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Ion-Pair-based Dispersive Liquid Liquid Microextraction Combined with Flame Atomic Absorption Spectrometry for a Sensitive Determination of Trace Amounts of Nickel in Food Samples

Soleiman Bahar
Department of Chemistry, Faculty of Science, University of Kurdistan, P. O. Box 416, Sanandaj, Iran
E-mail address: s.bahar@uok.ac.ir

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ABSTRACT
In this study, a sensitive method of dispersive liquid phase microextraction based on ion-pair combined with the flame atomic absorption spectrometry was proposed for the determination of trace Ni(II) using Aliquat 336-chloride as ion pair agent. Several factors which have effect on the microextraction efficiency of Ni(II), such as pH, extraction and dispersive solvent type and their volume, concentration of the Aliquat 336-chloride, extraction time were investigated and the optimized experimental conditions were established. After extraction, the enrichment factor was 47. The detection limit of the method was 8.0 µg L^{-1} and the relative standard deviation for eight determinations of 100 µg L^{-1} Ni(II) was 2.1 %. The results for the determination of Ni(II) in food samples (black tea, lettuce, parsley and carrot) have demonstrated the accuracy, recovery and applicability of the proposed method.

KEYWORDS: Ion-Pair; Dispersive Liquid Phase Microextraction; Flame Atomic Absorption Spectrometry; Ni(II); Food Samples.

1. INTRODUCTION

Heavy metal level in food and environmental samples is an important key for the environmental pollution [1-2]. The determination of trace heavy metal ions in environmental samples is restricted by the very low concentration of heavy metal ion, which may be lower than the detection limit of many analytical techniques including flame atomic absorption spectrometry (FAAS) and the interfering effects of the matrix. In order to achieve accurate, reliable and sensitive results, preconcentration and separation are needed when the concentration of analyte in the original material or the prepared solution is too low to be determined directly by FAAS [3-4].

The most widely used techniques for separation and preconcentration of Ni(II) are liquid–liquid extraction (LLE) [5-6], coprecipitation [7], ion exchange [8], solid-phase extraction (SPE) [9-10] and cloud point extraction (CPE) [11]. Although satisfactory results can be obtained with the above mentioned separation /preconcentration techniques, they have some drawbacks such as large consumption of reagent, low enrichment factor, multistage operation and lengthy separation.

Modern trends in analytical chemistry are towards the simplification and miniaturization of sample preparation, as well as the minimization of the used organic solvent. A new mode of liquid-phase microextraction (LPME) named dispersive liquid–liquid microextraction (DLLME) which is based on ternary component solvent system, such as CPE and homogeneous liquid–liquid extraction (HLLE), as high performance, rapid and inexpensive microextraction method has been proposed [12]. DLLME has been successfully applied to the preconcentration of several families of organic [13-18], and inorganic species [19-21], prior to analysis with gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS), high performance liquid chromatography (HPLC), ultra violet-visible (UV–Vis) and atomic absorption spectroscopy (AAS).

In the presented work, the conditions for the quantitative recovery of Ni(II) by DLLME and using Aliquat 336-chloride as an ion pairing agent have been investigated. The established procedure was applied to preconcentration of Ni(II) in various food samples.

2. EXPERIMENTAL

2.1. Apparatus

The measurement was performed with a Shimadzu atomic absorption/flame emission spectrometer (Kyoto, Japan) Model AA-670 equipped with a computer processor. A Ni(II) hollow-cathode lamp as the radiation source was used for absorbance measurements at a wavelength of 232 nm. All measurements were carried out in an air/acetylene flame. The instrumental parameters were adjusted according to manufacturer recommendations (slit width 0.15 nm, lamp current 4 mA). The pH values were measured with a metrohm E-691 pH/mV meter equipped with a combined glass calomel electrode (Switzerland). A laboratory centrifuge (Heraeus, Labofuge 400 model, Germany) was used to accelerate the phase separation.

