# Simultaneous preconcentration of Co(II), Ni(II), Cu(II), and Cd(II) from environmental samples on Amberlite XAD-2000 column and determination by FAAS

Celal Duran [a,*], Hasan Basri Senturk [a], Latif Elci [b], Mustafa Soylak [c], Mehmet Tufekci [a]

[a] Department of Chemistry, Faculty of Arts & Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey
[b] Department of Chemistry, Faculty of Arts & Sciences, Pamukkale University, 20020 Denizli, Turkey
[c] Department of Chemistry, Faculty of Arts & Sciences, Erciyes University, 38039 Kayseri, Turkey

## ARTICLE INFO

## ABSTRACT

A new method for the preconcentration of some trace metals (Co, Ni, Cu, and Cd) as complexed with ammonium pyrrolidynedithiocarbamate (APDC) was developed using a mini-column filled with Amberlite XAD-2000 resin. Metal contents were determined by flame atomic absorption spectrometry (FAAS) after the metal complexes accumulated on the resin were eluted with 1 M $HNO_3$ in acetone. The effects of the analytical parameters such as sample pH, quantity of complexing agent, eluent type, resin quantity, sample volume, sample flow rate, and matrix ions were investigated on the recovery of the metals from aqueous solutions. The relative standard deviation (R.S.D.) of the method was <6%. The validation of the method was confirmed using two certified reference materials (CRM TMDW-500 Drinking Water and CRM SA-C Sandy Soil C). The method was successfully applied to some stream waters and mushroom samples from Eastern Black Sea Region (Trabzon city) of Turkey.

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## 1. Introduction

Environmental pollution and its most important side water pollution increasing in parallel with technological development are important research subjects in terms of natural balance and the health of all organisms. Therefore, the determination of trace elements in environmental solid/liquid samples is nowadays made more demanding because of the large number of metal ions that have to be monitored for the quality and quantity of various samples. Various techniques have been applied for the determination of trace heavy metals over a large range of concentration in environmental samples [1]. The determination of trace metals by FAAS among the determination techniques has a number of advantages including high selectivity, speed and fairly low operational cost. However, preconcentration is usually required for the determination of trace metals in various samples by FAAS because of complex matrices of samples and low concentrations of some metals, which are near or below the limit of detection of the instrument [2].

The most widely used preconcentration methods are liquid–liquid extraction [3], solid-phase extraction (SPE) [4–8], co-precipitation [9,10], ion-exchange [11], electrochemical deposition [12], and cloud point extraction [13]. SPE technique has become increasingly popular in compared with the classical liquid–liquid extraction method because of its advantages of high preconcentration factor, high recovery, rapid phase separation, simplicity, low cost, low consumption of organic solvents and the ability of combination with different detection techniques in the form of on-line or off-line mode [14,15]. SPE normally involves the optimization of some parameters during the adsorption of the metals in the sorbent and their desorptions with an appropriate eluent [16].

One of batch, membrane filtration and column preconcentration systems is used in SPE. However, preconcentration based on column techniques seem to have undergone the most rapid development, probably due to the simplicity of the operation and the existence of a wealth of knowledge on related batch procedure. The column can be mostly packed either cross-linked polymeric resins with chelating groups or directly the resin adsorbed neutral metal complexes formed before the preconcentration step. The main requirements with respect to substances to be used as solid-phase materials in SPE based on adsorption mechanism are as follows: possibility of extracting a large number of elements over a wide pH range,

* Corresponding author. Tel.: +90 462 3772491; fax: +90 462 3253196.
E-mail address: cduran@ktu.edu.tr (C. Duran).

fast and quantitative adsorption, high capacity, regenerability and accessibility [17].

Various support materials are used in SPE [18–22]. Among the many available materials for SPE, Amberlite XAD resins having most of properties above have been used with success as adsorbent or support for various chelating agents such as 2,6-dihydroxyphenyl-diazoaminoazobenzene [23], 2-(2-benzothiazolylazo)-2-p-cresol [24] calmagite [25], dithiocarbamate [26], and sulfinylcalix[4]arene [27]. However, the metal adsorption properties of Amberlite XAD-2000 resin have been rarely explored [28–31].

Ammonium pyrrolidynedithiocarbamate (APDC) and sodium diethyldithiocarbamate (DDTC) are two of the most common chelating agents for preconcentration and separation of trace metals from aqueous solutions in the FAAS technique [17]. APDC forms much more stable complexes with some metals such as Co, Ni, Cu and Cd in a wide range of pH than DDTC. Because of the strong complexation ability of APDC, these metals can be successfully extracted in the pH range of 2–8 [32]. In addition, APDC-MIBK liquid–liquid extraction system has been validated as a standard preconcentration/separation method [33]. Hence, APDC was selected as a chelating agent in the present study.

Sorbents with higher surface area retained the metal-dithiocarbamate chelates more strongly [17]. Amberlite XAD-2000 has relatively higher surface area ($620\,m^2\,g^{-1}$) than some other XAD resins such as XAD-2 ($330\,m^2\,g^{-1}$), XAD-7 ($450\,m^2\,g^{-1}$), XAD-8 ($160\,m^2\,g^{-1}$) and XAD-1180 ($600\,m^2\,g^{-1}$), and also has good physical properties including porosity, uniform pore size distribution and chemically homogeneous non-ionic structure. In this sense, we thought that Amberlite XAD-2000/APDC column solid-phase extraction system may be effectively used for preconcentration and separation of Co, Ni, Cu and Cd from aqueous solutions.

