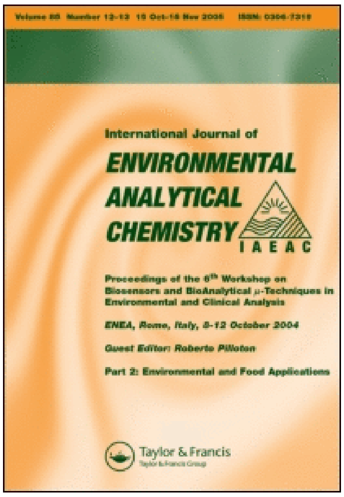

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Dispersive liquid–liquid microextraction and spectrophotometric determination of cobalt in water samples

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A new simple and rapid dispersive liquid–liquid microextraction has been applied to preconcentrate trace levels of cobalt as a prior step to its determination by spectrophotometric detection. In this method a small amount of chloroform as the extraction solvent was dissolved in pure ethanol as the disperser solvent, then the binary solution was rapidly injected by a syringe into the water sample containing cobalt ions complexed by 1-(2-pyridylazo)-2-naphthol (PAN). This forms a cloudy solution. The cloudy state was the result of chloroform fine droplets formation, which has been dispersed in bulk aqueous sample. Therefore, Co-PAN complex was extracted into the fine chloroform droplets. After centrifugation (2 min at 5000 rpm) these droplets were sedimented at the bottom of conical test tube (about 100 µL) and then the whole of complex enriched extracted phase was determined by a spectrophotometer at 577 nm. Complex formation and extraction are usually affected by some parameters, such as the types and volumes of extraction solvent and disperser solvent, salt effect, pH and the concentration of chelating agent, which have been optimised for the presented method. Under optimum conditions, the enhancement factor (as the ratio of slope of preconcentrated sample to that obtained without preconcentration) of 125 was obtained from 50 mL of water sample, and the limit of detection (LOD) of the method was 0.5 µg $L^{-1}$and the relative standard deviation (RSD, $n=5$) for 50 µg L^{-1} of cobalt was 2.5%. The method was applied to the determination of cobalt in tap and river water samples.

Keywords: dispersive liquid–liquid microextraction; cobalt; water samples; spectrophotometry

1. Introduction

Cobalt may enter the environment from both human activities and natural sources. It can benefit or harm human health. Cobalt is beneficial for humans because it is part of vitamin B_{12} [1]. We can be exposed to low levels of cobalt by breathing air, eating food, or drinking water. Food and drinking water are the largest sources of exposure to cobalt for the general population.

Toxicological effects of large amounts of cobalt include vasodilatation, flushing and cardiomyopathy in humans and animals [2]. Because human beings and animals cannot exist without drinking water, spring, well, tap, etc., as well as plants without water for

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irrigation, natural water has particular importance. Therefore, the development of accurate and rapid determination methods for monitoring the level of cobalt concentration in natural waters is necessary and indispensable [3].

Despite improvements in modern analytical instruments, direct determination of trace analytes at low concentrations is often a problem for analytical chemists and, as a result, a sample-preparation step is required. Sample preparation in the analytical process typically consists of an extraction-separation step which offers not only the ability to isolate the target analytes from the matrix solution, thus reducing or even eliminating the interferences originally present, but also the opportunity for these analytes to be preconcentrated and determined at very low levels.

There are a lot of methods for preconcentration and separation, such as liquid–liquid extraction [4–6] and solid phase extraction [7–15]. The applications of some of these techniques are limited because of their disadvantages such as significant chemical additives, solvent losses, complex equipment, large secondary wastes, unsatisfactory enrichment factors and high time consumption.

The continuous quest for novel sample preparation procedures has led to the development of new methods, whose main advantages are their speed and negligible volume of solvents used. The solvent microextraction technique effectively overcomes these difficulties by reducing the amount of organic solvent as well as allowing sample extraction and preconcentration to be done in a single step. Compared with conventional methods solvent microextraction is faster and simpler, inexpensive, more sensitive and effective for the removal of interfering matrices. Solvent microextraction is a form of solvent extraction with phase ratio values higher than 100 [16]. Compared with the conventional solvent extraction, microextraction may provide poorer analyte recovery, instead the concentration in the organic phase greatly enhances [17]. A big advantage is that the amount of the organic solvent used is highly reduced. In addition, only one operational step is required, therefore, problems of contamination and loss of analytes vanishes.

