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International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

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To cite this Article Ardakani, M. Mazloum, Karimi, M. A., Mashhadizadeh, M. H., Pesteh, M., Azimi, M. S. and Kazemian, H. (2007) 'Potentiometric determination of monohydrogen arsenate by zeolite-modified carbon-paste electrode', *International Journal of Environmental Analytical Chemistry*, 87: 4, 285 – 294

To link to this Article: DOI: 10.1080/03067310601068825

URL: <http://dx.doi.org/10.1080/03067310601068825>

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Potentiometric determination of monohydrogen arsenate by zeolite-modified carbon-paste electrode

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(Received 8 June 2006; in final form 13 October 2006)

A new carbon-paste electrode, based on natural zeolite (clinoptilolite) modified by the Fe^{2+} ion as carrier, was developed. The electrode exhibits a linear response to monohydrogen arsenate over a wide concentration range (5.0×10^{-8} – 1.0×10^{-3} M) with a Nernstian slope of -28.3 ± 1.0 mV per decade ($r^2 = 0.9998$). The limit of detection was 3.0×10^{-8} M. It has a fast response time 5–10 s and can be used for more than 2 months. Selectivity coefficients determined by the fixed interference method indicate that a good discriminating ability towards monohydrogen arsenate ion in comparison with other anions. The monohydrogen arsenate-selective electrode could be used in the pH range of 7.0–11.0. This chemically modified carbon-paste electrode was successfully used for the determination of arsenic in water and wastewater samples.

Keywords: HAsO_4^{2-} ; Zeolite; Potentiometry; Zeolite carbon-paste electrode

1. Introduction

Several drinking-water sources around the world [1–4] are contaminated by toxic arsenic originating from the oxidation of arsenic-containing minerals or mining activities. Using untreated water contaminated with arsenic causes numerous diseases of the skin and internal organs [5]. Therefore, one of the most pressing aims of the World Health Organization (WHO) [6] in solving the world's drinking-water problems is to develop and introduce low-cost procedures to determine various arsenic species from natural water.

Arsenic is a naturally occurring element in the environment and can be present in ground water as a result of minerals dissolving from rock and soils. It has many industrial uses such as hardening of copper and lead alloys, pigmentation in paints, glass manufacture, electrical semiconductors, pesticides, and food additives. Inorganic arsenic is highly toxic to mammals and damages most human organs. It is also toxic to

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aquatic species. When ingested, it is readily absorbed from the gastrointestinal tract, lungs, and, to a lesser extent, the skin, and is distributed throughout the body. The main objective of this study was to optimize a relatively inexpensive and specific method to determine arsenic species from drinking water.

Natural zeolites [7] are well-known aluminosilicate crystalline microporous materials exhibiting unique physicochemical properties including the ability to absorb heavy-metal cations from aqueous solutions [8]. Organo-modified natural zeolitic materials comprise a recently developed class of specialized sorbents based on zeolite-containing sedimentary rocks chemically pretreated with organic compounds, such as quaternary amines and polyamine [9]. These materials exhibit combined absorptive properties and are able to remove cations, anions, and even organic molecules from aqueous solutions.

Zeolite and zeolite-modified electrodes (ZMEs) have stimulated interest in electrochemical science. Such interest in the fields of electrochemistry and zeolite science can be discerned from the number of reviews on this topic in previous years [10–12]. However, even greater interest arises from the perception that examining the commonalities between electrochemistry and zeolite science and then exploring beyond them will lead us to new science and the discernment of new reactive schemes.

It has been demonstrated empirically that ion-exchange reactions occurring at ZMEs are of major importance in terms of their application as electrochemical sensors. Previously, fundamental studies involving ZMEs, based on ion-exchange equilibrium occurring on zeolite particles, have not been widespread [13]. Recently, intrazeolite effects observed with ZMEs have been reported [14]. Among these, Baker *et al.* [14, 15] focused on electron-transfer mechanisms and ion-exchange reactions (cation-site effects, intracrystalline cation exchange, and kinetics), especially for some zeolites embedded into a polystyrene film-coated on solid electrodes (especially for zeolites with low ability exchange), while Calzaferri's group [16] proposed intrazeolite ion and electron-transport mechanisms for dense zeolite monograin layers on substrate electrodes. Such studies are very informative, owing to their demonstrative ability of ZMEs to distinguish between electroactive species on the basis of their ion-exchange sites in the zeolite framework, but they are not directed towards analytical applications of ZMEs. In these methods, ZMEs should be preconcentrated with electroactive cations before their electrochemical sensing. All previously described fundamental investigations of ZMEs [13–16] were performed using pre-exchanged (completely or not) zeolite particles, so electroactive materials were initially located in bulk zeolite, not in external solution, in contrast to what is done when using ZMEs as preconcentrating systems via an ion-exchange route for electrochemical detection.