The aim of this work is to show the analytical potentiality of Amberlite XAD-2000/APDC system for separation/preconcentration of Co, Ni, Cu and Cd from aqueous solutions following FAAS determinations. For this purpose, effects of some analytical conditions such as sample pH, eluent type, quantity of APDC, sample flow rate and matrix interferences were examined.

## 2. Experimental

### 2.1. Instrumentation

A Unicam AA-929 flame atomic absorption spectrometer with hallow cathode lamp and air/acetylene mixture was used for the determination of trace metals. During the use of the instruments, recommendations of the manufacturer were taken into consideration for instrumental parameters. The wavelengths selected for the analyte determinations were 240.7, 232.0, 324.8, and 228.8 nm for Co, Ni, Cu, and Cd, respectively. Hanna 211 digital pH meter with a glass electrode was used for pH adjustments. Milestone Ethos D closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300 °C) was operated for digestion of mushroom samples.

### 2.2. Reagents and solutions

All the chemicals used were of analytical-grade and purchased from Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland). Distilled-deionized water was used in all determinations. Stock solutions of Co(II), Ni(II), Cu(II), and Cd(II) at $1000\,mg\,L^{-1}$ concentration prepared in 0.5 M HNO$_3$ were used. The model and standard solutions of the metals were prepared by diluting the stock solutions in appropriate ratios. 0.05% (w/v) solution of APDC in ethanol was used as the complexing agent. The complexing agent APDC

and the adsorbent resin Amberlite XAD-2000 with particle size of 20–60 mesh, $620\,m^2\,g^{-1}$ surface areas were purchased from Sigma Chem. Co. (St. Louis). Standard reference materials, CRM TMDW-500 Drinking Water and CRM SA-C Sandy Soil C were obtained from High-Purity Standards, Inc.

The pHs of the solutions were adjusted with the buffer solutions. The pH 2 buffer solution was prepared by mixing of appropriate volume of 1 M sodium sulfate and 1 M sodium hydrogen sulfate solutions. Acetate buffers prepared by mixing different amounts of 1 M sodium acetate and 1 M acetic acid were used to maintain the pH between 4 and 6. 0.1 M potassium dihydrogen phosphate and 0.1 M disodium hydrogen phosphate were used for pH 7. Ammonium chloride buffer solutions (0.1 M) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions to result in solutions of pH 8–10. pH 12 was obtained by mixing of appropriate amounts of 0.1 M sodium dihydrogen phosphate and 0.1 M sodium hydroxide solutions.

### 2.3. Preparation of the mini-column

The glass mini-column (13 cm length and 1.0 cm diameter), having a porous disk and a stopcock, used for preconcentration of the metals was manufactured by Ildam, Ankara, Turkey. Amberlite XAD-2000 resin was ground and sieved to 100–200 μm range. The resin was first washed successively with 1 M NaOH, water, 1 M HNO$_3$, water, acetone, and water and kept in a desiccator after drying until filled into the column.

### 2.4. Sampling and pre-treatments

The proposed method was applied to solid/liquid samples, mushroom and stream waters from Eastern Black Sea Region-Turkey. The metal contents of stream waters and mushroom samples collected from various districts of Trabzon city were determined. The water samples were kept in polyethylene bottles. The polyethylene bottles were thoroughly and consecutively washed with detergent, tap water, HNO$_3$, and distilled-deionized water prior to use. The water samples were acidified to pH ~2.0 with HNO$_3$ after collection and filtered through a cellulose nitrate membrane with 0.45 μm pore size. Mushroom sample (*Lactarius scrobiculatus*) (from Macka, Trabzon-Turkey) was dried at 80 °C for 24 h, and then ground in an agat mortar.

The solid samples were digested in closed microwave system prior to application of the preconcentration procedure. 0.250 g of CRM SA-C Sandy Soil C and 0.500 g of mushroom samples were separately weighed into teflon vessels. 1.5 mL of conc. HNO$_3$, 4.5 mL of conc. HCl and 2 mL of conc. HF for Sandy Soil, and 6 mL of conc. HNO$_3$, 2 mL of H$_2$O$_2$ for mushroom sample were added into the vessels. The contents of the vessels were digested by microwave irradiation. Digestion program for microwave system was given in literature [30]. The clear solutions obtained were evaporated to near dryness on a hot plate, and then diluted to 50 mL with distilled-deionized water. A blank digest was carried out in the same way.

### 2.5. Preconcentration procedure

The proposed method was tested first with model solutions prior to the determination of the trace metals in the real samples. The model solutions (50 mL) containing 25 μg of Co(II), Ni(II) and Cu(II), and 5.0 μg of Cd(II) were prepared. The pH of the model solutions was first adjusted to the desired values (in the range 2–12) by the addition of 2–5 mL of respective buffer solution, and 5.0 mL of 0.05% solution of the complexing agent was added. The mini-column was preconditioned with the buffer solution at the working pH. The solution containing metal complexes was passed through

the column with a flow rate of $5\,mL\,min^{-1}$ by using a water jet aspirator. After the metal complexes retained on the resin in the column were washed with 10 mL of distilled-deionized water, they were recovered into a beaker with 10 mL of the eluent solution, 1 M $HNO_3$ in acetone. The beaker content was evaporated to near dryness on a hot plate at 40–50 °C, and the residue was diluted to 5.0 mL with 1 M $HNO_3$. The metals in this solution were determined by FAAS. These procedures were repeated separately for all optimization parameters.

