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Homogeneous Liquid-Liquid Extraction and Determination of Cobalt, Copper, and Nickel in Water Samples by Flame Atomic Absorption Spectrometry

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Homogeneous Liquid–Liquid Extraction and Determination of Cobalt, Copper, and Nickel in Water Samples by Flame Atomic Absorption Spectrometry

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Abstract: A simple and effective homogeneous liquid–liquid extraction method has been used for the simultaneous extraction and preconcentration of cobalt, copper, and nickel after the formation of complex with 4-benzylpiperidinedithiocarbamate potassium salt (K-4-BPDC), and later they were determined by flame atomic absorption spectrometry (FAAS) using (water/tetrabutylammonium ion (TBA^+)/chloroform) as a ternary component system. The phase separation phenomenon occurred by an ion-pair formation of TBA^+ and perchlorate ion. After the optimization of complexation and extraction conditions ($[\text{K-4-BPDC}] = 2.0 \times 10^{-4}$ mol l^{-1}, $[TBA^+] = 2.0 \times 10^{-2}$ mol l^{-1}, $[CHCl_3] = 60.0$ μl, $[ClO_4^-] = 2.0 \times 10^{-2}$ mol l^{-1} and pH = 6.0), a preconcentration factor of 200 was obtained for only 10 ml of the sample.

The analytical curves were linear in the range of 20–1500, 15–2000, 35–1600 μg l^{-1} and the limits of detection were 10, 5, and 15 μg l^{-1} for Co^{2+}, Cu^{2+}, and Ni^{2+},

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respectively. The proposed method was applied for the extraction and determination of Co^{2+}, Cu^{2+}, and Ni^{2+} in natural water samples with satisfactory results.

Keywords: Homogeneous liquid–liquid extraction, cobalt, copper, nickel, FAAS

INTRODUCTION

Several analytical techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS), are available for the determination of trace metals with sufficient sensitivity in most applications. However, the determination of trace metal ions in natural waters is difficult due to various factors, particularly their low concentrations and matrix effects.

Preconcentration and separation can solve these problems and lead to a higher confidence level and an easy determination of the trace elements by less sensitive, but more accessible instrumentation such as flame atomic absorption spectrometry (FAAS). There are many methods of preconcentration and separation such as liquid–liquid extraction (LLE) (1, 2), ion-exchange techniques (3, 4), co-precipitation (5, 6), sorption on various adsorbents such as activated carbon (7, 8), Amberlite XAD resins (9, 10), and other sorbents (11, 12). However, these methods which are typically time-consuming and labor-intensive, have multi-step procedures prone to loss of analytes and need high volumes of samples. Therefore, simple, rapid, and efficient techniques that can be used easily are required.

Homogeneous liquid–liquid extraction (HLLE) is an excellent method that extracts the desired solute existing in the homogeneous solution into the water-immiscible phase by each kind of phase separation phenomenon. In homogeneous liquid–liquid extraction, the initial condition (before phase separation) is homogeneous solution; namely, there is no interface between the water phase and the organic solvent phase. In other words, the surface area of the interface is infinitely large initially. Accordingly, no vigorous mechanical shaking is necessary. The procedure is simple, rapid, and requires only the addition of the reagents (13).

The methods, which use phase separation that depends upon the temperature changes of the water-propylene carbonate system (14) or the salt effect in the water–acetonitrile system, etc., have been already reported (15). Recently, a homogeneous liquid–liquid extraction method using a ternary solvent system has been developed (13); it was applied as a simple and high-powered preconcentration for the instrumental analysis (16–19). Similarly, the methods based on the pH dependent phase separation, which used a water/acetic acid/chloroform ternary solvent system (16) and water/pyridine/ethyl chloroacetate system (20) have been reported. However, in these methods, the widespread application for target analytes has been limited by the inconvenient pH condition in extraction.

