and recognized alternative to liquid–liquid extraction for sample preparation that overcomes many drawbacks of the traditional extraction by using two immiscible liquids. SPE procedures are used not only to extract traces of organic compounds from samples, but also to remove the interfering components of the complex matrices [19]. SPE is also superior for preconcentration of trace metals in respect to minimum solvent waste generation and sorption of the target species on the solid surface in a more stable chemical form [20–22]. Various solid phases including chelex 100 [23], silica gel [24,25], Amberlite XAD resins [26–31], polyurethane foam [32], and activated carbon [33] have been used for the solid-phase extraction of traces heavy metals in environmental samples prior to their instrumental analysis.

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In the presented work, a multi elemental solid-phase extraction procedure for heavy metal ions in environmental samples has been established. The analytical parameters including pH, amounts of reagents and eluent type were investigated.

2. Experimental

2.1. Instrumentation

A flame atomic absorption spectrometer (Unicam model AA-929) equipped with a 10 cm air-acetylene burner head and a single element hallow-cathode lamp was used for all measurements. Selected spectral lines (nm) of all metals were as follows: Mn 279.5, Co 240.7, Ni 232.0, Cu 324.8, Cd 228.8, and Pb 217.0.

A digital pH-meter (Hanna Instruments model pH 211) with glass electrode was used for all pH measurements. Milestone Ethos D microwave oven with closed vessels and 1450 psi max pressure was used for digestion of solid materials.

2.2. Reagents and solutions

All chemicals were reagent-grade. All solutions were prepared in distilled-deionised water. Multi-element standard (various concentrations) and model solutions were prepared by dilution of single element stock solutions ($1000 \,\mu g \, mL^{-1}$) of Mn(II), Co(II), Ni(II), Cu(II), Cd(II) and Pb(II) ions purchased from Fluka. Amberlite XAD-2010 (specific surface area $660 \, m^2 \, g^{-1}$ and bead size 20–60 mesh) and sodium diethyldithiocarbamate (Na-DDTC) were purchased from Sigma Chem. Co., St. Louis. CRM-TMDW-500 and CRM-SA-C Sandy Soil reference materials were purhased from High-Purity Standards, Inc, and SRM 1568a Rice Flour from NIST, National Institute of Standards & Technology. All glass- and plastic-ware were rigorously cleaned and kept in $1 \, mol \, L^{-1}$ nitric acid for at least 24 h. The material was then rinsed three times with distilled-deionised water.

Buffer solutions were prepared from $1 \, mol \, L^{-1}$ sodium sulfate and $1 \, mol \, L^{-1}$ sodium hydrogen sulfate for pH 2, from $1 \, mol \, L^{-1}$ sodium acetate and $1 \, mol \, L^{-1}$ acetic acid for pH 3–6, from $0.1 \, mol \, L^{-1}$ potassium dihydrogen phosphate and $0.1 \, mol \, L^{-1}$ disodium hydrogen phosphate for pH 7, from $0.1 \, mol \, L^{-1}$ ammonium chloride and ammonia for pH 8–10, and from $0.1 \, mol \, L^{-1}$ sodium dihydrogen phosphate and $0.1 \, mol \, L^{-1}$ sodium hydroxide for pH 11–12.

2.3. Sampling

Stream and spring waters from Of Village-Trabzon and mineral water from Kisarna-Trabzon were collected in July, 2006. Polyethylene bottles were used for storage of the samples. The bottles were successively precleaned with detergent, distilled-deionized water, $1 \, mol \, L^{-1}$ of HNO_3, and distilled-deionized water. High-purity HNO_3 was added to keep the final acidity of the water at about pH 2 after sampling. The water samples were filtered through a Millipore nitrocellulose membrane (pore size 0.45 mm) immediately after sampling and stored at 4°C.

Rock samples were collected from Kumbet Plateau, Giresun-Turkey, and crushed, ground, and left to dry in an oven for 3 h at 105°C. Hazelnut and black tea samples were taken from Of-Trabzon and hazelnut was dried in an oven for 20 h at 80°C. The samples were ground into fine powder in an agate mortar.

2.4. Column preparation

A glass mini-column (10 cm × 1.0 cm i.d.), having a porous disk and a stopcock, was used for preconcentration procedures. Two-hundred-and-fifty milligrams of Amberlite XAD-2010 resin were loaded into the column after washing successively with $1 \, mol \, L^{-1}$ NaOH, water, $1 \, mol \, L^{-1}$ HNO_3, water, acetone and water. A small amount of glass wool was placed on the disk to prevent loss of the resin beads during flow. After each use, the resin in the column was washed thoroughly with water and related buffer solution, and then stored in water for the next application.

