ULTRASOUND-ASSISTED DISPERSIVE MICROSOLID-PHASE EXTRACTION FOR PRECONCENTRATION OF TRACE COBALT AND NICKEL IN ENVIRONMENTAL SAMPLES PRIOR TO THEIR DETERMINATION BY FLAME ATOMIC ABSORPTION SPECTROMETRY**

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A new, green, simple, and validated ultrasound-assisted dispersive microsolid-phase extraction method applying unprecedented adsorbent-modified multiwalled carbon nanotubes was achieved for preconcentration and separation of trace cobalt (Co(II)) and nickel (Ni(II)) ions in diverse ecological samples before determination by flame atomic absorption spectrometry. The suggested approach uses a novel chelating agent named 3-(2,4-dihydroxyphen-1-ylazo)-1,2,4-triazole, which is chelated with Co(II) or Ni(II) ions as efficient and selective sorbent at pH 8.0. The impact of many parameters has been studied and optimized. Under ideal conditions, the calibration curves were linear within 1.0–200 and 2.0–300 μg/L ranges, with limits of detection equaling 0.30 and 0.60 μg/L for Co(II) and Ni(II) ions, respectively. The preconcentration factor attained 200, while the highest sorption capacities of Co(II) and Ni(II) are around 300 and 380 mg/g, respectively. The relative standard deviation (%RSD) regarding repeatability for Co(II) and Ni(II) upon calculation was 1.30 and 1.70% for intraday, and 1.750 and 1.95% for interday. To ensure the correctness of the suggested preconcentration approach, certified reference materials (SRM 1570A spinach leaves and TMDA-52.3 enriched water) were employed. The proposed approach was applied to determine the concentration of Co(II) and Ni(II) ions in a range of genuine water, juice, and food samples, and the findings were excellent.

Keywords: *ultrasound-assisted dispersive microsolid-phase extraction, multiwalled carbon nanotubes, cobalt, nickel, environmental samples, flame atomic absorption spectrometry.*

ИСПОЛЬЗОВАНИЕ УЛЬТРАЗВУКОВОЙ ДИСПЕРСИОННОЙ МИКРОТВЕРДОФАЗНОЙ ЭКСТРАКЦИИ ДЛЯ КОНЦЕНТРИРОВАНИЯ СЛЕДОВ КОБАЛЬТА И НИКЕЛЯ И ИХ ПРЕЦИЗИОННОГО ОПРЕДЕЛЕНИЯ В ОБРАЗЦАХ ОКРУЖАЮЩЕЙ СРЕДЫ С ПОМОЩЬЮ ПЛАМЕННОЙ АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОМЕТРИИ

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Разработан простой и экологичный подход к ультразвуковой дисперсионной микротвердофазной экстракции с использованием новых модифицированных адсорбентом многостенных углеродных нанотрубок (MWCNTs) для разделения и предварительной концентрации ионов кобальта Co(II) и никеля Ni(II) в различных образцах окружающей среды перед определением методом пламенной атомно-абсорбционной спектрометрии. Предлагаемый метод основан на модификации MWCNTs

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комплексообразователем 3-(2,4-дигидроксифен-1-илазо)-1,2,4-триазолом, который образует комплекс с ионами Co(II) или Ni(II) в качестве селективного и эффективного сорбента при pH 8.0. Исследовано и оптимизировано влияние различных параметров. Калибровочные кривые линейные в пределах 1.0–200 и 2.0–300 мкг/л; пределы обнаружения при оптимальных условиях 0.30 и 0.60 мкг/л для ионов Co(II) и Ni(II). Коэффициент предварительной концентрации 200. Максимальная сорбционная способность Co(II) и Ni(II) ~300 и 380 мг/г. Показатели извлечения анализируемых веществ 96.0—102 %. Относительное стандартное отклонение (RSD%) для внутрисуточной и межсуточной повторяемостей 1.30, 1.70 % и 1.750, 1.95% для Co(II) и Ni(II) соответственно. Сертифицированные справочные материалы (листья шпината SRM 1570A и обогащенная вода TMDA-52.3) использованы для проверки точности предлагаемого протокола предварительной концентрации. Метод успешно применен для определения содержания ионов Co(II) и Ni(II) в образцах воды, соков и пищевых продуктов.

Ключевые слова: *ультразвуковая дисперсионная микротвердофазная экстракция, многостенные углеродные нанотрубки, кобальт, никель, образцы окружающей среды, пламенная атомно-абсорбционная спектрометрия.*

Introduction. It is well known that heavy metals are a major source of pollution that comes into the atmosphere from both natural and artificial origins [1, 2]. Toxic quantities of trace metals build in numerous organs, particularly aquatic tissues, posing major health hazards such as vomiting, cancer, liver damage, and renal failure. While some metals are necessary for human health and are essential components of enzymes and other vital proteins engaged in crucial metabolic processes in small concentrations, they can be hazardous when they surpass the limit values [3]. Nickel (Ni(II)) is employed as a catalyst in the hydrogenation process. Cobalt (Co(II)) is an element that people, plants, and animals all require. Both metals have the potential to be hazardous and poisonous [4–6]. As a result, the determination of both Co(II) and Ni(II) in various environmental matrices is critical, and chemical researchers, as well as environmental and food analysis groups, are interested in doing so. Inductively coupled plasma mass spectrometry (ICP-MS) [7], flame atomic absorption spectrometry (FAAS) [8, 9], and inductively coupled plasma optical emission spectrometry (ICP-OES) [10–12] have all been utilized to measure Co(II) and Ni(II) concentrations directly at trace levels in various samples.