The aim of this work was to investigate the determination of the HAsO_4^- anion from aqueous solutions using natural zeolite modified by Fe^{2+} . Chemically modified carbon-paste electrodes (CMCPEs) have been successfully applied as potentiometric sensors for determination of some species [17]. Most of these electrodes are based on the ion-exchange mechanism of the active component incorporated into the carbon-paste matrix.

These electrodes offer very attractive properties for the electrochemical investigation of various inorganic and organic species. In comparison with ion-selective electrodes based on polymeric membranes, CMCPEs possess advantages of simple preparation, ease of regeneration, and a very stable response in addition to the very low ohmic resistance [18], which is probably due to the formation of a very thin film of pasting

liquid coated onto small particles of carbon powder [19]. Therefore, CMCPes have direct application in a variety of analytical situations, such as amperometry [20] and voltammetry [21] in addition to potentiometry [22]. CMCPes have been successfully used to determine arsenic using both potentiometric titration [23] and potentiometric stripping analysis [24]. Recently, two As(V) selective electrodes (with and without an inner reference solution) have been made based on iron oxyhydroxide embedded on silica gel mixed with ultrapure graphite [25]. Also, a new differential pulse anodic stripping voltammetry (DPASV) method for the determination of arsenic in tapwater samples with a gold-film-plated carbon-paste microstructure have been developed [26].

Voltammetry, especially stripping voltammetry, is the most common electrochemical technique used to determine low levels of arsenic. Occasionally, potentiometric and/or amperometric titrations have been carried out. Construction and then application of ion-selective electrode as a potentiometric sensor offers interesting advantages such as simplicity, high speed, fast response, low cost, wide linearity range, and a simple procedure.

2. Experimental

2.1 Reagents and chemicals

All of the chemicals used were of analytical reagent grade. Doubly distilled water was used throughout all experiments. Graphite powder (1–2 μm) (Aldrich, St. Louis, MO), paraffin oil (Merck), and natural zeolites (clinoptilolite) modified by iron(II) (clinoptilolite) (Mianeh, Iran) were prepared.

Before use, flasks and containers were soaked in 6 M HNO_3 for at least 24 h, then rinsed with deionized water. Extra-pure fine graphite powder (Merck, Whitehouse Station, NJ) and paraffin oil (Merck) were used for the graphite pastes. Stock solutions of HAsO_4^{2-} were prepared from the corresponding analytical grade (Merck).

2.2 Preparation of modified zeolite

The natural zeolite was ground and wet-sieved to a particle size of 224–500 μm . The powder was then washed with distilled water in order to remove occluded soluble salts and dried at 50°C overnight. To prepare iron-modified zeolite, 5 g of zeolite powder was mixed with 50 mL of 1 M solution of FeCl_2 in a 100-mL polyethylene vessel, shaken for 72 h at 24°C, and then washed with diluted HCl solution to remove any occluded material and surface-adherent salt. Double-distilled water was then used to wash the sample to remove Cl^- ions. The modified zeolite was then characterized [27, 28].

2.3 Preparation of modified-zeolite carbon-paste electrode

Modified-zeolite carbon paste was prepared according to the following procedure: 3 g of solid particles, i.e. natural zeolite modified by iron(II) and graphite in a ratio 10 : 1, was ground into micro grains as small as possible in a mortar. Paraffin oil was added to

the above mixture using a 5-mL syringe and mixed for 20 min until a uniformly wetted paste was obtained. The paste was then packed into the end of a Teflon tube (e.d. 8 mm, i.d. 6 mm) equipped with a screwing stainless-steel piston. When necessary, a new surface was obtained by pushing an excess of paste out of the tube and polishing it on a weighing article. Unmodified carbon paste was prepared in the same way without adding zeolite to the mixture and was used for comparison purposes.

