Determination of Trace Nickel in Spinach Samples Using the Combination of Vortex-assisted Deep Eutectic Solvent-based Liquid Phase Microextraction and Slotted Quartz Tube - Flame Atomic Absorption Spectrometry

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ABSTRACT

A novel, green, and efficient analytical method was developed for the preconcentration of nickel in spinach samples, prior to the determination by slotted quartz tube (SQT) - flame atomic absorption spectrometry (FAAS). Diphenylcarbazone was employed as the ligand, and a deep eutectic solvent (DES)-based liquid phase microextraction (LPME) was used to enrich the analyte for its determination at trace levels. All parameters of the SQT-FAAS and DES method were systematically optimized to enhance the detection power of conventional FAAS.

Under the optimum experimental conditions, the optimized method (DES-LPME-SQT-FAAS) recorded a 60-fold improvement in detection power over the FAAS. The limits of detection and quantification were 3.8 and 12.6 μg L^{-1}, respectively. The calibration plot was linear over a wide concentration range, and the precision for replicate measurements was appreciably high. Nickel was not detected in the spinach samples analyzed, but the spiked recovery tests for three samples yielded results close to 100%, confirming the method's accuracy and applicability to this type of matrix.

INTRODUCTION

Nickel can be found on the surface of the Earth as a silvery-white metallic element which has been greatly utilized in everyday life by humans since its discovery. This element is very resistant to corrosion and increases the strength of steel alloy (1). For this reason, it is used primarily for computer components, dental and surgical prostheses, electroplating, magnetic cords, and Ni-Cd batteries (2). Nickel accumulates in the environment through processes such as volcanic eruptions, soil and rock dissolution, biological cycles, and waste disposal (3). Nickel is a toxic element, and its most common effect on human health is skin disorder (4). Prolonged or repeated exposure to nickel can lead to damage of target organs, such as the kidneys, lungs, and liver, and increases the risk of cancer (5). Therefore, the World Health Organization (WHO) has established that the concentration of Ni in water should not exceed 0.07 mg L^{-1} (1). Thus, determining nickel at trace levels in environmental samples is important for public health and the environment (3).

There are many instrumental techniques used for the determination of elements, but sensitivity, accuracy, and precision are the main factors in selecting the appropriate instrumentation for a variety of matrices (3). Nickel determination in foods could be done by electrothermal atomic absorption spectrometry (ETAAS) (6) or inductively coupled plasma mass spectrometry (ICP-MS) (7) due to their high sensitivities. Flame atomic absorption spectrometry (FAAS) is a common instrument used in most laboratories, and has the advantages of robustness, high precision and accuracy, and low operational cost (8). However, it has low sensitivity relative to ETAAS and ICP-MS and therefore, requires the use of analyte preconcentration methods or a system enhancement apparatus to achieve adequate sensitivity levels (9).

Some sample pretreatment techniques that have been used to isolate/preconcentrate nickel from sample matrices are liquid phase microextraction (LPME) (10), dispersive liquid-liquid microextraction (DLLME) (11), dispersive solid phase extraction (D-SPE) (12), and solid–liquid–solid dispersive extraction–ionic liquid-based dispersive liquid–liquid microextraction (SLSDE-ILDLLME) (13). The main benefit of these microextraction techniques is the use of green solvents, thus eliminating conventional toxic solvents which pose risks to humans and the environment.

In recent times, the use of deep eutectic solvents (DESs) have drawn attention as a viable option in place of the regular organic solvents. DESs are eutectic mixtures of at least two components with the capacity to join with one another by means of hydrogen bonds (14). The high melting point salts are mixed to the point where they form a eutectic product with a lower melting point than each component separately (15). DESs are ordinarily a low-cost mixture of non-toxic and biodegradable choline chloride salt with a safe hydrogen bond donor (HBD) such

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as urea, glycerol, sugars, and carboxylic acids (16). Preconcentration methods significantly enhance the analyte signals to obtain lower detection limits, but basic components such as slotted quartz tube (SQT) can be used to enhance the absorbance signals 2–5 fold, of course, subject to the type of element (17).

The aim of this study was to utilize deep eutectic solvents as a viable extraction solvent to isolate and preconcentrate nickel from spinach samples, followed by subsequent determination with SQT-FAAS.

