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## Fabrication of an Electrochemical Sensor Based on a New Nano-ion Imprinted Polymer for Highly Selective and Sensitive Determination of Molybdate

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In this work a new chemically modified carbon paste electrode (IIP@SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>) was constructed for accurate, simple, sensitive and selective determination of molybdenum(VI) ions. The results showed the stripping peak currents had a dramatic increase at the modified electrode. Under the optimal conditions, the linear dynamic range and limit of detection were 0.2-500.0 and 0.04 ng ml<sup>-1</sup>, respectively. The relative standard deviation for five successive measurements of 5.0 and 20.0 ng ml<sup>-1</sup> of Mo(VI) ions were 1.8 and 1.4%, respectively. The reproducibility and stability of the designed modified electrode response were also investigated. By examining the effect of different cations and anions on the determination of the target ion, it was found that the electrode is highly selective for the determination of Mo(VI) ions. Furthermore, the present method was applied to the determination of Mo in real samples with satisfactory results.

**Keywords:** Modified carbon paste electrode, Ion imprinted polymer, Determination, Mo(VI), Electrochemical sensor

### INTRODUCTION

Molybdenum as an essential trace element for both animals and plants play an important role in catalyzing enzymatic redox reactions, *e.g.* oxidation of aldehydes, xanthine and other purines, and reduction of nitrates and molecular nitrogen. Low and high doses of molybdenum in the body creates risks. A shortage of molybdenum in the human diet may lead to neurological disorders and even death and also adversely affects growth. On the other hand, the higher concentrations of molybdenum in the body may also cause teeth vulnerable to caries and disturbances in the metabolism of fats and proteins and bone deformation or results in severe gastrointestinal irritation and death due to cardiac failure.

The development of new methods with performing a pre-concentration step before the determination of trace metals, because of their low concentration in food and biological samples, is under discussion [1,2]. Therefore, for the determination of molybdenum in various matrices a

variety of analytical methods have been developed. Several techniques have been performed for the determination of molybdenum such as spectrophotometry [1,3-5] and spectrofluorimetry [6] which these methods suffer for low sensitivity values. Some sensitive techniques have also been reported for the determination of molybdenum such as inductively coupled plasma mass spectrometry (ICP-MS) [7], inductively coupled plasma atomic emission spectrometry (ICP-AES) [8], neutron activation analysis (NAA) [9], flame atomic absorption spectrometry [10] and electrothermal atomic absorption spectrometry [11,12]. But most of these methods are very expensive, have inappropriate detection limit, hard to use, use time consuming procedures and are not suitable for in situ monitoring. On the other hand, for routine analysis of metals, some methods that are sensitive and selective such as ICP-AES, ICP-MS and NAA are too expensive.

Several advantages of electrochemical methods such as quick response time, sensitivity, selectivity, precision, accuracy and with low cost of instrumentation and maintenance are better than the other techniques [2,13,14] for trace Mo detection.

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Over the past five decades, one of the most famous electrode materials has attracted much attention among different electrodes is carbon paste, *i.e.* a mixture of carbon (graphite) powder and a binder (pasting liquid). The advantages of this electrode comparison to other electrodes are convenient surface renewal, low cost, porous surface, wide potential range (from -1.40 to 1.30 V), and low residual current. The properties of chemically modified carbon paste electrodes (CMCPEs) that are made with the addition of suitable modifier to carbon paste, depends on the properties of the modifier materials used to impart selectivity and sensitivity towards the target species [15-17].

In order to enhance the sensitivity and selectivity for the determination of metals, molecular imprinted polymers (MIP) can be used. MIP technology has been progressing as a new highly selective method with synthetic receptors for a specific analyte. The base of this method is polymerization of self-assembled complexes, formed by functional monomers and a template in polymerization mixture. If the preparation of polymers be done for inorganic ion selective sites, this technology is named ion imprinted polymers (IIP) [18-22].

In this work, a new nano-IIP was made-up by using SiO<sub>2</sub> coated magnetite nanoparticles (SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>, SCMNPs) for the detection of Mo ions as the nanostructured core and supporting material in the IIPs construct. The SCMNPs directed selective polymerization of IIPs on the nanocomposite surface. In this work, the polymer was synthesized using a new functional monomer and the polymerization was not performed by the traditional monomers (*e.g.* methacrylate). Then, the nano-IIPs, with improved qualities such as simplicity of the electrode preparation, a wider linear range, lower detection limit, higher selectivity, in comparison to the some existing modified electrodes for the determination of Mo(VI), were synthesized as the recognition material for Mo(VI). The procedure is based on the oxidation of Mo(VI) after its selective accumulation and reduction at the modified carbon paste electrode. The proposed sensor was successfully applied to the determination of Mo(VI) in several real samples. Because of the better accumulation of Mo(VI) at the electrode surface the enhancements of the voltammetric responses of Mo(VI) can be explained on the surface of electrode modified with nano-IIP as a modifier.

## EXPERIMENTAL

### Apparatus

A Metrohm model 797 VA Computrace polarograph was used for voltammetric studies. All the reagents used were of analytical grade. Three-electrode cell systems were used to monitor the differential pulse voltammograms. An Ag/AgCl/KCl (3.0 M) electrode, a platinum wire, and a modified CPE electrode were used as the reference, auxiliary and working electrodes, respectively. A Metrohm Model 827 pH lab (Herisau, Switzerland) pH-meter with a combined glass electrode was used for pH measurements. Double distilled water (DDW) was used throughout. The prepared electrode was characterized by Fourier transform infrared (FT-IR) and transmission electron microscopy (TEM).

