Flame Atomic Absorption Spectrometry Determination of Trace Amounts of Nickel Ions in Water Samples after Ligandless Ultrasound-assisted Emulsification Microextraction

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In the present work, a new ligandless-ultrasound-assisted emulsification microextraction (LL-USAEME) method was developed for preconcentration trace amounts of nickel as a prior step to its determination by flame atomic absorption spectrometry. Some factors influencing the extraction efficiency of nickel and its subsequent determination were studied and optimized, such as type and volume of the extraction solvent, pH, extraction time, extraction temperature and ionic strength. Under the optimal conditions, the calibration curve was linear over the range of 1.0 ng mL⁻¹ – 1.0 μg mL⁻¹ for nickel with \( R^2 = 0.9997 \). The detection limit was 0.34 ng mL⁻¹ in the original solution (3 \( S_b/m \)) and the relative standard deviation for 8 replicate determination of 0.3 μg mL⁻¹ nickel was ±1.6%. The proposed method was successfully applied in the analysis of four real environmental water samples and good spiked recoveries over the range of 97 - 103% were obtained.

(Received January 11, 2010; Accepted June 11, 2010; Published September 10, 2010)

Introduction

Nickel is a moderately toxic element compared to other transition metals. However, it is known that the inhalation of nickel and its compounds can lead to serious problems, including respiratory system cancer. Moreover, nickel can cause a disease known as nickel-eczema.† Other studies show that nickel is toxic to patients who consumed food and beverages rich in nickel. Environmental pollution monitoring requires the determination of nickel at trace levels in various samples. Thus, it is clear that the determination of nickel, at trace levels, in water and environmental samples is of great significance from a public health and environmental point of view. The importance of determinations the trace-metal concentration in natural water samples is increasing in contamination monitoring studies.

Modern instrumental methods including spectrometry, ICP-MS, ICP-AES, AAS, etc., have been used for the determination of traces of metal ions in various media. However, in these determinations, low concentration levels of the analytes and high levels of matrices are the main problems. To solve these problems, a separation/preconcentration step prior to analysis is required. Up to now, several methods have been designed for the separation/preconcentration of cobalt and nickel from various matrices, including, solid-phase extraction (SPE), liquid-liquid extraction (LLE), ion-exchange, flotation, cloud point extraction (CPE), etc., which are among the most widespread used methods. Although relatively good analytical performance can be obtained with the above-mentioned pretreatment techniques, inconveniences such as lengthy separation, large consumption of reagents, multi-stage, and unsatisfactory enrichment factors can be listed as their disadvantages.

The applications of solid phase microextraction (SPME) and liquid phase microextraction (LPME) were developed to remove these disadvantages. A novel microextraction technique, dispersive liquid-liquid microextraction (DLLME), was recently introduced by Berijani et al. based on a ternary component solvent system, like homogeneous liquid-liquid extraction and cloud point extraction (CPE). It has the advantages of simplicity, rapidity, low sample volume, low cost, high recovery, and a high enrichment factor. DLLME has been widely used for the extraction of organic compounds (polycyclic aromatic hydrocarbons (PAHs), organophosphorus pesticides, triazine herbicides, phthalate esters, and antioxidants) and metal ions (palladium and cobalt, cadmium, and selenium). Recently, we reported a new DLLME method to preconcentrate silver and copper without the addition of a chelating agent. However, it still has some drawbacks, including a difficulty to automate and the necessity of using a third component (disperser solvent) that usually decreases the partition coefficient of the analytes into the extractant solvent. Furthermore, the extractant and disperser solvent used in DLLME are often volatile organic compounds.

The application of ultrasonic radiation in LLE methods (USALLE) has been reported by Luque de Castro and Priego-Capote. They also successfully applied ultrasound-assisted emulsification (USAEME) for the first time to determine some polar and non-polar compounds in solid plant samples. A high extraction efficiency in a short period of time is the main advantage of this method, but due to the volatilization of the disperser solvent, it is not suitable for the determination of volatile compounds. Moreover, adding the dispersed solvent to the sample is time-consuming and troublesome.

