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Enrichment of trace amounts Nickel (Π) in water samples and paraffin-embedded tissues from Liver loggerhead turtles specimens using nano-Fe_3O_4-encapsulated-chitosan/graphene oxide

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ABSTRACT

A simple, highly sensitive, accurate and selective method for determination of trace amounts of Ni^{2+}in water samples .In this paper, chitosan grafted with graphene oxide sheets showed an increased surface area was used to encapsulate nano-Fe_3O_4 and produce a nano-Fe_3O_4-encapsulated-chitosan/graphene oxide sorbent based new sorbent was prepared. Flame atomic absorption spectrometer was utilized for determination of Ni^{2+}.Some of the important parameters on the preconcentration and complex formation was selected and optimized. Under the optimized conditions the limit of detection (LOD) and limit of quantification (LOQ)were 0.30,0.750 and the proposedmethodhas a good reproducibility 0.90% (RSD %).The enrichment factor was 200 and the percentage of recovery was in the range of 95-100% .The method was successfully applied to the recovery of Ni^{2+}in different type of water samples. Graphene oxide and its derivates such as magnetic nano-Fe_3O_4-encapsulated-chitosan/graphene oxide in this studyis full of potential to use as an excellent adsorbent in the extraction method like solid phase extraction(SPE) and solid phase micro extraction(SPME).In the present study, we report the application of preconcentration techniques still continues increasingly for trace metal determinations by flame atomic absorption spectrometry (FAAS) for quantification of Ni^{2+} in Formalin-fixed paraffin-embedded (FFPE) tissues from Liver loggerhead turtles. This method exhibits the superiority in compared to the other adsorption reagents because of the fact that there is no necessity of any complexing reagent and optimum pH of solution presents in acidic media.

Keywords: nano-Fe_3O_4-encapsulated-chitosan/graphene oxide, preconcentration; SPE; Preconcentration; FAAS; Nickle; Formalin-fixed paraffin-embedded (FFPE) ; tissues from Liver loggerhead turtles.

INTRODUCTION

The properties of nano magnetic particles have attracted many studies on their functionality as magnetic carrier. This characteristic make these elements a fit candidate in a wide range of heavy metal ions application in biology and water samples [1-2],also in medical imaging uses such as magnetic resonance imaging(MRI) [3,4], in isolating substances and materials in anions– cations pre-concentration [5].

In recent years, SPE method have been well used for determination of Nickel (II) ions in numerous environmental samples[6,7]because of its simplicity, rapidity, minimal cost, low consumption of reagents and its ability to combine with different detection techniques either in on-line or off-line mode [8] . The main part of the SPE is the sorbent material that determines the selectivity and sensitivity of the technique. Though, the commonly used SPE sorbents, such as C_{18} silica and graphitic carbon, are often the only suitable option for a limited number of analytes. Reusability of the SPE column is also a problem. Thus, developing new SPE sorbent material is important [9].

Due to the very low concentration of most elements, including Nickle, in environmental samples (i.e. less than 10 µg l^{-1}), their separation and sensitive determination urgently necessitate the use of a preconcentration or trace enrichment method [13–15]. The liquid–liquid extraction and separation of Nickle in the presence of classical [16–18] and macrocyclic ligands [11,19–21] are frequently reported in the literature. However, classical extraction methods are usually time consuming and extensive and require relatively large volumes of high-purity solvents. Of additional concern is disposal of the solvents used, which creates a severe environmental problem. Solid-phase extraction (SPE) is an attractive technique that reduces the consumption of and exposure to a solvent, disposal costs and extraction time [22,23]. Recently, SPE disks were successfully utilized for the extraction of several organic [24–26] and inorganic analytes [27–32] from different matrices.

Chitosan has been reported to be a suitable biopolymer for the removal of heavy metals from industrial wastewater, due to its high amino and hydroxyl functional group content, low toxicity, biocompatibility, and biodegradability [33]. However, to improveits absorption capacity and enhance the separation rate, the design and synthesis of novel adsorbents are still critical [34]. The application of magnetic adsorbent technology to solve environmental problems is a relatively new and emerging field of research. Coating chitosan with magnetic fluids is a new method to improve separation speed, and the method has been reported that it canimprove the surface area for adsorption and reduce the required dosage for the adsorption of heavy metals.