Recently, a pH independent phase separation phenomenon using the ion-pair formation of tetrabutylammonium ion (TBA^+) and perchlorate (ClO_4^-) in homogeneous solution (water/TBA^+/chloroform) has been reported. In this method, chloroform is solvated by TBA^+ and dissolves in water. When $NaClO_4$ is added to the homogeneous solution that consists of a water/TBA^+/chloroform, the solvation effect of TBA^+ is excluded by the ion-pair formation of TBA^+ and ClO_4^-. Therefore, the chloroform in the homogeneous aqueous solution is postulated to form water-immiscible chloroform in aqueous solution by the phase separation. This method was applied for the extraction and determination of iron (II) in water sample (21).

In the present work, homogenous liquid–liquid extraction, using 4-benzylpiperidineditiocarbamate potassium salt (K-4-BPDC) as a complexing agent (Scheme 1) for Co^{2+}, Cu^{2+}, Ni^{2+}, and water/TBA^+/chloroform ternary component system, was applied to the separation and preconcentration of cobalt, copper, and nickel in natural water samples and their determination by flame atomic absorption spectrometry (FAAS).

EXPERIMENTAL

Apparatus

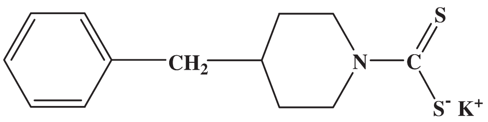
The experiments were performed using a Shimadzu atomic absorption spectrometer (model 6300). Shimadzu hollow cathode lamps were applied as the radiation sources.

Phase separation was assisted using a centrifuge (Centurion Scientific 1020D).

The pH of the solutions was controlled by Metrohm pH-meter model 713.

Reagents and Solutions

All reagents used were of analytical grade. Stock standard solutions of cobalt, copper, and nickel at a concentration of 1000.0 mg l^{-1} were prepared by dissolving appropriate amounts of $Co(NO_3)_2$, 6 H_2O, $Ni(NO_3)_2$, 6 H_2O, and



Scheme 1. Structure of 4-benzylpiperidinedithiocarbamate potassium salt (K-4-BPDC).

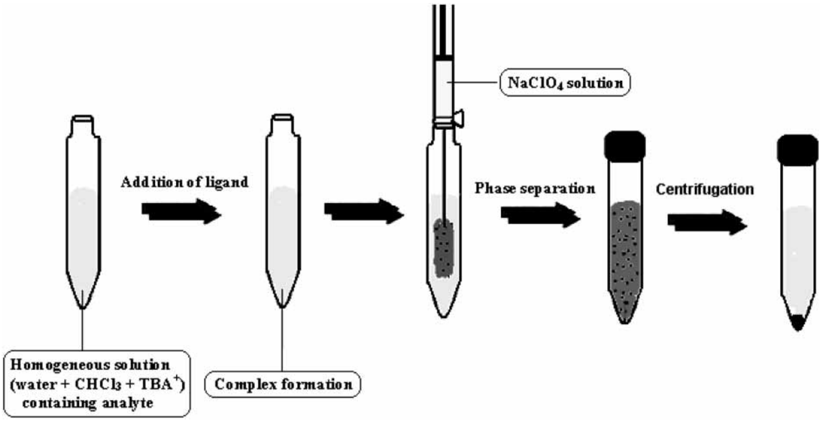
$Cu(NO_3)_2$, $3H_2O$ (Merck) in deionized doubly distilled water. Before each investigation, a series of metal standard solutions were prepared by diluting these stock solutions. 4-Benzylpiperidinedithiocarbamate potassium salt (K-4-BPDC) was prepared according to the procedure described by Andac et al. (22). Fresh 1.0×10^{-2} mol l^{-1} solution of K-4-BPDC was prepared daily by dissolving an appropriate amount of reagent in deionized water.

Chloroform and ethanol were of analytical grade from Merck. A stock standard buffer solution, 0.1 mol l^{-1}, was prepared by dissolving an appropriate amount of sodium acetate and hydrochloric acid. Other reagents used were: tetrabutyl ammonium bromide (Merck), nitric and hydrochloric acid (Merck), sodium hydroxide (Merck), and sodium perchlorate (Merck).

