

Preconcentration and separation of nickel, copper and cobalt using solid phase extraction and their determination in some real samples

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Abstract

A solid phase extraction method has been developed to separate and concentrate trace amounts of nickel, cobalt and copper ions from aqueous samples for the measurement by flame atomic absorption spectrometry. By the passage of aqueous samples through activated carbon modified by dithioamide (rubeanic acid) (DTO), Ni²⁺, Cu²⁺ and Co²⁺ ions adsorb quantitatively. The recoveries of analytes at pH 5.5 with 500 mg solid phase were greater than 95% without interference from alkaline, earth alkaline and some metal ions. The enrichment factor was 330. The detection limits by three sigma were 0.50 µg L⁻¹ for copper, 0.75 µg L⁻¹ for nickel and 0.80 µg L⁻¹ for cobalt. The loading capacity was 0.56 mg g⁻¹ for Ni²⁺, 0.50 mg g⁻¹ for Cu²⁺ and 0.47 mg g⁻¹ for Co²⁺. The presented procedure was applied to the determination of analytes in tap, river and sea waters, vegetable, soil and blood samples with successfully results (recoveries greater than 95%, R.S.D. lower than 2% for $n = 3$).

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1. Introduction

The determination of heavy metals at trace levels in environmental is one of the targets of analytical chemists, due to their important roles in our life [1–3]. There are many difficulties in determining trace amounts of heavy metals in environmental samples by flame atomic absorption spectrometry due to insufficient sensitivity of instrument and/or matrix interferences. In order to achieve detection limits within the range of flame atomic absorption spectrometry. An initial preconcentration step allows lower limits of detection for analytes, as well as the separation of the analytes from its matrix, which may interfere in atomic absorption spectrometric determinations.

Preconcentration procedure is required for the determination of low contents of trace elements in geological and technological samples. Of all preconcentration and separation procedures sorption possesses several advantages: large preconcentration

factors that can be obtained in a short time, simplicity of phase separation and suitability for automation [2–5]. Solid phase extraction consists of the recovery of hydrophobic metal species on solid support of hydrophobic functionality. Desorption of metals is simply achieved by the change in solvent polarity. It does not require the use of concentrated acids or other aggressive reagents.

Various solid phase extraction materials including Diaion HP-20 [6], cellulose [7], activated carbon [8], Lewatit S 100 [9], SDS coated alumina [10] polyurethane foam [11], Chelex 100 [12], microcrystalline naphthalene [13], modified silica [14] and diaion HP-2MG [15]. Among which activated carbon has been widely applied. The reasons for widespread application of the activated carbon as a trace collector for metal ion preconcentration are strong interaction. Because activated carbon is a type of hydrophobic adsorbent which adsorbs non-polar or little polar substances in aqueous solutions, metal ions to be preconcentrate need to be transformed corresponding metal chelates [16–32]. The sorption is quantitative when the chelate contains systems of Π -electrons in the molecule and when the centers for binding on carbon and those for the metal ions are spatially

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separated so that their orbital do not have a substantial influence [33,34].

The purpose of this work is preconcentration–separation of Co^{2+} , Ni^{2+} and Cu^{2+} on activated carbon modified with dithioamide (DTO). The influences of the some analytical parameters including pH and sample volume on the quantitative recoveries of the analytes were investigated.

2. Experimental

2.1. Instruments

The measurements of metal ions were performed with a 680 AA Shimadzu atomic absorption spectrometer equipped with a hollow cathode lamp and a deuterium background corrector, at respective wavelengths (resonance line) using an air-acetylene flame. The instrumental parameters were those recommended by the manufacturer. A Metrohm 691 pH/Ion meter with a combined glass–calomel electrode was used for adjustment of test solution pH.

2.2. Reagents

Acids and bases were of the highest purity available from Merck and were used as received. Doubly distilled deionized water was used throughout. Nitrate salts of lead, cadmium, mercury, cobalt, nickel, copper, zinc, magnesium, calcium, strontium, barium, silver, sodium and potassium (all from Merck) were of the highest purity available and used without any further purification. The pH adjustment was done by addition of dilute nitric acid or sodium hydroxide to phosphate solution for preparing the desired pH buffer solution. Activated carbon (AC) (gas chromatographic grade, 40–60 mesh from Merck), were soaked in hydrochloric acid for 2 days, it was then washed with water and dried at 110°C for 1 day. dithioamide (DTO) was purchased from Merck Company and used as received.

