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Research Article

Optimization of dispersive liquid-liquid micro extraction followed by HPLC-DAD determination of Cr (III) and Co (II) based on the complexation reaction with morpholin -4-carodithioate

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Abstract: In this study, a dispersive liquid-liquid microextraction (DLLME) method was used for preconcentration of Cr (III) and Co (II) cations in water samples. Morpholin -4-carodithioate (MDTC) was used as chelating agent prior to extraction. High-performance liquid chromatography-diode array detection (HPLC-DAD) was used for quantification of the analytes after preconcentration. The effects of extraction, nature and volume of disperser solvent, pH value of sample solution, extraction time and extraction temperature were investigated. Under the optimum conditions, the calibration graphs were linear in the range of (10-4000 $\mu\text{g L}^{-1}$) and (5-4000 $\mu\text{g L}^{-1}$) with detection limits of 3 $\mu\text{g L}^{-1}$ and 3 $\mu\text{g L}^{-1}$ for Co(II) and Cr(III) respectively. Recoveries and enrichment factors for Cobalt and Chromium were obtained (90%, 63.69) and (84%, 58.42), respectively. The DLLMEHPLC-DAD method was successfully applied to the analysis of Cr (III) and Co (II) in aqueous samples.

Keywords: Dispersive liquid-liquid microextraction. MDTC. HPLC-DAD

INTRODUCTION

The aquatic environmental pollution caused by heavy metals has become a subject of considerable public and scientific concern due to their toxicity to human health and biological systems. The

toxicological and biological properties of many elements depend on their chemical forms and oxidation state¹. Determination of toxic heavy metals, such as Co (II), Pb (II), Mn (II) and Cr (VI) has special importance in environmental samples. Yet, for many years the analysis of these elements has only resulted in determination of total concentration of the considered elements^{2,3}. The most extensively used methods for preconcentration and separation of trace Co and Cr in HPLC include liquid–liquid extraction (LLE)⁴, solid-phase extraction (SPE)^{5,6}, and cloud point extraction (CPE)^{7,8}, but drawbacks, such as time consumption, unsatisfactory enrichment factors, large organic solvent requirements, and secondary wastes, limit their applications. In recent years, liquid-phase microextraction (LPME) has been developed as a sample pretreatment procedure which needs very low amounts of solvents, and therefore it is inexpensive and has minimal exposure to toxic organic solvents. Recently, Assadi and co-workers has developed a simple and rapid preconcentration and microextraction method, called dispersive liquid–liquid microextraction (DLLME), as a highly promising environmentally friendly sample preparation technique with target analytical potential⁹⁻¹¹. This method applies an extracting solvent containing a dissolved dispersive solvent, which is miscible with both extraction solvent and water. In DLLME technique, the extraction solvent should be hydrophobic with a density of more than that of water. Hydrocarbons and halogenated hydrocarbons, such as chloroform¹², chlorobenzene¹³, carbon tetrachloride¹⁴, tetrachloroethane⁹, n-hexane¹⁵ and hexadecane¹⁶, are usually chosen as extraction solvents. In this method an appropriate mixture of extraction and disperser solvents is injected into the analyt containing aqueous sample. By dispersion of extraction solvent in an aqueous sample, very fine droplets are produced and the surface area between the extraction solvent and the aqueous sample increases^{4,17}. Recently we reported a DLLME preconcentration method for some polymer additives followed by their determination by HPLC-DAD¹⁸. In previous studies, we demonstrated a novel microextraction technique, named dispersive liquid–liquid microextraction (DLLME), which was successfully used for the extraction and determination of polycyclic aromatic hydrocarbons (PAHs) [9], organophosphorus pesticides (OPPs)¹⁹, chlorobenzenes (CBs)¹⁰, chlorophenols¹³, trihalomethanes [THMs]²⁰, cadmium²¹ and selenium²² in water samples. In addition, other researchers have used this method for the measurement of antioxidants¹⁸, volatile phenols¹⁴ and triazine herbicides²³. DLLME is a miniaturized sample pretreatment technique that uses microliter volumes of the extraction solvent. Some of DLLME advantages include operation simplicity, rapidity, low sample volume, low cost and high enrichment factor²⁴. We now report the DLLME application, as a separation and preconcentration technique, for the rapid determination of Cobalt and Chromium amounts in water samples using the Morpholin -4-carbodithioate (MDTC) as chelating agent. Eventually, High-performance liquid chromatography-diode array detection (HPLC-DAD) was used for detection.

EXPERIMENTAL

Chemicals and solutions: HPLC grade water and acetonitrile were obtained from Caledon (Canada). All chemicals such as methanol, chloroform, acetate, acetic acid were high-purity grade reagents from Merck Co. (Darmstadt, Germany). Morpholine-4-carbodithioate (MDTC) reagent was prepared in the lab according to method reported by Macrotrigiano *et al.*²⁴. It was purified through recrystallization with 2-propanol. The purity was checked by recording IR spectra on a Thermo Nicolet (Nexus-670 model) FTIR spectrometer.

Synthesis of morpholine-4-carbodithioate and complex formation: MDTC has been used as complexing agent. It was prepared according to method reported by Macrotrigiano *et al* (**Fig.1**).

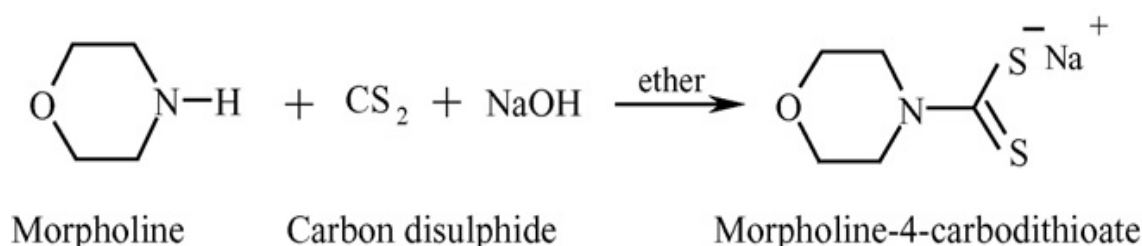


Fig. 1: Molecular structure of morpholin

Morpholine in dry ether was taken in 250 ml Erlenmeyer flask and to this solution; stoichiometric amount of CS_2 was added dropwise while constant stirring. Reaction mixture was cooled in an ice salt mixture thoroughly and stoichiometric amount of NaOH (dissolved in minimum quantity of water) was added dropwise while constant stirring. Addition was completed in about 3–4 h. The crude product was filtered over suction and washed several times with ether. Residue was recrystallized twice from isopropyl alcohol. Obtained product was in the form of white needle shaped crystals with melting point of 175°C and was highly soluble in water. FTIR studies showed characteristic bands for C=S str at 1083 cm^{-1} and two bands at 1437 and 1164 cm^{-1} corresponding to $\nu(\text{C-N})$ and $\nu(\text{C-O})$, respectively^{25,26}.

