



An Eco-Friendly Ultrasound-Assisted Emulsification Dispersive Liquid–Liquid Microextraction of Nickel in Environmental Samples Coupled with Spectrophotometry

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Abstract

A new, simple, rapid, sensitive and environmentally friendly ultrasound-assisted emulsification dispersive liquid–liquid microextraction (UAE-DLLME) has been developed for trace nickel Ni(II) separation and preconcentration in environmental samples prior to spectrophotometric determination. The proposed method based on using non-ionic water-soluble surfactant Triton X-114 (TX-114) as a disperser solvent and tetrachloroethylene as an extractive solvent. A 6-(1,3-thiazolylazo)-2-nitrophenol (TANP) as complexing agent was used for complexation of Ni(II) at pH 7.0. The influence of various variables on the performance of the UAE-DLLME method was optimized. Under the optimal conditions, the calibration graph was linear in the range of 1.0–300 $\mu\text{g L}^{-1}$. The detection and quantitation limits of the method were determined as 0.3 and 1.0 $\mu\text{g L}^{-1}$, respectively. The preconcentration factor and enhancement factor were obtained as 60 and 45. Relative standard deviation (RSD %) as precision at 100 and 200 $\mu\text{g L}^{-1}$ of Ni(II) were 1.4 and 2.1%, respectively ($n=10$). The validation of the developed method was proved by analysis of certified reference materials. Finally, the developed UAE-DLLME microextraction method was applied to preconcentrate and determine of trace levels of Ni(II) in real water, food and tobacco samples with satisfactory results.

Keywords: Ultrasound-assisted emulsification dispersive liquid–liquid microextraction; Preconcentration; Nickel; Non-ionic surfactant; Environmental samples; Spectrophotometry.

1. Introduction

Nickel (Ni(II)) is a very abundant natural element and it is toxic for living organisms according to concentration levels. Humans are exposed to nickel through the air, ingestion of contaminated food, water, and cigarette smoke. Ni(II) compounds was categorized as a carcinogen to humans and a wide variety of chronic problems related to the respiratory tract, lung cancer and skin dermatitis were caused by high exposure to Ni(II)[1]. Therefore, the estimation of trace Ni(II) in various samples is a very important aim using novel and sensitive methods[2, 3]. The concentration of Ni(II) in real samples are less than the detection limit of some instruments like FAAS or GFAAS and the co-existing ions interference are two limitations and common problems in the determination of trace Ni(II)[4]. Therefore, a preconcentration and separation step are substantial before the measurements to overcome these

limitations by increasing the sensitivity and enhancing estimation accuracy[5].

The development of several methods to separate and enrich of trace Ni(II) from various samples, such as solid-phase extraction (SPE)[6–13], cloud point extraction (CPE)[14–21], membrane filtration[22, 23] and co-precipitation[24, 25] has recently been documented in the literature. Analytical chemists have tried to reduce or omit the hazardous toxic and volatile extraction solvents using dispersive liquid–liquid microextraction (DLLME). DLLME is a simple and fast microextraction technique based on the use of a green extractant and disperser solvents with high miscibility in both extractant and aqueous phase. Recently, many advanced methods of DLLME have been developed and reported for the preconcentration and microextraction of inorganic and organic contaminants from environmental samples[26–40].

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Because the high cost and energy consuming of the analytical instruments coupled with DLLME, spectrophotometer is an ordinary instrument but very cost-effective and widely used even in some less developed area. Therefore, the utilization of UAE-DLLME method combined with spectrophotometry has some advantages such as simplicity, an economic, lower limit of detection, higher preconcentration factor and environment-friendly.

Thiazolyl azo and benzothiazolyl azo dyes have attracted much attention as they are sensitive chromogenic reagents in addition to being important complexing agents. These azo dyes have been applied to some microextraction methods for determinations of some metal ions due to its good selectivity and sensitivity over a wide range of pH and because they are relatively easy to synthesize and purify. Nevertheless, for conventional spectrophotometric analysis in aqueous solution, the low solubility of these azo compounds and their complexes is a significant drawback, that can be overcome by adding organic solvents or surfactants[41].

The aim of the proposed work was to develop green ultrasound-assisted emulsification dispersive liquid-liquid microextraction (UAE-DLLME) procedure in combination with spectrophotometer for preconcentration and accurate determination of trace levels of Ni(II) in real water, food and tobacco samples. Nonionic water-soluble surfactant Triton X-114 (TX-114) as a disperser solvent and tetrachloroethylene was investigated as an extractive solvent and 6-(1,3-thiazolylazo)-2-nitrophenol (TANP) as a complexing agent, were used. The influence of various variables on the performance of the UAE-DLLME method was optimized. The method validity was examined by the analysis of certified reference materials.

2. Experimental

2.1. Apparatus

Varian UV-Vis spectrophotometer (Cary 100 Conc., Australia) was used for the determination. A centrifuge (HERMLE, Germany) was utilized to facilitate and enhance the phase separation. To support analyte extraction from sample matrices and production of cloudy solution, Grant ultrasonic water bath (LabGear, Australia) was utilized. An AD1000 model pH-meter (Adwa instruments Kft., Szeged, Hungary) combined with a glass-electrode was utilized to control the pH-values of the solutions. Milli-Q purification device (Millipore, USA) was utilized to obtain deionized/bidistilled water that used for the preparation of solutions. Milestone Ethos UP (Milestone, Sorisole, Italy) closed vessel microwave digestion systems were used to digest the solid samples up to 300 °C and 100 bar pressure. All glass

wares were kept in HNO₃ (5.0 %, v/v) for at least 16 h, rinsed and cleaned with bidistilled water prior to the experiment.

