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The Development of pH Modulated Solidified Homogeneous Liquid Phase Microextraction Methodology for Preconcentration and Determination of Nickel in Water Samples

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Abstract. In this work, a new, fast and green pH assisted solidified homogeneous liquid phase microextraction method (pH-MS-HLPME) was developed. Initially, the complex formation of Ni-1-Phenylthiosemicarbazide (Ni-PTC) and the dissolution of the extraction solvent (caprylic acid) in water were achieved by addition of NaOH. After base addition caprylic acid (CA) become completely soluble as sodium caprylate in model solution. The phase separation of extraction solvent was accessed by addition of HCl. The analyse of nickel concentrations was carried out by micro-sampler adapted flame atomic absorption spectrometer. Under optimized parameters, linear range (10.0-450 µg L-1), detection limit (3.2 µg L-1), limit of quantification (10.0 µg L-1), relative standard deviation (2.0 %), relative error (-3.9 %), and preconcentration factor (45) were calculated, respectively. Finally, the developed pH-MS -HLPME methodology was successfully applied to LGC 6010 hard drinking water (CRM) and some water samples.

Keywords: Nickel, pH, liquid phase microextraction, drinking water samples, microsampler system.

Su Örneklerinde Nikelin Zenginleştirilmesi ve Tayini için pH Modülasyonlu Katılaştırılmış Homojen Sıvı Faz Mikroekstraksiyon Metodunun Geliştirilmesi

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Özet. Bu çalışmada yeni, hızlı ve yeşil bir pH destekli katılaştırılmış homojen sıvı faz mikroekstraksiyon metodu (pH-MS-HLPME) geliştirildi. İlk olarak, Ni-1-feniltiyosemikarbazit (Ni-PTC) kompleksinin oluşumu ve ekstraksiyon çözücüsünün (kaprilik asit) su içinde çözülmesi, NaOH ilave edilerek sağlandı. Baz ilave edildikten sonra kaprilik asit (CA), model çözeltide sodyum kaprilat halinde tamamen çözünür hale geldi. Ekstraksiyon çözücüsü fazının ayrılması HC1 ilavesiyle gerçekleştirildi. Nikel konsantrasyonlarının tayini, mikro örnekleyici uyarlanmış alevli atomik absorpsiyon spektrometresi ile gerçekleştirildi. Optimize edilmiş parametreler altında, doğrusal çalışma aralığı (10.0-450 µg L-1), gözlenebilme sınırı (3.2 µg L-1), tayin sınırı (10.0 µg L-1), bağıl standart sapma (% 2.0), bağıl hata (-3.9 %) zenginleştirme faktörü (45) hesaplandı. Son olarak, geliştirilen pH-SFO-HLPME yöntemi LGC 6010 sert içme suyu standard referans maddesine ve bazı su örneklerine başarıyla uygulandı.

Anahtar Kelimeler: Nikel, pH, sıvı faz mikroekstraksiyon, içme suları, mikro örnek verici sistem.

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1. INTRODUCTION

Nickel is widely used industrial element for making many products such as batteries, coins, keys, cooking equipments and cell phones etc. In addition, natural waters, foods, fruits and vegetables include trace amount of nickel and nickel compounds. It is also very important for

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hormonal activity and lipid metabolism [1–4]. However, the excessive amount uptake of nickel can cause cancer, allergic skin problems and psychological disorders. Because of these harmful effects determination of nickel is an essential obligation for analytical chemists. Many modern instrumental methods like inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES, electrothermal atomic absorption spectrometry (ETAAS), flame atomic absorption spectrometry (FAAS) can be used for determination of nickel in various samples. FAAS is the most favourable and used technique when it is compared to the other spectroanalytical techniques. However, for sensitive and reliable determination of nickel a sample pretreatment procedure is needed before FAAS measurements [5–9].

The aim of many analytic chemists is to develop high- performance, away from environmental pollution and matrix effects, less time consuming and economically feasible sample pretreatment methods. Nowadays, the popularity of liquid phase microextraciton (LPME) methods is increasing day by day when we compare with the other sample pretreatment methods. LPME was presented as a simpler and cheaper alternative to conventional liquid-liquid extraction in 1990s [10–12]. Many kinds of modified LPME techniques were reported in literature for separation and preconcentration of metals [13–18] such as dispersive liquid–liquid microextraction (DLLME) [19], single-drop microextraction (SDME) [20–22], hollow-fiber liquid-phase microextraction (HF-LPME) [23,24], solidification of floating organic droplets liquid phase microextraction (SFO-LPME) [25,26].