2.2. Reagents and materials

All reagents and solvents such as Aliquat 336-choloride, chloroform, carbon tetrachloride, dichloromethane, methanol, ethanol, acetone, tetrahydrofuran, acetonitrile, carbon disulfide, HCl (37%, supra pure) and HNO_3 were high purity grade reagents from Merck Co. (Darmstadt, Germany). All aqueous solutions were prepared using deionized water. Vessels in the experiments were kept in 10% nitric acid for at least 24 h and subsequently washed with deionized water. A stock standard solution (1000 mg L^{-1}) Ni(II) was by dissolving of $Ni(NO_3)_2.H_2O$ salt in 50 mL HNO_3 0.01 mol L^{-1} .Solutions of lower concentrations were prepared daily by a suitable dilution of the stock solution with deionized water. The solution of Aliquat 336-choloride was prepared by dissolving appropriate amount of Aliquat 336-choloride in tetrahydrofuran.

2.3. DLLME procedure

In a typical experiment, to 5.0 mL of aqueous solution Ni(II) in a 10-mL test tube with conical bottom, 0.5 mL of a 0.1 mol L^{-1} Aliquat 336-choloride solution produced in THF was added and then, a mixture containing 2 mL of ethanol and 200 µL of carbon tetrachloride was added by a 5.0-mL syringe. The mixture was gently shaken for 2 min and centrifuged for 5 min at 3500 rpm. The sedimented CCl_4 phase at the bottom of the centrifuge tube was transferred to another test tube and allowed to evaporate at room temperature. Finally the residue was dissolved in 0.5 mL DMF solvent and the cobalt concentration was determined by flame atomic absorption spectrometry.

2.4. Sample preparation

0.5 gram of vegetables sample was placed in a 250 mL beaker and 10 mL of concentrated HNO_3 (65% w/w) was added to the beaker. The mixture was evaporated on a hot plate at about 120 °C for 3 h. After cooling to room temperature, 3 mL of concentrated hydrogen peroxide (30%, w/w) was added. The mixture was again evaporated near to dryness. The residue was completely dissolved in 25 mL of 7 mol L^{-1} HCl and finally the DLLME procedure was applied.

For tea sample, 10 mg of the dry tea sample (dried at 110 ^{o}C) was placed in a 50-mL beaker, followed by the addition of 7 mL of concentrated nitric acid and the beaker was covered with a glass watch. The beaker was allowed to stand overnight and the contents were heated on a hot plate (150 ^{o}C for 15 min). Then the sample was cooled, 8 mL of perchloric acid was added and the mixture was heated again at 200 ^{o}C until the solution became clear (about 1 h). The glass watch was removed and the acid evaporated to dryness level at 150 ^{o}C. The residue was completely dissolved in 5 mL of 1 mol L^{-1} nitric acid and the solution was transferred to a 100- mL calibrated flask. Then, the solution was neutralized with a proper NaOH solution and diluted to the mark, and the recommended procedure was followed [22].

3. RESULTS AND DISCUSSION

In this study a microextraction method, DLLME, was investigated for the enrichment of Ni(II) ion from aqueous samples and determination by FAAS. In order to obtain a high enrichment factor (EF), the effect of different parameters affecting the ion pair formation and extraction conditions such as kind and volume of extraction and disperser solvents, pH, concentration of ion pairing agent and extraction time were optimized. One variable at a time optimization was used to obtain optimum conditions for DLLME procedure. The enrichment factor was defined as the ratio between the analyte concentration in the sedimented phase (C_{sed}) and the initial concentration of analyte (C_0) within the sample

$$EF = \frac{C_{sed}}{C_o}$$

The C_{sed} was calculated on the calibration graph which obtained from standard solutions of Ni(II) and the sedimented phase volume (140 µL).

