ISSN: 2279 - 0594

Available Online at www.jbpr.in

Journal of Biomedical and Pharmaceutical Research 2 (6) 2013, 65-73

RESEARCH ARTICLE

Optimization of dispersive liquid-liquid microextraction followed by flame atomic absorption determination of Cu (II), Ni (II) and Co (II) based on the complexation reaction with phenathrene-9, 10-dine dioxime (PD)

N. Samadi*, A. Chehregani, M. R. Vardast

Faculty of chemistry. Urmia University, Urmia-IRAN

Received 10 October 2013; Revised 22 October 2013; Accepted 25 October 2013

ABSTRACT

In this study, a dispersive liquid-liquid microextraction (DLLME) method was used for preconcentration of Cu (II), Ni (II) and Co (II) cations from water samples. Oxime (phenathrene-9, 10-dine dioxime (PD)) was used as a chelating agent prior to extraction. Flame atomic absorption spectrophotometry using an acetylene-air flame was used for quantitation of the analytes after preconcentration. The effects of various experimental parameters in extraction were investigated using two optimization methods, one variable at a time and central composite design. The experimental design was done at four levels of operating parameters. Under optimum conditions the calibration curves were linear in the range of (10-2000μg L^{-1}) with detection limits of 5 μg L^{-1} for both Cu (II) and Ni (II) (10-1000 μgL $^{-1}$) and 0.5 μg L $^{-1}$ for Co (II). Recoveries and enrichment factores for Copper, Cobalt and Nickel were obtained as (77.6%, 26.99), (76.53%, 29.95) and (74.23%, 29), respectively.

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 state [1-4].Separation and preconcentration procedures are often needed before FAAS application. The most widely used techniques for the separation and preconcentration of trace Cu, Ni and Co in FAAS include liquid–liquid extraction (LLE) [5], solid-phase extraction (SPE) [6,7], and cloud point extraction (CPE) [8,9], but disadvantages, such as time consumption, unsatisfactory enrichment factors, large organic solvents, and secondary wastes, limit their applications. In recent years, liquid-phase microextraction (LPME) has been developed as a solvent-minimized sample pretreatment procedure since 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 potential [10–12]. 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 has to be hydrophobic with a density more than that of water. Hydrocarbons and halogenated hydrocarbons, such as chloroform [13], chlorobenzene [14], carbon tetrachloride [15], tetrachloroethane [10], n-hexane [16] and hexadecane [17], 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, tiny droplets are produced and the surface area between the extraction solvent and the aqueous sample increases [5, 18]. 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) [10], organophosphorus pesticides (OPPs) [20], chlorobenzenes (CBs) [11], chlorophenols [14], trihalomathans [THMs] [21], cadmium [22] and selenium [23] in water samples. In addition, other researchers have used this method for the measurement of antioxidants [19], volatile phenols [15] and triazine herbicides [24]. DLLME is a miniaturized sample pretreatment technique that uses microliter volumes of the extraction solvent. Some of DLLME advantages include simplicity, rapidity, low sample volume requirement, low cost and high enrichment factor [25].We now report the DLLME application, as a

---

**Corresponding author:* *N. Samadi* | *Email:* *samadi76@yahoo.com* separation and preconcentration technique, for the rapid determination of Nickel, Cobalt and Copper in water samples using phenathrene-9, 10-dine dioxime (PD) as chelating agent(fig1). Eventually, flame atomic absorbtion spectrometry (FAAS) was used for detection. The analytic in the sample is extracted into the fine droplets of extraction solvent. After extraction, phase separation is performed by centrifugation, and the enriched analytic in the sediment phase is determined by chromatography or spectrometry methods. The advantages of the DLLME method are simplicity, rapidity, low cost, high recovery and enrichment factors.

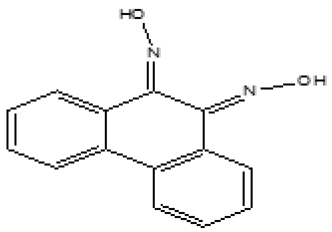

Figure 1: Moleccular structure of Indolenin

2. Experimental:

2.1 Chemicals and solution:

All chemicals such as ethanol, acetonitrile, Ammoniac, Ammonium chloride and nitric acid were high-purity grade reagents from Merck Co. (Darmstadt, Germany). Working standard solutions were obtained by appropriate dilution from 1000 µg ml^{-1} stock solutions. A solution 0.01 mol l^{-1} of PD was prepared by dissolving 0.2374 g of this reagent in 100 ml acetonitrile. Reagent oxime (phenathrene-9, 10-dine dioxime (PD) was prepared in the lab according to the reported method. The purity was checked by recording NMR spectra.