## 3. Results and discussion

### 3.1. Effect of pH on the recovery of the trace metals

The recovery efficiencies of each metal were investigated in the pH range 2–12 by use of relevant buffer solution given above. The recovery of Cd was found quantitative in the pH range of 2–9. The recoveries of Cu, Ni, and Co were quantitative in the pH range of 2–7 (Fig. 1). Judging from these results, the optimized sample pH is established as 6. Therefore, for the later optimization studies, pH 6 was selected as the pH of sample solution for the simultaneous preconcentrations of multi-elements in the solutions.

### 3.2. Effect of quantity of complexing agent

APDC quantity is the most important chemical variables affecting the preconcentration of the examined analytes. Therefore, the effect of APDC quantity on the retention was examined from 0.5 to 25.0 mg.

The results in Fig. 2 shows that the change in the concentration of APDC did not affect recovery much in the range of 1.25–12.5 mg and the recovery was slightly reduced at 25.0 mg of APDC. Accordingly, 2.5 mg of APDC (5.0 mL 0.05%, w/v) was used for further experiments. The considerable increase on the recoveries obtained by changing of APDC concentration from 0.5 to 1.25 mg indicates that the use of APDC is necessary for quantitative recovery. On the other hand, the expected low recoveries for the studies repeated without APDC addition in the pH range of 2–12 were confirmed. The recoveries of the elements with 1 M $HNO_3$ in water and in acetone separately were found in 0–13% range.
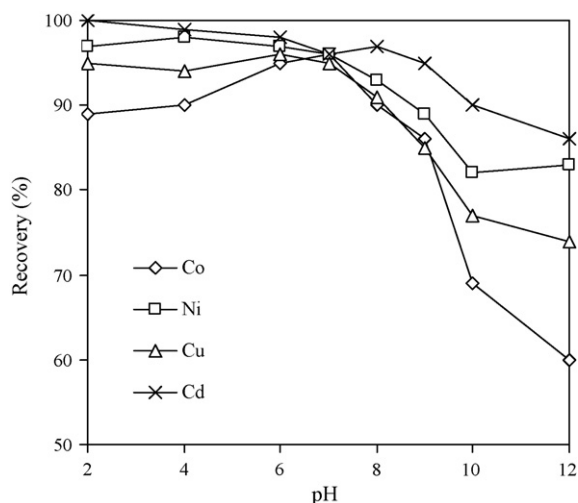


**Fig. 2.** Effect of complexing agent quantity (pH 6, $N = 4$).

### 3.3. Effect of eluent type, concentration and volume

The following considerations should be taken into account to select an appropriate eluent for effective desorption of metal complexes from the resin: (i) the eluent should desorb the metals complexes; (ii) the eluent should not destroy the sorbent; and (iii) the eluent should be suitable for the subsequent determination technique [34].

Various acids and organic solvents were tested to choose the best solution for the elution of the metal–APDC complexes accumulated on Amberlite XAD-2000 resin, and the percentage recovery for each eluent type was determined. Among the solvents studied, especially the acids with acetone provided higher recovery efficiency compared to the acids in aqueous and alcoholic solutions, and the highest recoveries were obtained with either $HNO_3$ or HCl in acetone. Finally, the acetone–$HNO_3$ mixture is specified as the eluent of choice for all the later determinations and for the optimizations of the other parameters (Table 1).

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 of 0.10, 0.25, 0.50, 1.00, 1.50, 2.00, and 4.00 M were studied for this purpose. The recovery values were increased with adding nitric acid to acetone. After 1 M $HNO_3$, the recovery values were almost quantitative for all the concentrations. Therefore, the optimum nitric acid concentration was



**Fig. 1.** Effect of pH on the recovery of the trace metals (resin quantity: 300 mg, resin particle size: 100–200 μm, eluent: 10 mL of 1 M $HNO_3$ in acetone, complexing agent: 5 mL of 0.05% APDC, sample volume: 50 mL, $N = 4$).
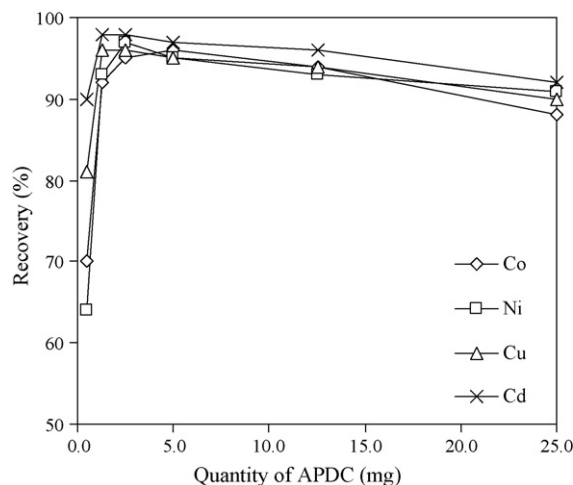
**Table 1**
Effect of eluent type on the recovery of the trace metals ($N = 4$)

