

## An Alternative Method Extraction of Trace Amounts of Cobalt (II) in Water Samples by Modified Nano Nickel Oxide

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### ABSTRACT

Metal nanoparticles have been studied for decades, and this is due to the properties that these materials do not have in bulk state. In nanoscale materials, the number of surface atoms is high and hence, have significant surface effects. In this proposed method for pre-concentration and measuring the trace amounts of cobalt (II) ions in aqueous samples, the modified nanostructured nickel oxide was used to improve the preconcentration and extraction procedure.  $\text{Co}^{2+}$  ion concentration in aqueous solution was carried out using flame atomic absorption spectrometry. Extraction parameters including, the effect of pH, amount and type of cleanser solvent, extraction time and the effect of other ions and..., were optimized. The enrichment factor of 36, the limit of detection of (LOD) method of  $1.768 \mu\text{g.L}^{-1}$  and relative standard deviation (RSD %) of 0.75% were obtained, respectively. The methodology was applied for determination of cobalt (II) in natural water samples and satisfactory results were obtained.

**Keywords:** modified nanonickel oxide, flame atomic absorption spectrometry, Co (II).

### INTRODUCTION

Detection and cleanup of toxic pollutants, especially heavy metal ions which are extremely dangerous for environment and living things, is a key issue to protect the environment. Biological samples or samples taken from natural resources, often contain very complex compounds which interfere in the process of decomposition and measurement as disturbing factors, or amounts of pollutants are so insignificant that may not be measurable even by the strongest detection systems or be incompatible with decomposition processes. As clear, the same small quantities of some hazardous materials have harmful biological effects. Therefore, highly sensitive and specific methods are required to be studied and developed, so that the trace amount of contaminants in the sample can be measured precisely and with high accuracy. Over the past few decades, tremendous growth has seen taken place in the use of sample measurement techniques. Analytical devices such as chromatography, spectroscopy, microscopy as well as micro sensors and instruments have been influenced by these developments. But despite the progress in the construction of analytical tools, extremely precise and non-destructive measurements, is not possible yet in most cases. So in order to help to improve existing methods,

in most cases, sample preparation in one or more steps is essential [1]. These advantages include: speed of analysis, easy process, possibility of automatic process, analysis of very trace amounts of analyte, concentration and cleaning of the samples, allowing the storage and transport of samples from the site, sampling to the analysis site, the use of low volume of organic solvents which most are toxic [2]. Metal oxides are important in many areas of chemistry, physics and materials science. In industrial applications, oxides used as in the production of microelectronic circuits, sensors, piezoelectric fuel cell devices, coating surfaces to disable against corrosion and also as catalysts.

The most active production technologies are plasma processes. There are several types of plasma methods. A study by Vollath in (2007) demonstrated that using metal precursors and using a plasma production methods, different nanoparticles can be produced [3]. Nanoparticles produced with this method are of proper distribution. But one of the limitations of these methods, is agglomeration of nanoparticles. To prevent the agglomeration in these methods, the low pressure microwave plasma process can be used. With this method, coating production is possible as well. Another method of synthesis of these materials is

synthesis methods based on laser vaporization, which may occur in the liquid or gas phase. In the latter case, the laser energy evaporates the metal from an appropriate target. Nanoparticles germinate from the metal in the gas phase. In the gas phase, sintering and agglomeration of particles take place. In the liquid phase, metal powder suspend in a carrier liquid and are driven into the laser. The particle size can be controlled by surfactants. Coating metal nanoparticles greatly increases their value, this is due that using this coating improves their resistance against oxidation. In addition, the carbon coating reduces the surface energy of particles, helps chemical bonds to lead to the formation of organic matters, and greatly affects the electromagnetic properties of materials. In biological applications, the coating also reduces the toxic effects of metal nanoparticles. In addition, the range of methods to create these particles is much wider. Therefore, the carbon is a common surface coating material for metal nanoparticles. This is a functional issue, for example the following examples can be mentioned: carbon coating in particles may be tens of nanometers thick and be amorphous or graphite. Other materials used in the coating of particles include polymers and silica. These coatings can be applied separately after production of nanoparticle or using a liquid method, on the nanoparticles. Of course, among the materials used for coating, carbon is one of the important materials.

Nickel oxide is of the transition metal oxides. Several studies have been conducted in recent years on the interesting electronic and magnetic properties of these materials [5]. NiO is an anti-ferromagnetic material with a Neel temperature over 524 °K [6]. Neel temperature of other anti-ferromagnetic transition metal oxides, is near or below room temperature. Therefore, investigation of the magnetic properties of nickel oxide is very interesting. In a pure ion image, nickel ions have an electron configuration of  $3d^8$  with the +2 ionic charge, and oxygen atoms with electron configurations as  $2p^6$  and ionic charge of -2. Since the *d* band of nickel is not completely filled, nickel oxide must be a conductor. However, the volume sample of nickel oxide (NiO) has a very high resistance and acts as a nonconductor. Nickel oxide conductivity is very low at room temperature and is of the order of  $10^{-11} \text{ohm}^{-1} \text{m}^{-1}$  [7]. Nickel oxide band gap has been reported about 3.5eV to 4 eV in the literature. This wide

band gap seems to be resulted from a strong on-site repulsion between 3d electrons of nickel, which increases the energy of one ion Ni with another one, such as ninth electron of 3d [8]. Nickel oxide conduction is inhibited by various impurities and lattice defects which exist even in the best crystal growth states.  $\text{Li}^+$  impurities are commonly used to reduce NiO resistance. For charge neutrality, one  $\text{Ni}^{2+}$  ion is produced per  $\text{Li}^+$  ion in the network. An  $\text{O}^{2-}$  vacancy can be replaced by two  $\text{Li}^+$  ions. Since an ion  $\text{Ni}^{3+}$ , is equivalent to a  $\text{Ni}^{2+}$  ion with an additional hole,  $\text{Li}^+$  impurity atoms acts as acceptors and conductivity type is p. In non-doped samples, the conductivity is p-type as well, which indicates that the single capacity impurities are suitable to increase the conductivity of nickel oxide. In the Stoichiometricnickel oxide, there is no Ni vacancy and thus is a nonconductor. But in non-stoichiometric nickel oxide thin films, conductivity increases significantly due to holes created through Ni vacancies in the network. Resistivity of nickel oxide films depends on Cation vacancy density (Ni) [9]. Nickel oxide layer resistance decreases by increasing  $\text{Ni}^{3+}$  ions [10 -23].

The most important of these elements in general are, lead, cadmium, chromium, cobalt, mercury, nickel, zinc, vanadium and other metals that are associated with toxic contamination. It can be said that the distribution of cobalt is very much in the body of living things and is in charge of different functions in plants and animals. Its little amount in the water is toxic for bacteria and single-celled organisms. Cobalt is one of the minor metals required in trace amounts in formation of the erythrocytes and hemoglobin, also its existence is essential for a number of oxidizing enzymes such as Katalaz, peroxidase and cytochrome oxidase, and others. Cobalt is important in cases such as preserving immune function of the body, bone strength, red and white blood cell development, cholesterol and glucose metabolism, preventing inflammation damages, maintaining a healthy heart and brain development. In 2005 Kasla et al, developed a new method for determination of trace amounts of cobalt using a coupled flow injection system and using solid phase extraction and FAAS as detector. Under optimal conditions of pH = 9 and leaching with hydrochloric acid 0.2 molar with preconcentration volumes of 2.13 and 4.26 ml, detection limit values of cobalt has been reported respectively as 1.1 and 0.9 ml/g, the relative standard deviation as 1.0 and 5.3%,

respectively, and sampling frequency of 25 and 13 samples per hour [24]. El Sheikh in 2008, measured cobalt (II) in piping water, reservoir water, and river water by flame atomic absorption spectroscopy. Activated carbon (oxidized by nitric acid, hydrogen peroxide and ammonium per sulfate) as solid phase was compared with oxidized and raw carbon nanotubes. Multi-walled nanotubes of external diameter of 10-30 and a length of 5  $\mu\text{m}$  were used – the detection limit was obtained as  $9\text{-}37\text{ngL}^{-1}$  [25]. In 2009 Khosravan et al, used a column filled with silica gel modified with 2-Amino thiophenol for pre-concentration of cobalt with FAAS. In this method, the inhibited cobalt filled in the ambient with  $\text{pH} = 5$  in a glassy column, has been leached with absorbent material with nitric acid detergent with a flow rate of 2 ml per minute. In this method, the detection limit and relative standard deviation of seven repetitive measurements for concentrations of 0.1 mg per liter, were obtained respectively as 0.125 nano-grams per milliliter and 1.8% [26]. Ozkan et al. in 2010, measured Co (II) in water and food samples by flame atomic spectroscopy. Multi-walled carbon nanotubes with outer diameter of 15-65 nm and a length of 10-50  $\mu\text{m}$  were used. Solid phase extraction was carried out steadily in the column. The limit of detection was obtained as  $3.5\text{ ngL}^{-1}$  and the recovery percentage as 99% [27]. In 2014, Mr. Pourreza and Rastgarzadeh studied nano-TiO<sub>2</sub> modified with MBT as a new absorbent for preconcentration of cadmium and cobalt. They adsorbed metal ions on the TiO<sub>2</sub>-MBT nanotubes, washed with nitric acid and examined with flame atomic spectrometry. This procedure was used for determining the cadmium (II), cobalt (II) and Pb (II) in water samples and ore.