The pipettes and vessels used for trace analysis were kept in 10% nitric acid for at least 24 h and subsequently washed four times with deionized water before use.

Recommended Procedure

A 10 ml homogeneous solution (water/TBA^+/chloroform) containing Co^{2+} (20–1500 μg l^{-1}), Cu^{2+} (15–2000 μg l^{-1}), and Ni^{2+} (35–1600 μg l^{-1}), chloroform (60.0 μl), K-4-BPDC (2.0×10^{-4} mol l^{-1}), TBA^+ (2.0×10^{-2} mol l^{-1}) and 1.0×10^{-3} mol l^{-1} sodium acetate (pH = 6.0) were kept in a thermostated bath at 25°C for 5 min. A $NaClO_4$ aqueous solution (2.0×10^{-2} mol l^{-1}) was added and the mixture was gently shaken. The mixture was then centrifuged for 3 min at 4000 rpm (Scheme 2). The sedimented phase (50 μl) was separated using a 100 μl



Scheme 2. Experimental scheme of preconcentration of metal cations from water sample by HLLE method.

micro-syringe and diluted to 2.0 ml with ethanol. The samples were introduced into the flame by conventional aspiration.

RESULTS AND DISCUSSION

Effect of pH

Because pH plays a unique role in metal-chelate formation and subsequent extraction, the pH was the first critical parameter evaluated concerning its effect on the determination of cobalt, copper, and nickel. The phase separation phenomenon does not depend upon the pH because this phenomenon occurs by the ion-pair formation of TBA^+ and ClO_4^- (21). Figure 1 shows the influence of pH on the extraction recovery of cobalt, copper, and nickel.

It was found that for copper and cobalt in the pH range of 4.0–10.0 and nickel in the range of 5.0–10.0 extraction was quantitative. At lower pH values recoveries decrease probably because of analytes release as a compotation with the excess of H^+. Hence, a middle range of pH at 6.0 was chosen for these analytes.

Effect of the Concentration of K-4-BPDC

The effect of the concentration of K-4-BPDC on the extraction of cobalt, copper, and nickel is shown in Fig. 2. The molar ratios of cobalt, copper, and nickel complexes with this complexing agent (4-BPDC) are 2:1. For the

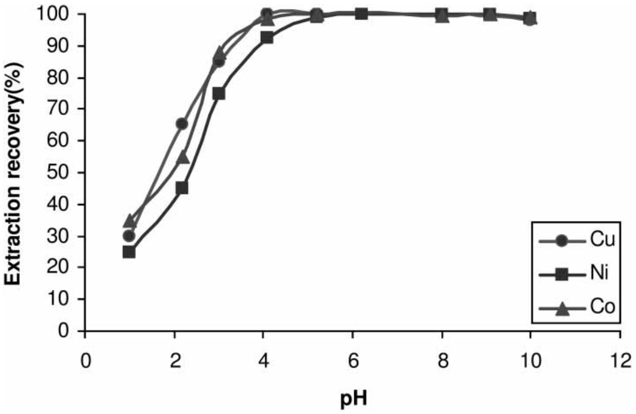


Figure 1. Effect of pH on the extraction recovery of cobalt, copper, and nickel. Conditions: Co^{2+}, Cu^{2+}, and Ni^{2+} 100.0 $\mu g\,l^{-1}$; K-4-BPDC 2.0×10^{-4} mol l^{-1}; TBA^+ 2.0×10^{-2} mol l^{-1}; $CHCl_3$ 60.0 µl and $NaClO_4$ 2.0×10^{-2} mol l^{-1}.

