



Dispersive liquid–liquid microextraction based on the solidification of floating organic drop followed by inductively coupled plasma–optical emission spectrometry as a fast technique for the simultaneous determination of heavy metals

Yadollah Yamini^{a,*}, Mohammad Rezaee^a, Alireza Khanchi^b, Mohammad Faraji^a, Abolfazl Saleh^a

^a Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran

^b Jaber Ibn Hayan Research Laboratories, Nuclear Fuel Cycle Research School, Nuclear Science & Technology Research Institute, Atomic Energy Organization of Iran, End of North Karegar Ave, P.O. Box 14395-836, Tehran, Iran

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ABSTRACT

A simple, rapid and efficient dispersive liquid–liquid microextraction based on the solidification of floating organic drop (DLLME–SFO) method, followed by inductively coupled plasma–optical emission spectrometry (ICP–OES) was developed for the simultaneous preconcentration and determination of heavy metals in water samples. One variable at a time method was applied to select the type of extraction and disperser solvents. Then, an orthogonal array design (OAD) with $OA_{16} (4^5)$ matrix was employed to study the effects of different parameters on the extraction efficiency. Under the best experimental conditions (extraction solvent: 140 μL of 1–undecanol; disperser solvent: 2.0 mL of acetone; ligand to metal mole ratio: 20; pH: 6 and without salt addition), the enhancement factor ranged from 57 to 96. The calibration graphs were linear in the range of 0.5–250 $\mu\text{g L}^{-1}$ for Mn, 1.25–250 $\mu\text{g L}^{-1}$ for Cr, Co and Cu with correlation coefficient (r) better than 0.990. The detection limits were between 0.1 and 0.3 $\mu\text{g L}^{-1}$. Finally, the developed method was successfully applied to extraction and determination of the mentioned metal ions in the tap, sea and mineral water samples and satisfactory results were obtained.

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1. Introduction

The determination of heavy metals at trace levels in environmental samples is one of the targets of analytical chemists [1–3]. Recently, the toxicity and the effect of trace elements which are dangerous to public health and environment are attracting more attention from pollution and nutritional fields [4]. However, direct determination of metal ions at trace levels is limited due to their low concentrations and matrix interferences. Therefore, in trace analysis, to improve the detection limits, preconcentration of trace elements is frequently necessary [5].

Various preconcentration techniques including solvent extraction [6,7] cloud point extraction [8,9] and ion–exchange [10,11] have been applied for extraction of trace levels of the heavy metal ions from various environmental samples.

Recently, a new liquid–liquid extraction technique namely “dispersive liquid–liquid microextraction” which uses microliter volume of extraction solvent along with a few milliliters of dispersive solvents such as methanol, acetonitrile or acetone was reported

[12]. In this method, cloudy solution is formed after injecting the appropriate mixture of extraction solvent and disperser solvent into the aqueous sample by syringe. Up to now, DLLME has been successfully applied to the determination of organic and inorganic species [12–26], in water samples.

Despite many benefits of DLLME, the choice of the extraction solvent has its main drawbacks. In DLLME, solvents with the densities higher than water are required and further, they are not often compatible with ICP–OES and reverse phase HPLC. DLLME needs extraction solvents and their toxicity is higher than solvents that are used in DLLME–SFO. DLLME have less extraction efficiency for the heavy metal ions. A novel dispersive liquid–liquid microextraction method based on the solidification of floating organic drop (DLLME–SFO) was introduced by Leong et al. [27]. It is based on DLLME and the solidification of floating organic drop [12,28]. In this method, the appropriate mixture of 1–undecanol (as extraction solvent) and dispersive solvent is injected into aqueous sample by syringe, rapidly. Thereby, cloudy solution is formed. The extraction solvent after DLLME, was collected in the top of the test tube and was then cooled by inserting it into an ice bath for 5 min. The solidified 1–undecanol was transferred into a suitable vial and immediately melted; then it was dissolved in 100 μL of 1–propanol (as eluent in ICP–OES) and was finally injected into an

* Corresponding author. Tel.: +98 21 82883417; fax: +98 21 88006544.
E-mail address: yyamini@modares.ac.ir (Y. Yamini).

ICP-OES by using flow injection system. DLLME–SFO was developed for the determination of halogenated organic compounds (HOCs) and polycyclic aromatic hydrocarbons (PAHs) in water samples [27,29]. This technique is easily carried out. The large contact surface between the sample and the droplets of extractants speeds up mass transfer, as fast as DLLME and shorter extraction time than liquid–liquid microextraction based on the solidification of floating organic droplet (LLME–SFO). In this method there is no need to use conical bottom glass tubes, which are easily damaged and hard to clean. The floated extractant is solidified and is easily collected for analysis.