The use of two types of solvent (disperser and extraction solvent) at DLLME, the instability of the extraction solvent drop at SDME, the use of expensive membranes at HF-LPME restrict the application of these methods [27]. Among these techniques, SFO-LPME draws more attention due to advantages such as easy removal of extraction solvent, use of less toxic extraction solvents and simplicity [28]. In this technique usually a low toxic extraction solvent with appropriate melting point (near room temperature) is mixed with a disperser solvent and injected into water sample for providing short extraction time and fast mass transfer. After phase separation by centrifugation, the sample tubes are placed in an ice bath for solidification of organic drop floats on the surface. The solidified organic drop including analyte removed with a spatula to a conical tube than the melted extraction solvent introduced to appropriate analytic techniques [29–31].

The aim of this work was to develop a modified SFO-LPME called pH modulated solidified homogeneous liquid phase microextraction (pH-MS-HLPME) method for determination of nickel. The concentration levels of nickel in various water samples were determined by microsampler adapted flame atomic absorption spectrometer. This method offers more green and economic alternative when compared to the other SFO-LPME methods. Because the dissolution of the extraction solvent (caprylic acid) and complex formation of Ni-1-Phenylthiosemicarbazide (Ni-PTC) was achieved by using any disperser solvent and buffer solution. Both were achieved by addition of appropriate amount of NaOH-HCl.

2. EXPERIMENTAL

2.1 Instruments and chemicals

A hand made micro-sampler adapted Perkin-Elmer Analyst 700 (Norwalk, CT, USA) atomic absorption spectrometer was used for Ni (II) determination. The operation conditions of FAAS were chosen according to manufacturer guides. A Sartorius pp-15 (Gottingen, Germany) model pH meter with glass-electrode and a Nüve NF 200 (Ankara, Turkey) model centrifuge were used for pH measuring and centrifuging test solutions, respectively.

All chemicals used during the pH-MS-HLPME were analytical reagent grade. Caprylic acid, 1-phenylthiosemicarbazide were purchased from Merck chemical company (Darmstadt, Germany). 0.1 % (w/v) PTC solution was prepared daily by dissolving in methanol. Sodium hydroxide and hydrochloric acid (E. Merck, Darmstadt, Germany) solutions at various concentrations were prepared by dissolving appropriate amount in deionized water. 1000 mg L^{-1} Ni (II) standard solution were prepared from $Ni(NO_3)_2.6H_2O$ (Sigma-Aldrich) and nickel solutions at other concentrations for test solutions were prepared by diluting from 1000 mg L^{-1} Ni (II) standard solution.

2.2 pH-MS-HLPME procedure

130 µL CA was added to conical test tube containing 9 mL test solution (containing 30 µg L^{-1} Ni(II), 1 ml PTC from 0.1 %) by a micropipette . Than 1.0 mL NaOH (1 mol L^{-1}) was added to test

solution and vortexed 20-30 seconds. CA became completely soluble as its salt form (sodium caprylate) and test solution was seen completely homogeneous. After addition of 1.0 mL HCl (1 mol L^{-1}), cloudy solution was appeared and complexes of Ni-PTC were extracted to CA phase. This cloudy solution was centrifuged for 3 min. at 3500 rpm and transferred to refrigerator for solidification. The solidified CA phase was removed by spatula and diluted to 200 µL with an acidified ethanol. The diluted CA phase was introduced to microsampler adapted flame atomic absorption spectrometer for determining Ni (II) concentrations.

2.3 Sample preparation procedure of pH-MS-LPME

The water samples (tap waters, hot spring water and river water) were filtered and acidified after collection (different places from TURKEY). The bottled samples were collected from local markets of Tokat, TURKEY. The samples were stored at refrigerator before application of procedure.

3. RESULTS AND DISCUSSION

3.1 Effect of added base-acid amount

The pH of sample is one of the most effective factor in metal enrichment studies for the formation of metal complexes with the high efficiency. In this work, the complex formation of Ni-PTC and the dissolution of the CA was achieved by addition of NaOH. After HCl addition a cloudy solution was appeared. For that purpose, the varied concentrations and volumes of NaOH and HCl in the range of 0.0-1.5 mol L^{-1} and 0.0-1.5 mL were added to test solutions. The recoveries of Ni (II) for pH-MS-LPME were not quantitative (< 95 %) for added NaOH and HCl in the range of 0.0-0.75 mol L^{-1} and 0.0- 0.75 mL. The quantitative recoveries (≥ 95 %) of Ni(II) were obtained after addition of 1 mol L^{-1} and 1.0 mL NaOH and HCl, respectively. As it can be seen table 1, addition of 1 mol L^{-1} and 1.0 mL NaOH and HCl were chosen as an optimal added base-acid amount for further studies.

