Dispersive Micro-solid Phase Extraction with Fibrous $\text{TiO}_2@\text{g-C}_3\text{N}_4$ Nanocomposites Coupled with ICP-MS for the Determination of Cobalt and Nickel in Environmental and Biological Samples

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ABSTRACT: In this work, fibrous $\text{TiO}_2@\text{g-C}_3\text{N}_4$ nanocomposites (FTGCNCs) were used for dispersive micro-solid phase extraction of Co and Ni prior to their determination by inductively coupled plasma mass spectrometry. As a new adsorbent, the surface on FTGCNCs have rich functional groups such as $-\text{NH}_2$, $-\text{NH}-$ and $=\text{N}-$, which can selectively adsorb target ions. The adsorption behaviors of Co and Ni on FTGCNCs were investigated. The results indicated that the analytes were quantitatively retained on FTGCNCs in the pH range of 5.0–8.0 and eluted completely with 1.0 mL of $0.5 \text{ mol L}^{-1} \text{ HNO}_3$ solution. The main factors influencing the preconcentration and determination of the analytes were investigated in detail, including the pH of the sample solution, dosage of adsorbent, extraction/elution time, elution parameters and sample volumes. Under the optimum conditions, the detection limits of this method were 0.12 pg mL^{-1} and 1.34 pg mL^{-1} for Co and Ni, respectively. The relative standard deviations were 3.9% for Co and 4.8% for Ni ($n=9$, $c=1.0 \text{ ng mL}^{-1}$). This method was used for the determination of trace/ultra-trace Co and Ni in environmental water samples with satisfactory results. In order to verify this method, three certified reference materials of stream sediment, human hair and mussel were analyzed using the proposed method, and the determined results were in agreement with the certified values.

INTRODUCTION

It is well known that cobalt (Co) and nickel (Ni) are elements widely dispersed in the environment due to their various industrial applications. Unlike organic pollutants, the heavy metal ions such as Co(II) and Ni(II) have long half-lives and degrade slowly. Moreover, they easily accumulate in living organisms.^{1,2} Co is an essential trace element in human dietary intake, possessing anti-anemic properties and acting as the central atom of vitamin B_{12} , which is widely responsible for the production of red blood cells.³ Ni is an essential element for humans at trace levels. However, if ingested in excess amounts, Ni can cause dermatitis, pulmonary fibrosis degeneration, cardiovascular and renal diseases.⁴ It is

worth noting that at higher concentration levels, these two metals are recognized as potentially toxic.^{5,6} Therefore, it is crucial to determine trace/ultra-trace Co and Ni in environmental and biological samples to study problems with respect to environmental pollution and public health.

Various analytical techniques are used for the determination of metals in real samples, including atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), X-ray fluorescence spectrometry (XRF), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS).^{7–12} However, the direct

analysis of real samples by these techniques is generally restricted due to the extremely low concentrations of the analytes and complex matrix interferences. This is the reason why sample pretreatment methods are often necessary prior to analysis.¹³⁻¹⁵ Solid phase extraction (SPE) is a preferred technique due to its merits such as simple operation, higher enrichment factor, and the ability to combine with other detection techniques.¹⁶⁻¹⁹ However, this procedure suffers from certain shortcomings such as solvent loss, large secondary waste, and a long procedure.²⁰ In addition, a liquid sample is passed through a column containing an adsorbent in conventional SPE. A small amount of adsorbent, such as nanoparticles, can escape from the SPE column and cause high column pressure.

In order to solve the above problems, various simplified and miniaturized sample preparation techniques were developed for the preconcentration and separation of elements and their speciation.²¹⁻²⁵ Among them, dispersive micro-solid phase extraction (DMSPE) has received increased attention. In comparison with SPE, DMSPE can provide many advantages, such as reduced solvent consumption, less adsorbent usage, short extraction time, and high extraction efficiency.²⁶⁻³⁰ In DMSPE, an adsorbent material is a key factor for the improvement of selectivity and sensitivity of a method. Thus, the development of new adsorption materials has become a consolidated trend in DMSPE/SPE. As a new nanomaterial, graphitic carbon nitride (g-C₃N₄) has many attractive merits, ranging from N-rich functional groups and easy surface modification to excellent thermal and chemical stability.³¹ In recent years, g-C₃N₄ has been developed and employed for the separation and preconcentration of organic compounds and metal ions.^{31,32-35}