Despite recent advances in instrumental research, direct identification of trace elements in various matrices appears to be problematic due to the lack of specificity and selectivity in the methodology used. Enrichment and separation techniques are required to analyze Ni(II) and Co(II) at trace levels due to low metal concentrations and matrix interferences in actual samples.

Several enrichment procedures involving various analytical techniques, such as membrane filtration [13, 14], coprecipitation [15–21], solid-phase extraction [22–29], cloud point extraction [30–35], and liquid–liquid microextraction [36–41], have been developed for the determination of Co(II) and Ni(II).

Dispersive microsolid-phase extraction (DMSPE) is the most important and widely used process for the separation and preconcentration of trace amounts of different metal ions in environmental samples with complex matrices due to its notable advantages such as high sensitivity, simplicity, extraction recovery, reusability of the adsorbent, economy, and short-term extraction. The adsorbent employed in DMSPE is crucial for achieving larger enrichment factors and superior recovery values, as well as enhancing the method's precision and accuracy [42–44].

Through the use of ultrasonic waves in DMSPE, new improvements have been made to obtain rapid extraction/adsorption of analytes in a relatively shorter period. In reality, the sonication phenomenon is increasingly being used to assist the extraction/adsorption of analytes of interest. Because it adheres to green chemistry principles, the DMSPE method for heavy metal separation and enrichment has recently gained a lot of attention [45].

The use of multiwalled carbon nanotubes (MWCNTs) as efficient SPE sorbents to preconcentrate small quantities of metal ions is a rather significant area of environmental analytical chemistry search [46]. MWCNTs have been utilized in DMSPE and/or SPE [47–49]; however, they are difficult to diffuse and insoluble in solvents due to strong van der Waals interactions that impede metal ion sorption. MWCNT surfaces can be changed to improve adsorption capability and usefulness, as well as dispersibility, by loading them with a range of ligands [50–56]. The elution of the analytes and the selection of the eluting solvent are the final steps in DMSPE to obtain a high enrichment factor and recovery of adsorbed metal ions on MWCNTs.

Oxidized MWCNTs (ox-MWCNTs) were used as a sorbent for the separation and preconcentration of trace levels of Co(II) and Ni(II) with the synthesized 3-(2,4-dihydroxyphen-1-ylazo)-1,2,4-triazole (DHPAT), which was applied as a complexing agent impregnated on their surface with the help of ultrasound in different environmental samples before FAAS. The suggested UA-DMSPE method, in contrast to a typical SPE process, encourages direct interaction between MWCNTs and metal chelates and minimizes sample preparation time. The MWCNTs also have a high dispersibility, which enhances the contact area between the MWCNTs and the sample. The impact of many analytical factors was studied and successfully optimized. The investigated method yielded satisfactory results in the precise and accurate measurement of trace levels of Co(II) and Ni(II) ion contents in several real-world samples.

Experimental. *Apparatus.* The pH values of buffer-used solutions were determined by applying an AD1000 pH meter fitted with a glass electrode (Adwa Instruments Kft., Szeged, Hungary). A Milestones Ethos D closed vessel microwave system (Milestone Inc., Italy) was used in the digestion of food samples. Before being rinsed and washed with bidistilled water, laboratory glassware was soaked overnight in a (5.0% v/v) HNO_3 solution. Polypropylene bottles were used to hold samples before the investigation. An Agilent (55B AA) FAAS (Agilent Technologies Inc., Santa Clara, USA) with a 10-cm burner for air (pressure 350 kPa, flow rate 11–20 L/min)-acetylene (pressure 75 kPa, flow rate 1.5–10 L/min) flame and hollow cathode lamps of cobalt (240.7 nm) and nickel (231.1 nm) were used to determine analyte concentrations in real samples and reference solutions. A Milli-Q system was used to collect deionized/bidistilled water (Millipore, USA; Millipore Australia Pty. Ltd., North Ryde, Australia), also used were a centrifuge (Isolab, GmbH, Germany) and a donated ultrasonic water bath (LabGear, Australia). Deionized/bidistilled water was obtained using Milli-Q (Millipore, USA).

