Enrichment of trace amounts Nickel (II) in water samples using nano-Fe$_3$O$_4$-encapsulated-dioctylphthalate and linked- ethylenediamine

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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, Dioctylphthalate (DOP) was used to encapsulate nano-Fe$_3$O$_4$ and produce a nano-Fe$_3$O$_4$-DOP sorbent based new sorbent was prepared. This was treated with ethylenediamine (ED) in another solvent-free procedure for the formation of a novel nano-Fe$_3$O$_4$-DOP-ED. Flame atomic absorption spectrometer was utilized for determination of Ni^{2+}. Some of the important parameters on the preconcentration and complex formation were selected and optimized. Under the optimized conditions the limit of detection (LOD) and limit of quantification (LOQ) were 0.25, 0.883 and the proposed method has a good reproducibility 0.88% (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 derivate such as magnetic nano- Fe$_3$O$_4$ -DOP- ED in this study is full of potential to use as an excellent adsorbent in the extraction method like solid phase extraction (SPE) and solid phase micro extraction (SPME).

Keywords: *Dioctylphthalate (DOP) [was used to encapsulate nano-Fe$_3$O$_4$ and produce a nano-Fe$_3$O$_4$-DOP]; FAAS; Nickle; Preconcentration; SPE*

INTRODUCTION

The properties of nano magnetic particles have attracted many studies on their functionality as magnetic carrier. This characteristic makes these elements a fit candidate in a wide range of heavy metal ions application in biology and water samples (Deng, *et al.*, 2005; Modo, *et al.*, 2005; Margel, *et al.*, 1997). Also in medical imaging uses such as magnetic resonance imaging (MRI)

(Bulte, *et al.*, 2006) in isolating substances and materials in anions– cations pre-concentration (Afkhami, *et al.*, 2010).

Ni, at trace concentrations, acts as both a micronutrient and a toxicant in marine and fresh water systems (Leyden, *et al.*, 1976; Narin, *et al.*, 2000; Akama, *et al.*, 2000; Ohta, *et al.*, 2001; Cuculic, *et al.*, 1997; Moghimi, *et al.*, 2012). The direct determination of trace met-

als especially toxic metal ions such as Ni, tin, arsenic, lead, antimony and selenium from various samples requires mostly an initial and efficient pre-concentration step (Leyden, *et al.*, 1976). This pre-concentration is required to meet the detection limits as well as to determine the lower concentration levels of the analyte of interest (Jones, *et al.*, 1983). This can be performed simply in many ways including liquid and solid phase extraction techniques (Nambiar, *et al.*, 1998; Caroli, *et al.*, 1991). The application of solid phase extraction technique for pre- concentration of trace metals from different samples results in several advantages such as the minimal waste generation, reduction of sample matrix effects as well as sorption of the target species on the solid surface in a more stable chemical form (Alexandrova, *et al.*, 1993).

The normal and selective solid phase extractors are those derived from the immobilization of the organic compounds on the surface of solid supports which are mainly polyurethane foams (Arpadjan, *et al.*, 1997), filter paper (Leyden, *et al.*, 1975), cellulose (Gennaro, *et al.*, 1983) and ion exchange resins (Grote, *et al.*, 1985). Silica gel, alumina, magnesia and zirconia are the major inorganic solid matrices used to immobilize the target organic modifiers on their surfaces (Unger, 1979) of which silica gel is the most widely used solid support due to the well documented thermal, chemical and mechanical stability properties compared to other organic and inorganic solid supports(Boudreau et al, 1989). The surface of silica gel is characterized by the presence of silanol groups, which are known as weak ion exchangers, causing low interaction, binding and extraction of the target analytes (Kvitek, *et al.*, 1982). For this reason, modification of the silica gel surface with certain functional groups has successfully been employed to produce the solid phase with certain selectivity characters (Bruening, *et al.*, 1991). Two approaches are known for loading the surface of solid phases with certain organic compounds and these are defined as the chemical immobilization which is based on chemical bond formation between the silica gel surface groups and those of the organic modifier, and the other approach is known as the physical adsorption in which direct adsorption of the organic modifier with the active silanol groups takes place (Unger, 1979). Selective solid phase extractors and pre-concentrators