EXPERIMENTAL

Chemicals and Reagents

In this study, nickel stock standard solution of 1000 mg L^{-1} was used (High Purity Standards (USA). The deep eutectic solvent (DES) was produced from the mixture of choline chloride (Acros, USA, 99%) and phenol (PhOl, Merck, Germany). Tetrahydrofuran (THF) was also obtained from Merck. Ultrapure water (resistivity 18.2 MΩ·cm) was used for the preparation of all working standard solutions. 1,5-diphenyl carbazone (DPC) was obtained from Riedel-de Haen® (Germany), and HNO_3 (nitric acid) (65%) and H_2O_2 (hydrogen peroxide) (30%) were purchased from Merck.

Instrumentation

A model AG NovAA 300 atomic absorption spectrometer, fitted with a flame burner head and deuterium (D_2) background correction system (Analytik Jena, Germany), was utilized for nickel determination. A nickel hallow cathode lamp (Varian, Australia) was used as the light source, operating at 240.7 nm, 0.5 nm slit width, and a recommended current of 15 mA. An air-acetylene flame was used for the atomization of nickel by FAAS. An upper slot (3.2 cm) and a lower slot (5.5 cm), situated at 180° angles to each other, were made on a 16 cm long slotted quartz tube, having a 1.5 cm inner and 1.8 cm outer diameter. The SQT was placed on the head of the burner and carefully adjusted so that the light coming from the lamp passes properly through the optical detector path. Centrifugation was performed using a model EBA 20 centrifuge (Hettich, Germany). A model M-100 ultrasonic water bath (Hapa, Germany) and a model VM-10 vortex (WiseMix, Germany) were used for mixing the samples throughout the extraction studies. The digestion process was studied with a model MWS-3+ microwave digestion system (Berghof, Germany).

Digestion of Spinach Samples

A few leaves of spinach (about 1.0 g in weight and obtained from a local market) were dried and placed into 100 mL microwave vessels. An amount of 6.0 mL HNO_3 and 2.0 mL H_2O_2 was transferred into the vessels for the digestion process. The temperature program for the digestion procedure is listed in Table I. The digested samples were adjusted to pH 7.0 using 1.0 M sodium hydroxide before diluting the final volume to 100 mL with distilled water.

Preparation of DES

In this study, choline chloride as an organic salt (ChCl) and phenol (PhOl) as a hydrogen bond donor were utilized for making the DES. In order to determine the ideal ratio, 1:2, 1:3, 1:4, and 1:5 molar proportions of ChCl and PhOl in 50 mL centrifuge tubes were vortexed at room temperature until clear and homogeneous fluids were obtained. The prepared DES was left in the ultrasonic bath for 60 seconds to eliminate air bubbles.

TABLE I
Temperature Program for Digestion of Spinach Samples

Steps	1	2	3
Temperature (°C)	100	150	180
Ramp time (min)	5	5	5
Hold time (min)	10	5	10

Procedure

Extraction studies were conducted in 15 mL centrifuge tubes containing 8.0 mL of aqueous sample/standard solutions. The Ni-DPC complex was formed by adding 0.50 mL of pH 7.0 buffer and 1.0 mL of 0.50% DPC ligand to the sample/standard solution and mixing by mechanical shaker for 15 seconds. The nickel complex solution was injected with 0.50 mL DES, and the resulting cloudy solution was vortexed for 15 seconds. Subsequently, 1.0 mL of THF was added to the solution as an emulsifier agent and vortexed 15 seconds to achieve homogeneous distribution. The final solution was centrifuged for 2.0 minutes at 6000 rpm, and the organic phase that settled on the top layer was transferred into a clean tube, then aspirated to the FAAS system for absorbance readings.

RESULT AND DISCUSSION

The influence of the DES-LPME parameters on the nickel absorbance signal for the selection of the proper experimental conditions was studied. The optimum parameters for complexation between nickel and DPC were obtained according to a study by Yolcu et al. (18) and are listed in Table II. The instrumental and SQT parameters were also optimized to boost the absorbance signal of nickel in order to achieve lower detection limits.

Optimization of FAAS and SQT-FAAS Systems

To increase the detection power of the FAAS and SQT-FAAS systems (see Figure 1), the parameters such as sample flow rate, acetylene flow rate and SQT height from the burner head were optimized prior to the extraction optimizations.