Although g-C₃N₄ exhibits great potential as a new sorbent, it has some problems from the DMSPE point of view. Pure g-C₃N₄ easily aggregates and results in a decrease of its specific surface area.³¹ The weak polarity of g-C₃N₄ causes its poor dispersion in water. Fortunately, these problems can be solved by the in-situ growth of g-C₃N₄ on the surface of TiO₂ nanofibers (TDNFs) to form fibrous TiO₂@g-C₃N₄ nanocomposites (FTGCNCs). In FTGCNCs, TDNFs provide hydrophilicity with the relative hydrophobic surface of g-C₃N₄ to enhance its dispersibility in polar media and affinity for metal ions.³⁶ Moreover, the formation of FTGCNCs greatly reduces the aggregation of g-C₃N₄, resulting in the increase of its specific surface area. Due to the high chemical stability, FTGCNCs can be used for the extraction/desorption of analytes using harsh acidic or basic media. These facts reveal that FTGCNCs may have great potential as an adsorbent. To the best of our knowledge, however, the application of FTGCNCs for DMSPE of trace elements and their speciation has received little attention so far.

This work aims to focus on the application of FTGCNCs as a new adsorbent in DMSPE for the preconcentration of trace Co and Ni before ICP-MS detection. The adsorption behaviors of the

Table 1. Operating Conditions for ICP-MS

Parameter	Value
Plasma power, kW	1.3
Plasma argon flow rate, L min ⁻¹	14
Auxiliary argon flow rate, L min ⁻¹	0.89
Nebulizer argon flow rate, L min ⁻¹	0.91
Sampler orifice (Ni), mm	1.1
Skimmer orifice (Ni), mm	0.7
Acquisition mode	Peak-jumping
Number of sweeps	100
Dwell time, ms	10
Acquisition time, s	40
Number of measurements per peak	3
Isotope	⁵⁹ Co, ⁶⁰ Ni and ⁶⁹ Ga

analytes on FTGCNCs were studied. The important parameters affecting preconcentration, separation and determination of the analytes were examined systematically. On the basis of the obtained results, a novel method of DMSPE with FTGCNCs coupled to ICP-MS was developed for the determination of trace/ultra-trace Co and Ni in environmental and biological samples.

EXPERIMENTAL

Instrumentation. An X-series ICP-MS system (Thermo Fisher Scientific, USA) was used for the determination of analytes. The operating parameters for ICP-MS are given in Table 1. A pH meter with a combined electrode was used to control the pH values of the solutions (Thermo Fisher Scientific, USA). The mixture was sonicated using a KQ-100E ultrasonic bath (Kunshan Ultrasonic Instrument Co., Ltd., Suzhou, P. R. China). A TG16-WS centrifuge (Hunan Xiangyi Centrifuge Instrument Co., Ltd., Changsha, P. R. China) was applied for phase separation. Sample digestion was carried out with an Ethos T microwave digestion device (Milestone, Italy). The surface morphology of FTGCNCs was examined by scanning electron microscopy (SEM), equipped with energy dispersive X-ray spectrometry (EDS; MAIA 3 LMH, TESCAN, Czech Republic). Infrared spectra were recorded on a Nicolet Instruments Research Series 5PC Fourier Transform Infrared (FT-IR) Spectrometer (Nicolet, USA).

Reagents and standard solutions. Stock solutions of Co, Ni and Ga (1.0 mg mL⁻¹) were obtained from the National Analysis Center of Iron & Steel (Beijing, P. R. China). Working solutions were prepared by stepwise dilution of the above stock solutions just before use. Poly (vinyl pyrrolidone) (PVP, Mw=1300 000) was supplied by Sigma-Aldrich Company (USA). Other chemicals used in this study were of analytical grade or better and obtained from Sinopharm Chemical Reagent Company (Shanghai, P. R. China). Certified reference materials were obtained from the Institute of Geophysical and Geochemical Prospecting (Langfang, Hebei, P. R. China). High purity deionized water was obtained with a Milli-Q A10 system (Millipore Corporation, USA) and used throughout this work. All glassware was kept permanently full of 2.0 mol L⁻¹ HNO₃ solution when not in use.