### Reagents

All chemical reagents were of analytical grade from Merck Company (Darmstadt, Germany) or Aldrich Company. For preparation all the solutions used double distilled water. Laboratory glassware was kept overnight in a 10% (v/v) HNO<sub>3</sub> solution and then rinsed with DDW. Stock standard solutions of Mo(VI) (100.0 µg ml<sup>-1</sup>) was prepared by dissolving adequate of Na<sub>2</sub>MoO<sub>4</sub>·H<sub>2</sub>O salt in water and diluting to 50.0 ml in a volumetric flask every day. Among various types of electrolyte solutions have been tested, the phosphate buffer solution was found to yield the best results. A phosphate buffer solution of pH 2.0 (consists of a mixture of 0.1 M H<sub>3</sub>PO<sub>4</sub> titrated with 0.2 M NaOH solution to the desired pH) served as a supporting electrolyte solution. For the preparation of conventional carbon paste electrode, graphite powder, with a 10-µm particle size and highly pure paraffin (both were purchased from Merck Company) were used.

### Preparation of IIP@SiO<sub>2</sub>@ Fe<sub>3</sub>O<sub>4</sub>

**Synthesis of magnetic Fe<sub>3</sub>O<sub>4</sub> particles and SiO<sub>2</sub>@ Fe<sub>3</sub>O<sub>4</sub>.** The magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles were synthesized using the solvothermal method according to a previous report [23]. Briefly, FeCl<sub>3</sub>·6H<sub>2</sub>O (1.35 g) dissolved in 50 ml of ethylene glycol under the magnetic stirring to obtain a clear solution. After rising sodium acetate (NaAc) (3.6 g) the mixture was placed in an ultrasonic bath during 30 min.

Then, the solution was refluxed at 180 °C for 8 h. After cooling the solution to ambient temperature, magnetic nanoparticles were washed several times with ethanol and double distilled water and then dried at 60 °C for 6 h. Then, Fe<sub>3</sub>O<sub>4</sub> nanoparticles (0.50 g) were firstly treated by the addition of NH<sub>3</sub> solution (60.0 ml) under the ultrasonic vibration for 15 min. After that, 1.0 ml ammonium hydroxide and 2.0 ml tetraethylortho-silicate (TEOS) was added to the mixture and reacted at room temperature for 24 h. At last, the obtained product was washed consecutively with DDW water and methanol, and finally dried at 70 °C for 12 h.

**Preparation of IIP@SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>.** For preparation of IIP@SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>, the sol-gel process was used [23,24]. Briefly, SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub> (0.2 g) was dispersed in the mixture of ethanol (80.0 ml) and deionized water (60.0 ml) under the ultrasonic vibration for 20 min. Then, 3-(2-aminoethyl-amino)propyltrimethoxysilane (AAPTS) (0.4 ml) and TEOS (0.8 ml) and concentrated ammonia solution (2.0 ml) were sequentially added to the above solution and was under vigorous stirring for 18 h. The product was washed with ethanol and dried at 80 °C.

In the next step, for the preparation of Mo-IIP, the magnetic nanoparticles from previous steps were dispersed homogeneously in 50.0 ml of ethanol /water mixture (50% v/v) by ultrasonic dispersion for 20 min (suspension A). Also separately isonicotinic acid (0.25 g) and Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O (0.8 g) were dissolved in 100 ml ethanol/water mixture (50% v/v) with stirring for 20 min (solution B). The polymerization reaction and obtaining the particles with highly cross linking structure was carried out by sequential addition of solution B to suspension A and stirring the solution for 18 h. Subsequently, the final product was washed several times with DDS and dried at 80 °C for 12 h.

Finally, the resulting particles were washed with a mixture of methanol and acetic acid to remove Mo(VI) template, for 12 h and after drying, the product washed for 3 times with hydrochloric acid (0.5 M) again and then dried at 80 °C for 12 h. The non-imprinted polymer nanoparticles (nano-NIP) was prepared by the same protocol without the template.

The different steps of synthesis of IIP@SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub> are shown in Scheme 1.