Actually, the SPE technique using graphene and derivates of graphene such as functionalization graphene oxide as a novel and great adsorbent [39].Chemical modification of graphene oxide has been a promising way to achieve mass production of chemically modified graphene (CMG) platelets. Graphene oxide contains a range of reactive oxygen functional groups, which renders it a good candidate to use in the above-mentioned applications. In the present work, nano-Fe_3O_4-encapsulated-chitosan/graphene oxide[40]was employed for production of solid phase. The synthesized and characterized new sorbent nano-Fe_3O_4-encapsulated-chitosan/graphene oxide was utilized for preconcentration of Nickel (II) from water samples. Determination of Nickel (II) concentration was achieved by FAAS after preconcentration procedure.

MATERIALS AND METHODS

2.1. Apparatus

The concentration of the metal ion solutions was determined by using the Varian model spectra AA-240 (Mulgrara, Victoria, Australia). The pH-measurements of the metal ion and buffer solutions were carried out by an Orion 420. The size and morphology of graphene oxide was observed by scanning electron microscopy (SEM model LEO 440i), before taken image with SEM the surface of sample was coated with gold. X-ray diffraction (XRD) measurements were carried out with Ni Kα radiation (40 kV, 60 mA, 2Ɵ from 5 -115). Fourier transform-infrared (FT-IR)spectra were taken in KBr pressed pellets on a FT-IR Thermo Nicolet (USA).

2.2. Materials and reagents

All the necessary materials and reagents were of analytical grade and were purchased Merck, Aldrich and Sigma Company. All the dilutions were prepared by ultrapure deionized water. Chitosan was purchased from Merck. $FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$ were purchased from Merck. The reagents 1-ethyl-3-(3-dimethylaminoprophy) carbon diimide hydrochloride(EDC), N-hydroxyl succinimide (NHS), acetic acid, glutaradehyde and sodium hydroxide were Merck. All other reagents used in this study were analytical grade, double distilled water was used in the preparation of all solutions. GO was purchased from Damao Chemical Agent Company (Tianjin, China). Other metal stock solutions (1000 mg l^{-1}) were prepared by dissolving appropriate amounts of nitrate in 1.0% (v/v) HNO_3 and further diluted daily prior to use. The pH was adjusted with the following buffer solutions: $H_2C_2O_4/NaHC_2O_4$ for pH 2.0 and 3.0; $NaCH_3COO$/ CH_3COOH for pH 4.0–6.0. Na_2HPO_4/NaH_2PO_4 for pH 7.0; $Na_2B_4O_7/NaOH$ for pH 8.0–11; NaOH for pH 12–14.

Synthesis of magnetic nano-Fe_3O_4 sorbent

The magnetic nano-iron oxide was first synthesized according to a previously reported method [2]. A 6.1 g sample of $FeCl_3$-$6H_2O$ and 4.2 g $FeSO_4$-$7H_2O$ were dissolved in 100 mL of distilled water. A total of 25.0 mL of 6.5 M-NaOH was slowly added to the above solution. The reaction mixture was stirred for 4 h using a magnetic stirrer. After the complete addition of NaOH, the formed black precipitate, nano-Fe_3O_4, was then washed several times with distilled water, collected in a pure form by the assistance of an external magnetic field and dried in an oven at 70 °C.

Preparation of nano-Fe_3O_4-encapsulated-chitosan/graphene oxide sorbent
graphene oxide (0.1 g) dispersion was prepared by sonicating graphene oxide for 3 h in ultrapure water. A solution of 1-ethyl-3-(3-dimethylaminoprophy) carbondiimide hydrochloride (0.05 M) and N-hydroxyl succinimide (0.05 M) was added to the graphene oxide dispersion with continuous stirring for 2 h in order to activate the carboxyl groups of graphene oxide [35]. The pH of the resulting solution was maintained at 7.0 using dilute sodium hydroxide. Magnetic chitosan (0.1 g) and the activated graphene oxide solution were added in a flask and dispersed in distilled water by ultrasonic dispersion for 10 min. After ultrasonic dispersion, the mixed solutions were stirred at 60 ˚C for 2 h. The precipitate was washed with 2% (w/v) NaOH and distilled water in turn until pH was about 7. Then, the obtained product was collected by the aid of an adscititious magnet and dried in a vacuum oven at 50 ˚C. The obtained product was nano-Fe_3O_4-encapsulated-chitosan/graphene oxide[40].