are mainly based on impregnation of the solid surface with certain donor atoms such as oxygen, nitrogen and sulfur containing compounds (Mahmoud, 1997; Mahmoud, *et al.*, 1997; Tong, *et al.*, 1990; Dadler, *et al.*, 1987). The most successful selective solid phases for soft metal ions are sulfur-containing compounds, which are widely used in different analytical fields. Amongst these sulfur-containing compounds are dithiocarbamate derivatives for selective extraction of Ni(II) (Mahmoud, 1998; Mahmoud, 1999) and pre-concentration of various cations (Leyden, *et al.*, 1976; Narin, *et al.*, 2000; Akama, *et al.*, 2000; Ohta, *et al.*, 2001; Cuculic, *et al.*, 1997; Moghimi, *et al.*, 2009; Thurman, 1998; Pawliszyn, 1997; Izatt, *et al.*, 1996; Hagen, *et al.*, 1990; Krueger, 1995; Yamini, *et al.*, 1994; Shamsipur, *et al.*, 1999; Shamsipur, *et al.*, 2001; Brunner, *et al.*, 2003; Zelder, *et al.*, 2004; Boll, *et al.*, 2005; Nayebi, *et al.*, 2006; Moghimi, *et al.*, 2007; Moghimi, 2007) and 2- mercaptobenzothiazol-modified silica gel for on-line pre-concentration and separation of silver for atomic absorption spectrometric determinations (Qiaosheng, *et al.*, 1998). Ammonium hexa-hydroazepin-1-dithiocarboxylate (HMDC)-loaded on silica gel as solid phase pre-concentration column for atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) was reported (Alexandrova, *et al.*, 1993). Mercapto-modified silica gel phase was used in pre-concentration of some trace metals from seawater (Moghimi, *et al.*, 2010). Sorption of Ni(II) by some sulfur containing complexing agents loaded on various solid supports (Tajodini, *et al.*, 2010) was also reported. 2-Amino-1-cyclopentene-1-dithiocaboxylic acid (ACDA) for the extraction of silver(I), Ni(II) and palladium(II) (Moghimi, *et al.*, 2009), 2-[2-triethoxys-ilyl-ethylthio] aniline for the selective extraction and separation of palladium from other interfering metal ions (Narin, *et al.*, 2000) as well as thiosemicarbazide for sorption of different metal ions (Campderros, *et al.*, 1998) and thioanilide loaded on silica gel for pre-concentration of palladium(II) from water (Narin, *et al.*, 2000) are also sulfur containing silica gel phases. 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-DOP-ED was employed for production of solid phase. The synthesized and characterized new sorbent nano-Fe_3O_4-DOP-ED was utilized for preconcentration of Nickel (II) from water samples. Determination of Nickel (II) concentration was achieved by FAAS after preconcentration procedure.

EXPERIMENTAL

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, 2θ from 5-115). Fourier transform-infrared (FT-IR) spectra were taken in KBr pressed pellets on a FT-IR Thermo Nicolet (USA).

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.

BDH Limited, Poole, England. Dioctylphthalate, DOP, (purity> 99.55%), sodium hydroxide (NaOH) and ethylenediamine (ED) was purchased from BDH, UK.

Synthesis of magnetic nano-Fe_3O_4 sorbent

The magnetic nano-iron oxide was first synthesized according to a previously reported method (Alexandrova & Arpadjan, 1993). 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 form 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.

Synthesis of nano-Fe_3O_4-DOP sorbent

The Fe_3O_4-encapsulated-DOP nano-sorbent was prepared by the addition of 20.0 mL of DOP to 10.0 g of nano- Fe_3O_4 sorbent. This mixture was heated under stirring at 80-90 °C for 3 hands the product nano-Fe_3O_4-DOP sorbent was filtered, washed with methanol, collected in a pure form by a magnetic field and dried in an oven at 70 °C until complete dryness.