2.2. Reagents and solutions

All reagents and chemicals used were of high purity and acquired from (Merck, Darmstadt, Germany) and (Sigma Aldrich, St. Louis, USA) companies. High-quality HNO₃ (65 %, v/v), HCl (37 %, v/v) and NH₃ (25 %, v/v) solutions were used. The stock solution of Ni(II) (1000 µg mL⁻¹) was intended from Ni(NO₃)₂·6H₂O of high purity, (Fluka Chemie AG, Basel, Switzerland). Diluted Ni(II) working solution was obtained through sequent dilution of the stock standard solution daily.

A stock solution (1.0 × 10⁻³ mol L⁻¹) of 6-(1,3-thiazolylazo)-2-nitrophenol (TANP) synthesized before[42] was prepared by dissolving an appropriate amount of the reagent in a minimum amount of absolute ethanol and diluting the mixture to 100 mL with ethanol in a 100 mL measuring flask. The working solution was prepared by its appropriate dilution with the same solvent.

Triton X-114 (TX-114) (Fluka, Buches, Switzerland) was used as the non-ionic surfactant without further purification. Aqueous 1.0 % (v/v) solution of TX-114 was prepared by dissolving 1.0 mL of TX-114 in 100 mL of bidistilled water in 100 mL volumetric flask with stirring. Cyclohexan, chloroform, carbon tetrachloride (CCl₄), dichloromethane, tetrachloroethylene, 1,2-dichloroethane were inspected as extraction solvents and purchased from (Sigma Aldrich, St. Louis, USA). The pH values were adjusted using a series of buffer solutions [43]. TMDA 51.3 fortified water and TMDA 53.3 fortified water (National Water Research Institute, Environment Canada, Burlington, Canada) and SRM 1570a spinach leaves and SRM 1573a Tomato leaves (National Institute of Standard Technology, Gaithersburg, MD, USA) were utilized as certified reference materials.

2.3. Preconcentration UAE -DLLME procedure

An aliquots of 30 mL of a sample solution containing 1.0-300 µg L⁻¹ of Ni(II) were placed in a conical-bottom glass centrifuge tube and mixed with 5.0 mL of phosphate buffer solution (pH 7.0). Subsequently, 2.0 mL of the 1.0×10⁻³ mol L⁻¹ TANP solution was added to form Ni(II)-TANP complex. A 1.0 mL of (1.0% v/v) TX-114 (disperser solvent) was added, and 200 µL of tetrachloroethylene (extractant solvent) was injected rapidly into the sample solution. After that, the extraction was completed by transferring the tube to an ultrasound bath and sonicated for 4.0 min. Then, the cloudy turbid solution in the tube was formed in an ice bath for 5.0

min. To speed up phase separation, the solution was centrifuged at 3500 rpm for 5.0 min. The dispersed fine droplets of tetrachloroethylene were subsequently sedimented at the bottom of the centrifuge tube. Using a syringe, the upper aqueous phase was removed. Finally, the remaining phase was diluted using acetone to 500 μL and the enriched Ni(II) was determined by spectrophotometer at 552 nm.

2.4. Pretreatment of real samples and CRMs

2.4.1. Water Samples

The proposed procedure was successfully applied to water samples "tap water, mineral water, sea water, well water, river water and wastewater" acquired from Egypt and stored in polyethylene bottles. All water samples are filtered through a cellulose membrane filter of 0.45- μm pore size (Millipore Corporation, Bedford, MA, USA) to eliminate hanging materials before being acidified with diluted HNO_3 and stored at 4°C. To oxidize the organic content of water samples, H_2O_2 (1.0 % v/v) and HNO_3 (65 % m/m) was utilized. The same preconcentration UAE-DLLME technique has been used to the CRM (TMDA-51.3 and TMDA 53.3 fortified water). The Ni(II) concentrations were evaluated from calibration graph.

2.4.2. Food and tobacco samples

The different fresh food samples (carrot, cabbage, spinach, mint, parsley, potato, apple, black tea and chocolate), canned foods (fish, peas, beans, kidney beans, corn, chickpea, tomato paste) and tobacco samples were collected from the supermarkets in Egypt. For 24 hours in an electric oven, the food samples are dried at 90 °C and homogenized by grinding in an agate porcelain mortar. Firstly, SRM 1570a spinach leaves, SRM 1573a tomato leaves, food, and tobacco samples (0.2 g) were treated with 15 mL of a mixture of concentrated HNO_3 - H_2O_2 (2:1, v/v) into Teflon tubes and the tubes were sealed. The microwave digestion procedure has been applied for sample preparation after necessary dilutions and pH adjustments[44]. After necessary dilutions and pH adjustments, the digested samples were subjected to the developed UAE-DLLME procedure.

3. Results and discussion

3.1. Absorption spectra

The absorption spectra of Ni(II)-TANP complex after extracted by UAE-DLLME at pH=7.0 was determined in the wavelength range between 400 and 650 nm which give a maximum absorbance at 552 nm against a reagent blank.

3.2. Optimization of the experimental conditions

Some analytical parameters such as pH, reagent and surfactant concentrations, temperature and centrifugation times, were investigated.

3.2.1. Influence of pH

The sample pH has a crucial impact on the extraction efficiency and the formation of a metal-chelate complex. Consequently, the influence of pH on the UAE-DLLME microextraction technique of Ni(II)-TANP complex was studied at pH range of 3.0-10. As illustrated in Fig. 1, the absorbance of Ni(II)-TANP complex increased with increasing pH and the largest quantitative values are accomplished until the pH range 6.0-8.0. The metal-ligand interaction is probably less effective at low pH values due to proton competition with the analyte. At pH values above 8.0, the absorbance also decreases due to the formation of the corresponding hydroxide and Ni(II)-TANP and aqua complexes of Ni(II) ions competed with each other. In subsequent studies, 4.0 mL of phosphate buffer solution (pH 7.0) was employed.

