Determination of Copper, Cobalt, Cadmium, Lead, Nickel and Chromium by Atomic Absorption Spectrometry in Bottled Mineral Water from Turkey after Preconcentration/Separation in Activated Carbon

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Copper, cobalt, cadmium, lead, nickel and chromium concentrations were determined in some bottled mineral water samples purchased from local markets in Nigde and Kayseri-Turkey by atomic absorption spectrometry after preconcentration/separation procedure on the activated carbon column as pyrocatechol violet complexes. The concentration ranges of copper, cobalt, chromium, lead and nickel were found to be as 10.3–37.4 µg/L, 2.0–2.3 µg/L, 2.0–4.6 µg/L, 2.0–3.4 µg/L 4.7–16.7 µg/L respectively. The cadmium concentrations of all the samples were found to be below 0.1 µg/L.

INTRODUCTION

Determination of the trace element concentrations of natural water samples is an important procedure for investigation of the chemical cycles of these elements. Modern instrumental techniques including atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), etc. have been widely used for determination of trace heavy metals in the natural water samples[1-3]. Because of the low metal concentrations and interferic effects of the matrix, an enrichment/separation procedure is necessary.

Various preconcentration/separation techniques for the determination of trace heavy metal ions have been proposed including extraction, chelation, coprecipitation, electroanalytical techniques, ion-exchange, etc., prior to their spectrometric determinations of metal ions[4-9]. Solid phase extraction has an important place in the determination traces of metal ions from natural waters. Loss of sorbents including silica gel, amberlite XAD resins, etc. have been used for the solid phase

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extraction of metal ions from the water samples[10–15]. Separation and enrichment methods based on adsorption of complexed metals on activated carbon have found widespread application[16–20]. In general, activated carbon filter was prepared and could be used only one time. The elution techniques for using activated carbon are limited many times. In these works activated carbon was filled onto a short column, then metal-chelate solution was passed through the column. Metal ions were adsorbed on the activated carbon column and were then eluted with a suitable eluting agent.

In the present study, the concentrations of copper, cobalt, cadmium, lead, nickel and chromium contents of the bottled mineral waters from Turkey were determined by atomic absorption spectrometry (AAS) after preconcentration/separation procedure using an activated carbon column.

EXPERIMENTAL

A Hitachi Z-8000 model atomic absorption spectrometer equipped with a Zeeman background corrector and a graphite furnace (Hitachi Model 180–704) was used in the determinations. 20 µL of sample was introduced into the graphite tube using an Eppendorf pipette. The operating parameters for working elements were set up as recommended by the manufacturer. A pH meter, Delta 320 Mettler, was employed for measuring pH values in the aqueous phase.

Analytical reagent-grade chemicals were employed for the preparation of all solutions. Freshly prepared double distilled water from a quartz still, was used in all experiments. All chemicals used were the same as previously described by Narain *et al.*[21] 500 mg of activated carbon as a slurry in water was added to a glass column 1.0 cm long and of 1.0 cm diameter. The column was preconditioned with 10–15 mL of working buffer solution prior to percolation of sample. After elution, the activated carbon column was regenerated with large volume of acetone.

Preconcentration procedure for water samples

For the preconcentration and separation of the trace metal ions, the procedure given by Narin *et al.*[21] was applied. Bottled mineral water samples were bought from local markets in Nigde and Kayseri. The pH of 200 mL of the sample was adjusted to 6 with acetate buffer. Then 10 mL of 0.02% of pyrocatechol violet was added. After 10 min, the sample was passed through the activated carbon column, with a 5 mL/min flow rate. Then the metal chelates adsorbed on activated carbon were eluted with 2 M HCl in acetone. The effluent was evaporated to near dryness at 35°C in a hood, then cooled. It was transferred into a calibrated volumetric flask and made up to 5 mL with 2 M HCl.

