

*Original Research Article*

# Preconcentration of trace Ni (II) using C<sub>18</sub> disks nano graphene with aminopropyltriethoxysilane (APTES)

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Abstract

A selective and simple method has been developed for preconcentration of Ni on C<sub>18</sub> disks nano graphene with aminopropyltriethoxysilane (APTES). Simple chemical bonding method to synthesize nano graphene with aminopropyltriethoxysilane (APTES) was reported. The adsorption behaviors of Ni (II) in aqueous solution on APTES were systematically investigated. The procedure is based on the selective formation of Ni (II) at optimum pH by elution with organic effluents and determination by flame atomic absorption spectrometry. The method is based on complex formation on the surface of the ENVI-18 DISK™ disks nano graphene with amino propyltriethoxysilane (APTES) followed by stripping of the retained species by minimum amounts of appropriate organic solvents. The elution is efficient and quantitative. The effect of potential interfering ions, pH, APTES amount, stripping solvent, and sample flow rate were also investigated. Under the optimal experimental conditions, the break-through volume was found to about 1000mL providing a preconcentration factor of 600. The maximum capacity of the disk nano graphene with aminopropyltriethoxysilane (APTES) was found to be  $398 \pm 3 \mu\text{g}$  for Ni<sup>2+</sup>. The limit of detection of the proposed method is 5ng per 1000mL. The method was applied to the extraction and recovery of Ni in different water samples.

**Keywords:** Ni (II), SPE, Octadecyl silica disk, FAAS, nano graphene with aminopropyltriethoxysilane (APTES)

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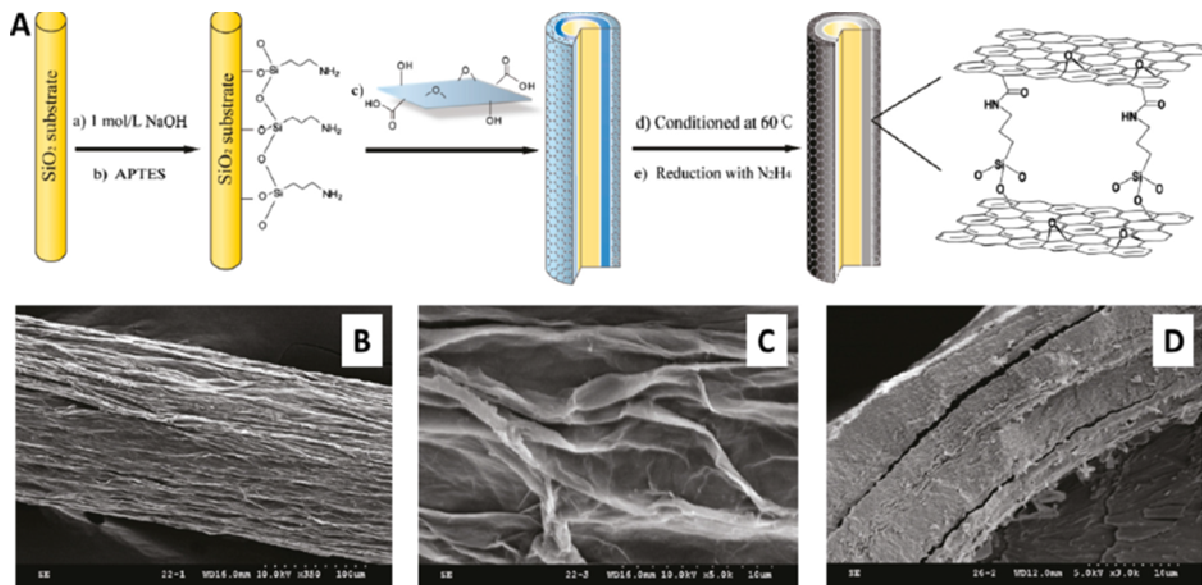
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## INTRODUCTION

Ni as trace concentrations acts as both a micronutrient and a toxicant in marine and fresh water systems (Izatt et al., 1991; Izatt et al., 1985; Izatt et al., 1995; Blake et al., 1996; Arca et al., 2001; Ghoulipour et al., 2002; Hashemi et al., 2001; Shcherbinina et al., 1990). This element is needed by plants at only very low levels and is toxic at higher levels. At these levels, Ni can bind to the cell membrane and hinder the transport process through the cell wall. Ni at nearly  $40\text{ng mL}^{-1}$  is required for normal metabolism of many living organisms (Gomes-Gomes 1995; Unger et al., 1979). On the other hand, Ni is an important element in many industries. Thus, the development of new methods for selective separation, concentration and determination of it in sub-micro levels

in different industrial, medicinal and environmental samples is of continuing interest. The determination of Ni is usually carried out by flame and graphite furnace atomic absorption spectrometry (AAS). (Boudreau et al., 1989) as well as spectrometric methods (Bruening et al., 1991; Mahmoud and Soliman, 1997a).