The advantages of DLLME–SFO method are simplicity of operation, rapidity, low cost, high recovery, compatibility of the extraction solvent with the instruments analyses such as ICP-OES in contrast to dispersive liquid–liquid microextraction (DLLME) and using extracting solvent with lower density rather than water and lower toxicity in contrast to DLLME and having higher extraction efficiency for heavy metal ions in contrast to DLLME.

In this paper, DLLME–SFO followed by ICP-OES has been investigated for the simultaneous determination of Mn, Cr, Co and Cu in water samples. Furthermore, experimental variables, such as type of extraction and disperser solvents, volumes of extraction and disperser solvents, ligand to metal mole ratio, pH and salt addition were assessed and optimized with the aid of one variable at a time and orthogonal array design (OAD) optimization methods. Orthogonal array design (OAD) is a type of fractional factorial design [31,32] in which orthogonal array is used to assign factors to a series of experimental combination, whose results can then be analyzed using a common mathematical procedure. Several applications of this method have been reported [32,33]. A more detailed description of an orthogonal array design was given elsewhere [34]. One variable at a time was used to choose the extractant and disperser solvents. In the OAD, with an $OA_{16} (4^5)$ matrix, significant factors that can affect the extraction recovery were identified as the volumes of extraction and disperser solvents, ligand to metal mole ratio, pH and salt addition.

2. Experimental

2.1. Chemicals and reagents

All chemicals used were of analytical reagent grade. Stock solutions (1000 mg L^{-1}) of Co^{2+} , Cu^{2+} and Mn^{2+} were prepared by the direct dissolution of proper amount of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ salts from Merck (Darmstadt, Germany) in ultra-

pure water. The stock standard solution of Cr^{3+} (1000 mg L^{-1}) was purchased from Sigma–Aldrich Company (Milwaukee, WI, USA). The standard solutions were diluted with ultrapure water to prepare the mixed standard solutions. Reagent grade 1-(2-thenoyl)-3,3,3-trifluoroacetone (TTA) (Merck) was used as chelating agent. A 0.5 mol L^{-1} solution of TTA in methanol was prepared by dissolving proper amount of the reagent. The pH of solutions was adjusted by dissolving proper amount of ammonium acetate in distilled water ($2.5 \times 10^{-3} \text{ mol L}^{-1}$) and drop wise addition of nitric acid (0.5 mol L^{-1}) and/or sodium hydroxide solutions (0.5 mol L^{-1}).

Carbon tetrachloride (GR), chloroform, 1-undecanol and chlorobenzene were obtained from Merck. Acetone, acetonitrile and methanol used as dispersive solvents and sodium chloride were obtained from Merck. The water used was purified on a Youngling ultra pure water purification system (Aqua Max™–Ultra, South Korea).

2.2. Apparatus

Determination of metal ions were performed with a simultaneous inductively coupled plasma-optical emission spectrometry (ICP-OES) model Vista PRO from Varian Company (Springvale, Australia) coupled to V-groove nebulizer and Scott spray chamber made from quartz glass and equipped with a charge coupled device (CCD) detector. Electrothermal atomic absorption spectrometry (ET-AAS) measurements were carried out by an atomic absorption spectrometer GBC, Avanta PM (Australia) equipped with a graphite furnace atomizer GF 3000 and an autosampler (Pal 3000). Deuterium background correction was employed to correct non-specific absorbance. Peak height was chosen as the analytical signal. The instrumental parameters and temperature program for the ET-AAS are tabulated in Table 1.

A silicon tube ($L = 4.0 \text{ cm}$, I.D. = 2.52 mm) was used as a loop and was connected to a six-port two-position injection valve (Tehran University, Iran) to introduce the final solution to ICP-OES. The pH of the solutions was determined and adjusted using a pH meter model WTW (Inolab, Germany) with a combined glass-calomel electrode.

The effects of different instrumental parameters including RF generator power, viewing height, nebulizer pressure and pump rate of ICP-OES on the emission intensities of the heavy metal ions were investigated and optimized by the direct introduction of 20 ppm of the heavy metal standards into the instrument. Table 2 shows the optimal instrumental conditions and emission lines which were used for determination of the metal ions via ICP-OES.

Table 1
Instrumental parameters for the metal ions determination using ET-AAS.