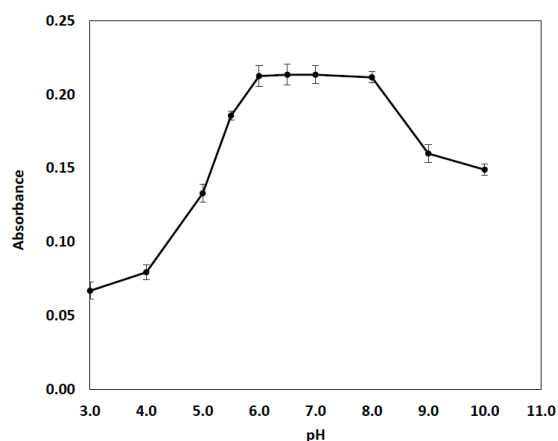


Fig. 1. Effect of pH on the recoveries of Ni(II) through UAE-DLLME method. Conditions: (Ni(II) concentration, 250 $\mu\text{g L}^{-1}$; concentration of TANP, $(1.0 \times 10^{-3} \text{ mol L}^{-1})$; TX-114 (1.0% v/v) volume, 1.0 mL; ultrasonication time, 4.0 min; tetrachloroethylene volume, 200 μL ; volume of the sample, 30 mL).

3.2.2. Influence of concentration of TANP reagent

The reagent concentration has an important effect on the absorbance of Ni(II)-TANP complex to give quantitative results. Various concentrations of TANP were examined within the range of 2.0×10^{-4} - $3.0 \times 10^{-3} \text{ mol L}^{-1}$ and results curvature is shown in Fig. 2. The absorbance has been increased by increasing the TANP concentration up to $1.0 \times 10^{-3} \text{ mol L}^{-1}$ and higher amounts of TANP have no significant effect in the absorbance. At TANP concentration higher than $2.0 \times 10^{-3} \text{ mol L}^{-1}$, the absorbance slightly decreased due to co-extract of excessive chelating agents into

the organic phase, thus the extraction efficiency decreased. Therefore, $1.0 \times 10^{-3} \text{ mol L}^{-1}$ of TANP was utilized as the optimum concentration for complexation and maximum extraction efficiency in further studies.

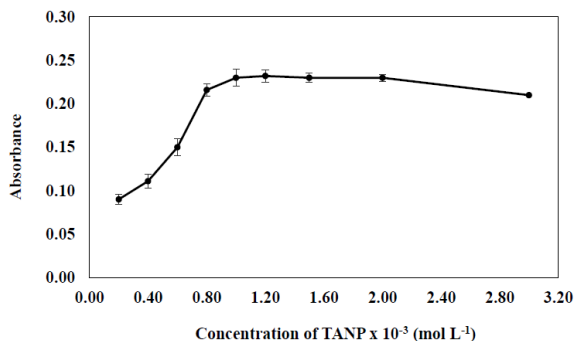


Fig. 2. Effect of the TANP concentration on the Ni(II) pre-concentration using UAE-DLLME method. Conditions: (Ni(II) concentration, $250 \mu\text{g L}^{-1}$; pH 7.0; TX-114 (1.0% v/v) volume, 1.0 mL; ultrasonication time, 4.0 min; tetrachloroethylene volume, 200 μL ; volume of the sample, 30 mL).

3.2.3. Influence of type and amount of extraction solvent

In microextraction technique, choice of type and volume of extraction solvent was important which has a large influence on the extraction efficiency of analyte based on higher density than water and low solubility in water. In the present experiment, cyclohexane, chloroform, carbon tetrachloride, dichloromethane, 1,2-dichloroethane, and tetrachloroethylene water-insoluble extractants were investigated. The results demonstrated in Fig. 3. The results showed that higher absorbance was obtained when tetrachloroethylene was used as the extraction solvent. So, tetrachloroethylene was selected as the extraction solvent in further experiments. Consequently, the volume of tetrachloroethylene was studied in the range of 50-400 μL (Fig. 4). The absorbance of the complex was enhanced with increasing tetrachloroethylene volume up to 200 μL which can dissolve Ni(II) complex. At volume higher than 200 μL , the absorbance decreased due to some of tetrachloroethylene adhered to the centrifuge tube and could not be dispersed into the aqueous solution as infinitesimal drops and existed as larger drops which decreased the contact area between Ni(II) complex and organic drop, that is reduced the transfer of Ni(II) complex into the tetrachloroethylene phase. Hence, 200 μL of tetrachloroethylene was chosen as an optimum volume for all the subsequent studies and to get a better enrichment factor.

3.2.4. Influence of dispersive solvent type and volume

In microextraction technique, the choice of the dispersive solvent is a significant parameter to form dispersed fine droplets because it must be miscible in both the aqueous and the extractant phases.

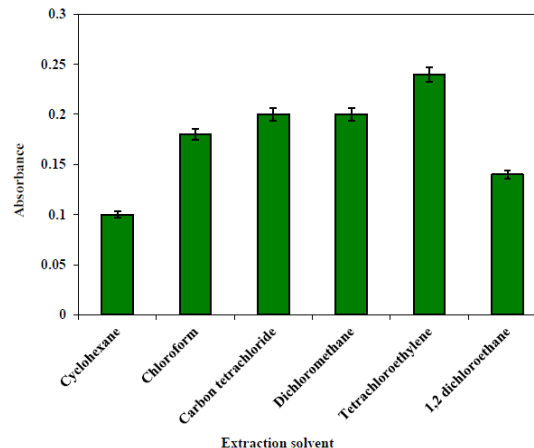


Fig. 3. Effect of types of extraction solvent. UAE-DLLME method. Conditions: (Ni(II) concentration, $250 \mu\text{g L}^{-1}$; pH 7.0; concentration of TANP, ($1.0 \times 10^{-3} \text{ mol L}^{-1}$); TX-114 (1.0% v/v) volume, 1.0 mL; ultrasonication time, 4.0 min; volume of the sample, 30 mL).