Table 1. Effect of added base-acid concentration and volume (N=3)

The concentration of NaOH-HCl (mol L^{-1})	**Added base-acid (mL)**	**Recovery of Ni(II), %**
0.25	0.25	28±2*
0.50	0.50	49±3
0.75	0.75	73±3
1.00	1.00	95±4
1.25	1.25	96±2
1.50	1.50	96±3

*mean ± standard deviation

3.2 Effect of PTC amount

The type and amount of the ligand is one of the important step that should be optimized for the formation of hydrophobic chelates with high efficiency. We noticed that PTC has not been used before for extraction of nickel in the solidification based microextraction processes. For that purpose the amount of PTC were investigated to obtain high complex yield. As shown in figure 1, the increase in recovery was seen by the addition PTC in the range of 0-1.0 mL (0.1 %, w/v). As a result of the obtained data, the amount of ligand was optimized as 1 mL.

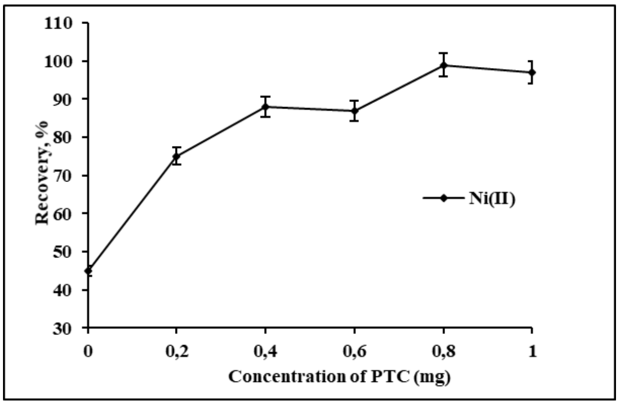

Figure.1 Effect of PTC concentration on pH-MS-HLPME (N:3)

3.3 Effect of volume of CA

Many extraction solvents (1-Undecanol, 1-Dodecanol, 1-Decanol, 1-Undecanoic acid) for SFO-LPME procedures were used in literature [32]. According to our literature survey we saw that caprylic acid was not yet used for extraction of Ni (II) solidification based studies in water samples. For that purpose, effects of volume of CA were tested in the range of 80-150 µL. the resuls were shown in figure 2. According to our results, the recoveries of Ni (II) were not quantitative up to volume 120 µL. It was quantitative in the range of 120-130 µL. After volume of 130 µL a decrease was seen. Therefore 130 µL CA volume was chosen for other experimental parameters.

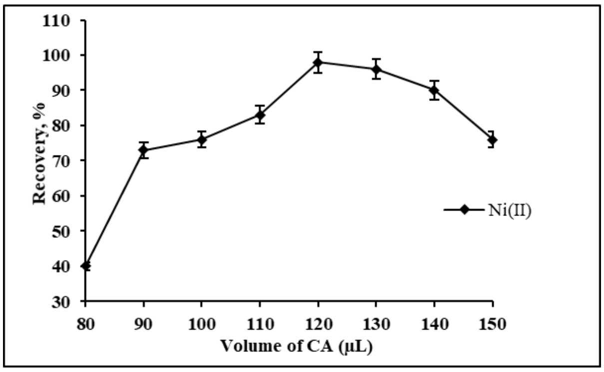

Figure.2 Effect of volume of CA (N:3)

3.4 Optimization of the other experimental parameters

The mixing time is an important parameter that plays a major role for increasing the extraction efficiency and reducing the extraction time. The effective mixing of the aqueous and organic phases is very important to ensure the mass transfer of the solution. The mass transfer coefficient of the aqueous phase increases with increasing mixing ratio. Therefore, in this study, the effects of shaking and centrifugation times on recovery rates of 1 to 5 minutes were examined. As it can be seen from figure 3, it was found that the best recovery was achieved the 20-30 seconds vortex time and 3 minute centrifugation time for the experimental conditions and all of the studies were completed at this time period.