2.5. Model workings

The preconcentration procedure was tested with the model solutions containing known amounts of the metal ions before application to real samples, and percentage recoveries were calculated. For this, a 100 mL of multi-element solution containing $12.5 \,\mu g$ of Mn(II), Co(II), Ni(II) and Cu(II), $2.5 \,\mu g$ of Cd(II), and $25 \,\mu g$ of Pb(II) ions was prepared. Five milliliters of related buffer solution (in the range of 2–12) and 5.0 mg of the ligand (5.0 mL of 0.1%, w/v), the complexing agent, Na-DDTC, were added to the solution. After 10 min, the solution was passed through the Amberlite XAD-2010 column, at a flow rate of $10 \, mL \, min^{-1}$. Then, the metal chelates were stripped from the column with 10 mL of $1 \, mol \, L^{-1}$ HNO_3 in acetone. The acetone in the eluent solution was evaporated in a vacuum desiccator. The residue was quantitatively completed to 10 mL with $1 \, mol \, L^{-1}$ HNO_3, and the solution was analyzed by FAAS.

2.6. Analysis of the real samples

The solid samples were digested in a closed microwave digestion system prior to preconcentration step. The following were weighed into the Teflon vessels: 0.250 g of CRM-SA-C Sandy Soil and 0.500 g of NIST SRM 1568a Rice Flour standard reference materials, and 1.000 g of hazelnut, black tea and rock samples. Eight milliliters HNO_3, 1.0 mL H_2O_2, and 0.5 mL HF for black tea sample, 4.5 mL HCl, 1.5 mL HNO_3, 2.0 mL HF for rock sample and CRM-SA-C Sandy Soil, and 7.0 mL HNO_3, 1.0 mL H_2O_2 for NIST SRM 1568a Rice Flour and hazelnut samples were added into the vessels. Then, content of the vessels were digested by microwave irradiation at 45 bar pressure. After digestion, the suspension from rock and soil samples were filtered through a blue-ribbon filter paper and completed to 50 mL with distilled-deionized water. The clear solutions obtained from the other samples were completed to 50 mL with distilled-deionized water. After preconcentration step, final volumes were made to 5.0 mL, and the solutions were analyzed by FAAS.
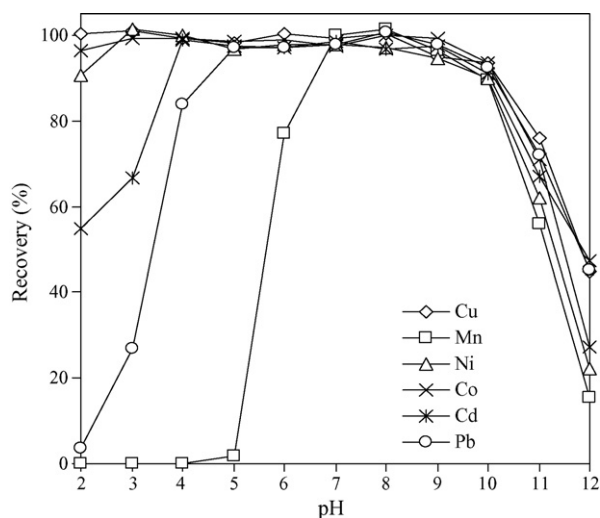
Fig. 1. Effect of pH on the retention of the metal ions (eluent: 10 mL of 1 mol L^{-1} HNO$_3$ in acetone, complexing agent: 5 mL of 0.1% Na-DDTC, resin quantity: 250 mg, sample volume: 100 mL, sample flow rate: 10 mL min^{-1}, $n = 4$).

The preconcentration procedure was also applied to CRM TMDW-500 Drinking Water standard reference material (100 mL), spring and mineral waters (500 mL). The final volumes were made to 5.0 mL, and the solutions were analyzed by FAAS.