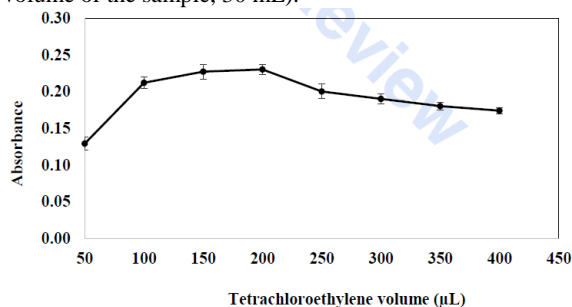


Fig. 4. Effect of the tetrachloroethylene volume on the Ni(II) pre-concentration using UAE-DLLME method. Conditions: (Ni(II) concentration, $250 \mu\text{g L}^{-1}$; pH 7.0; concentration of TANP, ($1.0 \times 10^{-3} \text{ mol L}^{-1}$); TX-114 (1.0% v/v) volume, 1.0 mL; ultrasonication time, 4.0 min; volume of sample, 30 mL).

Firstly, various dispersive solvents like (methanol, ethanol, acetonitrile, acetone, and tetrahydro furan) were utilized. However, tetrachloroethylene was very viscous. Ni containing extractant adhered to the walls of the centrifuge tube; therefore, quantitative extraction could not be obtained. Water-soluble nonionic surfactants Triton X-100, TX-114, Tween 20, and Tween 80 were used. Surfactants were preferred because they acted in the aqueous solution as both disperser solvents and anti-sticking agents. TX-114 had the best extraction efficiency and higher absorbance; therefore, it was selected as the optimum disperser solvent as given in Figure 5. The effect of dispersive solvent (TX-114, 1.0% v/v) volume on the

absorbance of Ni(II)-TANP complex was tested in the range of 0.1–2.0 mL (Fig. 6). The absorbance of the complex was increased with increasing TX-114 volume up to 1.0 mL. For subsequent studies, the suitable volume of TX-114 (1.0 mL) was selected as optimal and provided the highest absorbance.

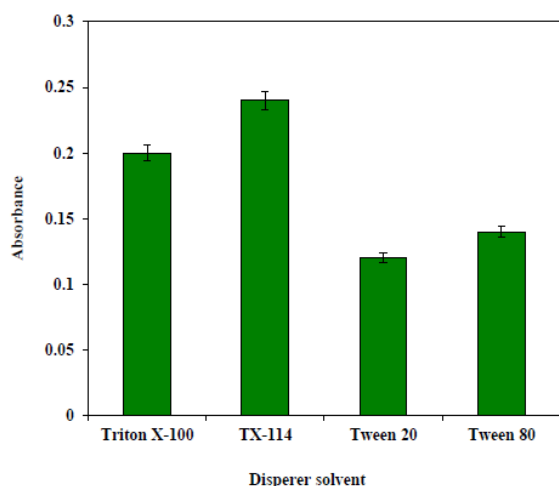


Fig. 5. Effect of types of disperser solvent. UAE-DLLME method. Conditions: (Ni(II) concentration, $250 \mu\text{g L}^{-1}$; pH 7.0; concentration of TANP, $(1.0 \times 10^{-3} \text{ mol L}^{-1})$; tetrachloroethylene volume, $200 \mu\text{L}$; ultrasonication time, 4.0 min; volume of the sample, 30 mL).

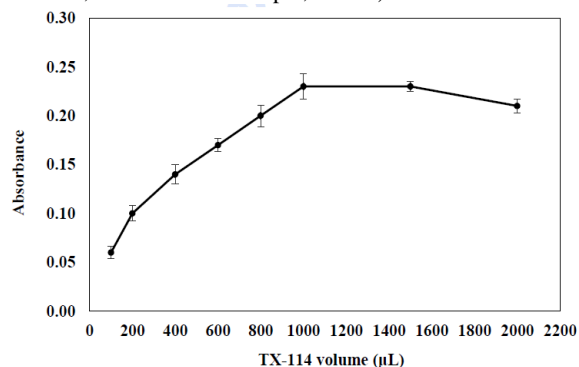


Fig. 6. Effect of TX-114 volume on the Ni(II) preconcentration using UAE-DLLME method. Conditions: (Ni(II) concentration, $250 \mu\text{g L}^{-1}$; pH 7.0; concentration of TANP, $(1.0 \times 10^{-3} \text{ mol L}^{-1})$; tetrachloroethylene volume, $200 \mu\text{L}$; ultrasonication time, 4.0 min; volume of the sample, 30 mL).

3.2.5. Influence of ultrasonication time

In microextraction technique, Ultrasound radiation has a significant effect on the extraction efficiency due to increasing mass transfer and emulsification of solution. The impact of ultrasonication time was optimized between 1.0–10 min (Figure 7). The results indicated that the absorbance was increased up to 4.0 min. after this time no significant change in absorbance till 6.0 min. At time more than 6.0 min, the absorbance slightly decreased due to increase the temperature of solution, and the complexation of

Ni(II)-TANP would be affected thus the extraction efficiency decreased. As a result, 4.0 min was chosen as the optimum ultrasonication time for subsequent studies.