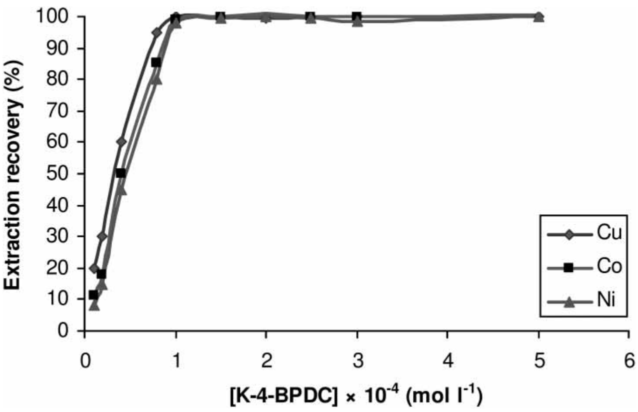


Figure 2. Effect of K-4-BPDC concentration on the extraction recovery of cobalt, copper, and nickel. Conditions: Co^{2+}, Cu^{2+}, and Ni^{2+} 100.0 μg l^{-1}; TBA^+ 2.0×10^{-2} mol l^{-1}; $CHCl_3$ 60.0 μl; $NaClO_4$ 2.0×10^{-2} mol l^{-1} and pH = 6.0.

three cations studied, 10 ml of a solution containing 1.0 μg of each cation at a medium buffer of pH 6.0 containing various amounts of K-4-BPDC were subjected to HLLE process. The yield increases up to a K-4-BPDC concentration of 1.0×10^{-4} mol l^{-1} and reaches near quantitative extraction efficiency. A concentration of 2.0×10^{-4} mol l^{-1} was chosen to account for other extractable species.

Effect of TBA^+ Concentration

In this method, TBA^+ concentration has a critical effect on increasing the solubility of chloroform in water to produce a homogeneous solution. In order to investigate the optimum amount of TBA^+ in the quantitative homogeneous liquid–liquid extraction of cobalt, copper, and nickel ions, the extraction of these ions from 10 ml of the sample solutions under the optimal experimental conditions was conducted by varying the concentration of TBA^+ (Fig. 3).

As seen, the extraction of cobalt, copper, and nickel is quantitative above 2.0×10^{-2} mol l^{-1} of TBA^+. Hence, subsequent homogeneous liquid–liquid extraction experiments were carried out with 2.0×10^{-2} mol l^{-1} of TBA^+. At lower concentrations, the system remains in two-phase condition and the extraction is not quantitative.

Effect of ClO_4^- Concentration

The phase separation phenomenon and the volume of sedimented chloroform are dependent on ClO_4^- concentration. In order to investigate the optimum

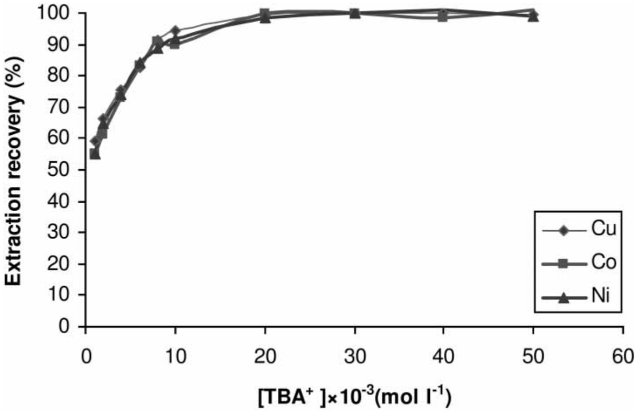


Figure 3. Effect of TBA$^+$ concentration on the extraction recovery of cobalt, copper, and nickel. Conditions: Co^{2+}, Cu^{2+}, and Ni^{2+} 100.0 µg l^{-1}; K-4-BPDC 2.0×10^{-4} mol l^{-1}; CHCl$_3$ 60.0 µl; NaClO$_4$ 2.0×10^{-2} mol l^{-1} and pH = 6.0.

amount of ClO$_4^-$ in the quantitative homogeneous liquid–liquid extraction of cobalt, copper, and nickel, the extraction of these ions from 10 ml of the sample solutions under the optimal experimental conditions was conducted by varying the concentration of ClO$_4^-$ (Fig. 4).

As seen, the extraction of cobalt, copper, and nickel is quantitative above 2.0×10^{-2} mol l^{-1} of ClO$_4^-$. In addition, above this concentration the volume of sedimented chloroform remained constant. Hence, subsequent homogeneous liquid–liquid extraction experiments were carried out with 2.0×10^{-2} mol l^{-1} of ClO$_4^-$.