2. 3 .Preparation of Solid Phase

Sorption characteristics of Ni(II) ions by magnetic nano-sorbents by the batch equilibrium technique. The applicability of magnetic nano-Fe_3O_4-encapsulated-chitosan/graphene oxide sorbent for extraction of Ni(II) ions was studied by the batch equilibrium technique under several experimental controlling factors. These include the effect of pH, contact time, sorbent dosage, initial metal ion concentration and interfering ions.

2.4. General procedure

100 ml solution with 50 $ngml^{-1}$ Ni content was prepared as a sample. This solution was added to the magnetic nano-Fe_3O_4-encapsulated-chitosan/graphene oxide sorbent and by using buffer solution ,its pH was modified to 3.0, followed the container was shaken for 25min in order to allow easier Ni ions absorption of the nano-Fe_3O_4-encapsulated-chitosan/graphene oxide sorbent [36]. At the end of this stage ,thenano-Fe_3O_4-encapsulated-chitosan/graphene oxide sorbent which had been formed on the bottom layer of the beaker was removed through applying an external field with1.4T magnetic powers and was immediately decanted outside the supernatant. 1 ml of 1$molL^{-1}$ ion of eluent was injected into FAAS for measurement of Ni(II) ions concentrations.

2.5. Analysis of sample paraffin-embedded tissues from liver loggerhead turtles

Specimens: Selected areas from fresh frozen tissues from liver loggerhead turtles specimens were sliced in three pieces (numbered as 1, 2 and 3) of approximately 10 mm × 5 mm × 2 mm each. Sets of pieces of set 1 (controls), were placed into a vacuum chamber at 50 ºC overnight to dry (until a constant weight was obtained) and the sets 2 and 3 were subjected to the standard 10 % buffered formalin fixation and paraffin embedding31 histological process using a tissue processor (Tissue-Tek VIP, Sakura Finetek USA Inc., Torrance, CA). After the paraffin embedding process, tissues were subsequently excised from the blocks with a titanium knife and deparaffinized in xylene at 55 ºC for 1 h in the tissue processor (the set 2), or with hexane at 20 ºC for 1 week with frequent changes of the solvent in handling-based procedure (the set 3). Xylene was of a grade routinely used for the FFPE process and hexane was of "Optima" grade (Fisher Scientific). Upon deparaffinization, the tissue samples were dried in a vacuum chamber until constant weight was obtained. Each dried sample (of the sets 1-3) was divided into three portions (5-10 mg each) to be further analyzed as triplicates.

