

## Development of a selective and sensitive flotation method for determination of trace amounts of cobalt, nickel, copper and iron in environmental samples

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### Abstract

A simple, selective and rapid flotation method for the separation–preconcentration of trace amounts of cobalt, nickel, iron and copper ions using phenyl 2-pyridyl ketone oxime (PPKO) has been developed prior to their flame atomic absorption spectrometric determinations. The influence of pH, amount of PPKO as collector, type and amount of eluting agent, type and amount of surfactant as floating agent and ionic strength was evaluated on the recoveries of analytes. The influences of the concomitant ions on the recoveries of the analyte ions were also examined. The enrichment factor was 93. The detection limits based on 3 sigma for Cu, Ni, Co and Fe were 0.7, 0.7, 0.8, and 0.7 ng mL<sup>-1</sup>, respectively. The method has been successfully applied for determination of trace amounts of ions in various real samples.

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### 1. Introduction

The direct determination of heavy metals at trace level in saline samples by flame atomic absorption spectrometer (FAAS) or electrothermal atomic absorption spectrometer (ETAAS) [1–4] has been failed due to particularly their low concentrations and matrix effects. Many authors indicated that matrix interferences are possible and to overcome them, the addition of different matrix modifiers [5,6], as well as the use of preconcentration–separation procedures [7–13]. Preconcentration and separation techniques, such as liquid–liquid extraction, ion exchange, co-precipitation, cloud point extraction, solid phase extraction, etc. can solve these problems and lead to a higher confidence level and easy determination of the trace elements [7–17]. Some of these methods suffer from inconveniences such as, lengthy separation, limitation of the volume of sample solution investigated, time consuming, multi stage, lower enrichment factor and consumption of organic harmful

solvents. These problems can be overcome by replacement of filtration or centrifugation by flotation. The major advantages of the flotation preconcentration method are the rapidity in addition to excellent recoveries of analytes. The equipments necessary for flotation preconcentration are simple and inexpensive. The small amount of a surfactant and the tiny air bubbles require to perform the proper flotation prevent serious contamination risks, which could be manifested by the high blank value. Because the physical and chemical properties of aragonite aqueous solution are similar to those of the natural waters with higher water hardness, a method of flotation is applied as the second way to eliminate the matrix effects [18–21]. Several methods have been developed for the flotation of heavy metal ions [22–27].

Based on the spectrophotometric and potentiometric studies in non-aqueous and water sample, we revealed that phenyl 2-pyridyl ketone oxime (PPKO) forms very stable and almost water insoluble 2:1 (ligand to metal ratio) complexes with a number of transition metal ions such as Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> and Fe<sup>3+</sup>. According to our literature survey, there is no work on the flotation of heavy metal ions by using PPKO.

The purpose of the presented work is preconcentration by flotation of copper(II), cobalt(II), nickel(II) and iron(III) using

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PPKO. 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 metals were performed with a Shimadzu 680 AA spectrometer equipped with a hollow cathode lamp and a deuterium background corrector, at respective wavelengths 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

All chemicals were analytical reagent grade and were used without further purification. Acids and bases were of the highest purity available from Merck and were used as received. Doubly distilled deionized water was used throughout. All the plastic and glassware were cleaned by soaking in dilute  $\text{HNO}_3$  (1 + 9) and were rinsed with distilled water prior to use. The element standard solutions used for calibration were produced by diluting a stock solution of  $1000 \text{ mg L}^{-1}$  of the given element supplied by Sigma and Aldrich. Stock solutions of diverse elements were prepared from high purity compounds. The pH adjustment was done by addition of dilute nitric acid or sodium hydroxide to phosphate solution for preparing the desired pH buffer solution. The ligand PPKO was synthesized according to literature [28].