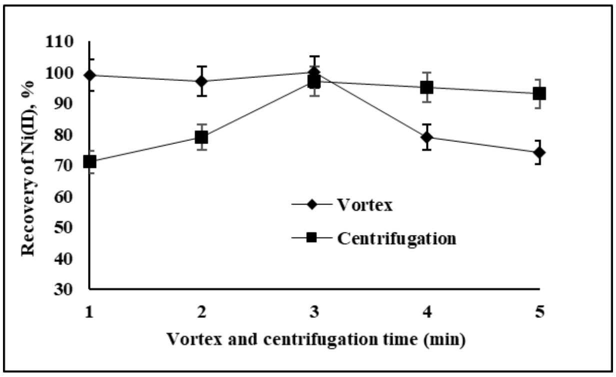

Figure 3. The effects of vortex and centrifugation and vortex time on recovery Ni (II) (N:3)

The increase in the ratio of the aqueous phase volume to the organic phase will increase the preconcentration factor, but this can reduce the extraction efficiency in a given extraction time. The effects of sample volume on the recovery of Ni (II) were investigated in the range of 8-14 mL in this study. The results are shown in figure 4. The recovery of 95 % and higher than 95 % was achieved between 8-9 mL. Therefore, the sample volume was chosen as 9 mL. In addition, the final volume was completed with 1M HNO3 (in ethanol) to 200 mL before the analysis step.

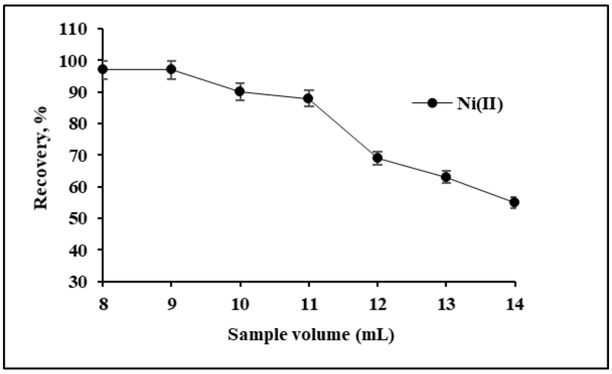

Figure 4. The effect of sample volume on pH-MS-HLPME (N:3)

3.5 Effect of interferences on pH-MS-HLPME

Some components which can be present in the water samples may interfere and cause negative or positive errors during the preconcentraiton studies. Therefore, the effects of some ions in different concentrations and types were investigated for pH-MS-HLPME technique. The results (table 2.) showed that ions had no effect until added concentrations. It demonstrates that our pH-MS-HLPME method was applicable for water samples.

Table 2. Effect of interferes on pH-MS-HLPME (N=3)

Ion	Interference/metal ratio	Recovery of Ni(II),%
Na^+	400	99±3*
K^+	500	96±2
Ca^{2+}	200	96±2
Mg^{2+}	200	99±4
Cl^-	800	102±3
NO_3^-	500	102±5
SO_4^{2-}	500	96±3
PO_4^{3-}	600	103±3

* mean ± standard deviation

3.5 Analytical performance criteria of the proposed method

To evaluate analytical performance criteria of the proposed method, limit of detection, calibration curve equation, linear range, reproducibility and preconcentration factor were calculated under optimized conditions. The limit of detection (3Sb, Sb is the standard deviation of ten replicates of the blank measurement) and limit of quantification (10Sb) were found as 3.2 µg L^{-1} and 10 µg L^{-1}, respectively. The linear range was found as 10.0-450 µg L^{-1}. The calibration curve equation was $A=1.73x10^{-2}C + 3.2x10^{-3}$ ($r^2=0.9993$). The reproducibility defined as relative standard deviation (R.S.D.) was calculated as 2.0 % after application (N=11) of pH-MS-LPME to model solutions containing 30 µg L^{-1} of Ni (II). The preconcentration factor of 45 was calculated from the ratio of the highest sample volume (9 mL) to final completed volume (200 µL).

3.6 Accuracy and application of optimized pH-MS-HLPME

In order to test the accuracy of the developed method, the method was applied to standard reference material (LGC 6010 hard drinking water). The experimental obtained value was found 49 ± 2 µg L^{-1} and the certificate value was 51 µg L^{-1}. The values of SRM shoved that pH-MS-HLPME method was found to be applicable to water samples. The relative error was calculated as -3.9 %.

Also, the developed method was applied to two different tap water samples, river water, hot spring water, sea water and 7 different bottled water samples purchased from local markets in Tokat city (TURKEY) for the determination of Ni (II). The obtained results were given in Table 3. together with the recoveries. The recovery values were quantitative. The results of pH-MS-HLPME shoved that the method was applicable for the determination of Ni (II) in natural and bottled water samples.

