

Flame Atomic Absorption Spectrometric Determination of Cd(II), Ni(II), Co(II) and Cu(II) in Tea and Water Samples after Simultaneous Preconcentration of Dithizone Loaded on Naphthalene

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A simultaneous preconcentration procedure for the determination of Cd(II), Ni(II), Co(II) and Cu(II) by atomic absorption spectrometry is described. The method is based on solid phase extraction of the metal ions on dithizone loaded on naphthalene in a mini-column, elution with nitric acid and determination by flame atomic absorption spectrometry. The sorption conditions including NaOH concentration, sample volume and the amount of dithizone were optimized in order to attain the highest sensitivity. The calibration graph was linear in the range of 0.5-75.0 ng ml⁻¹ for Cd(II), 1.0-150.0 ng ml⁻¹ for Ni(II), 1.0-150.0 ng ml⁻¹ for Co(II) and 1.0-125.0 ng ml⁻¹ for Cu(II) in the initial solution. The limit of detection based on 3S_b was 0.13, 0.32, 0.33 and 0.43 ng ml⁻¹ for Cd(II), Ni(II), Co(II) and Cu(II), respectively. The relative standard deviations (R.S.D) for ten replicate measurements of 20 ng ml⁻¹ of Cd(II), 100 ng ml⁻¹ of Ni(II), Co(II) and 75 ng ml⁻¹ of Cu(II) were 3.46, 2.43, 2.45 and 3.26%, respectively. The method was applied to the determination of Cd(II), Ni(II), Co(II) and Cu(II) in black tea, tap and river water samples.

Keywords: Solid-phase extraction, Dithizone, Naphthalene, Metal ions, Flame atomic absorption spectrometry

INTRODUCTION

The determination of heavy metals at trace levels in environmental samples is one of the targets of analytical chemists. Some of these are essential elements and play an important role in human metabolism. However, at higher concentrations, all metals are recognized as potentially toxic. Therefore, accurate determination of trace metals in environment is very important [1]. Flame atomic absorption spectrometry (FAAS) is one of the most widely used techniques for the determination of heavy metals because it has the advantages of low cost of operation, high sample throughput, high precision and specificity. However, this technique suffers from some drawbacks such as chemical

interference from the sample matrix and high detection limit. Therefore, direct determination at trace concentration levels is not possible by this technique. These problems can be overcome by applying a preconcentration procedure to enrich the metal ion concentration and remove the analyte from the sample matrix.

Different techniques such as liquid-liquid extraction [2], cloud point extraction [3,4], coprecipitation [5,6] and solid phase extraction (SPE) [7-9] are available for preconcentration of metal ions. Solid phase extraction is an attractive separation preconcentration technique for heavy metal ions with some important advantages such as simplicity, flexibility and high enrichment factors. Various solid phase extraction materials have been successfully used for the preconcentration and separation of metal ions at trace levels. These include Chromosorb 108 [10], Diaion SP-850 resin [11], cellulose

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functionalized with 8-hydroxyquinoline [12], chemically modified silica gel with aminothioamidoanthraquinone [13] and polyurethane foam functionalized with α -naphthol [14]. Naphthalene coprecipitated with methyl trioctyl ammonium chloride [15] or tetraoctyl ammonium bromide [16], naphthalene loaded with different ligands such as 2,6-bis(N-phenyl carbamoyl) pyridine [17], 1-(2-pyridylazo)-2-naphthol (PAN) [18], N,N-(4-methyl-1,2-phenylene)diquinoline-2-carboxamide [19] and dithizone [20,21] have also been used as solid phase extractors for determination of trace metal ions.

In this paper, a simultaneous solid-phase extraction method for the determination of Cd(II), Ni(II), Co(II) and Cu(II) is described. These metal ions are retained by dithizone loaded on naphthalene in a mini-column, eluted by nitric acid solution and determined by FAAS.

EXPERIMENTAL

Instrumentation

A Chemtech Analytical Instrument model CTA-3000 atomic absorption spectrometer (Bedford, England) equipped with cadmium, nickel, cobalt and copper hollow cathode lamps and air-acetylene flame was used for analysis. All instrumental settings were those recommended by the manufacturer. The selected wavelengths for the determination of cadmium, nickel, cobalt and copper were 228.8, 232.0, 240.7 and 324.7 nm, respectively. Lamp currents were 2, 4, 4 and 3 mA for cadmium, nickel, cobalt and copper, respectively. The selected band widths were 0.4 nm for copper and 0.2 nm for cadmium, nickel and cobalt. Other conditions such as air-acetylene flow rates and burner height were adjusted by the instrument for each element. A deuterium background correction was also used for Cd, Ni and Co.