Dispersive liquid–liquid microextraction (DLLME) is a modified solvent extraction method and its acceptor-to-donor phase ratio is greatly reduced comparing with the other methods [18–20]. In DLLME, the appropriate mixture of the extraction and disperser solvents is rapidly injected by syringe into aqueous samples containing analytes. Thereby, a cloudy solution forms. In fact, the cloudy state results from the formation of fine droplets of the extraction solvent, which disperse in the sample solution. Then, this cloudy solution is centrifuged and the fine droplets sediment at the bottom of the conical test tube. Determination of analytes in sedimented phase can be performed by instrumental analysis. In this extraction method any component in the solution, directly or indirectly after the previous (or simultaneous) derivatization reaction, interacts with the fine droplets of the extraction solvent and consequently gets extracted from the initial solution and concentrates in the small volume of the sedimented phase. The simplicity of the operation, speed, low sample volume, low cost, high recovery and high enrichment factor are some advantages of DLLME [17].

The aim of this work is to introduce a reliable, simple, inexpensive method for determination of cobalt in water samples by spectrophotometric determination after preconcentration by the dispersive microextraction technique. Preconcentration of a 50 ml sample solution allowed an enrichment factor approaching 125, which is favourably comparable with other preconcentration methods.

2. Method

2.1 *Instrumentation*

A UV-Vis spectrophotometer (Perkin Elmer, lambda 25) with a 500 µL quartz cell was used for recording the spectra or measuring the absorbance of the complex at 577 nm. Phase separation was assisted using a refrigerated centrifuge (Hettich, Universal 320R) equipped with an angle rotor (6 place, 9000 rpm, cat no 1620A).

2.2 *Reagents and solutions*

All reagents used were of analytical reagent grade. Doubly distilled water was used throughout the experiment. A stock solution of cobalt (II) (1000 mg L^{-1}) was prepared by dissolving the appropriate amount of $CoCl_2 \cdot 6H_2O$ (Merck, Darmstadt, Germany).

Working standard solutions were prepared freshly by appropriate dilution of the standard stock solution. A 10^{-3} mol L^{-1} solution 1-(2-pyridylazo)-2-naphthol (PAN) (Merck, Darmstadt, Germany) was prepared by dissolving the appropriate amount of PAN in absolute ethanol. Chloroform and carbon tetrachloride as extraction phase, ethanol as a disperser solvent, acetone as a dilution solvent, HCl, NaOH and $NaNO_3$ were obtained from Merck (Darmstadt, Germany).

2.3 *Dispersive liquid–liquid microextraction procedure*

A 50.00 mL sample of standard solution containing 30 µg L^{-1} of cobalt and sodium nitrate (0.25 mol L^{-1}) was poured in a test tube with a conical bottom and 0.1 mL of PAN (10^{-3} mol L^{-1}) as chelating agent was added into the solution. After a few minutes a greenish complex of cobalt was formed and the solution pH was adjusted to 1 by concentrated HCl. Then a binary solution containing 2.1 mL of ethanol (disperser solvent) and 400 µL of chloroform (extraction solvent) was injected rapidly into the sample solution using a syringe and a stable cloudy solution (water, ethanol and chloroform) was obtained. Then, Co-PAN complex was extracted into fine droplets of chloroform. After that the mixture was centrifuged for 2 min at 5000 rpm. After this process the fine droplets of chloroform were joined together and sedimented at the bottom of the conical test tube. After removing the whole aqueous solution, the extraction phase was diluted with 250 µL acetone and transferred to a 500 µL cell and the absorbance was measured at 577 nm. The volume of the sedimented phase was determined to be about 100 µL.

3. Results and discussion

It is necessary to investigate the effect of all the parameters that can probably influence the extraction performance. In this methodology these parameters are the ligand concentration, pH, the kind and volume of extraction solvent, the kind and volume of disperser solvent, extraction time and salt concentration that were investigated and optimised in order to achieve a high recovery and enrichment factor.

3.1 *Effect of pH*

Separation of metal ions by DLLME involves prior complex formation with sufficient hydrophobicity to be extracted into the extraction phase, thus, obtaining the desired preconcentration. pH plays a unique role on metal-chelate formation and subsequent extraction. The effect of pH on complex formation and extraction of cobalt from water samples was studied in the range of 0.5–6.0 using HCl and NaOH.

The results illustrated in Figure 1 reveal that the absorbance is slightly reduced by increasing pH. As in low pH, cations are less likely to precipitate, pH 1 seems a proper choice for both complexation and extraction.