Synthesis of adsorbent. FTGCNCs were fabricated by in-situ evaporation and calcination of melamine on the surface of TiO₂ nanofibers (TDNFs), respectively. Briefly, a certain amount of TDNFs was mixed with 50 mL H₂O in a three-necked flask with a stirrer. The resulting mixture was sonicated at 200 W for 5 min to break the TDNFs. Then, 3.0 g of melamine was added into the above suspension solution with vigorous stirring at 95 °C for 10 min. The slurry was evaporated at 100 °C to crystallize out the melamine on the surface of the TDNFs. The white mixtures of melamine and TDNFs were placed into the crucible with a cover and calcined in a muffle furnace at 520 °C for 2 h at 5 °C min⁻¹. Finally, the FTGCNCs were achieved. For comparison, the pure g-C₃N₄ was prepared by the same procedure without addition of TDNFs. In addition, the TDNFs were synthesized using the same procedure reported in the literature.³⁷

Dispersive micro-solid phase extraction. Aliquots of 20 mL sample solutions containing the analytes were transferred to a 50 mL centrifuge tube and adjusted to pH 6.0 with 0.1 mol L⁻¹ NH₃·H₂O or 0.1 mol L⁻¹ HNO₃. Then, 15 mg of FTGCNCs was added to the test tube. The mixture of sorbent and sample was sonicated with a vortex for 3.0 min to facilitate the dispersion of the FTGCNCs in the sample solution. After complete extraction, the adsorbent was separated from the solution by a centrifugation method for 4.0 min at 4500 rpm. The aqueous phase was discarded, and the FTGCNCs remained in the test tube. To elute the analytes, 1.0 mL of 0.5 mol L⁻¹ HNO₃ solution was added to the test tube containing the FTGCNCs, and the test tube was ultra-sonicated for 2.0 min. The sorbent was separated again using the same method as mentioned above. Finally, the eluent was taken out with a pipette for ICP-MS detection. The blanks, samples and standards were spiked with 1.0 ng mL⁻¹ of ⁶⁹Ga as the internal standard.

Sample preparation. A 0.1000 g of stream sediment was accurately weighed into PTFE digestion vessels. Then, 4.0 mL of HNO₃ (65–68%, w/w), 2.0 mL of HCl (36–38%, w/w) and 2.0 mL of HF (40%, w/w) were immediately added to the vessels. The samples were left standing overnight for pre-digestion at room temperature. Then, the vessels were tightly capped and placed into the digestion instrument. The samples were digested at 180 °C (ramp, 10 min; hold, 15 min) at 1.0 kW power. After cooling, the solution was transferred into a Teflon beaker, then heated to near dryness. The residues were dissolved with 0.1 mol L⁻¹ HNO₃ solution and diluted to a desired volume.

The digestion steps used for human hair or mussel (0.1000 g) were the same as those of the stream sediment, except for 4.0 mL of HNO₃ (65–68%, w/w) and 2.0 mL of H₂O₂ (30%, w/w) as the digestion reagents. The water samples (Wuhan, P. R. China) were immediately filtered through a 0.45 µm membrane filter, then kept at 4 °C before use. The blank was prepared in an identical manner without the addition of samples.

RESULTS AND DISCUSSION

Characterization of material. The morphologies of g-C₃N₄, TDNFs and FTGCNCs were characterized by SEM. It can be seen from Fig. 1A that g-C₃N₄ seriously aggregates with a particle size of about 3 µm. Fig. 1B shows that the TDNFs possess the mean diameter of 185 nm, and the rough surface with many pores. It is worth noting that with an increase in dosage of the TDNFs, the aggregation of g-C₃N₄ is gradually slight, and almost disappears when the content of the TDNFs reaches 40.36% (Fig. 1C). In the EDS spectrum (Fig. 1D), only Ti, O, C and N were detected from the sample pretreatment, but Au was not. Fig. 1E vividly shows

Fig. 1 SEM images of g-C₃N₄ (A), TiO₂ nanofibers (B), fibrous TiO₂@g-C₃N₄ nanocomposites (C), EDS spectrum of fibrous TiO₂@g-C₃N₄ nanocomposites (D), schematic presentation of fibrous TiO₂@g-C₃N₄ nanocomposites (E), and FTIR spectra (F) of g-C₃N₄ (a), fibrous TiO₂@g-C₃N₄ nanocomposites (b), and TiO₂ nanofibers (c).

the schematic presentation of the FTGCNCs. This phenomenon can be explained by the following facts. The melamine in the solution is crystallized out and deposited on the surface of the porous TDNFs in the evaporation process. At the same time, g-C₃N₄ is formed on the surface of the TDNFs during calcination. Fig. 1F indicates the FTIR spectra of g-C₃N₄, TDNFs and FTGCNCs. It can be seen from Fig. 1F(a) that the characteristic peaks for pure g-C₃N₄ are located at 3000-3300, 1200-1600 and 810 cm⁻¹. The adsorption band at 3000-3300 cm⁻¹ can be related to the stretching vibrations of N-H. The regions of 1200-1600 cm⁻¹ with feature peaks at 1241, 1319, 1403, 1465 and 1573 cm⁻¹ are assigned to the stretching vibration of the C-N heterocycles. The absorption peak at 810 cm⁻¹ arises from the breathing mode of the triazine units. In Fig. 1F(c), the adsorption band in the range of 400 to 800 cm⁻¹ corresponds to the Ti-O-Ti stretching vibration. Fig. 1F(b) demonstrates that all the feature peaks of both the g-C₃N₄ and the TDNFs are coexisting in the FTGCNCs. These facts further validate the formation of FTGCNCs in the calcination step.