A digital pH-Meter model 632, Metrohm (Herisau, Switzerland) with a combined glass electrode was used for pH adjustments. A Tebazma vacuum pump (Iran) was used for pumping the solutions.

Reagents

Analytical reagent-grade chemicals were used. 1000 $\mu\text{g ml}^{-1}$ stock solutions of Co(II), Cu(II) Cd(II) and Ni (II) were prepared by dissolving appropriate amounts of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Merck), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Merck), $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ (Merck) and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (Merck), respectively in water and diluting to

100 ml in volumetric flasks. The working solutions were prepared by appropriate dilution of these stock solutions. The stock solutions were standardized by EDTA titration [22]. A 0.10 M solution of NaOH was prepared by dissolving 2.0 g of sodium hydroxide (Merck) in water and diluting to 500 ml in a volumetric flask.

Sorbent Preparation

Dithizone was loaded on microcrystalline naphthalene and used as a sorbent for preconcentration of metal ions. To prepare this sorbent, 0.04 g of dithizone and 20 g of naphthalene were dissolved in 60 ml of acetone and heated on a hot-plate stirrer at 40 °C. This solution was transferred to 1000 ml of water while stirring the solution at room temperature. It was stirred for 2 h on a stirrer. This sorbent slurry was stored in a dark bottle for further use.

Sample Preparations

0.1 g of dry black tea sample was precisely weighed into a 100 ml beaker; 4.0 ml of 1:1 (v/v) nitric acid solution was added and gently heated at 150 °C. A number of sub-samples were also spiked with a known amount of each analyte. After cooling at room temperature, the residue was dissolved in water and the pH of the final digest was adjusted by suitable addition of 10% (w/v) sodium hydroxide solution. This solution was transferred to a 250 ml volumetric flask and subjected to the general procedure.

Tap and river water samples were acidified with 5 ml of nitric acid and stored in polyethylene bottles and kept in the refrigerator before use and filtered prior to analytical procedure.

Recommended Procedure

A glass tube (10 cm length and 7 mm i.d) with a very fine bore was used as a preconcentration column. It was filled with the sorbent to a height of about 7 cm and slightly pressed in the column with a flat glass rod. 250 ml solutions containing 0.5-75.0 ng ml^{-1} of Cd(II), 1.0-150.0 ng ml^{-1} of Ni(II), 1.0-150.0 ng ml^{-1} of Co(II), 1.0-125.0 ng ml^{-1} of Cu(II) and 1.0×10^{-3} M of NaOH were passed through the column packed with dithizone-naphthalene sorbent at a flow rate of 8.0 ml min^{-1} . The sorbed metal ions were eluted with 3.0 ml of 2.0 M of nitric acid. The metal content of the eluent was determined by FAAS. A blank solution was also run under the same

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analytical conditions without adding any Cd(II), Ni(II), Co(II) and Cu(II).

RESULTS AND DISCUSSION

Dithizone (dipheylthiocarbazone) forms chelate complexes with a number of heavy metal ions in neutral or alkaline solutions. Due to the differences in the stabilities of chelate complexes formed, the separation and determination of various metal ions is possible [23]. Therefore, dithizone was chosen as a ligand and was loaded on naphthalene by a simple procedure and used as a sorbent in a mini-column for simultaneous preconcentration of Cd(II), Ni(II), Co(II) and Cu(II). The retained analytes were then eluted by nitric acid solution and determined by FAAS.

Effect of NaOH Concentration

The sorption of metal ions was performed in both acidic and alkaline media. The preliminary investigation showed that the metal ions were retained by the sorbent in the alkaline solution. Thus, the effect of sodium hydroxide concentration was studied. As presented in Fig. 1, the highest recoveries were obtained for all metal ions at sodium hydroxide concentration of 1×10^{-3} M. Therefore, this concentration was selected for further investigations. Since the first formation constants for the hydroxide complexes of these metal ions were high (pK_f values were 6.38, 6.66, 2.8 and 3.08 for $Cd(OH)_3^-$, $Cu(OH)_3^-$, $Co(OH)_3^-$ and $Ni(OH)_3^-$, respectively), they were probably in these forms in alkaline media.