2.3. Preparation of DTO coated activated carbon

Ligand loaded activated carbon was prepared by dissolving a weighed amount of DTO in 0.005 mol L^{-1} NaOH to the required amount of activated carbon. After 18 h, the solutions were filtered through the filter paper and activated carbons was washed with distilled water until the filter out was no longer alkaline. Finally, the mixtures were dried at 70°C overnight. The solid phase columns were initially preconditioned with solution with desired pH. For the final optimum experiments the solid phase was prepared as follow: 25 mg DTO per 500 mg of activated carbon.

2.4. Preconcentration procedure

The pH of solutions containing analyte ions was adjusted to pH 6 by adding phosphate buffer solution. The buffered solutions were passed through the column of DTO coated activated carbon at a flow rate of 5 mL min^{-1} . The adsorbed ions were then eluted with 5 mL of 3.0 mol L^{-1} nitric acid in acetone with a flow rate

of 1 mL min^{-1} . The analyte ions in the eluent were determined by flame atomic absorption spectrometer.

2.5. Analysis of the real samples

A 40 g of spinach was heated in silica crucible for 3 h on a hot plate and the charred material was transferred to furnace for overnight heating at 650°C . The residue was cooled, treated with 10.0 mL concentrated nitric acid and 3 mL 30% H_2O_2 again kept in furnace for 2 h. The final residue was treated with 3 mL concentrated hydrochloric acid and 2–4 mL 70% perchloric acid and evaporated to fumes. The solid residue was dissolved in water, filtered and by keeping the pH at 6.0 by addition of KOH and phosphate buffer. The preconcentration procedure given above was applied to these solutions.

River, tap and waste water samples were collected from Zohre River, Nourabad, Iran, Abshar spring, Yasouj, Iran, respectively. Before the analysis, the samples were filtered through a cellulose membrane filter (Millipore) of pore size $0.45\text{ }\mu\text{m}$. The organic content of the water samples were oxidized in the presence of 1% H_2O_2 and addition of concentrated nitric acid. The water samples were filtered through a filter paper. After acidification to 1% with concentrated nitric acid, they were stored in polyethylene bottles.

For the preconcentration procedure, pH of the 800 mL of water samples was adjusted to 6 using phosphate buffer and the sample passed through the column at flow rate of 4 mL min^{-1} . The analyte ions retained on column were eluted with 5 mL of 3 mol L^{-1} HNO_3 in acetone. The effluent was sent to flame atomic absorption spectrometry for evaluation of their metal content evaluation.

The soil and blood samples were digested as follow, 40 g (soil sample) or 40 mL (blood sample) or put in a beaker and 20 mL of distilled deionized water, 24 mL HNO_3 and 6 mL of H_2O_2 (30%) added to solution. While stirring heat on a plate until decrease its volume to half, it was filtrate and completed in 200 mL volumetric flask with distilled water. The preconcentration procedure given above was applied to these solutions.

3. Results and discussion

Due to the existence of a donating nitrogen atom as well as =S (SH) group and =O (OH) group and NH group in DTO was expected to increase both the stability and selectivity of its complex toward ions.

3.1. Effect of activated carbon

The DTO-activated carbon can retain all of the mention metal ions while the untreated activated carbon cannot quantitatively retain Co, Ni and Cu. Evidently; the preconcentration of the metals with the untreated activated carbon is not suitable for Co, Ni and Cu. Therefore, DTO-activated carbon seems to be a better sorbent in simultaneous sorption of Co, Ni and Cu. The effects of the amount of activated carbon at fix value of DTO on the sorption of metal ions at pH 6 were examined in the range of 100–1200 mg. The results are given in Fig. 1. Quantitative

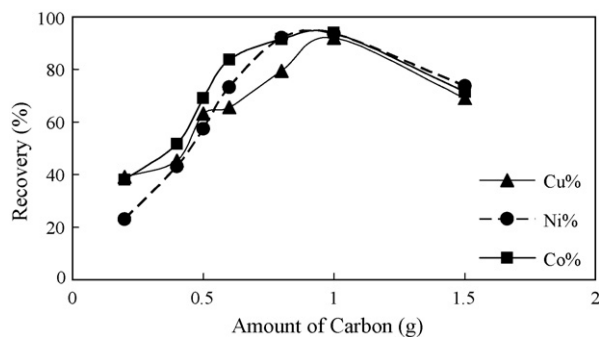


Fig. 1. Effect of amount of activated carbon on recovery of metal ions ($N=3$), pH 5.5, eluent: 5 mL, 3.0M HNO_3 in acetone.

recoveries (>95%) of the working elements were observed in the range of 500 mg. Above 500 mg, the recoveries were below 95% with 10 mL of the eluent. In the proposed procedure, 500 mg of activated carbon is recommended.