3.1. Optimization of DLLME procedure

In this method, extraction solvent should have special characteristics including higher density than water, high efficiency in the extraction of the desired compounds and low solubility in water. Special attention should be paid to the selection of disperser solvent. It should be miscible in both extraction solvent and aqueous sample. In this work methanol, ethanol, acetone, tetrahydrofuran and acetonitrile were studied as the disperser solvent and chloroform ($CHCl_3$), carbon tetrachloride (CCl_4) and carbon disulfide (CS_2) were studied as the extraction solvent. The experiments were performed by using 2 mL of disperser solvent containing 200 µL extraction solvent. Fig. 1 shows the recovery and EF for all combinations of the disperser and extraction solvents. Regarding the recovery and EF, the combination of carbon tetrachloride as extraction solvent with ethanol as disperser solvent is the best one and an EF higher than 30 is attainable.

The effect of ethanol volume as the disperser solvent on the extraction efficiency was also examined. To obtain the optimized volume of ethanol, various experiments were performed using different volumes of ethanol in the range of 0–3 mL along with 200 µL carbon tetrachloride as an extraction solvent for the extraction of Ni(II) using the DLLME procedure. The obtained results (Fig. 2) show that the highest recovery and a reasonable EF and sedimented phase volume are attainable using 2 mL ethanol. At lower volumes, ethanol could not disperse CCl_4 properly and cloudy solution was not formed completely. Reversely, at higher volumes, the solubility of the complex in water increased by volume of ethanol. Finally, 2 mL ethanol was chosen as the optimum volume.

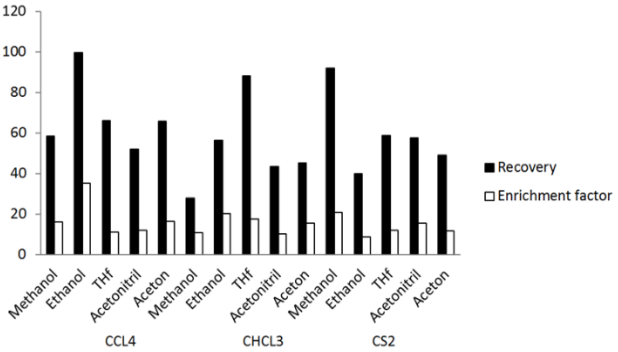

Fig. 1. Selection of extraction and disperser solvent in DLLME. Conditions: sample volume, 5 mL; volume of disperser solvent, 2 mL; volume of extraction solvent, 200 mL; HCl concentration, 7.0 mol L^{-1}; Aliquat 336-chloride solution, 0.5 mL (0. 1 mol L^{-1}) in THF.

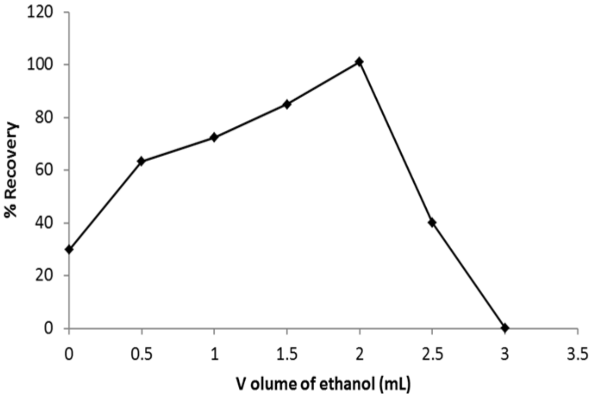

Fig. 2. Effect of disperser solvent volume on the extraction of Ni(II) by DLLME. Conditions: sample volume, 5 mL; volume of extraction solvent, 200 mL; HCl concentration, 7.0 mol L^{-1}; Aliquat 336-chloride solution, 0.5 mL (0. 1 mol L^{-1}) in THF.

In order to examine the effect of the extraction solvent volume on the extraction efficiency, different volumes of CCl_4 (50-250 μL) and a constant volume of the disperser solvent (ethanol, 2 mL) were investigated. Fig. 3 illustrates the variations of the extraction recovery versus the volume of the extraction solvent. According to Fig. 3, the extraction recovery increased with the increase of the volume of CCl_4 and with more than 200 μL the enrichment factor decreased because of increasing the sediment phase volume. Therefore, 200 μL CCl_4 was used as the optimum volume of the extraction solvent in the subsequent experiments.