### 2.3. Potentiometric studies

The pH measurement method for speciation of different forms of complexes between analyte ions and PPKO were carried out according to previous publication [29,30]. Each time, two separate solutions were prepared as follow: the first solution contains, 5 mL  $0.02735 \text{ mol L}^{-1}$  PPKO, 10 mL  $0.5 \text{ mol L}^{-1}$  potassium nitrate, 2 mL  $0.1 \text{ mol L}^{-1}$  hydrochloric acid and 33 mL water; the second solution contain 5 mL  $0.02735 \text{ M}$  PPKO, 5 mL  $0.01346 \text{ mol L}^{-1}$   $\text{MCl}_2$  or  $\text{M}(\text{NO}_3)_3$ , 10 mL  $0.5 \text{ mol L}^{-1}$  potassium nitrate, 2 mL hydrochloric acid and 28 mL water. Both solutions were titrated potentiometrically with  $0.0965 \text{ mol L}^{-1}$  sodium hydroxide. From the titration curve of the first solution the acidic dissociation constants of the ligand and from the second titration curve the formation constant of different form of complex were evaluated.

### 2.4. Flotation–separation procedure

A combined glass electrode was immersed into a 1 L beaker of sample solution containing  $0.5 \mu\text{g mL}^{-1}$  of each ion. After 6 mL of saturated  $\text{KNO}_3$  solution and 2 mL of 1% (w/w) solution of SDS and 5 mL of  $0.01 \text{ mol L}^{-1}$  of PPKO were added, the pH of medium was carefully adjusted to 8.5 with NaOH solution. After stirring for 15 min, the mixture was diluted to 750 mL and then

transferred quantitatively to the flotation cell (type 1) and filled to the 750 mL mark with DDW. An air stream ( $50 \text{ mL min}^{-1}$ ) was kept flowing for 2–4 min to raise the foam layer to the water surface. A foamy layer was thus obtained and the aqueous solution in the cell became clear. Then the glass pipette tube was immersed into the cell through the foam layer and a water sample (10 mL) was sucked off. The floated layer was dissolved in  $3.0 \text{ mol L}^{-1}$  nitric acid in methanol and analyzed by FAAS.

### 2.5. Application to real samples

Analysis of water sample was performed as following: 400 mL of sample was poured in a beaker and 8 mL concentrated  $\text{HNO}_3$  and 3 mL of  $\text{H}_2\text{O}_2$  of (30%) for elimination and decomposition of organic compound were added. The samples, while stirring was heated to one-tenth volume. After adjustment of samples pH to desired value the flotation were performed according to procedure given in Section 2.4.

Homogenized soil sample 20 g or blood sample 20 mL was weighed accurately and in a 200 mL beaker was digested in the presence of an oxidizing agent with addition of 10 mL concentrated  $\text{HNO}_3$  and 2 mL  $\text{HClO}_4$  70% was added and heated for 1 h. The content of beaker was filtered through a Whatman No. 40 filter paper and diluted to 250 mL with distilled water. Then its pH was adjusted to 8.5 and the procedure given in Section 2.4 was applied.

Spinach sample was purchased from Gachsaran, Iran. Afterwards, they were taken in small mesh. A 40 g sample was heated in silica crucible for 3 h on a hot plate and the charred material was transferred to furnace for overnight heating at  $650^\circ\text{C}$ . The residue was cooled, treated with 10.0 mL concentrated nitric acid and 3 mL 30%  $\text{H}_2\text{O}_2$  again kept in furnace for 2 h at the same temperature so that no organic compound traces are left. The final residue was treated with 3 mL concentrated hydrochloric acid and 3 mL 70% perchloric acid and evaporated to fumes, so that all the metals change to respective ions. The solid residue was dissolved in water, filtered and by keeping the pH at 8.5 made up to 25 mL. Then the procedure given in Section 2.4 was applied.