Apparatus: Separation and determination of copper and chromium were carried out on an HP 1100 series high-performance liquid chromatography (Agilent technologies, Wilmington, DE, USA) controlled by Chemstation software, equipped with a diode array detector and a $20\ \mu\text{L}$ injection loop. The analytical column used for reverse phase liquid chromatographic analysis was a ZORBAX Eclips XDB-C18 $25\text{ cm}\times 4.6\text{ mm}$ packed with $5\ \mu\text{m}$ particles. All pH measurements were made at $25\pm 1^\circ\text{C}$ with a Metrohm pHmeter Model 827 (Switzerland) using a combined glass electrode.

Extraction process: The DLLME procedure was carried out according to our previous report²⁷. 5.0 mL of doubly distilled water spiked with analytes was placed in a 10 mL glass centrifugal tube with conical bottom and were spiked at copper and chromium concentration of 1 mgL^{-1} . 1 mL acetate buffer and 0.5 mL MDTC solution were added. By using a 5 mL syringe, 2.5 mL methanol containing $250\ \mu\text{L}$ chloroform was added to the above solution. Chloroform was dispersed in all parts of sample and there was no need to homogenize the sample. The mixture was immediately centrifuged for 5 min at 3500 rpm. The enriched analytes in the [MDTC] [Co^{+2} , Cr^{+3}] phase were withdrawn by microsyringe. The sedimented phase was quantitatively transferred to another test tube and allowed to evaporate at room temperature. Finally the residue was dissolved in 0.5 mL water and acetonitrile solution (50/50) and was determined by HPLC. The elution of analytes was done by using acetonitrile: water (50:50) as mobile phase at a flow rate of 1 ml/min .

RESULTS AND DISCUSSION

The extraction performance of proposed method was described by the enrichment factor (EF) and the extraction recovery (ER). EF is defined as $\text{EF} = C_{\text{sed}}/C_0$, where C_{sed} and C_0 are the concentration of analytes in the extraction phase and in the sample phase, respectively. ER is the percentage of total analyte amount extracted to the [MDTC] [Cation] phase and is a function of EF and the phase volume ratio (V_{sed}/V_0) (where V_{sed} and V_0 are the volumes of the extraction phase and the aqueous sample, respectively). In the [MDTC] [Co^{+2} , Cr^{+3}]-DLLME procedure, various extraction parameters could have influences on EF and ER and thus were investigated to obtain optimum value. Triplicate

extractions were performed for all experiments and the average of the results was used to plot curves or in tables.

Selection of dispersive and extracting solvents: The main criterion for the selection of the disperser solvent is its miscibility in the organic phase (extraction solvent) and the sample. Five solvents: methanol, acetone, tetrahydrofuran, ethanol and acetonitrile, were studied as a dispersive solvent in this work. The selection of the extracting solvent is critical and should meet the following criteria: (a) higher density than water, (b) good chromatographic behavior, (c) extraction capability for the relevant compounds and (d) low solubility in water^{9,18,27}.

In this work, chloroform, dichloromethane, trichloromethane and carbon tetrachloride were investigated. For this purpose, a series of sample solutions were treated with 250 μL of disperser solvents containing 1.5 mL of the extraction solvents. The obtained average recovery results using the different extraction solvents are shown in **Fig. 2**. Regarding recovery, the combination of chloroform as extracting solvent with methanol as dispersive solvent is the best one. Therefore, the combination of chloroform and methanol was selected for further studies. It should be noted that for tetrahydrofurane no absorption occurred in the samples although the amount of organic phase precipitates were relatively high, so no extraction was occurred and the EF and RF were both zero.

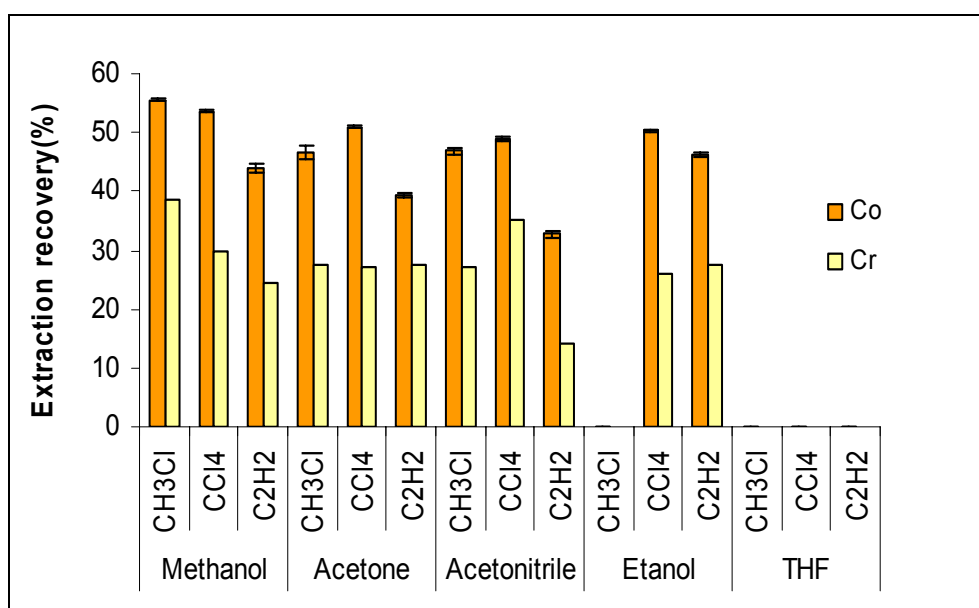


Fig.2: Selection of extracting and dispersive solvents in DLLME. Conditions: sample, 5mL Co^{2+} and Cr^{3+} 1 mgL^{-1} ; volume of dispersive solvent, 1.5 mL; volume of extracting solvent, 250 μL ; buffer, 1mL acetate buffer ($C=1 \text{ mol L}^{-1}$, pH 6) and morpholin -4-carodithioate solution, 0.5mL 0.1 mol L^{-1} in water. The bars show the maximum and minimum levels of determinations.