Chemicals and reagents. At –5.0 to 0°C, the diazonium salt of 3-amino-1H-1,2,4-triazole was combined with 1,3-dihydroxybenzene to make the DHPAT reagent. The particles were filtered, washed several times with bidistilled water, refined by recrystallization from hot ethanol to provide the pure azo ligand, and then dried in a desiccator over anhydrous calcium chloride [57, 58]. A DHPAT stock solution (1.0×10^{-3} mol/L) was made by dissolving an adequately weighed amount (0.032 g) of purified azo (DHPAT) in methanol in a 100-mL flask. The pH of the solutions was adjusted using buffer solutions. Acetate buffer solution CH_3COONa/CH_3COOH) with pH values from 3.0 to 5.0 was produced by mixing sufficient amounts of acetic acid (2.0 mol/L) and sodium acetate solution (2.0 mol/L). Phosphate buffer solutions (NaH_2PO_4/Na_2HPO_4) with pH values of 6.0 and 7.0 were obtained by mixing sufficient amounts of Na_2HPO_4 (1.0 mol/L) and NaH_2PO_4 (1.0 mol/L). Sodium tetraborate and boric acid were used in the preparation of borate buffer solutions covering pH values of 8.0–10 where HCl and NaOH are used in adjusting the pH values [59]. MWCNTs (Sigma-Aldrich, USA) with a purity of > 95% were used (length 10–30 μm, diameter 20–30 nm, surface area 300 m^2/g, and density 2.1 g/mL). Merck (Darmstadt, Germany) and Sigma Aldrich (St. Louis, MO, USA) provided high-quality reagents and chemicals. HCl (37%, v/v), HNO_3 (65%, v/v), and NH_3 aq. (25%, v/v) were applied and a PVDF membrane Millex® syringe filter (diameter 33 mm, pore size 0.45 μm, and γ-irradiated sterility) was used. To prepare standard stock solutions of Ni(II) and Co(II) ions (1000 mg/L), high purity $Ni(NO_3)_2{\cdot}6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ (Fluka Chemie AG, Basel, Switzerland) were dissolved in HNO_3 (1.0 mol/L). The calibration operations were carried out by diluting the stock standard solutions with HNO3 (1.0 mol/L). After suitable dilution in bidistilled water, interference study solutions of various cations and anions were produced from high-quality inorganic salts (Sigma-Aldrich, USA). Analyzing certified reference material spinach leaves (SRM 1570a) from the National Institute of Standards and Technology (Gaithersburg, MD, USA) and fortified water TMDA 52.3 proved the method's accuracy (National Water Research Institute, Environment Canada, Burlington, Canada).

Preparation of oxidized multiwalled carbon nanotubes (ox-MWCNTs). Before use, MWCNTs were oxidized with concentrated HNO_3 (65% v/v) to create binding sites on their surface. MWCNTs (2.0 g) were suspended and dispersed in 100 mL of concentrated HNO_3 (65% v/v) and then refluxed for 6.0 h at 100°C. In the end, the washing and filtration processes of the mixture proceeded with deionized water, and the pH of the filtrate was corrected to 7.0. In an oven, the filtered material was dried at 60°C. To make a suspension of ox-MWCNTs, deionized water was employed (5.0 mg/mL). Prior to use, the ox-MWCNT suspension was sonicated in an ultrasonic bath for 30 min to obtain a homogenous dispersion.

UA-DMSPE preconcentration procedure. A DHPAT (1.0×10^{-3} mol/L) solution (2.0 mL) and an ox-MWCNT suspension (1.5 mg/mL) were added to 100 mL of the studied solutions containing Co(II) and Ni(II). Using borate buffer solution, the pH was then increased to 8.0. The mixture was immersed in an ultrasonic bath for approximately 5.0 min at room temperature to increase analyte adsorption onto the sorbent

(50 kHz, 100 W). At a rate of 2.0 mL/min, the sample was then run through a syringe filter. At a 2.0 mL/min flow rate, the adsorbed Ni(II) and Co(II) ions were eluted with HNO_3 solution (2.0 mL of 1.0 mol/L). The concentrations of Co(II) and Ni(II) ions in the final eluent solution were determined using FAAS.

Application to real environmental samples. *Water and fruit juice samples.* Before acidification with (1.0% v/v) HNO_3, well water (Zagazig, Egypt), samples of tap, mineral and seawater (Red Sea), and fruit juice (apple, grape, orange, and peach) were purchased from the local market in Zagazig, Egypt, stored in polyethylene bottles and filtered through a cellulose membrane filter (Millipore; 0.45-μm pore size). The pH of the samples was raised to 8.0 using a buffer solution. The water samples were then treated to the aforementioned UA-DMSPE technique. Using the suggested approach, the concentrations of analyte ions in the final solution of water samples and CRMs (fortified water TMDA 52.3) were preconcentrated and measured applying FAAS.

Food samples. Certified reference materials – SRM 1570A spinach leaves (0.25 g) – and 1.0 g of food samples (green tea, black tea, cabbage, mint, potato, parsley, spinach, hazelnut, and tomato) were obtained from a supermarket in Zagazig, Egypt, and were dried in an oven at 90°C until a constant weight was reached. The samples were microwave digested with 10 mL of HNO_3 (65% v/v) and 3.0 mL of H_2O_2 (30% v/v) and evaporated to near dryness using the same method. The samples were combined with 10-mL deionized water after evaporation. The solution was then filtered on filter paper before being diluted to 50 mL with deionized water. All of the samples were kept in polyethylene bottles and blanks were created in the same way that the sample was [60]. The aforementioned preconcentration technique was applied to the samples. The analytes in the final solution were determined using FAAS.

Results and discussion. Important parameters were evaluated using the "one-factor-at-a-time" approach to investigate the optimum experimental conditions of the proposed preconcentration method that affect extraction efficiency and achieve high efficiency and recovery of both Co(II) and Ni(II) ions, and are discussed in detail in the following sections.

Effect of pH. The pH is a critical factor that impacts the analyte recovery levels when utilizing the proposed approach. Using buffer solutions, the pH value was investigated in a pH range of 3.0–10. Hydrophobic DHPAT complexes with Co(II) and Ni(II) ions were generated and adsorbed on ox-MWCNTs at pH 3.0–10. At pH 3.0–6.0, the adsorption of Co(II) or Ni(II)–DHPAT complexes increases fast, as shown in Fig. 1, and quantitative recoveries (>95%) were obtained at pH 7.0–9.0. At higher pH values, metal hydroxides developed, resulting in a reduction in recoverable quantities. As a result, a borate buffer solution with a pH of 8.0 was chosen as the best pH in all following studies.