### Preparation of the Electrodes

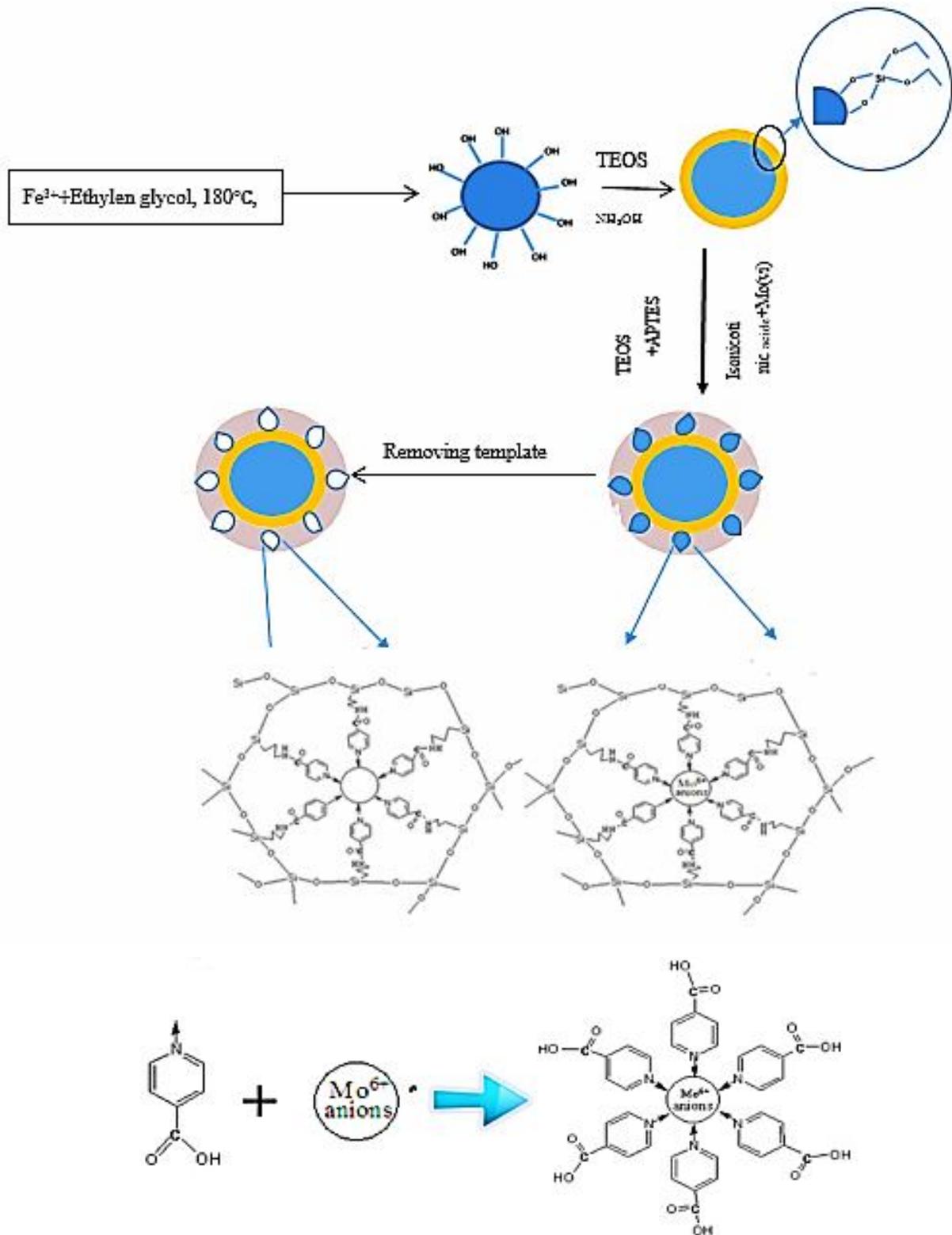
In order to the prepare the unmodified carbon paste electrode (CPE), fine graphite powder with the appropriate amount of paraffin was mixed thorough hand in a mortar and pestle. The homogenized mixture was inserted into a plastic needle type capillary tube with 1.5 mm diameter and 5 cm length, using a 0.5-mm diameter copper wire connected to the measurement system. The CPE modified with nano-IIP (IIP@SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>) and nano-NIP (NIP@SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>) were prepared by mixing the modified mixture with nano-IIP or nano-NIP (both of them 15%) and transferred into the syringe. The paste was carefully packed into the syringe tip to avoid possible air gaps, which often enhance the electrode resistance. This prepared composite has the advantages such as renewal characteristics, high mechanical stability, and low electrical resistance and simple polishing. For receiving a low background current the prepared modified CPEs were immersed in the supporting electrolyte in the electrolysis cell and several sweeps were applied. Also, to refresh the electrode surface before each measurement the pastes surface was smoothed and rinsed with double-distillated water.

### Recommended Procedure

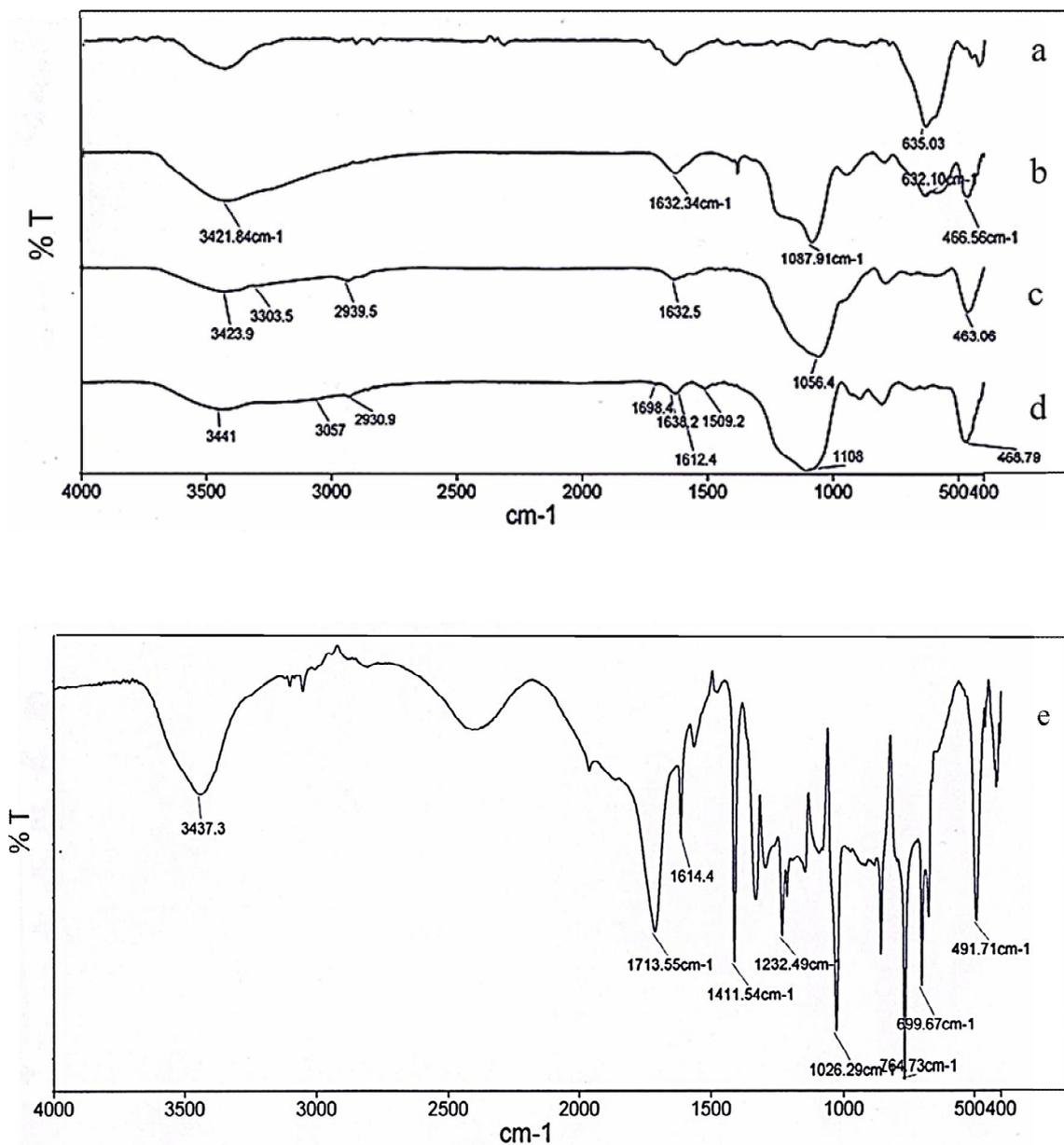
A 25.0 ml volume of the solution, containing an appropriate concentration of Mo(VI) and 0.1 M phosphate buffer (pH 2.0) was transferred into a voltammetric cell. The differential pulse (DP) parameters including pulse amplitude, pulse time, resting time and voltage step height were 0.16 V, 0.014 s, 10 s and 0.02 V, respectively. The preconcentration step for 15 min at the potential of -0.5 V vs. Ag/AgCl was performed in the stirred solution. The stirring was then stopped and after a resting time of 10 s, to settle the solution and decrease the background current, differential pulse voltammograms were recorded in the positive potential direction. The surface of the electrode was cleaned by a simple polishing of the electrode on a paper. The renewed active surface of the electrode permits to eliminate the irreversible contamination of the surface and to minimize the memory effects, especially in real sample analysis.