Spectrometer parameters	Cu		Co		Cr		Mn
Wavelength (nm)	324.7		242.5		357.9		279.5
Slit width (nm)	0.5		0.2		0.5		0.2
Lamp current (mA)	3.0		7.0		5.0		5.0
Step	Temperature ($^{\circ}\text{C}$)				Time (s)		Gas flow (L min^{-1})
	Cu	Co	Cr	Mn	Ramp	Hold	
Electrothermal atomizer							
Pre-warming	50	50	50	50	1	2	3.0
Inject step	Inject sample				–	–	3.0
Drying I	90	90	90	90	10	15	3.0
Drying II	120	120	120	120	15	10	3.0
Ashing	600	750	850	650	10	5	3.0
Gas stop step	600	750	850	650	0	1	3.0
Atomization	2600	2300	2500	2200	0.9	1.2	0
Cleaning	2600	2400	2600	2600	1	2	3.0

Table 2
ICP-OES operating conditions and metal ions emission lines.

RF generator power	1.65 kW
Frequency of RF generator	40 MHz
Plasma gas flow rate	15 L min ⁻¹
Auxiliary gas flow rate	1.5 L min ⁻¹
Viewing height (above coil)	6 mm
Nebulizer pressure	150 kPa
Pump rate	3.0 mL min ⁻¹
Analytical lines (nm)	238.892 (Co), 267.716 (Cr)
	324.754 (Cu), 257.610 (Mn)

2.3. Dispersive liquid–liquid microextraction based on the solidification of floating organic drop (DLLME–SFO) procedure

Aliquots of the solutions were selected and their pH and ionic strength were adjusted at appropriate amount. A 20.0 mL of solutions was placed in a 40.0 mL screw cap glass tube and spiked with the ions at 100 µg L⁻¹ level and suitable amount of TTA was added. The ions in the aqueous solution were complexed with TTA. Suitable volume of acetone containing microliter volume of 1-undecanol was injected into the sample solution by using a 5.0 mL of gastight syringe, rapidly. A cloudy solution was formed in the test tube (the cloudy state was stable for a long time). The mixtures were centrifuged for 3 min at 6000 rpm. Accordingly, the dispersed fine droplets of the extraction solvent were collected at the top of test tube. The sample solution was transferred into a beaker containing ice pieces and the organic solvent was solidified after 5 min and then, the solidified solvent was transferred into a conical vial where it was melted immediately. Finally it was dissolved in 100 µL of 1-propanol and injected into ICP-OES by a flow injection system.

3. Result and discussion

In the present work, DLLME–SFO combined with ICP-OES was developed for the simultaneous determination of Mn, Cr, Co and Cu in water samples. In first step, in order to obtain high ICP signals, the effect of extractant and disperser solvents was optimized using one variable at a time optimization method.

3.1. Selection of extraction solvent

Selection of the extractant is a key step in the optimization of DLLME conditions. Three chlorinated solvents, carbon tetrachloride (CCl₄), chloroform (CHCl₃) and chlorobenzene (C₆H₅Cl), showing densities above 1 g mL⁻¹, low water solubility and different polarities were considered for the dispersive liquid–liquid microextraction of metal ions. Formation of a sedimented phase was investigated with 20.0 mL samples. A series of sample solutions containing the metal ions were selected and DLLME procedure was followed by using 2.0 mL of acetone containing different volumes of extraction solvent to obtain about 100 µL of the sedimented phase. Thereby, 117, 135 and 190 µL of chlorobenzene, carbon tetrachloride and chloroform were used, respectively. After DLLME procedure the sedimented phase was evaporated and the residue was dissolved in 200 µL of 1-propanol and was injected into the ICP-OES. The intensities of ICP-OES signals (original intensities in counts unit) for different metal ions using different extraction solvents are shown in Fig. 1. The results revealed that in the presence of studied solvents very low ICP-OES intensities were observed for the metal ions. Thus, 1-undecanol was introduced first time as extraction solvent for the extraction of the ions from water samples. A sample solution containing the metal ions was selected and 2.0 mL of acetone containing 140 µL of 1-undecanol was injected into the solution to achieve about 100 µL volume of floating droplet.

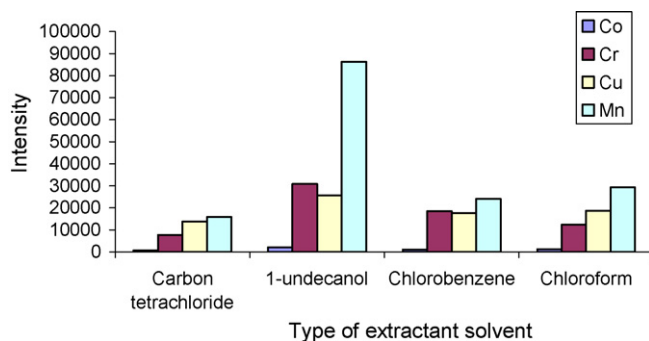


Fig. 1. Effect of type of the extraction solvent on the intensities of metal ions obtained from DLLME and DLLME–SFO. Extraction conditions: water sample volume, 20.0 mL; disperser solvent (acetone) volume, 2.0 mL; extraction solvent volumes, 190 µL CHCl₃, 135 µL C₆H₅Cl, 117 µL CCl₄ and 140 µL 1-undecanol; concentration of metal ions, 100 µg L⁻¹.