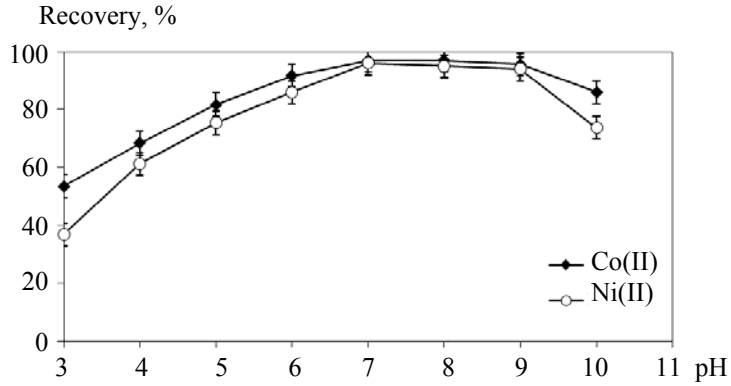

Fig. 1. Adsorption of the Co(II)–DHPAT and Ni(II)–DHPAT complexes on ox-MWCNTs (N = 3.0) as a function of pH.

Effect of sorbent quantity. To discover the optimal amount of sorbent required for the preconcentration of Co(II) and Ni(II) ions, the amount of ox-MWCNTs added was varied from 0.5 to 2.0 mg. Quantitative adsorption was impossible at 1.5 mg sorbent mass. The effective and quantitative adsorption of metal ions was discovered in the range of 1.25–2.0 mg ox-MWCNTs (Fig. 2). As a result, 1.50 mg of ox-MWCNTs was chosen as the best mass for future testing.

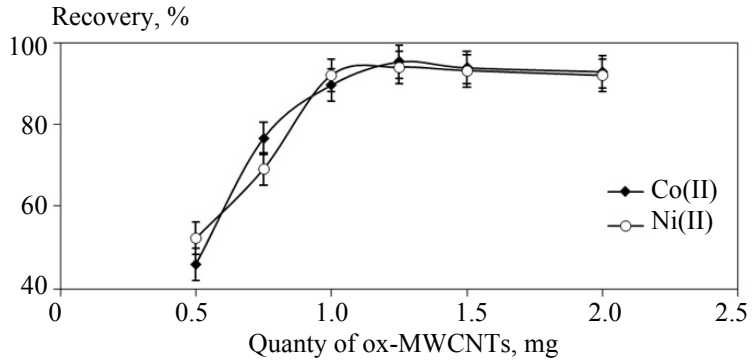

Fig. 2. Influence of ox-MWCNT quantity on Ni(II)–DHPAT and Co(II)–DHPAT chelates recovery (N = 3.0).

Effect of DHPAT amount. The influence on the performance of UA-DMSPE and quantitative recovery was examined by changing the volume (1.0×10^{-3} mol/L) of the DHPAT solution in the range of 0.5–5.0 mL. Higher Co(II) and Ni(II) ion recoveries were achieved with a DHPAT volume of 2.0 mL, as shown in Fig. 3, and this amount was regarded as the most efficient and optimum in the following steps.

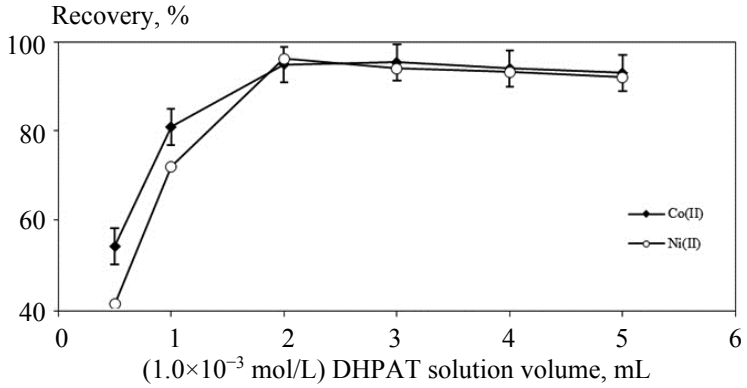

Fig. 3. Effect of DHPAT solution volume on Co(II) and Ni(II) recovery (N = 3.0).

The impact of sample volume. To achieve high analyte recoveries, different quantities of the sample in the range of 50–500 mL were analyzed using the proposed UA-DMSPE procedure. Quantitative recoveries were achieved up to a volume of 400 mL. When the sample volume was more than 400 mL, the recovery of Co(II) and Ni(II) was lower. As a result, the optimal sample volume was 400 mL. When the final eluent volume was 2.0 mL, a preconcentration factor of 200 was obtained (Fig. 4).

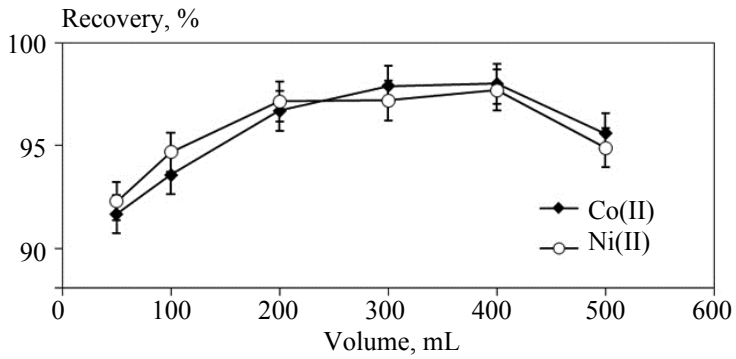

Fig. 4. Co(II) and Ni(II) recovery as a function of sample volume (N = 3.0).

