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Development of a dispersive liquid–liquid microextraction combined with flame atomic absorption spectrometry using a microinjection system for the enrichment, separation, and determination of nickel in water samples

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ABSTRACT

A simple, rapid dispersive liquid–liquid microextraction procedure was combined with flame atomic absorption spectrometry and has been established for the determination of trace amounts of nickel. A mixture of carbon tetrachloride, 2-(5-bromo-2-pyridylazo)-5-diethyl-amino-phenol (5-Br-PADAP), and acetonitrile was swiftly injected with a syringe into a sample containing nickel(II) resulting in the formation of a cloudy solution. The cloudy solution was centrifuged and fine droplets settled at the bottom of the test tube. After centrifuging, the settled organic phase was dissolved to a total volume of 250 μL in concentrated nitric acid, from which 25 μL was introduced into the flame atomic absorption spectrometer using the microinjection system. The effect of parameters such as pH, the amount of 5-Br-PADAP, the volume and types of the extraction, and dispersion solvents have been examined. The limit of detection, the preconcentration factor, and enhancement factors were 0.13 $\mu g\,L^{-1}$, 200, and 99, respectively. The calibration graph was linear in the rage of 5–186 $\mu g\,L^{-1}$. The developed method was validated by analyzing certified reference materials (TMDA-25.3, TMDA-51.3). The microextraction method was satisfactorily used for the determination of nickel(II) in various environmental waters.

Keywords: Preconcentration; Microextraction; Nickel; Water; Atomic absorption spectrometry

1. Introduction

Transition metal such as nickel can be essential or toxic to human beings depending on its concentration. Nickel is apparently essential for proper functioning of the liver; however, some nickel compounds are carcinogens [1–4]. Therefore, the accurate and precise determination of nickel in environmental samples is very important. Many instrumental techniques, such as flame and electrothermal atomic absorption spectrometry, atomic fluorescence spectrometry, and inductively coupled plasma mass spectrometry, are available for determining trace quantities of nickel and other metal ions [5,6]. However, enrichment and separation are generally required prior to the determination step because of low levels of metal ions and interferences of the sample matrix [7–9]. Solvent

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extraction, membrane filtration, electrodeposition, solid phase extraction, coprecipitation, and cloud point extraction have been used and developed to overcome the problems [10–16]. However, the applications of these preconcentration methods are limited because of the disadvantages, such as not being green due to a high consumption of organic chemicals, being time-consuming, expensive, and having unsatisfactory enrichment factors.

Within the last 5 years, researchers have proposed the development of miniaturized separation and preconcentration procedures that are generally green techniques. Microextraction systems are important for these procedures. The dispersive liquid–liquid microextraction (DLLME) technique has been widely used for the preconcentration and separation of metal ions in real samples because of the advantages, such as simplicity and swiftness [17,18].

The aim of this study was to develop a simple, rapid DLLME method for the extraction of nickel(II) from water samples. 5-Br-PADAP was used as a complexing agent because it forms stable complexes with a number of metals and it has numerous applications in trace element separation and preconcentration methods [19–21].

2. Experimental

2.1. Apparatus

Nickel content was determined using a flame atomic absorption spectrometer (Perkin Elmer model 3110; Norwalk, CT) equipped with a nickel hollow cathode lamp. The instrumental conditions were adjusted according to the manufacturer's suggestions. The air/acetylene flow rates and the burner height were adjusted to provide the maximum analytical signal.

Samples were aspirated to the nebulizer of flame atomic absorption spectrometer (FAAS) by using a microinjection method [22,23]. Then 25 μL of the samples were introduced into a mini self-made Teflon funnel with a micro pipette, and the peak height signals were recorded. The pH was measured using a Sartorius PT-10 model pH meter (Germany). The solutions were centrifuged using ALC PK 120 model centrifuges. The water used was purified using a Human model RO 180 (HUMAN Corp., Seoul, Korea) purification system, which resulted in the water having a conductivity of 1 $\mu S\,cm^{-1}$.

2.2. Reagents

All chemicals used throughout the experiments were at least of analytical grade. The water used during the experiments was purified using reverse osmosis. A stock solution of 1,000 $mg\,L^{-1}$ nickel(II) was prepared by dissolving a proper amount of $Ni(NO_3)_2{\cdot}6H_2O$ (Sigma-Aldrich) in 0.1 $mol\,L^{-1}$ of nitric acid (HNO_3). Sodium hydroxide and HCl (Merck) were used to adjust the sample solution to a desired pH. A 0.1% (m/v); solution of 2-(5-bromo-2-pyridylazo)-5-diethylamino-phenol (Merck) in ethanol was prepared daily. Standard reference materials comprised of TMDA-25.3 and TMDA-51.3 fortified water were used in the experiments.