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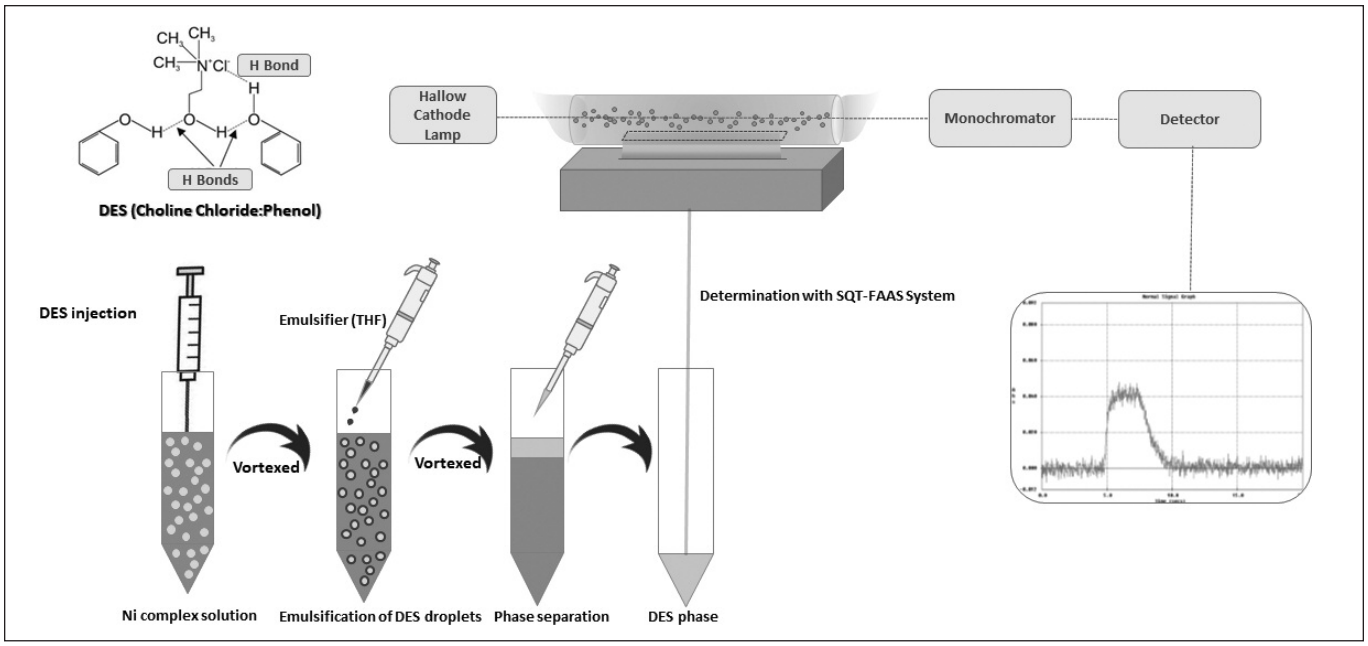

Fig. 1. Steps involved for the determination of Ni with SQR-FAAS system.

To determine the optimum flame atomization temperature, acetylene flow rates of 40, 45, 50, and 55 L h^{-1} were tested with equivalent standard solutions. The highest absorbance value corresponded to an acetylene flow rate at 40 L h^{-1}. The sample flow rate determines the amount of analyte in the sample that goes through the nebulization process to reach the flame and where it undergoes atomization. The optimum nickel sample flow rate of 7.44 mL min^{-1} was taken from a study performed by our research group with the same instrument (18). Using these flow rates, the SQT position on the flame burner head was examined, because it influences the rate of aspiration and atomization and the interaction between analyte atoms and light emanating from the hollow cathode lamp. After testing 0.0 mm (direct placement of SQT on the burner head), then 1.0 mm and 2.0 mm, the SQT height from the burner head of 1.0 mm was selected as optimal due to its high absorbance values with lower standard deviation value.

Optimization of Deep Eutectic Solvent

The choice of an extraction solvent ought to be made based on the rule of "like dissolves like" (19). That is, the extractant should have appreciably high affinity for the analyte of interest to be able to extract substantive amounts from the aqueous solution. The use of DES as an extraction solvent in this work offers these advantages, in addition to being a green solvent for rapid extraction. Choline chloride and phenol at the ratios of 1:2, 1:3, 1:4, and 1:5 were mixed to their eutectic points and used to extract the nickel complex from aqueous solution. As the phenol ratio decreased, there was a decrease in the viscosity of the solution and the absorbance signals increased accordingly (as shown in Figure 2).