2.4 Potential measurement and calibration

The potential build-up across the zeolite carbon-paste electrode was measured using the following type of galvanic cell: Cu | zeolite-modified carbon paste | test solution ||| SCE. All potentials were measured at $25 \pm 1^\circ\text{C}$ using a digital pH/mV meter, model 691 Metrohm. A saturated calomel electrode (SCE, Metrohm) with a fibre junction was used as the external reference electrode. Activities were calculated according to the Debye–Hückle procedure [29] for the calibration curve, and concentration instead of activity was used. The pH of the sample solution was monitored simultaneously with a conventional glass pH electrode (Metrohm).

The performance of the modified-zeolite carbon-paste electrode was investigated by measuring its potential in monohydrogen arsenate solutions prepared in the concentration range 1.0×10^{-8} – 1.0×10^{-3} M by serial dilution at constant pH. All solutions were freshly prepared by dilution from the stock standard solution, 1.0×10^{-1} M, with doubly distilled water. The solutions were stirred and potential readings recorded when they became stable. The data were plotted as observed potential vs. the logarithm of the HAsO_4^{2-} concentration.

3. Results and discussion

3.1 Optimization of the modified-zeolite carbon-paste electrode composition

Preliminary experiments were carried out to obtain an optimum zeolite carbon-paste electrode composition. The optimized zeolite carbon-paste electrode was used to test the performance of the zeolite carbon-paste characteristics.

In the preliminary experiment, carbon pastes with and without zeolite were constructed. The carbon pastes with no zeolite displayed insignificant selectivity toward arsenate, and their response was not reliable, whereas in the presence of the proposed modified zeolite, the optimized carbon paste demonstrated a Nernstian response and remarkable selectivity for arsenate over several common inorganic and organic anions.

Several zeolite carbon-paste compositions were investigated by varying the ratio of graphite, paraffin, and the active material, zeolite (table 1). The potentiometric response of the modified-zeolite carbon-paste electrode was greatly improved in the presence of lipophilic anionic additive, NaTPB. The ratio of paste ingredients and concentration of the equilibrating solution were optimized so that the electrode would develop reproducible, noiseless, and stable potentials. The paste compositions which resulted in the best performance are listed in table 2 along with their potentiometric characteristics. The use of paraffin oil requires lower amounts of zeolite in electrodes and also improves the homogeneity of the electrodes so that in the presence of paraffin

Table 1. Optimization of the zeolite modified carbon paste ingredients (values are mass ratios in percent).

Electrode	Composition (%)				Slope (mV decade ⁻¹)
	Graphite	Zeolite	NaTBP	Oil	
A	70.0	7.0	0	23.0	-26.0 ± 1.0
B	69.0	8.0	0	23.0	-11.5 ± 1.0
C	71.0	6.0	0	23.0	-6.2 ± 1.0
D	70.0	6.0	1.0	23.0	-28.3 ± 1.0
E	50.0	25.0	0	25.0	-
F	39.0	39.0	0	22.0	-
J ^a	70.0	6.0	1.0	23.0	-

^aUnmodified zeolite.

Table 2. Characteristics of optimized modified-zeolite carbon-paste electrode (ZMCPE).

Linear range (M)	5.0×10^{-8} – 1.0×10^{-3}
Slope (mV/decade)	-28.3 ± 1.0
pH range	7.0–11.0
Precision	At a concentration of 1.0×10^{-4} mol L ⁻¹ , the arsenate standard deviation was ± 0.90 mV
Detection limit (M)	3.0×10^{-8}
Lifetime (month)	2
Response time (s)	10

oil, the potential readings will be stable and reproducible. This could be attributed to a significant increase in homogeneity and lipophilicity by using the paraffin oil. Electrodes made from 6.0% w/w zeolite in the presence of 70.0% graphite, 23.0% paraffin oil, and 1.0% NaTBP were found to be the most suitable, and show a rapid response and good signal stability (electrode D; table 1). Thus, this electrode composition was used for subsequent studies. The composition was, therefore, used to study the performance of the electrode, viz. working concentration range, sensitivity, selectivity, life time, response time, and effect of pH.

The potential response of the optimized monohydrogen arsenate-selective electrode to varying concentrations of HAsO_4^{2-} ions was examined. All the emf values were corrected for liquid junction potential using the Henderson equation. The average slope of the calibration plot was -28.3 ± 1.0 mV/decade. The calibration plot is shown in figure 1; this indicates a linear range from 5.0×10^{-8} to 1.0×10^{-3} M ($R^2 = 0.9998$). The practical limit of detection, defined as the concentration of arsenate ion obtained from the intersection of two extrapolated segments of the calibration graph, was about 3.0×10^{-8} M. The optimum equilibration times for arsenate-selective electrode in the presence of 1.0×10^{-3} M monohydrogen arsenate was 1 h, after which the electrode would generate stable potentials in contact with HAsO_4^{2-} solutions. The characteristic properties of the optimized paste are summarized in table 2.