Choice of Eluent

A satisfactory eluent should quantitatively elute the sorbed analytes with small volume, which is needed for a high enrichment factor. For this reason, various solutions such as nitric acid, hydrochloric acid and thiourea were used to identify the best eluent for the sorbed metals on the naphthalene-dithizone sorbent. Among the eluents studied, nitric acid provided higher recoveries compared to thiourea and hydrochloric acid. Therefore, the effect of nitric acid concentration was studied. The results indicated that the highest recoveries were obtained when nitric acid concentration was above 1.5 M. Thus, 2.0 M of nitric acid was chosen as the eluent. The effect of volume of nitric acid was

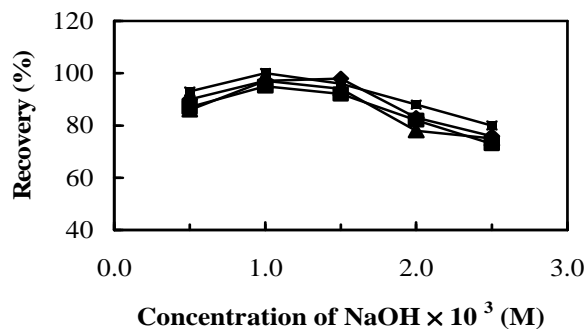


Fig. 1. Effect of NaOH concentration on the recovery 20 ng ml^{-1} of Cd(II) and 100 ng ml^{-1} of Ni(II), Co(II) and Cu(II). Conditions: Flow rate 8.0 $ml\ min^{-1}$, Column height 7 cm and 3 ml of 2.0 M of nitric acid as eluent: (♦) Cd, (■) Ni, (▲) Co, (●) Cu.

also investigated and quantitative recoveries were obtained for 3-5 ml of the eluent. The optimum eluent volume was specified as 3 ml for the subsequent studies.

Effect of the Amounts of Dithizone Loaded on Naphthalene

The quantity of ligand loaded on the sorbent is an important chemical variable affecting the preconcentration of the examined analytes. Therefore, the effect of the amount of dithizone loaded on naphthalene was investigated in the range of 0.02-0.08 g at optimum conditions. The results showed that the recovery was constant above 0.04 g. When the amount of dithizone was less than 0.04 g, there were not enough sites to capture the ions. Therefore, 0.04 g of dithizone loaded on 20 g of naphthalene ($2\ mg\ g^{-1}$) was chosen for further work.

Effect of Column Height

100 ml solutions containing 20 ng ml^{-1} of Cd(II) and 100 ng ml^{-1} of Ni(II), Co(II) and Cu(II) was passed through the column packed with heights of 3 to 7 cm. The recovery increased up to a height of 6 cm which was constant above that value. A column height of above 7 cm was chosen as a suitable height for this purpose.

Effect of the Sample Volume on the Recoveries

For samples containing very low concentrations of metal ions, the maximum applicable sample volume must be established. For this purpose, Cd(II), Ni(II), Co(II) and Cu(II) were pre-concentrated from sample volumes of 50, 100, 150, 200, 250 and 500 ml containing equal amounts of metal ions (5 μg of cadmium and 25 μg each of nickel, cobalt and copper), and applying the recommended procedure. The recovery of Cd(II), Ni(II), Co(II) and Cu(II) was quantitative for the sample volumes up to 250 ml. Thus, in this procedure, by using 3 ml of elution solution, a preconcentration factor of 83.3 was obtained.

Effect of Sample Flow Rates

The sorption of the metal ions on the sorbent was investigated at various flow rates. This was done by pumping 250 ml of the solution containing Cd(II), Ni(II), Co(II) and Cu(II) at flow rates in the range of 2.0-12.5 ml min^{-1} . As shown in Fig. 2, above 8.5 ml min^{-1} , the analytical signal decreased because the metal ions could not equilibrate properly with the sorbent due to the increase in the velocity of the ions. At low flow rates, sample throughput was decreased and the time of analysis was increased. In further experiments, the flow rate was kept constant at 8.0 ml min^{-1} in order to increase sample throughput.

Sorption Capacity

The sorption capacity of solid phase extractor was studied using batch method. 1.0 g of dry sorbent was added to 100 ml solutions containing different amounts of the metal ions and sodium hydroxide (1×10^{-3} M). After shaking the solutions for 2 h, the mixture was filtered and the remaining metal ions in the aqueous phase were determined by flame atomic absorption spectrometry. The amount of metal ions loaded on the sorbent phase was calculated by mass balance. The results showed that one gram of naphthalene-dithizone sorbent was able to retain up to 10 μg of Cd(II) and 50 μg of Ni(II), 50 μg of Co(II), and 50 μg of Cu(II).