## 3. Results and discussion

In preliminary experiments, our potentiometric studies revealed that PPKO could form a fairly stable and selective complex with copper, nickel, iron and cobalt ions with mole ratio of M:L of 1:2. The possible complexation form and their stability between these ions and PPKO has been presented in Fig. 1 show that type and percent of major form of complexes has strong dependency to pH and the corresponding data for their stability constant in binary system of them are displayed in Table 1. This reagent has sufficient hydrophobic nature to be used as a complexing agent in flotation extraction. As it can be seen from the results in Fig. 1 and Table 1, in the alkaline pH only  $\text{M}(\text{PPKO})_2$  with abundance about 100% would be formed, decreasing pH lead to protonation of PPKO and extremely reduce its ability for complexation with ions.

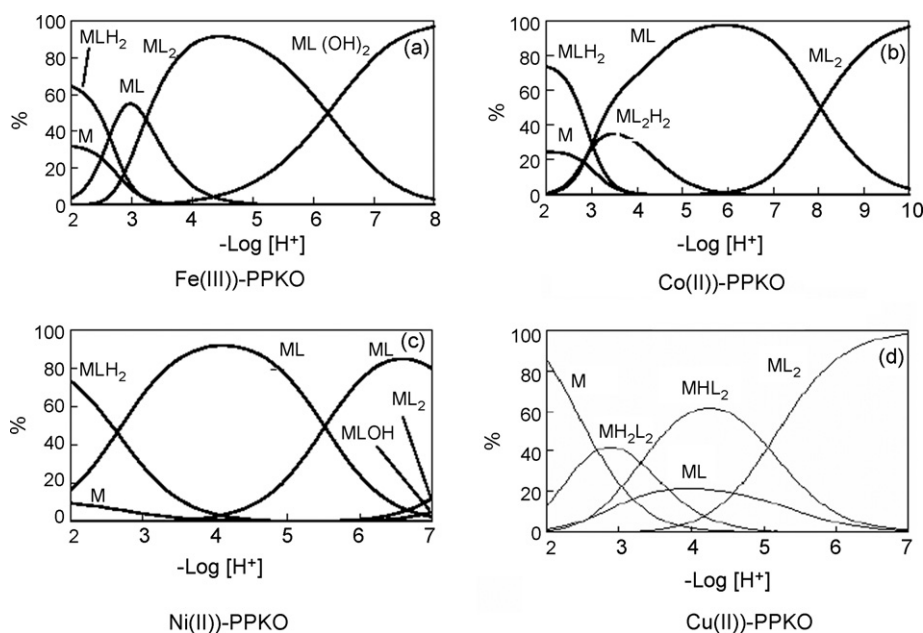


Fig. 1. The nature of different form of complex of analytes with PPKO.

The presence of 2-pyridyl ketone oxime ligand and hydroxyl group results in selective interaction with these ions while oxygen atoms of the ligand mostly interact with these ions as a soft acid through ion–dipole interactions, while all resulting in fast complexation and higher sensitivity.

We decided to examine its capability as a suitable reagent for sensitive and selective flotation of copper, nickel, iron and cobalt ions. The influence of affective parameters including pH, amount of PPKO, type and amount of surfactant on sensitivity were examined.

Table 1

Logarithm of cumulative stability constants for the interaction of  $H^+$  and  $Fe^{3+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$  and  $Cu^{2+}$  with the PPKO at 25 °C

System	<i>m</i>	<i>l</i>	<i>h</i>	Log $\beta$
Co(II)–PPKO	1	1	0	12.54
	1	1	2	18.55
	1	2	0	18.89
	1	2	1	22.20
	1	2	2	30.75
Ni(II)–PPKO	1	1	0	10.72
	1	1	1	16.24
	1	1	2	18.86
	1	2	0	16.94
	1	2	1	20.65
	1	1	–1	2.78
Fe(III)–PPKO	1	1	0	13.08
	1	1	2	18.36
	1	2	0	25.03
	1	1	–2	4.39
Cu(II)–PPKO	1	1	0	11.53
	1	2	0	21.45
	1	2	1	26.51
	1	2	2	29.81

### 3.1. Effect of pH

The influences of pH on the quantitative recoveries of copper, nickel, iron and cobalt ions by the presented flotation method were investigated at the pH range of 2–10 with model solutions. Due to possible hydroxide formation of the analytes, the investigation on the pH values higher than 10 were not carried out. The results are given in Fig. 2. In the pH range of 8.0–9.0, PPKO is de-protonated and its complexes with the metal ions of interest have higher stability. Quantitative recoveries were obtained in the pH range of 8.0–9.0. In subsequent experiments, adjustment of pH on 8.5 was recommended.