3. Results and discussion

3.1. Effect of pH on the recoveries of the metal ions

Among the chemical variables, sample acidity, specified by pH of the sample solution, is the most critical parameter for effective formation and retention of the metal-DDTC complexes onto the sorbent. The effect of the pH was studied in the range 2–12 by adjusting the metal solutions with buffer solutions. Copper and cobalt were quantitatively recovered (≥95%) in the pH range 2–9. Quantitative recoveries were obtained in the pH range 3–9 for nickel, 4–9 for cadmium, 5–9 for lead, and 7–9 for manganese (Fig. 1). According to the results, the optimum pH was six for multi-element preconcentration of the metals in question, except for manganese for which the value is eight.
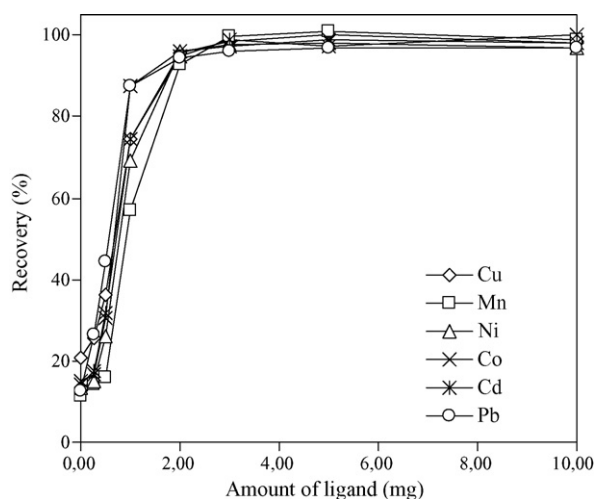

Fig. 2. Effect of ligand quantity on the recoveries.

Hence the following optimization work was carried out at these pHs.

3.2. Effect of ligand concentration

Effects of the quantity of Na-DDTC as a chelating agent were also studied. In order to determine this, quantities of Na-DDTC on the retention were examined from 0.0 to 10.0 mg. Fig. 2 indicates that preconcentration yields of the six metal ions are 11–21% without chelating agent. The preconcentration yields increased with the addition of Na-DDTC. The quantitative values were obtained after 2.0 mg of Na-DDTC (Fig. 2). After this point, the recoveries were quantitative in all working range of Na-DDTC. For all further works, 5.0 mg of Na-DDTC (5.0 mL of 0.1%, w/v) was added.

3.3. Selection of the best eluent and optimization of its concentration and volume

For selection of the best eluent, various acidic solutions on the preconcentration yields of the metals were studied under the optimum conditions. Especially the acids with acetone provided higher recovery efficiency compared to the acids in aqueous

Table 1
The eluent solution type and the recovery of the metal ions (sample volume: 100 mL, $n = 3$, concentrations of eluents: 1.0 mol L^{-1})

Type of eluent	Recovery (%)					
	Cu	Mn	Ni	Co	Cd	Pb
HCl in acetone	95 ± 4	100 ± 3	102 ± 4	91 ± 3	93 ± 3	95 ± 5
H$_2$SO$_4$ in acetone	96 ± 3	97 ± 3	101 ± 3	88 ± 3	97 ± 2	88 ± 4
HNO$_3$ in acetone	100 ± 3	101 ± 2	98 ± 2	99 ± 3	97 ± 2	97 ± 4
HCl in water	48 ± 2	93 ± 3	69 ± 2	38 ± 2	60 ± 2	86 ± 3
HNO$_3$ in water	49 ± 2	98 ± 3	63 ± 2	41 ± 2	56 ± 2	83 ± 4
H$_2$SO$_4$ in water	53 ± 2	92 ± 4	71 ± 3	54 ± 2	54 ± 2	78 ± 3
HCl in methanol	62 ± 2	98 ± 3	91 ± 3	92 ± 4	64 ± 3	96 ± 4
HNO$_3$ in methanol	60 ± 1	101 ± 4	99 ± 2	94 ± 3	68 ± 2	97 ± 4
H$_2$SO$_4$ in methanol	66 ± 2	98 ± 3	95 ± 3	92 ± 3	75 ± 2	80 ± 3
Acetone	91 ± 3	< 10	96 ± 3	91 ± 3	66 ± 3	91 ± 3
Methanol	59 ± 2	< 10	75 ± 2	<10	31 ± 1	27 ± 1

Table 2
Concentration of the eluent and the recovery of the metal ions (sample volume: 100 mL, $n = 3$)

Concentration of the eluent (M)	Recovery (%)					
	Cu	Mn	Ni	Co	Cd	Pb
0.10	95 ± 3	101 ± 3	95 ± 2	94 ± 3	91 ± 3	90 ± 4
0.25	99 ± 2	98 ± 2	100 ± 2	95 ± 3	94 ± 3	94 ± 3
0.50	100 ± 2	100 ± 2	99 ± 3	97 ± 2	96 ± 2	97 ± 3
1.00	100 ± 3	101 ± 2	98 ± 2	99 ± 3	97 ± 2	97 ± 4
2.00	96 ± 2	98 ± 3	94 ± 3	95 ± 3	96 ± 2	95 ± 4
4.00	85 ± 3	91 ± 3	89 ± 3	83 ± 2	90 ± 2	85 ± 4

and alcoholic solutions (Table 1). Quantitative recoveries for all metals were obtained with HNO_3 in acetone and therefore it was selected as an eluent for further applications.