Detection limit for cadmium, cobalt, and lead was respectively, 0.12, 0.15, and  $1.38\text{ ngml}^{-1}$  [28]. In 2015, a new method of solid-phase extraction was provided for description of cobalt (II), cobalt (II) and Ni (II) covered with silica gel as an adsorbent. The proposed method can be suggested as an accurate, easy and inexpensive way to determine cobalt (II), cobalt (II) and nickel (II) [29]. In 2016, Zhou et al., proposed a simple method for solid-phase extraction of chromium (III), iron (III), cobalt (II) and manganese (II) in wastewater by graphene oxide carbon nanotubes. The limit of detection based on the GO-MCNTs-DETA, has been reported respectively 16, 50, 24, and

$1.38\text{ngml}^{-1}$ , respectively for chromium (III), iron (III), cobalt (II) and manganese (II) [30].

In the present work, modified nano structured nickel oxide was employed for production of solid phase. The synthesized and characterized new sorbent modified nano structured nickel oxide was utilized for preconcentration of cobalt (II) from water samples. Determination of cobalt (II) concentration was achieved by FAAS after preconcentration procedure.

## EXPERIMENTAL

### Instrumentation

Determination of  $\text{Co}^{2+}$  by PG-990 flame atomic absorption spectrometer equipped with HI-HCL according to the recommendations of the manufacturers. These condition are tabulated in (Table 3). The pH measurements used by Sartorius model PB-11.

### Chemicals and Reagents

$\text{Co}(\text{NO}_3)_2$  were prepared from Darmstadt, Germany of Merck, 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 [17]. All solutions were prepared with doubly distilled deionized water from Darmstadt, Germany of Merck.  $\text{C}_{18}$  powder for chromatography with diameter of about  $50\text{ }\mu\text{m}$  obtained from Katayama Chemicals from Supelco. It was conditioned before use by suspending in 4 M nitric acid for 20 min, and then washed two times with water.

### Preparation of Solutions and Standards

Preparation of  $\text{Co}^{2+}$  solution with a concentration of 1000ppm: was prepared solving 0.33 grams of cobalt nitrate and bringing to the volume of 100 mL. Required solutions were prepared by diluting the stock solution.

Through consecutive dilution of 1000ppm solution, solutions with concentrations of (100, 50, 10, and 2 ppm) were prepared, and from 10 ppm solution, solutions with concentrations of (10, 5, 3, 1, 0.5 ppm) were prepared as standard.

### Method of Preparation of Nano Nickel Oxide

For this purpose, the three following solutions were provided.

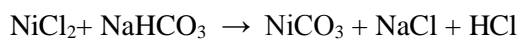
Beaker A: 0.46grams of nickel chloride is dissolved in 20 ml of distilled water.

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Beaker B: 2 g of CTAB is dissolved in 200 cc of distilled water.

Beaker C: 3 g of NaHCO<sub>3</sub> is dissolved in 20 ml of distilled water.

Then beaker A was stirred for 30 minutes with a stirrer and beaker B was added to it drop by drop. After one hour of stirring, beaker C was added drop by drop, then after one hour of stirring, the sediment was separated from the funnel and then rinsed with distilled water and ethanol, then dried in a 100 °C oven for 3 hours and then was placed in the oven for 2.5-3 hours at 600 degrees, until the deposition of nickel oxide nanoparticles obtained [31]. Here CTAB has the molecular framework and is used for the stability of the structure of nickel oxide and nickel oxide particles' small dimensions, and because of being an organic material, burns and disappears during the reaction. The formation mechanism of nano nickel oxide with the deposition method is as follows:



### Initial Co<sup>2+</sup> Extraction and Recovery Test to Determine the Appropriate Ligand

Extraction and recovery of cobalt ion by nickel oxide nanoparticles is as follows: 50 mL of 2 ppm solution was provided in pH of 2.5 set relative to Co<sup>2+</sup>, and 0.05 g of nano-nickel oxide and (100ppm) 2mL of lig and were added to it. The resulting mixture is placed inside the shaker for 20 minutes, and at a speed of 150 and temperature of 25 °C, and then the mixture is centrifuged, and the concentration of Co<sup>2+</sup> was measured by flame atomic absorption spectrometry. This experiment is performed once more without adding ligand.

### Effect of pH on the extraction and recovery of Co<sup>2+</sup>

To investigate the effect of pH on Co<sup>2+</sup> ion adsorption, first a number of 2ppm solutions of volume 50 mL relative to Co<sup>2+</sup> were prepared, in which the effect of aqueous solution on recovery of ion Co<sup>2+</sup> at pH 2, 2.5, 3, 4, 5, 6, 10 was examined. The buffer was used to adjust the pH. The method applied to adjust the pH of the solution was as the 2ppm solutions are poured inside the beaker and pH meter electrode is floated inside it and by adding highly suitable volumes of buffer, the pH is set to the desired

values (2, 2.5, 3, 4, 5, 6, and 10). After adjusting the pH of the solution, 0.05g of nano nickel oxide adsorbents was added to each solution, and were placed for 20 minutes in the shaker, and then the above mixture was centrifuged and the solution above the test tube was put aside and the concentration of Co<sup>2+</sup> inside it was measured by the flame atomic absorption spectrometry.

### Effect of adsorbent amount to recover Co<sup>2+</sup>

First, 7 solutions of 1.0 ppm with a volume of 50 mL relative to Co<sup>2+</sup>, were prepared and poured within seven flasks and the solutions were adjusted at a pH of 5 (optimum pH), and different values of nano nickel oxide (0.01, 0.05, 0.07, 0.09, 0.11, 0.15, 0.2 g) were added, and were placed into a shaker for 20 minutes and then, the above mixtures were centrifuged, then the solution above the test tube was measured by flame atomic absorption spectrometry.

### Stirring effect on the extraction and recovery of ion Co<sup>2+</sup>

For this purpose, first 5 balloons were selected, and 0.5 ml of 100 ppm cobalt nitrate solution along with 1 mL of buffer 5 were poured into each solution and were reached to the volume. Then, 0.07g of adsorbent was added to them and were placed inside the shaker for times (25, 15, 10, 6, 2) minutes, then were centrifuged and the top solution absorption was determined by flame atomic absorption spectrometry.

### Effect of different detergents to recover ion Co<sup>2+</sup>

First, 6 solutions of 1.0 ppm with a volume of 50 mL relative to Co<sup>2+</sup>, were prepared and poured within six flasks and the solutions were adjusted at a pH of 5 (optimum pH), and 0.07g of nano nickel oxide was added, and were placed into a shaker for 15 minutes and then, the above mixtures were centrifuged, then the top solution is put aside and the sediment obtained is poured into the flasks and into which, 7mL of the following detergents HNO<sub>3</sub>(0.1M), HNO<sub>3</sub>(1M), HNO<sub>3</sub>(3 M), NaOH (0.1 M), H<sub>2</sub>SO<sub>4</sub>(0.1 M), and H<sub>2</sub>SO<sub>4</sub>(0.1 M) were added and then put inside the shaker for 20 minutes then the resulting mixture was centrifuged and the concentration of Co<sup>2+</sup> of the top solution of the test tube was measured by flame atomic absorption spectrometry.

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### *Optimizing volume of the eluting solvent to recover Co<sup>2+</sup> ion*

In order to select the suitable solvent volume to recover ion Co<sup>2+</sup>, first inside 5 small flasks, an amount of 50 mL of 1.0 ppm solution relative to Co<sup>2+</sup> adjusted at a pH of 5, and 0.07g of nano nickel oxide was added to each of them, and were placed into a shaker for 15 minutes and then, the above mixtures were centrifuged, then the top solution is emptied and the sediments are poured into the 5 flasks and into which, volumes of (5, 7, 9, 11 and 13 mL) of 1M nitric acid (optimal detergent) are added and the mixture is centrifuged for 20 minutes and then is put inside the shakes and finally, Co<sup>2+</sup> ion concentration of the solution above the centrifuge tube is measured by flame atomic absorption spectrometry.