### Real Sample Preparation

In order to verify the applicability and reliability of the



Scheme 1. The different steps of synthesis of IIP@SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>

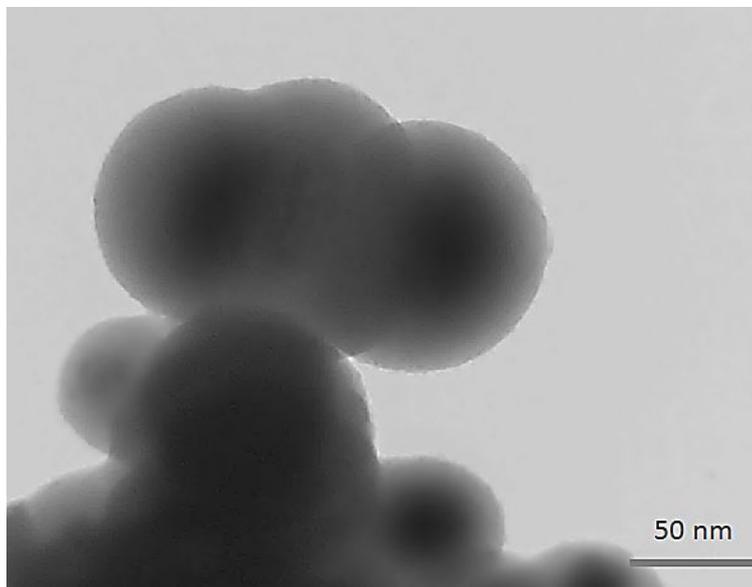


**Fig. 1.** FT-IR spectra for  $\text{Fe}_3\text{O}_4$  (a),  $\text{SiO}_2@\text{Fe}_3\text{O}_4$  (b), amino  $\text{SiO}_2$  (c), IIP (d) and isonicotinic acid (e).

method, water and food samples were prepared and analyzed using the method. Water sample was taken in our lab. Tomato sample and tea samples were purchased from local markets in Hamedan. After sampling of water, the sample was filtered through a Millipore cellulose membrane filter (0.45  $\mu\text{m}$  pore size), acidified to pH 2.0 with  $\text{HNO}_3$ ,

and stored in pre-cleaned polyethylene bottles.

For the determination of Mo(VI) in plant foodstuffs, at first, about 1.000 g of the dried sample (tomato, tea) was ashed for 6 h at 500  $^\circ\text{C}$  and after cooling, with addition of 5.0 ml of 1:1 concentrated nitric acid:  $\text{H}_2\text{O}$  the mixture were heated on a hotplate to near dryness. After dissolving of the



**Fig. 2.** TEM image for synthesized nano-IIP.

residue in 20.0 ml of triply distilled water and filtering the solution using filter paper (Whatman No. 1), the filtration was collected into a 50.0 ml volumetric flask and diluted to the mark with triply distilled water [1].

## RESULT AND DISCUSSION

### Characterization of the Modified Magnetite Nanoparticles

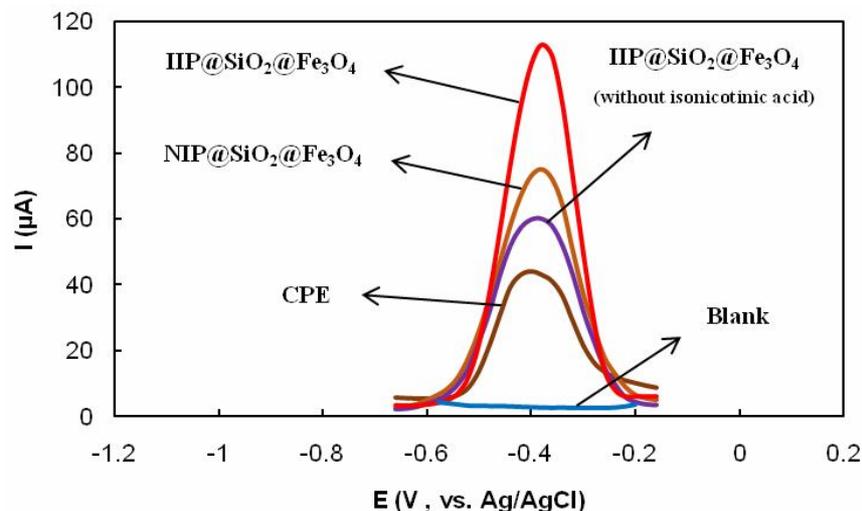
To verify the synthesized products in different steps of nano-IIP fabrication, the FTIR spectra for  $\text{Fe}_3\text{O}_4$ ,  $\text{SiO}_2@\text{Fe}_3\text{O}_4$ , amino  $\text{SiO}_2$  and IIP were recorded and showed in Figs. 1a-d, respectively. The characteristic absorption band for Fe-O in  $\text{Fe}_3\text{O}_4$  (around  $635\text{ cm}^{-1}$ ) is observed in Fig. 1a. In Fig. 1b, the appeared peaks at around  $1087\text{ cm}^{-1}$  and  $810\text{ cm}^{-1}$  referred to Si-O-Si and Si-OH stretching vibrations, respectively. Moreover new absorption peaks at around  $3303\text{ cm}^{-1}$  in Fig. 1c, are assigned to the stretching mode of the amino group (N-H). In Fig. 1d, the peaks around  $1612\text{ cm}^{-1}$ ,  $1502\text{ cm}^{-1}$ , in the spectrum, which indicated the vibration peaks of pyridine ring. The bands near  $3057\text{ cm}^{-1}$  and  $1695\text{ cm}^{-1}$  were attributed to C-H stretching vibrations of pyridine ring and