After DLLME–SFO procedure; the extraction solvent was dissolved in 100 µL of 1-propanol and then injected to ICP-OES by using 80% 1-propanol (v/v) in water as FIA carrier. Intensity of ICP-OES for the ions in the presence of 1-undecanol is very higher than the other tested solvents that were used in DLLME procedure (Fig. 1). It is probably, because of higher solubility of the complexes of the metal ions in 1-undecanol in comparison with the other tested solvents. Also the other advantages of 1-undecanol are compatibility of the solvent with ICP-OES instrument and easily collection of it after solidification.

3.2. Selection of disperser solvent

Miscibility of disperser solvent with extraction solvent and sample solution is the most important point for the selection of disperser solvent. Thereby, acetone, acetonitrile and methanol, which have these properties, are selected as disperser solvents. A series of sample solutions was extracted using 2.0 mL of each disperser solvent containing 140 µL 1-undecanol. The intensity values of metal ions in the presence of different disperser solvents are as follows: acetone [Co (3004), Cr (30,754), Cu (24,049) and Mn (96,050) counts], acetonitrile [Co (2105), Cr (31,536), Cu (25,031) and Mn (86,869) counts] and methanol [Co (1380), Cr (17,084), Cu (25,488) and Mn (79,229) counts]. The total ICP-OES intensities for acetone, acetonitrile and methanol were 1,53,857, 1,45,541 and 1,23,181 counts, respectively. The total ICP-OES intensity for acetone is higher than other solvents, thus, acetone was selected as disperser solvent because of its low toxicity, cost and higher ICP-OES signal.

3.3. Experimental design and data analysis

A five-factor, four-level factorial design was used to evaluate the effects of the volume of extraction solvent, the volume of disperser solvent, ligand to metal mole ratio, pH and salt addition on the extraction efficiency of the metal ions. In order to estimate the best condition for the extraction of the ions, 16 experiments were performed. Each experiment was repeated twice and the factors and their respected levels are reported in Table 3. In this study, the focus was on the main effects of the five most important factors. The effects of different parameters on the DLLME–SFO method combined with ICP-OES experiments based on the total normalized ICP-OES intensity of the metal ions are given in Fig. 2. To normalize the intensities of the metal ions, first, all of the experiments were performed based on Table 3. Then the intensity of each metal ion was divided over its smallest intensity that was obtained in all the experiments. Then normalized intensities for different metal ions

Table 3
OA₁₆ (4⁵) experimental design for the extraction of metal ions.

Trial	A ^a	B ^b	C ^c	D ^d	E ^e
1	1	0	5	3	60
2	1	3	10	4.5	100
3	1	6	20	6	140
4	1	10	30	8	170
5	2	0	10	6	170
6	2	3	5	8	140
7	2	6	30	3	100
8	2	10	20	4.5	60
9	4	0	20	8	100
10	4	3	30	6	60
11	4	6	5	4.5	170
12	4	10	10	3	140
13	6	0	30	4.5	140
14	6	3	20	3	170
15	6	6	10	8	60
16	6	10	5	6	100

^a Volume of disperser solvent (mL).^b Concentration of NaCl (w/v) %.^c Ligand/metal (L/M) ratio.^d pH.^e Volume of extractant solvent (μL).

were added for each run and used in calculation of total normalized intensity.

The best values of the selected factors for the extraction of the ions were obtained as: volume of extraction solvent (V_{ex}), 140 μL, volume of disperser solvent ($V_{dis.}$), 2.0 mL; ligand to metal molar ratio (L/M), 20; pH, 6 and without salt addition. The ANOVA results for the selected factor are shown in Table 4. The ANOVA results indicate that the pH play an important role in DLLME-SFO of the

ions from aqueous samples. The effect of other parameters was less significant.