2.2. Apparatus:

A Shimadzu atomic absorption spectrometer (Model AA-670G) was used for the determination of cobalt, nickel and copper using the manufacturer recommendations.

2.3. Procedure:

The DLLME procedure required the following steps according to our previous report [26]. 5.0mL of doubly distilled water spiked with analytes was placed in a 10mL glass centrifugal tube with conical bottom and were spiked at cobalt and copper concentration of $1mgL^{-1}$ and nickel concentration of $4mgL^{-1}$. 1mL ammonic buffer and 0.5mL PD solution were added. By using a 5mL syringe, 2.5mL ethanol containing 250µL 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 3000 rpm. The volume of the sedimented phase (chloroform) was determined using a 250µL GC syringe. The enriched analytes in the [PD] [Co^{+2}, Cu^{+2} and Ni^{+2}] phase were withdrawn by microsyringe. The sedimented phase was quantitatively transferred to another test tube and allowed to evaporate at room temperature.The remaining micellar phase was dissolved in 0.5mL of 1.0 M HNO3 in methanol and then the ions contents were readily evaluated by FAAS. Copper standard solutions (0.1–10 mg L^{-1}), Nickel standard solutions (.2-20 mg L^{-1}) and Cobalt standard solutions (.2 – 10 mg L^{-1}) in methanol were prepared daily and their absorbance was read along with samples.

2.4. Statistical software:

Essential Regression and Experimental Design for Chemists and Engineers, EREGRESS, as a Microsoft Excel Add-In software[27,28] was used to design the experiments and to mode and analyze the results.

2.5. Experimental design:

Central composite design was used to optimize the preconcentration of Co^{2+}, Cu^{2+} and Ni^{2+} by cloud point extraction Four independent variables, namely the Dispersive solvent volume (F1), Extracting solvent volume (F2), Sample volume (F3) and pH (F4) were studied at five levels with four repeats at the central point, using a circumscribed central composite design. The PD concentration was selected 0.01 mol L^{-1} in all experiments. For each of the five studied variables, high (coded value: +1.607) and low (coded value: -1.607) set points were selected as shown in Table 1. Also Table 2 shows the coded values of designed experiments based on CCD methodology achieved using EREGRESS software by the use of EREGRESS, polynomial equations, response by the use of EREGRESS, polynomial equations, response surface and central plots for a particular response are produced. For an experimental design with four factors, the model including linear, quadratic, and cross terms can be expressed as the following equation:

$$\text{Response} = b_0 + b_1F_1 + b_2F_2 + b_3F_3 + b_4F_4 + b_5F_1 * F_1 + b_6F_2 * F_2 + b_7F_3 * F_3 + b_8F_4 * F_4 + b_9F_1 * F_2 + b_{10}F_1 * F_3 + b_{11}F_1 * F_4 + b_{12}F_2 * F_3 + b_{13}F_2 * F_4 + b_{14}F_3 * F_4$$

3. 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 EF = C_{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 [PD] [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 this work, optimization was performed both via one variable at a time and with central composite design methods. Factors such as selection of the dispersive and extracting solvents and their volumes, sample size, pH, salting out effect, etc., were studied and the optimum conditions were selected. Enrichment factor was calculated using ratio of the analyte concentration in the sedimented phase to the analyte concentration in the aqueous sample.

3.1. One variable at a time method (Optimization of Chemical Variables)

3.1.1. 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. In this work five solvents: methanol, acetone, tetrahydrofuran, ethanol and acetonitrile, were studied as dispersive solvent. 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 [10, 19 and 30]. In this work, chloroform, dichloromethane 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 and ethanol as dispersive solvent is the best. Therefore, the combination of chloroform and ethanol 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 was relatively high, so no extraction was occurred and the EF and RF were both zero.