the C=O band, respectively [14,24]. The IR spectra of isonicotinic acid is shown in Fig. 1e.

The morphology of  $\text{IIP}@\text{SiO}_2@\text{Fe}_3\text{O}_4$  were characterized with transmission electron microscopy. As shown in Fig. 2, the particles size of nano-IIP was about 80 nm. This image shows that the  $\text{Fe}_3\text{O}_4$  nanoparticles were well-enwrapped by  $\text{SiO}_2$  shell and further by IIP layer.

### Preliminary Investigation of Behavior of the Electrodes

The performance of different electrodes for the preconcentration, reduction and oxidation of Mo(VI), the electrochemical behavior of them in  $0.20\text{ }\mu\text{g ml}^{-1}$  of Mo(VI) in phosphate buffer solution of pH 2.0 was studied. As shown in Fig. 3, the differential pulse voltammograms of  $0.20\text{ }\mu\text{g ml}^{-1}$  of Mo(VI) at CPE,  $\text{NIP}@\text{SiO}_2@\text{Fe}_3\text{O}_4$ ,  $\text{IIP}@\text{SiO}_2@\text{Fe}_3\text{O}_4$ ,  $\text{IIP}@\text{SiO}_2@\text{Fe}_3\text{O}_4$  (without isonicotinic acid) and the modified electrode in blank solution after 15 min deposition time and the deposition potential of  $-0.50\text{ V}$  vs. Ag/AgCl were recorded. As can be seen in Fig. 3, under the optimum conditions, the performance of  $\text{IIP}@\text{SiO}_2@\text{Fe}_3\text{O}_4$  electrode is better than the other electrodes, because the electrochemical signal of the modified electrode is higher than that for the others. The results indicated that the



**Fig. 3.** Differential pulse voltammograms of  $0.20 \mu\text{g ml}^{-1}$  of Mo(VI) at CPE, NIP@SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>, IIP@SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>, IIP@SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub> (without isonicotinic acid) under the optimum conditions,  $E_{\text{acc}}$ :  $-0.5 \text{ V}$ ,  $t_{\text{acc}}$ :  $15 \text{ min}$ .

modified electrode (IIP@SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>) can enhance the accumulation of Mo(VI) ions at the surface of electrode (compared with NIP@SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>). The main reason for enhancement of signal response and selectivity is excellent preconcentration of ions at the surface of modified electrode because of the presence of active sites and good interaction of Mo ions and isonicotinic acid.