Solid phase extraction (SPE) methods are the best alternatives for traditional classic methods due to selective removal of trace amounts of metal ions from their matrices. Solid phase extraction determinations can be carried out on different efficient ways. One of the most appropriate performance features of SPE is achieved by using octadecyl silica membrane disks. SPE reduce the use of toxic solvent, disposal costs, and extraction



**Figure 1.** (A) Layer-by-layer fabrication processes of chemical-bonded graphene-coated SPE fiber. (B–D) SEM images of an SPME fiber coated with graphene. The surface images at magnifications of (B) 350 $\times$  and (C) 5000 $\times$ ; the cross-section image at magnifications of (D) 3000 $\times$  (Karousis et al., 2011).

time (Mahmoud et al., 1997b, 45; Mahmoud et al., 1997b). The octadecyl silica membrane disks involves shorter sample processing time and decreased plugging due to the large cross-sectional area of the disk and small pressure drop which allows higher flow-rates; reduced channeling resulting from the use of sorbent with smaller particle size and a greater mechanical stability of the sorbent bed (Tong et al., 1990).

In our previous we modified SPE membrane disks with suitable for selective measurement of chromium (Dadler et al., 1987; Moghimi 2007) and lead (Mahmoud et al., 1990). Meanwhile, other investigators have successfully utilized these sorbents for separation and determination trace amounts of lead (Leyden et al., 1976; Moghimi et al., 2009; Liu et al., 1992), copper (Liu et al., 1996; Mishenina et al., 1996; Wang et al., 1999), silver (Wang et al., 1997; Zhang et al., 1982), mercury (Zhou et al., 1983; Zargarani et al., 2008), cadmium (Tabarzadi et al., 2010), palladium (Shin et al., 2004), Ni (Moghimi et al., 2012) and  $\text{UO}_2$  (Mahmoud et al., 1998; Moghimi et al., 2006).

The  $\beta$ -cyclodextrin–chitosan nanoparticles have attracted attentions due to its many excellent properties such as easy separation and high adsorption capacity (Fang et al., 2007; Guo et al., 2010). In this work,  $\beta$ -cyclodextrin–chitosan/nano graphene oxide materials were prepared via a step procedure route that the carboxyl group of GO chemically reacts with the amine group of magnetic  $\beta$ -cyclodextrin–chitosan with consequent formation of chemical bond between GO and chitosan.

In the present report, we wish to describe a proper concentrative method for assessment of trace levels of Ni

in different water samples. To the best of our knowledge, octadecyl silica membrane disks modified by (APTES) have not been used for Ni isolation and preconcentration, previously of this work was the development of a rapid, efficient and highly sensitive method for selective extraction and concentration of ultra trace amounts of  $\text{Ni}^{2+}$  ions from aqueous media using octadecyl silica membrane disks nano graphene with aminopropyltriethoxysilane (APTES) and Flame Atomic Absorption Spectrometric (FAAS) determination.

## Experimental

### Reagents

Graphite oxide was prepared from purified natural graphite (SP-1, Bay Carbon, Michigan, average particle size 30  $\mu\text{m}$ ) by the Hummers (Hummers et al., 1958). Method and dried for a week over phosphorus pentoxide in a vacuum desiccators before use. 4-Isocyanatobenzenesulfonyl azide was prepared from 4-carboxybenzenesulfonyl azide via a published procedure (Ibarra et al., 1993). All solutions were prepared with doubly distilled deionized water from Merck (Darmstadt, Germany).  $\text{C}_{18}$  powder for chromatography with diameter of about 50  $\mu\text{m}$  obtained from Katayama Chemicals from supelco. It was conditioned before use by suspending in 4M nitric acid for 20min, and then washed two times with water. Sodium dodecyl sulfate (SDS) obtained from Merck (Darmstadt, Germany) and used without any further purification. The stock standard solution of  $\text{Ni}^{2+}$

**Table 1.** The operational conditions of flame for determination of Ni

|                               |                          |
|-------------------------------|--------------------------|
| Slit width                    | 0.7 nm                   |
| Operation current of HI-HCL   | 15 mA                    |
| Resonance fine                | 324.8nm                  |
| Type of background correction | Deuterium lamp           |
| Type of flame                 | Air/acetylene            |
| Air flow                      | 7.0 mL.min <sup>-1</sup> |
| Acetylene flow                | 1.7 mL.min <sup>-1</sup> |

was prepared by dissolving 0.1000g of the Ni powder in 10mL concentrated nitric acid and diluted to 1000mL with water in a calibrated flask. Working solutions were prepared by appropriate dilution of the stock solution.