After the findings above, the experiments were carried out for selecting the concentration of nitric acid solution in acetone. HNO_3 solutions in acetone at the concentrations between 0.10 and 4.00 mol L^{-1} were studied for this purpose. The recovery values were increased with adding nitric acid to acetone. After 0.25 mol L^{-1} HNO_3, the analytes were quantitatively recovered. The optimum nitric acid concentration was determined as 1 mol L^{-1} HNO_3 in acetone (Table 2).

The influence of the volume of 1 mol L^{-1} HNO_3 in acetone between 2.5 and 15 mL was also examined (Table 3). The optimum eluent volume is specified as 10 mL for the subsequent studies.

3.4. Effect of sample and eluent flow rates

The flow rate of the sample solution through the Amberlite XAD-2000 column is a very important parameter. While the recovery increases with the decreasing flow rate, the preconcentration time increases. To obtain the quantitative recovery and to decrease the preconcentration time, the sample flow rate was investigated in the range 2–40 mL min^{-1} by using a waterjet aspirator. The results show that the recoveries were decreased after 25 mL min^{-1} flow rate (Fig. 3). A sample flow rate of 10.0 mL min^{-1} was selected. This rate is high enough to load the sample in a moderate short time and allowing metal/Na-DDTC chelates to interact with XAD–2010.

The flow rates of eluent solution were investigated in the range 1–20 mL min^{-1}. After 12 mL min^{-1} of eluent solution,

Table 3
The eluent volume and the recovery of the metal ions (sample volume: 100 mL, concentrations of eluents: 1.0 mol L^{-1}, $n = 3$)

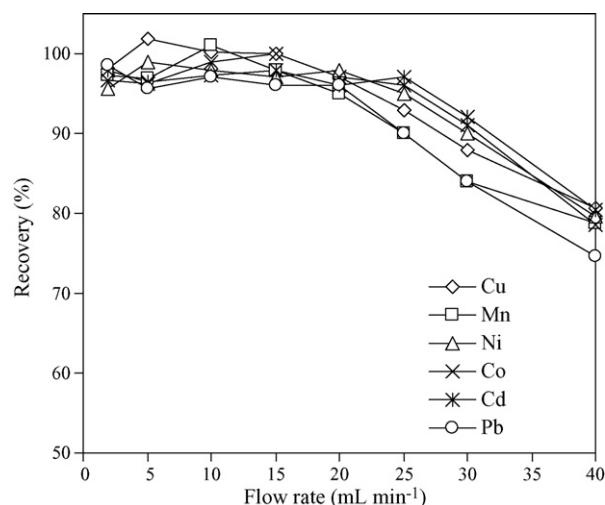| Eluent volume (mL)	Recovery (%)					
	Cu	Mn	Ni	Co	Cd	Pb
2.5	83 ± 2	92 ± 3	88 ± 2	66 ± 2	85 ± 2	87 ± 4
5.0	94 ± 3	99 ± 2	98 ± 1	94 ± 3	95 ± 2	94 ± 4
7.5	97 ± 2	100 ± 2	101 ± 2	96 ± 3	97 ± 3	98 ± 3
10.0	100 ± 3	101 ± 2	98 ± 2	99 ± 3	97 ± 2	97 ± 4
12.5	99 ± 2	98 ± 3	100 ± 1	98 ± 2	98 ± 3	96 ± 3
15.0	98 ± 3	98 ± 2	98 ± 1	99 ± 2	100 ± 3	97 ± 4

Fig. 3. Effect of flow rate on the recoveries.

the recovery values of the analytes were not quantitative. For the all experiments, 7 mL min^{-1} was selected as eluent flow rate.

3.5. Effect of sample volume

In order to deal with real samples, especially water samples, containing very low concentrations of the metal ions, the maximum applicable sample volume must be determined. The recoveries of the metal ions from different volumes of aqueous solutions containing the same amounts of the metal ions are shown in Fig. 4. The recoveries were found to be stable until 500 mL and, hence, 500 mL was chosen as the largest sample volume to work. In this study, the final solution volume to be measured by FAAS was 5.0 mL, therefore the preconcentration factors were 100 for six metal ions.