Optimization of extraction conditions. Owing to its effect on the surface-active sites of the FTGCNCs, the pH values play a key role in DMSPE. Therefore, the effect of pH on the extraction of analytes was studied in the pH range of 1.0-8.0. It can be seen in Fig. 2A that the sorption percentages of the analytes on the FTGCNCs increased with an increase in pH value of the sample solution from 1.0 to 5.0, and the quantitative recoveries (>90%) of the analytes were obtained at pH 5.0-8.0. Finally, pH 6.0 was utilized for subsequent experiments.

The different dosage of adsorbent was investigated in the range of 5-30 mg per sample solution (20 mL). The results in Fig. 2B indicate that quantitative recoveries (>90%) of the analytes can be achieved using an adsorbent dosage of 10-30 mg. Thus, 15 mg adsorbent was used in this work.

During DMSPE, the mass transfer of the analytes between the sorbent and the aqueous phase takes place at the dispersive step. Therefore, the effect of sonication time was examined within the time range of 0.5 to 4.0 min. The results from Fig. 2C indicate that the recoveries of the analytes increased within the first 2.0 min, and then remained approximately constant after exceeding 2.0 min. Therefore, a sonication time of 3.0 min was used in the following experiments.

Selection of eluent parameters. Fig. 2A shows that H⁺ competes with Co²⁺ and Ni²⁺ for the binding sites on the FTGCNCs and results in very poor recoveries of the analytes (pH < 2.0). Thus, an acid medium can be considered to be an eluent. Moreover, HNO₃ is the most recommended solvent for ICP-MS analysis. For this reason, different concentrations of the HNO₃ solutions were used as the eluent to desorb the analytes on the FTGCNCs. The results showed that the analytes can be eluted quantitatively with 0.5 mol L⁻¹ HNO₃. The effect of eluent volume on the recovery of the analytes was also tested in the experiments. The results showed that 1.0 mL of 0.5 mol L⁻¹ HNO₃ was sufficient to quantitatively

elute the analytes. Additionally, the elution time of the analytes was optimized by varying the time from 0.5 to 3.0 min. The results showed that the analytes were quantitatively eluted within 2.0 min. Finally, 1.0 mL of 0.5 mol L⁻¹ HNO₃ and an elution time of 2.0 min were employed in this work.

Effect of sample volume. The sample volume is a key parameter influencing the enrichment factor of an analytical method. In order to obtain a higher enrichment factor, the effect of sample volume on the recovery of the analytes was studied with sample volumes ranging from 10 mL to 150 mL and containing 5.0 ng of the analytes (Fig. 2D). The experimental results showed that the adsorption percentages of the analytes were quantitative when the sample volume was up to 100 mL, and then the recovery gradually decreased with a further increase of sample volume. Because the elution volume was 1.0 mL, an enrichment factor of 100 was achieved. Based on real need, the subsequent experiments were carried out using a 20 mL sample solution.

Effect of diverse ions. To assess the possible application of this method, the different concentrations of potentially interfering ions were individually added to the sample solution containing 2.0 ng mL⁻¹ of analytes, and their effects on the recovery of the analytes were investigated under the optimized conditions. The tolerance limit of the coexisting ion is defined as the largest amount making variations of less than 10% in the recovery of the analytes. The results in Table 2 show that the presence of major cations and anions had no significant effect on the extraction and determination of the analytes.

Fig. 2 Optimization of extraction conditions. Effect of sample pH (A), adsorbent dosage (B), extraction time (C), and (D) sample volume.