### *Effect of the volume of the sample solution (determination of the break through volume)*

After finding the best value of sample solution pH and suitable solvent detergent for thorough washing of cobalt (II) off the adsorbent, the maximum volume of aqueous solution containing ion cobalt (II) must be determined. To investigate the effect of the volume of the sample, 6 solutions of 1 ppm cobalt nitrate solution were prepared at the optimum conditions other than pH adjustment, nothing was added to the first solution, but 350, 200, 150, 100, 50 ml of distilled water were added to the first solutions, and the pH was adjusted and then, was stirred inside the shaker for 20 minutes (optimal time) and then the mixture was centrifuged, and finally, was placed back into the shaker and washed with 7 ml of 1M nitric acid for 20 minutes. In the following, the mixture was centrifuged and then the cobalt ion concentration in the top solution of centrifuge tube was measured by flame atomic absorption spectrometry.

### *Determination of standard deviation of the control (Sb)*

First, 4 solutions were made with optimal conditions, then the 5 and 0.07 grams buffer of absorbent were added to them, and brought to the volume. By pH meter, pH was set to 4.9-5 and was stirred inside the shaker and centrifuged, and the supernatant was removed and 7 cc of 1M nitric acid was added to the absorbent and placed back into the shaker. The mixture was centrifuged, and the absorption was

measured by flame atomic absorption spectrometry.

### *Determination of the accuracy and repeatability of the method (% RSD)*

To determine the accuracy, first 4 solutions were made with optimal conditions, then the 5 and 0.07 grams buffer of absorbent and stock solution were added to them, and brought to the volume. By pH meter, pH was set to 4.9-5 and was stirred inside the shaker and centrifuged, and the supernatant was removed and 7 cc of 1M nitric acid was added to the absorbent and placed back into the shaker. The mixture was centrifuged, and the absorption was measured by flame atomic absorption spectrometry.

### *Linear range and calibration curve*

To determine the linear range, first 50 ml of solution (800, 500, 200, 100, 80, 40, 20, 10 ppb) relative to Co<sup>2+</sup> in the pH of 4.9-5 set, were poured into 8 balloons and 0.07g of nano nickel oxide was added to each of them, and were placed into a shaker for 20 minutes and then, the mixture was centrifuged, and then finally washed with 7mL of 1M nitric acid and at last, the mixture was centrifuged and Co<sup>2+</sup> ion absorption in the solution above the centrifuge tube was measured by flame atomic absorption spectrometry.

### *Disturbances on the extraction of Co<sup>2+</sup> ions*

To investigate the effect of disturbing other ions on the extraction of ions Co<sup>2+</sup>, a number of 1ppm solutions relative to Co<sup>2+</sup> set in pH 5 set, were prepared with volume (limit volume) and a certain amount of disturbing factors and diverse ions were added in the initial solution and then, the amount 0.07g of nano nickel oxide was added to each of solutions, and were placed into a shaker for 15 minutes and then, the mixture was centrifuged, and then finally washed with 1M nitric acid and were placed into the shaker for 20 minutes and then, the Co<sup>2+</sup> ion concentration in the solution above the centrifuge tube was measured by flame atomic absorption spectrometry.

### *Application on real samples*

Once the extraction is completed with nano-oxide and optimal conditions for which were found, several water samples were analyzed. Real samples studied include: drinking water, well water, water for fish farming. First, 6 balloons of 100 ml volume were prepared for sampling of each sample. The bottles were

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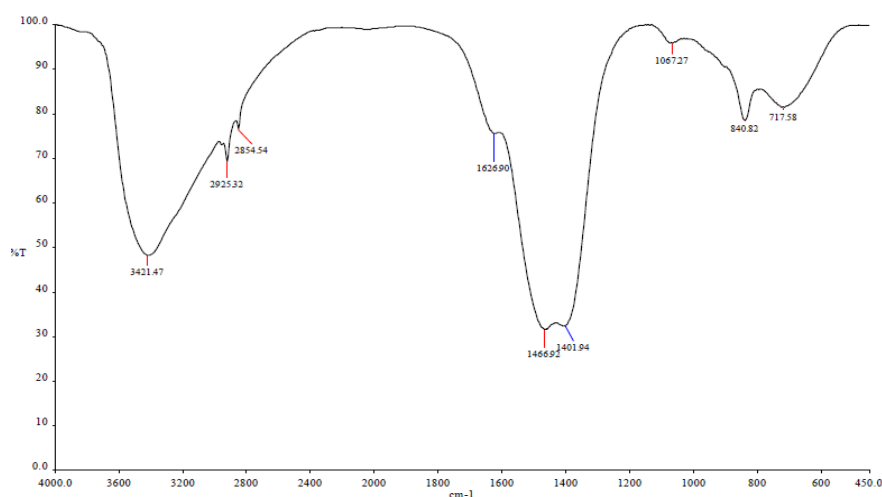
rinsed with tap water and distilled water, after completing drying of balloons, the appropriate label was attached on them. To take water samples, previously cleaned and dried beakers were used. To start the analysis of samples, the colloidal and suspended particles must be taken into consideration; to do this, samples are then passed through a 0.45 $\mu$ m filter, then to 3 of bottles, the drinking water, well water or water for fish farming with 2 ml buffer 5 and 0.07

grams of absorbent are poured and into 3 other bottles, 0.5 mL of 50 ppb stock solution are added, stirred for 15 minutes and the mixture is centrifuged and finally, washed with 1M nitric acid and was placed into the shaker for 20 minutes and then, after centrifuging the mixture, absorption of the cobalt ion in the solution below the filter was determined by flame atomic absorption spectrometry.

### RESULTS AND DISCUSSION

#### Assessment of the Results of FT-IR and XRD Spectrums

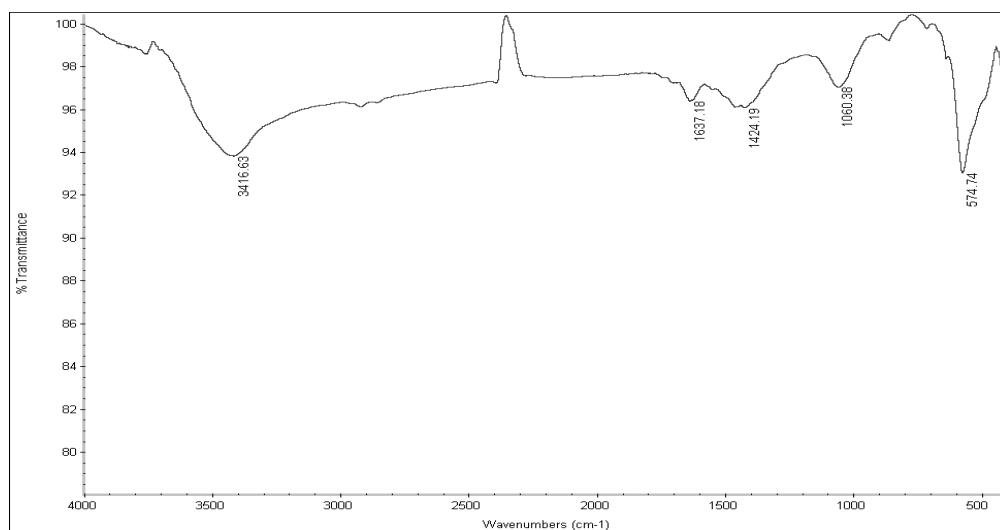
Figure 1. shows the nano nickel oxide Fourier transform infrared spectrum.



**Figure1.** Nano nickel oxide Fourier transform infrared spectrum after the absorption

The IR spectrum of nickel oxide nanoparticles prior to peak absorption can be seen in the area of 1620  $\text{cm}^{-1}$  showing that OH molecule is trapped between Ni and O, and peak observed in

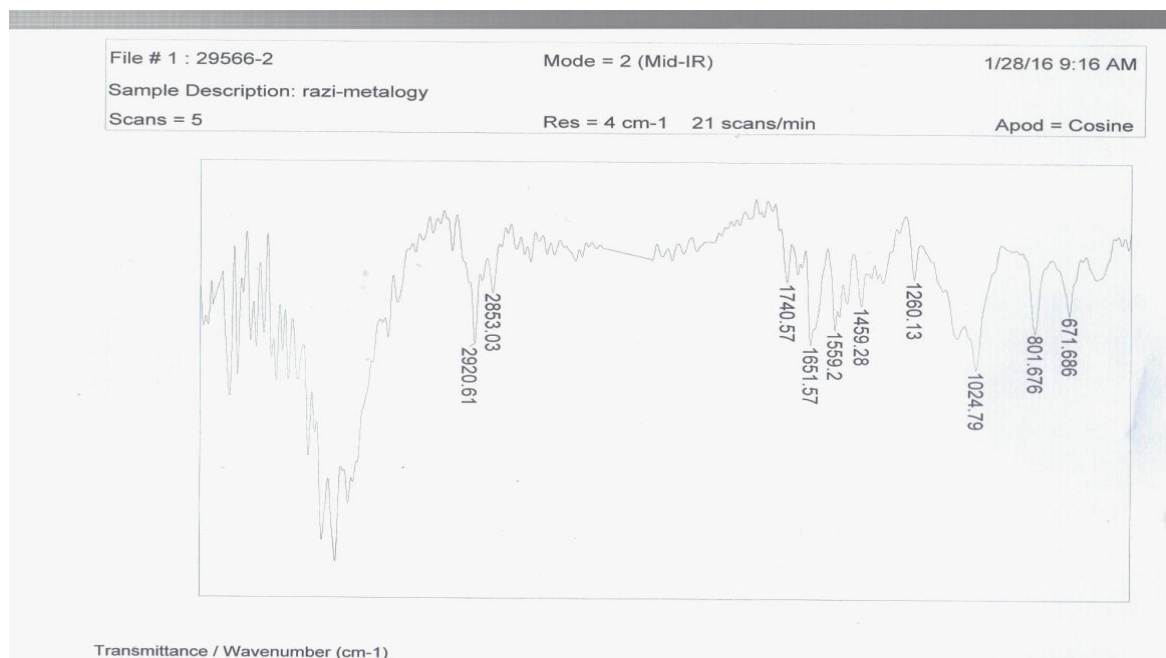
the area 3421  $\text{cm}^{-1}$  and 2925  $\text{cm}^{-1}$ , is related to the OH functional group which can be attributed to water molecules absorbed by NiO.