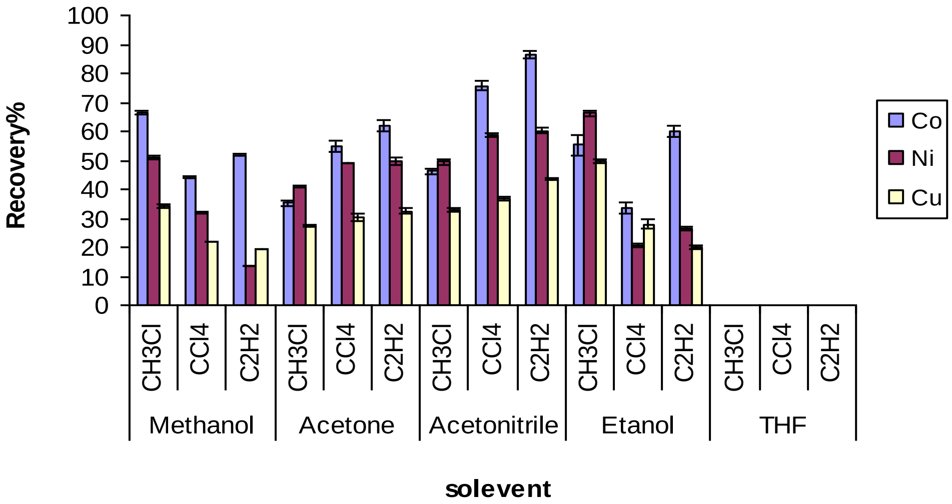

Figure 2: Selection of extracting and dispersive solvents in DLLME. Conditions: sample, 5mL Co^{2+} and Cu^{2+} 1 mgL^{-1} and Ni^{+2} concentration of 4mgL^{-1}; volume of dispersive solvent, 1.5 mL; volume of extracting solvent, 250µL; buffer, 1mL ammonic buffer (*C*= 1 mol L^{-1}, pH 10) and oxim solution, 0.5mL 0.01 mol L^{-1} in acetonitrile. The bars show the maximum and minimum levels of determinations.

3.1.2. Dispersive solvent volume:

Ethanol as a dispersive solvent in different volumes in the range 0–5mL along with 250µL chloroform as an extracting solvent was used to extract nickel, copper and cobalt ions at pH 10 using DLLME procedure. The obtained results (Fig. 3) show that in the case of 2.5mL ethanol the highest recovery and a reasonable EF are attainable. With 3mL or higher volume of ethanol no sedimented organic phase was achieved.

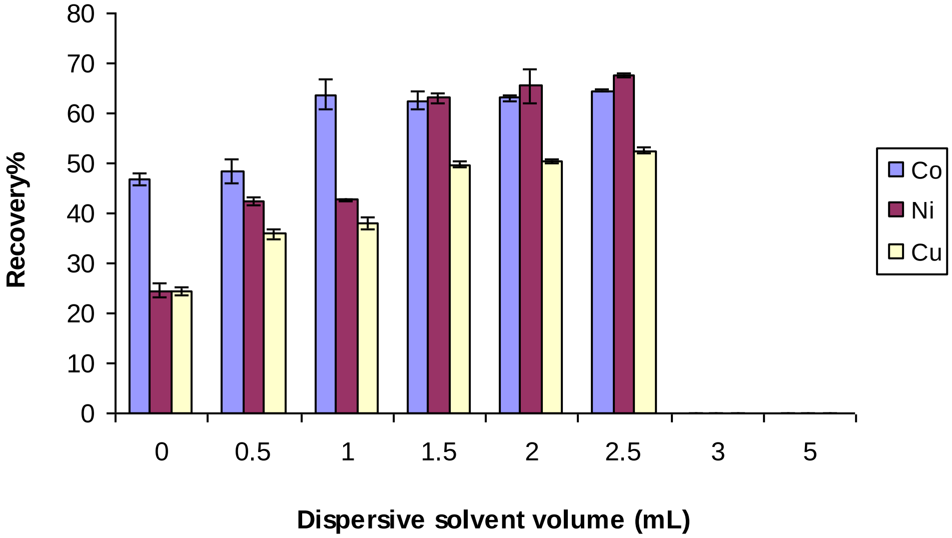

Figure 3: Dispersive solvent volume study. Other conditions are the same as Fig. 1.3.1.3. Extracting solvent volume

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 100µL and the system became useless. On the other hand by using 250µL chloroform, EF 31.45 and recovery 64% for cobalt, EF 25.56 and recovery 52.03% for copper and EF 33.22 and recovery 67.62% for nickel were obtained. The volume of sedimented phase was 183µL under these circumstances. Therefore, we chose initially 250µL as optimum volume of chloroform as extracting solvent for further study (optimization of sample size).