Dispersive solvent volume: Methanol as a dispersive solvent in different volumes in the range 0–5mL along with 250 μL chloroform as an extracting solvent was used to extraction copper and chromium ions at pH 6 using the DLLME procedure. The obtained results (**Fig. 3**) show that in the case of 2.5mL methanol the highest recovery and a reasonable EF are attainable. With 4mL or higher volume of methanol no sedimented organic phase was achieved.

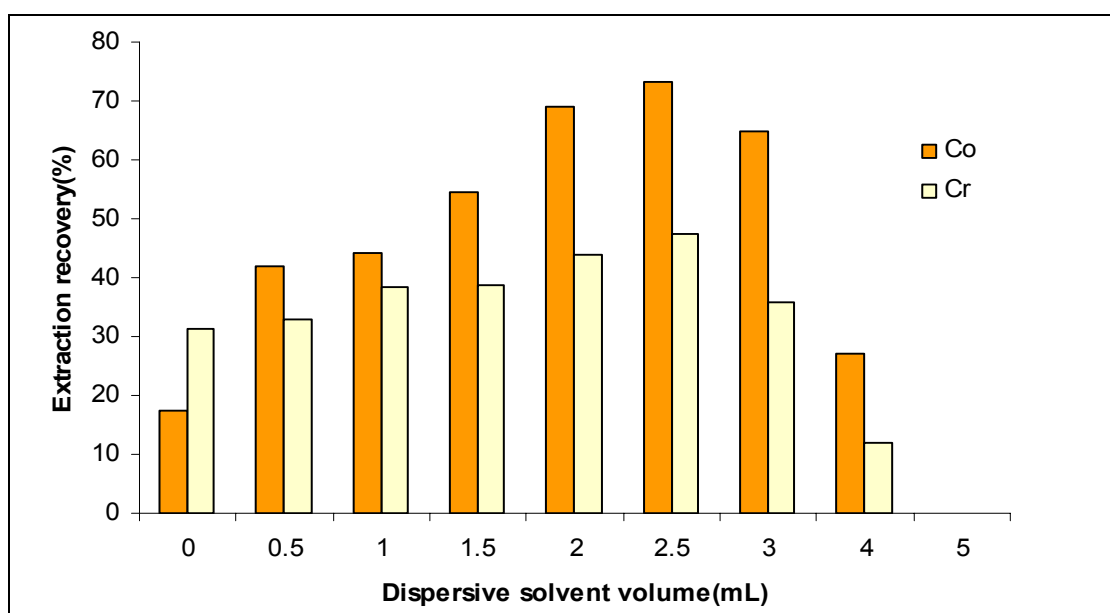


Fig.3: Dispersive solvent volume study. Other conditions are the same as Fig. 1.

Extracting solvent volume: In order to evaluate the effect of the extraction solvent volume on the extraction efficiency, additional experiments were performed using 2.5mL methanol containing different volumes of chloroform, in the range of 50–500 μL . As can be seen in **Fig. 4** there was no sedimented organic phase in the cases of 50 and 100 μL and the system became useless. By using 250 μL chloroform on the other hand, EF 47.44 and recovery 75% for cobalt and EF 31 and recovery 47% for chromium were obtained. The volume of sedimented phase was 137 μL under these circumstances. Therefore, we chose initially 250 μL as optimum volume of chloroform as extracting solvent for further study (optimization of sample size).

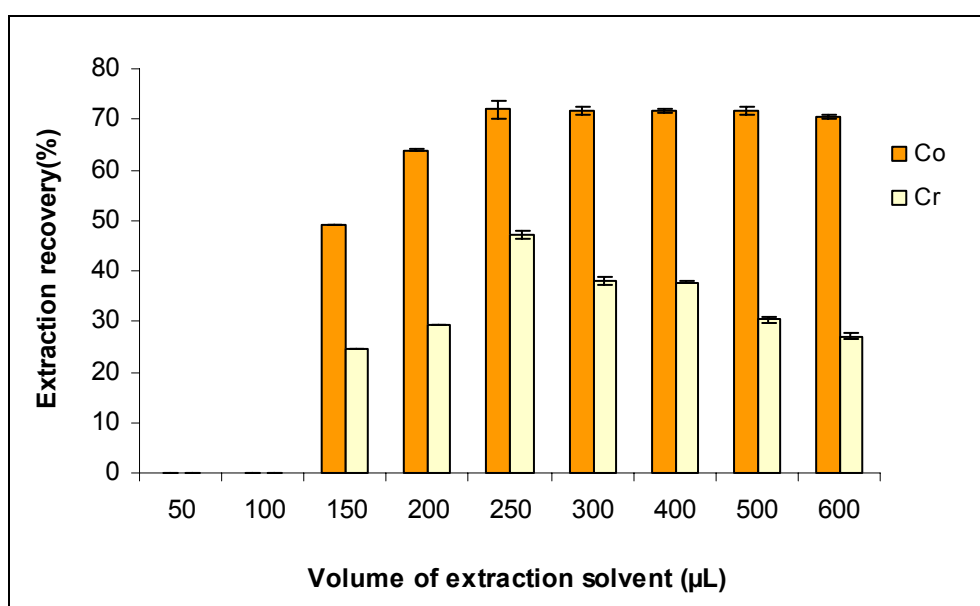


Fig.4: Selection of extracting solvent volume. Volume of dispersive solvent, 2.5 mL. Other conditions are the same as Fig. 1.

pH effect: Because pH plays a unique role in the metal-chelate formation and the subsequent extraction, the pH of the sample solution was the next critical factor evaluated for its effect on the DLLME preconcentration of Co (II) and Cr (III). In this study morpholin -4-carodithioate was used as a complexing agent for Co^{2+} and Cr^{3+} ions to produce a neutral thionate chelate, which is extractable into chloroform. Because the production of thionate chelate is pH-dependent, DLLME was performed at different pH values in the range 2–12. The results, shown in **Fig. 5**, indicated the enrichment factor and extraction recovery of analytes all reached a better level at pH 6. Therefore pH 6 was selected for the following studies.