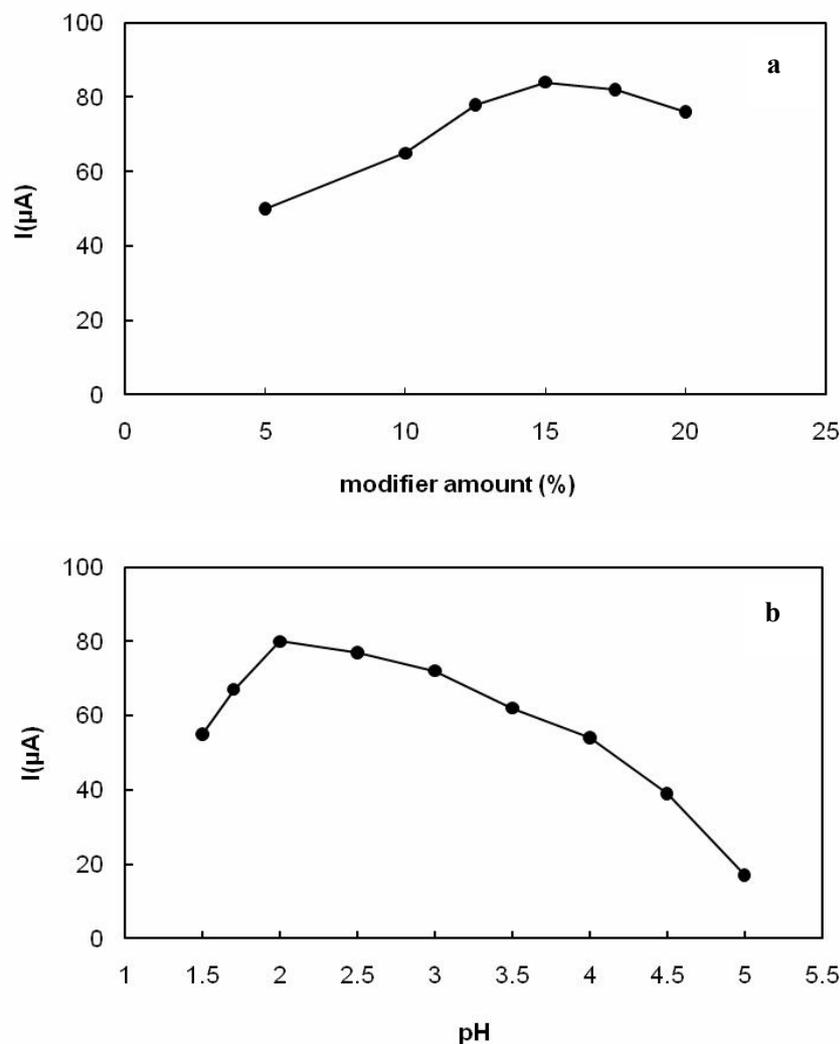
### Effect of Experimental Parameters

In order to obtain the optimum experimental conditions, the effects of different variables including supporting electrolyte, pH, the amount of modifier, deposition potential, deposition time and instrumental parameters on the determination of Mo(VI) in a solution containing  $0.2 \mu\text{g ml}^{-1}$  of ion were studied.

**Electrode composition.** One of the important parameters affecting the sensitivity and selectivity of the electrode is the binder/graphite ratio and the amount of nanomaterial as the modifier in the electrode composition. The effect of nano-IIP on enhancing the signal of the modified electrode on the preconcentration of Mo(VI) is shown in Fig. 4a. By increasing the nano-IIP to the electrode composition up to 15%, the signal of the deposition of Mo on the surface of electrode increased and then decreased. The increase in the signal by increasing IIP up to 15% is due to the increase in the recognition sites at

the electrode surface. Also, in the presence of higher amounts of the nano-IIP the electrode conductivity reduced. So, for the further investigations the 15% of modifier was selected as optimum amount of nano-IIP.

**Effect of supporting electrolyte and pH.** The influence of various types of supporting electrolytes, including phosphate buffer, B-R buffer, acetate buffer and KCl solution on peak current of  $0.20 \mu\text{g ml}^{-1}$  were investigated. Among different buffer solutions, the height of the peak reached a maximum and the shape of the curves was better in phosphate buffer solution. Then the influence of the pH using phosphate buffer solution between 1.5 and 5.0 on the anodic peak current of  $0.20 \mu\text{g ml}^{-1}$  Mo(VI) ion was also studied (Fig. 4b). As Fig. 4b shows, the maximum signal of oxidation of Mo observed at pH 2.0 and then decreased at higher pHs. At pH 2.0 the predominant form of Mo is as  $\text{HMoO}_4^-$  [25] which can interact with the surface of modified electrode through electrostatic interactions with the protonated ligand (isonicotinic acid). At pHs lower than 2.0 the predominant form of Mo is as  $\text{H}_2\text{MoO}_4$  which cannot have good interaction with the modifier at the electrode surface. On the other hand, as pH rise to higher values, Mo is converted to  $\text{MoO}_4^{2-}$  which is not electroactive [25]. Also, the decrease in the currents at pHs lower than 2.0 can be mentioned to the competition between proton ions and the metal ion for binding to the donating atoms of the cavities

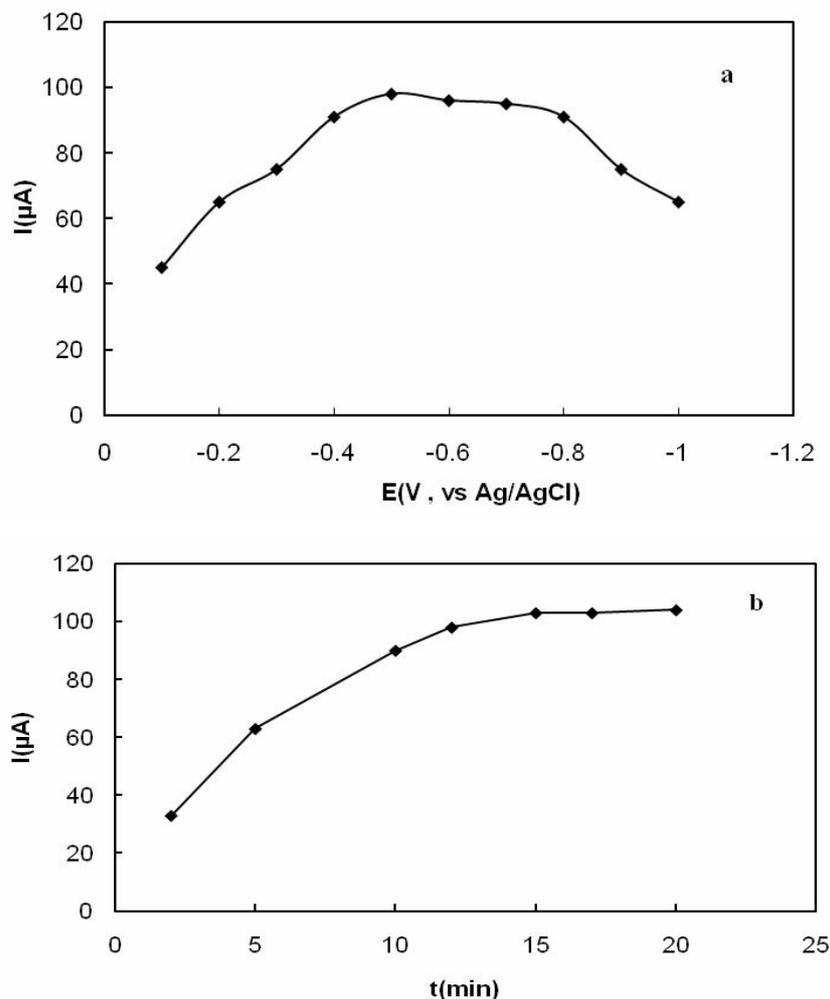


**Fig. 4.** Effect of (a) amount of modifier and (b) pH on the analytical signal of  $0.2 \mu\text{g ml}^{-1}$  of Mo(VI) at  $E_{\text{acc}}: -0.7 \text{ V}$ ,  $t_{\text{acc}}: 10 \text{ min}$ .

of nano-IIP at the surface of the electrode [26]. Therefore, for the further investigates the optimal pH of 2.0 was chosen.