3.2 *Effect of ligand concentration*

The effect of PAN (complexing agent) amount on the absorption is shown in Figure 2. As is well expected, following an ML2 stoichiometry of complex the absorption is increased by increasing the PAN concentration. We investigated PAN concentration in the range of 1.5×10^{-8}–2.5×10^{-6} mol L^{-1}. Maximum absorbance was obtained at a concentration of 2.0×10^{-6} mol L^{-1} of the ligand (the molar ratio of PAN/Co = 3.93) and after that, absorbance approximately stays constant.

3.3 *Effect of type and volume of the extraction solvent*

Selecting the extraction solvent by paying attention to its characteristic properties is very important. It must have a higher density than water, be capable of extracting the compounds of interest, and have low solubility in water. Chloroform and carbon tetrachloride were compared in this extraction and obtained recoveries were higher for chloroform. To examine the effect of the extraction solvent volume, solutions containing 1.5 mL of ethanol and different volumes of chloroform in the range of 200–800 µL were subjected to the same procedures. According to Figure 3, which shows the curve of absorbance versus volume of the chloroform, increasing the volume of chloroform, initially increases the absorbance until at 330 µL it reaches the maximum amount, and at 650 µL starts to decrease. This drop off is due to the rise of the sedimented phase volume. The high sensitivity was obtained using 400 µL of chloroform.

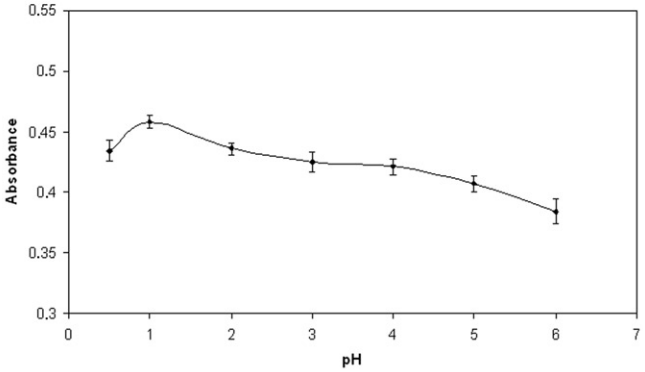

Figure 1. Effect of pH on the absorbance of Co-PAN complex.
Notes: Utilised conditions: Cobalt 30 µgL^{-1}, PAN 2.0×10^{-6} molL^{-1}, Chloroform 500 µL, Ethanol 1500 µL, Diluting agent 250 µL.

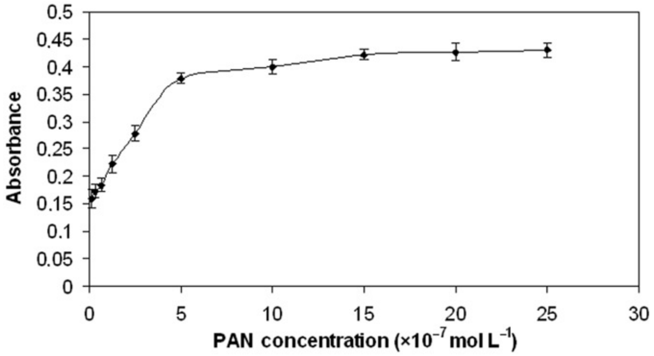

Figure 2. Effect of PAN concentration on the absorbance of Co-PAN complex.
Notes: Utilised conditions: Cobalt 30 μgL^{-1}, $NaNO_3$ 0.2 molL^{-1}, pH = 1, Chloroform 500 μL, Ethanol 1500 μL, Diluting agent 250 μL.

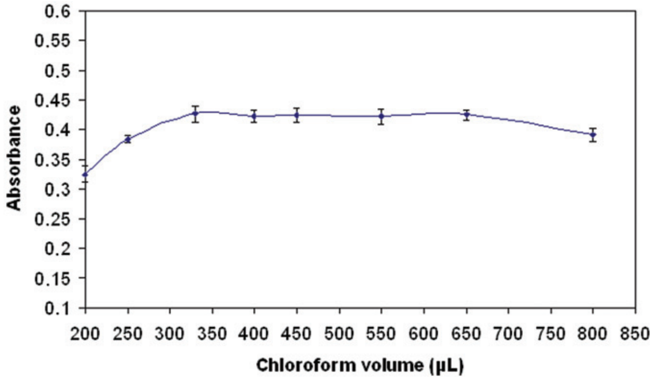

Figure 3. Effect of amount of chloroform on the absorbance of Co-PAN complex.
Notes: Utilised conditions: Cobalt 30 μgL^{-1}, PAN 2.0×10^{-6} molL^{-1}, $NaNO_3$ 0.2 molL^{-1}, pH = 1, Ethanol 1500 μL, Diluting agent 250 μL.