In order to overcome these disadvantages, a new method for the determination of nickel ions in water samples is introduced. This method is based on the previously reported USAEME technique. Due to the high enrichment factor of this technique, it is suitable for the determination of nickel ions in water samples. The main advantage of USAEME is the rapidity, low sample volume, low cost, high recovery, and a high enrichment factor. In this work, the method was optimized for the preconcentration of nickel ions in water samples. The main factors influencing the extraction efficiency of nickel and its subsequent determination were studied and optimized.
advantages of USALLE. Regueiro et al. applied a miniaturized approach to USALLE by using a micro volume of the organic phase to provide the advantages of both DLLME and USALLE. They successfully applied ultrasound-assisted emulsification microextraction (USAEME) to determine some emergent contaminants and pesticides in environmental waters. Fontana et al. applied this method for the determination of polybrominated flame retardants in water samples. They demonstrated that USAEME is an efficient, simple, and rapid as well as cheap extraction technique prior to GC analysis. Zhou et al. dispersed an ionic liquid (1-hexyl-3-methylimidazolium hexafluorophosphate) by ultrasonication to determine some aromatic amines in real water samples. According to our literature survey, until now there were two references to the application of USAAE for the separation and preconcentration of trace amounts of cadmium.

This paper describes the application of ligandless-ultrasound-assisted emulsification microextracion (LL-USAEME) for the determination of trace nickel in water samples without the addition of a dispersive solvent and chelating agent, thereby overcoming DLLME disadvantages. In order to obtain a high enrichment factor, the effect of different parameters affecting the extraction conditions (such as type and volume of the extraction solvent, pH, extraction time, extraction temperature and ionic strength) were tested. USAEME can be employed as a simple and efficient extraction and preconcentration procedure for heavy metals in aqueous samples with satisfactory results.

**Experimental**

**Chemicals**

All chemicals were of analytical-reagent grade and all solutions were prepared with deionized water. The laboratory glassware was kept overnight in a 1.4 mol L⁻¹ HNO₃ solution. Before using, all of the glassware was washed with deionized water and dried. A stock solution of nickel at a concentration of 1000.0 μg mL⁻¹ was prepared by dissolving appropriate amounts of Ni(NO₃)₂·6H₂O (Merck, Darmstadt, Germany) in deionized water containing 1 mL concentrated nitric acid (Merck). Working reference solutions were obtained daily by stepwise dilution from the stock solution with deionized water. A solution of 10% NaCl (Merck) was prepared by dissolving of 10 g of NaCl in 100 mL of deionized water. Solutions of alkali metal salt (1%) and various metal salts (0.1%) were used to study the interference of anions and cations, respectively.

**Apparatus**

A SensAA GBC (Dandenong, Australia) atomic absorption spectrometer equipped with deuterium background correction and nickel hollow cathode lamp was used for absorbance measurements at a wavelength of 232.0 nm. The instrumental parameters were adjusted according to the manufacturer’s recommendations. The acetylene flow rate and the burner height were adjusted in order to obtain the maximum absorbance signal, while aspirating the analyte solution. A Metrohm 692 pH meter (Herisau, Switzerland) was used for pH measurements. A Centurion scientific centrifuge Model 1020 D.E. (UK) was used to accelerate the phase separation. An ultrasonic bath with temperature control (FALC Instruments S.V.I Treviglio, Italy). Model LBS2, was used to assist the emulsification process of the microextraction technique.

**LL-USAEME procedure**

All standards and samples were prepared for analysis according to the following procedure. Seven milliliters of each sample were placed in a screw-cap glass test tube with a sonic bottom. To each test tube, 1 mL of 0.2 mol L⁻¹ phosphate buffer (pH 11) and 1 mL of 10% (w/v) NaCl were added. Then, 30.0 μL of carbon tetrachloride (CCl₄) was injected into each solution, and the tube was immersed into an ultrasonic bath for 10 min at 55°C. As a result, oil-in-water emulsions of CCl₄ in water were formed. Emulsions were then disrupted by centrifugation at 4000 rpm for 5 min, which resulted in the organic phase sedimenting at the bottom of the conical tube. The sediment phase was removed and 0.5 mL of 0.5 mol L⁻¹ HNO₃ in methanol was added to it. The final solution was aspirated directly into flame atomic absorption spectrometry (FAAS) for nickel determination.