Table 2. Effect of Coexisting Ion Concentration on Recovery of Analytes

Coexisting ion	Concentration (mg L ⁻¹)
Na ⁺ , K ⁺	10000
Ca ²⁺ , Mg ²⁺	5000
Fe ³⁺ , Al ³⁺	50
Cu ²⁺ , Zn ²⁺ , Mn ²⁺	200
Cl ⁻ and NO ₃ ⁻	10000

Table 3. Comparison of Analytical Characteristics for This Method with Those of Other Techniques

Method	EF	DL (pg mL ⁻¹)		RSD (%)		Ref.
		Co	Ni	Co	Ni	
SPME-ICP-MS	50	0.9	6.0	-	-	38
CP-ICP-MS	-	0.6	16	11	11	39
CME-ICP-MS	50	0.6	6.4	1.8	4.2	40
SPE-ICP-MS	10	2.5	2.3	1.2	2.9	41
CME-ICP-MS	20	0.45	4.6	4.8	5.1	42
FI-ICP-MS	5	8.2	38	3.0	2.8	43
DMSPE-ICP-MS	100	0.12	1.34	3.9	4.8	This work

SPME, solid phase microextraction; CP, coprecipitation; CME, capillary microextraction; SPE, solid phase extraction; FI, flow injection; EF, enrichment factor; DL, detection limit; RSD, relative standard deviation.

Table 4. Analytical Results and Recovery of Analytes in Water Samples

Sample	Added (ng mL ⁻¹)		Found ^a (ng mL ⁻¹)		Recovery (%)	
	Co	Ni	Co	Ni	Co	Ni
Lake water	0	0	0.25 ± 0.01	1.17 ± 0.06	-	-
	0.5	0.5	0.74 ± 0.03	1.69 ± 0.09	98.0	104
	1.0	1.0	1.26 ± 0.05	2.12 ± 0.13	101	95.0
Waste water	0	0	15.7 ± 0.6	23.7 ± 0.8	-	-
	5	5	20.6 ± 0.9	28.5 ± 1.2	98.0	96.0
	10	10	25.0 ± 1.1	33.1 ± 1.5	97.0	93.0

^a Mean value ± standard deviation, n=3.

Table 5. Analytical Results and Recovery of Analytes in Certified Reference Materials

Sample	Found (μg g ⁻¹) ^a		Certified (μg g ⁻¹)	
	Co	Ni	Co	Ni
Stream sediment	3.51 ± 0.10	2.56 ± 0.09	3.6 ± 1.2	2.7 ± 1.3
Human hair	0.064 ± 0.003	0.75 ± 0.05	0.071 ± 0.008	0.83 ± 0.15
Mussel	0.83 ± 0.04	1.10 ± 0.06	0.94 ± 0.06	1.03 ± 0.13

^a Mean value ± standard deviation, n=3.

Analytical merits. The analytical performances of this method were evaluated under the optimal conditions. The detection limits (DLs) of this method, defined as the concentration of analytes equals 3 times the standard deviation for 11 replicate detections of the blanks, were 0.12 pg mL⁻¹ and 1.34 pg mL⁻¹ for Co and Ni, respectively. The relative standard deviations (RSDs) of the proposed method were 3.9% for Co and 4.8% for Ni with nine replicate measurements of the solutions containing 1.0 ng mL⁻¹ Co and Ni. The linear range of calibration covered over four orders of magnitude with a correlation coefficient higher than 0.9983. The analytical merits of the proposed method were compared with those of other methods.³⁸⁻⁴³ As shown in Table 3, the DLs of this method are lower than previously published reports. The RSDs are superior or similar to other methods. Moreover, the present method has a higher enrichment factor.

Application of method. The proposed method was applied successfully to determine Co and Ni in lake water and wastewater (Table 4). The recoveries for the spiked samples were found to be in the range of 93.0 and 104%. In addition, three certified reference

materials of stream sediment (GBW 07308), human hair (GBW 07601) and mussel (GBW 08571) were used to validate the accuracy of the proposed method. The results in Table 5 show that the determined values were in good agreement with the certified values despite the complex sample matrices.

CONCLUSIONS

In summary, FTGCNCs as a new sorbent material were prepared for the dispersive micro-solid phase extraction of Co and Ni prior to their detection by ICP-MS. The in-situ formation of g-C₃N₄ on the surface of the TDNFs greatly reduces the aggregation of g-C₃N₄ to increase its specific surface area and active sites. Furthermore, the TDNFs provide hydrophilicity with the relative hydrophobic surface of g-C₃N₄ to enhance its dispersibility in polar media and affinity for metal ions. Moreover, the adsorption behaviors of Co(II) and Ni(II) on the FTGCNCs were investigated in detail. The analytes were quantitatively adsorbed in the pH range of 5.0-8.0 and diluted completely with 1.0 mL of 0.5 mol/L HNO₃ solution. An enrichment factor of 100 was obtained in this study. This work reveals the potential application of FTGCNCs for the preconcentration, separation and determination of trace/ultra-trace heavy metals and their speciation in biological and environmental samples with complex matrices.

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Notes

The authors declare no competing financial interest.

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