## Synthetic procedures

### Preparation of GO-APTES

Zhang et al. reported the preparation of chemical bonded graphene coating for SPME in a layer-by-layer manner (Figure 1A) (Karousis et al., 2011). The silica fiber was first treated with NaOH and 3- amino propyltriethoxysilane (APTES) to introduce amino groups to the surface. Then, GO was bonded to the fiber via reaction of the carboxyl groups of GO with the amino groups. Repeating the treatment with APTES and GO four times gave a coating of 20 μm thickness (Figure 1D). Finally, the fiber was aged at 60°C and reduced with hydrazine. SEM showed a rough tree-bark-like structure with a striped appearance (Figure 1B), and the high-resolution image revealed a continuous folded, wrinkled structure (Figure 1D).

### Column preparation

GO-APTES (40 mg) were packed into an SPE mini-column (6.0 cm ×9 mm i.d., polypropylene). A polypropylene frit was placed at each end of the column to prevent loss of the adsorbent. Before use, 0.5 mol L<sup>-1</sup> HNO<sub>3</sub> and DDW were passed through the column to clean it.

### Apparatus

Determination of Ni<sup>2+</sup> contents in working samples were carried out by a Varian spectra A.200 model atomic absorption spectrometer equipped with a high-intensity hollow cathode lamp(HI-HCL) according to the recommendations of the manufacturers. These characteristics are tabulated in (Table 1).

GO-APTES (40mg) were packed into an SPE ENVI-

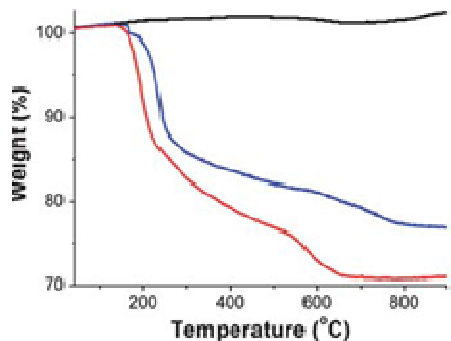
18 DISK™ disks. Solid phase extractions were carried out by glassy membrane disks, ENVI-18DISK™ 47mm diameter ×0.6 mm thickness containing octadecyl silica bonded phase (30 μm particles, 70 Å pore size) obtained from Supelco in conjunction with a standard Millipore 47 mm filtration apparatus equipped with a vacuum pump. The pH measurements were carried out by an ATC pH-meter (EDT instruments, GP 353).

### Sample extraction

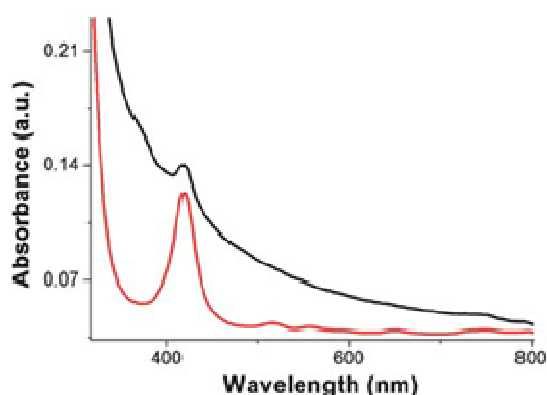
Extraction were performed with glassy membrane disks, ENVI-18 DISK™ 47mm diameter ×0.6 mm thickness containing octadecyl silica bonded phase (30 μm particles, 70 Å pore size) from Supelco. The disks were used in conjunctions with a standard Millipore 47mm filtration apparatus connected to water aspirator (Moghimi 2007).

1) Sample Treatment: The water samples were filtered through 45μm nylon filters. Sampling vessels were polyethylene bottles soaked in 1 mol.L<sup>-1</sup> HNO<sub>3</sub> overnight and rinsed twice with deionized water. The analysis must be done within 2 days of sample collection to limit the risk of interconversion of Ni (II). Then, 5mL of methanol was added to a 90mL portion of each before analysis. The surface of the ENVI-18 DISK™ disks is modified with GO-APTES and therefore could retain Ni<sup>2+</sup> ions properly. Instead, 10 mg of GO-APTES an appropriate volume of an organic solvent (5mL) miscible with water. The most suitable solvent under the experimental conditions was acetone.