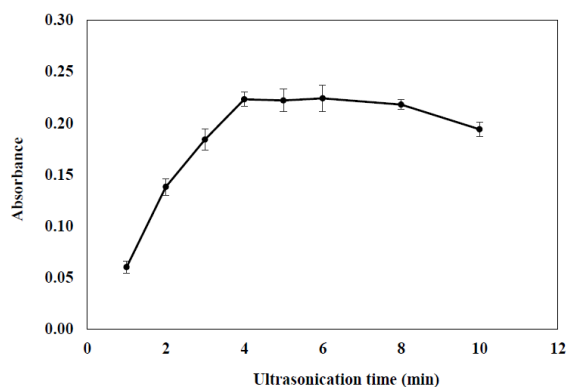


Fig. 7. Effect of ultrasonication time on the Ni(II) preconcentration using UAE-DLLME method. Conditions: (Ni(II) concentration, $250 \mu\text{g L}^{-1}$; pH 7.0; concentration of TANP, $(1.0 \times 10^{-3} \text{ mol L}^{-1})$; TX-114 (1.0% v/v) volume, 1.0 mL; tetrachloroethylene volume, $200 \mu\text{L}$; volume of the sample, 30 mL).

3.2.6. Influence of centrifugation conditions

Centrifuge rate and time have an important impact on the separation of tetrachloroethylene from the aqueous phase. The centrifugation rate was tested in the range of 1000 and 5000 rpm. The centrifugation rate was increased up to 3500 rpm which chosen as the optimum rate. Also, the centrifugation time effect on the absorbance was evaluated between 2.0 and 15 min. The maximum absorbance was obtained at 5.0 min to ensure complete phase separation. At centrifugation time longer than 5.0 min the absorbance decreased due to generation of heat which may enhance the dissolving the metal complex into the aqueous phase. So, 3500 rpm and 5.0 min were chosen as optimum centrifuge rate and time, respectively for further studies.

3.2.7. Effect of type of dilution solvent

The type of dilution solvent could affect the detection such as the ratio of volumes between water phase and organic phase and the enrichment factor[45]. In this experiment, some conventional solvents including methanol, ethanol, and acetone were studied. The results showed that acetone was the best dilution solvent for determination of Ni(II) ion.

3.2.8. Influence of sample volume

The sample volume is an important factor for achieving a high preconcentration factor and maximum absorbance based on UAE-DLLME procedure. The sample volume effect was investigated using (5.0–50.0 mL) model solutions. Higher than 30 mL, Ni(II) ion recoveries were not

quantitative. Hence, Ni(II) solution (30 mL) was chosen as the highest sample volume in all the subsequent studies. The preconcentration factor (PF) has been described as the sample volume ratio to the final dilute volume (0.5 mL). Therefore, PF was attained as 60.

3.3. Influence of matrix ions

The possible effect of the potential matrix constituents on the preconcentration and determination of the Ni(II) ions in different real environmental samples was examined. The results of tolerance limits obtained are shown in Table 1. The tolerance limit is defined as the highest amount of interfering ions creating a relative error $\leq \pm 5\%$. No obvious interference effect of matrix ions was observed in the determination of Ni(II) ions under the experimental conditions which confirm the applicability of UAE-DLLME method for Ni(II) determination in various real samples.

Table 1

Tolerance limits of some coexisting matrix ions on the recovery of Ni(II)-TANP complex using the developed UAE-DLLME procedure (N=3.0).

Ions	Added as	Concentration (mg L ⁻¹)	Recovery (%) ^a
Na ⁺	NaCl	7000	98 ± 2
K ⁺	KCl	7000	97 ± 1
Ca ²⁺	CaCl ₂	2000	95 ± 3
Mg ²⁺	MgCl ₂	5000	97 ± 2
Cl ⁻	KCl	7000	98 ± 3
SO ₄ ²⁻	Na ₂ SO ₄	4000	98 ± 1
PO ₄ ³⁻	Na ₃ PO ₄	1000	100 ± 2
NO ₃ ⁻	NaNO ₃	5000	99 ± 2
Fe ³⁺	FeCl ₃	500	96 ± 2
Al ³⁺	Al(NO ₃) ₃ .9H ₂ O	300	99 ± 3
Mn ²⁺	MnSO ₄ .H ₂ O	500	97 ± 4
Cr ³⁺	Cr(NO ₃) ₃ .9H ₂ O	200	98 ± 2
Co ²⁺	Co(NO ₃) ₂ .6H ₂ O	50	98 ± 2
Cu ²⁺	Cu(NO ₃) ₂ .3H ₂ O	50	97 ± 3
Cd ²⁺	Cd(NO ₃) ₂ .6H ₂ O	50	99 ± 1
Pb ²⁺	Pb(NO ₃) ₂	50	96 ± 2
Zn ²⁺	Zn(NO ₃) ₂ .6H ₂ O	50	100 ± 4

^a Mean ± standard deviation.

3.4. Analytical performance and validation studies of the proposed method

Using the optimized experimental conditions described above, a satisfactory linear relationship was obtained in the 1.0-300 $\mu\text{g L}^{-1}$ range with the following linear regression equation, $A = 9.0 \times 10^{-4} C + 3.1 \times 10^{-3}$ with a correlation coefficient (R^2 0.9999, $n=8$), where A is the absorbance and C is the Ni(II) concentration ($\mu\text{g L}^{-1}$) (Fig. 8). The limits of detection (LOD) and quantification (LOQ) were calculated as $3S_b/m$ and $10S_b/m$, respectively, where S_b is the standard deviation from ten replicate measurements of blank solutions and m is the slope

of the calibration graph. The LOD and LOQ were 0.3 and 1.0 $\mu\text{g L}^{-1}$, respectively. The low detection limit of the present UAE-DLLME method indicates high sensitivity and suggests its efficient application for the determination of very low concentrations of Ni(II) in real samples.

The performance of the proposed UAE-DLLME procedure was assessed by calculating two parameters including the enrichment factor (EF) and the consumptive index (CI). The enrichment factor (EF), defined as the ratio between the calibration graph slopes with and without preconcentration procedure (EF= 45). The consumptive index (CI) was determined using the expression $CI = V_s/EF$, where V_s is the analyte solution volume and CI is 0.67. The reliability and precision of the proposed UAE - DLLME system as the relative standard deviation (RSD %) was examined by applying ten replicate determinations of 100 and 200 $\mu\text{g L}^{-1}$ of Ni(II), and RSD % of the recoveries was found to be 1.40 and 2.10%, respectively which illustrate a good precision of the method.