The formation of ion pair and its chemical stability are two important subjects influencing the extraction of Ni(II) and the HCl concentration plays a unique role on $[HNiCl_4]^-$ formation and its subsequent extraction. The effect of HCl concentration on the extraction of Ni (II) from the solution in the range of 1.0–10.0 mol L^{-1} was studied. Fig. 4 shows the recovery percentage of extracted Ni (II) as a function of the HCl concentration. It can be seen that recovery increases steadily with increasing HCl concentration from 1.0 to 7.0 mol L^{-1} and remains constant at higher concentrations, hence HCl concentration of 7.0 mol L^{-1} was taken as optimal concentration for the extraction of Ni (II).

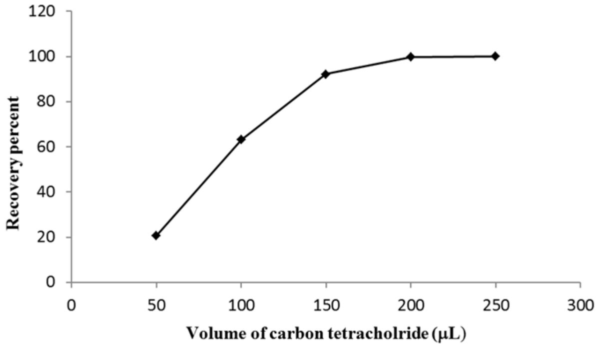

Fig. 3. Effect of extraction solvent volume on the extraction of Ni(II) by DLLME. Conditions: sample volume, 5 mL; volume of disperser solvent, 2 mL; HCl concentration, 7.0 mol L^{-1}; Aliquat336-chloride solution, 0.5 mL (0. 1 mol L^{-1}) in THF.

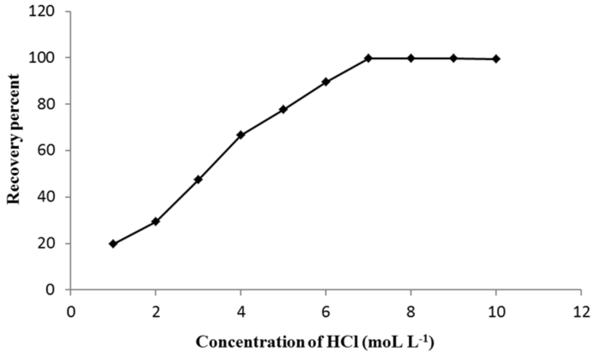

Fig. 4. Effect of HCl concentration on the extraction of Ni(II) by DLLME. Conditions: sample volume, 5 mL; volume of disperser solvent, 2 mL; volume of extraction solvent, 200 μL and Aliquat 336-choloride solution, 0.5 mL (0. 1 mol L^{-1}) in THF.

In this method Ni(II) ions were extracted as $A^+[HCoCl_4]^-$ that A^+ is methyltrioctylammonium. The amount of Aliquat 336-chloride is a critical factor to obtain the high recoveries. For this purpose, the influence of Aliquat 336-chloride concentration on the extraction in the the range of 0.01-0.3 mol L^{-1} in THF was studied. The best results were obtained when concentrations in the range of 0.1 to 0.3 mol L^{-1} were used. Hence, 0.1 mol $L^{-1}$of Aliquat 336-chloride solution was taken as optimal amount for the extraction of Ni(II).

In DLLME, the extraction time is defined as interval time between the injection of the disperser and extraction solvents and the starting of centrifuge. The effect of extraction time was examined in the range of 15 s to 10 min with the constant other experimental conditions. The obtained results showed that the extraction time did not significantly influence on the signal of Ni(II). Therefore, the DLLME method was time-independent, which was the most important advantage of this technique.