### 3.2. Effect of PPKO concentration on recoveries

The effects of the concentration of PPKO on the recoveries of analytes was evaluated over the range 0.4–7.0 mmol PPKO. Seven hundred and fifty milliliters of a solution contain-

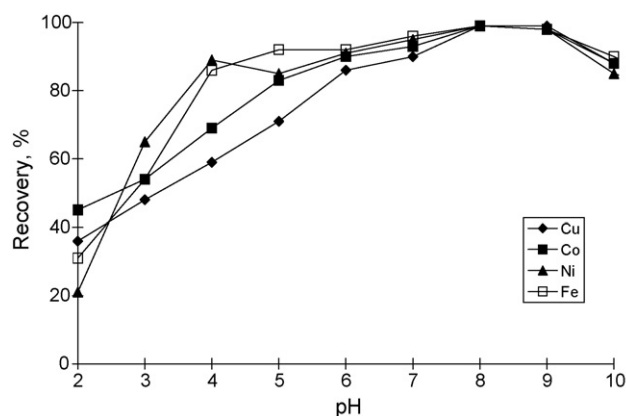


Fig. 2. Effect of pH on ions recoveries.

Table 2

Effect of type of surfactant on sensitivity, pH  $8.5 \pm 0.5$ , 5.0 mmol PPKO, 0.0027% (w/v) of each surfactant

Surfactant	Recovery (%)			
	Cu	Co	Ni	Fe(III)
CTAB	Foam—no floated	Foam—no floated	Foam—no floated	Foam—no floated
DTAB	Foam—no floated	Foam—no floated	Foam—no floated	Foam—no floated
SDS	98.4	98.6	98.5	98.3
Triton X-100	36.4	43.7	34.9	32.4
No surfactant	30.3	32.1	25.6	24.8

ing analyte ions in 0.005% (w/v) SDS with various amounts of PPKO was subjected to the flotation preconcentration process. The results are shown in Fig. 3. Quantitative flotation efficiency was achieved for a PPKO concentration of 3.0–7.0 mmol, therefore 5.0 mmol concentrations was chosen for subsequent experiments. It is worth mentioning that the presence of excess amounts of the ligands revealed no adverse effect on the flotation process. This is an advantageous point, as the procedure could thus be applied to the analysis of these ions in real samples.

### 3.3. Selection of surfactant

A number of tests under optimized conditions were carried out to find suitable surfactant for quantitative recoveries of analytes. The results are presented in Table 2. Cationic surfactants DTAB and CTAB foamed very well over the whole pH range investigated and a copious white scum was formed at the top of the aqueous phase, but the color precipitate of coagulated  $ML_2$  was not separated by flotation and remained in water. The flotation by use of the non-ionic tenside Triton X-100 was also ineffective. The anionic surfactants were more effective. The ions flotation recoveries obtained by SDS within the optimal pH were greater than 95%. The anionic surfactant, SDS, was chosen because of its commercial availability in a high purified homogeneous form, low toxicological properties and cost.