**Sample preparation**

Two certified reference materials (CRMs) furnished by the National Institute for Environment Studies (NIES) No. 1 Pepperbush and NIES No. 7 Tea leaves have been analyzed. Approximately 1.0 g of this material was accurately weighed into a Teflon cup and dissolved in concentrated nitric acid (~10 mL) with heating on a water bath. The solution was cooled, diluted and filtered. The filtrate was made to 50.0 mL with deionized water in a calibrated flask. An aliquot of the sample solution was taken individually and Ni(II) ion was determined by the LL-USAEME procedure.

River and well-water samples were collected in acid-leached polyethylene bottles. The river-water samples were collected from Rayen, Shahdad and Kheypah in Kerman in Iran. The well-water sample was collected from Payame Noor University, Kerman, Iran. The only pretreatment was acidification to pH 2 with nitric acid, which was performed immediately after collection, in order to prevent adsorption of the metal ions on the flask walls. The samples were filtered before analyses through a cellulose membrane (Millipore, Bedford, MA) of 0.45 μm pore size.

**Results and Discussion**

In this study, the combination of USAEME with FAAS was developed for the determination of trace amounts of nickel. Several factors that may affect the extraction process, such as the type and volume of the extraction solvent, pH, extraction time, extraction temperature and ionic strength were optimized. The optimizations were carried out on an aqueous solution containing 7.0 μg of nickel.

**Selection of type and volume of the extraction solvent**

The type of extraction solvent used in USAEME is an essential consideration for efficient extraction. It should have a higher density than water, a high extraction capability of the interested compounds and low solubility in water. Dichloromethane (CH₂Cl₂), chloroform (CHCl₃), 1,2-dichlorobenzene (1,2-DCB) and carbon tetrachloride (CCl₄) were studied as extraction solvents. The effect of these solvents on the extraction efficiency of LL-USAEME was investigated using 30 μL of each solvent. After the addition of CHCl₃ and CH₂Cl₂, not only was the cloudy state formed, but there was also no sedimented phase on the bottom of the test tube after centrifugation. This was due to the higher solubility of this solvent in water than the other tested solvents. Three replicate tests were performed for each of these solvents under the same conditions. The results showed that, the extraction efficiency of CCl₄ is higher than 1,2-DCB. Therefore, CCl₄ was selected as the extraction solvent for...
In order to examine the effect of the extraction solvent volume, different volumes of CCl₄ (15 – 90 μL) were used as the extraction solvent for the same LL-USAEME procedure. The results are shown in Fig. 1. It was observed that the extraction efficiency increased with an increase of the volume of CCl₄ to 30 μL. A reduction in the extraction efficiency was observed after the volume of CCl₄ exceeded 30.0 μL. Based on these observations, a volume of 30.0 μL was used for further experiments.

**Effect of pH on USAEME**

The pH of the sample solution is one of the important factors affecting the formation of nonionic compounds and subsequent extraction. The effect of the pH on the LL-USAEME extraction of nickel was studied in the pH range of 3 – 12. As can be seen in Fig. 2, the highest extraction efficiency of nickel was obtained in the pH range of 10 – 12. Therefore, pH 11 was selected for further studies.

**Effect of the extraction time**

In USAEME, the extraction time is defined as the interval time between injection of the extraction solvent (CCl₄) and the end of the sonication stage. The effect of the extraction time was examined over the range of 5 to 30 min under constant experimental conditions. The results are shown in Fig. 3. It was observed that the extraction efficiency increased allows with an increase of the extraction time up to 10 min. A reduction in the extraction efficiency was observed after 10 min. Based on these observations, an extraction time of 10 min was used for further experiments.