**Figure2.** Nano nickel oxide Fourier transform infrared spectrum before the absorption

In figure 3, the new peak can be seen also in the area of 1620  $\text{cm}^{-1}$  which represents cobalt metal and the area of 1424  $\text{cm}^{-1}$  represents nitrate as well.

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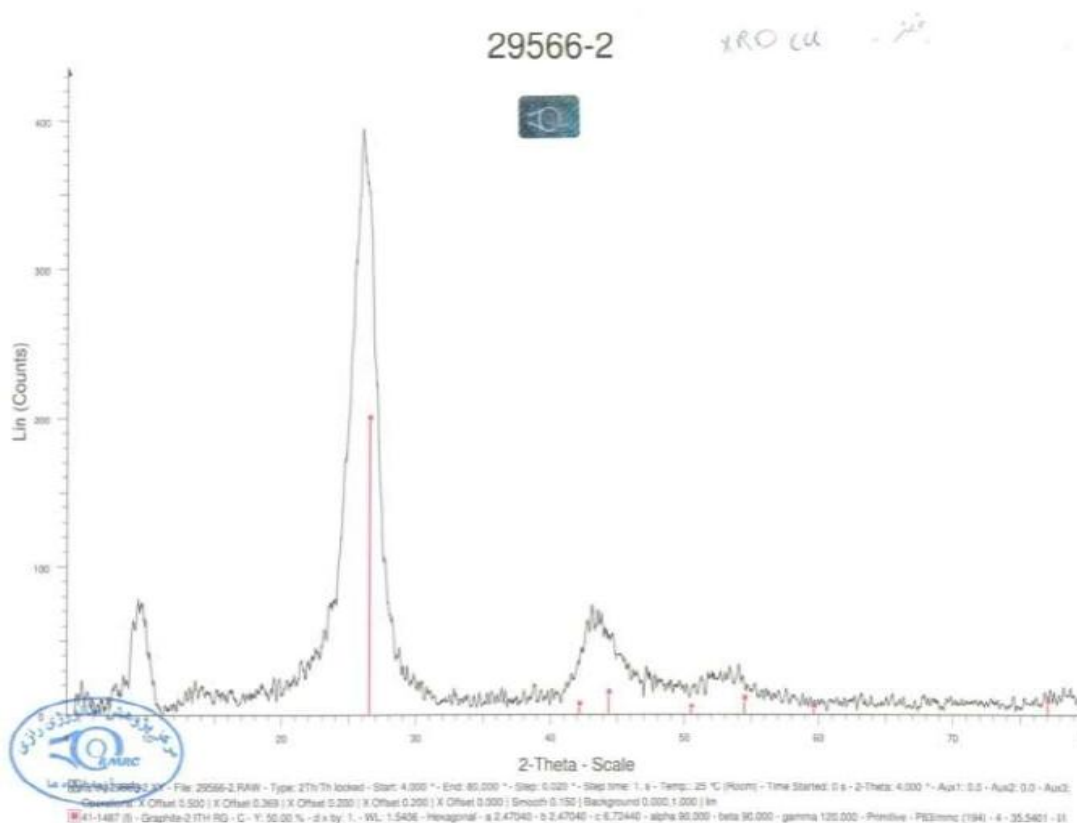
**Figure3.** Cobalt (II) Fourier transform infrared spectrum

This figure shows that cobalt, is absorbed to nano nickel oxide. The two peaks identified in the areas 1400-1500  $\text{cm}^{-1}$ , denote cobalt and nitrate, respectively. And peak 2920  $\text{cm}^{-1}$  is related to OH stretching vibration.

Here Scherrer equation was used to determine the size of nano-nickel oxide. The equation is as follows:

$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad (1-1)$$

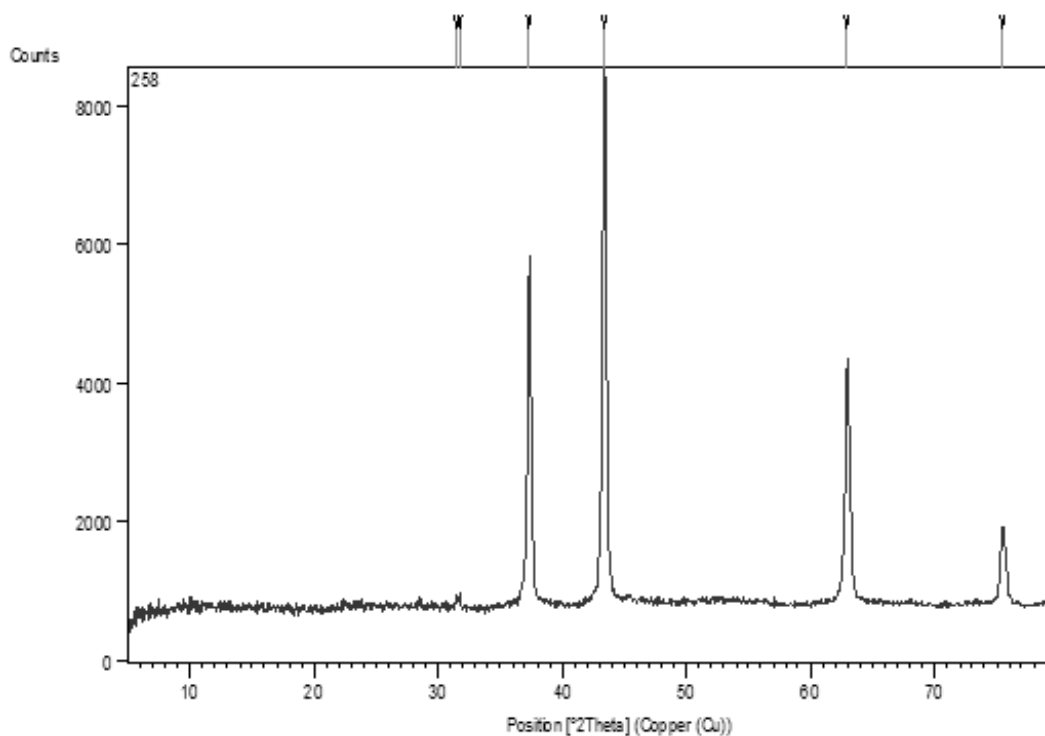
$\tau$ : average crystallite size (nm), K: crystal form factor (usually 0.9 is considered),  $\lambda$ : wavelength of X-ray tube producer (nm),  $\beta$ : peak width,  $\theta$ : diffraction angle.



**Figure4.** Images of XRD spectra of cobalt ion

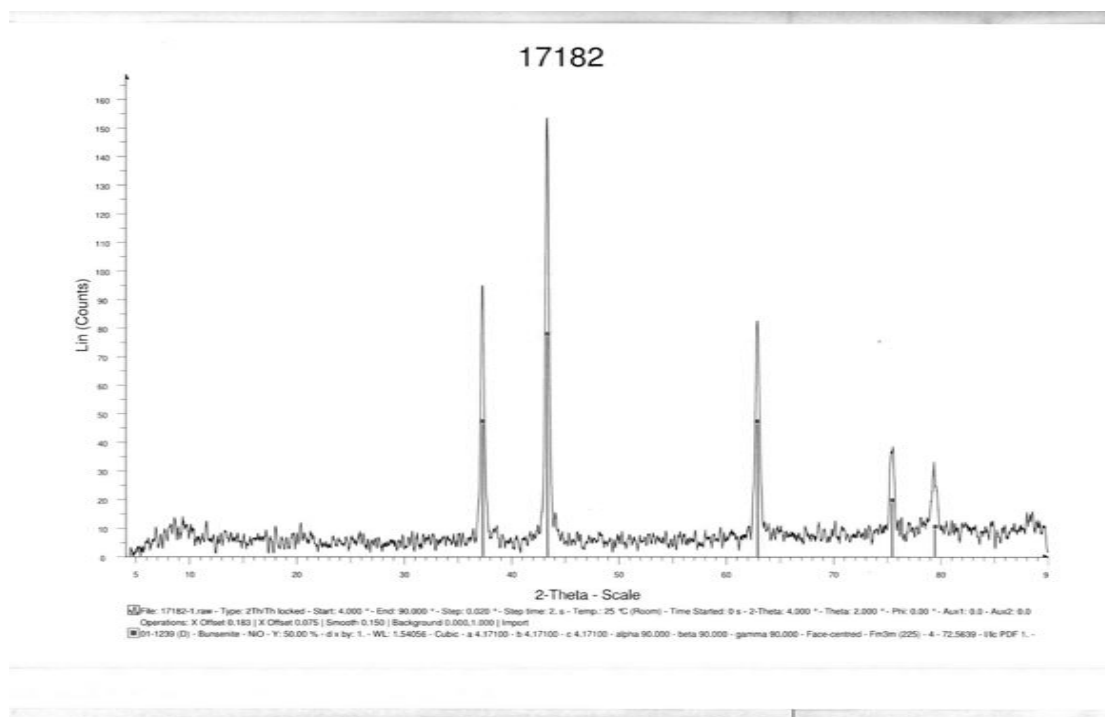
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The following figure shows the diffraction pattern of nano-nickel oxide, which the diffraction peak of  $2\theta = 26.5$  can be observed.