2.3. Analytical procedure

A 20 mL solution containing 30–50 $\mu g\,L^{-1}$ of nickel (II) was prepared in a 50 mL centrifuge tube and the pH was adjusted to 9.0. A mixture of 1.5 mL acetonitrile, 50 μL carbon tetrachloride, and 0.1 mg 5-Br-PADAP was swiftly injected into the solution using a syringe; a cloudy solution was formed when the nickel(II) ions reacted with the 5-Br-PADAP. Nickel, which was chelated with 5-Br-PADAP, was extracted into fine droplets of CCl_4. The mixture was then centrifuged at 4,000 rpm for 10 min, obtaining the aqueous and organic phases. The aqueous phase was easily removed using a pipette. The remaining organic phase (30 μL) was dissolved in concentrated HNO_3 to achieve a total volume of 250 μL. A 25 μL aliquot of the solution was injected into the FAAS using the microinjection method for analyte determination from the sample solutions [22,23].

2.4. Sample preparation

Different samples of water, including TMDA-25.3 and TMDA-51.3 fortified water, tap water from Ordu city and bottled mineral water were analyzed. The tap water was filtered through membrane filters with 0.45 μm pores. Then, the above procedure was used for all the samples.

3. Results and discussion

3.1. Effects of pH

The effects of pH on the microextraction of nickel (II) were studied in the pH range of 2.0–10.0, while the other experimental conditions were kept constant. As shown in Fig. 1, the nickel(II) was effectively extracted at a pH of 9.0; thus, this pH was selected for further experiments.

3.2. Effects of the amount of 5-Br-PADAP

The amount of complexing agent is an important factor in the extraction process to obtain quantitative

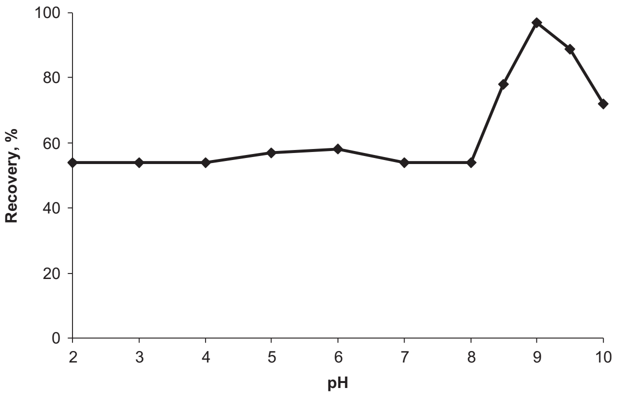

Fig. 1. Relationship between pH and recoveries in the presented microextraction system ($N = 3$).

recoveries of analyte elements [24,25]. The effects of amount of ligand were examined in the ranges of 0.0–3.0 mg. The results are given in Fig. 2. The amount of nickel recovered increased with increasing amounts of 5-Br-PADAP. The recovery reached to a stable value that was greater than 95% when at least 0.1 mg was added. Therefore, all the experiments were performed using 0.1 mg of 5-Br-PADAP.

3.3. Extraction and disperser solvent

The potential extraction solvents that were examined were 100 µL of chloroform, carbon tetrachloride, dichloromethane, and carbon disulphide. The results indicate that the maximum recovery can be attained by using carbon tetrachloride as an extraction solution in 1.0 mL of acetonitrile containing 5-Br-PADAP. All further experiments were performed using carbon tetrachloride as the extraction solvent.

Acetonitrile, acetone, ethanol, and methanol were examined for use as dispersion solvents. Capability of each solvent was assessed with understudy sample solution containing the complexing agent and 100 µL of CCl_4. The results show that the use of acetonitrile as a dispersion solvent yields the maximum extraction efficiency.

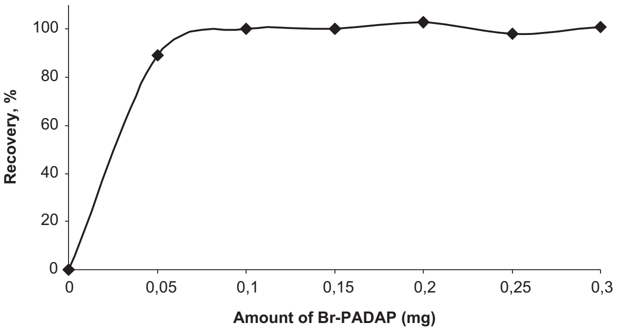

Fig. 2. Influences of the amounts of 5-Br-PADAP on the recovery values of nickel ($N = 3$).