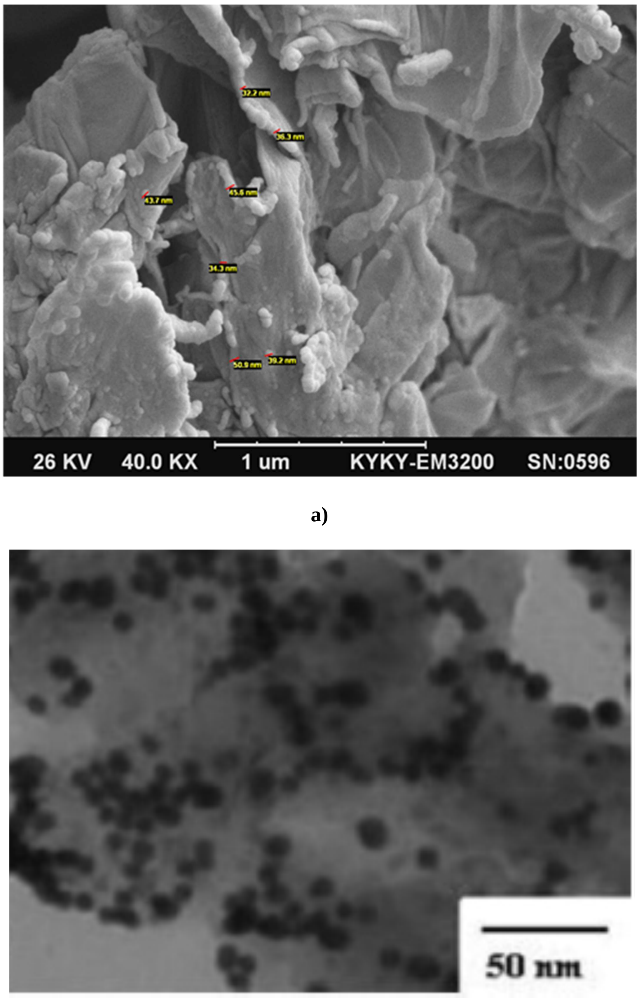
RESULTS AND DISCUSSION

Fig. 1a and b show the morphology and size of magnetic nano-Fe_3O_4-encapsulated-chitosan/graphene oxide sorbent as shown in Fig. 1a and b. The particles of nano-Fe_3O_4-encapsulated-chitosan/graphene oxide 339 sorbent retained a homogenous distribution in the range of 340 5.0–20.0 nm.

3.2. Optimization of SPE procedures

3.2.1 Effect of pH

The metal chelate stability constant and its chemical stability considerably influence the SPE recovery. The pH plays a very important role on metalchelate formation and following extraction. Therefore, pH was the first optimized parameter. pH of the analyte solutions was adjusted to desired values with diluted hydrochloric acid (0.1 mol L^{-1}) and/or ammonia solution (0.1 mol L^{-1}) The variation in recovery of Ni(II) with pH is shown in Fig.2. . According to the results shown in Fig 4 up to pH 4.5-6.0, complete recoveries are obtained. However, at higher pH values, percentage recovery decreases. This is due to fact that in an acidic solution the protonation of magnetic nano-Fe_3O_4-encapsulated-chitosan/graphene oxide occurs and there is a weak tendency for retention between Ni (II) and magnetic nano-Fe_3O_4-encapsulated-chitosan/graphene oxide, whereas at higher values (pH>6), Ni (II) reacts with hydroxide ions to produce Ni $(OH)_2$. Accordingly, pH 5.0 was selected for subsequent work and real sample analysis.



a)

b)

Fig.1. Images of (a) Scanning Electron Microscopy (SEM) and (b) Transmission Electron Microscopy (TEM) of magnetic nano-Fe_3O_4-encapsulated-chitosan/graphene oxide.distance

3.2.2 Effect of flow rates of sample and eluent solution

The effects of flow rates of sample solution and eluent solution on the recovery of Ni (II) was also examined between under the optimum conditions in the range of 1–10.0 mL min^{-1} by controlling the flow rate with peristaltic pump. The recovery of the ions were independent of flow rate in the range of 0.5–2.0 mL min^{-1} for eluent solution and range of 1–5.0 mL min^{-1} for sample solution.

3.2.3 Effect of sample solution volume

Another parameter studied to find the best experimental conditions is the volume of sample solution and/or analyte concentration. For this purpose, 50.0–1100.0 mL of sample solutions containing 5ppm Ni (II)were processed according to the suggested procedure. The recovery of Ni(II) was quantitative (>96%) obtained up to a sample volume of 1000.0 mL and the adsorbed Ni(II) can be eluted with 5 mL eluent. Therefore, an enrichment factor of 200 was achieved by this technique. Finally In our suggested procedure, a sample volume of 50.0 mL was chosen for preconcentration method.

3.2.4 Effect of amount of sorbent

To achieve a high extraction recovery, different amounts of magnetic nano-Fe_3O_4-encapsulated-chitosan/graphene oxide ranging from 50 to 300 mg were applied to extract the target compounds from the sample solutions. The results are shown in Fig 3 from which it can be seen that the extraction recovery achieved by 100 mg, but almost the same as obtained with 300 mg or more than of the adsorbent. Based on the above results, 100 mg of magnetic nano-Fe_3O_4-encapsulated-chitosan/graphene oxide was selected for the following experiments.