3.6. Effect of diverse ions

To assess the usefulness of the proposed method, the effect of diverse ions on the trace level determination of the metal ions has
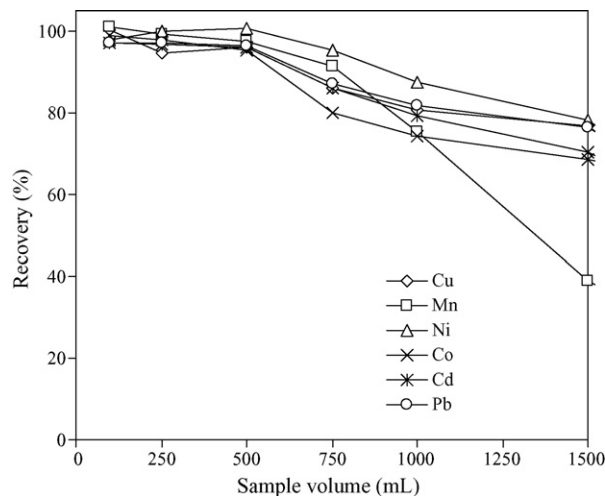

Fig. 4. Effect of sample volume.

Table 4
The matrix ions and the recovery of the metal ions (sample volume: 100 mL, $n = 3$)

Ions	Quantity	Added as	Recovery (%)					
			Cu	Mn	Ni	Co	Cd	Pb
Na^+	100 mg	NaCl	98 ± 3	96 ± 2	98 ± 2	97 ± 3	96 ± 3	96 ± 4
	1000 mg		101 ± 4	102 ± 4	101 ± 3	95 ± 2	98 ± 3	101 ± 5
K^+	100 mg	KCl	97 ± 2	98 ± 3	100 ± 3	97 ± 3	97 ± 3	97 ± 4
Ca^{2+}	100 mg	$CaCl_2$	100 ± 4	101 ± 4	99 ± 2	100 ± 3	98 ± 4	97 ± 4
Mg^{2+}	100 mg	$MgCl_2$	97 ± 3	98 ± 3	97 ± 3	96 ± 2	96 ± 4	95 ± 4
Fe^{3+}	25 μg	$Fe(NO_3)_3$	98 ± 3	100 ± 3	99 ± 3	96 ± 3	97 ± 3	96 ± 4
Zn^{2+}	25 μg	$Zn(NO_3)_2$	99 ± 2	97 ± 3	96 ± 4	97 ± 4	98 ± 2	97 ± 4
Cr^{3+}	25 μg	$Cr(NO_3)_3$	100 ± 2	99 ± 2	98 ± 3	100 ± 3	101 ± 3	95 ± 4
Hg^{2+}	25 μg	$Hg(NO_3)_2$	101 ± 3	101 ± 4	97 ± 3	99 ± 3	97 ± 2	96 ± 3
As^{3+}	25 μg	As_2O_3	99 ± 2	100 ± 3	100 ± 2	97 ± 2	96 ± 3	97 ± 4
Sb^{3+}	25 μg	Sb_2O_3	100 ± 2	98 ± 3	99 ± 2	96 ± 3	95 ± 4	96 ± 3
V^{5+}	25 μg	V_2O_5	101 ± 3	101 ± 4	100 ± 3	97 ± 3	96 ± 4	98 ± 4
Mo^{6+}	25 μg	$(NH_4)_6Mo_7O_{24}\cdot4H_2O$	99 ± 3	98 ± 4	101 ± 4	100 ± 3	100 ± 3	99 ± 3
Mixed[a]			97 ± 3	101 ± 4	98 ± 3	97 ± 2	98 ± 3	97 ± 4
Mixed[b]			102 ± 4	102 ± 5	101 ± 3	96 ± 3	96 ± 3	99 ± 4

[a] A sample containing 100 mg of Ca^{2+}, Mg^{2+}, Na^+ and K^+, 25 μg of Fe^{3+}, Zn^{2+}, Cr^{3+}, Hg^{2+}, As^{3+}, Sb^{3+}, V^{5+} and Mo^{6+}.
[b] A sample containing 1000 mg of Na^+, 100 mg of K^+, Ca^{2+} and Mg^{2+}, 10 mg of SO_4^{2-}, 1500 mg of Cl^-, and 1000 mg of NO_3^-.

been investigated. A 100 mL of multi-element model solution containing 12.5 μg of Mn(II), Co(II), Ni(II) and Cu(II), 2.5 μg of Cd(II), 25 μg of Pb(II), and individual and/or mixed foreign ions at various concentrations was prepared. Then, the procedure was applied under the optimal conditions and the recoveries of studied metal ions were calculated. As can be seen in Table 4, the trace metals were not affected by the medium containing either individual or mixed ions.

3.7. Adsorption capacity of the resin

The relationships between adsorbent and adsorbate described by adsorption isotherms, usually the ratio between quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium, can be described by adsorption isotherms [34].

Langmuir isotherms were used for the determination of resin capacity defined as the amount of metal adsorbed by 1.0 g of resin. Na-DDTC complexes of the metals, of which total amounts varied in the range 100–2000 μg, were loaded onto the column filled with 100 mg resin, and the recoveries were investigated.