The flotation efficiency was evaluated using SDS concentrations ranging from 0.001% to 0.1% (w/v). The quantitative recovery values for copper, iron, nickel and cobalt ions were obtained with 0.005% (w/v) SDS. By decreasing the surfactant concentration to 0.0002% (w/v) the recovery was reduced. The

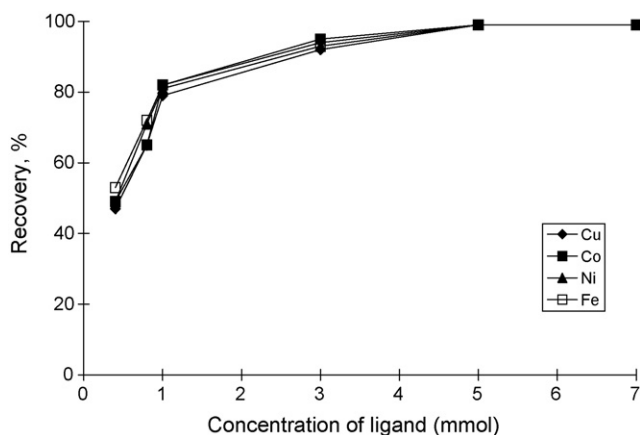


Fig. 3. The effect of amount of ligands on copper and lead ion recoveries.

recovery values were also decreased for a higher SDS concentration (0.1%, w/v). In addition, the viscosity of the surfactant-rich phase increases, leading to poor sensitivity [29–31]. At lower SDS concentrations (below 0.005%, w/v), the preconcentration efficiency of the complex was very low, probably due to assemblies that were inadequate to quantitatively entrap the hydrophobic complex and float the complex [31,32]. Since, 0.005% (w/v) of SDS showed the highest copper, nickel, iron and cobalt ions recovery; a surfactant concentration of 0.005% (w/v) was selected.

### 3.4. Effect of eluting solutions

Since the surfactant-rich phase foam obtained after flotation is rather viscous, experiments were carried out in order to choose a proper eluent for the retained ions on the foam layer and respective results are presented in Table 3. These solutions were directly introduced into the nebulizer of atomic absorption spectrometer. The ions were stripped with varying volumes of various concentrations of different acids containing methanol. Quantitative recoveries for analyte ions were obtained with. Optimum volume for  $3.0 \text{ mol L}^{-1}$  nitric acid in methanol with respect to quantitative recoveries of the analytes was 8 mL. An 8 mL volume of  $3.0 \text{ mol L}^{-1}$  nitric acid in methanol was therefore used throughout the remaining experiments.

### 3.5. Effect of $KNO_3$ as electrolyte

$KNO_3$  was investigated as electrolyte in the concentration range from 0.5 to saturated and the highest copper, nickel, iron and cobalt ions recovery was obtained at  $1.5 \text{ mol L}^{-1}$   $KNO_3$  concentration. The recovery decreased considerably with increasing  $KNO_3$  concentrations ( $>1.5 \text{ mol L}^{-1}$ ). This effect might be explained by the additional surface charge when the

Table 3

The effect of eluting solution on the recoveries of the analytes

Eluting condition	Recovery (%)			
	Cu	Ni	Co	Fe(III)
$3 \text{ mol L}^{-1} \text{ HCl}^a$	97.5	99.7	89.4	94.6
$1.0 \text{ mol L}^{-1} \text{ HNO}_3^a$	63.2	65.6	67.4	68.6
$2.0 \text{ mol L}^{-1} \text{ HNO}_3^a$	79.8	90.2	86.4	85.9
$2.5 \text{ mol L}^{-1} \text{ HNO}_3^a$	95.2	96.4	94.9	93.7
$3.0 \text{ mol L}^{-1} \text{ HNO}_3^a$	98.8	99.3	98.6	98.6
$3 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4^a$	49.3	51.5	50.3	54.2

<sup>a</sup> Solutions are prepared in methanol.