Synthesis of magnetic nano-Fe_3O_4 -DOP- ED sorbent

A 10.0 g sample of nano-Fe_3O_4-DOP addition to 5 mL of ED and these two reactants were combined together by heavy grinding and mixing in a mortar for 5 h. The produced nano- Fe_3O_4 DOP-TETA sorbent was heated to dryness in an oven at 60 °C.

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-DOP- ED 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.

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-DOP- ED sorbent and by using buffer solution, its pH was modified to 3.0, followed the container was shaken for 25 min in order to allow easier Ni ions absorption of the nano-Fe_3O_4-DOP-ED sorbent. At the end of this stage, the nano-Fe_3O_4 -DOP-ED sorbent which had been formed on the bottom layer of the beaker was removed through applying an external field with 1.4T magnetic power 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.

RESULTS AND DISCUSSION

Fig. 1a and b show the morphology and size of magnetic nano- Fe_3O_4 -DOP- ED sorbent as shown in Fig. 1a and b. The particles of nano-Fe_3O_4-DOP- ED 339 sorbent retained a homogeneous distribution in the range of 340 5.0–20.0 nm.

Optimization of SPE procedures
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 solu-

Fig. 1. Images of (a) Scanning Electron Microscopy (SEM) and (b) Transmission Electron Microscopy (TEM) of magnetic nano- Fe_3O_4 -DOP- ED
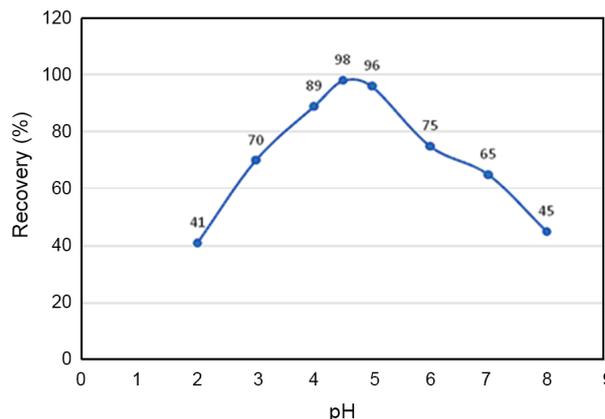

Fig. 2. Influence of sample pH on the percentage recovery of Ni (II), conditions: 100 mg adsorbent, 50 ml of 5 mg/L of nickel ions

tion the protonation of magnetic nano-Fe_3O_4 -DOP-ED occurs and there is a weak tendency for retention between Ni (II) and magnetic nano-Fe_3O_4 -DOP- ED, 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.

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.

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 5 ppm Ni (II) was 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.
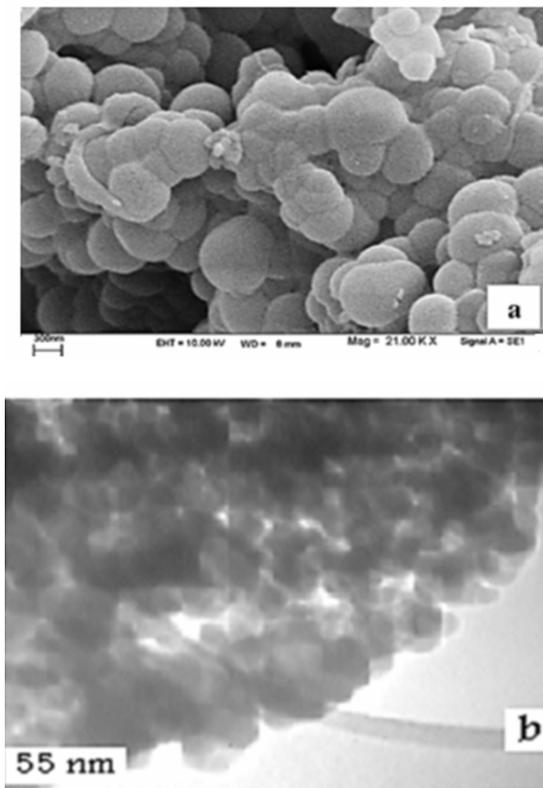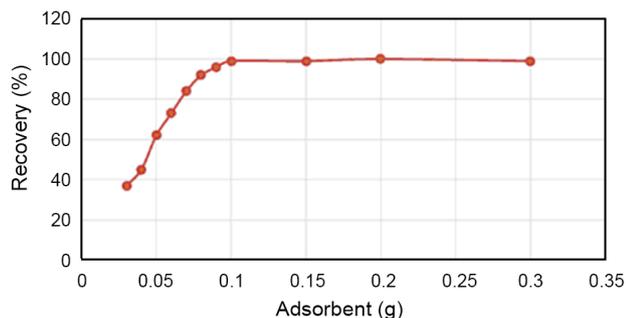
Fig. 3. Removal percentages of nickel ions at different amounts of magnetic nano- Fe_3O_4 -DOP- ED, conditions: 50 ml of 5 mg/L of nickel ions, pH= 5.0