Langmuir adsorption isotherm is one of the most well-known and applied adsorption isotherms and described by the equation below:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{a_L q_{max}} \tag{1}$$

A plot of C_e versus C_e/q_e shows linearity; hence Langmuir constants q_{max} and a_L can be calculated from the gradient and intercept of the plot, respectively. The amount of maximum metal (q_{max}) adsorbed by 1.0 g resin was calculated in mg g^{-1} from Langmuir isotherms (Fig. 5). The results are given in Table 5.
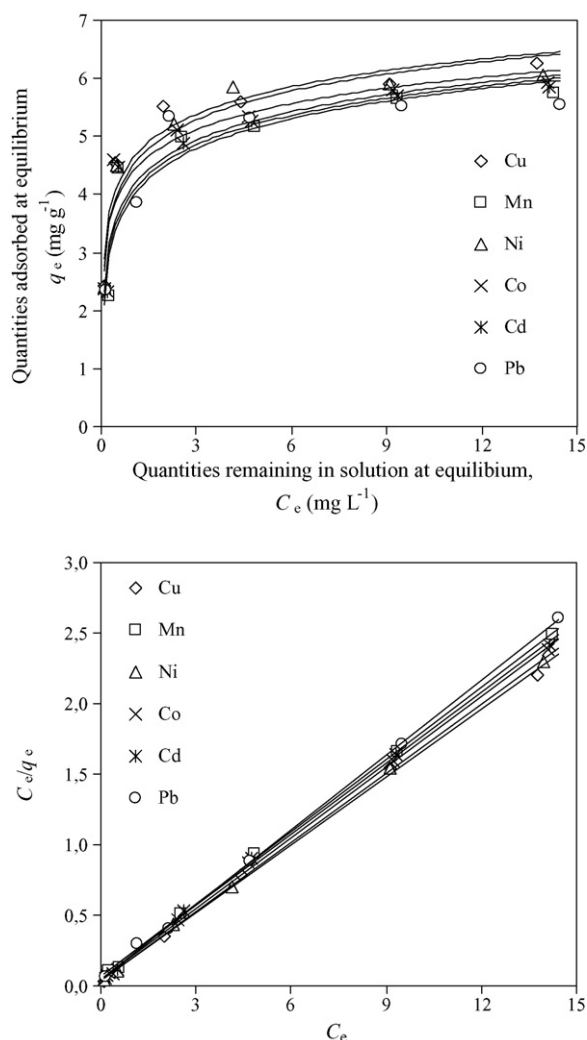

Fig. 5. Langmuir isotherms for determination of the resin capacities.

Table 5
Langmuir constants and equations from Fig. 5 for the resin capacity

	Cu	Mn	Co	Ni	Cd	Pb
Equation, $y = mx + n$	$y = 0.1599x + 0.0435$	$y = 0.1704x + 0.0668$	$y = 0.1668x + 0.0498$	$y = 0.1633x + 0.0389$	$y = 0.1676x + 0.0668$	$y = 0.1762x + 0.0528$
R^2	0.9983	0.9991	0.9991	0.9996	0.9989	0.9994
Q_{max}, $1/m$ (mg g^{-1})	6.3	5.9	6.0	6.1	6.0	5.7
a_L, $1/(Q_{max} \times n)$ (L mol^{-1})	$\sim2.3 \times 10^5$	$\sim1.4 \times 10^5$	$\sim2.0 \times 10^5$	$\sim2.5 \times 10^5$	$\sim2.8 \times 10^5$	$\sim6.9 \times 10^5$

Table 6
The accuracy test results for spiked recovery (sample volume: 100 mL, $n = 3$)

	Added (µg)	Solakli stream		Kisarna mineral water		Spring water	
		Found (µg)	R (%)	Found (µg)	R (%)	Found (µg)	R (%)
Cu	0	0.64 ± 0.03	–	0.51 ± 0.04	–	ND	–
	10	10.1 ± 0.04	99	10.6 ± 0.3	101	10.1 ± 0.2	101
	25	24.8 ± 0.6	99	24.7 ± 0.5	97	24.3 ± 0.5	97
Mn	0	12.2 ± 0.4	–	26.3 ± 1.0	–	0.23 ± 0.03	–
	10	21.1 ± 0.8	95	34.2 ± 1.2	94	9.9 ± 0.02	97
	25	36.5 ± 1.1	98	48.6 ± 2.2	95	23.7 ± 0.6	94
Ni	0	0.35 ± 0.02	–	ND	–	ND	–
	10	10.0 ± 0.4	97	10.1 ± 0.3	101	9.6 ± 0.3	96
	25	24.1 ± 1.0	95	25.1 ± 0.7	100	23.2 ± 0.5	93
Co	0	ND	–	ND	–	ND	–
	10	9.4 ± 0.4	94	10.0 ± 0.3	100	10.2 ± 0.2	102
	25	24.3 ± 0.8	97	24.5 ± 0.6	98	23.9 ± 0.6	96
Cd	0	ND	–	ND	–	ND	–
	10	10.1 ± 0.4	101	9.8 ± 0.2	98	9.4 ± 0.2	94
	25	25.5 ± 1.0	102	25.0 ± 0.5	100	24.1 ± 0.7	96
Pb	0	0.51 ± 0.05	–	ND	–	ND	–
	10	9.8 ± 0.6	93	10.1 ± 0.3	101	9.6 ± 0.6	96
	25	25.0 ± 1.5	98	23.7 ± 1.1	95	23.5 ± 1.0	94