**Effect of deposition potential and time.** When preconcentration of the analyses at the electrode surface is studied, the effects of the accumulation potential and the accumulation time, as the important factors, should be checked. The preconcentration conditions, therefore, have a significant impact on the stripping signals of the analytes. The effect of the accumulation potential on the anodic peak current of the solution of  $0.20 \mu\text{g ml}^{-1}$  of Mo(VI), was

examined in the range  $-0.3$  to  $-1.0 \text{ V vs. Ag/AgCl}$  under the above optimum pH by recording the voltammograms at different deposition potentials. Figure 6a shows the curve of the current response as a function of deposition potential for the modified electrode. As shown in Fig. 5a the peak current increased by changing the potential to  $-0.5 \text{ V}$  and then leveled off and decreased after  $-0.8 \text{ V vs. Ag/AgCl}$ . Therefore, a potential of  $-0.5 \text{ V vs. Ag/AgCl}$  was selected as the accumulation potential in the procedure. Then, the effect of the accumulation time on the peak current of  $0.20 \mu\text{g ml}^{-1}$  of Mo(VI), in pH 2.0 phosphate buffer solution and



**Fig. 5.** Effect of accumulation potential (a) and accumulation time (b) on analytical signal of  $0.2 \mu\text{g ml}^{-1}$  of Mo(VI) at pH: 2.0.

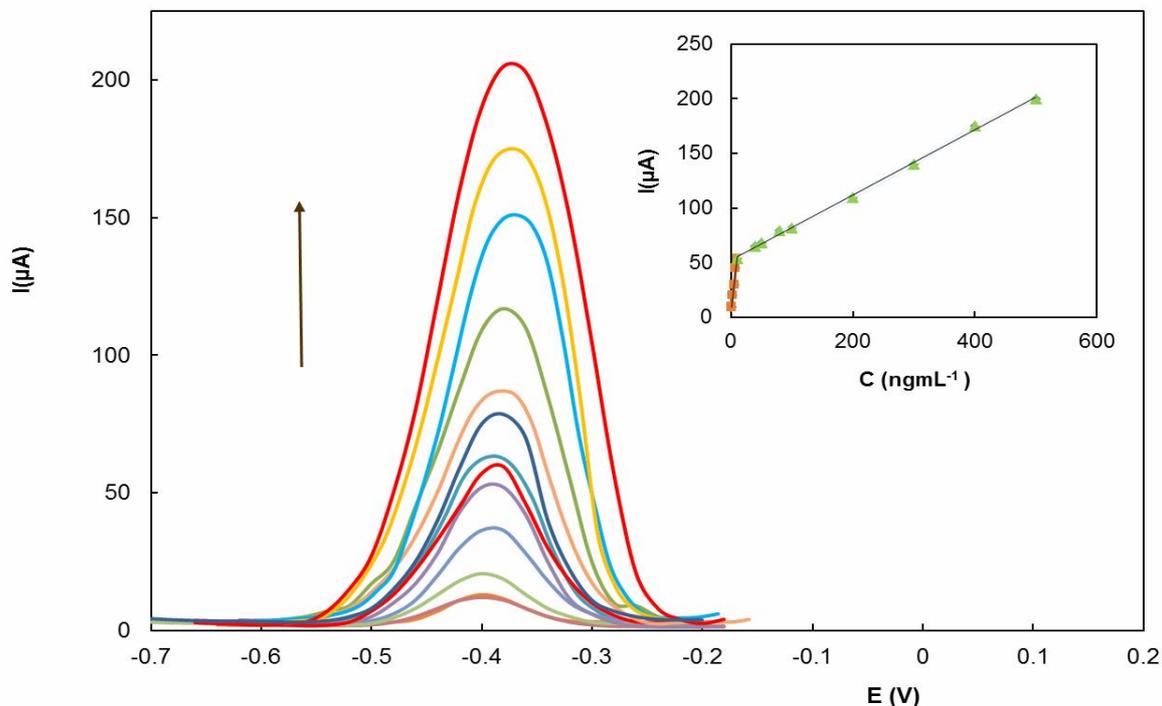
deposition potential of  $-0.5 \text{ V Ag/AgCl}$ , in the range 2-20 min was studied (Fig. 5b). The peak current was proportional to the accumulation time up to 15 min. For longer preconcentration times, because of the saturation loading of the active sites at the electrode surface, the current was found to level off. Therefore, a deposition time of 15 min was selected for further works.

The optimum instrumental parameters affecting the DPV peak current of the analyte were also obtained. These parameters were optimized to obtain maximum signal-to-noise ratio. Optimum values for the studied parameters were

chosen as  $0.16 \text{ V}$ ,  $10 \text{ s}$ ,  $0.014 \text{ s}$ ,  $0.02 \text{ V}$  and  $0.7 \text{ s}$ , for pulse amplitude, resting time, pulse time, voltage step and voltage step time, respectively.

### Analytical Parameters

After optimization of the conditions described above, calibration graph was constructed using the modified electrode and different concentrations of Mo(VI). Registered voltammograms for Mo(VI) revealed that there is a linear relationship between the oxidation peak current of the molybdenum and the concentration of Mo(VI) in given



**Fig. 6.** DPVs at the surface of modified electrode in PBS (pH 2.0) containing different concentrations of Mo(VI) (from down to up, the concentrations: 0.5, 3.0, 5.0, 8.0, 10.0, 40.0, 50.0, 80.0, 100.0, 200.0, 300.0, 400.0 and 500.0  $\text{ng mL}^{-1}$  of Mo(VI)) under the optimized conditions. Inset: Plot of the oxidation peak currents as a function of Mo(VI) concentrations.

concentration ranges. As seen in Fig. 6, two linear ranges of 0.2-10.0 and 10.0-500.0  $\text{ng mL}^{-1}$  were observed with the line equations of  $I_p = 4.924C_{\text{Mo}} + 5.184$ , ( $R^2 = 0.9998$ ) and  $I_p = 0.297C_{\text{Mo}} + 52.615$  ( $R^2 = 0.9986$ ), respectively, where  $I_p$  is the anodic peak current in  $\mu\text{A}$  and  $C_{\text{Mo}}$  is the concentration of Mo(VI) in  $\text{ng mL}^{-1}$ . The detection limit, calculated from three times the standard deviation of the blank ( $S_b$ ) divided by the slope of the calibration graph, was 0.04  $\text{ng mL}^{-1}$ .  $S_b$  was estimated by 10 times determination of the blank signals.