| Eluent solution | Recovery (%) | | | |
|---|---|---|---|---|
| | Co | Ni | Cu | Cd |
| HCl (1 M) in water | <10 | <10 | <5 | $39 \pm 2$ |
| $HNO_3$ (1 M) in water | <10 | <10 | <10 | $28 \pm 2$ |
| HAc (1 M) in water | <5 | <5 | <10 | $13 \pm 1$ |
| Methanol | $11 \pm 1$ | <10 | <10 | $15 \pm 1$ |
| HCl (1 M) in methanol | $15 \pm 2$ | $36 \pm 3$ | $13 \pm 1$ | $86 \pm 2$ |
| $HNO_3$ (1 M) in methanol | $20 \pm 1$ | $52 \pm 3$ | $14 \pm 1$ | $80 \pm 3$ |
| HAc (1 M) in methanol | $11 \pm 1$ | $25 \pm 2$ | $12 \pm 1$ | $72 \pm 2$ |
| Ethanol | $20 \pm 2$ | $12 \pm 1$ | $13 \pm 1$ | $29 \pm 1$ |
| HCl (1 M) in ethanol | $24 \pm 1$ | $37 \pm 2$ | $42 \pm 2$ | $89 \pm 2$ |
| $HNO_3$ (1 M) in ethanol | $33 \pm 2$ | $35 \pm 2$ | $17 \pm 1$ | $28 \pm 1$ |
| HAc (1 M) in ethanol | $21 \pm 1$ | $31 \pm 2$ | $26 \pm 1$ | $76 \pm 2$ |
| Acetone | $81 \pm 3$ | $80 \pm 3$ | $84 \pm 3$ | $85 \pm 2$ |
| HCl (1 M) in acetone | $94 \pm 3$ | $95 \pm 2$ | $96 \pm 2$ | $95 \pm 3$ |
| $HNO_3$ (1 M) in acetone | $95 \pm 2$ | $97 \pm 3$ | $96 \pm 2$ | $98 \pm 2$ |
| HAc (1 M) in acetone | $92 \pm 3$ | $93 \pm 3$ | $94 \pm 3$ | $94 \pm 2$ |
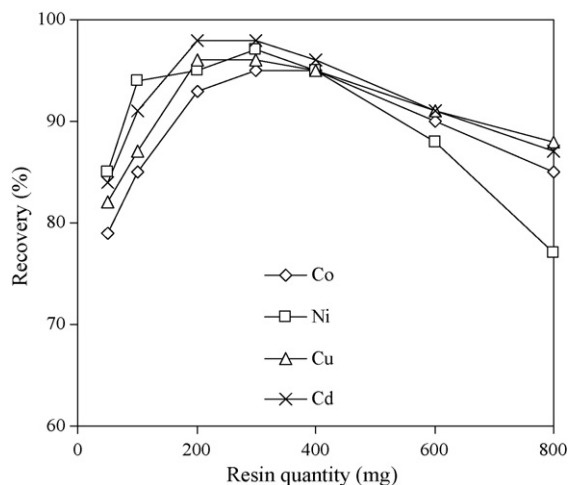
Fig. 3. Effect of resin quantity on the recovery of the trace metals ($N=4$).
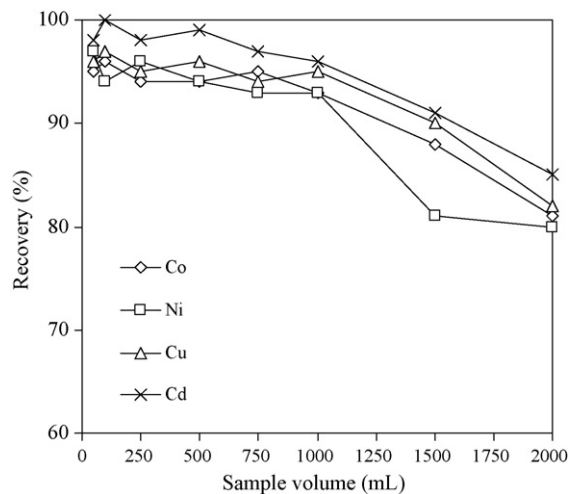


Fig. 4. Effect of sample volume on the recovery of the trace metals ($N=4$).

determined as 1 M HNO$_3$ in acetone and used in the subsequent experiments.

The effect of the volume of 1 M HNO$_3$ in acetone solution on the recovery was investigated. The almost quantitative recoveries were found after 7.5 mL of eluent volume. The optimum eluent volume was specified as 10.0 mL and used in the subsequent experiments.

### 3.4. Effect of resin quantity

In order to estimate the optimum resin quantity, the recoveries of the metals were examined by use of the resin quantities between 50 and 800 mg, and the best recoveries were achieved between 200 and 400 mg (Fig. 3). The optimum resin quantity was

selected as 300 mg for the later tests. The relationship between eluent volume and decrease in the recoveries obtained with increasing resin was investigated using 800 mg resin and quantitative recovery (>95%) for the analytes with 800 mg of the resin was achieved with 25 mL eluent volume. Thus, when higher amounts of sorbent were used, the more eluent should be used to obtain the quantitative recovery.

### 3.5. Effect of sample volume

Because of the low concentrations of trace metals in real samples, the sample volume is one of the most important parameters to reach high preconcentration factors for the analysis of a real sam-