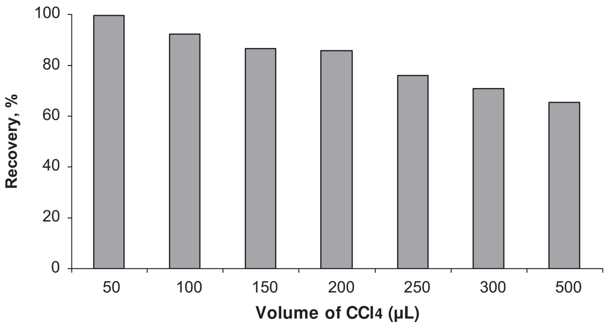

Fig. 3. Influences of the volume of CCl_4 on the recovery of nickel ($N = 3$).

The volumes of the extraction and dispersion solvents were examined to evaluate their impact on the recovery. To find the optimum volume of extraction solvent, solutions containing varying volumes of carbon tetrachloride (in the range of 50–500 µL) were prepared in 1 mL acetonitrile. It can be seen from Fig. 3 that nickel was quantitatively recovered when the extraction solvent volume was 50 µL. Therefore, 50 µL of carbon tetrachloride was selected as the extraction solvent volume.

After selecting the volume of CCl_4, the volume of acetonitrile was optimized by examining varying volumes of acetonitrile in the range of 0.5–3.0 mL. The recovery of nickel increased with increasing volume of acetonitrile up to 1.5 mL. Volumes greater than 1.5 mL acetonitrile caused a decrease in the recovery of nickel (Fig. 4). The stable cloudy solution was not established well when used less volume of acetonitrile, therefore the recovery decreased. 1.5 mL of acetonitrile was selected.

3.4. Effects of the extraction and centrifugation times

The effect of the extraction time was examined over the range of 1–30 min. There was no notable effect on the nickel(II) recovery values using the

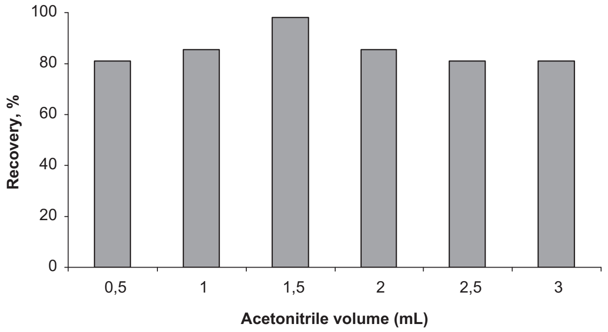

Fig. 4. Influences of the volume of acetonitrile on the recovery of nickel ($N = 3$).

Table 1
Effect of the coexisting ions on the recovery of nickel ($N = 3$)

Interference	Concentration of interfering ions in the model solution (mg/L)	Concentration ratio of interfering ions to the analyte (w/w)
Na^+	1,000	25,000
K^+	1,000	25,000
Ca^{2+}	500	12,500
Mg^{2+}	500	12,500
Mn^{2+}	5	125
Fe^{3+}	10	250
Zn^{2+}	10	250
Co^{2+}	2.5	62.5
Cl^-	1,600	40,000
SO_4^{2-}	1,000	25,000

current microextraction system. This is because the surface area between the extraction solvent and aqueous phase became large after the formation of a large amount of fine droplets [26,27]. Centrifugation times over the range of 1–10 min at a rate of 4,000 rpm were investigated. Quantitative results were obtained after 10 min centrifugation. Therefore, 10 min centrifugation was selected as the optimum value.

3.5. Matrix influences

The effects of other ions on extraction were studied using the optimized conditions to demonstrate the selectivity of the developed microextraction method for the determination of nickel(II). A 20 mL solution, which contained 40 $\mu g\,L^{-1}$ of Ni and different concentrations of other ions, was prepared and subjected to the extraction procedure. The tolerance limits of the coexisting ions are listed in Table 1. They show that the recovery are quantitative and satisfactory in the presence of most foreign cations and the major cations in the water and real samples have no obvious influence on presented microextraction procedure of nickel((II) ions.

Table 2
Determination of nickel content in the certified reference materials ($N = 3$)

	Observed[a] ($\mu g\,L^{-1}$)	Certified value ($\mu g\,L^{-1}$)	Recovery (%)
TMDA-25.3	15.5 ± 0.6	15.5	100
TMDA-51.3	65.7 ± 6.2	68.3	96

[a] Mean of three determinations ± standard deviation.