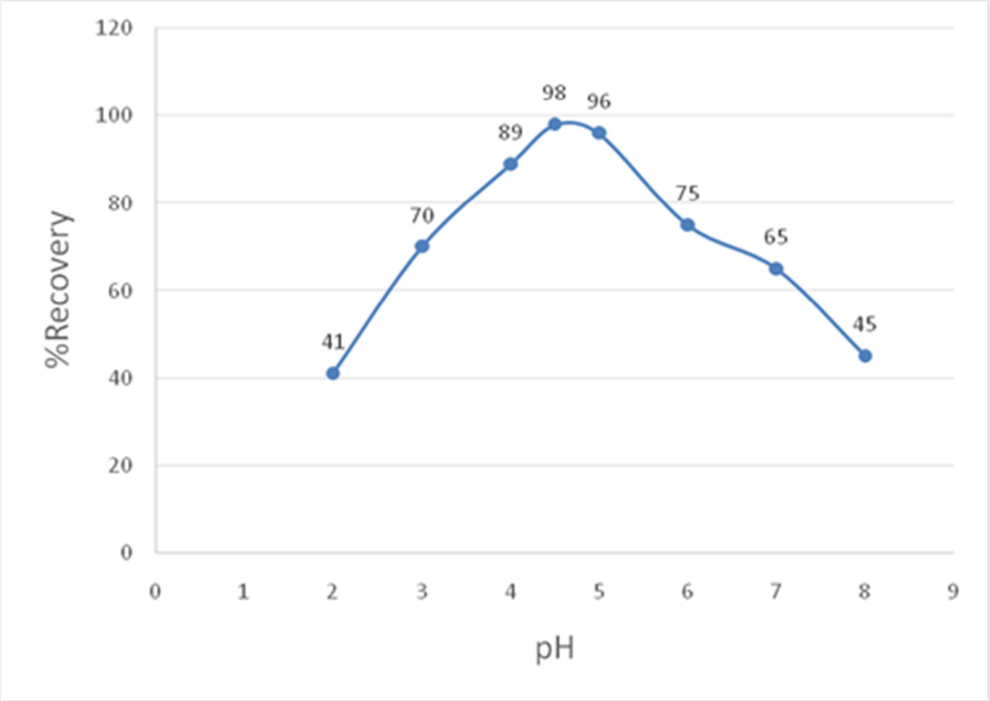


Fig. 2. Influence of sample pH on the percentage recovery of Ni (II), conditions: 100 mg adsorbent, 50 ml of 5 mg/L of nickel ions

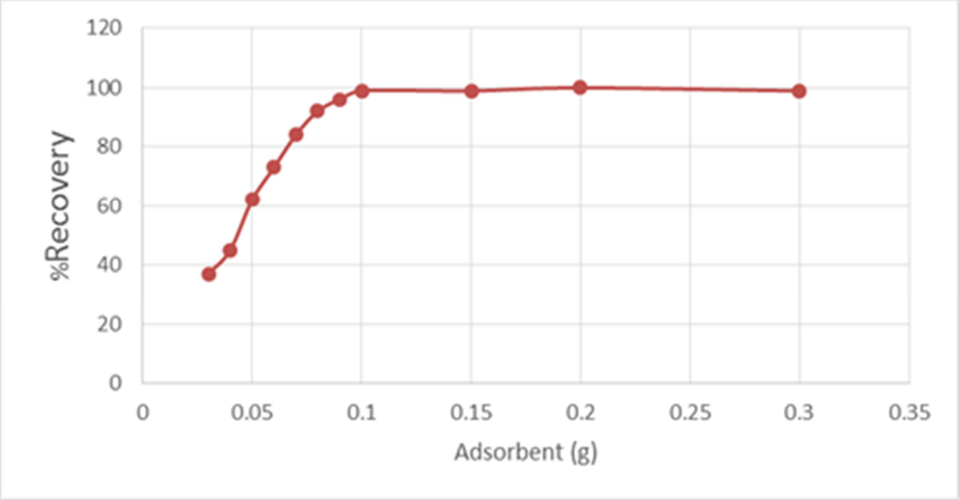


Fig 3.Removal percentages of nickel ions at different amounts of magnetic nano-Fe_3O_4-encapsulated-chitosan/graphene oxide , conditions: 50 ml of 5 mg/L of nickel ions, pH= 5.0

3.2.5 Eluent type and its volume

Another important factors which affect the percent of recovery are the type, volume, and concentration of the eluent solution used for the removal of metal ions from the sorbent. For this purpose, various type of eluents were examined according to the suggested procedure. The results for this study are listed in Table 1. 4.0 mol L^{-1} HNO_3 was found to be adequate for quantitative elution (≥95%).The effect of eluent volume on the recovery of Ni (II) was also studied and listed in table.2. the results show the best quantitative recovery is 5.0 mL of 4.0 mol $L^{-1}HNO_3$. As a result 5.0 mL of 4.0 mol L^{-1} HNO_3 was selected in the subsequent preconcentration method.