**Figure5.** Images of XRD spectra of nano-nickel oxide before the absorption

XRD spectra of this combination is three peaks with very high intensity, which is related to the nano nickel oxide, which shows the strongest peak in the region of  $2\theta = 43.34$ , and a very weak peak in the region of  $79.43$  degrees, which has respectively, a very sharp and small peaks.



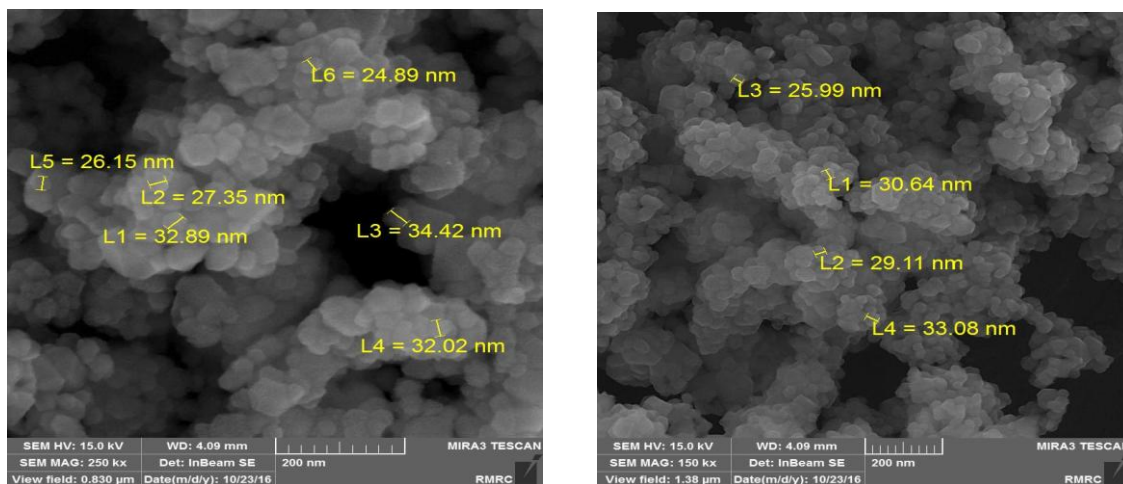
**Figure6.** Images of XRD spectra of nano-nickel oxide after the absorption

### Assessment of the Results of SEM Images

The following figure shows SEM images of nano-nickel oxide.

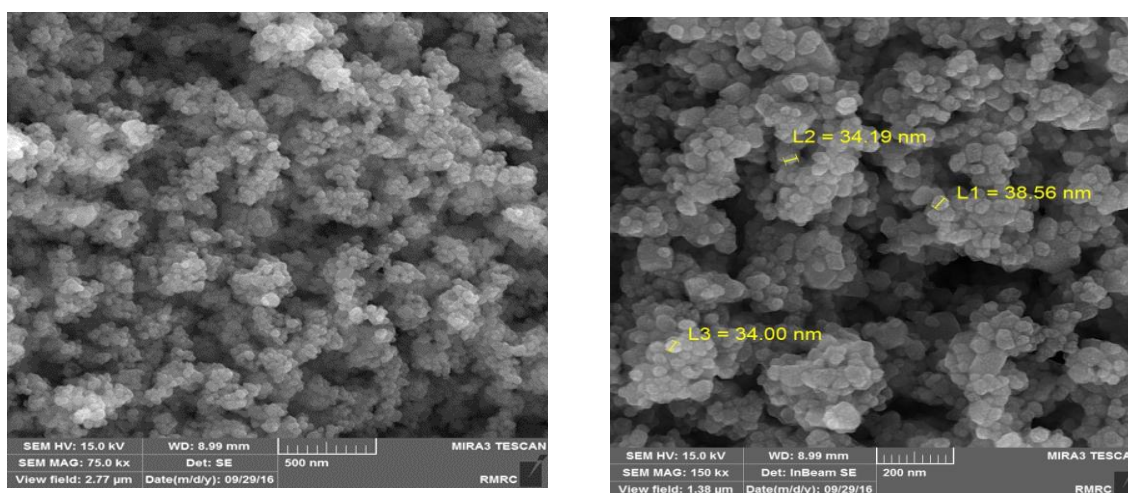


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**Figure7.** Images of SEM of nano-nickel oxide before the absorption

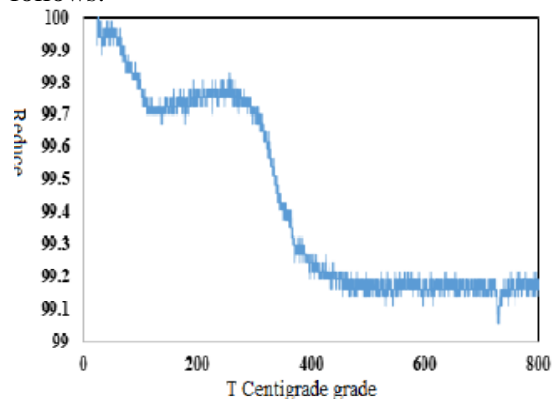
Also the figure after SEM image absorption, shows deposition of the desired metal on nano nickel oxide; it can be concluded from the above images that the thickness of plates has increased.



**Figure8.** Images of SEM of nano-nickel oxide after the absorption

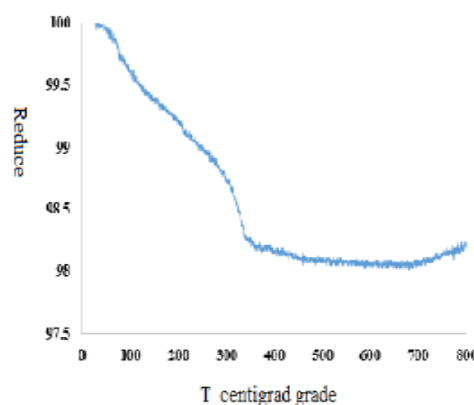
### Results of TGA spectrum

The results of the TGA spectrum in the two steps before and after absorption of cobalt are as follows.



**Figure9.** TGA spectrum of nano-nickel oxide before the absorption

As can be seen, in this spectrum in temperatures of 25 to 210 °C, half of crystallized water (8.8%) and in the second step, at a temperature of 210 to 400 °C, removal of water from Ni(OH)<sub>2</sub> and conversion into NO nanoparticles and 17.7 percent weight loss can be seen.



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**Figure10.** TGA spectrum of nano-nickel oxide after the absorption

In TGA spectrum after the absorption, the change is only seen in one step, which represents cobalt absorbed by the nano absorber.

*Investigation of parameters affecting the extraction and recovery of ion  $Co^{2+}$*

*Investigation of effect of pH on extraction and*

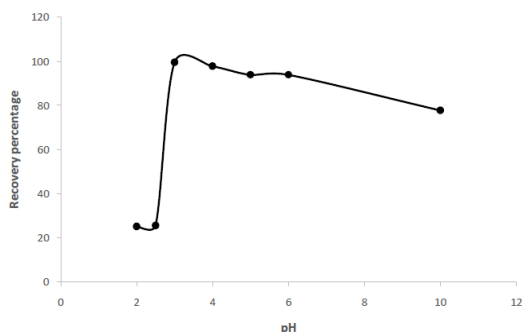
*recovery of ion  $Co^{2+}$*

The results of this survey were demonstrated in (Table 1) and (Figure 13), as the results show in pH = 5, absorption percentage and recovery of cobalt ions reach the maximum and at lower and higher pHs, the absorption rate decreases will, which specifies that the extraction in the amounts of pH>5, can be reduced by nano nickel oxide and in pH<5, inhibition of ions cannot be completely done.