2) Disk cleaning and conditioning: A disk was placed in the apparatus and was washed with 10mL of methanol to remove all contaminants arising from the manufacturing process and the environment. Then, the disk was dried by passing air through it for several minutes. In order to insure optimal extraction of the analytes of interest, the disk was again washed with 10mL of methanol, immediately followed by 10mL of water, without letting the surface of the disk dry. This step pre-wets the disk surface before to extraction. Improper performance of this step causes slow flow – rate and poor analyte recoveries. It is important to avoid any air contact with the surface of the disk before the addition of the sample.



**Figure 2.** The TGA graphs of graphite (black), GO (blue) and GO-APTES (red), obtained under an inert atmosphere.



**Figure 3.** The UV-vis spectra of GO-APTES (black) and free APTES (red), obtained in DMF.

3) Sample addition: After complete homogenization, accurate volumes of the sample solutions (100mL portions) were transferred to the top reservoir of the disk apparatus. At the same time, the solution was drawn through the disk by applying a mild vacuum. Application of vacuum was continued until the disk was completely dry (about 5 minutes).

4) Analyte elution: In order to elute the analyte selectively, exactly 5 mL of acidified solvents 0.1M HCl in methanol was passed through the disk and collected into a 5.0 mL volumetric flask under the extraction funnel. It was found that ultra pure alcoholic organic solvents were the best eluting agents. The concentration of Ni (II) in the effluent was then determined by FAAS using an external calibration graph.

## RESULTS AND DISCUSSION

The treatment of nano graphene with aminopropyltriethoxysilane (APTES) can lead to the derivatization of both the edge carboxyl and surface hydroxyl functional groups via formation of amides (Karousis et al., 2011) or carbamate esters (Smith 2001), respectively.

## Morphology

The amount of nano graphene with aminopropyltriethoxysilane (APTES) sheet was evaluated by thermogravimetric analysis. As compared with the TGA results of pure graphite, which is thermally stable up to 900 °C under nitrogen, and GO which decomposes above 600°C, after having lost the oxygenated species at 240°C (i.e. 14.7% weight loss), the 6% weight loss occurred in the temperature range 250–550 °C for the GO-APTES material., is attributed to the decomposition of APTES (Figure 2).

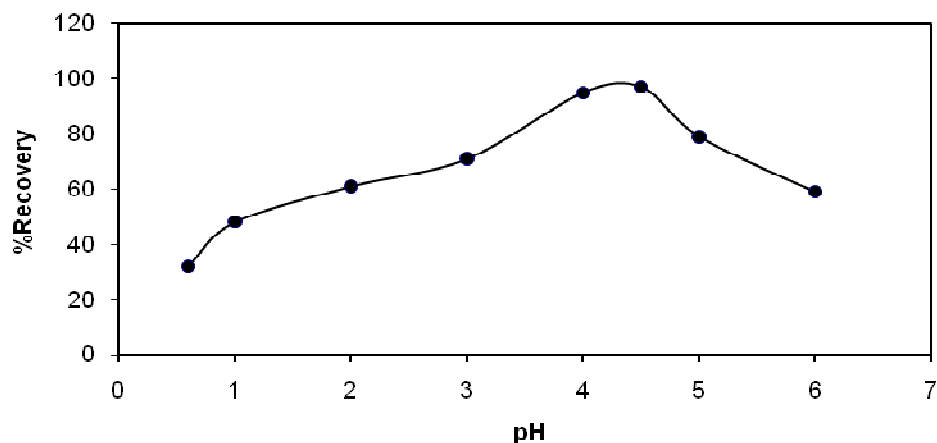
The GO-APTES material forms a stable dispersion in DMF at a concentration not exceeding 1 mg mL<sup>-1</sup>. The electronic absorption spectrum of GO-APTES in DMF (Figure 3), shows (i) a broad signal monotonically decreasing from the UV to the visible region, which is attributed to GO and (ii) a characteristic band at 420 nm (Soret-band) corresponding to the covalently grafted APTES units (the Q-bands at 516, 557, 589 and 648 nm were flattened to the base line in the GO-APTES material). Interestingly, the absorption of porphyrin in the GO-APTES material is broadened, shortened and bathochromically shifted (ca. 2 nm) as compared to that

**Table 2.** The effect of presence of GO-APTES on extraction percent of Ni(II)<sup>a</sup>.

| GO-APTES | pH  | Extraction percent of Ni (II) |
|----------|-----|-------------------------------|
| Absence  | 2-6 | 0.03(7.3) <sup>b</sup>        |
| Presence | 2-6 | 98.9(2.5) to 63(2.2)          |

<sup>a</sup>Initial samples contained 10µg of Ni (II) in 100mL of water.