The proper amount of extraction solvent is another crucial parameter that was determined, because it influences the efficiency of the analyte extraction and the preconcentration factor. An ideal extraction solvent volume should be enough to collect the analyte of interest without diluting it further after extraction. Here, 0.50, 0.60, and 0.75 mL volumes were injected into equivalent aqueous standards. It was observed that by increasing the DES volume, the settled upper phase increased and the absorbance values decreased. The optimum value was chosen to be 0.50 mL because of its high absorbance value and regular phase formation. DES volumes below 0.50 mL did not produce separate phases after addition of THF to the solution. The mixing type and period of time after injection of the DES into the aqueous solution were optimized to enhance homogenous mixing and mass transfer of the analyte. Mechanical shaking, ultrasonication, vortexing, manual shaking, and no mixing were performed, and vortexing was selected as being optimum. Periods of 5.0, 10, 15, 30, and 60 seconds were tried, and the highest extraction output was recorded for 15 seconds of vortexing, which was employed in subsequent extraction processes.

Effect of THF Volume

After injection of the DES into the aqueous solution, THF was utilized as an aprotic solvent to separate the DES from the aqueous phase. The THF acts as an emulsifier agent which facilitates the formation of insoluble aggregates of the DES and subsequent suspension over the aqueous solution. The effect of THF amount was investigated by testing voulumes of 0.50, 1.0, 1.5, and 2.0 mL. No phase formation was observed for 0.50 mL of THF. The optimum volume was recorded as 1.0 mL (Figure 3) and was used for further experiments. Mixing by vortex was used to expedite the emulsifying process, and the optimum time was studied at 5.0, 10, 15, 30 and 60 seconds. The highest absorbance signal was obtained within 15 seconds.

Analytical Performance of DES-LPME-SQT-FAAS Method

All optimum extraction and instrumental conditions obtained in this study are presented in Table II and were used to determine the analytical performance of the different systems studied. The detection limit (LOD) and the quantification limit (LOQ) were calculated using the equations 3 s/m and 10 s/m, respectively, where s is the standard deviation of six replicate measurements (lowest concentration) and m is the slope of the calibration plot. The LOD and LOQ values calculated for the optimum method (DES-LPME-SQT-FAAS) were 3.8 and 12.6 μg L^{-1}, respectively. Relative to conventional FAAS, the optimum method recorded about 60-fold enhancement in detection power.

Table III summarizes the figures of merit obtained in this study and a comparison to other preconcentration methods for the determination of nickel reported in the literature is also given. The calibration plots of the different systems were linear (>0.9994) over broad concentration ranges, and the low percent relative standard deviation (%RSD) values proved the method's precision.

Table II
Optimized Parameters of DES-LPME-SQT-FAAS

Parameters	Value
*pH of buffer solution (volume)	pH 7.0 (0.50 mL)
*Ligand concentration (volume)	0.50% (w/v) (1.0 mL)
*Complexing period	15 s (Mechanical shaking)
DES type, molar ratio and volume	ChCl:Ph (1:2) (0.50 mL)
THF volume	1.0 mL
Mixing type (period)	Vortex-assisted (15 s)
SQT height	1.0 mm
*Sample flow rate	7.44 mL min^{-1}
Acetylene flow rate	40 L h^{-1}

*Parameters obtained from Yolcu et al. (18).

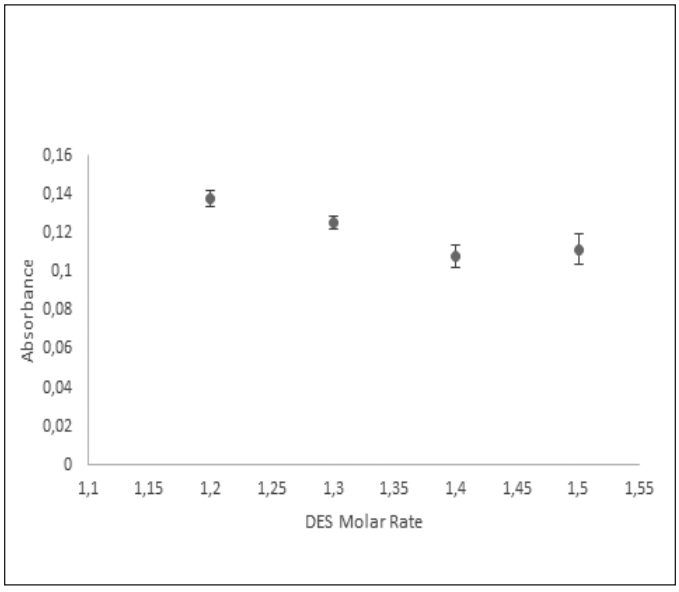

Fig. 2. Effect of DES molar ratio on the absorbance of nickel (n=3 error bars). Conditions: 8.0 mL of 0.25 mg L^{-1} Ni standard, 0.50 mL pH 7.0 buffer solution, 1.5 mL of 0.50% (w/v) ligand solution, 0.60 mL DES, 1.0 mL THF.