**Effect of the extraction temperature**

The temperature affects the organic solvent solubility in water as well as the emulsification phenomenon. Thus, this affects the mass-transfer process and the extraction efficiency. To determine the influence of the extraction temperature, 7.0 mL of an aqueous solution containing 7.0 μg of nickel was extracted at different temperatures ranging from 30 to 70°C. The results are shown in Fig. 4. It was observed that the highest extraction efficiency was obtained at 55°C. At a temperature higher than 60°C, CCl₄ was partially dissolved into the aqueous bulk, leading to a reduction of the analytical signal. Hence, 55°C was used for further experiments.

**Salting-out effect**

In the extraction, the solubility of many analytes in aqueous solutions decreases with increasing of the ionic strength, due to the salting-out effect. Sodium chloride was used to investigate the influence of the ionic strength on the extraction efficiency. For investigating the influence of the ionic strength on the LL-USAEME performance, several experiments were performed by adding varying amounts of NaCl from 0.025 to 0.2 g. The remainder of the experimental conditions was kept constant. The resulting data showed that the maximum extraction efficiency was obtained in the presence of 0.1 g of NaCl. Below or above this amount, a decrease on the extraction efficiency was observed. Therefore, 1 mL of NaCl 10% was used in all further experiments.

**Effect of interference ions**

In view of the high selectivity provided by flame atomic absorption spectrometry, the only interference may be attributed to the preconcentration step. The interferences studied were...
those related to the preconcentration step, species that may react with the analytes and decrease the extraction efficiency. To perform this study, interference ions in different aqueous solutions were added to a solution containing 7.0 μg of Ni(II), and were subjected to the recommended procedure. Table 1 gives the tolerance limits of the interference ions (±5% error). The results demonstrate that the presence of large amounts of species commonly present in water samples have no significant effect on the LL-USAEME of nickel.

### Calibration, precision and detection limit

The repeatability, linearity and detection limit were investigated under the optimized experimental conditions. For a sample volume of 7.0 mL, the calibration curve exhibited linearity over the range of 1.0 ng mL⁻¹ - 1.0 μg mL⁻¹ with a correlation coefficient of 0.9997 (A = 0.9871C + 0.0037, where A is the absorbance value of the eluent and C is the concentration of Ni (μg mL⁻¹)). Eight replicate determinations of 0.3 μg mL⁻¹ nickel gave a mean absorbance of 0.296 with a relative standard deviation of ±1.6%. The detection limit was 0.34 ng mL⁻¹ (3Sb/m).

### Accuracy of the method

The accuracy and applicability of the proposed method has been applied to the determination of Ni(II) ion in National Institute for Environment Studies (NIES) No. 1 Pepperbush, NIES No. 7 Tea leaves. An aliquot of these samples was subjected to the LL-USAEME procedure for the preconcentration and determination of nickel by using the standard addition method. The results are given in Table 2. It was found that there is no significant difference between results obtained by the proposed method and the certified results. These results indicate the applicability of the developed procedure for nickel determination.

### Analysis of water samples

The proposed procedure has been applied to the determination of nickel in different water samples after standard addition. The results are given in Table 3. The recovery of nickel from water samples spiked with Ni(II) was also studied. The results are tabulated in Table 3. According to this table, the added nickel ion can be quantitatively recovered from the water samples by the proposed procedure. These results demonstrate the applicability of the proposed procedure for nickel determination in water samples.

### Conclusions

LL-USAEME combined with the FAAS was evaluated for the preconcentration and determination of trace amounts of nickel (at ng mL⁻¹ level) from water samples. LL-USAEME is a sensitive, efficient, and simple method for the preconcentration and separation of trace amounts of nickel using low sample volumes. In addition, it is important to point out that LL-USAEME is a low organic solvent-consuming extraction technique, which turns it into a low-cost, environmentally friendly technique. In this method, consumption of the toxic organic solvent (at μL level) was minimized without affecting the method sensitivity.

### References