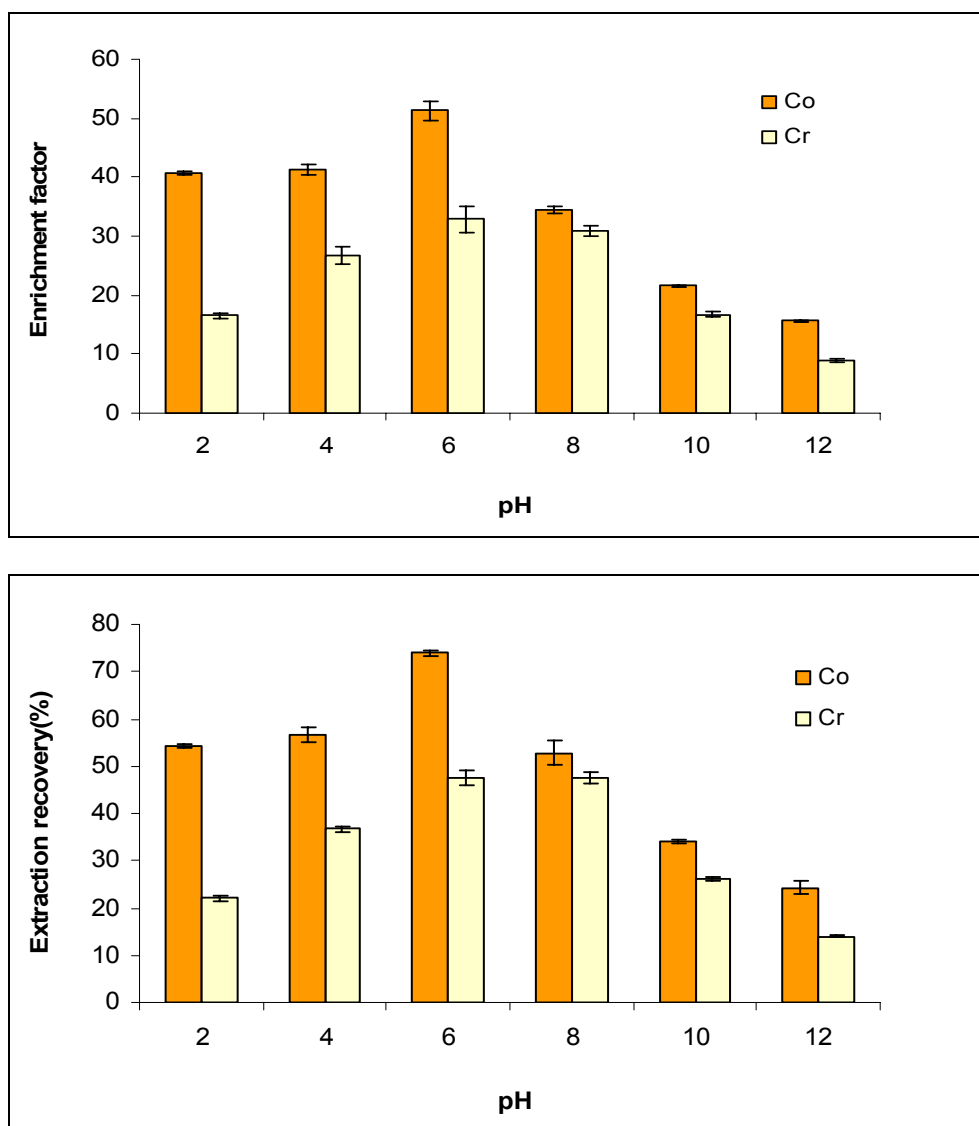


Fig.5: Effect pH. Conditions: sample, 5mL Co^{2+} and Cr^{3+} 1 mgL^{-1} ; volume of dispersive solvent, 2.5 mL; volume of extracting solvent, 250 μL ;and morpholin -4-carodithioate solution, 0.5mL 0.1 mol L^{-1} in water.

Sample volume: Different volumes of analyte solution from 1 to 11 mL were used to study the effect of sample volume with a constant volume of extracting solvent (250 μL) and dispersive solvent (2.5 mL). The results (**Fig. 6**) show that a sample size of 5 mL is optimum volume of chloroform as extracting solvent for further study.

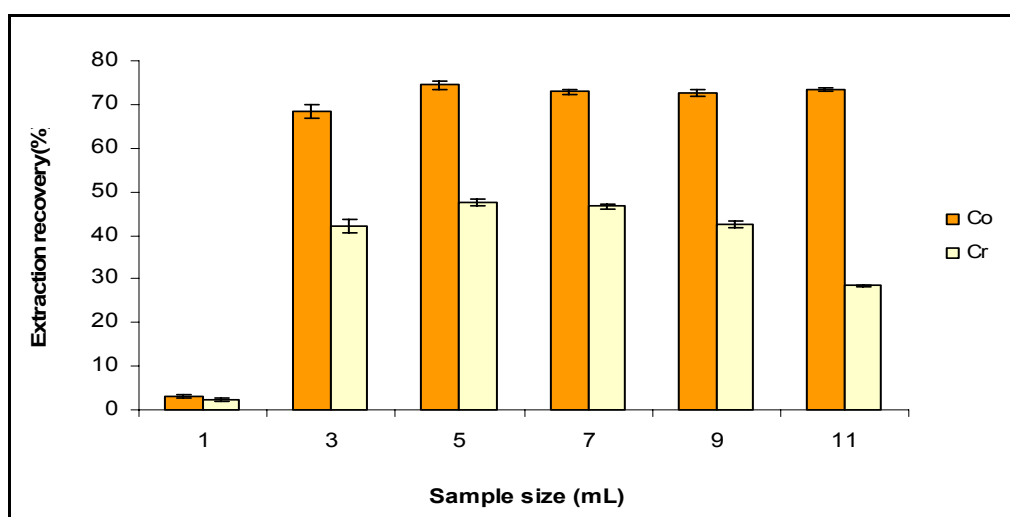


Fig.6: Sampel volume. Conditions: volume of dispersive solvent, 2.5 mL; volume of extracting solvent, 250 μ L; 1mL acetate buffer ($C= 1 \text{ mol L}^{-1}$, pH 6) and morpholin -4-carodithioate solution, 0.5mL 0.1 mol L^{-1} in water.

Effect of the ionic strength: To investigate the influence of the ionic strength on the performance of DLLME, various experiments were performed by addition of different NaCl amounts (0–1g). The other experimental conditions were kept constant. With the increase in ionic strength (from 0 to 1g), the solubility of the extraction solvent in the aqueous phase diminished. Subsequently, the volume of the sedimented phase and extraction recovery increased until 0.2g. These observations offered the possibility of utilizing this method for the lead separation from saline solutions up to 0.2gram (**Fig.7**).