Effect of ultrasonic time. The influence of ultrasonication time on the performance of analyte preconcentration was evaluated in the range of 1.0–20 min. As the sonication period was extended, the recoveries improved, with full analyte recovery happening at 5.0 min. After that, the ultrasonication time was set to 20 min. Consequently, 5.0 min of sonication was judged to be the best extraction time.

Effect of the eluent. To discover the most selective eluent for the quantitative desorption of Co(II) or Ni(II) ions from the solid phase, the effects of various types of eluents, such as HCl, HNO_3, and CH_3COOH, were examined. According to the data, HNO_3 had a quantitative recovery rate of >95%. The effect of HNO_3 concentration on enriched ion recoveries was examined using sonication at concentrations ranging from 0.2 to 4.0 mol/L. According to the observations reported in Fig. 5, the recovery improves before HNO_3 (1.0 mol/L) and remains consistent from 1.0 to 3.0 mol/L HNO_3. The results of testing several quantities of HNO_3 (1.0 mol/L) revealed that 2.0 mL was the best eluent volume for all following tests. The influence of the eluent solution flow rate on the desorption of Co(II) or Ni(II) ions from the sorbent surface was examined in the range of 0.5–5.0 mL/min. The ions Co(II) and Ni(II) were completely desorbed with precise and quantitative elution at a flow rate of 2.0 mL/min. A flow rate of 2.0 mL/min at room temperature, helped by ultrasound, was used for future studies, resulting in greater quantitative recoveries of the examined analytes.

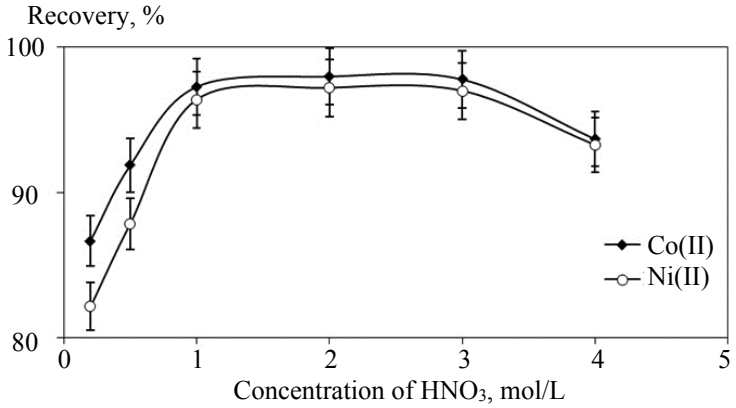

Fig. 5. Effect of HNO_3 concentration on the elution of Co(II) and Ni(II) (N = 3.0).

Effect of matrix ions. One of the primary issues in trace metal identification in varied real environmental samples is the influence of probable matrix ions on the viability of the proposed approach. To increase the selectivity of the proposed method, the effect of varying amounts of foreign ions on the preconcentration and determination of Co(II) and Ni(II) ions under ideal conditions was investigated. Table 1 summarizes the quantitative recoveries (95%) for the metal ions.

TABLE 1. Effect of Coexisting Ions on Co(II) and Ni(II) Ion Recovery (N = 3.0)

Ion	Added	Concentration, mg/L	Recovery, % (Mean ± SD)	
			Co(II)	Ni(II)
Na^+	NaCl	7000	97.0±1.0	96.0±2.0
K^+	KCl	7000	96.0±2.0	98.0±2.0
Ca^{2+}	$CaCl_2$	3000	98.0±3.0	100.0±3.0
Mg^{2+}	$MgCl_2$	3000	99.0±3.0	95.0±2.0
Al^{3+}	$Al(NO_3)_3 \cdot 9H_2O$	1000	95.0±2.0	98.0±2.0
Fe^{3+}	$FeCl_3$	1000	96.0±1.0	97.0±3.0
Mn^{2+}	$MnSO_4 \cdot H_2O$	500	95.0±2.0	100.0±2.0
Cr^{3+}	$Cr(NO_3)_3 \cdot 9H_2O$	400	95.0±1.0	96.0±2.0
Cd^{2+}	$Cd(NO_3)_2 \cdot 4H_2O$	300	96.0±2.0	95.0±3.0
Cu^{2+}	$Cu(NO_3)_2 \cdot 3H_2O$	300	98.0±3.0	97.0±1.0
Pb^{2+}	$Pb(NO_3)_2$	200	97.0±2.0	95.0±2.0
Zn^{2+}	$Zn(NO_3)_2 \cdot 6H_2O$	300	99.0±3.0	97.0±3.0

Adsorption capacity. Individual study of the sorption isotherm for Co(II) and Ni(II) ions was used to evaluate the sorption behavior of the developed UA-DMSPE at starting concentrations of 200–600 and 100–500 mg/L, respectively. The adsorption capacities for Co(II) and Ni(II) were determined using the equation $q_e = [(C_0 - Ce)V]/m$), where C_0 is the initial concentration (mg/L), Ce is the equilibrium concentration (mg/L), V is the volume of metal ion solution, and m is the mass of ox-MWCNTs (g). For Co(II) and Ni(II), the adsorption capabilities were 300 and 380 mg/g, respectively.