Further experiments were performed under proposed conditions. The results showed that under the best conditions, obtained from the OA₁₆ (4⁵) matrix, total ICP-OES intensity of the metal ions is similar to the intensities calculated from the following equation:

$$Y_{opt} = \frac{T}{N} + \left(\overline{V_{dis.}} - \frac{T}{N} \right) + \left(\overline{L/M} - \frac{T}{N} \right) + \left(\overline{pH} - \frac{T}{N} \right) + \left(\overline{V_{ex.}} - \frac{T}{N} \right) \quad (1)$$

where T is the grand total of all results, N the total number of results, Y_{opt} the performance under optimum conditions, $\overline{V_{dis.}}$, $\overline{L/M}$, \overline{pH} and $\overline{V_{ex.}}$ are the average total normalized responses of the volume of disperser solvent, ligand to metal mole ratio, pH and the volume of extraction solvent at their optimum levels. Based on the above equation at the best conditions the total normalized intensity response is estimated using these significant factors [35]. Estimated total normalized intensities calculated by the Taguchi method = 300.27 ± 13.59 and empirical total normalized intensities = 281.97, these results show that there are satisfactory agreement between the results for the total intensity response of these metals estimated based on Eq. (1) and obtained under the best conditions in which the confidence interval (C.I.) of the normalized response is calculated using the following expression:

$$C.I. = \pm \sqrt{\frac{F(1, n_2)V_e}{N_e}} \quad (2)$$

where $F(1, n_2)$ is the F value from the F table at a required confidence level at degree of freedom (dof) 1 and dof of error, n_2 ; V_e is the

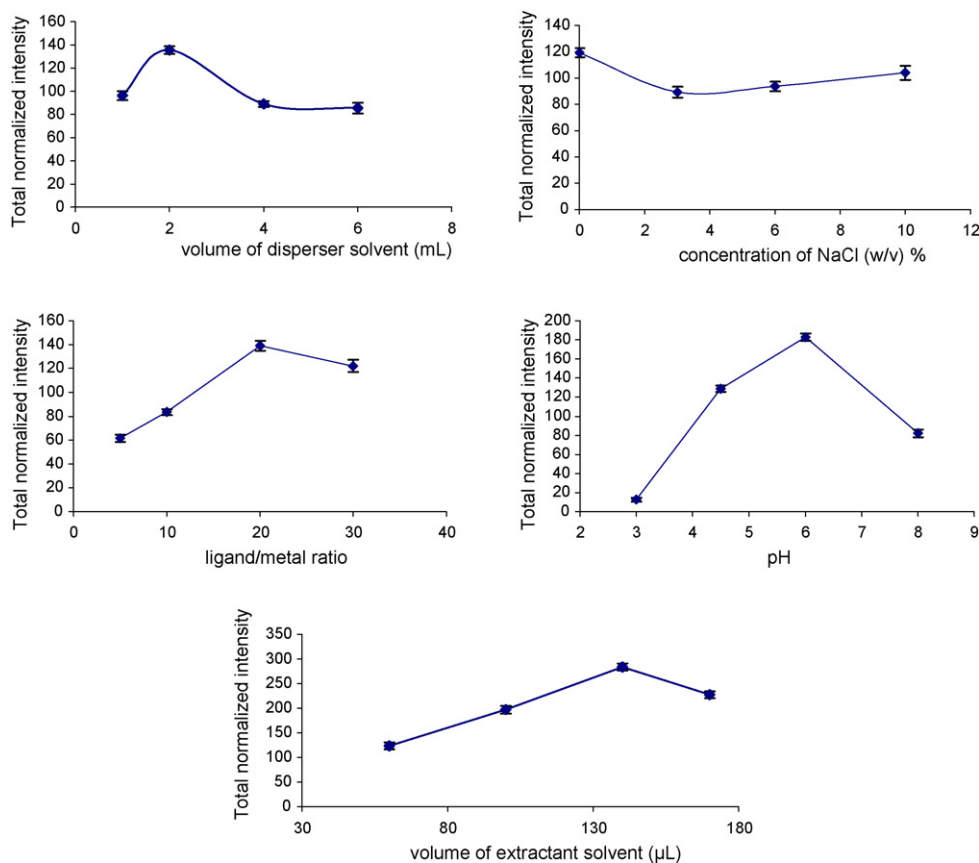


Fig. 2. Effect of the volume of disperser solvent, the volume of extraction solvent, pH, ligand to metal mole ratio and salt amount on the DLLME-SFO-ICP-OES. Extraction conditions: water sample volume, 20.0 mL; concentration of metal ions, $100 \mu\text{g L}^{-1}$.

Table 4
ANOVA of the metal ions extractions.