**Table 2**
Effect of matrix ions on the recovery of the trace metals (sample volume: 50 mL, $N=3$)

| Ion | Added as | Conc. (mg L$^{-1}$) | Recovery (%) | | | |
|---|---|---|---|---|---|---|
| | | | Co | Ni | Cu | Cd |
| Na$^+$ | NaCl | 2500 | $97 \pm 3$ | $98 \pm 2$ | $99 \pm 1$ | $97 \pm 3$ |
| | | 5000 | $98 \pm 4$ | $102 \pm 3$ | $97 \pm 3$ | $101 \pm 3$ |
| | | 10000 | $100 \pm 4$ | $100 \pm 4$ | $96 \pm 2$ | $101 \pm 2$ |
| K$^+$ | KCl | 2500 | $97 \pm 3$ | $99 \pm 3$ | $98 \pm 2$ | $99 \pm 2$ |
| | | 5000 | $98 \pm 2$ | $96 \pm 3$ | $97 \pm 3$ | $97 \pm 2$ |
| Ca$^{2+}$ | CaCl$_2$ | 2500 | $97 \pm 2$ | $95 \pm 2$ | $96 \pm 2$ | $100 \pm 1$ |
| | | 5000 | $99 \pm 3$ | $100 \pm 3$ | $98 \pm 1$ | $100 \pm 1$ |
| Mg$^{2+}$ | MgCl$_2$ | 2500 | $93 \pm 3$ | $96 \pm 4$ | $96 \pm 2$ | $94 \pm 4$ |
| | | 5000 | $92 \pm 2$ | $102 \pm 4$ | $96 \pm 2$ | $95 \pm 3$ |
| Mixed | Chlorides | 2500 | $96 \pm 3$ | $94 \pm 3$ | $101 \pm 3$ | $100 \pm 1$ |
| (Na$^+$, K$^+$ Ca$^{2+}$, Mg$^{2+}$) | | 5000 | $98 \pm 2$ | $98 \pm 2$ | $103 \pm 3$ | $102 \pm 3$ |
| | | 10000 | $102 \pm 3$ | $102 \pm 3$ | $100 \pm 2$ | $101 \pm 3$ |
| Cl$^-$ | NaCl | 20000 | $96 \pm 3$ | $93 \pm 3$ | $98 \pm 2$ | $100 \pm 1$ |
| F$^-$ | NaF | 2500 | $97 \pm 3$ | $96 \pm 2$ | $97 \pm 1$ | $99 \pm 2$ |
| NO$_3$$^-$ | KNO$_3$ | 5000 | $97 \pm 2$ | $98 \pm 4$ | $100 \pm 1$ | $97 \pm 2$ |
| SO$_4$$^{2-}$ | Na$_2$SO$_4$ | 2500 | $96 \pm 4$ | $95 \pm 3$ | $101 \pm 3$ | $99 \pm 3$ |
| PO$_4$$^{3-}$ | Na$_3$PO$_4$ | 2500 | $95 \pm 3$ | $97 \pm 3$ | $96 \pm 3$ | $98 \pm 3$ |
| CH$_3$COO$^-$ | CH$_3$COONa | 2500 | $96 \pm 4$ | $96 \pm 3$ | $98 \pm 2$ | $99 \pm 3$ |
| HCO$_3$$^-$ | NaHCO$_3$ | 2500 | $97 \pm 3$ | $95 \pm 3$ | $97 \pm 2$ | $97 \pm 1$ |
| Fe$^{3+}$ | Fe(NO$_3$)$_3$ | 10 | $98 \pm 4$ | $97 \pm 2$ | $96 \pm 2$ | $96 \pm 1$ |
| Mn$^{2+}$ | Mn(NO$_3$)$_2$ | 10 | $97 \pm 2$ | $98 \pm 2$ | $98 \pm 3$ | $97 \pm 2$ |
| Pb$^{2+}$ | Pb(NO$_3$)$_2$ | 10 | $96 \pm 3$ | $97 \pm 3$ | $96 \pm 3$ | $98 \pm 2$ |
| Al$^{3+}$ | Al$_2$(SO$_4$)$_3$ | 10 | $97 \pm 3$ | $96 \pm 4$ | $96 \pm 3$ | $97 \pm 3$ |
| Hg$^{2+}$ | Hg(NO$_3$)$_2$ | 10 | $94 \pm 4$ | $95 \pm 3$ | $98 \pm 2$ | $96 \pm 3$ |
| Zn$^{2+}$ | Zn(NO$_3$)$_2$ | 10 | $96 \pm 3$ | $97 \pm 2$ | $100 \pm 1$ | $98 \pm 2$ |
| Cr$^{3+}$ | Cr(NO$_3$)$_3$ | 10 | $97 \pm 3$ | $96 \pm 3$ | $96 \pm 2$ | $95 \pm 2$ |
| Co$^{2+}$ | Co(NO$_3$)$_2$ | 10 | – | $96 \pm 3$ | $99 \pm 1$ | $96 \pm 2$ |
| Ni$^{2+}$ | Ni(NO$_3$)$_2$ | 10 | $94 \pm 3$ | – | $99 \pm 2$ | $97 \pm 2$ |
| Cu$^{2+}$ | Cu(NO$_3$)$_2$ | 10 | $95 \pm 3$ | $97 \pm 3$ | – | $99 \pm 1$ |
| Cd$^{2+}$ | Cd(NO$_3$)$_2$ | 10 | $96 \pm 2$ | $98 \pm 2$ | $96 \pm 3$ | – |

**Table 3**
Analysis of the certified reference materials for accuracy test

| | CRM TMDW-500[a] Drinking Water | | | CRM SA-C[b] Sandy Soil C | | |
|---|---|---|---|---|---|---|
| | Certified ($\mu g\,L^{-1}$) | Found[c] ($\mu g\,L^{-1}$) | Error (%) | Certified ($\mu g\,g^{-1}$) | Found[c] ($\mu g\,g^{-1}$) | Error (%) |
| Cu | 20.0 ± 0.1 | 19.4 ± 0.3 | −3.0 | 63.6 ± 4.0 | 61.1 ± 4.2 | −3.9 |
| Co | 25.0 ± 0.1 | 24.2 ± 0.4 | −3.2 | 12.4 ± 0.6 | 11.9 ± 0.3 | −4.0 |
| Ni | 60.0 ± 0.3 | 61.4 ± 2.8 | +2.3 | 48.4 ± 3.0 | 50.6 ± 3.1 | +4.5 |
| Cd | 10.00 ± 0.05 | 9.4 ± 0.5 | −6.0 | 109.0 ± 8.0 | 107.9 ± 6.3 | −1.0 |