<sup>b</sup>Values in parentheses are RSD<sub>s</sub> based on five individual replicate analyses.

**Figure 4.** Influence of sample pH on the percentage recovery of Ni (II).

of the free APTES, a result that corroborates not only the linkage of porphyrin with the GO sheets but also electronic interactions between the two species (i.e. GO and APTES) in the ground state. These results are in agreement with studies based on other hybrid systems consisting of porphyrins covalently grafted to carbon nanotubes and nanohorns (Karousis et al., 2011).

### Evaluation of the role of the GO-APTES

Some preliminary experiments were performed for investigation of absence or presence of GO-APTES on the quantitative extraction of Ni (II). It was concluded that the membrane disk itself does not show any tendency for the retention of Ni (II), but introduction of 100mL portions of aqueous Ni (II) samples containing 10µg of Ni (II) and 10mg of GO-APTES leads to satisfactory its retention (Table 2). The latter case is most probably attributed to the existence of a considerable interaction between Ni (II) and the GO-APTES. It should be mentioned that formation of stable complexes between Ni (II) and GO-APTES at pH=2 is probably due to an ion pair formation mechanism. However, at pH higher than 2 the retention and percentage recovery of Ni (II) are negligible.

### Choice of effluent

In order to select the most appropriate effluent for the

quantitative stripping of the retained Ni (II) on the disks, 5mL of various non organic (each containing 10% V.V-1 methanol) and different organic solvents were tested. The results tabulated in Table 2. As can be seen, the best eluting solvents were found to be 5mL of methanol or ethanol, resulting in quantitative elution of Ni (II) from the disk. It should be emphasized that presence of methanol in any kind of employed solvents helps to better the contact of effluent with hydrophobic surface of the disk.

### Choice of pH

The pH of the sample solutions were adjusted to different values between 2-9 by addition of HCl or a buffer such as CH<sub>3</sub>COONa- CH<sub>3</sub>COOH or NaH<sub>2</sub>PO<sub>4</sub>, and then solutions passed through the sorbent.

Usually, the metal ions were stripped by pure methanol solutions followed by FAAS determination of the eluted Ni (II). Then, percentage recovery at various pH values was determined (Figure 4). According to the results shown in Figure 4 up to pH 4.0-4.5, complete percentage recoveries are obtained. However, at higher pH values, recovery decays. This is due to fact that in an acidic solution the protonation of GO-APTES occurs and there is a weak tendency for retention between Ni (II) and GO-APTES, whereas at higher values (pH>5), Ni (II) reacts with hydroxide ions to Ni(OH)<sub>2</sub>. Therefore, CH<sub>3</sub>COONa- CH<sub>3</sub>COOH buffer with pH=4.5 was used for the preconcentration step. Other solvents used for

**Table 3.** Effect of different eluting solvents on Percentage recovery of Ni (II) adsorbed on the disk<sup>a</sup>

| Stripping solution                                 | % Recovery             |            |           |
|--|------------------------|------------|-----------|
|  | 2mL                    | 5mL        | 10mL      |
| Methanol   | 82.3(2.6) <sup>b</sup> | 92.5(2.7)  | 98.7(2.0) |
| Acidified methanol <sup>c</sup>                    | 54.5(2.3)              | 83.5(2.6)  | 83.8(2.9) |
| Ammoniacal methanol <sup>d</sup>                   | 53.4 (2.5)             | 87.5(2.6)  | 86.3(2.8) |
| Ethanol  | 82.5(1.3)              | 99.6(1.5)  | 99.0(2.3) |
| Acetonitril  | 36.6(4.3)              | 46.5(5.5)  | 69.5(2.9) |
| Formic acid(1M)10% V.V <sup>-1</sup> mthanol       | 55.2(1.2)              | 68.3(2.0)  | 71.5(2.8) |
| Hydrochloric acid(1M)10% V.V-1 mthanol             | 54.3(1.9)              | 92.0(2.6)  | 91.6(2.0) |
| Hydrochloric acid(1M)10% V.V <sup>-1</sup> mthanol | 55.6(2.5)              | 65.3 (2.5) | 97.7(1.6) |
| Nitric acid(2M)10% V.V <sup>-1</sup> mthanol       | 59.8(1.9)              | 85.9(2.3)  | 85.4(2.0) |
| Nitric acid(1M)10% V.V <sup>-1</sup> mthanol       | 64.0(2.5)              | 85.8(2.1)  | 87.7(1.6) |
| Ethanol  | 85.1(2.8)              | 95.7(2.0)  | 97.7(2.2) |

a Initial samples contained 10 µg of each Ni in 100 mL water.