Analytical figures of merit. Table 2 shows an acceptable linear relationship and regression equations for Co(II) and Ni(II) derived using the optimal experimental conditions stated previously. The IUPAC definitions of the limit of detection (LOD = 3σ/S) and limit of quantification (LOQ = 10σ/S), where σ is the standard deviation of ten blank measurements and S is the calibration curve slope [61]. The suggested UA-DMSPE method's LODs and LOQs were determined and are displayed in Table 2. The suggested method's intraday and interday precisions were assessed using the relative standard deviation (%RSD), as shown in Table 2. The method was precise and accurate, as evidenced by the lower %RSD and excellent recovery values.

The suggested UA-DMSPE approach for preconcentration and detection of Co(II) and Ni(II) concomitants was validated using certified reference materials (CRMs; SRM 1570A spinach leaves and TMDA-52.3 enriched water). The recovered values were quite close to the certified values (Table 3). The suggested UA-DMSPE protocol for CRMs demonstrates that it is accurate, dependable, and interference free.

TABLE 2. Analytical Characteristics of the Proposed UA-DMSPE Method

Parameter	Co(II)	Ni(II)
Linear range, μg/L	1.0–200	2.0–300
Regression equations		
Slope	7.0×10^{-4}	4.0×10^{-4}
Interference	7.0×10^{-4}	1.6×10^{-3}
Correlation coefficient, R^2	0.9998	0.9997
Limit of detection (LOD), μg/L	0.3	0.6
Limit of quantification (LOQ)	1.0	2.0
Preconcentration factor	200	200
Relative standard deviation, RSD% (Intraday, 150 μg/L, n = 6)	1.30	1.70
Relative standard deviation, RSD% (Interday, 150 μg/L, n = 6)	1.75	1.95

TABLE 3. Validation of the Proposed UA-DMSPE Procedure Using CRMs (N = 3.0)

Analyte	SRM 1570A spinach leaves			TMDA-52.3 fortified water		
	Certified value, μg/g	Found*, μg/g	Recovery, %	Certified value, μg/L	Found*, μg/L	Recovery, %
Co(II)	0.39±0.05	0.36±0.06	95.0	136	130	95.6
Ni(II)	2.14±0.10	2.07±0.08	96.70	274	263	96.0

* Mean ± SD.

Applications of the UA-DMSPE method. The current UA-DMSPE preconcentration procedure was used to separate, enrich, and determine Co(II) and Ni(II) in real-world samples such as mineral water, tap water, seawater, and well water, as well as apple, peach, orange, and grape juice and food (tomato, parsley, cabbage, mint, hazelnut, potato, spinach, and green and black tea). The method's dependability was assessed using the standard addition method, which involved spiking the samples with known amounts (100 and 200 μg/L) of metal ions. The percentage recoveries were quantifiable, ranging from 95.0 to 102%, with a %RSD of less than 3.0%. The results in Tables 4 and 5 show that the UA-DMSPE approach was effective in separating, enriching, and detecting Co(II) and Ni(II) ions at trace levels in genuine environmental samples. Table 6 shows a comparison of the UA-DMSPE described with several contemporary preconcentration methods. High preconcentration factor, low LOD, low RSD, and greater dependability (as a percentage of recovery) were the key advantages of the devised approach (PF). The approach has a high level of repeatability.

TABLE 4. Additional Recovery Studies for the Preconcentration of Co(II) and Ni(II) Ions from Water and Juice Samples (N = 3.0)

Samples	Added, μg/L	Co(II)			Ni(II)		
		Found [a]±SD, μg/L	Recovery [b], %	RSD%	Found [a]±SD, μg/L	Recovery [b], %	RSD%
Tap water	–	BDL[c]	–	–	BDL[c]	–	–
	100	95.0±0.65	95.0	0.68	96.0±1.25	96.0	1.30
	200	200.0±1.75	100	0.88	196.0±3.20	98.0	1.63
Mineral water	–	BDL[c]	–	–	BDL[c]	–	–
	100	97.0±0.80	97.0	0.82	95.50±1.10	97.0	1.05
	200	198.0±3.20	99.0	1.62	198.0±4.10	99.0	2.07
Well water	–	3.40±0.10	–	–	BDL[c]	–	–
	100	101.3±1.10	98.0	1.09	95.0±1.70	95.0	1.79
	200	195.3±3.50	96.0	1.79	196.0±3.0	98.0	1.53
Sea water	–	27.0±0.32	–	–	10.0±0.40	–	–
	100	126.0±1.40	99.0	1.11	106.0±2.0	96.0	2.25
	200	222.0±3.90	98.0	1.76	204.0±4.50	97.0	2.21
Grape juice	0.0	1.70±0.07	–	–	3.40±0.09	–	–
	100	97.60±1.36	96.0	1.39	101.3±0.95	98.0	0.94
	200	200.0±2.90	99.0	1.45	197.3±3.50	97.0	1.77
Peach juice	0.0	2.0±0.05	–	–	BDL[c]	–	–
	100	97.0±1.50	95.0	1.55	96.0±1.60	96.0	1.67
	200	194.0±3.70	96.0	1.91	198.0±4.20	99.0	2.12
Orange juice	0.0	BDL[c]	–	–	2.70±0.08	–	
	100	96.0±1.25	96.0	1.30	100.7±1.37	98.0	1.36
	200	200.0±3.68	100.0	1.84	193.0±3.90	95.0	2.02
Apple juice	0.0	2.40±0.04	–	–	BDL[c]	–	–
	100	99.30±1.20	97.0	1.21	95.0±1.30	95.0	1.37
	200	195.0±2.90	96.50	1.49	197.0±3.0	98.50	1.52

[a] Mean ± SD.
[b] Recovery% = [Observed value of analyte/expected value of analyte] × 100.
[c] BDL below detection limit.