Table.1.Effect of type and concentration of various eluent on the recovery of Ni

	%Recovery			
Eluent concentration (M)	1	2	3	4
NaOH	8	11	15	15
NH_3	10	12	14	13
HCl	11	16	17	18
H_2SO_4	17	19	22	22
$HClO_4$	25	30	34	35
HNO_3	58	79.8	96	100

Table.2.Effect of eluent volume on the recovery of Ni

Volume of eluent	%Recovery
HNO_3 (4M) 2 ml	47.3
HNO_3 (4M) 4 ml	79
HNO_3 (4M) 5 ml	98
HNO_3 (4M) 8 ml	85
HNO_3 (4M)10ml	84

Reusability of Column

The stability and potential regeneration of the column were studied. After every time extraction, the column was washed with 10 mL of MeOH and 10mL of deionized water. Thus, the column was available for a next extraction immediately at least 50 adsorption elution cycles without significant decrease in the recovery of Ni (II) ions.

3.2.7 Effect of foreign ions

The influence of common foreign ions on the adsorption of Ni (II) onmagnetic nano-Fe_3O_4-encapsulated-chitosan/graphene oxide were studied. In these work, 50.0 ml solutions containing 5ppm of Ni and various amounts of interfering ions were treated according to the suggested procedure. The tolerance level was defined as the maximum concentration of the foreign ion causing a change in the analytical signal no higher than 5%, when compared with the signal of 5ppm nickel alone. The results, listed in Table 3, demonstration that the presence of major cations and anions in natural water has no important influence on the adsorption of Ni (II) ions under the designated conditions.

Table.3.Effect of foreign ions on the percent recovery of 5 ppm Ni in water samples

Ions	Amount taken (mg)	%Recovery
Na^+	10	101 (1.5)[a]
K^+	10	101 (1.5)
Ca^{2+}	10	100 (0.2)
Mg^{2+}	10	99 (0.8)
Fe^{3+}	8	100(1.2)
Cr^{3+}	8	99(1.2)
Co^{2+}	5	100(1.2)
Cl^-	5	100(1.0)
Br^-	2.5	97(1.5)
F^-	2.5	100 (2)
Mn^{2+}	2.5	99(0.2)
Zn^{2+}	2.5	97(1.7)

a:Values in parentheses are RSD based on three replicate analyses.

3.2.8 Analytical figures of merits

Under optimized conditions, a calibration curve for Ni (II) was found by preconcentrating a series of Ni (II) standards according to the procedure mentioned. The curve was linear from 1.0 mg/l to 7.0 mg/l for Ni. As analytical figures of merit, limit of detection (LOD), limit of quantification (LOQ) defined as $3S_B/m$ and $10S_B/m$, relative standard deviation (RSD) for the proposed preconcentration and speciation method have been determined and listed in table 4.

Table.4.Analytical figures of merits for Ni.

Parameters	
RSD% n=10	0.88%
LOD(μm/L)	0.25
LOQ(μm/L)	0.883
Enrichment factor	200
flow rates of sample (mL/min)	5
calibration equation	Y = 0.06x - 0.0002
correlation coefficient	0.999

3.2.9. Determination of nickel in real water samples

Three type of water samples (information described in section 2.7sampling) were used for the determination of nickel. The analytical results, are given in Table 5. The percent of recoveries for the addition of different concentrations of Ni (II) to water samples and sample paraffin-embedded tissues from liver loggerhead turtles were 98 and 100.5%.These satisfactory percent of recoveries indicate no significant effects from the matrix composition of the real water samples.As is seen, the recovered Ni (II)ion reveals that the results are quite reliable and are in satisfactory agreement with those obtained by ICPAES.

The proposed method was used for the determination of Ni (II) in several water samples. The results, along with the recovery for the spiked samples, are given in Table 5. The recoveries for the addition of different concentrations of Ni (II) to water samples were in the range of 95.8–98.6%. To verify the accuracy of the proposed procedure, the method was used to determine of the content of Ni (II) in the National Standard Reference Material for Environment Water (GSBZ 50030-94) after the appropriate dilution. The results for this test are presented in Table 5. A good agreement between the determined values and the certified values was obtained.