Analytical Performance

Linear calibration graphs were obtained in the range of 0.5-75.0 ng ml^{-1} for Cd(II), 1.0-150.0 ng ml^{-1} for Ni(II), 1.0-

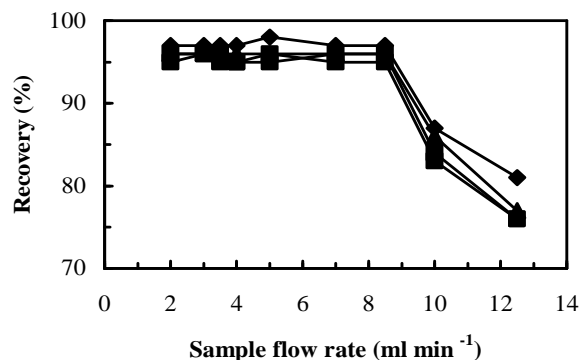


Fig. 2. Effect of sample flow rate on the recovery of 20 ng ml^{-1} of Cd(II) and 100 ng ml^{-1} of Ni(II), Co(II) and Cu(II). Conditions: Column height 7 cm, 3 ml of 2.0 M of nitric acid as eluent and NaOH concentration; 1×10^{-3} M.

150.0 ng ml^{-1} for Co(II) and 1.0-125.0 ng ml^{-1} for Cu(II) in the initial solution. The equations of the lines are $A = 1.26 \times 10^{-2}C + 0.068$, $A = 6.30 \times 10^{-3}C + 0.041$, $A = 6.10 \times 10^{-3}C + 0.033$ and $A = 7.40 \times 10^{-3}C + 0.068$ for Cd(II), Ni(II), Co(II) and Cu(II), respectively, where A is the absorbance and C is the concentration of metal ions in ng ml^{-1} . The regression coefficients for the lines are 0.9993, 0.9997, 0.9996 and 0.9995 for Cd(II), Ni(II), Co(II) and Cu(II), respectively. The limit of detection based on $3S_b$ was 0.13, 0.32, 0.33 and 0.43 ng ml^{-1} for Cd(II), Ni(II), Co(II) and Cu(II), respectively. The relative standard deviations (R.S.D) for ten replicate measurements of 20 ng ml^{-1} of Cd(II), 100 ng ml^{-1} of Ni(II), Co(II) and 75 ng ml^{-1} of Cu(II) were 3.46, 2.43, 2.45 and 3.26%, respectively.

Effect of Foreign Ions

The effect of foreign ions on the recovery of cadmium, nickel, cobalt and copper was tested. Different amounts of common ions were added to the test solution containing 20 ng ml^{-1} of Cd(II) and 100 ng ml^{-1} of Ni(II), Co(II), and Cu(II) and the developed procedure was applied. The tolerance limits were determined for a maximum error of $\pm 5\%$. The results presented in Table 1 demonstrate that the common coexisting ions did not have any significant effect on the separation and determination of cadmium, nickel, cobalt and copper ions.

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Table 1. Effect of Foreign Ions on the Determination of 20 ng ml⁻¹ of Cd(II) and 100 ng ml⁻¹ of Ni(II), Co(II) and Cu(II)

Interfering ion	Tolerance limit (mg l ⁻¹)
SO ₄ ²⁻ , Ca ²⁺ , Mg ²⁺ , Br ⁻ , F ⁻ , Cl ⁻ , I ⁻ , Na ⁺ , K ⁺	100
Mn ²⁺ , Zn ²⁺ , Cr ³⁺ , NO ₃ ⁻	50
Pb ²⁺ , CO ₃ ²⁻	20
NH ₄ ⁺ , HPO ₄ ²⁻	10
Hg ²⁺ , Bi ³⁺ , Fe ³⁺	1

APPLICATION

The solid phase extraction procedure presented for cadmium, nickel, cobalt and copper ions was applied to black tea, tap and river water samples. The results are given in Table 2. In order to estimate the accuracy of the procedure, the river water sample was also analyzed by graphite furnace atomic absorption spectrometry (GFAAS). A comparison of the results, presented in Table 3, indicated that there was a good agreement between the two methods and there was no significant difference between the results obtained by performing t-test at 95% confidence limit. Different amounts of the investigated metal ions were also spiked to water, and tea samples for recovery measurements. In most cases, good agreement was obtained between the added and found analyte content using the recommended procedure. The recovery values were quantitative and show that the presented method could be applied to the preconcentration of cadmium, nickel, cobalt and copper ions in black tea, tap and river water samples.