The influence of ionic strength of the aqueous solutions on the extraction efficiency was evaluated by adding various amounts of sodium chloride (NaCl) in the range of 0.0-5.0 % (W/V). Other experimental conditions were kept constant. It was found (Fig. 5) that salt addition has no significant effect on the recovery. However, by increasing sodium chloride concentration from 0.0 to 5.0 %, the solubility of the extraction solvent in the aqueous phase decreased. As a result, the volume of sedimented phase increases from 120 to 161 µL and the enrichment factor reduces from 41.5 to 27. Therefore, all the extraction experiments carried out without adding salt.

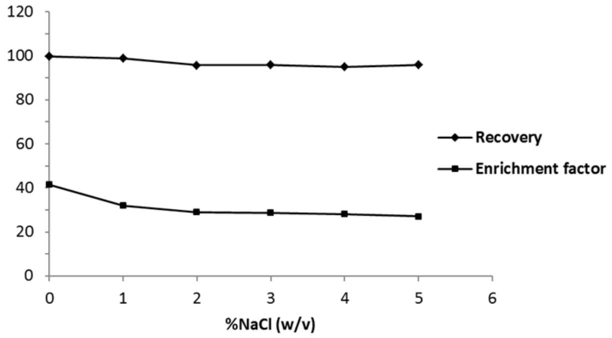

Fig. 5. Effect of ionic strength on the extraction Ni(II) by DLLME. Conditions: sample volume, 5 mL; volume of disperser solvent, 2 mL; volume of extraction solvent, 200 µL; HCl concentration, 7.0 mol L^{-1}; Aliquat336-chloride solution, 0.5 mL (0. 1 mol L^{-1}) in THF.

3.2. Interferences

Interferences were studied in the presence of a constant concentration of analyte (1 mg L^{-1}) and different amounts of foreign ions. The tolerance limits of the coexisting ions is defined as the ion concentration causing a relative error of less than ± 5%. The results obtained are given in Table 1. It can be seen that the presence of major cations and anions has no significant influence on the extraction of Ni(II) ion under the selected conditions.

Table 1. Effect of foreign ions on DLLME of Ni(II)

Coexiting ions	Added as	Telorance limit ion ratio (C_{ion}/C_{Ni})^a
Hg^{2+}	$Hg(NO_3)_2.6H_2O$	100
Cd^{2+}	$Cd(NO_3)_2.4H_2O$	100
Pb^{2+}	$Pb(NO_3)_2$	100
Cu^{2+}	$Cu(NO_3)_2.4H_2O$	10
Ba^{2+}	$Ba(NO_3)_2$	100
Zn^{2+}	$Zn(NO_3)_2.6H_2O$	100
Mg^{2+}	$Mg(NO_3)_2.6H_2O$	100
Mn^{2+}	$Mn(NO_3)_2.6H_2O$	100
K^+	KNO_3	1000
Cl^-	KCl	1000
I^-	KI	100
MnO_4^-	$KMnO_4$	100

[a] At this ratio interfering effect was not observed.

3.3. Evaluation of the method performance

For the purpose of quantitative analysis, under the optimum conditions; sample size, 5 mL; volume of disperser solvent (ethanol), 2 mL; extraction solvent (CCl_4) volume, 200 µL and Aliquat336-chloride solution, 0.5 mL (0. 1 mol L^{-1}) in THF, some analytical characteristics of the proposed DLLME were obtained. Analytical characteristics of the optimized method, including linear range, coefficient of determination (R^2), limit of detection (LOD), relative standard deviation (RSD) and EF are listed in Table 2. The calibration curve was linear in the range of 40-1200 µg L^{-1} of Ni(II). The LOD (S/N =3), was 8.0 µg L^{-1}. The RSD for 8 replicate measurements of 100 µg L^{-1} nickel was 2.1 % and the EF was found to be 47.

Table 2. Analytical characteristics of DLLME-FAAS for determination of nickel.