[a] 25 mL of Drinking Water CRM was taken, and the method was applied. Final volume was 5.0 mL.
[b] 0.250 g of Sandy soil CRM was taken, and after digestion in microwave irradiation, the method was applied. Final volume was 5.0 mL.
[c] The confidence interval was calculated at $P = 0.95$ ($N = 3$).

ple using preconcentration. Therefore, the effect of sample volume on the recoveries of the analytes were investigated by using model solutions containing the same amount of trace metals in the volume range of 50–2000 mL which were passed through the column under optimum conditions. The recoveries were found to be stable until 1000 mL and, hence, 1000 mL was chosen as the largest sample volume to work (Fig. 4).

### 3.6. Effect of sample flow rate

One of the parameters affecting recovery and preconcentration time is sample flow rate. There is contradiction between recovery and preconcentration time changing with flow rates. 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 1–25 mL min$^{-1}$ by using a waterjet aspirator. The results showed that the recovery did not change at the flow rates studied. The sample flow rate was chosen as 5 mL min$^{-1}$ in further studies.

From the results, the developed system, Amberlite XAD-2000/APDC column solid-phase extraction is independent from the flow rates in the range 1–25 mL min$^{-1}$. This may be an evidence showing that the resin is retained the metal-dithiocarbamate chelates more strongly because of its high surface area. On the other hand, though the metal-chelates were retained strongly on the resin surface, they were eluted easily with 1 mol L$^{-1}$ HNO$_3$ in acetone (Section 3.3).

### 3.7. Effect of matrix ions (salt effect)

Natural water samples contain commonly alkali, alkaline earth and some transition element salts. Therefore, the effects of some anions and cations at various concentrations on the recovery were evaluated. This salts either individually or mixing in the model solution did not affect on the recovery in the examined concentration range of the salts (Table 2). As expected, matrix ions cause no interferences due to the group-specific character of APDC.

**Table 4**
The accuracy test results for spiked recovery (sample volume: 50 mL, final volume: 5.0 mL, $N = 3$)

| Element | Yomra stream | | | Yanbolu stream | | Karadere stream | | Mushroom[a] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Added ($\mu g$) | Found ($\mu g$) | R (%) | Found ($\mu g$) | R (%) | Found ($\mu g$) | R (%) | Added ($\mu g$) | Found ($\mu g$) | R (%) |
| Co | 0 | ND | – | ND | – | ND | – | 0 | 1.5 ± 0.1 | – |
| | 10 | 9.8 ± 0.3 | 98 | 9.6 ± 0.3 | 96 | 9.5 ± 0.4 | 95 | 5 | 6.1 ± 0.3 | 95 |
| | 25 | 23.7 ± 1.6 | 95 | 24.0 ± 1.4 | 96 | 23.5 ± 1.1 | 94 | 15 | 16.9 ± 0.7 | 103 |
| Ni | 0 | ND | – | ND | – | ND | – | 0 | 21.7 ± 0.9 | – |
| | 10 | 9.6 ± 0.5 | 96 | 9.5 ± 0.3 | 95 | 9.6 ± 0.7 | 96 | 5 | 25.6 ± 1.3 | 96 |
| | 25 | 23.4 ± 1.1 | 94 | 24.4 ± 1.0 | 98 | 23.8 ± 1.2 | 95 | 15 | 37.5 ± 1.7 | 102 |
| Cu | 0 | ND | – | ND | – | ND | – | 0 | 15.7 ± 0.7 | – |
| | 10 | 10.0 ± 0.3 | 100 | 9.7 ± 0.2 | 97 | 9.6 ± 0.1 | 96 | 5 | 21.0 ± 1.1 | 101 |
| | 25 | 24.4 ± 1.0 | 98 | 24.2 ± 0.9 | 97 | 24.0 ± 0.8 | 96 | 15 | 29.5 ± 1.4 | 96 |
| Cd | 0 | ND | – | ND | – | ND | – | 0 | 8.8 ± 0.4 | – |
| | 10 | 9.9 ± 0.3 | 99 | 9.6 ± 0.4 | 96 | 9.7 ± 0.2 | 97 | 5 | 12.9 ± 0.5 | 94 |
| | 25 | 24.5 ± 0.7 | 98 | 23.8 ± 0.7 | 95 | 24.0 ± 0.5 | 96 | 10 | 18.1 ± 0.7 | 96 |

[a] Sample quantity: 0.500 g.