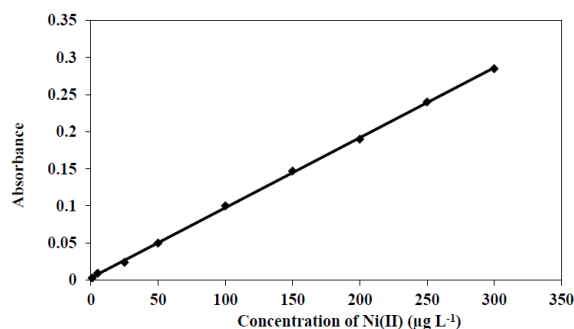


Fig. 8. Calibration graph for the determination of Ni(II) using the proposed preconcentration UAE-DLLME method under optimum conditions.

3.5. Validation studies

Additionally, the applicability of the developed UAE-DLLME method was checked and validated by two different studies. The first study was the determination of Ni(II) concentrations in four certified reference materials (TMDA-51.3 fortified water; TMDA-53.3 fortified water; SRM 1570a Spinach leaves, and SRM 1573a Tomato leaves) by the developed method. The concordant resulting values of recoveries levels were in a good agreement with the reported certified values (Table 2). The application of the proposed method to the real samples and CRMs shows that this method is highly accurate and reliable, is free of interference and validates the estimation of Ni(II) ion at trace levels in real samples. The t_{crit} values for 2.0 degrees of freedom at the 95% confidence level of was statistically greater than the t_{exp} values. It indicates that the results showed no significant error (Table 2).

Table 2
The validation of the proposed UAE-DLLME procedure for Ni(II) estimation in CRMs (N= 3.0).

CRMs	Certified value ($\mu\text{g L}^{-1}$)	Found ^a ($\mu\text{g L}^{-1}$)	RSD (%)	Recovery (%)	t_{exp} ^b
TMDA-53.3 fortified water	311	304 ± 2.30	0.76	97.75	2.40
TMDA-51.3 fortified water	68.3	65.0 ± 1.0	1.54	95.20	3.0
SRM 1570a Spinach Leaves	2.14 ± 0.1	2.10 ± 0.09	4.29	98.10	0.30
SRM 1573a Tomato leaves	1.582 ± 0.041	1.52 ± 0.03	1.97	96.15	0.53

^a Mean ± standard deviation based on three replicate determinations.

$$t_{\text{exp}} = \frac{|\mu - \bar{x}| \sqrt{N}}{s}$$

^b , where t_{exp} was statistical value (for 2 degrees of freedom, the tabulated value of t at the 95% confidence level is 4.30), s was the standard deviation, N was number of independent determinations, x was the mean found value, and μ was the certified value.

In the second validation study, intra-day and inter-day studies were performed with recovery test for spiked samples. The RSD% for the intra-day precision was determined by performing five replicate extractions and analysis of three Ni(II) concentrations (50, 100 and 200 $\mu\text{g L}^{-1}$) in the same day. Also, the RSD% for the inter-day precision was determined by extractions in five consecutive days for analyzing the same Ni(II) concentrations. The RSD% for intra-day precision ranged from 2.30 to 3.60% and, inter-day precision as RSD% ranged from 2.70 to 4.0%. As can be seen, acceptable precision (with RSD < 4.0%) was obtained in both studies, too. In addition, recovery values were calculated in two studies for three different concentrations. The results showed that quantitative recovery (> 95.80%) was achieved. Comprehensive results were given in Table 3.

Table 3
Intra-day and inter-day accuracy (as recovery %) and precision (as RSDs%) of the proposed method.

Added concentration ($\mu\text{g L}^{-1}$)	Intra-day (Recovery ± RSD) %	Inter-day (Recovery ± RSD) %
50	97.60 ± 2.30	96.90 ± 2.80
100	95.80 ± 3.2	97.50 ± 4.0
200	98.0 ± 3.60	99.0 ± 2.70

3.6. Analytical applications to real samples

The potential application of the developed UAE-DLLME preconcentration method to identify and separate Ni(II) ion in different real water and acid digested samples including food and tobacco samples were tested. The sample solutions were spiked with known quantities of Ni(II) ion using the standard

addition method to verify the reliability and accuracy of the developed process. Tables 4 and 5 shows the percentage of the analyte recovered from the spiked real sample and the RSD%. The quantitative recoveries for the Ni(II) analyte were great, in the range of 95.0–102 % with RSD ≤ 2.11%. Such results show that the approach is accurate and therefore, be used in to separate, preconcentrate and evaluate trace amounts of Ni(II) in real water, food and tobacco samples.

Table 4
The results for the standard addition-recovery method for the preconcentration of Ni(II) in water samples using the developed UAE-DLLME method (N=3.0).

Sample	Added ($\mu\text{g L}^{-1}$)	Found ^a ± SD ($\mu\text{g L}^{-1}$)	RSD (%) ^b	Recovery (%) ^b
Tape water	0	3.80 ± 0.07	-	-
	50	52.83 ± 1.10	2.08	98.20
	100	100.40 ± 1.60	1.59	96.70
Mineral water	0	< LOD ^c	-	-
	50	48.50 ± 0.94	1.94	97.0
	100	99.0 ± 1.50	1.52	99.0
Sea water	0	34.60 ± 0.35	-	-
	50	85.45 ± 1.04	1.22	101.0
	100	132.60 ± 1.80	1.36	98.50
Well water	0	< LOD ^c	-	-
	50	48.0 ± 0.82	1.70	96.0
	100	100.50 ± 1.40	1.40	100.50
River water	0	4.50 ± 0.05	-	-
	50	52.0 ± 0.65	1.25	95.40
	100	100.30 ± 1.80	1.80	96.0
Waste water	0	21.0 ± 0.30	-	-
	50	69.20 ± 1.20	1.73	97.50
	100	118.60 ± 2.0	1.69	98.0

^a Mean ± standard deviation.