3.7 Comparison of pH-MS-HLPME with the other solidification based microextraction methods in literature

The developed pH-MS-HLPME was compared with some SFODME based studies for preconcentration of Ni (II) in the literature (Table 4). In many DLLME and SFODME studies, a disperser solvent was often used to mix the extraction solvent in the samples. However, the dissolution of the extraction solvent, the formation of the Ni-PTC complex and the phase separation of extraction solvent were carried out only with the addition of NaOH-HCl in our study. This showed that the developed method reduces use of the amount of organic toxic solvent during the sample preparation step and because of this reason, the developed pH-MS-HLPME was a more environmentally and economically efficient method.

Table 3. Application of optimized pH-MS-HLPME (N:3)

Element	**Added (µg L^{-1})**	**SAMPLES**			
		Tap water 1		**Tap water 2**	
		Found (µg L^{-1})	Recovery (%)[a]	Found (µg L^{-1})	Recovery (%)
Ni(II)	0	ND[b]	-	ND	-
	50	49.6±1.5	99±3	48.5±1.4	97±3
	100	98.2±2.6	98±3	96.5±3.4	97±3
		River water		**Spring water**	
		Found (µg L^{-1})	Recovery (%)	Found (µg L^{-1})	Recovery (%)
Ni(II)	0	ND	-	17±0.4	-
	50	48.0±2.0	96±3	65.2±3.1	96±4
	100	98.3±3.1	98±3	114±3.0	97±4
		Sea water		**Bottled water 1**	
		Found (µg L^{-1})	Recovery (%)	Found (µg L^{-1})	Recovery (%)
Ni(II)	0	ND	-	ND	-
	50	48.0±1.3	96±1	47.5±1.9	95±1
	100	95.0±3.4	95±3	96.3±2.7	96±3
		Bottled water 2		**Bottled water 3**	
		Found (µg L^{-1})	Recovery (%)	Found (µg L^{-1})	Recovery (%)
Ni(II)	0	ND	-	ND	-
	50	49.1±1.1	98±2	48.6±1.2	97±2
	100	96.6±3.2	97±3	95.2±3.4	95±3
		Bottled water 4		**Bottled water 5**	
		Found (µg L^{-1})	Recovery (%)	Found (µg L^{-1})	Recovery (%)
Ni(II)	0	ND	-	ND	-
	50	48.3±2.0	99±3	49.1±1.4	98±2
	100	97.5±2.7	98±3	98.5±2.2	99±2
		Bottled water 6		**Bottled water 7**	
		Found (µg L^{-1})	Recovery (%)	Found (µg L^{-1})	Recovery (%)
Ni(II)	0	ND	-	ND	-
	50	47.5±3.0	95±3	49±2.0	98±3
	100	97.8±3.3	98±4	99.2±2.0	99±2

a: mean ± standard deviations

b: Not detected

Table 4. Comparison of pH-MS-HLPME with the other solidification based microextraction procedures

Element	Method	Extraction solvent	Disperser agent	LOD	PF	R.S.S %	Ref.
Ni(II), Co(II), Pb(II), Cr(III)	GFAAS	1-dodecanol	Ethanol	1.3 ng L^{-1}	800	7.20	[33]
Ni	FAAS	1-dodecanol	Ethanol	1.27 µgL^{-1}	-	2.55	[34]
Ni, Co	GFAAS	1-undecanol	-	0.3 ng L^{-1}	497	3.60	[35]
Ni, Co	FAAS	1-dodecanol	Ultrasonication	1.7 µg L^{-1}	65	3.60	[36]
Ni,Co, Cu	GFAAS	1-undecanol	Acetone	1.2 ngL^{-1}	277	3.20	[37]
Ni,Cd	FAAS	1-dodecanol	Ultrasonication	0.20 µgL^{-1}		2.10	[38]
Ni	FAAS	Caprylic acid	-	3.2 µg L^{-1}	45	2.0	This work

4. CONCLUSIONS

In this study, a new, fast, useful and sensitive pH modulated solidified homogeneous liquid phase microextraction method for preconcentration and determination of nickel in water samples was developed for determination of Ni (II) in water samples. The developed pH-MS-LPME method had many advantages such as having a lower detection limit, better reproducibility and higher preconcentration factor compared to some established studies. Moreover the established methodology provides greener microextraction procedure with using any disperser solvent. Because, the dispersing of the extraction solvent, the formation of the Ni-PTC complex and the phase separation of extraction solvent were provided by only addition of NaOH-HCl. Under optimized conditions, the developed pH-MS-HLPME successfully applied to water samples for determination of Ni (II).

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