**Table 5**
Statistical evaluation of the method

| Statistical parameters | Co | Ni | Cu | Cd |
|---|---|---|---|---|
| Regression equations | $A = 0.0307C + 0.0007$ | $A = 0.0322C + 0.0021$ | $A = 0.0557C + 0.0017$ | $A = 0.1479C + 0.0009$ |
| Correlation coefficients, $r^2$ | 0.9999 | 0.9989 | 0.9996 | 0.9993 |
| Relative std deviation, R.S.D. (%) | 3.3 | 3.0 | 2.2 | 2.1 |
| Confidence intervals ($\pm ts/\sqrt{N}$) | 2.3 | 2.0 | 1.6 | 1.6 |
| Limit of detection, LOD ($\mu g\,L^{-1}$) | 0.21 | 0.23 | 0.14 | 0.07 |
| Limit of quantification, LOQ ($\mu g\,L^{-1}$) | 0.71 | 0.76 | 0.46 | 0.23 |
| Linear ranges (mg L$^{-1}$) | 0.05–6.0 | 0.05–6.0 | 0.03–7.0 | 0.015–1.2 |
| Working ranges (mg L$^{-1}$) | 0.15–5.0 | 0.15–5.0 | 0.1–5.0 | 0.05–1.0 |
| Sensitivity ($\mu g\,L^{-1}$) | 0.52 | 0.36 | 0.24 | 0.12 |

$A$: Absorbance; $C$: Concentration (mg L$^{-1}$).

**Table 6**
The metal contents determined by XAD–2000/APDC method of the water and mushroom samples taken from various locations in Trabzon (Sample volume: 1000 mL, final volume: 5.0 mL, $N = 4$)

| Sample no. | Sample locations | Concentration, $\mu g\,L^{-1}$, $\bar{x} \pm s$ | | | |
|---|---|---|---|---|---|
| | | Co | Ni | Cu | Cd |
| 1 | Yomra Stream, Yomra | 1.4 ± 0.1 | 1.2 ± 0.1 | 2.8 ± 0.3 | ND |
| 2 | Yanbolu Stream, Arsin | 1.8 ± 0.2 | 1.7 ± 0.7 | 4.1 ± 0.4 | ND |
| 3 | Karadere Stream, Araklı | 1.0 ± 0.1 | 2.1 ± 0.2 | 5.0 ± 0.4 | ND |
| 4 | Mushroom ($\mu g\,g^{-1}$) | 2.9 ± 0.1 | 43.3 ± 1.8 | 31.3 ± 1.4 | 17.5 ± 0.7 |

### 3.8. Adsorption capacity of the resin

Langmuir isotherms were used for the determination of resin capacity defined as the amount of metal adsorbed by 1 g of resin. APDC complexes of the metals, of which total amounts varied in the range of 50–3000 $\mu g$, 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 widely used adsorption isotherms and described by the equation below:

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

where $q_e$ is the amount of metal adsorbed per unit weight of the resin ($mg\,g^{-1}$) at equilibrium, $C_e$ the final concentration in the solution ($mg\,L^{-1}$), $q_{max}$ the maximum adsorption in mono-layered adsorption systems ($mg\,g^{-1}$), and $a_L$ the adsorption equilibrium constant related to adsorption energy ($L\,mg^{-1}$).

The equation given above can be rearranged as follows:

$$\frac{C_e}{q_e} = \left(\frac{C_e}{q_{max}}\right) + \left(\frac{1}{a_L q_{max}}\right) \tag{2}$$

A plot of $C_e/q_e$ versus $C_e$ showed a linear relationship, and Langmuir constants $q_{max}$ and $a_L$ can be calculated from the slope and intercept of the plot. Adsorption capacity of the Amberlite XAD-2000 resin for Co(II), Cu(II), Cd(II), and Ni(II) were evaluated as 6.1, 6.4, 6.2, and 6.3 $mg\,g^{-1}$, respectively.

### 3.9. Analytical performance

The analytical performance of the proposed procedure can be shown for the results from FAAS measurements. The accuracy of the developed procedure for solid/liquid samples was checked with standard reference materials, CRM TMDW-500 Drinking Water and CRM SA-C Sandy Soil C. The preconcentration procedure was applied to 25 mL of CRM TMDW-500 Drinking Water and 50 mL of the clear solution of CRM SA-C Sandy Soil C obtained from microwave digestion system, and then final volumes were made 5.0 mL.

The results obtained were given in Table 3. The relative errors are in the range of 0.6–4.5% for trace metals in the analyzed samples.

Analytical recoveries for the investigated ions was assessed for two concentration levels, after spiking solid/liquid samples (50 mL of the samples) with analyte quantities between 5 and 25 $\mu g$ for each metal. Good recoveries were reached for all studied metals (Table 4).

The preconcentration procedure was repeated 10 times with the model solutions at the optimum working conditions determined for each metal. The percent relative standard deviations (%R.S.D.) and the confidence intervals at confidence level of 95% were calculated. The detection limits (3 s, $N = 20$) for the examined analytes were calculated as defined by IUPAC [35]. In the current study, the detection limit (DL) was determined as three times the standard deviation of the absorbance (20 replicate measurements of blank sample) with the pre-concentration step. The absorbance values

**Table 7**
The metal contents determined by APDC-MIBK liquid–liquid extraction method in the water samples (sample volume: 1000 mL, final volume: 10.0 mL, $N = 4$).

| Sample no. | Sample locations | Concentration, $\mu g\,L^{-1}$, $\bar{x} \pm s$ | | | |
|---|---|---|---|---|---|
| | | Co | Ni | Cu | Cd |
| 1 | Yomra Stream, Yomra | 1.5 ± 0.2 | ND | 2.7 ± 0.2 | ND |
| 2 | Yanbolu Stream, Arsin | 1.9 ± 0.3 | 1.9 ± 0.3 | 4.4 ± 0.3 | ND |
| 3 | Karadere Stream, Araklı | ND | 2.0 ± 0.4 | 5.1 ± 0.5 | ND |

were divided by the slope of analytical curve, and then the detection limits were calculated by dividing the instrumental detection limit by the pre-concentration factor. The linear response ranges were determined from the calibration curves for each metal. The lower limits of the working ranges were taken as 10-fold of the standard deviation (limit of quantity). Upper limits of the linear ranges for each metal were determined with analysis of a series of metal solutions (up to 10.0 $mg\,L^{-1}$) by FAAS. The point that the linearity was ended was evaluated as high limit of the linear range. The sensitivity was chosen as the concentration giving 0.0044 absorbance value. The analytical parameters defined above were given in Table 5.