The stability and reproducibility of the electrodes were also tested. The standard deviation of 10 replicate measurements at 1.0×10^{-4} M HAsO_4^{2-} was ± 0.9 mV. The long-term stability of the electrode was studied by periodically recalibrating in standard solutions and calculating the response slope over the range of 1.0×10^{-8} – 1.0×10^{-3} M. The detection electrode was very stable and could be used over a period of at least 2 months. The slopes of the electrode response decreased from -28.3 to -27.0 mV decade⁻¹ over a period of 2 months (table 3).

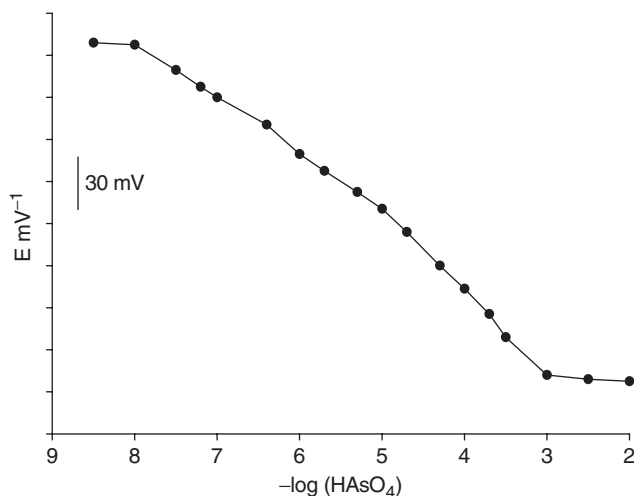


Figure 1. Potentiometric response of the monohydrogen arsenate modified-zeolite carbon-paste electrode.

Table 3. Stability and reproducibility of the monohydrogen arsenate zeolite carbon paste electrode ($n = 5$).

Time (day)	Slope (mV decade ⁻¹)	Linear range (mol L ⁻¹)
1	-28.3	5.0×10^{-8} – 1.0×10^{-3}
7	-28.3	5.0×10^{-8} – 1.0×10^{-3}
20	-28.2	8.0×10^{-8} – 1.0×10^{-3}
25	-28.1	8.0×10^{-8} – 1.0×10^{-3}
40	-28	1.0×10^{-7} – 1.0×10^{-3}
55	-27.4	1.0×10^{-7} – 1.0×10^{-3}
75	-27	3.0×10^{-7} – 1.0×10^{-3}

3.2 Effect of pH

The effect of the pH of the test solution on the response of the modified-zeolite carbon-paste electrode was examined at 1.0×10^{-5} M concentration of HAsO_4^{2-} . The pH was adjusted with dilute hydrochloric acid and sodium hydroxide as required. As illustrated in figure 2, the potentials remained constant within a pH range of approximately 7.0–11.0. Variation of the potential at $\text{pH} < 7.0$ could be related to protonation of HAsO_4^{2-} in the paste phase, which results in a loss of its ability to interaction with zeolite. At higher pH, i.e. > 11.0 , the potential drop (negative slope) may be due to interference from hydroxide ions and a noticeable decrease of HAsO_4^{2-} by conversion into AsO_4^{3-} .

3.3 Response time

For analytical applications, the response time of an electrode is of critical importance. The response time was defined as the time elapsed from the dipping of the electrode in the solution until the equilibrium potential was reached. Also, the average time required