Table.5 .Determination of nickel in real water samples

Sample	Taken amount (μg)	Flame atomic absorption (μg)	ICP-AES
Tap water (Tehran, Iran)	0	4.2(0.4)[a]	4.3
	30	33.08(1.2)	34.6
Tap water (Pakdasht,Tehran,iran)	0	1.2(0.8)	1.23
	30	33.1(0.1)	33.3
Mineral water (Damavand company)	0	N.D[b]	N.Db
	30	30.09(1.2)	31.1
GSBZ 50,030-94 (μg L^{-1})	0	13.65	14.1
Development of a methodology for the determination of Ni^{2+} in FFPE tissue	0.0	N.D[b]	ND
	10.0	9.95(2.2)	10.1

a.Values in parentheses are RSD based on four replicated analyses.
b.No adsorption, passes through column

Table. 6.Comparison of the total results of the proposed method with ICP-AES [a]

Sample	Ni^{2+} (mg.mL^{-1}) SPE-FAAS	Ni^{2+} (mg.mL^{-1}) ICP-AES	F-test [c]	T-test [d]
1	16.5±0.5[b]	16.6±0.7	3.1	0.5
2	14.6±0.3	14.7±0.5	1.8	0.8
3	7.9±0.8	8.1±0.7	2.7	0.9
4	3.6±1.3	3.5±1.1	2.0	0.6
5	1.8±0.9	1.7±0.9	2.1	0.7

[a] *.All real samples were diluted 50 times before analysis.*
[b] *Mean ±standard deviations based on five individual replicate analyses.*
[c] *Tabulated F-value for (4,4) degrees of freedom at p (0.95) is 6.39.*
[d] *Tabulated T-value for 8 degrees of freedom at p (0.95) is 2.306.*

Real samples marked 1 to 5, were collected at the at the distances of 5, 100, 250, 350 and 500 metres of the total waste water of electroplating plants in the eastern parts of Varamin, respectively. The total results obtained by the recommended procedure and ICP-AES have compared in Table 6. As it is seen, the results obtained by the proposed method and ICP-AES are in agreement with each other.

The results were shown in Table 6, together with results of a recovery test by added known amounts of nickel in water sample. A standard method with ICP-MS has also been used as reference method.

Table 7. Comparison of published results of several on-line or several methods for determination of Ni^{2+}

Technique	Sorbent	RSD(%)	Duration of SPE	Enhancement factors	LOD (µg /L)	Ref
SPE & FAAS	Dimethylglyoxim/sodiumdodecyl sulfate-immobilized on alumina-coated magnetite nanoparticles (DMG/SDS-ACMNPs)	1.9%	15	25	4.6	44
SPE & FAAS	2-{4-[2-(1H-Indol-3-yl)ethyl]-3-(4-chlorobenzyl)-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl}-*N′*-(pyrrol-2-ylmethyliden)acetohydrazide (ICOTPA)	4.0%	25	30	0.27	45
SPE & FAAS	N- propylsalicylaldimine based on porous silica	3.5	10	18	7.0	46
SPE & FAAS	Amino-Functionalization of Multiwall Carbon Nanotubes	2.23	30	100	0.3	47
SPE & FAAS	magnetic nano-Fe_3O_4-encapsulated-chitosan/graphene oxide	0.88%	20	50	0.25	Present method

CONCLUSION

The proposed SPE method possesses advantages such as easiness, and considerable selectivity in comparison with the previously reported procedures for isolation and determination of Ni^{2+} contents (Table 7). In conclusion, the proposed SPE possesses the following advantages: the technique is rapid when compared with the previously reported procedures for the separation and determination of nickel, the time taken for the separation and determination of nickel in a 500 mL sample is at the most 30 min. Furthermore, it is a simple, highly sensitive, selective and reproducible method for the separation of Ni^{2+} and in this work the recovery yields obtained with magnetic nano-Fe_3O_4-encapsulated-chitosan/graphene oxide were about 95-100% then it show graphene oxide and its derivation e.g. in this work magnetic nano-Fe_3O_4-encapsulated-chitosan/graphene oxide is full of potential for use as a adsorbent in the extraction method like SPE and SPME .consequently it can be applied to the preconcentration and determination of nickel and the large number of heavy metal that are dangers for human from real samples.

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