Table 4  
Effects of the matrix ions on the recoveries of the examined metal ions ( $N=3$ )

Ion	Added as	Tolerance limit (mg L <sup>-1</sup> )
Cl <sup>-</sup> , K <sup>+</sup> , Na <sup>+</sup> , Mg <sup>2+</sup> , HCO <sub>3</sub> <sup>-</sup>	KCl, NaCl, MgCl <sub>2</sub> , NaHCO <sub>3</sub>	1000
Pb <sup>2+</sup>	PbCl <sub>2</sub>	300
PO <sub>4</sub> <sup>3-</sup>	Na <sub>3</sub> PO <sub>4</sub>	1000
Zn <sup>2+</sup> , Cd <sup>2+</sup> , Ba <sup>2+</sup> , Ca <sup>2+</sup> , Ag <sup>+</sup> , Al <sup>3+</sup> , Cr <sup>3+</sup> , Hg <sup>2+</sup>	Nitrate salts	600

KNO<sub>3</sub> concentration is very high, thus changing the molecular structure of the surfactant and consequently the micelle formation process. It is necessary to emphasize that different blank solutions were also evaluated and no significant signal was obtained. In this way, 1.5 mol L<sup>-1</sup> KNO<sub>3</sub> was used in all further experiments.

### 3.6. Effect of foreign ions

Interferences studied were those related to the preconcentration step, cations that may react with PPKO or species that may react with analytes and decrease the extraction efficiency. Flotation procedures for trace elements in the high salt content samples can be strongly affected by the matrix constituents of the sample [24–27]. Before the application of the preconcentration method for the determination of analyte ions in samples with complicated matrix, the influences of some alkaline and earth alkaline ions on the recoveries of the analyte ions were also investigated. The results are given in Table 4. The tolerance limit is defined as the ion concentration causing a relative error smaller than  $\pm 5\%$  related to the preconcentration and determination of analytes. Analyte ions were quantitatively recovered at large amounts for alkaline and earth alkaline ions and some anions.

Table 5  
Recovery studies of trace metal ions from some real samples

Ion	Added ( $\mu\text{g g}^{-1}$ )	Found ( $\mu\text{g g}^{-1}$ )	R.S.D. (%)	Recovery (%)
<b>Spinach</b>				
Co	0	68.6	1.2	–
	100	170.1	0.9	101.5
Ni	0	74.9	1.3	–
	100	177.6	0.8	102.7
Cu	0	78.6	1.2	–
	100	180.1	0.9	101.5
Fe	0	89.6	1.2	–
	100	192.3	0.9	102.7
<b>Soil</b>				
Co	0	0.256	1.4	–
	0.4	0.662	1.0	101.5
Fe	0	0.374	1.4	–
	0.4	0.618	1.1	102.8
Ni	0.0	0.249	1.3	–
	0.4	0.654	0.8	101.3
Cu	0	0.284	1.3	–
	0.4	0.693	1.0	102.3

### 3.7. Characteristics of the method

Calibration graphs were obtained by flotation of 750 mL of a sample containing known amounts of analytes ions under the experimental conditions. Under the specified experimental conditions the calibration curves for Ni and Co were linear from 15 to 850 and for iron and copper from 10 to 900 ng mL<sup>-1</sup>. To determine the relative standard deviation (R.S.D.%) of the method, 10 similar solution containing 0.2  $\mu\text{g mL}^{-1}$  all ions were floated, i.e. extracted by the recommended procedure, and then the concentrations of cobalt, iron, nickel and copper ions were determined by FAAS. The R.S.D.% was in the range of 0.8–1.0%.

The detection limit of the method (DL) was estimated as three times the standard deviation of the blank. The values of DL for cobalt, iron, nickel and copper ions were calculated as 0.8 ng mL<sup>-1</sup>, 0.7 ng mL<sup>-1</sup>, 0.7 ng mL<sup>-1</sup>, and 0.7 ng mL<sup>-1</sup>, respectively. The preconcentration factor is calculated by the ratio of the highest sample volume (750 mL) and the lowest final volume (8 mL). The preconcentration factor was 93.