TABLE 5. Additional Recovery Studies for the Preconcentration of Co(II) and Ni(II) Ions from Food Samples (N = 3.0)

Samples	Added, μg/g	Co(II)			Ni(II)		
		Found [a] ± SD, μg/g	Recovery [b], %	RSD%	Found [a] ± SD, μg/g	Recovery [b], %	RSD%
Parsley	0	2.60±0.37	–	–	3.10±0.50	–	–
	100	98.50±1.10	96.0	1.12	98.0±1.60	95.0	1.57
	200	202.6±4.30	100.0	2.12	199.0±3.70	98.0	1.86
Mint	0	3.60±0.64	–	–	2.60±0.52	–	–
	100	98.40±1.60	95.0	1.63	100.5±1.0	98.0	1.0
	200	200.0±3.80	98.0	1.90	196.5±4.30	97.0	2.19
Tomato	0	4.0±0.60	–	–	3.80±0.43	–	–
	100	100.9±1.50	97.0	1.49	98.60±0.85	95.0	0.86
	200	204.0±3.30	100	1.62	201.80±3.10	99.0	1.54
Cabbage	0	2.90±0.37	–	–	2.40±0.27	–	–
	100	98.80±1.20	96.0	1.21	101.4±2.0	99.0	1.97
	200	197.0±2.80	97.0	1.42	202.0±4.60	100.0	2.28

Continue Table 5

Samples	Added, μg/g	Co(II)			Ni(II)		
		Found [a] ± SD, μg/g	Recovery [b], %	RSD%	Found [a] ± SD, μg/g	Recovery [b], %	RSD%
Potato	0	2.0±0.21	–	–	2.30±0.30	–	–
	100	100.0±1.15	98.0	1.15	98.20±1.70	96.0	1.73
	200	194.0±3.0	96.0	1.55	196.2±3.50	97.0	1.78
Spinach	0	2.50±0.27	–	–	3.40±0.39	–	–
	100	101.5±1.40	99.0	1.38	98.20±0.92	95.0	0.94
	200	196.4±4.10	97.0	2.09	199.3±3.30	98.0	1.66
Hazelnut	0	2.30±0.31	–	–	BDL [c]	–	–
	100	98.20±1.80	96.0	1.83	97.0±1.30	97.0	1.34
	200	198.3±4.70	98.0	2.37	200.0±3.0	100	1.50
Black tea	0	4.60±0.57	–	–	5.70±0.64	–	–
	100	99.40±1.30	95.0	1.31	102.5±1.60	97.0	1.56
	200	198.5±5.30	97.0	2.67	197.5±3.80	96.0	1.92
Green tea	0	3.0±0.29	–	–	4.20±0.41	–	–
	100	101.0±1.90	98.0	1.88	99.0±1.50	95.0	1.52
	200	203.0±2.70	100	1.33	200.0±4.30	98.0	2.15

[a] Mean ± SD.
[b] Recovery % = [Observed value of analyte/Expected value of analyte] × 100.
[c] BDL below detection limit.

TABLE 6. Comparison of Analytical Features of the Proposed Method with Several Methods Reported for Separation and Preconcentration of Co(II) and Ni(II)

Analyte	Method	Reagent	Detection system	Linearity range	DL, μg/L	PF/EF	Samples	Reference
	Coprecipitation	QAN	FAAS	–	0.83 Co(II)	50	Food	[14]
Co(II) NI(II)	Coprecipitation	$Pr(OH)_3$	FAAS	– –	0.71 2.80	45	Environmental water	[15]
Co(II) NI(II)	Coprecipitation	IMOTPA	FAAS	– –	0.40 0.17	100	Food and water	[16]
Co(II) NI(II)	Coprecipitation	$Ho(OH)_3$	FAAS	– –	13.3 0.48	10 100	Food	[17]
Co(II) NI(II)	Coprecipitation	$Tm(OH)_3$	FAAS	– –	0.5 1.41	120	Food and environmental	[18]
Co(II) NI(II)	Coprecipitation	$Zr(OH)_4$	FAAS	– –	1.42 1.05	25	Natural water and food	[19]
Co(II) NI(II)	DLLME	ChCL/ 4-aminophenol	FAAS	0.5–50 0.8–50	0.22 0.30	24.0 24.2	Water and fruit juice	[20]
Co(II) NI(II)	IL-USE-AALLME	5-Br-PADAP	FAAS	3.0–570 7.0–667	3.0 7.0	21 158	Food and biological	[21]
Co(II) NI(II)	AA-HLLME	PAN	FAAS	8.0–500 10–450	2.7 3.6	333/360 333/340	Water	[22]
Co(II) NI(II)	UA-IPSE-DLLME	CR/DDMAC	FAAS	10–400 20–300	2.4 11.7	48 65	Vegetable and herb	[23]
Co(II) NI(II)	HLLME	8-HQ	FAAS	0.5–20 1.0–30	0.36 0.20	24 23.8	Water, juice, and soda	[24]
Co(II) NI(II)	DES-ME	ChCl/urea	FAAS	5.0–30 10–50	4.6 7.5	100	Oil	[25]
Co(II) NI(II)	UA-CPE	HNB/CTAB/ TX-114	FAAS	2.0–160 3.0–180	0.56 0.78	53.9 48.6	Milk-based samples	[26]