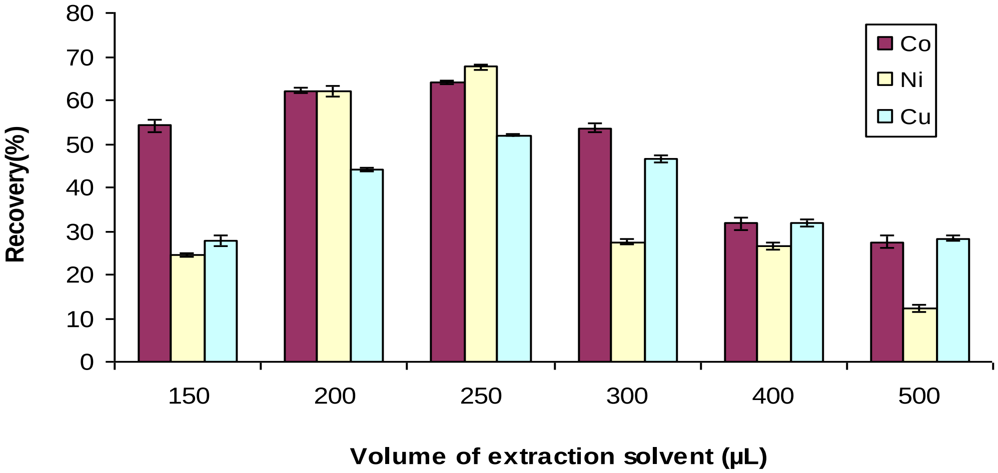

Figure 4: Selection of extracting solvent volume. Volume of dispersive solvent, 2.5 mL. Other conditions are the same as Fig. 1.

3.1.4. pH effect:

Because pH plays a unique role in the metal-chelate formation and the subsequent extraction, in this study we used PDD since protonation of nitrogen which is present in the structure of the compound occures in acidic environments, it works better in basic situations and forms more stable complexes with the cations. the pH of the sample solution was the next critical factor evaluated for its effect on the DLLME preconcentration of Ni(II), Co (II) and Cu (II). In this study phenathrene-9, 10-dine dioxime was used as a complexing agent for Co^{2+} and Cu^{2+} ions to produce a neutral metalchelate, which is extractable into chloroform. Because the production of nitro 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 10. Therefore pH 10 was selected for the following studies.

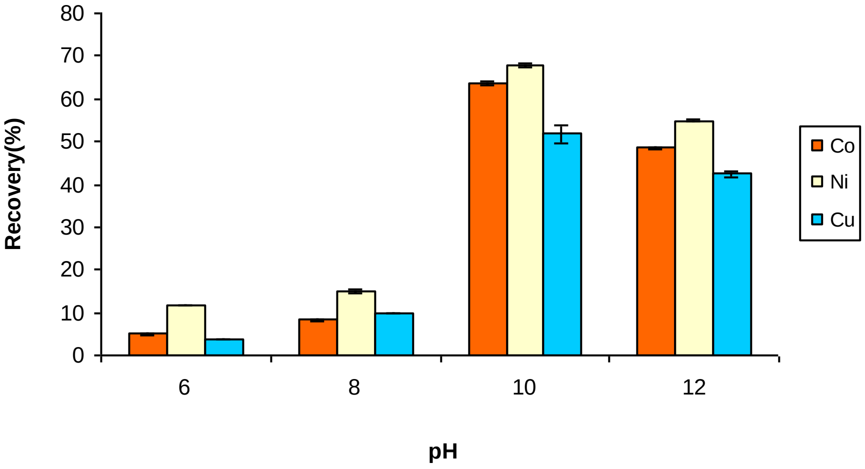

Figure 5: Effect pH. Conditions: sample, 5mL Co^{2+} and Cu^{2+} 1 mgL^{-1} and Ni^{+2} concentration of 4mgL^{-1}; volume of dispersive solvent, 2.5 mL; volume of extracting solvent, 250µL;and oxim solution, 0.5mL 0.01 mol L^{-1} in acetonitrile.