CONCLUSIONS

The results of this work demonstrate the possibility of using dithizone loaded on naphthalene as a sorbent for simultaneous preconcentration of Cd(II), Ni(II), Co(II) and Cu(II) with an enrichment factor of 83.3 fold. The proposed sorbent is very economical and easy to prepare. The method is highly sensitive and selective for the determination of trace amounts of Cd(II), Ni(II), Co(II) and Cu(II) by flame atomic

Table 2. Determination of Cd(II), Ni(II), Co(II) and Cu(II) in Black Tea, Tap and River Water Samples

Sample	Added (ng ml ⁻¹)	Found (ng ml ⁻¹) ^a	Recovery (%)	
River water	Co	-	1.3 ± 0.1	-
	Co	2.5	3.6 ± 0.1	94
		5.0	6.2 ± 0.1	98
		-	1.2 ± 0.1	-
	Ni	2.5	3.7 ± 0.1	100
		5.0	6.3 ± 0.1	102
		-	22.4 ± 0.3	-
	Cu	2.5	25.0 ± 0.3	104
		5.0	27.6 ± 0.3	104
		-	9.2 ± 0.2	-
	Cd	1.0	10.3 ± 0.2	110
		2.0	11.3 ± 0.2	105
-		ND ^b	-	
Tap water	Co	-	2.5 ± 0.1	100
	Co	2.5	2.5 ± 0.1	100
		5.0	5.2 ± 0.1	104
		-	ND	-
	Ni	2.5	2.6 ± 0.1	104
		5.0	5.2 ± 0.1	104
		-	19.7 ± 0.3	-
	Cu	2.5	22.0 ± 0.3	92
		5.0	24.6 ± 0.3	98
		-	ND	-
	Cd	1.0	1.0 ± 0.1	100
		2.0	2.1 ± 0.1	105
-		1.1 ± 0.1	-	
Black tea	Co	-	3.6 ± 0.1	100
	Co	2.5	3.6 ± 0.1	100
		5.0	6.2 ± 0.1	102
		-	1.5 ± 0.1	-
	Ni	2.5	4.1 ± 0.1	104
		5.0	6.5 ± 0.1	100
		-	11.9 ± 0.2	-
	Cu	2.5	14.6 ± 0.2	108
		5.0	16.7 ± 0.2	96
		-	ND	-
	Cd	1.0	1.0 ± 0.1	100
		2.0	2.0 ± 0.1	100

^a $\bar{x} \pm ts / \sqrt{n}$ at 95% confidence (n = 5). ^b Not detected.

Table 3. Comparison of the Results for the Determination of Cd(II), Ni(II), Co(II) and Cu(II) in River Water with Graphite Furnace Atomic Absorption Spectrometry (GFAAS)

Ion	Proposed method (ng ml ⁻¹) ^a	GFAAS (ng ml ⁻¹) ^a	Ion	Proposed method (ng ml ⁻¹) ^a	GFAAS method (ng ml ⁻¹) ^a
Co ²⁺	1.3 ± 0.1	1.36 ± 0.2	Cu ²⁺	22.4 ± 0.3	21.6 ± 0.5
Ni ²⁺	1.2 ± 0.1	1.15 ± 0.1	Cd ²⁺	9.2 ± 0.2	9.5 ± 0.4

^a $\bar{x} \pm ts / \sqrt{n}$ at 95% confidence (n = 5).

Table 4. Comparison of the Proposed Method with some of the Methods Reported in Literature

System	Preconcentration factor	DL (ng ml ⁻¹)				Ref.
		Cd	Ni	Co	Cu	
Chromosorb 108	80.0	0.24	0.44	0.25	0.16	[10]
Diaion SP-850 resin	50.0	0.47	-	0.73	0.30	[11]
Cellulose functionalized with 8-hydroxyquinoline	90.0	2.59	1.61	1.09	0.79	[12]
Modified silica gel with aminothioamidoanthraquinone	50.0	1.10	2.90	0.95	1.00	[13]
Dithizone loaded on naphthalene	83.3	0.13	0.32	0.33	0.43	This work

absorption spectrometry. The limits of detection and preconcentration factors attained for cadmium, nickel, cobalt and copper ions were more favorable than those reported by Spinola Costa *et al.* [20] using dithizone loaded on naphthalene in a batch mode. They reported limits of detection values of 44, 11, 30, 47 and 11 ng ml⁻¹ for Zn, Ni, Cd, Pb and Cu which are higher than those obtained by this method (0.13, 0.32, 0.33 and 0.43 ng ml⁻¹ for Cd, Ni, Co and Cu, respectively). A comparison with some of the previous works is also given in Table 4. The analytical parameters together with the values obtained in the analyzed samples show the usefulness of the method for measuring Cd(II), Ni(II), Co(II) and Cu(II) in black tea, tap and river water samples.

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