### 3.10. Application of the method to real samples

The proposed preconcentration method was applied to water and mushroom samples. pHs of all the samples were adjusted to 6. The trace metals contents of the samples were complexed with APDC and passed through the mini-column filled with XAD-2000 resin. The metal complexes retained in the column were then eluted with 1 M HNO$_3$ in acetone. Final volumes were made 5.0 mL and the studied metals were analyzed by FAAS. The results of FAAS determinations obtained for Co, Ni, Cu, and Cd are presented in Table 6.

The accuracy of the developed procedure for stream water samples was also checked with standard MIBK-APDC liquid–liquid extraction method [33]. The results were given in Table 7. The relative errors are calculated to be 2.0–10.5% for studied metals in the analyzed samples.

## 4. Conclusions

A new method was developed for the determination of trace metals in various environmental solid/liquid samples. As a result of a 200-fold preconcentration factor, the method was found to be applicable to surface waters, including streams, rivers, and lakes, as well as to seawater because of competency with high saline concentrations. The system was also successful in preconcentrating metal ions from large sample volume such as 1000 mL. In conclusion, the metal contents at $\mu g\,L^{-1}$ (ppb) levels were determined easily and with high accuracy.

The other main advantages of the method include simplicity, time saving, no requirements of sophisticated instruments, and cost-effectiveness. Instead of the use of fresh solvent as an extracting phase for each sample, the reusability of XAD-2000 was as high as greater than 500 cycles without any loss in its sorption behavior.

**Table 8**
Comparative data from some recent studies for preconcentration of trace metals using SPE methods using with Amberlite XAD resin or APDC as a complexing agent and detection by FAAS

| Preconcentration system | Studied metals | pH | Eluent | Flow rate (mL min$^{-1}$) | PF | Resin capacity (mg g$^{-1}$) | LOD ($\mu$g L$^{-1}$) | Ref. |
|---|---|---|---|---|---|---|---|---|
| XAD-2010/8-hydroxyquinoline | Mn, Fe, Co, Ni, Cu, Zn, Pb, Cd | 8.0 | 1 M HNO$_3$ in acetone | 20.0 | 100 | 8.7–11.2 | 0.10–0.40 | [4] |
| XAD-2/calmagite | Cu | 4.75 | 2 M HCl | 1.8 | 50 | 0.10 | 0.15 | [25] |
| XAD-2000/APDC | Cr(III), Cr(VI) | 2.0 | 0.05 mol L$^{-1}$ H$_2$SO$_4$ | 10.0 | 80 | 7.4 | 0.6 | [26] |
| XAD-2000/diethyldithiocarbamate | Fe, Cu, Mn, Zn, Co, Ni, Cd, Pb | 8.0 | 1 M HNO$_3$ in acetone | 20.0 | 100 | 3.80–6.08 | 0.20–0.45 | [29] |
| XAD-2000/8-hydroxyquinoline | Fe, Cu, Mn, Zn, Co, Ni, Cd, Pb | 6.0 (8.0 for Mn) | 1 M HNO$_3$ in acetone | 10.0 | 100 | 6.83–9.43 | 0.3–2.2 | [30] |
| XAD-7/xylenol orange | Cd, Co, Cu, Ni, Zn, Fe | 4.0–7.0 | 1.0–2.0 M HCl | 2.0–5.0 | 50–200 | 1.6–2.6 | 0.003–0.024 | [36] |
| XAD-2/1-(2-pyridylazo)-2-naphthol | Cu, Cd, Pb | 8.5 | 3 M HNO$_3$ | 4.5 | 50 | 1.35–6.86 | 0.8–23.2 | [37] |
| XAD-4/AMPDAA | Cd, Co, Cu, Ni, Zn | 7.0 | 1 M HCl + 1 M NaCl | 2.0 | 80 | 3.92–20.22 | 0.023–0.16 | [38] |
| XAD-4/APDC | Cd, Cu, Mn, Ni, Pb, Zn | 5.0 | 4 N HNO$_3$ | 0.6 | 120–230 | 7.21–11.08 | 0.1–0.6 | [39] |
| Activated carbon/APDC | Cd, Cu, Ni, Zn | 5.0 | 1 M HNO$_3$ in acetone | 1.0 | – | – | 0.019–0.028 | [40] |
| XAD-2000/APDC | Cu, Co, Ni, Cd | 6.0 | 1 M HNO$_3$ in acetone | 5.0 | 200 | 5.7–6.4 | 0.07–0.23 | This work |

LOD: limit of detection; PF: preconcentration factor; SPE: solid-phase extraction; AMPDAA: 2-acetylmercaptophenyldiazoaminoazobenze; APDC: ammonium pyrrolidyn-dithiocarbamate.

A comparison of the proposed system with other preconcentration procedures with Amberlite XAD resins is given in Table 8. Some parameters obtained were comparable to those presented by other methods described in the literature. As seen from the data in Table 8, the proposed method developed by using Amberlite XAD-2000/APDC system has relatively high preconcentration factor, flow rate and resin capacity, and low LOD when compared to other methods reported in Table 8.

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