ND: not detected.

Table 7
Analysis of the certified reference materials for the determination of analytes after application presented procedure

	Mn	Co	Ni	Cu	Cd	Pb
CRM TMDW-500 drinking water						
Certified value (µg L^{-1})	40.0 ± 0.2	25.0 ± 0.1	60.0 ± 0.3	20.0 ± 0.1	10.0 ± 0.05	40.0 ± 0.2
Amount found[a] (µg g^{-1})	39.1 ± 1.1	24.2 ± 0.8	57.0 ± 2.2	19.8 ± 0.4	9.8 ± 0.3	37.2 ± 1.4
Recovery (%)	98	97	95	99	98	93
CRM-SA-C sandysoil						
Certified value (µg g^{-1})	310 ± 1.6	12.60 ± 0.06	44.9 ± 0.2	60.6 ± 0.3	109.0 ± 0.5	133.0 ± 0.6
Amount found[a] (µg g^{-1})	297 ± 15	13.0 ± 0.5	43.2 ± 2.5	58.8 ± 3.2	110.0 ± 5.4	128.0 ± 8.6
Recovery (%)	96	103	96	97	101	96
NIST[b] SRM 1568a rice flour						
Certified value (µg g^{-1})	20.0 ± 1.6	0.018[c]	–[d]	2.4 ± 0.3	0.022 ± 0.002	<0.010[c]
Amount found[a] (µg g^{-1})	18.7 ± 1.1	ND	ND	2.6 ± 0.3	ND	ND
Recovery (%)	94	–	–	108	–	–

ND: not detected.

[a] The confidence interval was calculated at $P = 0.95$ ($n = 3$).
[b] NIST: National Institute of Standards & Technology.
[c] Not certified.
[d] No value reported.

Table 8
Statistical evaluation of the method

Statistical parameters	Mn	Co	Ni	Cu	Cd	Pb
Analytical LOD (μg L^{-1})	0.10	0.18	0.15	0.12	0.08	0.26
Relative standand deviation, RSD (%)	2.1	3.2	2.8	2.1	1.9	5.1
Working range (mg L^{-1})	0.05–5.0	0.08–6.0	0.07–5.0	0.06–5.0	0.03–1.1	0.13–8.0

Table 9
Trace metals contents of real water samples with the proposed method ($n = 3$)

	Cu	Mn	Ni	Co	Cd	Pb
Water samples (μg L^{-1})						
Solakli stream	6.14 ± 0.12	119 ± 3	3.28 ± 0.10	ND	ND	4.38 ± 0.26
Kisarna mineral water	4.93 ± 0.13	256 ± 5	ND	ND	ND	1.93 ± 0.14
Of stream water	1.20 ± 0.05	2.20 ± 0.07	ND	ND	ND	1.90 ± 0.13
Solid samples (μg g^{-1})						
Hazelnut	12.5 ± 0.4	196 ± 9	3.33 ± 0.20	1.10 ± 0.10	ND	8.72 ± 0.50
Black tea	12.8 ± 0.5	40.0 ± 2.0	6.90 ± 0.42	ND	ND	2.80 ± 0.25
Rock[a]	983 ± 42	315 ± 13	4.40 ± 0.30	2.11 ± 0.13	ND	1.18 ± 0.07

ND: not detected.

[a] Trace metal contents of rock sample was determined by ACME Analytical Lab. (ISO 9002 Accredited Co.) in Canada as follows: Mn 309, Co 1.9, Ni 4.1, Cu 1096, Cd 0.02, Pb 1.11 mg kg^{-1} (RSD ≤5%).

3.8. Analytical figure of merits

The standard addition technique was applied to the real water samples for two concentration levels and the recoveries obtained revealed that the proposed method has good accuracy. The results are described in Table 6.