b Values in parentheses are RSDs based on five individual replicate analysis.

c Acidified solvents obtained by addition of 0.1M HCl.

d Ammoniacal solvents obtained by addition of 0.1M NH<sub>3</sub>

**Table 4.** Percent recovery of Ni from the modified membrane disk in the presence of 0.01 M of different counter anions<sup>a</sup>

| Counter anion                 | %Recovery |
|-------------------------------|-----------|
| Cl <sup>-</sup>               | 13.8      |
| Br <sup>-</sup>               | 23.9      |
| ClO <sub>4</sub> <sup>-</sup> | 35.0      |
| SCN <sup>-</sup>              | 45.8      |
| Picrate                       | 76.9      |
| Acetate                       | 98.7      |

<sup>a</sup>Initial samples contained 10µg of Ni (II) in 100mL of water.

dissolving GO–APTES were methanol. The influences of these solvents on the percentage recoveries as a function of pH are compared and shown in Figure 4. Meanwhile, other organic solvents were not tested because of their restricted solubility and formation of two phases with aqueous solutions and incompatibility with flame higher pH values (>7) were not tested because of the possibility of the hydrolysis of C<sub>18</sub> in the disks (Moghimi 2007). Ni (II) ions can be retained quantitatively by the modified membrane disk through the pH range from 4.0 to 4.5 However, at lower pH (< 4.0), nitrogen atoms of the GO–APTES could be protonated and the stability of complex is reduced.

#### Effect amount of counter anion

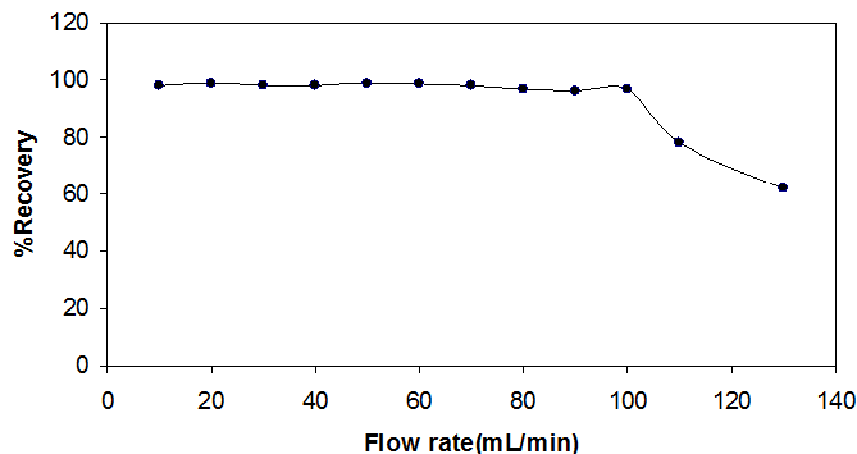
In order to investigate the effect of counter ion on the recovery Ni<sup>2+</sup> ions by the modified disks, different counter anions were tested Table 4, it is immediately obvious that the nature of the counter anion strongly influences the retention of Ni<sup>2+</sup> ions by the disk. The results revealed

that the GO–APTES behaves in pH range 4.0-4.5 (Leilei et al., 2013) so that the Ni<sup>2+</sup> ions are retained as ion pair complexes by the membrane disks. As seen, CH<sub>3</sub>COO<sup>-</sup> ion is the most efficient counter anion for the SPE of Ni<sup>2+</sup> ions. The influence of the concentration of CH<sub>3</sub>COONa ion on Ni recovery was investigated, and the results are shown in Table 4. As seen, the percent recovery of Ni<sup>2+</sup> increased with the CH<sub>3</sub>COO<sup>-</sup> concentration until a reagent concentration of about 0.1 M is reached, beyond which the recovery remained quantitative.

Moreover, acetate ion acts as a suitable buffering agent, while it effectively contributes to the ions- pair formation; thus, in the SPE experiments, there was no need for the addition of any buffer solution.