3.4 *Effect of type and volume of the disperser solvent*

The main criterion for the selection of the disperser solvent is its miscibility in the extraction solvent and aqueous solution. In addition, the type of disperser directly influences the viscosity of the binary solvent. Thus, this solvent can control droplet production and extraction efficiency. To study this effect, two different solvents such as acetone and ethanol were tested. A series of sample solutions were studied using 1500 μL of each disperser solvent with 400 μL of chloroform as the extraction solvent. The obtained enrichment factors for these two dispersers show no statistically significant differences between them; however we selected ethanol as the disperser because it was cheaper and more accessible than acetone.

The effect of the volume of ethanol on the extraction recovery was also studied. The different volumes of ethanol in the range of 1500–2700 μL with the addition of 400 μL of chloroform were examined. For the first three tests, the droplets were big and the surface area was low, so the droplets rapidly settled at the bottom of the tube and low

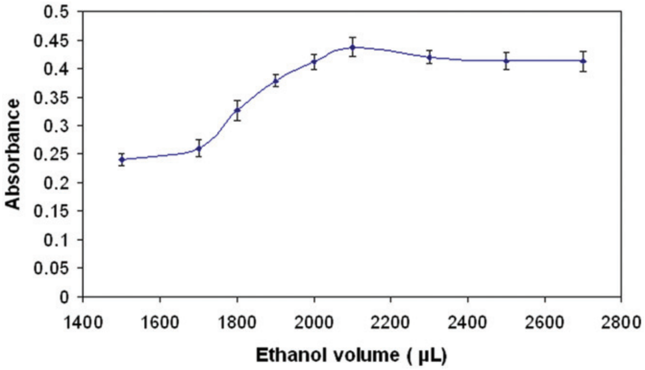

Figure 4. Effect of amount of ethanol on the absorbance of Co-PAN complex.
Utilised conditions: Cobalt 30 µgL^{-1}, PAN 2.0×10^{-6} molL^{-1}, $NaNO_3$ 0.2 molL^{-1}, pH = 1, Chloroform 400 µL, Diluting agent 250 µL.

extraction efficiencies were obtained. As it is shown in Figure 4, the absorbance increases up to 2100 µL of disperser solvent volume and after that it decreases slowly. Thus 2100 µL of ethanol was chosen as the proper amount.

3.5 *Effect of centrifuging rate*

A series of same solutions were tested at various rates of centrifugation. The rate of centrifugation was adjusted at 1000, 2000, 3000, 4000, 5000 and 6000 rpm for 3 minutes. The absorbance slowly increases with increasing the rate to 4000 rpm and after that, it approximately stays constant. 5000 rpm was selected as the best rate for centrifuging.

3.6 *Effect of extraction time*

Extraction time is one of the most important factors in most extraction procedures. In DLLME, extraction time is defined as the time between the injection of the binary solvent and starting to centrifuge. The effect of extraction time was examined in the range of 1–6 min with constant experimental conditions. The surface area between extraction solvent and aqueous phase (water sample) is infinitely large. Thereby, transfer of complex from aqueous phase (water sample) to extraction solvent is fast. Subsequently, equilibrium state is achieved quickly; therefore, the extraction time is very short, which is the advantage of DLLME technique. In this method, the most time-consuming step is the centrifuging of sample solution, which is about 2 min.

3.7 *Effect of salt*

For studying the influence of ionic strength on the performance of DLLME, we investigated $NaNO_3$ concentration in the range of 0–0.5 mol L^{-1} while other experimental conditions were kept constant. By increasing $NaNO_3$ concentration extraction efficiency slowly increases due to salting-out effect and then slightly decreases. These observations showed the possibility of using this method for the separation of cobalt from saline solutions up to 0.5 mol L^{-1} (4.25%).

3.8 *Effect of coexisting ions*

The effects of coexisting ions in real water samples on the recovery of cobalt were also studied. In these experiments, 50 mL of solutions containing 50 µg L^{-1} of cobalt and various amounts of interfering ions were treated. A given species was considered to interfere if it resulted in a ±5% variation of the absorbance. The results obtained are given in Table 1.