3. 1.5. Effect of oxim concentration:

In order to determine the concentration of oxime(PD) required for quantitative recoveries, the proposed method was applied. In order to study the effect of PD concentration on the analytical response of nickel, cobalt and copper, different concentrations of PD in the range of 0.001 to 0.01 (M) were used, and the general procedure was applied. The results are shown in (Fig.6). The recovery of the metal ions increased with increasing oxim concentrations. The optimum amount of ligand was taken as 0.01 for further experiments.

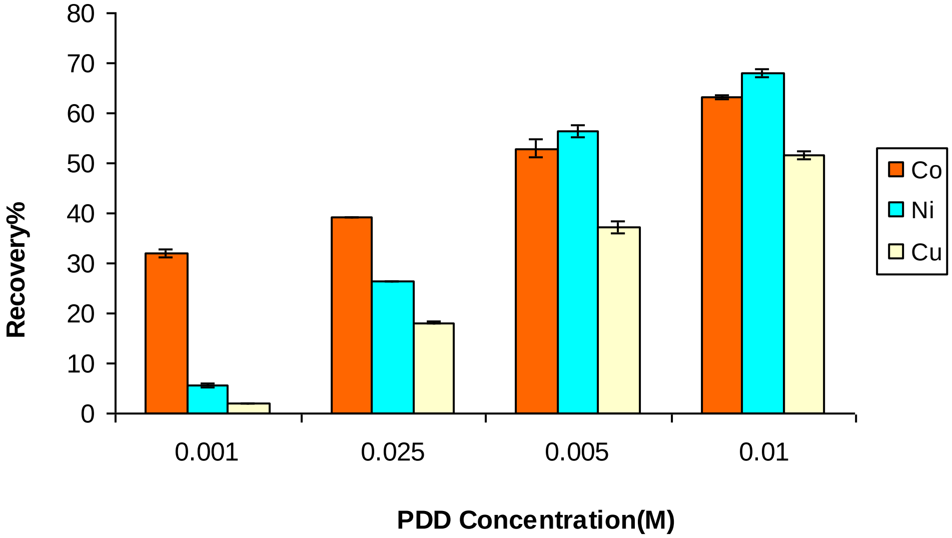

Figure 6: Effect of oxim(PD) concentration. Conditions: sample, 5mL Co^{2+} and Cu^{2+} 1 mgL^{-1} and Ni^{+2} concentration of 4mgL^{-1}; volume of dispersive solvent, 2.5 mL; volume of extracting solvent, 250µL; and oxim solution.

3.1.6. Effect of centrifuge rate:

The centrifuge rates above the DLLME was the next parameters considered. DLLME of copper, silver and cobalt ions was performed in solutions with the rates ranging from 500 to 3500(rpm). Fig.7 shows the effect of centrifuge rates on the extraction of the complexes of these ions. In subsequent experiments the rate of 3000(rpm) was selected. In general, centrifugation time hardly ever affects micelle formation but accelerates phase separation in the same way as in conventional separations of a precipitate from its original aqueous environment. Therefore, a centrifugation time of 5min at 3000rpm was selected for subsequent uses.