**Table1.** Recovery percentage changes in terms of pH of the sample solution relative to the cobalt (II)

pH	Recovery percentage
2	25(0.9) <sup>a</sup>
2.5	25.5 (0.6)
3	99.5(0.7)
4	97.7(0.3)
5	93.85(0.9)
6	93.85(0.6)
10	77.7(0.5)

a) RSD of measurements after 3 times of repetition



**Figure11.** Recovery percentage changes of cobalt ion recovery relative to pH

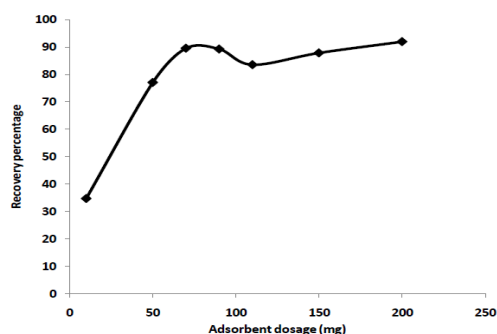
*Assessment of the effect of nano nickel oxide to recover  $Co^{2+}$*

The results of this survey were demonstrated in (Table 2) and (Figure 12), as the results of the table show, in the amount of 0.07grams of nano-nickel oxide, absorption percentage and cobalt ions recovery have reached the maximum.

**Table2.** Recovery percentage changes of adsorbent grams relative to Co (II) ion

Adsorbent dosage (mg)	Recovery percentage
10	34.8 (1.2) <sup>a</sup>
50	77.1 (0.9)
70	89.6 (1.6)
90	89.3 (0.8)
110	83.6 (1.2)
150	87.9 (1.6)
200	92 (1.5)

a) RSD of measurements after 3 times of repetition



**Figure12.** Recovery changes of cobalt ion percentage recovery relative to adsorbent

*Assessment of the effect of mixing time to recover  $Co^{2+}$*

The results of this survey were demonstrated in (Table 3) and (Figure 13), as the results of the table show, within 15 minutes of stirring, the maximum absorption and recovery of cobalt ions is carried out by nano nickel oxide.

*Effects of different types of detergent to recover ion  $Co^{2+}$*

According to the results of (Table 4), sodium hydroxide cannot be used as an appropriate

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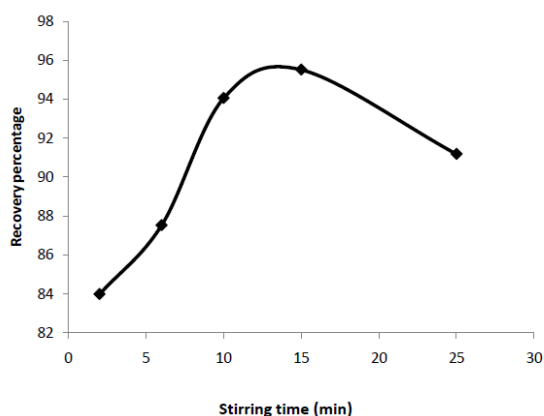
detergent and these bases do not have full power of washing, so the mineral acids with certain concentrations were used, including  $H_2SO_4$  and  $HNO_3$ . According to (Table 5), the results show that all the acids are of good washing power for cobalt ions, but the percentage recovery of nitric acid is far more than that of other acids. Acidic

environment causes solution of the possible deposition and increased recovery of these ions, but the results obtained in the case of  $HNO_3$ , were better than  $H_2SO_4$  acid. So that its 1M solution washed 102.47 percent the cobalt ions from the adsorbent. So to continue studies, 1M nitric acid was used as a detergent solution.

**Table3.** Recovery percentage changes of stirring time relative to Co (II) ion

Stirring time (min)	Recovery percentage
2	83.98 (2.9) <sup>a</sup>
6	87.52 (1.9)
10	94.05 (1.3)
15	95.51 (0.5)
25	91.18 (1.8)

a) RSD of measurements after 3 times of repetition

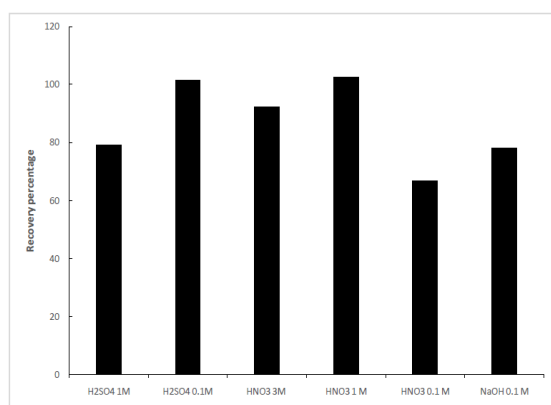


**Figure13.** Change curve of cobalt ion percentage recovery relative to stirring time

**Table4.** Choosing the appropriate detergent to recover cobalt (II)

Solvent	Disadsorption percentage
$H_2SO_4$ 1M	79.21 (0.5) <sup>a</sup>
$H_2SO_4$ 0.1M	101.47 (0.2)
$HNO_3$ 3M	92.17 (0.3)
$HNO_3$ 1M	102.47 (0.3)
$HNO_3$ 0.1M	66.89 (0.4)
NaOH 0.1M	78.22 (0.8)

a) RSD of measurement after 3 times of repetition



**Figure14.** Change curve of cobalt ion recovery percentage relative to different detergent solutions

### Assessment of optimizing the effect of detergent solvent volume to recover ion $Co^{2+}$

After the assessment and selection of the optimal detergent, the volume of this solvent was evaluated and the results are collected in (Table 5) and (Figure 17), the 7 mL volume of nitric acid was selected as the optimal volume for washing.

### Assessment of the effect of the volume of the sample solution (determining the limit volume)

After optimizing the parameters of the sample solution pH and solvent detergent and so on, for thorough washing of cobalt (II) off the

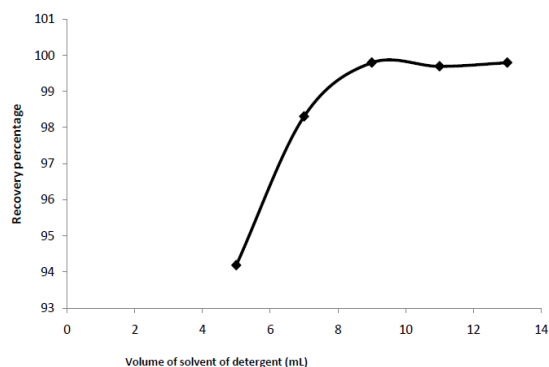
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adsorbent, the maximum volume of aqueous solution containing cobalt (II) must be determined.

**Table5.** Determination of the optimal volume of detergent solvent

Solvent volume	Recovery percentage
5 ml	94.19 (1.5) <sup>a</sup>
7ml	98.31 (1.9)
9 ml	99.8 (2.4)
11 ml	99.7 (0.9)
13 ml	99.8 (1.3)

a)RSD of measurement after 3 times of repetition



**Figure15.** Recovery percentage change based on changes in the volume of solvent detergent

The limit volume for pre-concentration is referred to a volume which crossing more than this volume from the solid phase, all of the analyte ions on the sorbent, are not kept and some of the ions of the analyte pass on them without being hampered, while if the volume of test solution is less than the limit volume, by passing this volume, all of analyte ions are kept on the solid phase. The results of (Table 6) and (Figure 18) show that up to the volume of 250 mL, ions are absorbed to the nano adsorbent and if the sample volume is greater than this value, some of cobalt (II) were not kept on the adsorbent will pass the adsorbent without retention. According to the definition of the limit volume, it can be said that the limit volume in this test is 250 mL and if the volume of the sample solution which contains cobalt (II), is more than 250 mL, Cation absorption is not completely done, and if the sample size is 400 mL and pass over the sorbent and is then washed with 7 mL of detergent solution, the

**Table7.** calibration curve to measure the cobalt (II) ion

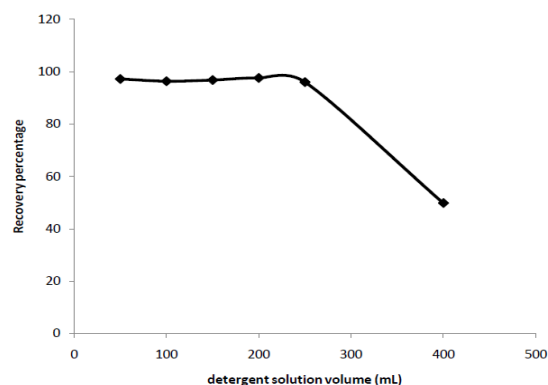
Primary standard solution concentration(µg/L) ppb	Absorption of the main concentrations according to the calibration curve of the device
10	0.415 (0.6) <sup>A</sup>
20	0.514 (0.4)
40	0.843 (0.1)
80	1.254 (0.1)
100	1.155 (0.1)
200	1.922 (0.1)

concentration factor of 36 is achieved. Namely, the concentration of cobalt ion in 7 mL of detergent solution passed over the absorber, becomes 36 times of the cobalt concentration in the initial test solution. According to (Table 6), limit volume calculations are as follows

**Table6.** of the effect of the solution volume in the sample

Total volume (mL)	Recovery percentage
50	97.2 (2.3) <sup>A</sup>
100	96.35 (1.7)
150	96.8 (1.5)
200	97.6 (2.1)
250	96 (1.9)
400	49.8 (1.8)

a)RSD of measurement after 3 times of repetition



**Figure16.** Determination of the limit volume on the determination of cobalt (II)

$$\text{Condensation Factor} = \frac{\text{limit volume}}{\text{detergent solution volume}}$$

$$\text{Condensation Factor} = 250.7 = 36$$

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500	4.125 (0.3)
800	6.57 (0.4)

a)RSD of measurement after 3 times of repetition

### Linear range and calibration curve method

To determine the linear range in the analysis, it is necessary to draw a calibration curve. This graph is not linear at all concentrations, and several factors cause the calibration curve to be linear in the range and follow the Birlaw. According to (Table 7) and (Figure 17), calibration curve method is as follows and equation of the line is as  $Y = 0.0075 X + 0.4469$  and  $R^2 = 0.9975$ .