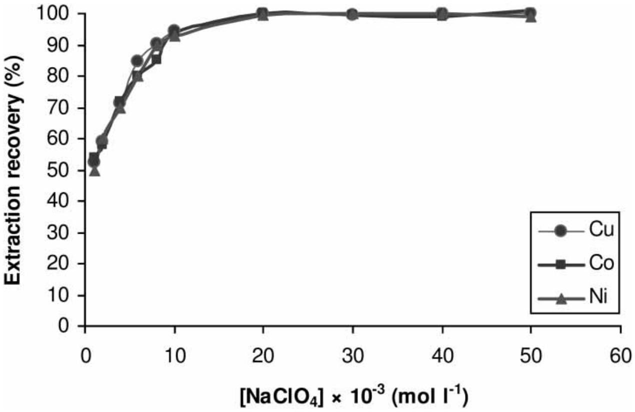


Figure 4. Effect of ClO$_4^-$ concentration on the extraction recovery of cobalt, copper, and nickel. Conditions: Co^{2+}, Cu^{2+}, and Ni^{2+} 100.0 µg l^{-1}; K-4-BPDC 2.0×10^{-4} mol l^{-1}; CHCl$_3$ 60.0 µl; TBA$^+$ 2.0×10^{-2} mol l^{-1} and pH = 6.0.

Effect of Volume of Chloroform

In this extraction method, the extraction efficiency and concentration factor are strongly dependent on the volume of the sedimented chloroform phase. Therefore, the relationship between the volume of added chloroform and the concentration factor and extraction efficiency was investigated. The concentration factor was calculated as the volume ratio (Va/Vs) of the aqueous phase (Va) and sedimented phase (Vs) after phase separation.

Figure 5 shows the influence of the volume of added chloroform on the extraction efficiency and concentration factor of cobalt (the results of this investigation for copper and nickel was similar to cobalt). As seen, the extraction of cobalt, copper, and nickel was quantitative above 60.0 μl of $CHCl_3$. Hence, In order to achieve a maximum concentration factor, 60.0 μl of added $CHCl_3$ was selected.

Effect of Buffer Concentration

The influence of buffer amount was investigated in which the other experimental variables remained constant. The results have shown that above the 1.0×10^{-3} mol l^{-1} buffer solution, no obvious variation took place in the extraction yield. Thus, 2.0×10^{-3} mol l^{-1} of the buffer solution was chosen as the optimal to achieve higher buffering capacity. At lower

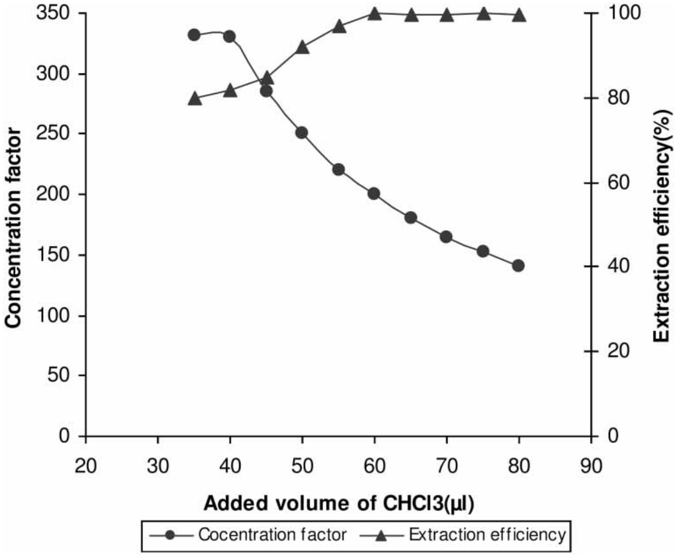


Figure 5. Effect of $CHCl_3$ concentration on the extraction of cobalt and concentration factor. Conditions: Co^{2+} 100.0 μg l^{-1}; K-4-BPDC 2.0×10^{-4} mol l^{-1}; TBA^+ 2.0×10^{-2} mol l^{-1} and pH = 6.0.