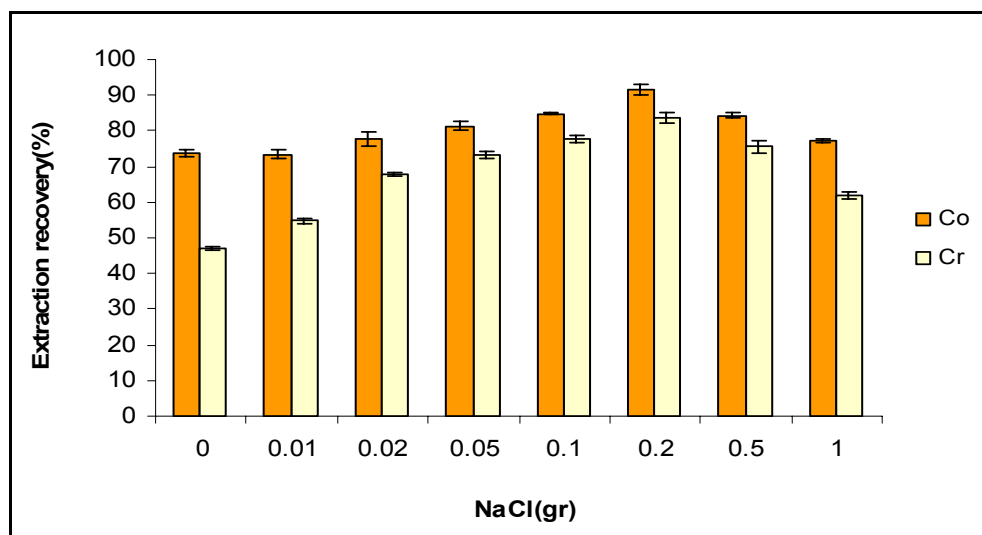


Fig.7: Effect of the ionic strength in DLLME. Conditions: sample, 5mL Co^{2+} and Cr^{3+} 1 mgL^{-1} ; volume of dispersive solvent, 2.5 mL; volume of extracting solvent, 250 μ L; buffer, 1mL acetate buffer ($C= 1 \text{ mol L}^{-1}$, pH 6) and morpholin -4-carodithioate solution, 0.5mL 0.1 mol L^{-1} in water.

Effect of MDTC concentration: In order to determine the concentration of MDTC required for quantitative recoveries, the proposed method was applied. In order to study the influence of MDTC concentration on the analytical response of cobalt and chromium, different concentrations of MDTC

in the range of 0.001 to 1 (M) were used, and the general procedure was applied. The results are shown in (Fig.8). At ligand concentration of 0.001 mol L⁻¹; recoveries of metals were not quantitative. The recovery of the metal ions increased with increasing indolenin concentrations. The optimum amount of ligand was taken as 0.2 for further experiments.

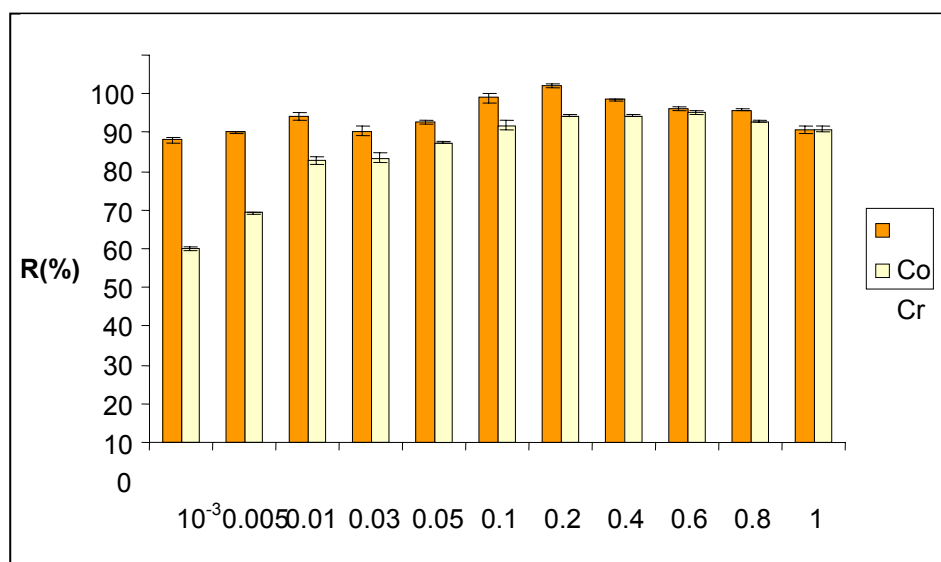


Fig. 8: Effect of MDTC concentration. Conditions: sample, 5mL Co²⁺ and Cr³⁺ 1 mgL⁻¹; volume of dispersive solvent, 2.5 mL; volume of extracting solvent, 250μL; buffer, 1mL acetate buffer (C= 1 mol L⁻¹, pH 6) and NaCl 0.2 g.

Study of other parameters: Other parameters such as effect of centrifuge time and rates and reaction time were studied. Reaction time was also studied over the range of 0–30 min. It was defined as the time spent between addition of MDTC solution and the addition of extraction solvent (chloroform) dissolved in dispersive solvent (methanol). It was found that both the reaction and the extraction procedures are rapid and time did not affect on the EF, recovery and sedimented phase volume. The results indicate that the experiment in the optimized reagent concentration after centrifuging by 5 min at 3500 rpm lead to high recovery of chromium, and cobalt ions in short time.

Analytical features of DLLME of Co²⁺ and Cr³⁺ ions: Under the optimum conditions obtained by one variable at a time optimization; sample size, 5 mL; 0.2gram Neck, volume of dispersive solvent (methanol), 2.5 mL; extracting solvent (chloroform) volume, 250μL; buffer, 1mL acetate buffer (C= 1 mol L⁻¹, pH 6) and volume of MDTC solution, 0.5mL 0.2 mol L⁻¹ in water, some analytical characteristics of the proposed DLLME method were obtained. Calibration curve is linear ($A = 2.5165 C + 16.37$ for Co²⁺ and $A = 2.488 C + 7.5313$ for Cr³⁺, where A is absorbance intensity and C is concentration of cations in μg L⁻¹) in the range of (10-4000μg L⁻¹) for Co (II) and (5-4000μg L⁻¹) for Cr (III) respectively. Square of correlation coefficients (R²) are 0.99. The relative standard deviations for cobalt and chromium were obtained to be 3.3% and 2.6% respectively (n = 6, C =1000 μg L⁻¹ for cations). Limit of detections were 3 μg L⁻¹ for both Co (II) and Cr (III). It can be observed that the recovery agrees well, as expected. In another study of EF, relative enrichment factor (REF) (EF/EF_{max} , where EF_{max} is the ratio of sample volume to sedimented phase volume) and recovery were obtained in three different concentrations of analyte and the results are summarized in **Table 1**. It can be observed that the recovery and the relative enrichment factor agree well, as expected.