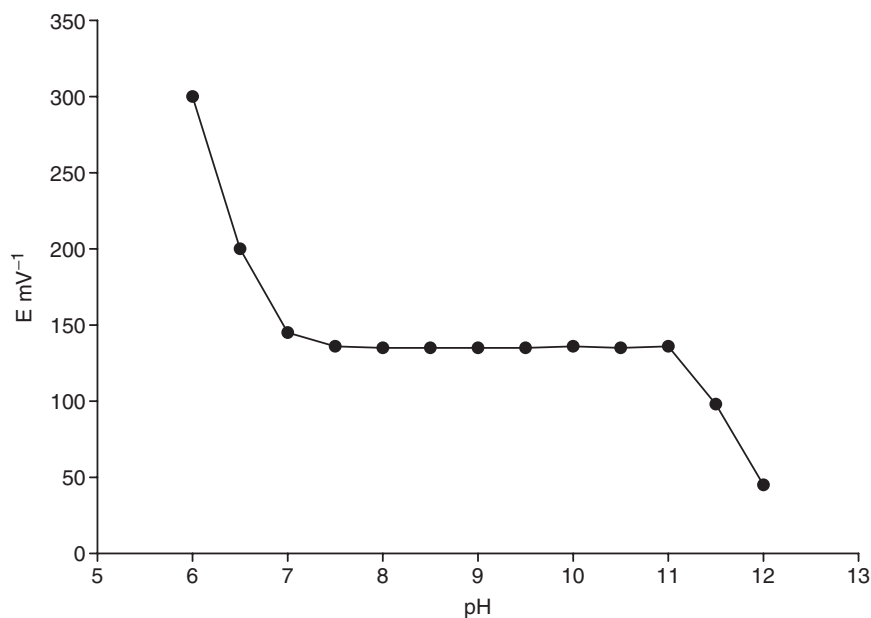


Figure 2. Influence of pH on the potential response of the optimized monohydrogen arsenate modified-zeolite carbon-paste electrode for a monohydrogen arsenate concentration of 1.0×10^{-5} M.

for the electrode to reach a steady potential response within ± 1 mV of the final equilibrium value after successive immersion of a series of HAsO_4^{2-} solutions, each having a tenfold difference in concentration was investigated. Response times inherent to ion-selective electrodes are only measurable if the overall response time of the potentiometric system is governed by the properties of the paste of electrode, i.e. if the time constant of the response function of the electrode is much larger than the time constants of the electrochemical cell and the electronic EMF-measuring device. Indeed, the overall response time is affected by a series of factors, for example the time constant of the measuring instrument, the impedance of the equivalent electrical circuit of the paste, the rate of the ion-transfer reaction across the paste/sample interface, the diffusion of the ion to be measured through the stagnant layer in the sample, and establishment of a liquid-junction potential at the reference electrode [30].

An important advantage of the electrodes is that they respond much faster to concentration changes than do zeolite-epoxy electrodes. The static response time of electrode thus obtained was less than 10 s over the entire linear concentration range (figure 3). The equilibrium potentials essentially remained constant for over 5 min.

3.4 Selectivity and interference

The potentiometric selectivity coefficient defines the ability of a selective electrode to distinguish between different ions in the same solution. It is not identical to the similar term used in the separation process. The selectivity coefficient should preferably be evaluated by measuring the response of an electrode in solutions of the primary ion, monohydrogen arsenate, and interfering ion, A^- (fixed interference method).

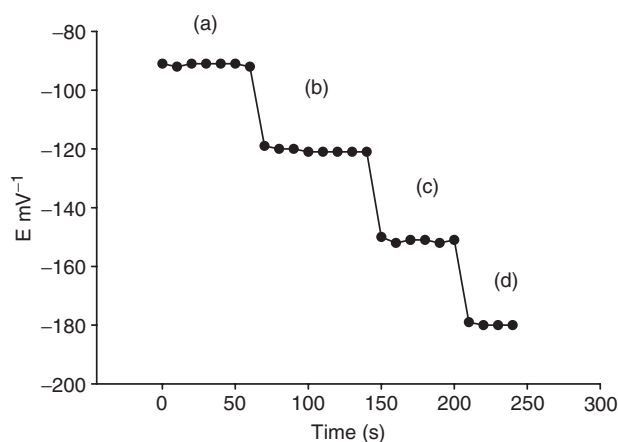


Figure 3. Response time of the optimized monohydrogen arsenate modified-zeolite carbon-paste electrode for step changes in concentration of monohydrogen arsenate: from (a) 1.0×10^{-7} M to 1.0×10^{-6} M, (b) 1.0×10^{-6} M to 1.0×10^{-5} M, (c) 1.0×10^{-5} M to 1.0×10^{-4} M, and (d) 1.0×10^{-4} M to 1.0×10^{-3} M.

Table 4. Selectivity coefficients, determined by use of the fixed interference method for the modified-zeolite carbon-paste electrode (ZMCPE).