Table 1. Analytical characteristics of proposed method

Element	Linear range (μg l^{-1})	RSD (%) (n =10)[c]	Concentration factor[a]	LOD[b] (μg l^{-1})
Co^{2+}	20–1500	2.3	200	10
Cu^{2+}	15–2000	2.1	200	5
Ni^{2+}	35–1600	2.7	200	15

[a] Concentration factor is the volume ratio (Va/Vs) of the aqueous phase (Va) and sedimented phase (Vs) after phase separation.

[b] LOD: limit of detection, calculated as three times the standard deviation (S_B) of the blank signal.

[c] Cobalt, copper, and nickel concentration were 100.0 μg l^{-1} for which the RSDs were obtained; number of results $n = 10$.

concentrations than 1.0×10^{-3} mol l^{-1} of the buffer solution, the buffering capacity is not sufficient for adjusting pH.

Figures of Merit

Table 1 summarizes the analytical characteristics of the optimized method, including the linear range, the limit of detection, the reproducibility, and the concentration factor. The limit of detection, defined as $C_L = 3\ S_B/m$ (where C_L, S_B and m are the limit of detection, standard deviation of the blank and slope of the calibration graph, respectively), were 10, 5, and

Table 2. Effect of foreign ions on the extraction and determination of cobalt, copper, and nickel (100 μg l^{-1})

Ion	Concentration (mg l^{-1})	Recovery (%)		
		Co^{2+}	Cu^{2+}	Ni^{2+}
K^+	1000	99.8	99.5	100.0
Li^+	1000	99.6	>100.0	97.8
Ca^{2+}	1000	99.8	>100.0	99.1
Mg^{2+}	1000	99.8	>100.0	>100.0
Cr^{3+}	100	>100.0	>100.0	100.0
Pb^{2+}	100	98.9	99.5	98.6
Mn^{2+}	50	97.1	98.2	97.5
Cd^{2+}	50	>100.0	99.6	98.9
Fe^{2+}	10	>100.0	99.2	97.8
Fe^{3+}	10	>100.0	100.0	99.3
Zn^{2+}	10	98.5	99.2	97.5
Ag^+	10	97.9	98.5	97.6

Table 3. Determination of Co^{2+}, Cu^{2+}, and Ni $^{2+}$ ($\mu g\ l^{-1}$) in natural water sample

		Tap water[a]		River water[b]		Sea water[c]	
Metal	Added	Found[d]	Recovery (%)	Found[d]	Recovery(%)	Found[d]	Recovery (%)
Co^{2+}	—	24.6 ± 0.5	—	63.5 ± 1.4	—	68.3 ± 1.4	—
	50	74.2 ± 1.5	99.4	113.9 ± 2.5	>100.0	118.7 ± 2.6	>100.0
	100	123.5 ± 2.1	99.1	165.1 ± 3.4	>100.0	170.6 ± 3.5	>100.0
Cu^{2+}	—	35.0 ± 0.8	—	56.2 ± 1.2	—	58.3 ± 1.3	—
	50	83.8 ± 1.8	98.5	106.5 ± 2.2	>100.0	109.6 ± 2.3	>100.0
	100	134.6 ± 2.8	99.7	156.8 ± 3.3	>100.0	160.1 ± 3.4	>100.0
Ni^{2+}	—	48.6 ± 1.3	—	55.6 ± 1.5	—	65.3 ± 1.8	—
	50	98.2 ± 2.7	99.6	105.9 ± 2.9	>100.0	113.8 ± 3.1	98.7
	100	148.1 ± 4.0	99.7	156.2 ± 4.2	>100.0	161.0 ± 4.4	97.4

[a] From drinking water system of Tehran, Iran.

[b] Sefidrood river water (local river).

[c] Caspian sea water.

[d] Mean ± S.D. (n = 3).