Table-1: The variables and values used for central composite design (CCD)

Variable Name		Coded factor levels				
		-1.607 (low)	-1	0	+1	+1.607 (high)
F1	Sample volume (mL)	1.8	3	5	7	8.2
F2	Dispersion solvent (mL)	0.7	1	1.5	2	2.3
F3	Chloroform (μL)	170	200	250	300	330
F4	Concentration of H_2SO_4 (M)	0.17	0.2	0.25	0.3	0.33

Application of the proposed cloud point extraction method to real samples and comparison with a standard method:

Table-2: List of experiments in the central composite design (CCD) for model optimization (coded values)

Design points	Factors levels			
	F1	F2	F3	F4
1	1	1	-1	-1
2	1	-1	-1	-1
3	-1	-1	-1	-1
4	1	-1	1	-1
5	-1	-1	-1	1
6	0	0	0	-1.607
7	0	0	-1.607	0
8	0	-1.607	0	0
9	0	1.607	0	0
10	0	0	0	1.607
11	-1	-1	1	-1
12	1	1	1	1
13(cp) ^a	0	0	0	0
14(cp) ^a	0	0	0	0
15	-1.607	0	0	0
16	1.607	0	0	0
17	1	1	-1	1
18(cp) ^a	0	0	0	0
19	-1	1	1	-1
20(cp) ^a	0	0	0	0
21	0	0	1.607	0
22	-1	-1	1	1
23	-1	1	-1	-1
24	-1	1	1	1
25	-1	1	-1	1
26	1	-1	1	1
27	1	1	1	-1
28	1	-1	-1	1

a. 4 Center points

To evaluate the efficiency of the proposed cloud point extraction method, four water samples including tap water, Aras river water from three different spots and mineral water were selected and the proposed cloud point extraction methods as well as a standard method^{28,29} were applied to determine the cobalt and chromium content. In the cloud point extraction method standard addition technique was used. For the standard method Co^{+2} and Cr^{+3} ions were extracted as the pyrrolidine chelate into methyl isobutyl ketone and then the absorbance of organic phase was read using HPLC-DAD lines of cobalt and chromium. The obtained results are summarized in **Table 2**. The obtained concentrations from both methods were in agreement. **Fig. 9** shows the typical chromatogram of the above mentioned samples after standard addition.

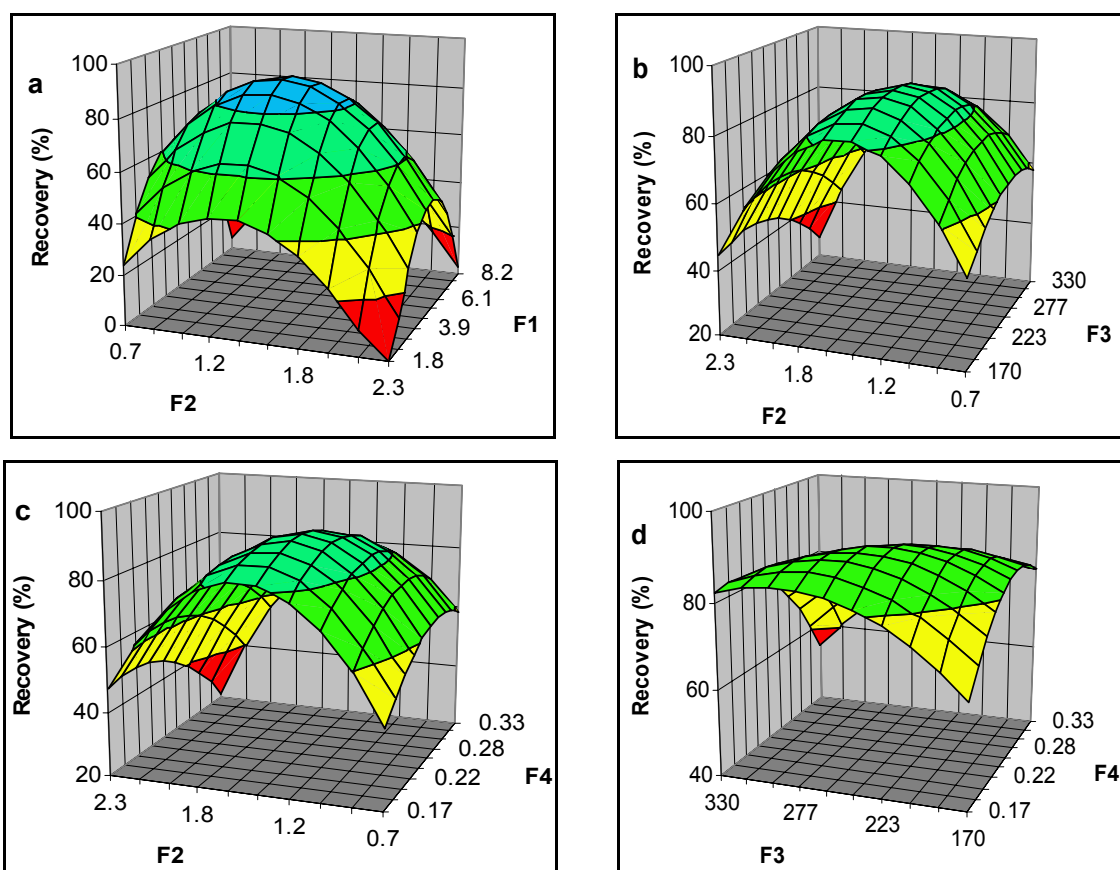
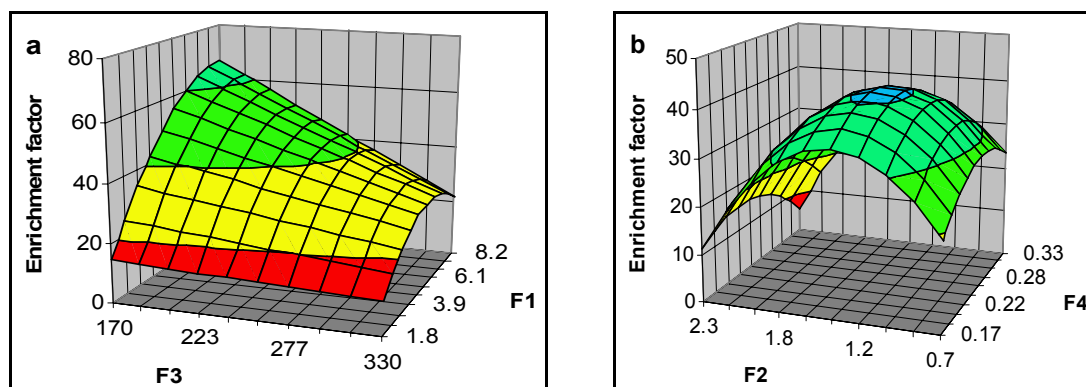