Most of the cations and anions examined did not interfere with the extraction and determination of Co^{2+}. However, some of the species tried, such as Fe^{3+}, Cu^{2+}, Pd^{2+} and especially, Ni^{2+}, interfered with the determination of Co^{2+} ion. These interferences were eliminated in the presence of proper masking agents, such as 1.9×10^{-4} mol L^{-1} acetylacetone for Pd^{2+}, 4.0×10^{-3} mol L^{-1} oxalate for Fe^{3+} (and Ca^{2+}) and 2.8×10^{-3} mol L^{-1} ascorbic acid and 3.9×10^{-3} mol L^{-1} iodide for Cu^{2+}. In the presence of the masking agents, no interference was observed for Ca^{2+} up to 1000, Fe^{3+} and Cu^{2+} up to 100 and Pd^{2+} up to 10 times relative to Co^{2+} concentration. Thus, quantitative extraction of Co^{2+} was possible.

3.9 *Figures of merit*

Table 2 summarises the analytical characteristics of the optimised method, including linear range, limit of detection, reproducibility, and enhancement factor. The calibration graph was linear in the range of 2–50 µg L^{-1} of cobalt. The limit of detection, defined as $C_L = 3S_B/m$ (where C_L, S_B and m are the limit of detection, standard deviation of the blank and slope of the calibration graph, respectively), was 0.5 µg L^{-1}. The relative standard deviation (RSD) for five replicate measurements of 30 µg L^{-1} Co(II) was 2.5%. The enhancement factor was obtained from the slope ratio of the calibration graph after and before extraction, which was about 125. The equation of the calibration curve after the preconcentration procedure was given in Equation (1). The equation of the calibration curve before the preconcentration procedure is given by Equation (2). (These standard samples of cobalt were chosen up to 200 µg L^{-1} with excess PAN to measure their absorbance and obtain the equation of the calibration curve accurately).

$$A = 0.0145C_{(Co)} + 0.0241 \quad (r_2 = 0.9944, r = 0.9972) \tag{1}$$

$$A = 1.16 \times 10^{-4}C_{(Co)} + 0.0342 \quad (r^2 = 0.9885, r = 0.9942) \tag{2}$$

3.10 *Comparison with other methods*

A comparison of the method under discussion with other reported preconcentration methods is given in Table 3. In comparison with other reported methods, DLLME has low LOD (0.5 µg L^{-1}), high enrichment factor (125) and short extraction procedure

Table 1. Effect of interferents on the recovery of 50 μg L^{-1} Co(II) in water sample using DLLME.

Interferent	Interferent/Co(II) ratio	Recovery (%)
Ba^{2+}	1000	92.2
	750	98.3
Mn^{2+}	1000	106.0
	750	100.8
Zn^{2+}	1000	109.6
	750	104.7
Cd^{2+}	1000	105.4
Cr^{3+}	1000	111.2
	750	108.5
	500	102.7
Ag^{+}	1000	62.7
	500	97.4
Pb^{2+}	1000	85.0
	500	100.5
Al^{3+}	1000	79.3
	500	100.5
Mg^{2+}	1000	83.9
	500	93.4
	400	99.8
Ca^{2+}	1000	80.2
	500	88.5
	1000	98.3[a]
Hg^{2+}	500	79
	100	92.8
	50	97.6
Pd^{2+}	10	224
	10	102.8[b]
Fe^{3+}	100	189
	100	101.6[c]
Cu^{2+}	100	–[d]
	100	97.2[e]
Ni^{2+}	100	–[d]
NO_2^-	1000	93.6
	750	100.7
I^-	1000	99.0
SO_4^{2-}	1000	99.5
NO_3^-	1000	99.0
PO_4^{3-}	1000	94.2
	750	99.9
CH_3COO^-	1000	101.0

Notes: [a]Ca^{2+} masked with 4.0×10^{-3} mol L^{-1} oxalate; [b]Pd^{2+} masked with 1.9×10^{-4} mol L^{-1} acetylacetone; [c]Fe^{3+} masked with 4.0×10^{-3} mol L^{-1} oxalate; [d]In the presence of this interferent the shape of spectrum is changed completely; [e]Cu^{2+} masked with 2.8×10^{-3} mol L^{-1} ascorbic acid and 3.9×10^{-3} mol L^{-1} iodide.