3.2. Effect of pH on recovery

In the solid phase extraction studies for heavy metal ions enrichment based on chelation, the pH of the aqueous solution is one of the main effective factor for quantitative recoveries of the analytes. Due to this important point, the influences of pH were investigated at the pH ranges 2–9 for both sorbents with model solutions, keeping the other parameters constant. Analyte deposition depended on the sample pH, and as shown in Fig. 2, high deposition efficiency was achieved at a pH of 5.8–6.1. The progressive decrease in the retention of analytes at a low pH is due to the competition of the hydrogen ion with the analytes for reaction with dithioxamide (rubeanic acid). To achieve high efficiency and good selectivity, a pH of 6.0 was selected for subsequent work.

3.3. Influences of the amounts DTO

The effects of the ligand amount on the retention of the analyte ions on DTO were also examined. The results are depicted in Fig. 3. The recoveries of analytes were quantitative till by the addition of 25 mg ligand. After that, the recovery values

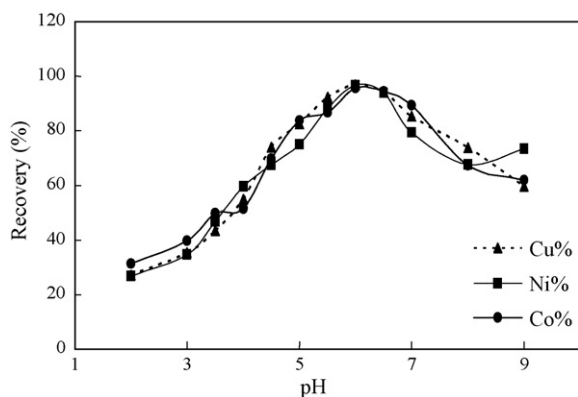


Fig. 2. Effect of pH on recovery of metal ions ($N=3$), pH 5.5, eluent: 5 mL, $3.0 \text{ mol L}^{-1} \text{ HNO}_3$ in acetone.

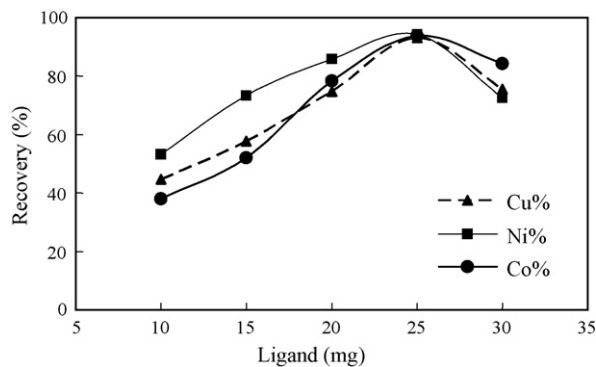


Fig. 3. Effect of amount of ligand loaded on recovery of metal ions ($N=3$), pH 5.5, eluent: 5 mL, 3.0M HNO_3 in acetone.

decreased, probably due to the formation of charged complex which could not be completely retained on solid phase.

3.4. Flow rates

Two important factors for the quantitative recoveries and desorption of metal chelates on the solid-phase extraction studies are flow rates of the sample and eluent solutions. The influences of the flow rates of the sample and eluent solution for the recoveries of analytes were investigated in the flow rate ranges of $1\text{--}10 \text{ mL min}^{-1}$. The recovery values for analyte ions were quantitative in all the working range of sample flow rates. The quantitative recovery values for eluent solution were obtained at the flow rate range of $1\text{--}5 \text{ mL min}^{-1}$. All further studies were performed at the sample and eluent flow rates of 5.0 mL min^{-1} .