Table 3
Addition/recovery tests for Ni determination in water samples ($N = 3$)

Added (μg)	Tap water from Ordu city		Bottled mineral water	
	Found[a] (μg)	Recovery (%)	Found[a] (μg)	Recovery (%)
0.00	UDL	–	UDL	–
0.50	0.51 ± 0.02	102	0.50 ± 0.01	100
0.75	0.75 ± 0.02	100	0.76 ± 0.03	101
1.00	1.01 ± 0.04	101	1.00 ± 0.02	100

UDL: Under of the detection limit.
[a] Mean ± standard deviation.

3.6. Sample volume

The sample volume is an important parameter in the preconcentration of traces of heavy metal ions [28–38]. The effect of the sample volume on the extraction of nickel was examined over the volume range of 10–50 mL sample. The quantitative recovery values (>95%) were obtained over the volume range of 10–50 mL. The largest sample volume observed to work was 50 mL. The final volume of solution was 0.25 mL, therefore, the preconcentration factor for nickel(II) is 200.

Table 4
Concentration of nickel in select real samples after application of the DLLME procedure ($N = 4$)

Samples	Concentration of Ni[a] ($\mu g\,L^{-1}$)
Bottled Cherry mineral water	3.2 ± 0.3
Bottled Pomegranate mineral water	1.3 ± 0.0
Bottled Lemon mineral water	3.1 ± 0.0
Bottled Strawberry mineral water	UDL
Tap water from Ordu city	UDL
Bottled mineral water	UDL

UDL: Under of the detection limit.
[a] Mean ± standard deviation.

Table 5
Comparison of the current procedure with select preconcentration methods

Method	Detection limit ($\mu g L^{-1}$)	Relative standard deviation (%)	Preconcentration factor	References
DLLME-FAAS[a]	1.59	2.17	51.8	[39]
ILDLLME-FAAS[b]	12.5	3.1	40.2	[40]
SPE-FAAS[c]	1.03	8.0	50	[41]
CP-FAAS[d]	1.05	3.9	25	[42]
SPE-FAAS[c]	1.42	2.0	50	[43]
CPE-FAAS[e]	1.1	–	10	[44]
DLLME-FAAS[a]	0.13	4.2	200	This work

Flame atomic absorption spectrometry (FAAS), [a]Dispersive liquid–liquid microextraction (DLLME), [b]Ionic liquid-based liquid–liquid extraction (IL-DLLME), [c]Solid phase extraction (SPE), [d]Coprecipitation (CP), [e]Cloud point extraction (CPE).

3.7. Figures of merit

The detection limit (LOD), quantification limit (LOQ), and relative standard deviation (RSD) were investigated under the optimized experimental conditions. The limit of detection, described as LOD = 3SD, and the limit of quantification, as LOQ = 10SD, are $0.13\,\mu g\,L^{-1}$ and $0.43\,\mu g\,L^{-1}$, respectively (Sd is the standard deviation of the blank and the slope of calibration curve after extraction) [39]. The RSD using this method was calculated to be 4.2% ($N = 10$). The enhancement factor was found to be 99 and was calculated from the slope ratio of two standard calibration curves with and without microextraction. Under the optimum conditions the calibration graph was linear in the rage of $5–186\,\mu g\,L^{-1}$.

3.8. Application of the presented procedure

To demonstrate the validity of the presented method, the latter was used to analyze TMDA-25.3 and TMDA-51.3 fortified water standard reference materials. The results are presented in Table 2, and they are in good agreement with the certified values.

The method was then used for determination of Ni in bottled mineral and tap water samples using the method of standard addition. Varying amounts of nickel were added to these samples (Table 3). Nickel recovery was found to be in the range of 95–100%. This method could be useful for the determination of nickel ions in natural waters. The DLLME procedure was applied to various water samples and the results are provided in Table 4.

4. Conclusions

An alternative DLLME method, which has advantages that include an excellent preconcentration factor, low detection limits, high sensitivity, simple operation, and being economical and green, has been developed. The matrix effects are tolerable. The method can be used as a routine and effective technique. We compared our method with other preconcentration procedures in Table 5. Our DLLME method shows a comparatively lower LOD ($0.13\,\mu g\,L^{-1}$) and a high preconcentration factor (200). The preconcentration factor found in the current work is comparable with some preconcentration factors that are found in literature [40–52].

Acknowledgments

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