15 μg l^{-1} for Co^{2+}, Cu^{2+}, and Ni^{2+}, respectively. The concentration factor (the volume ratio (Va/Vs) of the aqueous phase (Va) and sedimented phase (Vs) after phase separation) was 200, that is, 50 μl of chloroform phase was obtained from 10 ml of the homogenous aqueous solution. The preconcentration factor of 200 makes the method very promising for use at sub μg l^{-1} level in combination with a more sensitive technique that needs a low injection volume such as the electrothermal atomic absorption spectrometry (ET-AAS).

Interferences

In the view of the high selectivity provided by FAAS, the only interferences studied were those related to the preconcentration step. Cations that may react with K-4-BPDC were studied. To observe these effects, various salts with different concentrations were added to each sample solution containing 100.0 μg l^{-1} of Co^{2+}, Cu^{2+}, and Ni^{2+}. An ion was considered to interfere when its presence produced a variation in the extraction recovery of samples more than $\pm 5\%$. The results of the interference studies are summarized in Table 2. The results show that cobalt, copper, and nickel recoveries are nearly quantitative in the presence of other cations.

Application to Samples

In order to test the reliability of the proposed methodology suitable for the assay of the three targeted metal ions, it was applied for the extraction and determination their concentrations in tap water, river water and seawater. For this purpose, 10 ml of each of the samples were preconcentrated with 60.0 μl chloroform and 2.0×10^{-4} mol l^{-1} K-4-PBDC following the proposed method. The results are shown in Table 3. For calibration purposes, the working standard solutions were subjected to the same preconcentration procedure as used for the analyte solutions. In addition, the recovery experiments for different amounts of Co^{2+}, Cu^{2+}, and Ni^{2+} were carried out. The results confirm the validity of the proposed method.

CONCLUSION

Homogenous liquid–liquid extraction that utilizes a pH independent phase separation phenomenon from the homogeneous solution was applied for the extraction and determination of Co^{2+}, Cu^{2+}, and Ni^{2+}. This technique could concentrate analytes rapidly and powerfully. HLLE is an easy, safe, rapid, and inexpensive methodology for the preconcentration and separation of trace metals in aqueous solutions. K-4-BPDC is a stable, and fairly selective complexing reagent. The proposed method gives low LODs (10, 5, and 15 $\mu g\, l^{-1}$ for Co^{2+}, Cu^{2+}, and Ni^{2+}, respectively), high concentration factor 200 and good RSDs and can be applied to the determination of trace metals in various water samples.

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REFERENCES

1. Malvankar, P.L. and Shinde, V.M. (1991) Ion-pair extraction and determination of copper (II) and zinc (II) in environmental and pharmaceutical samples. *Analyst*, 116 (10): 1081–1084.
2. Akdogan, A., Deniz, M., Cebecioglu, S., Sen, A., and Deligoz, H. (2002) Liquid–liquid extraction of transition metal cations by nine new azo derivatives calix[*n*]arene. *Sep. Sci. Technol.*, 37 (4): 973–980.
3. Bae, S.Y., Zeng, X., and Murray, G.M. (1998) Photometric method for the determination of Pb^{2+} following separation and preconcentration using a templated ion-exchange resin. *J. Anal. At. Spectrom.*, 13 (10): 1177–1180.
4. Prakashi, N., Csanady, G., Michaelis, R.A., and Knapp, G. (1989) Automatic off/on-line preconcentration for ICP-OES: Powerful instrumentation for water analysis. *Mikrochim. Acta.*, 99 (3–6): 257–265.
5. Vircaus, M., Rone, V., Palne, A., and Vircava, D. (1994) Coprecipitation behaviour of 5,8-polyquinolyl polydisulphide for trace element preconcentration from aqueous solution. *Anal. Chim. Acta.*, 299 (2): 291–298.
6. Elci, L., Sahin, U., and Oztas, S. (1997) Determination of trace amounts of some metals in samples with high salt content by atomic absorption spectrometry after cobalt-diethyldithiocarbamate coprecipitation. *Talanta*, 44 (6): 1017–1023.
7. Gucer, S. and Yaman, M. (1992) Determination of vanadium in vegetable matter by flame atomic absorption spectrometry. *J. Anal. At. Spectrom.*, 7 (2): 179–182.
8. Santhy, K. and Selvapathy, P. (2004) Removal of heavy metals from wastewater by adsorption on coir pith activated carbon. *Sep. Sci. Technol.*, 39 (14): 3331–3351.
9. Ramesh, A., Mohan, K.R., and Seshaiah, K. (2002) Preconcentration of trace metals on Amberlite XAD-4 resin coated with dithiocarbamates and determination by inductively coupled plasma-atomic emission spectrometry in saline matrices. *Talanta*, 57 (2): 243–252.
10. Soylak, M., Sahin, U., and Elci, L. (1996) Spectrophotometric determination of molybdenum in steel samples utilizing selective sorbent extraction on Amberlite XAD-8 resin. *Anal. Chim. Acta*, 322 (1–2): 111–115.
11. Suttun, R.M.C., Hill, S.J., and Jones, P. (1996) Comparison of the chelating ion exchange properties of dye coated cellulose and polystyrene substrates for the separation and determination of trace metals from aqueous media. *J. Chromatogr. A*, 739 (1–2): 81–86.