Factor	dof	Sum of Sqrs.	Variance	F ratio	Pure sum of Sqrs.	Percent (%)
A ^a	3	12788.378	4262.845	12.383	11755.819	5.998
B ^b	(3)	(4264.441)		POOLED	(CL=99.94%)	
C ^c	3	30062.101	10020.7	29.109	29029.382	14.811
D ^d	3	125172.775	41724.258	121.207	124140.056	63.341
E ^e	3	21422.885	7140.961	20.744	20390.167	10.403
Other/error	19	6540.551	344.239			5.447
Total	31	195986.852				100.00

^a Volume of disperser solvent.

^b Concentration of NaCl (w/v) %.

^c Ligand/metal ions (L/M) molar ratio.

^d pH.

^e Volume of extractant solvent.

variance of error term (from ANOVA) and N_e is the effective number of replications. C.I. value is 13.59.

3.3.1. Effect of the volume of extraction solvent

The effect of the volume of 1-undecanol on the analytical signal was studied in the range of 60–170 μL . The results are shown in Fig. 2. As can be seen, when the volume of 1-undecanol is increased, the analytical signal of the ions increases until 140 μL , by further increasing the volume of 1-undecanol, it decreases, because of dilution effect. Therefore, 140 μL of 1-undecanol was chosen as the optimum extracting solvent volume.

3.3.2. Effect of the volume of disperser solvent

The effect of the volume of disperser solvent on the analytical signal was studied in the range of 1.0–6.0 mL. The results are shown in Fig. 2. As can be seen, at the low volume of acetone, the analytical signals of these ions are low, because the cloudy state is not formed well. At the high volumes of acetone, the analytical signals of the ions are low, because the solubility of complexes of them in the aqueous samples increases. Based on the above results, the highest analytical signal was obtained at 2.0 mL of the acetone. Therefore, 2.0 mL of acetone was selected as the volume of disperser solvent.

3.3.3. Influence of pH

The pH of the solution plays a unique role on metal-chelate formation and subsequent extraction. The extraction yield depends on the pH at which the complex formation occurs. In the present work, the effect of pH upon the complex formation of target ions was studied within the pH range of 3.0–8.0, using ammonium acetate solution and addition of 0.5 mol L⁻¹ of NaOH or HNO₃. As shown in Fig. 2 and based on the ANOVA results, the effect of pH on the analytical signal of the metal ions was significant and at the pH of 6, the highest signal was obtained. Hence, the pH of 6 was chosen for the subsequent extractions.

3.3.4. Influence of ligand to metal mole ratio

The effect of the TTA amount on the analytical signals is shown in Fig. 2. The intensity was increased by increasing the TTA amount, which is well expected. Accordingly, at TTA/metal ions molar ratio of 20, the highest intensity was obtained. It seems that slight reduction of extraction efficiency at higher concentration of TTA is due to the extraction of TTA itself, which can easily saturate the small volume of extraction solvent. Therefore, for further studies, a TTA/metal ions molar ratio of 20 was selected.

3.3.5. Salt addition

To study the effect of salt addition on the analytical signal of the metal ions, the concentration of NaCl was changed in the range of 0–10% (w/v). The ANOVA results showed that extraction efficiency of the analytes was independent of NaCl concentration. Thus, according to Table 4, the strategy of no salt addition was performed.

3.4. Effect of extraction time

In DLLME–SFO, extraction time is defined as interval time between injecting the mixture of disperser solvent and extraction solvent, before starting to centrifuge. The effect of extraction time on the extraction efficiency was examined in the range of 0–30 min under constant experimental conditions. The obtained results showed that the extraction time did not have significant influence on the ICP signals of the metal ions. Because, in DLLME–SFO after the formation of cloudy solution, the surface area between extraction solvent and aqueous sample is infinitely large. Thereby, transition of complex from aqueous sample to extraction solvent is fast. This is the great advantage of DLLME–SFO technique, which is independent of time. In this method, time-consuming step is centrifuging of sample solution, which is about 3 min and solidification of 1-undecanol, which is about 5 min.

3.5. Interferences

The potential interferences of some ions on the preconcentration and determination of metal ions were examined. In these experiments, solutions of 100 $\mu\text{g L}^{-1}$ of the analytes containing the interfering ions were treated according to the optimized procedures. Table 5 shows tolerance limits of the interfering ions. In the

Table 5
Effect of interferences ions on preconcentration and determination of metal ions.