Figure 9



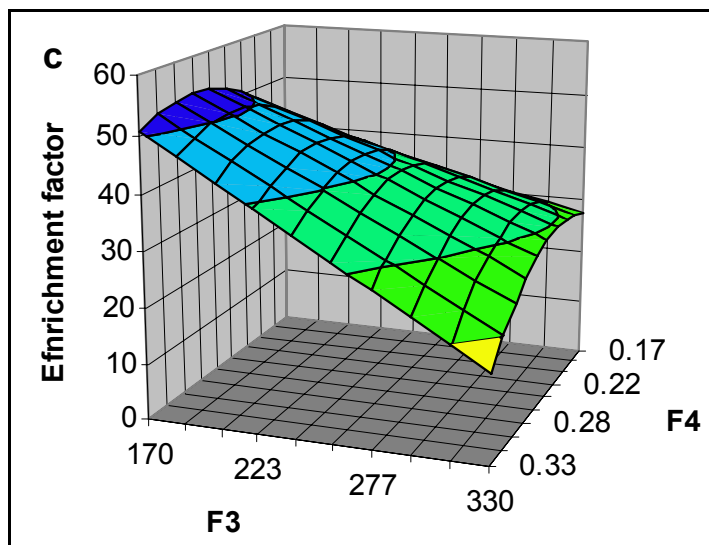
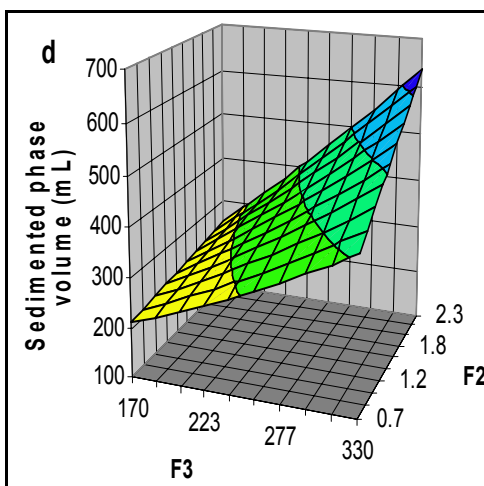
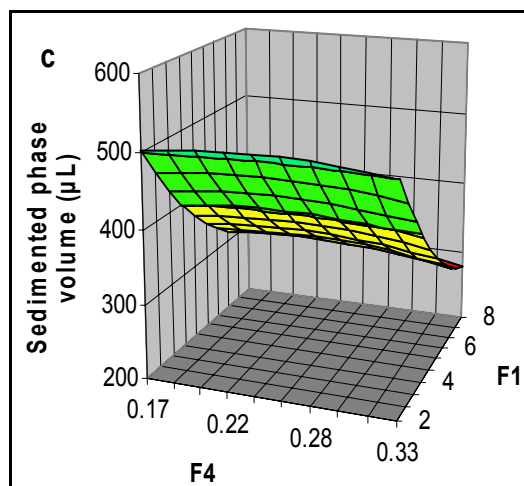
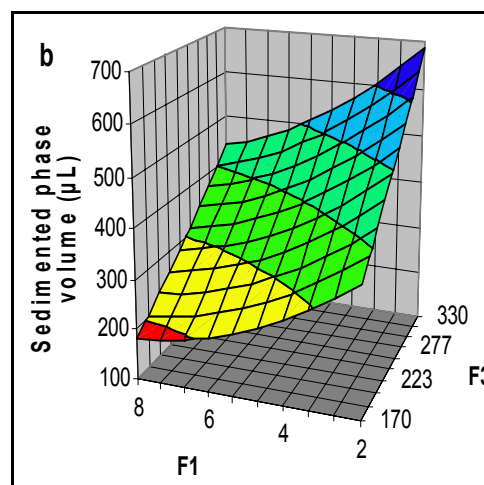
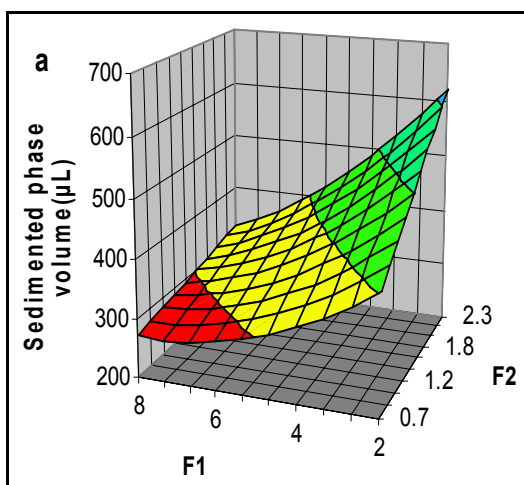


Figure 10



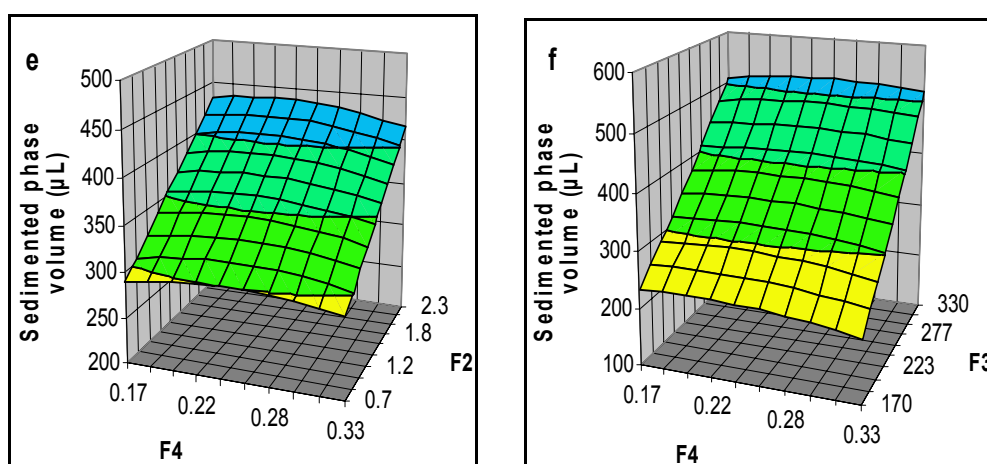


Figure 11

Table-3: List of experiments in the central composite design (uncoded values) for model optimization and the responses