12. Mohammad, B., Ure, A.M., and Littlejohn, D. (1992) On-line preconcentration of aluminium with immobilized 8-hydroxyquinoline for determination by atomic absorption spectrometry. *J. Anal. At. Spectrom.*, 7 (4): 695–699.
13. Takagai, Y. and Igarashi, S. (2000) Homogeneous liquid–liquid extraction as a simple and powerful preconcentration method for capillary gas chromatography and capillary electrophoresis. *Am. Lab. News*, 34: 29–30.
14. Murata, K., Yokoyana, Y., and Ikada, S. (1972) Homogeneous liquid–liquid extraction. *Anal Chem.*, 44 (4): 805–810.
15. Matkovich, C.E. and Chisian, G.D. (1973) Salting-out of acetone from water basis of a new solvent extraction system. *Anal. Chem.*, 45 (11) 1915–1921.
16. Igarashi, S., Arai, T., and Kawakami, T. (1994) A homogeneous liquid–liquid extraction method based on pH dependent phase-separation phenomena in the water/acetic acid/chloroform ternary component system. *Bunseki Kagaku*, 43: 1183–1188.
17. Igarashi, S., Ide, N., and Takagai, Y. (2000) High-performance liquid chromatographic–spectrophotometric determination of copper (II) and palladium (II) with 5,10,15,20-tetrakis(4N-pyridyl)porphine following homogeneous liquid–liquid extraction in the water-acetic acid-chloroform ternary solvent system. *Anal. Chim. Acta*, 424 (2): 263–269.
18. Ghiasvand, A.R., Shadabi, S., Mohagheghzadeh, E., and Hashemi, P. (2005) Homogeneous liquid–liquid extraction method for the selective separation and preconcentration of ultra trace molybdenum. *Talanta*, 66 (4): 912–916.
19. Takagai, Y., Maekoya, C., and Igarashi, S. (2000) Determination of chlorophenol derivatives using the homogeneous liquid–liquid extraction in ternary component system-GC/MS method. *Nippon Kaguka Karishi*, 4: 291–293.
20. Igarashi, S., Ide, N., Takahata, K., and Takagai, Y. (1999) HPLC spectrophotometric determination of metal-porphyrin complexes following a preconcentration method by homogeneous liquid–liquid extraction in a water/pyridine/ethyl chloroacetate ternary component system. *Bunseki Kagaku*, 48: 1115–1121.
21. Oshite, S. and Igarashi, S. (2001) Homogeneous liquid–liquid extraction as preconcentration method using water/tetrabutylammonium bromide/chloroform ternary component system and its application to the flame-less atomic absorption spectrometry. *Anal. Sci.*, 17: i1329–i1131.
22. Andak, M., Asan, A., Isildak, I., and Cesur, H. (2001) Flow-injection spectrophotometric determination of cobalt (II) at low $\mu g\ l^{-1}$ levels with 4-benzylpiperidinedithiocarbamate. *Anal. Chim. Acta*, 434 (1): 143–147.