Table 2. Analytical characteristics of DLLM for determination of Co(II).

Parameter	Analytical feature
Linear range (μg L^{-1})	2–50
r^2	0.9944
Limit of detection (μg L^{-1}) (3σ, $n = 5$)	0.5
Repeatability (R.S.D.[a], %) ($n = 5$)	2.5
Enhancement factor	125
Sample volume (mL)	50
Extraction time (min)	<3

Table 3. Characteristic performance data obtained by using DLLME and other techniques in determination of cobalt in water.

Method	LOD[a] (μg L^{-1})	R.S.D.[b] (%)	Enhancement factor	Sample consumption (mL)	Time (min)	Calibration range (μg L^{-1})	References
CPE–FAAS	5	1.71	20[c]	10	>30	0–200	[21]
CPE–FAAS	0.24	2.1	57[d]	50	>30	0–120	[22]
SPE–	10	2.23	100[e]	250	>15	10–400	[23]
CPE–FAAS	1.06	5.41	28.5	12.5	>30	25–200	[24]
CPE–	7.5	2.2	10[f]	10	>30	20–200	[25]
SPE–ETAAS	0.004	4.5	87	11.5	>1	0.01–0.25	[26]
DLLME–	0.5	2.5	125	50	<3	2–60	This work

Notes: [a]Limit of detection: [b]Relative standard deviation; [c]Preconcentration factor; [d]The enhancement factor, as the ratio of absorbance of preconcentrated sample to that obtained without preconcentration; [e]Ratio of the aqueous phase to final volume of eluent phase; [f]Ratio of the aqueous phase to final volume of surfactant-rich phase.

(less than 3 min). These characteristics are of key interest for routine laboratories in trace metal ion analysis.

3.11 *Accuracy*

For evaluating the accuracy of the method, a certified reference material (CRM) was analysed. The Reference Standard "SCP-ES-L-1" (SCP SCIENCE Canada, ground water (Low level)) is a ground water that has been spiked with metals. The certified value and the analytical results are presented in Table 4. The result indicates the effectiveness and accuracy of the proposed method.

3.12 *Analysis of natural waters*

The proposed DLLME methodology was applied for the determination of cobalt in two different water samples. Tap and river water samples were collected from the north of Iran and were analysed by DLLME as a prior step for spectrophotometric determination. The concentration of cobalt in the river water sample was determined to be 1.0 ± 0.5 μg L^{-1} and no concentration of cobalt in the tap water was detected. As shown

Table 4. Determination of cobalt in a standard reference material using the DLLME.

Certified reference material	Unit	Certified[a]	Found[b]	Recovery (%)
SCP-ES-L^{-}1	Mg L^{-1}	0.051 ± 0.008	0.0532 ± 0.0004	104.3

Notes: [a]Results after dilution 1: 500; [b]Mean value ± standard deviation based on five replicate measurements.

Table 5. Determination of Co(II) in tap and river water samples and relative recovery of spiked Co(II) in tap and river water samples.

Sample	Concentration of Co^{2+} Mean ± S.D.[a] (µg L^{-1})	Added Co^{2+} (µg L^{-1})	Found Co^{2+} Mean ± S.D.[a] (µg L^{-1})	Relative recovery (%)
Tap water[b]	n.d.[c]	30	31.0 ± 0.1	102
River water[d]	1.0 ± 0.1 [e]	30	29.8 ± 0.6	96

Notes: [a]Standard deviation ($n = 5$); [b]From drinking water system of Tehran, Iran; [c]Not detected; [d]Tajan river water, north of Iran, [e]Was determined by GFAAS.

in Table 5, tap and river water samples were spiked with cobalt standards to assess matrix effects. The relative recoveries of cobalt from tap and river water samples at spiking level of 30 µg L^{-1} were 102% and 96%, respectively. These results demonstrated that the tap and river water samples matrices, in our present context, had little effect on DLLME of cobalt.

4. Conclusion

We have proposed the use of dispersive liquid–liquid microextraction for preconcentration of cobalt from real water samples as a prior step to their determination by spectrophotometric detection.

This method is simple, rapid, sensitive, low cost and has high enrichment factor and low toxicity since only a very small amount of extraction solvent is used. Also using spectropotometry as a detection system exhibits a low primary and operational (no need for consumption of gases) cost in comparison with other methods such as FAAS and ICP/OES.

Acknowledgement

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