The analytical procedure was also validated by determining the certified reference materials, CRM TMDW-500 drinking

Table 10
Comparative data from some recent studies for preconcentration of trace metals using column SPE methods and detection by FAAS

System	Studied metals	pH	Eluent	Flow rate (mL min^{-1})	PF	Resin capacity (mg g^{-1})	LOD (μg L^{-1})	Reference
Diaion SP-850/Alpha-benzoin oxime	Cr, Mn, Fe, Co, Cu, Cd, Pb	8.0	1 mol L^{-1} HNO$_3$	5.0	50	2.2–6.0	0.28–0.73	[12]
Modified natrolite zeolite/2-(5-bromo-2-pyridylazo)-5-Diethylaminophenol	Cu, Zn	8.5	2 mol L^{-1} HNO$_3$	4.0	160	0.85–1.23	0.006–0.03	[13]
Amberlite XAD-2000/8-hydroxyquinoline	Fe, Cu, Mn, Zn, Co, Ni, Cd, Pb	6.0 (8.0 for Mn)	1 mol L^{-1} HNO$_3$ in acetone	10.0	100	6.83–9.43	0.3–2.2	[27]
Activated carbon/ammonium pyrrolidinedithiocarbamate	Cd, Cu, Ni, Zn	5.0	1 mol L^{-1} HNO$_3$ in acetone	1.0	–	–	19–28	[33]
Amberlite XAD-4/DDTC	Cd, Cu, Fe, Cu, Ni, Bi	6.0	Acetone	5.0	–	–	2.0–23.0	[35]
Polyurethane foam/ammonium pyrrolidinedithiocarbamate	Cu, Pb, Cr(VI)	1.6	Isobutylmethylketone	12.0	28–170	3.0–7.0	0.2–2.0	[36]
Polychlorotrifluoroethylene/ diethyldithiophosphate	Cu, Pb	0.1–2.0	Isobutylmethylketone	11.6	250		0.07–2.7	[37]
Dowex Optipore V-493/dibenzyldithiocarbamate	Cd, Pb	2.0	1 mol L^{-1} HNO$_3$ in acetone	4.0	50	7.3–8.6	0.43–0.65	[38]
Amberlite XAD-4/di-2-pyridyl ketone thiosemicarbazone	Co, Ni, Fe, Cu	6.0	1 mol L^{-1} HNO$_3$ in acetone	0.5	200	2.0	30–50	[39]
Amberlite XAD-2010/DDTC	Cu, Mn, Co, Ni, Cd, Pb	6.0 (8.0 for Mn)	1 mol L^{-1} HNO$_3$ in acetone	10.0	100	5.7–6.3	0.08–0.26	This work

LOD: limit of detection; PF: preconcentration factor; SPE: solid-phase extraction.

water, CRM-SA-C Sandy Soil and NIST SRM 1568a rice flour. The results revealed good agreement between the observed values and certified values (Table 7).

The limit of detection (LOD) was calculated as three times the standard deviation (3σ) of 20 replicate measurements of blank sample with the preconcentration step. The detection limits were calculated by dividing the instrumental detection limit by the preconcentration factor. The precision of the method, evaluated as the R.S.D. obtained after analyzing a series of ten replicates with the preconcentration step, was between 1.9 and 5.1% for the six metals. The working ranges for FAAS determinations were also established. The calculated values for statistical evaluation of the method are given in Table 8.

3.9. Application to real samples

Six sample collection sites were determined and the proposed procedure was applied to each sample under optimal conditions. The results of FAAS determinations obtained for the six metals are given in Table 9.

3.10. Comparison with other methods

A comparison of the proposed system with other preconcentration procedures is given in Table 10. Some parameters obtained were comparable to those presented by other methods described in the literature. As seen from the data in Table 10, the proposed method developed by using Amberlite XAD-2010/DDTC system has relatively high preconcentration factor, flow rate and resin capacity, and low LOD when compared to other methods reported in Table 10.

4. Conclusion

A new method was developed for the determination of trace metals. The procedure offers a useful multi-element preconcentration technique in various samples including streams, rivers, lakes, seawaters, and various environmental solid samples with acceptable accuracy and precision. In conclusion, the metal contents at $\mu g\,L^{-1}$ (ppb) levels were determined easily. The other main advantages of the method include simplicity, time saving, no requirements of sophisticated instruments, and cost-effectiveness. Amberlite XAD-2010 on the column could be used all through the studies without any lost of its adsorption properties. The possibilities of using the extraction system in solid phase XAD-2010/DDTC for the preconcentration and separation of the metallic cations in solutions with relatively high contents of salts are extended.

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