Interference	Interference to metal ions ratio (w/w) ^a	Recovery (%)			
		Co	Cr	Cu	Mn
Na ⁺	2000	98	102	100	94
K ⁺	2000	96	92	87	96
Ba ²⁺	1000	99	94	99	98
Ba ²⁺	500	98	93	97	95
Ca ²⁺	1000	92	101	98	89
Ca ²⁺	500	95	100	99	91
Mg ²⁺	1000	85	83	84	86
Mg ²⁺	500	88	87	89	92
Hg ²⁺	500	71	88	93	89
Hg ²⁺	100	108	104	102	101
Al ³⁺	200	17	25	65	13
Al ³⁺	50	101	85	109	89
Pb ²⁺	200	36	32	69	23
Pb ²⁺	50	94	93	97	98
Ni ²⁺	200	25	39	36	14
Ni ²⁺	50	99	86	83	98
Zn ²⁺	200	23	12	62	15
Zn ²⁺	30	85	86	101	87
Cd ²⁺	200	63	56	68	46
Cd ²⁺	50	88	92	97	86
Fe ³⁺	50	51	58	62	41
Fe ³⁺ + 0.02 SCN ⁻	5	98	112	94	96

^a Concentration of each metal ion is 100 $\mu\text{g L}^{-1}$.

Table 6

Figures of merit of the proposed method.

Analyte	Enhancement factor	Detection limit ($\mu\text{g L}^{-1}$) ^a	RSD% ^b (n = 6)	Dynamic linear range ($\mu\text{g L}^{-1}$)	R ²
Co	76	0.2	3.4	1.25–250	0.995
Cr	96	0.1	4.1	1.25–250	0.994
Cu	93	0.2	6.7	1.25–250	0.996
Mn	57	0.3	7.5	0.5–250	0.990

^a Detection limits were calculated based on $3 S_b/m$.^b Percent relative standard deviation for six replicate measurements of the elements with the concentration of $100 \mu\text{g L}^{-1}$ in the water samples.**Table 7**

Comparison of the proposed method with CPE and SPE of the metal ions in water samples.

Metal ions	System	Method	EF	DLR	DL ^a	R.S.D.%	Detection	Ref.
Mn–Fe	TMBP ^b /Triton X-100	Off-line CPE	25–31		0.02–0.08	3.5–4.2	GF-AAS	[36]
Cr(III)/Cr(VI)	PMBP ^c /Triton X-100	Off-line CPE	20		0.81		FAAS	[37]
Fe, Cu, Mn, Zn, Co, Ni, Cd, pb	Amberlite XAD-2000/DDTC ^d	On-line SPE	100	0.04–7.0 mg L ⁻¹	0.15–0.45		FAAS	[38]
Cu, Cd, Pb, Zn, Mn, Fe, Cr, Ni, Co	Chromosorb 108/bathocuproinedsulfonic	On-line SPE	80	0.02–10.0 mg L ⁻¹	0.16–0.60	1–17	FAAS	[39]
Cd, Co, Cr, Cu, Fe, Mn	TTA/Triton X-114	On-line CPE	42–97	0.5–100 $\mu\text{g L}^{-1}$	0.1–2.2	2.2–4.6	ICP-OES	[40]
Co, Cr, Cu, Mn	DLLME-SFO	Flow injection	57–96	1.25–250 $\mu\text{g L}^{-1}$	0.1–0.3	3.4–7.5	ICP-OES	This work

^a Detection limit ($\mu\text{g L}^{-1}$).^b 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone.^c 2-[2'-(6-Methyl-benzothiazolylazo)-4-bromophenol.^d Diethyldithiocarbamate.

present study the tolerance limits of the coexisting ions, defined as the largest amounts of the coexisting ions, change the recovery of the metal ions as large as $\pm 10\%$. The results showed that Hg^{2+} could be tolerated up to $10 \mu\text{g mL}^{-1}$, Al^{3+} , Pb^{2+} , Ni^{2+} and Cd^{2+} could be tolerated up to $5 \mu\text{g mL}^{-1}$, Zn^{2+} and Fe^{3+} could be tolerated up to 3 and $0.5 \mu\text{g mL}^{-1}$, respectively. In addition, a number of common anions like Cl^- , SO_4^{2-} , NO_3^- , I^- and F^- were tested. The results showed that they did not interfere at the concentrations up to 100mg L^{-1} .

3.6. Figures of merit of the proposed method

The figures of merit of the proposed method are summarized in Table 6. The percent relative standard deviations (RSDs %) were between 3.4 and 7.5. The detection limits (DLs) were calculated from $\text{C}_{\text{LOD}} = K S_b/m$, where K is a numerical value of 3, S_b is the standard deviation of six replicate blank measurement and m is the slope of the calibration graph. The DLs were obtained between