^b Recovery% = [Observed value of Ni(II) / Expected value of Ni(II)] × 100

^c LOD: limit of detection.

3.7. Comparison with other preconcentration methods

The developed UAE-DLLME method was compared to the other extraction procedure documented in the literature [6-11, 14-19, 23-40]. The comparison allows easier analysis, relative to other approaches, of the positive aspects of the proposed method. As illustrated in Table 6, the main advantages of the method were low limit of detection, the large working ranges, better reliability or accuracy (as recovery%) and precision as (RSD%) and high PF, as well as the use of green chemicals. According to these properties, the UAE-DLLME technique has the potential to be a good alternative to the extraction methods used toxic organic solvents. Such results showed that the proposed UAE-DLLME protocol could be implemented successfully without any systematic error to analyse Ni(II) in different real samples.

4. Conclusions

In the current study, new, simple, sensitive, efficient, stable, fast and environmentally friendly UAE-DLLME method was developed and validated to preconcentrate Ni(II) ions in real water, food and tobacco samples prior to its spectrophotometric determination. The method is based on complexation of Ni(II) with TANP at pH 7.0 and using TX-114 non-ionic surfactant as a disperser solvent and tetrachloroethylene as an extractive solvent. Good characteristics of the proposed method such as low LOD of $0.30 \mu\text{g L}^{-1}$, wide linear range and high PF of

Table 5

The results for the standard addition-recovery method for the preconcentration of Ni(II) in food and tobacco samples using the developed UAE-DLLME method (N=3.0).

Fresh Foods sample	Added ($\mu\text{g g}^{-1}$)	Found \pm SD ($\mu\text{g g}^{-1}$)	RSD (%) ^b	Recovery (%) ^b	Canned foods sample	Found \pm SD ($\mu\text{g g}^{-1}$)	RSD (%) ^b	Recovery (%) ^b
Carrot	0	3.0 ± 0.06		-	Fish	12.0 ± 0.18		-
	50	52.15 ± 1.10	2.11	98.40		59.15 ± 1.20	2.03	95.40
	100	100.73 ± 2.0	1.99	97.80		113.12 ± 1.60	1.41	101.0
Cabbage	0	< LOD ^c		-	Peas	< LOD ^c		-
	50	48.35 ± 0.70	1.45	96.70		48.15 ± 0.40	0.83	96.30
	100	100.80 ± 1.30	1.29	100.80		97.60 ± 1.70	1.74	97.60
Spinach	0	1.80 ± 0.07		-	Beans	2.70 ± 0.05		-
	50	49.73 ± 0.85	1.71	96.0		51.12 ± 0.92	1.80	97.0
	100	95.20 ± 1.15	1.21	95.20		101.67 ± 1.90	1.87	99.0
Mint	0	1.50 ± 0.04		-	Kidney beans	3.0 ± 0.06		-
	50	50.21 ± 0.67	1.30	97.50		53.26 ± 0.73	1.37	100.50
	100	100.49 ± 1.0	1.0	99.0		101.66 ± 1.62	1.59	98.70
Parsley	0	3.70 ± 0.05		-	Corn	2.90 ± 0.03		-
	50	52.63 ± 0.60	1.14	98.0		51.31 ± 0.63	1.23	97.0
	100	100.07 ± 1.90	1.90	96.50		102.39 ± 1.18	1.15	99.50
Potato	0	2.40 ± 0.07		-	Chickpea	3.40 ± 0.04		-
	50	52.30 ± 0.70	1.34	99.80		51.05 ± 0.51	1.0	95.60
	100	99.64 ± 1.60	1.61	97.30		99.33 ± 1.72	1.73	97.0
Apple	0	3.0 ± 0.08		-	Tomato paste	6.0 ± 0.09		-
	50	50.88 ± 0.90	1.77	96.0		57.12 ± 0.68	1.19	102.0
	100	101.46 ± 1.40	1.38	98.50		101.76 ± 1.80	1.77	96.0
Black tea	0	1.40 ± 0.03		-	Tobacco	17.0 ± 0.14		-
	50	51.14 ± 0.65	1.27	99.50		66.33 ± 0.79	1.19	99.00
	100	102.41 ± 1.13	1.10	101.0		114.70 ± 1.45	1.26	98.0
Chocolate	0	3.20 ± 0.1		-				
	50	53.41 ± 0.60	1.12	100.40				
	100	98.0 ± 0.90	0.92	95.0				

^a Mean \pm standard deviation.

^b Recovery% = [Observed value of Ni(II) / Expected value of Ni(II)] \times 100

^c LOD: limit of detection.

60, high precision with RSDs of 1.40-2.1%, and high recovery (>95%). Moreover, the high tolerance to coexisting ions is also an outstanding feature of effective separation by the developed method. Satisfactory repeatability and reproducibility. The proposed method has good analytical performance indicated that this method was successfully applied to the determination of trace Ni(II) ions in real water, food and tobacco samples and certified reference materials.

Table 6

Comparison between the proposed UAE-DLLME procedure and other reported preconcentration methods for Ni(II) determination in various samples.