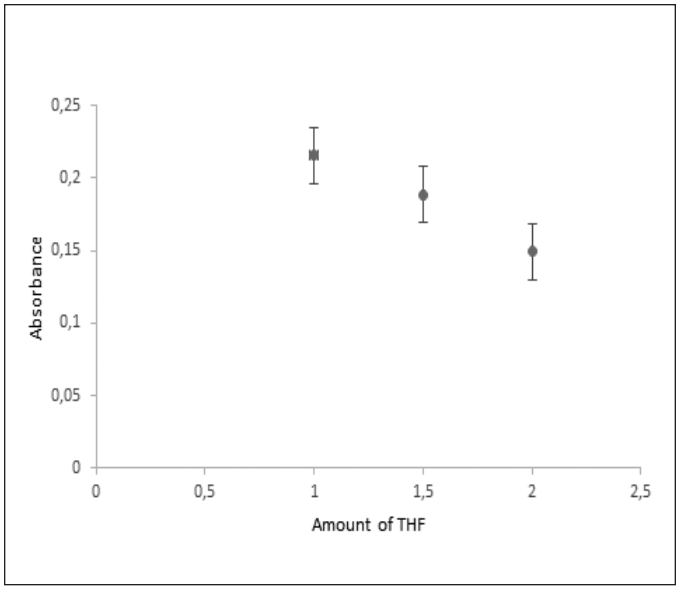

Fig. 3. Effect of THF volume on the absorbance of nickel (n=3 error bars). Conditions: 8.0 mL of 0.25 mg L^{-1} Ni standard, 0.50 mL pH 7 buffer solution, 1.0 mL of 0.50% (w/v) ligand solution, 0.60 mL DES (1:2; ChCl:PhOl).

Table III
Analytical Performance of Proposed Method and Comparison to Other Preconcentration Methods for the Determination of Nickel

	LOD ($\mu g\ L^{-1}$)	LOQ ($\mu g\ L^{-1}$)	Range ($\mu g\ L^{-1}$)	RSD (%)	R^2
FAAS	227.2	757.4	500-7500	4.9	0.9997
SQT-FAAS	70.4	235.4	200-5000	6.8	0.9998
DES-FAAS	7.5	25.1	25-500	4.9	0.9995
DES-SQT-FAAS	3.8	12.6	10-150	3.1	0.9996
CPE/UV–VIS SPECTROMETRY (20)	5	-	30-1000	1.3	0.9982
CPE/ICP-OES (21)	6.3	-	50-2500	2.6	
ETAAS (22)	1.7	5.6	-	-	-
DES-FAAS (23)	7.5	24.8	10-50	-	0.992
HR-CS SS-GF AAS (24)	12	37	-	0.6-4.9	0.995
EIEB-GFAAS (25)	3.5	11.5	-	9.6	-

Recovery Study

Spinach samples were purchased from a local market in Istanbul, Turkey, then cleaned and dissolved in a microwave digester. The resulting acidic solution was neutralized with sodium hydroxide. A blank analysis of the digested sample was performed to determine its nickel content but no analytical signal was determined for all three replicates. Spiked recovery tests were therefore performed to validate the method's suitability to real samples and the accuracy of nickel quantification. The digested sample solution was spiked at 60 and 100 ng mL^{-1} and extracted under the optimum DES conditions for SQT-FAAS measurements. A calibration plot of the aqueous standard solutions was used to calculate the percent recoveries found at 104.4 ± 7.7 and 99.4 ± 8.0% for 60 and 100 ng mL^{-1}, respectively. These results confirm the high accuracy and suitability of the developed method for nickel extraction and its determination in a spinach matrix.

CONCLUSION

A green, sensitive, efficient, and simple analytical method is proposed with liquid phase microextraction using a deep eutectic solvent (DES) for the preconcentration of nickel from spinach samples and determination by slotted quartz tube-flame atomic absorption spectrometry (DES-LPME-SQT-FAAS). Choline chloride was utilized in synthesizing DES with phenol due to its non-toxic and economically friendly nature. The slotted quartz tube enhanced the detection power of the FAAS system by approximately 2-fold, and in combination with the DES method provided a 60-fold enrichment. Under the optimum conditions, the analytical performance of the different systems was studied and the optimum values of the proposed method were calculated as 3.8 and 12.6 $\mu g\ L^{-1}$, respectively. To check the validity of the method, recovery studies were performed for the spinach samples, and the recovery results were satisfactory and validated the applicability to the spinach matrix.

Conflicts of interest: None.

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