#### The influence of flow-rate

One of the most important parameters affecting solid phase extraction is the speed of the process. Hence, the effect of flow-rates on extraction efficiencies was investigated. It was found that in the range of 10-100



**Figure 5.** The effect of the flow-rate on extraction percent of Ni (II).

**Table 5.** Influence of the GO-APTES amount on the recovery of Ni (II) ions a.

| GO-APTES amount (mg) | Recovery(%) of Ni (II)  |
|----------------------|-------------------------|
| 2                    | 34.25(2.6) <sup>b</sup> |
| 5                    | 44.46(2.0)              |
| 8                    | 83.20(2.6)              |
| 10                   | 95.5(2.5)               |
| 15                   | 98.5(2.5)               |
| 20                   | 98.6(2.8)               |

<sup>a</sup>Initial samples contained 10 µg of each Ni in 100 mL water.

<sup>b</sup>Values in parentheses are RSDs based on five individual replicate analysis.

mL.min<sup>-1</sup>, the retention of Ni (II) was not considerably affected by the sample solutions flow-rates and leads to reproducible and satisfactory results (Figure 5). Thus, the flow-rate was maintained at 89mL.min<sup>-1</sup> throughout the experiment.

### Quantity of the GO-APTES

The optimum amount of GO-APTES for the quantitative extraction of Ni (II).was also investigated by adding various amounts of it to solution (between 2-20 mg). The results are listed in Table 5. The experimental results revealed that the extraction of Ni (II).was quantitative using a sample solution containing more than 10 mg GO-APTES. Hence, subsequent extractions were performed with 15mg of GO-APTES.

### Disk efficiency

Undoubtedly, one of the major parameters affecting in the SPE determinations is the efficiency of the used

membrane disks. However, to the best of our knowledge this case has not been discussed elsewhere in similar reports. Under the optimum experimental conditions, it was found out that each ENV-18 DISK™ disk could perform at least 14 replicate analyses if organic eluting solvents are used. On the other hand, acidic, effluents practically decrease the number of time a disk could be used to 10replicates. These observations are represented in Figure 6.

### Analytical Performance

When solutions of 10µg Ni in 10, 50, 100, 600, 1000, 2000, 2500 and 3000mL solutions under optimal experimental conditions were passed through the disks, the Ni (II).was quantitatively retained in all cases. Thus, the breakthrough volume for the method must be greater than 2500mL, providing a concentration factor of >600. The limit of detection (LOD) of the method for the determination of Ni (II) was studied under the optimal experimental conditions. The LOD based on 3σ of the blank (5mL of methanol) is 5mg per 1000mL.



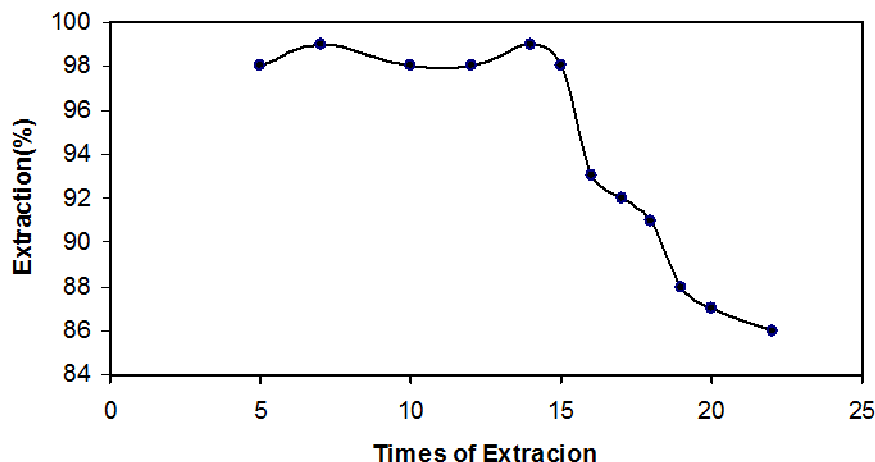


Figure 6. Influence of eluent(5mL of methanol )type on disk efficiency.