3.5. Type and volume of the eluent

Various eluent solutions for desorption of the analytes-complex loaded on activated carbon were evaluated at 5 mL min^{-1} flow rate of the each eluent. The results are summarized in Table 1. When elution analyte ions using acetone or inorganic acids at various concentrations ($1 \text{ mol L}^{-1} \text{ HNO}_3$, $2 \text{ mol L}^{-1} \text{ HNO}_3$, $1 \text{ mol L}^{-1} \text{ HCl}$ and $2 \text{ mol L}^{-1} \text{ HCl}$, etc.) from the modified activated carbon column, the values of recovery were not quantitative (lower than 90%). The desorption of the

Table 1
Effect of eluent condition on ion recoveries efficiency

Acid ^a	Recovery (%)		
	Cu	Ni	Co
$1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$	23.3	39.7	34.4
$2 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$	39.7	45.7	38.9
$2 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$	41.8	49.9	43.9
$1 \text{ mol L}^{-1} \text{ HCl}$	43.8	39.3	39.9
$2 \text{ mol L}^{-1} \text{ HCl}$	71.8	59.8	63.8
$3 \text{ mol L}^{-1} \text{ HCl}$	98.7	96.9	97.9
$1 \text{ mol L}^{-1} \text{ HNO}_3$	56.7	52.9	62.9
$2 \text{ mol L}^{-1} \text{ HNO}_3$	79.8	81.7	80.7
$3 \text{ mol L}^{-1} \text{ HNO}_3$	97.8	96.4	97.9
$1 \text{ mol L}^{-1} \text{ H}_3\text{PO}_4$	29.8	21	30.9

^a All in acetone.

Table 2

Effects of the matrix ions on the recoveries of the examined metal ions ($N=3$)

Ion	Tolerance limit ion (mg L^{-1})
Na^+ , K^+ , Cl^- , SO_4^{2-} , Al^{3+} , Cr^{3+} , Zn^{2+} , Mn^{2+} , Sn^{2+} , Mg^{2+} , HCO_3^- , PO_4^{3-} , Ba^{2+} , Ca^{2+}	1000
Zn^{2+} , Cd^{2+} , Fe^{2+} , Fe^{3+}	500
Ag^+ , Pb^{2+} , Hg^{2+}	150

investigated metal ions from column was studied by using different eluents that were mixtures of inorganic acids and organic solvents such as 1 mol L^{-1} HCl in acetone, 1 mol L^{-1} HNO_3 in acetone (Table 1). Quantitative recoveries for all investigated were obtained when 3 mol L^{-1} HNO_3 in acetone used as eluent solution. Three moles per litre HNO_3 in acetone is the most effective eluent for quantitative recovery of metal ions.

To investigate the effect of the volume of 3 mol L^{-1} HNO_3 in acetone solution, the recommended preconcentration procedure were applied to the model solutions. In these investigations, the rest of the eluent in the resin bed was removed. The investigated metal ions were quantitatively recovered from the column with the eluent volume range of more than 5 mL. In the eluent volume lower than 5 mL, because of insufficient eluent volume, the recoveries of the analyte ions were not quantitative. For achieving higher enrichment factor, 5 mL of eluent was recommended for subsequent work.

3.6. Sample volume

The effect of the sample solution volume on the metal sorption was studied by passing 10–2000 mL volumes through the column at a 5 mL min^{-1} flow rate. The adsorption of the metal ions was not affected by sample volume below 1650 mL. Above this volume of sample solution, the percent sorption decreased for the analytes. The recoveries of analytes decrease probably due to the excess analytes loaded over the column capacity with increasing sample volume above 1650 mL. In the present study 1650 mL of sample solution was adopted for the preconcentration of the investigated ions, the adsorbed metals can be eluted with 5 mL of 3 mol L^{-1} HNO_3 in acetone and a preconcentration factor of 330 is achieved.

3.7. Interferences

In order to examine the effect of the various tested metal ions in the optimum conditions, extraction of these metal ions in the presence of some selected metal ions by and have been carried out which prompted us to perform an intensive selectivity study to evaluate the possible interference of some metal ions in the process of selective solid phase extraction of Co^{2+} , Ni^{2+} and Cu^{2+} .

Interferences that may be concomitant with this ion were investigated. The interference effect of calcium, magnesium and other alkali and alkaline earth ions were presented in Table 2 display that these ions up to 1000 fold are negligible and this high selectivity able the method for accurate and precise determination of Co^{2+} , Ni^{2+} and Cu^{2+} ion content in real samples.