### 3.8. Applications

The procedure was applied to the determination of copper, nickel and cobalt ions in different samples, including spring water, tap water, spinach, soil and blood sample and spinach samples by standard addition method. The results are presented

Table 6  
Recovery of trace elements from spiked environmental samples after application of presented flotation procedure

Ion	Added ( $\mu\text{g L}^{-1}$ )	Found ( $\mu\text{g L}^{-1}$ )	R.S.D. (%)	Recovery (%)
<b>Spring water</b>				
Co	0	19.7	1.2	–
	50	71.1	1.0	102.8
Ni	0	20.3	1.3	–
	50	71.9	1.0	103.2
Cu	0	32.8	1.2	–
	50	83.8	0.9	102.0
Fe	0	39.6	1.2	–
	50	91.6	0.8	104.0
<b>Tap water</b>				
Co	50	51.3	1.2	102.3
	200	203.6	0.8	99.8
Ni	50	51.8	0.8	100.6
	200	204.1	0.9	100.7
Cu	50	48.8	1.1	97.6
	200	202.3	0.8	101.2
Fe	50	51.6	1.1	103.2
	200	203.7	0.9	101.9
<b>Blood</b>				
Co	0	46.7	1.4	–
	50	98.7	1.0	104.6
Ni	0	49.8	1.5	–
	50	101.4	1.0	103.2
Cu	0	58.9	1.5	–
	50	110.1	1.2	102.4
Fe	0	64.3	1.4	–
	50	115.9	1.0	103.2

Table 7  
Comparative data from recent papers on preconcentration studies

Analytes	Method and instrumental detection	PF	DL ( $\mu\text{g L}^{-1}$ )	R.S.D. (%)	Reference
Co(II)	SPE on surfactant-coated alumina/AAS	100	–	1.4–4.0	[37]
Ni(II)	SPE on surfactant-coated alumina/AAS	300	40	2.4	[38]
Cu(II), Co(II)	CPE/CE	15.9–16.3	0.12–0.26	0.74–1.8	[39]
Cd(II)	SPE on naphthalene/DDP	40	70	0.98	[40]
Cd(II)	SPE on surfactant-coated alumina/AAS	100	0.024	1.6	[41]
Cu(II), Cd(II), Pb(II)	SPE on Amberlite XAD-2/AAS	50	0.8–23.2	<5	[43]
Ni(II)	SPE on aminocarboxylic amphoteric resin/DRS	–	50	<5	[44]
Co(II), Ni(II), Co(II), Fe(III)	Flotation with 2-pyridyl ketone oxime (PPKO)/AAS	93	0.7–0.8	<1	Present work

DL: detection limit, R.S.D.%: relative standard deviation, %PF: preconcentration factor, CPE: cloud point extraction, SPE: solid phase extraction, CE: capillary electrophoresis, AAS: atomic absorption spectrometry, DDP: differential pulse polarography, and DRS: diffuse reflection spectroscopy.

in Tables 5 and 6. The recovery of spiked samples is satisfactory reasonable and was confirmed using addition method, which indicate the capability of the system in the determination of analytes in natural water samples.

#### 4. Conclusion

The flotation of copper, nickel iron and cobalt ions with PPKO into SDS has been investigated. Analytes extractions were shown to be achieved with PPKO due to the hydrophobic complex compound formation. The sensitivity, metrological characteristics, ecological safety, simplicity, and convenience of the suggested procedure are competitive with respect to the methods based on the extraction with organic solvents.

The method presented in this study is most promising for the analytes as the preconcentration factor is 93. The preconcentration factor achieved with presented procedure is superior to some preconcentration procedures including cloud point extraction, solid phase extraction, electroanalytical techniques [2,3,6,16,24,33–36]. The detection limits of analytes are superior to those of preconcentration techniques for analyses [33–44]. The matrix effects with the method were reasonably tolerable. The good features of the proposed method showed that it is a convenient and low cost one. Also the method is relatively rapid as compared with previously reported procedures for the enrichment of analytes (Table 7).

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