Interference ion	$\log K_{\text{HAsO}_4^{2-}, \text{A}^-}^{\text{pot}}$	Interference ion	$\log K_{\text{HAsO}_4^{2-}, \text{A}^-}^{\text{pot}}$
I^-	-3.8	SO_4^{2-}	-1.6
SCN^-	-2.5	$\text{S}_2\text{O}_3^{2-}$	-1.7
BrO_3^-	-2.0	ClO_4^-	-2.4
CrO_4^{2-}	-3.6	F^-	-2.6
OAc^-	-4.6	NO_2^-	-1.2
NO_3^-	-3.4	IO_3^-	-1.4
Cl^-	-2.1	$\text{C}_2\text{O}_4^{2-}$	-2.6
CO_3^{2-}	-2.3	-	-

The selectivity coefficient ($K_{\text{HAsO}_4^{2-}, \text{A}^-}^{\text{pot}}$) for various anions was evaluated by the mixed solution method with a fixed concentration of interference ion and varying amounts of monohydrogen arsenate concentrations. Table 4 lists the potentiometric selectivity coefficient data of the sensor for several anions relative to arsenate. The selectivity coefficients clearly indicate that the electrode is selective to monohydrogen arsenate over a number of other inorganic and organic anions. In this work, interference studies were carried out for F^- , Cl^- , I^- , CH_3COO^- , SCN^- , and IO_3^- monovalent ions. As can be seen from table 4, the most interfering anion at the electrode is nitrite. The interference effect of the ions is as follows: $\text{NO}_2^- > \text{IO}_3^- > \text{SO}_4^{2-} > \text{S}_2\text{O}_3^{2-} > \text{BrO}_4^- > \text{Cl}^- > \text{CO}_3^{2-} > \text{ClO}_4^- > \text{SCN}^- > \text{F}^- = \text{C}_2\text{O}_4^{2-} > \text{NO}_3^- > \text{CrO}_4^{2-} > \text{I}^- > \text{OAc}^-$.

The sequence is characterized by the Hofmeister series: $\text{R}^- > \text{ClO}_4^- > \text{SCN}^- > \text{I}^- > \text{NO}_3^- > \text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{HPO}_4^{2-}$. The reason that the selectivity coefficients of this electrode do not comply with the Hofmeister series, and show an anti-Hofmeister behaviour, is perhaps due to the possible interaction of the anions with Fe in zeolite.

Table 5. Recovery of monohydrogen arsenate ions from different water samples.

Sample	HAsO ₄ ²⁻ (μg mL ⁻¹)		Recovery (%)
	Added	Found	
Well water	1.5	1.52 (±0.05)	101.3
Tap water	2.5	2.56 (±0.03)	102.4
River water	1.0	1.05 (±0.02)	105.0

Table 6. Recovery of monohydrogen arsenate from wastewater.

Sample	HAsO ₄ ²⁻ (μg mL ⁻¹)	
	ET-AAS	ZMCPE
Wastewater	0.030 ± (0.003)	0.028 ± (0.002)

The fact that this electrode could be used over a wide pH range and good selectivity coefficient seems to be an advantage. As is evident from the data in table 4, the monohydrogen modified-zeolite carbon-paste electrode has a relatively high selectivity toward monohydrogen arsenate relative to anions such as nitrite, bromate, and several common anions. The modified zeolite has higher interaction with the monohydrogen arsenate ion than any of the other anions tested.

3.5 Practical applications

The high degree of monohydrogen arsenate selectivity exhibited by the electrode makes them potentially useful for monitoring concentration levels of monohydrogen arsenate in spiked water samples. To assess the applicability of the modified-zeolite carbon-paste electrode real samples, an attempt was made to determine monohydrogen arsenate in different water samples spiked with increasing concentrations of monohydrogen arsenate ranging from 1.0 to 2.5 μg mL⁻¹ and the recovery factor calculated. The results presented in table 5 indicate a good recovery. Also, the accuracy of the method was further assessed by repeated measurement ($n=5$) of total arsenic in the wastewater sample by electrothermal atomic absorption spectrometry (ET-AAS). The mean concentration and standard deviation of the results are presented in table 6. There are no significant differences between the results given by two methods and confirming the accuracy of the potentiometric method.

4. Conclusion

The results of this study show that the modified-zeolite carbon-paste electrode may provide an attractive alternative for the detection of monohydrogen arsenate. This electrode is very easy to prepare and use, and shows a Nernstian response. The very low detection limit, wide dynamic range, fair selectivity, rapid response time, and relatively long-term stability make these sensors suitable for measuring the

concentration of monohydrogen arsenate in a real samples, without the need for preconcentration or pretreatment steps and without any significant interactions from other anionic species present in the samples.

Acknowledgements

The authors express their appreciation to the Payam Noor University Research Council (Ardakan center) for financial support of this work.

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