RESULTS AND DISCUSSION

The determination of the trace metal contents of the mineral water samples has been made after separation and preconcentration by sorbing the metal/pyro-catechol violet (PV) complexes on the activated carbon column[21]. The method has been modified for the preconcentration of trace metal ions in mineral water

samples. The optimum conditions for the preconcentration method were: pH 6, sample volume 500 mL, ligand amount 10 mL of 0.02% pyrocatechol violet, amounts of activated carbon on the column 500 mg, eluent 2 M HCl in acetone, eluent volume 10 mL. The main components of the mineral spring waters were not allowed to interfere in determinations.

The method has been applied for the preconcentration and separation of the trace metal contents in bottled mineral water samples. The concentrations of copper, cobalt, cadmium, lead, nickel and chromium in the samples given in Table-1 have been calculated on the assumption of 100% recovery of the trace metal ions. The relative standard deviations (RSD) of the procedure were less than 10 %.

TABLE-1

METAL LEVELS IN BOTTLED MINERAL WATER SAMPLES FROM TURKEY (N = 4)

Sample	Concentration, µg/L ($x \pm SD$)				
	Cu	Co	Cr	Pb	Ni
Kizilcahamam	30.5 ± 0.2	2.2 ± 0.2	4.6 ± 0.2	2.2 ± 0.1	5.0 ± 0.4
Beypazari	16.8 ± 1.1	BDL	BDL	3.4 ± 0.3	BDL
Akmina	30.6 ± 3.3	BDL	2.0 ± 0.1	BDL	BDL
Uludag	37.1 ± 0.3	2.3 ± 0.4	BDL	2.0 ± 0.1	16.7 ± 1.2
Çelik	39.5 ± 0.7	BDL	3.1 ± 0.4	BDL	12.3 ± 0.8
Kinik	24.6 ± 1.7	2.0 ± 0.2	BDL	BDL	4.7 ± 0.4
Özkaynak	10.3 ± 0.5	BDL	BDL	BDL	5.4 ± 0.2

BDL: Below Detection Limit.
$x \pm SD$: mean ± standard deviation.

The lowest and highest levels of elements detected ranged between 2.0 µg/L for cobalt and 39.5 µg/L for copper. The highest levels of total trace heavy metal ions were found in Kizilcahamam Mineral Water sample. As can be seen in Table-1, in this sample copper, cobalt, chromium, lead and nickel levels were (µg/L) 30.5 ± 0.2, 2.2 ± 0.2, 4.6 ± 0.2, 2.2 ± 0.1 and 5.0 ± 0.4, respectively. The lowest level of total heavy metal contents in the samples was found in the Özkaynak Mineral Water. Apart from nickel and copper, the investigated metal ions were below the LD of these ions in this station, while copper and nickel were 10.3 ± 0.5 and 5.4 ± 0.2 µg/L, respectively.

The maximum copper level (39.5 µg/L) was found in Çelik Mineral Water. The minimum level of copper (10.3 µg/L) was found in Özkaynak Mineral Water. The cadmium contents of the all mineral water samples were found to be below 0.1 µg/L. The cobalt level in the samples was in the range of 2.0–2.3 µg/L (the minimum being in Kinik Mineral Water, and the maximum in Uludag Mineral Water). The cobalt levels in four water samples were below the limit of detection (Table-1).

The chromium levels in the samples were in the range of 2.0–4.6 µg/L. The lowest and highest values were in Akmina Mineral Water and Kizilcahamam

Mineral Water, respectively. The lead concentrations in four samples were below the LD. The highest lead (3.4 ± 0.3 µg/L) was found at Beypazari Mineral Water and the lowest at Uludag Mineral Water (2.0 ± 0.1 µg/L). Nickel was found to be below the LD in only two samples. The highest nickel level of was found in Uludag Mineral Water (16.7 ± 1.2 µg/L) and the lowest in Kinik Mineral Water (4.7 ± 0.4 µg/L) (Table-1).

In conclusion, the activated carbon method can be easily applied for the preconcentration and separation of copper, cobalt, cadmium, lead, nickel and chromium ions in the other matrices such as geological samples.

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