The repeatability of the proposed electrode was investigated with analysing five successive measurements of 5.0 and 20.0  $\text{ng mL}^{-1}$  of Mo(VI). The relative standard deviation of 5.0 and 20.0  $\text{ng mL}^{-1}$  of Mo(VI) were calculated as 1.8 and 1.4%, respectively. The reproducibility of the electrode response was also studied. Five electrodes were prepared from the same materials and the performance of

these electrodes were evaluated by the determination of 0.20  $\mu\text{g mL}^{-1}$  of Mo(VI) solution. The RSD for the response between electrodes was 2.8%. Also, the response of electrode maintained more than 95% over 6 weeks. After that, the sensitivity decreased and the noise in the responses increased. The high reproducibility and stability indicated that the modified electrode was suitable for the analysis of real samples.

### Interference Study

In order to investigate the selectivity of the prepared electrode the influence of coexisting substances on determination of Mo(VI) was studied under the optimum conditions. The effects of various interfering species, by the addition of the interfering ions to the solution containing 0.20  $\mu\text{g mL}^{-1}$  of Mo(VI) solution were studied. The tolerance limit was defined as the concentration of foreign species

**Table 1.** Tolerance Ratio of Interfering Ions in the Determination of 0.2  $\mu\text{g ml}^{-1}$  of Molybdenum(VI)

Species	Tolerance limit for Mo(VI)
$\text{Na}^+$ , $\text{Cl}^-$ , $\text{Br}^-$ , $\text{Ca}^{2+}$ , $\text{K}^+$ , $\text{Ba}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Co(II)}$ , $\text{Ni(II)}$ , $\text{Al(III)}$ , $\text{CO}_3^{2-}$ , $\text{SO}_3^{2-}$ , $\text{NO}_3^-$ , $\text{CH}_3\text{COO}^-$ , $\text{Mn}^{2+}$ , $\text{SO}_4^{2-}$ , $\text{Cu}^{2+}$	1000
$\text{I}^-$	500
$\text{Pb(II)}$	200
$\text{NO}_2^-$	100
$\text{W(VI)}$	20

**Table 2.** Results of Determination of Mo(VI) in Real Samples

Sample	Added ( $\text{ng ml}^{-1}$ )	Found ( $\text{ng ml}^{-1}$ )	Recovery (%)
Tap water	-	N.D. <sup>a</sup>	-
	5.00	$4.85 \pm 0.07$	97.0
	8.00	$8.07 \pm 0.10$	100.8
Tomato	-	$3.25 \pm 0.09$	-
	5.00	$8.31 \pm 0.14$	101.2
	8.00	$11.19 \pm 0.29$	99.2
Tea	-	$0.19 \pm 0.01$	-
	5.00	$5.07 \pm 0.11$	97.6
	8.00	$8.10 \pm 0.23$	98.8

<sup>a</sup>Not Detected.

that causes less than 5% change in the height of peak current. The maximum tolerable concentrations of foreign species are shown in Table 1. Based on the results, it was found that most of the foreign ions did not interfere and the designed electrode was selective for Mo(VI) determination.

#### Applications and Comparison of the Proposed Method with other Methods

According to the results, given in Table 2, the modified sensor was successfully applied to the determination of Mo(VI) in water and food samples. Mo(VI) was also

**Table 3.** Comparison of Some Critical Points in Present Work Compared with Some Previous Works for Determination of Mo(VI)

Electrode	Relative standard deviation (%)	Linear dynamic range (ng ml <sup>-1</sup> )	Detection limit (ng ml <sup>-1</sup> )	Ref.
CPE/CTAB	3.9	0.5-500.0	0.04	[27]
HMDE	-	48.0-240.0	14.4	[28]
HMDE	3.6	-	4.0	[29]
Acetylene black paste electrode	2.4	0.5-960.0	0.19	[30]
Lead film electrode	3.9	0.19-4.8	0.08	[31]
HMDE	1.9-6.0	0.5-150.0	0.1	[32]
HMDE	-	0.1-20.0	0.06	[33]
HMDE	-	Up to 70.0	0.45	[34]
IIP@SiO <sub>2</sub> @Fe <sub>3</sub> O <sub>4</sub>	1.4	0.2-500.0	0.04	This work

determined after addition to the samples and recovery values were calculated. As shown in Table 2, the acceptable recovery and RSD suggest that the method can be applied for the successful determination of the target ion in water and food samples.

In Table 3 a comparison is given between the proposed electrode with the previously reported modified electrodes for the determination of Mo(VI). As seen in Table 3, the linear ranges and detection limit of this work are better than many other reported electrodes [27-34]. In addition, the selectivity of this method is better than the other method.

## CONCLUSIONS

In this study, a novel electrochemical sensor based on ion imprinted polymer for the determination of Mo(VI) was constructed and applied. This method is based on sensitive and selective interaction between target ion and nano-IIP at the surface of modified electrode that leads to high sensitivity and wide linear range for the determination of Mo(VI). The investigation of interference effect of different substances confirmed the high selectivity of proposed

sensor for Mo determination. Finally, the applicability of the modified electrode was evaluated by the determination of analyte in real samples and the result showed good performance of the designed electrode.

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