Table 6. Separation of Ni from binary mixtures a

| Diverse ion      | Amounts taken(mg) | % Found                | %Recovery of Ni <sup>2+</sup> ion |
|------------------|-------------------|------------------------|-----------------------------------|
| Na <sup>+</sup>  | 92.4              | 1.15(2.4) <sup>b</sup> | 98.5(2.7)                         |
| K <sup>+</sup>   | 92.5              | 1.36(2.3)              | 98.0(2.2)                         |
| Mg <sup>2+</sup> | 24.5              | 0.70(2.6)              | 98.5(1.7)                         |
| Ca <sup>2+</sup> | 26.3              | 2.65(3.0)              | 98.5(1.8)                         |
| Sr <sup>2+</sup> | 2.45              | 2.85(2.1)              | 98.4(2.0)                         |
| Ba <sup>2+</sup> | 3.66              | 3.16(2.1)              | 98.7(2.3)                         |
| Mn <sup>2+</sup> | 2.66              | 1.75(2.2)              | 96.3(2.3)                         |
| Co <sup>2+</sup> | 2.17              | 6.44(2.3)              | 93.0(1.9)                         |
| Cu <sup>2+</sup> | 1.64              | 2.43(2.4)              | 93.7(2.4)                         |
| Zn <sup>2+</sup> | 2.76              | 4.97(2.1)              | 97.6(2.4)                         |
| Cd <sup>2+</sup> | 2.77              | 2.96(2.4)              | 97.2(2.7)                         |
| Pb <sup>2+</sup> | 1.74              | 2.74(1.9)              | 97.7(2.7)                         |
| Hg <sup>2+</sup> | 1.67              | 2.71(2.1)              | 97.7(2.7)                         |
| Ag <sup>+</sup>  | 2.6i              | 3.47(2.9)              | 97.6(2.3)                         |
| UO <sup>2+</sup> | 2.76              | 2.74(2.1)              | 98.3(2.7)                         |

a. Initial samples contained 10 $\mu$ g Ni<sup>2+</sup> and different amounts of various ions in 100 mL water(0.1 M acetate ion).

b Values in parentheses are RSDs based on five individual replicate analysis.

The capacity of modified disks (5mg GO-APTES) was determined by passing 50mL portions of sample solutions containing 8mg of Ni and 0.1M sodium acetate-acetic acid buffer with pH 4.0-4.5, followed by the determination of the retained metal ions in the eluting solution using AAS. The maximal capacity of the disk obtained from three replicate measurements was 398 $\pm$ 3 $\mu$ g of Ni<sup>2+</sup> on the disk.

In order to investigate the selective separation and determination of Ni<sup>2+</sup> ions from its binary mixtures with various metal ions, an aliquot of aqueous solutions (50mL) containing 10 $\mu$ g Ni<sup>2+</sup> and mg amounts of other cations was taken and the recommended procedure was followed. The results are summarized in Table 6. The results show that the Ni (II) ions in binary mixtures are retained almost completely by the modified disk, even in the presence of up to about 100mg of various ions.

Meanwhile, retention of other cations by the disk is very low and they can separated effectively from the Ni<sup>2+</sup> ion. Its is interesting to note that, in other experiments, we found that in the presence of high enough concentrations NH<sub>2</sub>OH.HCl as a suitable reducing agent(> 0.5M) (Moghimi 2007).

#### Analysis of water samples

In order to assess the applicability of the method to real samples, it was applied to the extraction and determination of Ni from different water samples. Tap water(Tehran, taken after 10 min operation of the tap),rain water (Tehran, 20January, 2013), Snow water (Tehran, 16 February, 2013) and Sea water(taken from Caspian Sea, near the Mahmoud-Abad shore) samples



**Table 7.** Recovery of Ni added to 1000mL of different water samples (containing 0.1M acetate at pH= 4.0-4.5).

| Sample     | Ni <sup>2+</sup> added (µg) | Ni <sup>2+</sup> determined(ng.mL <sup>-1</sup> ) | ICP-AES |
|------------|-----------------------------|---|---------|
| Tap water  | 0.0                         | 1.72(2.8) <sup>a</sup>                            | ND      |
|            | 10.0                        | 11.93(2.0)  | 11.8    |
| Snow water | 0.0                         | 4.85(2.5)   | ND      |
|            | 10.0                        | 14.94(2.6)  | 14.5    |
| Rain water | 0.0                         | 2.65(2.3)   | ND      |
|            | 10.0                        | 12.85(2.4)  | 12.9    |
| Sea Water  | 0.0                         | 12.96(2.3)  | 12.8    |
|            | 10.0                        | 22.50(2.5)  | 23.0    |

a Values in parentheses are %RSDs based on five individual replicate analysis

b Not detected.

were analyzed (Table 7). As can be seen from Table 4 the added Ni ions can be quantitatively recovered from the water samples used. As is seen, the recovered Ni ion reveals that the results are quite reliable and are in satisfactory agreement with those obtained by ICPAES.

## CONCLUSION

Results presented in this work demonstrate well the tremendous possibilities offered by the solid phase extraction of trace amounts of Ni (II) in water samples using Octadecyl Silica membrane disks modified by (GO-APTES) and its determination by FAAS. The developed method was simple, reliable, and precise for determining Ni in water. In addition, the proposed method was free of interference compared to conventional procedures to determine Ni (Moghimi et al., 2012; Zargarani et al., 2008). The method can be successfully applied to the separation and determination of Ni in binary mixtures.

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