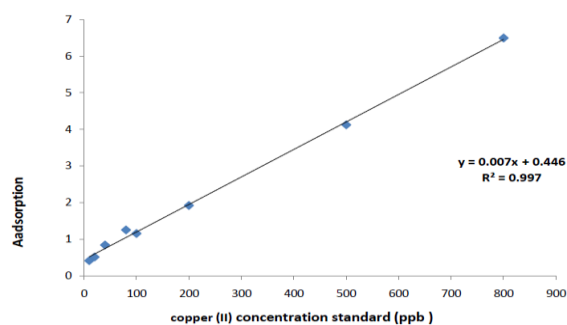


Figure17. Calibration curve of the proposed method

### Assessment of the effect of disturbances on the measurement of ion $Co^{2+}$

Disturbing ion is defined as an ion which causes certain change more than  $\pm 5\%$  in cobalt absorption and recovery. To investigate the effect of disturbing other ions on the extraction of cobalt ions, a certain amount of disturbing factors are added, and the experiment and investigation are performed in the limit volume. Recovered solution absorption is measured by flame atomic absorption and is compared by absorbing the solution resulted from the sample recovery which is without disturbing ions. As can be seen in (Table8), in the presence of external ions, cobalt recovery is performed with changes of  $\pm 5\%$  and the external ions have little effect on the measurement and do not disturb.

Table8. Effect of disturbing ions on the recovery of cobalt (II)

Ions	Added value (ppm)	Recovery percentage $Co(II)$
$Mg^{2+}$	100	93.08 (1.6) <sup>a</sup>
$Zn^{2+}$	5	89.84 (0.9)
$Na^{2+}$	200	90.34 (2.5)
$K^+$	200	92.90 (1.9)
$Pb^{2+}$	5	102.08 (0.6)
$Co^{2+}$	5	96.16 (2.1)

a) RSD measurement after 3 times of repetition

### Determination of Control Standard Deviation (Sb)

Repeatability or accuracy of each method is an important factor in determining its validity and

reliability. To evaluate the repeatability of the method, results of the four blank solution (deionized water) are collected in (Table 9).

Table9. Preparation of blank solution and determining Sb

Sample	Device response
1	0.023 (0.8) <sup>A</sup>
2	0.015 (0.8)
3	0.017 (0.1)
4	0.024 (0.6)

According to the results obtained in (Table9), blank standard deviation is obtained as follows:  $S_b = 0.004425$

### Determining detection limit of the method

The lowest concentration or weight of the sample measured by a specified confidence level, is called the detection limit, which is defined as follows. A method detection limit, is a concentration of the test sample the device response of which is significantly different from

the control response, which is defined as follows: The concentration of the test sample the signal of which is equivalent to the blank signal plus three times the standard deviation of the solution. The limit of detection is the least amount of cobalt ions whom the proposed method is able to detect. According to the

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definition given, limit of detection (LOD) can be calculated by the following equation:

$$\%R = \frac{S}{\bar{X}} \times 100 \quad \%RSD = 0.00404/0.54066 \times 100 = 0.75\%$$

$$LOD = \frac{3 \times S_b}{m}$$

*Assessment of the results obtained on real samples*

Where,  $S_b$  is the blank signal standard deviation and  $m$  is the calibration curve slope. According to tests carried out,  $S_b=0.004425$  and the calibration curve slope is equal to 0.0075.

As a result, the detection limit can be calculated as follows:

$$LOD = \frac{(3 \times 0.004425)}{(0.0075)} = 1.77 \mu\text{gL}^{-1}$$

The detection limit of the method was obtained as  $1.77 \mu\text{gL}^{-1}$

### *Determining the accuracy and RSD% of the method*

This parameter is to verify the accuracy of the test data and near study data. According to the results of (Table 10),  $\bar{X}$  or average recovery and standard deviation  $S$  are calculated for 3 times of measurement and relative standard deviation (RSD) for 3 times of measurement are obtained.

**Table10.** *Determining the RSD of the method*

sample	Absorption
1	0.537 (0.3) <sup>A</sup>
2	0.545 (0.3)
3	0.540 (0.4)

Once the optimal conditions of the method were obtained, to verify the applicability of the method on real samples, the amount of cobalt in several different water and biological samples in the limit volume (250mL) was measured. In the first stage, the sample itself without raising a certain amount of cobalt (II) ion of the method, absorption and cleaning were done and injected to the device, which showed insignificant absorption. In the second time, with the increase of cobalt (II) ion according to the proposed method, the condensation and separation were carried out. In fact, to determine a certain amount of cobalt in water samples, the standard additions method was used. The results of this analysis are shown in (Table 11). As seen in water samples, the water for fish farming compared to water samples tested, the greater amount of cobalt exist, but in samples of well water a smaller amount of cobalt is available; the performance and power of preconcentration and determination of cobalt can be realized. In the case of fish farming water, a considerable amount of cobalt was found, which has been investigated with flame atomic absorption spectrometry device, and this device can be used to measure cobalt in water samples.

**Table11.** *Results of cobalt measurements on real samples*

Sample	Cobalt (II) added ( $\mu\text{g}$ )	Cobalt (II) found in ( $\mu\text{g}$ ) in flame atomic absorption
drinkable water	0	1.12 (3.0) <sup>A</sup>
	50	51.21 (2.3) <sup>A</sup>
Well water	0	N.D. <sup>B</sup>
	50	49.8 (1.8) <sup>A</sup>
Fish Farming	0	4.1 (1.7) <sup>A</sup>
	50	54.3 (2.6) <sup>A</sup>

### *Assessment of the analytical parameters*

In (Table 12), some analytical parameters such as the concentration factor, limit of detection, correlation coefficient and calibration equation for flame atomic absorption spectrometry method are given.

In the analytical methods, a method is more appropriate that the analytical parameters of which such as detection limit and the concentration factor have lower results. The present method with a detection limit of 1.77 and the concentration factor of 36, is a relatively good method.

**Table12.** *Analytical parameters of the proposed method*

Parameter	Analytical parameters
Detection limit	1.77
Concentration factor	36

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Correlation coefficient	0.9975
Calibration equation	$Y=0.0075X+0.4469$
%RSD	0.75%

### Comparison between the proposed method and other methods

According to the results of (table 13), the superiority of this method compared with other methods is in this case that the absorbent used in this method: 1) has high characteristic surfaces, which is a key factor in choosing this material for use as absorbent of metal ions. 2) Adsorbent used in the proposed method is able to be

recovered, that is able to be tested many times. 3) Another advantage of the proposed method compared to other methods which can be seen in the table below, is that the speed of the proposed method is more than the 105 reference, and a detection limit of less than most proposed methods, and has concentration factor better than many other methods and is of easy technique and high accuracy.

**Table13.** Comparison between the proposed method and other methods

Technique	Repeatability Percentage	Concentration factor	Detection limit (mg/L)	Correlation coefficient	Calibration equation	References
FAAS	3	100	0.3	0.9987	$Y=0.0076X+0.00005$	[30]
FI-FAAS	2.1	220	1.2	0.9993	$Y=0.0017X+0.0022$	[31]
GFAAS	2.77	100	0.26	0.9981	$Y=0.0067X+0.0025$	[32]
ICP-AES	2.7	140	0.2	0.993		[33]
FAAS	0.75	36	1.77	0.9975	$Y=0.0075X+0.4469$	Present work

### CONCLUSION

The proposed approach compared to the methods which have been reported previously to isolate and measure the cobalt (II), has significant advantages including: This method is simple and cheap and is quickly used for environmental samples containing natural water. In addition, minimizes the use of toxic and expensive organic solvents. Also, the design and development of this method for preconcentration, separation and measurement of cobalt (II) due to its importance in various industries, and low concentrations of these ions in most cases, is a basic requirement. Therefore, the aim of this study is to provide an efficient, selective, inexpensive and easy way to measure the amount of cobalt (II) in different samples. (In this research, the amount of limit volume, the detection limit and RSD are obtained). Recent research showed that the measurement of cobalt (II) takes place at an acceptable level without any other disturbing agents, and therefore the proposed method can easily be used to measure the amount of cobalt (II) in water samples.