Design points	Factors levels				Response		
	F1	F2	F3	F4	Recovery (%)	Enrichment Factor (EF)	<i>Sedimented phase volume (μL)</i>
1	7	2	200	0.2	50	42.5	250
2	7	1	200	0.2	46	46	212
3	3	1	200	0.2	55	18.7	330
4	7	1	300	0.2	56	33.8	355
5	3	1	200	0.3	66	25	300
6	5	1.5	250	0.17	78	37.5	361
7	5	1.5	170	0.25	73	54.2	220
8	5	0.7	250	0.25	53	28.2	308
9	5	2.3	250	0.25	45	17	430
10	5	1.5	250	0.33	72	32	350
11	3	1	300	0.2	63	15.2	460
12	7	2	300	0.3	32	17	422
13(cp) ^a	5	1.5	250	0.25	94	40.5	375
14(cp) ^a	5	1.5	250	0.25	92	40.7	368
15	1.8	1.5	250	0.25	38	20	500
16	8.2	1.5	250	0.25	38	39	308
17	7	2	200	0.3	54	48	238
18(cp) ^a	5	1.5	250	0.25	92	41.2	362
19	3	2	300	0.2	55	10.2	620
20(cp) ^a	5	1.5	250	0.25	91	39.7	370
21	5	1.5	330	0.25	79	26.7	530
22	3	1	300	0.3	63	15	475
23	3	2	200	0.2	51	14.5	400
24	3	2	300	0.3	26	4.75	635
25	3	2	200	0.3	42	12.2	390
26	7	1	300	0.3	48	29	350
27	7	2	300	0.2	45	21.2	450
28	7	1	200	0.3	58	54.7	225

a. 4 Center points

Table-4: Some characteristics of the constructed models.

Response	R ²	R ² adjustment	R ² for prediction	Regression equations
Enrichment factor	0.965	0.944	0.879	EF = b ₀ + b ₁ *F ₁ + b ₂ *F ₂ + b ₃ *F ₃ + b ₄ *F ₄ + b ₅ *F ₁ *F ₁ + b ₆ *F ₁ *F ₃ + b ₇ *F ₂ *F ₂ + b ₈ *F ₂ *F ₄ + b ₉ *F ₃ *F ₄ + b ₁₀ *F ₄ *F ₄
Recovery	0.948	0.906	0.789	R = b ₀ + b ₁ *F ₁ + b ₂ *F ₂ + b ₃ *F ₃ + b ₄ *F ₄ + b ₅ *F ₁ *F ₁ + b ₆ *F ₁ *F ₂ + b ₇ *F ₂ *F ₂ + b ₈ *F ₂ *F ₃ + b ₉ *F ₂ *F ₄ + b ₁₀ *F ₃ *F ₃ + b ₁₁ *F ₃ *F ₄ + b ₁₂ *F ₄ *F ₄
Sedimented phase volume	0.997	0.994	0.979	SPV = b ₀ + b ₁ *F ₁ + b ₂ *F ₄ + b ₃ *F ₁ *F ₁ + b ₄ *F ₁ *F ₂ + b ₅ *F ₁ *F ₃ + b ₆ *F ₁ *F ₄ + b ₇ *F ₂ *F ₃ + b ₈ *F ₂ *F ₄ + b ₉ *F ₃ *F ₃ + b ₁₀ *F ₃ *F ₄ + b ₁₁ *F ₄ *F ₄

Table-5: Constants and coefficients for the constructed quadratic models (Eqs. presented in Table 4) for each response

	Recovery (%)	Enrichment Factor (EF)	Sedimented phase volume (μL)
b ₀	-488.06	-213.83	136.13
b ₁	40.90	26.89	-23.88
b ₂	210.28	91.39	735.94
b ₃	1.276	0.257	3.597
b ₄	1404.9	798.67	-16.18
b ₅	-4.597	-1.183	-0.07153
b ₆	2.875	-0.04059	-13.75
b ₇	-56.36	-29.72	0.716
b ₈	-0.110	-41.13	-54.57
b ₉	-155.00	-0.821	0.00166
b ₁₀	-0.00142	-1073.3	1.078
b ₁₁	-1.700		-1822.3
b ₁₂	-1573.7		

Table-6

Concentration (μgmL-1)	Mean EF ± SDa		Mean recovery ± SDa	
	Co ²⁺	Cr ³⁺	Co ²⁺	Cr ³⁺
0.50	61.5 ± 1.78	58.9 ± 1.94	88.2 ± 1.83	84.11 ± 2.06
1.00	63.69 ± 1.21	58.42 ± 1.13	90.06 ± 1.19	83.39 ± 1.18
2.00	60.6 ± 2.71	59.8 ± 3.65	83.9 ± 2.51	87.4 ± 3.38

a) n = 3

Table7

Sample	Concentration ($\mu\text{g mL}^{-1}$) obtained by			
	This method ^a		Standard method ^b	
	Co ²⁺	Cr ³⁺	Co ²⁺	Cr ³⁺
Tap water	ND ^c	ND	ND	ND
Aras river water (point 1)	0.4	ND	0.5	2.3
Aras river water (point 2)	10.8 \pm 1.2	ND	11.11 \pm 4.5	2.1
Aras river water (point 3)	16.9 \pm 3.1	0.38	18.12 \pm 3.7	0.4
Mineral water	ND	ND	ND	ND

a. Obtained by standard addition method

b. Mean \pm standard deviation (n=3)

c. Not detected

CONCLUSIONS

A dispersive liquid–liquid microextraction method was used for preconcentration of Co²⁺ and Cr³⁺ ions prior to determination by HPLC-DAD technique. Enrichment factor and recovery for the target analyte were obtained about 63.69 and 90% for cobalt and 58.42 and 84% for chromium, respectively. The proposed extraction method was used for the quantification of Co²⁺ and Cr³⁺ ions in different water samples and the obtained results were compared to those obtained by a standard method. A relatively good agreement was observed between them. The method is simple, efficient and very rapid and it uses extracting solvent at μL level.

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