Table 3

Specification of presented method at optimum conditions for each element

Parameters	Cu	Ni	Co
Linear range (ng mL^{-1})	10–950	17–850	18–900
Detection limit ($\mu\text{g L}^{-1}$)	0.50	0.75	0.80
Loading capacity (mg g^{-1})	0.56	0.50	0.47
R.S.D. (%)	0.90	0.90	0.85
Recovery (%)	98.3	97.6	98.3

3.8. Calibration graphs and precisions

The calibration curve were obtained by using 250 mL $0.05\text{--}1.5 \mu\text{g mL}^{-1}$ ions solutions at pH 5.5 at the optimum condition. The eluting solution was sent to AAS for evaluating ion content and results are shown in Table 3. The results indicate that linear range for Cu is 10–950, Ni 17–850 and for Co is

Table 4

Recovery of trace elements from spiked soil waters sample after preconcentration on activated carbon modified with DTO ($N=3$)

Ion	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	R.S.D. (%)	Recovery (%)
$\text{Co}^{\text{a,b}}$	0	N.D.	–	–
	50	57.6	1.1	–
	100	108.3	0.8	101.4
$\text{Ni}^{\text{a,b}}$	0	N.D.	–	–
	50	58.7	1.1	–
	100	109.6	0.8	101.8
$\text{Cu}^{\text{a,b}}$	0	N.D.	–	–
	50	59.6	1.1	–
	100	110.7	0.8	102.2
Co^{c}	0	73.2	1.2	–
	75	146.7	0.9	98.0
Ni^{c}	0	68.9	1.2	–
	75	146.3	0.9	103.2
Cu^{c}	0	80.3	1.1	–
	75	156.3	0.9	101.3
Co^{d}	0	62.3	1.2	–
	100	164.6	0.9	102.3
Ni^{d}	0	64.9	1.2	–
	100	166.2	0.8	101.3
Cu^{d}	0	78.4	1.0	–
	100	179.8	0.8	101.4

^a Recovery was calculated as (found 3–found 2/added 3–added 2).

^b Spring Abshar water.

^c Waste water.

^d Fahlian (Zohreh)River water.

Table 5
Recovery of trace elements from blood sample after preconcentration on activated carbon modified with different ligand ($N=3$)

Analyte	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	R.S.D. (%)	Recovery (%)
Co ^a	0	27.3	1.3	–
	50	78.9	1.1	103.2
Ni ^a	0	29.4	1.3	–
	50	80.2	1.0	101.6
Cu ^a	0	27.2	1.2	–
	50	78.1	0.9	101.8
Co ^b	0	60.1	1.1	–
	50	111.7	0.8	103.2
Ni ^b	0	63.8	1.2	–
	50	114.9	1.0	102.2
Cu ^b	0	69.3	1.3	–
	50	120.1	0.9	101.6
Cu ^c	0	63.7	1.0	–
	75	140.3	0.7	102.1
Ni ^c	0	60.3	1.3	–
	75	136.4	1.0	101.5
Co ^c	0	58.6	1.2	–
	75	136.4	0.9	103.7

^a Soil sample.

^b Blood sample.

^c Spinach sample.

18–900 $\mu\text{g mL}^{-1}$ using DTO. Relative standard deviation of measurement was found to be less than 0.6% at 0.5 for each ion.

In order to investigate reproducibility of method at optimum condition six experiments for separation–preconcentration of these ions on activated carbon modified with The efficiency based on modified activated carbon are 98.3, 97.6 and 98.3% for Co^{2+} , Ni^{2+} and Cu^{2+} that indicate repeatable results.

3.9. Analytical performance of the method

The correctness of results was verified by analyzing the concentration after the addition of known amounts of analytes into a river and spring water samples or soil, blood or vegetable samples. The results were summarized in Table 4. Satisfactory recoveries were obtained for spiked analyte ions. The recoveries were higher than 95%, thus confirming the accuracy of the presented procedure (Table 5).

4. Conclusion

The ligand loaded on activated carbon is sensitive and accurate method for determination of trace amounts of nickel, cobalt and copper ions in low concentrations. The results presented in this paper have confirmed the applicability of the separation and preconcentration of metals. This method is simple and there is no necessity for elaborate cleanup procedure. Each column can be used for at least 10 successive analyses without considerable change in metal ions recovery. After the use by passing sim-

ple solution of ligand the column could be used for at least 100 times.

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