Effect of amount of sorbent

To achieve a high extraction recovery, different amounts of magnetic nano-Fe_3O_4-DOP- ED 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-DOP- ED was selected for the following experiments.

Eluent type and its volume

Other 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 types of eluents were examined according to the suggested procedure. The results for this study are listed in Table 1. 4.0 molL^{-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 recov-

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

Eluent concentration (M)	%Recovery			
	1	2	3	4
NaOH	8	11	15	15
NH$_3$	10	12	14	13
HCl	11	16	17	18
H$_2$SO$_4$	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) 10 ml	84

ery is 5.0 mL of 4.0 molL^{-1} HNO$_3$. As a result 5.0 mL of 4.0 molL^{-1} HNO$_3$ was selected in the subsequent preconcentration method.

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.

Effect of foreign ions

The influence of common foreign ions on the adsorption of Ni (II) on magnetic nano-Fe_3O_4-DOP- ED was studied. In these work, 50.0 ml solutions containing 5 ppm 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 5 ppm 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.

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 3SB/m and 10SB/m, relative standard deviation (RSD) for the proposed preconcentration and speciation method

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.

have been determined and listed in Table 4.

Determination of nickel in real water samples

Three type of water samples (information described in section 2.7 sampling) 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 were 98

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

and 100.5%. These satisfactory percent of recoveries indicate no significant effects from the matrix composition of the real water samples.

Real samples marked 1 to 5, were collected 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. Moreover, as it is expected, the Ni (II) concentration decreases as the distance from the electroplating plants increases.

Table 5. Determination of nickel in real water samples

Sample	Taken amount (μg)	Flame atomic absorption (μg)	%Recovery
Tap water (Tehran, Iran)	0	4.2 (4.0)[a]	-
	30	33.08 (1.2)	98.5
Tap water (Pakdasht, Tehran, Iran)	0	1.2 (0.8)	-
	30	33.1 (0.1)	100.5
Mineral water (Damavand company)	0	N.D[b]	-
	30	30.09 (1.2)	98

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.

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/sodium dodecyl sulfate -immobilized on alumina-coated magnetite nanoparticles (DMG/SDS-ACMNPs)	1.9%	15	25	4.6	Tuzen, et al., 2009
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	Graf, et al., 2007
SPE & FAAS	N- propylsalicylaldimine based on porous silica	3.5	10	18	7.0	Moghimi, et al., 2014
SPE & FAAS	Amino-Functionalization of Multiwall Carbon Nanotubes	2.23	30	100	0.3	Shojai, et al., 2015
SPE & FAAS	as magnetic nano- Fe_3O_4 -DOP- ED	0.88%	20	50	0.25	Present method

CONCLUSIONS

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-DOP- ED were about 95-100% then it show graphene oxide and its derivation e.g. in this work magnetic nano-Fe_3O_4-DOP- ED 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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