Parameter	Analytical feature
Sample consumption (mL)	5
EF	47
Linear range (µg L^{-1})	40–1200
LOD, µg L^{-1}	8.0
Precision (R.S.D., $n = 8$) (%) (100 µg L^{-1})	2.1
Correlation coefficient (R^2)	0.999

3.4. Comparison with other methods

Some characteristics of the previously reported methods such as enrichment factor and limit of detection are summarized in Table 3 for comparison. As it can be seen, the proposed method in this work, for the precocentration of Ni(II) ions, showed a higher EF and liner range than other methods and LOD was comparable in comparison to the mentioned methods. All these results demonstrate that DLLME–FAAS is a sensitive, fast and reproducible technique for the preconcentration and determination of nickel in real samples.

3.5. Application to real samples

The proposed method was applied to the determination of Ni(II) in real samples (black tea, parsley, lettuce and carrot). The accuracy of the method was verified by the analysis of the samples spiked with known nickel amounts. The results are shown in Table 4. The recovery values calculated for the added standards were higher than 98.7%, which confirms the validity of the method. Also, in order to investigate the accuracy of the proposed method, further experiments were done on carrot, lettuce and parsley samples and results were compared with those obtained using liquid-liquid extraction method and FAAS [28]. According to the paired t-test, one can see (Table 5) that a satisfactory agreement exits between the results obtained for Ni(II) in the real samples by the proposed method and those by LLE-FAAS.

4. CONCLUSIONS

A new method of DLLME combined with FAAS has been proposed for the determination of Ni(II) in real samples. In the proposed procedure, the reagent of Aliquat336-chloride was successfully used as ion pair agent for the preconcentration of Ni(II) using DLLME. The method is simple, rapid and the low consumption of carbon tetrachloride and ethanol also minimizes the toxicity of the method. The proposed method possesses

Table 3. Comparison of the proposed method with other methods for determining nickel.

Method	Extraction method	Concentration range (ng mL^{-1})	r^2	RSD%	R%	EF	LOD	Ref.
ICP-OE	SPE	-	-	8	97.2-100.8	5	2.37	[23]
Spectrometry	CPE	20-500	0.998	3.6	99-105.9	-	10	[24]
MPT-AES	F.I.A	10-200	0.9995	4.2	95.5	17.85	1.8	[25]
Spectrometry	F.I	25-500	0.9997	1	-	-	17	[26]
FAAS	SPE	100-800	0.9993	1.2	<96.6	-	20	[27]
FAAS	CPE	2-100	0.9988	3.24	99-103	83.3	0.71	[29]
FAAS	CPE	0-240	0.9996	2.89	96-102	29	1.09	[30]
FAAS	SPE	2-100	-	1.9	92-107	43	0.8	[31]
FAAS	DLLME	40-1200	0.999	2.1	98-100	47	8	this study

Table 4. The analytical results for determination of Ni (II) in real food samples.

Sample	Concentration μg g^{-1} ± SD (%) (n=3)	Added (μg g^{-1})	Found μg g^{-1} ± SD (%) (n=3)	Relative Recovery (%)
Black tea	<LOD	5000	4973.54±13.09	99.4
Parsley	23.43 ± 0.25	100	123.35± 0.13	99.9
Lettuce	37.94 ±0.68	100	137.4±0.89	99.3
Carrot	37.64 ±0.45	100	136.39±1.02	98.7

Table 5. Analytical results for determination of Ni (II) by the proposed and LLE method.

Sample	DLLME (μg g^{-1}) ± SD (%) (n=3)	LLE (μg g^{-1}) ± SD (%) (n=3)
Parsley	23.43 ± 0.25	23.07 ± 0.43
Lettuce	37.94 ± 0.68	37.1 ± 0.44
Carrot	37.64 ± 0.45	37.7 ± 0.68

a higher EF and liner range than other reported preconcentration methods and LOD was comparable in comparison to the mentioned methods, which makes it suitable for the determination of trace amounts of Ni(II) in various real samples.

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