0.1 and $0.3 \mu\text{g L}^{-1}$ for different metal ions. In order to find linear dynamic range (LDR, which defines as concentration range that a linear relation between signal of ICP-OES and concentration of the metal ion exists) of the proposed method for the metal ions, nine standards containing mixture of the ions were prepared in the distilled water and extracted under the optimal conditions. After the extraction of the metal ions by DLLME-SFO procedure, the floating droplet of 1-undecanol was dissolved in $100 \mu\text{L}$ of 1-propanol and was then injected into ICP-OES by using FI system. LDRs of $0.5\text{--}250 \mu\text{g L}^{-1}$ for Mn and $1.25\text{--}250 \mu\text{g L}^{-1}$ for other metal ions were obtained. The correlation coefficient of the calibration curves were in the range of 0.990–0.996. Comparison of the proposed method with off-line CPE and on-line SPE methods to extract and determine the similar metal ions is shown in Table 7. In the present work, better enhancement factors were obtained for most of the metal ions in comparison with the off-line CPE methods and that these obtained enhancement factors are comparable with those of

Table 8

Determination of the metal ions in different water samples.

Sample	Concentration ($\mu\text{g L}^{-1}$) \pm RSD (%) (n = 3)				Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$) \pm RSD (%) (n = 3)				Relative recovery (%)			
	Co	Cr	Cu	Mn		Co	Cr	Cu	Mn	Co	Cr	Cu	Mn
Sea water ^a	–	–	3.3 ± 5.7	7.8 ± 2.2	10	9.3 ± 10.4	8.9 ± 7.3	12.4 ± 12.3	17.4 ± 11.5	93	89.5	91	96
Mineral water ^b	–	–	–	5.3 ± 5.3	10	8.6 ± 1.0	8.3 ± 8.1	9.2 ± 10.3	14.5 ± 4.5	86.5	83.2	92.3	87.4
Tap water ^c	–	–	4.8 ± 9.8	2.8 ± 10.3	10	9.7 ± 6.3	8.6 ± 9.8	14.3 ± 4.1	11.6 ± 10.6	97.2	85.6	95	88

^a The sample was collected from Caspian Sea (Mazandaran, Iran).^b Mineral water was prepared from Pars Mineral Water Company (Tehran, Iran).^c The water was taken from Tarbiat Modares University (Tehran, Iran).**Table 9**

Determination of Cu, Cr, Co and Mn ions in different water samples.

Sample	ET-AAS method ($\mu\text{g L}^{-1}$) ^a				Proposed method ($\mu\text{g L}^{-1}$) ^a			
	Cu	Cr	Co	Mn	Cu	Cr	Co	Mn
River water ^b	2.3 ± 2.2	N.D. ^e	N.D. ^e	4.6 ± 5.3	2.0 ± 3.1	N.D.	N.D.	5.2 ± 6.1
Tap water ^c	4.4 ± 3.8	N.D.	N.D.	2.5 ± 1.6	4.8 ± 9.8	N.D.	N.D.	2.8 ± 10.3
Mineral water ^d	N.D.	N.D.	N.D.	5.8 ± 4.7	N.D.	N.D.	N.D.	5.3 ± 5.3

^a Concentrations of metal ions were determined using standard addition method.^b The sample was collected from Langrud River (Gilan, Iran).^c The water was taken from Tarbiat Modares University (Tehran, Iran).^d Mineral water was prepared from Pars Mineral Water Company (Tehran, Iran).^e Not detected.

on-line SPE methods. Precision of the proposed method is comparable with off-line CPE methods and it is better than on-line SPE methods.

In the on-line mode of CPE, heating of sample and trapping of the surfactant-rich phase on a column and elution of the entrapped analytes are need. These steps are time-consuming and labour intensive. In comparison with on-line SPE and on-line CPE, the proposed method is simple, fast and cheap.

3.7. Analysis of real samples

To demonstrate the performance of the present method, it was utilized to determine the analytes concentration in different water samples. The obtained results are given in Table 8. As seen, the relative recoveries for the spiked samples are in acceptance range (83.2–97.2%). Also, in order to investigate the accuracy of the proposed method, further experiments were done on new water samples and the results were compared with those obtained by direct determination using ET-AAS (Table 9). One can see that satisfactory agreement exists between the results obtained for the cations in the water samples by the proposed method and ET-AAS.

4. Conclusion

For the first time, orthogonal array designs were efficiently employed to optimize the dispersive liquid–liquid microextraction based on the the solidification of floating organic drop (DLLME–SFO) method. The results of ANOVA showed that pH has significant effect on the DLLME–SFO of the metal ions. The results showed that the Taguchi optimization approach is a suitable method for the optimization of DLLME–SFO of metal ions from aqueous samples. The proposed method in comparison with on-line CPE and on-line SPE has advantages such as simplicity, short extraction time and low cost. The preconcentration method allows analytes determination in different aqueous samples with good accuracy and reproducibility.

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