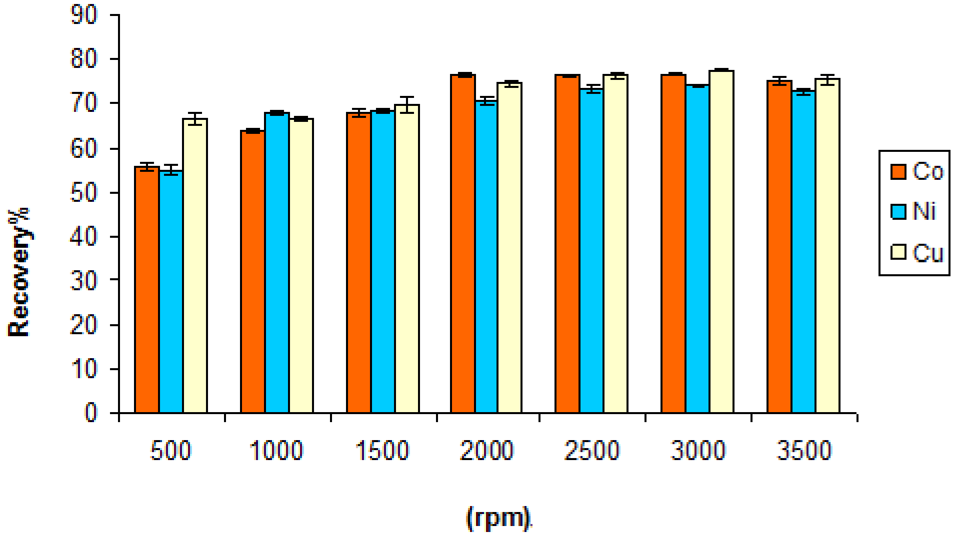

Figure 7: Effect of centrifuge rate in DLLME. Conditions: sample, 5mL Co^{2+} and Cu^{2+} 1 mgL^{-1} and Ni^{+2} concentration of 4mgL^{-1}; volume of dispersive solvent, 2.5 mL; volume of extracting solvent, 250µL; buffer, 1mL ammoniac buffer (C= 1 mol L^{-1}, pH 10) and oxim, 0.5mL 0.01 mol L^{-1} in water.

3.1.7. Study of other parameters:

Other parameters such as effect of the ionic strength 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 oxim solution and the addition of extraction solvent (chloroform) dissolved in dispersive solvent (ethanol). It was found that both the reaction and the extraction procedures are rapid and time did not affect the EF, recovery and sedimented phase volume.

3.2. Experimental design:

Recovery was investigated as responses in order to optimize five variables, namely the Dispersive solvent volume (F1), Extracting solvent volume (F2), Sample volume (F3) and pH (F4). These four parameters were chosen to be optimized simultaneously among all parameters based on their importance and their probable interaction. Tables 1 and 2 present the levels of coded and actual experimental variables that were tested. Table 2 also presents the corresponding responses. The aims of the CCD strategy were: (1) to maximize the recovery (2) to determine which variables have higher impact on extraction recovery (3) to give an insight on the robustness of the method close to the optimum conditions and (4) to show possible variable interactions [29].

3.3. Analytical features of DLLME of Ni^{+2}, Co^{2+} and Cu^{+2} ions:

Under the optimum conditions obtained by one variable at a time optimization; sample size, 5 mL; volume of dispersive solvent (ethanol), 2.5 mL; extracting solvent (chloroform) volume, 250µL; buffer, 1mL ammoniac buffer (C= 1 mol L^{-1}, pH 10) and volume of oxim solution, 0.5mL 0.01 mol L^{-1} in actonitrile, some analytical characteristics of the proposed DLLME method were obtained. Calibration curve is linear ($A_{(Co^{2+})}$ = 107.55 C +16.14, $A_{(Ni^{2+})}$ = 149 C + 17 and $A_{(Cu^{2+})}$ = 202.5 C + 21.77, where A is absorbance intensity and C is concentration of cations in µgL^{-1}) in the range of (5-4000µgL^{-1}) for Ni(II) , (10-3000µgL^{-1}) for Co (II) and (5-4000µgL^{-1}) for Cu (II) respectively. Square of correlation coefficients (R^2) are 0.99. The relative standard deviations for nickel, cobalt and copper were obtained to be 5.6%, 5.3% and 4.8% respectively (n = 6, C =1000 µgL^{-1} for cations). Limit of detections were 1 µg L^{-1} for Ni (II), 3 µg L^{-1} for Co (II) and 2 µg L^{-1} for Cu (II). 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 5. It can be observed that the recovery and the relative enrichment factor agree well, as expected.

3.4. Application of the proposed DLLME method for real samples and comparison with a standard method:

To evaluate the efficiency of the proposed DLLME 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 [29] were applied to determine the cobalt and chromium content. In the

DLLME method standard addition technique was used. For the standard method Ni^{+2}, Co^{+2} and Cu^{+2} ions were extracted as the pyrrolidine chelate into methyl isobutyl ketone and then the absorbance of organic phase was read using FAAS lines of copper, cobalt and nickle. The obtained results are summarized in Table 2. The obtained concentrations from both methods were in agreement.