Continue Table 6

Co(II) NI(II)	CPE	BTANP	FAAS	5.0–100 5.0–150	1.4 1.0	100 100	Water and food samples	[27]
Co(II) NI(II)	CPE	1-nitroso-2-naphthol/SDS	SP	5–300 10–320	0.73 0.85	20.1	Water	[28]
Co(II) NI(II)	CPE	Na-DDTC/ TX-114	SP	20–210 20–440	8.0 9.2	– –	Natural and wastewater	[29]
Co(II) NI(II)	CPE	5-Br-PADAP/ TX-114	FAAS	10–100 10–10	2.4 1.7	25	Water	[30]
Co(II) NI(II)	CPE	MPKO/TX-114	FAAS	10–200 10–200	2.1 1.9	58 67	Biological, natural, and wastewater, soil and blood	[31]
Co(II) NI(II)	MF	Cellulose acetate/cochineal red	FAAS	– –	2.6 2.4	40 40	Water, hair, urine, and fish	[32]
Co(II) Ni(II)	MF	Cellulose acetate/5-Br-PADAP	FAAS	– –	8.9 19.5	15 15	Natural water and fertilizer	[33]
Co(II) Ni(II)	SPE	Amberlite XAD-4/ DMMDTC	SP	20–4000 10–1500	26.1 1.37	100 20	Water	[34]
Co(II) Ni(II)	SPE	Functionalized curdled milk N-acetic acid	FAAS	10–200 10–250	2.95 2.74	206 205	Food, water, and blood	[35]
Co(II) Ni(II)	SPE	ACC/TDADT	FAAS	– –	2.9 2.7	120	Water and fertilizer	[36]
Co(II) Ni(II)	SPE	Amberlite XAD-4/SAB	FAAS	– –	0.7 0.9	240	Water	[37]
Co(II) Ni(II)	SDSPE	PAN/$Zn(OH)_2$	FAAS	10–1000 10–1000	2.4 1.7	20	Water	[38]
Co(II) Ni(II)	SPE	ACC/EDTA	FAAS	– –	0.99 0.91	50	Fertilizer and water	[39]
Co(II) Ni(II)	SPE	Diaion SP-850/TAR	FAAS	– –	2.3 2.8	60	Water and food	[40]
Co(II) Ni(II)	SPE	MWNTs/*o*-cresolphthalein	FAAS	– –	5.31 5.68	40	Water	[41]
Co(II) Ni(II)	UA-DMSPE	MWNTs/ DHPAT	FAAS	1.0–200 2.0–300	0.3 0.6	200	Water, juice, and food	The present study

N o t e. DL detection limit; PF preconcentration factor; EF enrichment factor; FAAS flame atomic absorption spectrometry; QAN 2-[(E)-(8-hydroxy-2-methylquinolin-5-yl) diazenyl] benzoic acid; $Pr(OH)_3$ praseodymium hydroxide; IMOTPA 2-{4-[2-(1H-indol-3-yl)ethyl]-3-(4-methylbenzyl)-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl}-N'-(pyridin-2-yl methylidene) acetohydrazide; $Ho(OH)_3$ holmium hydroxide; $Tm(OH)_3$ thulium hydroxide; $Zr(OH)_4$ zirconium(IV) hydroxide; DLLME dispersive liquid–liquid microextraction; IL-USE-AALLME ionic liquid-based ultrasound-enhanced air-assisted liquid–liquid microextraction; 5-Br-PADAP 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol; AA-HLLME aeration-assisted homogeneous liquid–liquid microextraction; PAN 1-(2-pyridylazo) 2-naphthol; UA-IPSE-DLLME ultrasound-assisted ion pair-based surfactant-enhanced dispersive liquid–liquid microextraction; HLLME homogeneous liquid–liquid microextraction; 8-HQ 8-hydroxyquinoline; CR Congo Red; DDMAC didecyldimethylammonium chloride; DES-ME deep eutectic solvent microextraction; UA-CPE ultrasound-assisted cloud point extraction; ChCl choline chloride; HNB hydroxy naphthol blue; CTAB cetyltrimethylammonium bromide; TX-114 Triton X-114; CPE cloud point extraction; BTANP 2-(benzothiazolylazo)-4-nitrophenol; SDS sodium dodecyl sulfate; SP spectrophotometry; Na-DDTC sodium diethyldithiocarbamate; MPKO methyl-2-pyridyl ketone oxime; MF membrane filtration; SPE solid-phase extraction; DMMDTC 2.6-dimethyl morpholine dithiocarbamate; ACC activated carbon cloth; TDADT 1,3,4-thiadiazole-2,5-dithiol; SAB salicylaldehyde benzoyl hydrazone; SDSPE suspension dispersive solid-phase extraction; $Zn(OH)_2$ zinc hydroxide; EDTA ethylenediaminetetraacetic acid; TAR 4-(2-thiazolylazo)resorcinol; MWNTs multi-walled carbon nanotubes; UA-DMSPE ultrasonic-assisted dispersive microsolid phase extraction.

Conclusions. An environmentally friendly UA-DMSPE approach was developed and validated for the enrichment of Co(II) and Ni(II) ions in food, juice and real water samples with subsequent FAAS detection using modified ox-MWCNTs with DHPAT as a novel adsorbent. The suggested UA-DMSPE process extracted the examined analytes at trace levels from genuine environmental samples with excellent extraction efficiency, high sensitivity, cheap cost, low LODs, high enrichment factor, high tolerance, low RSD values <3.0%, and no substantial interference from coexisting ions. Furthermore, the approach established was effectively applied to verified reference materials.

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