### REFERENCES

- [1] Al-Saidi, A. Emar, A. 2011, "The recent developments in dispersive liquid-liquid microextraction for preconcentration and determination of inorganic analytes" Journal of Saudi Chemical Society, 754-761.
- [2] Paleologos, E. K. 2002, "Micelle Mediated Methodology for the Determination of Free and Bound iron in Wines by Flame Atomic Absorption Spectrometry", Analytica Chimica Acta, 241-248.
- [3] Vollath, D. 2007, Plasma Synthesis of Nanoparticles, KONA Powder and Particle Journal, 39-55 .
- [4] Chen, H. L., Yang, Y. S. 2008, "Effect of crystallographic orientations on electrical properties of sputter-deposited nickel oxide thin films" Thin Solid Films., 5590-5596.
- [5] Cox, P.A. Transition Metal Oxides. University Press, Oxford. 1992.
- [6] Germann, K.H. ,Maier K., Strauss E., 1976, "Linear optische Anisotropie von anti ferromagnetischem NiO in magnetischen Magnetfeld" J. Magn. Magn.Mater., 73-79 .
- [7] Makhlof, S. A. 2008, "Electrical properties of NiO films obtained by high temperature oxidation of nickel" Thin Solid Films., 3112-3116.
- [8] Janssen, G.J.M., Nieuwpoort, W.C. 1988, "Band gap in NiO: A cluster study" Phys. Rev. B., 3449-3458.
- [9] Ai, L., Fang, G., Yuan, L., Liu, N., Wang, M., Li, C., Zhang, Q., Li, J., Zhao, X., 2008, "Influence of substrate temperature on electrical and optical properties of p-type semitransparent conductive nickel oxide thin films deposited by radio frequency sputtering" Applied Surface Science., 2401-2405.
- [10] Chang, H.L., Lu, T.C., Kuo, H.C., Wang, S.C. 2006, "Effect of oxygen on characteristics of nickel oxide/indium tin oxide hetero junction diodes" J. Appl. Phys Lett., 124503.
- [11] Moghimi A. Shabanzadeh M., 2012. Extraction and Determination of Trace Cobalt

- (II) Using Octadecyl Silica Membrane Disks Modified 1-(2-Pyridyl Azo) 2-Naphtol(Pan) in Water Samples and Paraffin-Embedded Tissues from Liver Loggerhead Turtles Specimens by FAAS. *Journal of chemical Health Risks.*2(2), 1-7.
- [12] Moghimi A., 2014. Extraction of Ni (II) on micro crystalline naphthalene modified with organic-solution-processable functionalized nano graphene. *Russian Journal of Physical Chemistry A.* 88 (7), 1177-1183.
- [13] Moghimi A., Abdouss M., 2013. Extraction of Co (II) by Isocyanate Treated Graphite Oxides (iGOs) Adsorbed on Surfactant Coated C<sub>18</sub> Before Determination by FAAS. *Int J Bio-InorgHybrNanomater.* 2(2), 319-327.
- [14] Moghimi A., Sabertehrani M., Waquif-Husain S., 2007. Preconcentration and determination of chromium species using octadecyl silica membrane disks and flame atomic absorption spectrometry. *Chinese Journal of Chemistry.* 25 (12), 1859-1865.
- [15] Moghimi A., Shabanzadeh M., 2012. Extraction and Determination of Trace Cobalt (II) Using Octadecyl Silica Membrane Disks Modified 1-(2-Pyridyl Azo) 2-Naphtol (Pan) in Water Samples and Paraffin-Embedded Tissues from Liver Loggerhead Turtles Specimens by FAAS. *J Chem Health Risk.* 2(2), 7-12.
- [16] Moghimi A., Poursharifi M.J., 2012. Preconcentration of Ni (II) from Sample Water by Modified Nano Fiber. *Orient J. Chem.* 28(1), 353-356.
- [17] Moghimi A., 2014. Separation and extraction of Co (II) using magnetic chitosan nanoparticles grafted with  $\beta$ -cyclodextrin and determination by FAAS. *Russ J Phys Chem A.* 88(12), 2157-2164.
- [18] Moghimi A., Siahkalrodi S.Y., 2013. Extraction and Determination of Pb (II) by Organic Functionalisation of Graphenes Adsorbed on Surfactant Coated C18 in Environmental Sample. *Journal of Chemical Health Risks.* 3(3), 1-12.
- [19] Moghimi A., Yari M., 2014. Preconcentration of trace Ni (II) using C18 disks nano graphene with amino propyltriethoxysilane (APTES). *Merit Research Journal of Environmental Science and Toxicology.* 2(5), 110-119.
- [20] Moghimi A., Akbarieh S.P., 2014. Evaluation of Solid-phase Extraction Sorbent with Octadecane-functionalized Nano Graphene (ODG) for the Preconcentration of Chromium Species in Water, *International Journal of Scientific Research in Knowledge.* 2(1), 8-21.
- [21] Moghimi A., 2013. Detection of trace amounts of Pb(II) by schiff base-chitosan-grafted multi-walled carbon nanotubes. *Russian J Physic Chem A.* 87 (7), 1203-1209.
- [22] Moghimi A., Esfanjani S., Mazloomifar H., 2012. Extraction and Perconcentration of Lead(II) using Octadecyl Bonded Silica Cartridge and Its Determination by Flame Atomic Absorption Spectrometry. *Asian J Chem.* 24(10), 4697- 312-319.
- [23] Moghimi A., Abdouss M., Ghooshchi G., 2013. Preconcentration of Pb(II) by Graphene Oxide with Covalently Linked Porphyrin Adsorbed on Surfactant Coated C18 before Determination by FAAS. *Int J Bio-InorgHybrNanomater.* 2(2), 355-364.
- [24] Ozcan, S.G., Satiroglu ,N., Soylak, M.,2010 "Column solid phase extraction of iron(III), cobalt(II), manganese(II) and lead(II) ions food and water samples on multi-walled carbon nanotubes", *Food and chemical Toxicology,* 2401-2406.
- [25] Pourreza N., Rastegarzadeh S., Larki A., 2014 "Simultaneous preconcentration of Cd(II), Cu(II) and Pb(II) on nano-TiO<sub>2</sub> modified with 2-mercaptobenzothiazole prior to atomic absorption spectrometric determination", *Industrial and Engineering Chemistry,* 2680-2686 .
- [26] Tokay, F., Bagdat, S., 2015. "preconcentration of Co(II), Cu(II) and Ni(II) using an optimized enrichment procedure: useful and alternative methodology for flame atomic absorption spectrometry", *Industrial and Engineering Chemistry,* 75-79.
- [27] Zhu, X., Cui, Y., Chang, X., Wang, H.,2016 ."selective solid-phase extraction and analysis of trace-level Cr(II), Fe(II), Cu(II) and Mn(II) ions in wastewater using diethylenetriamine-functionalized carbon nanotube dispersed in graphene oxide clloids", *Talent,* 358-363 .
- [28] Jalal Uddin, M., Khatun, R., Nasir Uddin Khan, M. ,Momin ,M.A., Khairul Islam ,M., Helal Uddin ,M. ,Alam, M.M. ,2016. *Journal of Multidisciplinary Engineering Science and Technology (JMEST),* 3713-3715.
- [29] Moghimi, A. 2007. "Preconcentration and Determination of Cobalt(II) Using Octadecyl Silica Membrane Disks Modified by 1,5-Diphenylcarbazide and Flame Atomic Absorption Spectrometry", *Chinese Journal of Chemistry,* 640-644.
- [30] Anthemidis, A.N., Koussoroplis, S.V., 2007. "Determination of chromium(VI) and lead in water samples by on-line sorption preconcentration coupled with flame atomic absorption spectrometry using a PCTFE-beads packed column", *Talent,* 1728-1733.
- [31] Moghimi A., 2014. *Journal of Chemical Health Risks ,*4(2), 15-22.



## An Alternative Method Extraction of Trace Amounts of Cobalt (II) in Water Samples by Modified Nanonickeloxide

- [32] khosravan , M.,saljooghi, A., 2009. "Synthesis, characterization of silica gel phases chemically immobilized with-2-aminothiophenol and the use of it for separation and preconcentration of trace amounts of manganese ions", European Journal, 228 – 236.
- [33] Tazen, M., Saygi ,Q., Soylak, M.,2008 ,“Solid phase extraction of heavy metal ions in environmental samples on multiwalled carbon nanotubes”, J.Hazardous Mat, 632-639.

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