Preconcentration method	Detection system	Reagent	LOD ^a ($\mu\text{g L}^{-1}$)	Linearity ($\mu\text{g L}^{-1}$)	PF/EF ^b	Samples	References
SPE	FAAS	Amberlite CG-120	0.58	5.0-50	400	Water	[6]
USA-SLTPE	AT-FAAS	MWCNTs-Ph-SO ₃ H	0.35	1.5-165	50	Wastewater	[7]
SPE	SP	CPAHPD	3.0	10-370	100	Water, food, biological and soil	[8]
SPE	Imaging analysis	TAC	0.8	2.6-20	148	river water, coffee, and cigarette	[9]
SPE	FAAS	GO-p-aminophenol	0.7	3.0-70	67	Water	[10]
SPE	FAAS	Graphene	0.588	2.0-200	96.5	Vegetable	[11]
CPE	SP	DMG	4.0	10-150	20	Water	[14]
CPE	SP	BTAO	2.0	10-250	50	Water	[15]
CPE	FAAS	ATDP	1.30	5.0-150	100	Water	[16]
CPE	FAAS	8-HQ	0.52	4.0-15	50/61	Drinking and wastewater	[17]
CPE	GF-AAAS	5-Br-PADMA	0.031	0.1-5.5	200	Well and river water	[18]
UA-CPE	FAAS	HNB	0.78	3.0-180	50/48.6	Chocolates	[19]
Membrane filtration	FAAS	8-HQ	4.87	-	20	Environmental samples	[23]
Coprecipitation	FAAS	Thulium hydroxide	1.41	-	120	Environmental samples	[24]
Coprecipitation	FAAS	BNBATT	0.6	5.0-150	100	Water and food	[25]
VA-DLLME	HPLC	DDTC	1.0	5.0-100	130	Water	[26]
VA-IL-DLLME	FAAS	Ninhydrin	0.3	1.0-350	62.5	Chocolate-based	[27]
IL-DLLME	SP	BTAHQ	9.8	30-1500	200	Environmental and biological samples	[28]
DLLM-SFOD	FAAS	APDC	1.27	4.23-250	158	Water	[29]
CIAME	FAAS	TAN	0.85	2.0-100	90	Water	[30]
DLLME	FAAS	1-Nitroso 2-naphthol	1.59	10-250	51.8	Water and vitamin B12	[31]
DLLME	FAAS	BTAC	1.4	4.7-100	29	Water	[32]
SAE-DLLME	SP	PAN	0.24	Up to 100	23	Water	[33]
DES-DLLME	FAAS	2,2'-furildioxime	1.7	5.0-100	40	Water	[34]
IL-CIAME	FAAS	DMG	0.47	8.0-200	186	Water	[35]
IL-DLLME	SP	PAN	0.32	2.0-15	27	Water and food	[36]
LL-USAEME	FAAS	-	0.34	1.0-1000	-	Water	[37]
SLLME	FAAS	N,N'-Dihydroxy-1,2-cyclohexanedii mine	1.30	-	40	Water, tobacco and fertilizer	[38]
EADLLME	GFAAS	Phthalic Acid	15	50-1000	196.4	Water and fruit juice	[39]
DLLME	FAAS	PAN	12.5	50-500	40.2	Water	[40]
UAE-DLPME	SP	TANP	0.30	1.0-300	60/45	Water, food and tobacco	Proposed work

^a LOD: Limit of detection.^b PF: Preconcentration factor and EF: Enrichment factor.

^c SPE: solid phase extraction; USA-SLTPE: ultrasound-assisted solid-liquid trap phase extraction; AT-FAAS: atom trapping flame atomic absorption spectrometry; CPAHPD: 5-(4'-chlorophenylazo)-6-hydroxypyrimidine-2,4-dione; TAC: 1-(2-thiazolylazo)-p-cresol; GO-p-aminophenol: graphene oxide-based poly(p-aminophenol) composite; CPE: cloud point extraction; RTIL-CPE room temperature ionic liquids cloud point extraction; DDTC: diethyldithiocarbamate; SAN: salicylideneaniline; BTAO: 2-(benzothiazolyl azo) orcinol reagent; ATDP: 2-amino-6-(1,3-thiazol-2-diazyl)-phenol; 8-HQ: 8-hydroxyquinoline; 5-Br-PADMA: 2-(5-bromo-2-pyridylazo)-5-dimethylaminoaniline; UA-CPE: ultrasound-assisted cloud point extraction; HNB: hydroxy naphthol blue; BNBATT: 3-benzyl-4-p-nitrobenzylideneamino-4,5-dihydro-1,2,4-triazole-5-thiol. VA-DLLME: vortex assisted dispersive liquid-liquid microextraction; VA-IL-DLLME: vortex

assisted-ionic liquid based dispersive liquid liquid microextraction; IL-DLLME: ionic liquid dispersive liquid-liquid microextraction; BTAHQ: 5-(2-benzothiazolylazo)-8-hydroxyquinolene; DLLM-SFOD: dispersive liquid-liquid microextraction based on solidification of floating organic drop; APDC: Ammonium pyrrolidine dithiocarbamate; CIAME: Cold induced aggregation microextraction; TAN: 1-(2-thiazolylazo)-2-naphthol; DLLME: dispersive liquid-liquid microextraction; BTAC: 2-(2'-benzothiazolylazo)-p-cresol; SAE-DLLME: surfactant assisted emulsification dispersive liquid-liquid microextraction; PAN: 1-(2-pyridylazo) 2-naphthol; DES-DLLME: deep eutectic solvent based dispersive liquid-liquid microextraction; IL-CIAME: ionic liquid Cold-induced aggregation microextraction; DMG: dimethylglyoxime; LL-USAEME: ligandless-ultrasound-assisted emulsification microextraction; SLLME: supramolecular solvent liquid-liquid microextraction; EADLLME: effervescence assisted dispersive liquid-liquid microextraction; FAAS: flame atomic

absorption spectrometry; GFAAS: graphite furnace flame atomic absorption spectrometry; SP: spectrophotometry; UAE-DLLME: surfactant assisted emulsification dispersive liquid-liquid microextraction.

Conflicts of interest

The authors declare that they have no competing interests.

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