3.5. Study of interferences:

Interferences were studied in the presence of a constant concentration of analyte (1 µg mL^{-1}) and different amounts of foreign ions (analyte: foreign ion ratio 1:1, 1:10, 1:100 and 1:1000). Tolerable concentration of foreign ions was considered as the concentration in which less than 10% deviation in absorbance reading was observed in comparison with the case in which interfering ion was absent. The obtained results are given in Tables 7. As can be seen most of the studied ions do not have interfering effect at 1:10 ratio but have serious interference at 1:100 ratio.

4. CONCLUSIONS:

A dispersive liquid–liquid microextraction method was used for preconcentration of Ni^{+2}, Co^{2+} and Cu^{2+} ions prior to determination by FAAS technique. Enrichment factor and recovery for the target analyte were obtained about 29.95 and 76.53 for nickel, 29 and 74.23% for cobalt and 26.99 and 77.6% for ccopper, respectively. The proposed extraction method was used for the quantification of Ni^{+2}, Co^{2+} and Cu^{2+} 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.

Table: 1

Cu^{2+}

Concentration (µg mL^{-1})	Mean EF ± SD[a]	Mean recovery ± SD[a]
0/50	26/1 ± 0/9	74/19 ± 1.8
1/00	26/99 ± 1/1	77/59 ± 2/17
2/00	30/7 ± 1.6	81/3 ± 2/4

[a] n = 3

Table: 2

Co^{2+}

Concentration (µg mL^{-1})	Mean EF ± SD[a]		Mean recovery ± SD[a]
0/05	29/11 ± 1/9		75/32 ± 2/1
0/10	29/95 ± 0/9		76/54 ± 2/34
0/20	30/68 ± 1/3		77/17 ± 2/8

[a] n = 3

Table: 3

Ni^{2+}

Concentration (µg mL^{-1})	Mean EF ± SD[a]		Mean recovery ± SD[a]
0.05	29 ± 1.8		73.6 ± 1.7
0.10	29.05 ± 2		74.23 ± 2.06
0.20	29.14 ± 2.1		74.9 ± 2.23

[a] n = 3

Table: 4

Sample	Concentration (μg mL^{-1}) obtained by							
	This method[a]				Standard method[b]			
	Co^{2+}	Cu^{2+}	Ni^{2+}		Co^{2+}	Cu^{2+}	Ni^{2+}	
Tap water	ND[c]	ND	ND		ND	ND	ND	
Aras river water (point 1)	0.37	0.4	ND		0.48	0.38	ND	
Aras river water (point 2)	9.7	3.9	ND		10.4 ± 4.9	3.65	ND	
Aras river water (point 3)	16.9	0.26	0.38		17/6 ± 5/2	2.2	0.4	
Mineral water	ND	ND	ND		ND	ND	ND	

a. Obtained by standard addition method

b. Mean ± standard deviation (n=3)

c. Not detected

Table: 5

Ni^{+2}

Interfering ions	Tolerable concentration Analyte: interfering ion
Fe^{2+}, Ag^{+} , Mg^{2+}	1:1
PO_4^{3-}	1:10
Cl^{-}, Pb^{2+},Hg^{2+}	1:100
CO_3^{2-}	1:500
F^{-}, SO_4^{2-},Ca^{2+}, Zn^{2+}	1:1000

Cu^{+2}

Table: 6

Interfering ions	Tolerable concentration Analyte: interfering ion
Fe^{2+}, Ag^{+} , Mg^{2+}	1:1
-	
PO_4^{3-+},Hg^{2+}	1:10
Ca^{2+}, Zn^{2+}	
F^{-}	1:100
	1:500
	1:1000

Co^{+2}

Table: 7

Interfering ions	Tolerable concentration Analyte: interfering ion
Fe^{2+} , Ag^{+}	1:1
-	1:10
PO_4^{3-}, Hg^{2+}, CO_3^{2-}	1:100
Cl^{-}, Ca^{2++}, Mg^{2+}	1:500
F^{-}, Zn^{2}, Pb^{2+} CO_3^{2-}	1:1000

REFERENCES:

1. J.L. Manzoori, M.H. Sorouraddin, A.M. HajiShabani, Microchem. J. 63 (2) (1999) 295.
2. J.L. Manzoori, M.H. Sorouraddin, A.M. HajiShabani, J. Anal. At. Spectrom. 13 (1998) 305.
3. J.L. Manzoori, M.H. Sorouraddin, F. Shemirani, Anal. Lett. 29 (11) (1996) 2007.
4. J.L. Manzoori, F. Shemirani, J. Anal. At. Spectrom. 10 (1995)881.
5. M.A. Farajzadeh, M. Bahram, B. Ghorbani Mehr, Talanta 75 (2008) 832.
6. M.A. Farajzadeh, M. Bahram, S. Zorita, B. Ghorbani-Mehr, J. Hazard. Mater. 161 (2009) 1535.
7. P. Liang, H. Sang, Analytical Biochemistry 380 (2008) 21.
8. M. Ghaedi, E. Asadpour, A. Vafaie, Sensitized spectrophotometric determination of Cr(III) ion for speciation of chromium ion in surfactant media using alpha-benzoin oxime, Spectrochim. Acta 63A (2006) 182.
9. M. Ghaedi, A. Shokrollahi, F. Ahmadi, H.R. Rajabi , M. Soylak, Journal of Hazardous Materials 150 (2008) 533–540
10. Rezaee M, Assadi Y, Milani Hosseini MR, Aghaee E, Ahmadi F, Berijani S (2006). J Chromatogr A 1116:1–9
11. Rahnama Kozani R, Assadi Y, Shemirani F, Milani Hosseini MR, Jamali MR (2007). Talanta 72:387–393
12. Bidari A, Hemmatkhah P, Jafarvand S, Milani Hosseini MR, Assadi Y (2008). Microchim Acta doi: 10.1007/s00604-008-0003-8
13. Q.H. Wu, X. Zhou, Y.M. Li, X.H. Zang, C. Wang, Z. Wang, Anal. Bioanal. Chem. 393 (2009) 1755.Fatahi N, Assadi Y, Milani Hosseini MR, Zeini Jahromi E (2007). J Chromatogr A 1157:23–29
14. L. Farina, E. Boido, F. Carrau, E. Dellacassa, J. Chromatogr. A 1157 (2007) 46.
15. S. Moinfara, M.R. Milani Hosseinia, J. Hazard. Mater. 169 (2009) 907.
16. M.I. Leong, S.D. Huang, J. Chromatogr. A 1216 (2009) 7645.
17. R. Maleki, N. Mohammad Nezhad, N .Samadi, K .Farhadi, Talanta 75 (2008) 832–840
18. M.A. Farajzadeh, M. Bahram, J.A. Jo¨nsson, Anal. Chim. Acta 591 (2007)69.
19. S. Berijani, Y. Assadi, M. Anbia, M.R. Milani Hosseini, E. Aghaee, J. Chromatogr. A 1123 (2006) 1.
20. R. Rahnama Kozani, Y. Assadi, F. Shemirani, M.R. Milani Hosseini, M.R. Jamali, Chromatographia 66 (2007) 81.
21. E. Zeini Jahromi, A. Bidari, Y. Assadi, M.R. Milani Hosseini, M.R. Jamali, Anal. Chim. Acta 585 (2007) 305.
22. A. Bidari, E. Zeini Jahromi, Y. Assadi, M.R. Milani Hosseini, Microchem. J. 87 (2007) 6.
23. D. Nagaraju, S.D. Huang, J. Chromatogr. A 1161 (2007) 89.
24. K. Demeestere, J. Dewulf, B.D. Witte, H.V. Langenhove, J. Chromatogr. A 1153 (2007) 130.
25. L.J. He, X.L. Luo, H.X. Xie, C.J. Wang, X.M. Jiang, K. Lu, Anal. Chim. Acta 655 (2009) 52.
26. D.D. Stephan, J.Werner, R.P.Yeater, MS Excel Add-in Software Package, 1998–2001.
27. J. Bulacov, J. Jirkovsky, M. Muller, R.B. Heimann, Surf. Coat. Technol. 201 (2006) 255.
28. M.A.M. Silva, V.L.A. Frescura, F.J.N. Aguilera, A.J. Curtius, J. Anal. At. Spectrom. 13 (1998) 1369.
29. Farahani H, Norouzi P, Dinarvand R, Ganjali MR (2007). J Chromatogr A 1172:105– 112