

Full Paper

Novel All-Solid-State Potentiometric Sensor for Monitoring Hg²⁺ in Waste Water Samples

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Received: 30 December 2014 / Received in revised form: 9 March 2015 /

Accepted: 15 March 2015 / Published online: 30 April 2015

Abstract- A novel all-solid-state (ASS) potentiometric poly vinyl chloride (PVC) membrane sensor is introduced, and to evaluate its applicability in the analyses of real samples it was used for monitoring of mercury ions in waste water samples. The ASS electrode is composed of a conductive composite of graphite and epoxy resin loaded with multi-walled carbon nanotubes (MWCNTs) acting as intermediary layer between an inner copper wire, and an outer thin PVC membrane which is coated on the conducting transducer. The optimal composition of the outer polymeric membrane was found to be 30% of PVC, 60% of nitro benzene (NB) as a plasticizer, 5% of an ionophore L, 2% of an ionic liquid, and 3% NaTPB. The resulting sensor showed a good Nernstian response of 29.4 ± 0.3 mV/decade, in a rather wide range of 1.0×10^{-8} - 1.0×10^{-3} M of the mercury concentration and its detection limit was found to be as low as 3.2×10^{-9} M. The proposed electrode was also found to have good selectivity towards the target ion in the presence of a wide range of commonly occurring ionic species and was further used to determine the concentration of Hg²⁺ ions in waste water samples.

Keywords- All solid state, Mercury, Potentiometry, Sensor

1. INTRODUCTION

Free Hg²⁺ and its compounds are among the most hazardous materials to humans and hence monitoring this ion is for great importance in a variety of fields. Like many other heavy metal ions, Hg²⁺ and its derivatives bio-accumulate in human body leading to

symptoms ranging from weakness sleeplessness, excessive salivation, skin itching and swelling, to fever, paranoia, memory loss, elevated blood pressure, tremors, gingivitis, and excitability [1-3].

Conventionally instrumental techniques like spectrophotometry, flameless or cold-vapour atomic absorption spectrometry, inductively coupled plasma (ICP), fluorimetry, and X-ray fluorescence have been used to the determination of Hg^{2+} [2,4-6]. Although the advantages of such methods are undeniable, the advent of simple and portable devices that can be used for off- and online monitoring of the concentrations of species like Hg^{2+} in real samples has always been of interest in analytical chemical applications.

In the light of the above mentioned and regarding the capabilities and advantages of potentiometric ion-selective sensors, as extensive a class of analytical instruments, which can be applied to the direct and indirect analysis of different ionic species for many years, these devices are known as a suitable alternative for many of such instrumental techniques, which enjoy the advantages of less complexity speed, simplicity and low cost. These portable, offer nondestructive analysis routes for facile monitoring of the concentration of a wide range of ionic species, without the need for using harmful solvents or time consuming sample preparation techniques.

Ion selective sensors have been developed into several different categories including PVC membrane electrodes (PME), coated wire electrodes (CWE), carbon paste electrodes (CPE), all-solid-state (ASS) electrodes and field effective transistors (FET). PMEs suffer the disadvantage of low mechanical resilience, especially if the device is repetitively used. The instruments also have comparatively higher detection limits in the range of 10^{-5} to 10^{-7} M, as compared to the other ASS, CWE, FET and CPEs, which are also known as asymmetric electrodes, due to the difference in the chemical environment of the two sides of the sensing membrane in these devices. The detection limits in asymmetric sensors like CWEs, which do not use an internal filling solution as opposed to PMEs and in turn are based on the direct contact of the internal conducting element with the sensing element, reach improved values in the range of 10^{-8} M. Such devices are also much more mechanically stable and offer advantages of renewability of the outer surface, as well as the possibility of carbon modifying the composition of the sensing element which is a carbon paste in the case of CPEs.

Another improvement in the ion selective sensors is the advent of ASS electrodes in which the sensing PVC membrane is coated on the surface of the conductive composite, which acts as a modified contact between the sensing elements, further improving the characteristics of the sensor. The focus of the present research has hence been the application of a conductive polymeric composite (CPC) of epoxy resin loaded with multi-walled carbon nanotubes (MWCNTs) as the internal contact and transducer.

2. EXPERIMENTAL SECTION

2.1. Chemicals

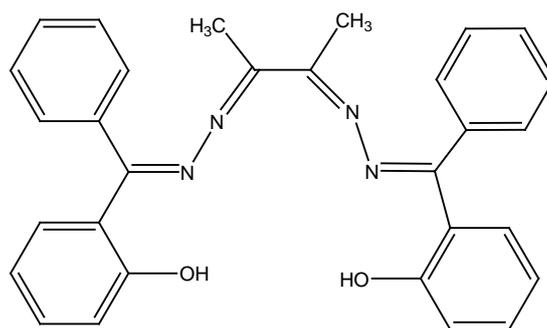
Tetrahydrofuran (THF), dibutyl phthalate (DBP), nitrobenzene (NB), benzyl acetate (BA), and sodiumtetraperenyl borate (NaTPB) and high-molecular weight polyvinylchloride (PVC) and the room temperature ionic liquids used, i.e. 1-n-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF₆), were Merck Co and Fluka Co. The ionophore L (Scheme 1), used in the composition of the sensing PVC membrane was synthesized as described in the literature [7].

Epoxy (macroplast Su 2227) from Henkel (Germany) and hardener (desmodur RFE) were from Bayer Ag (Germany) and the graphite powder of a 1–2 μm particle size, and all solvents and nitrate salts of all cations were of analytical reagent grade and were obtained from Merck Co.

2.2. Construction of the sensors

The typical method for constructing the ASS-PVC membrane electrodes included the two sub-phases of preparing the CPC and the PVC membrane [8-11]. For the constructing the conductive polymer composite (CPC) which is composed of an epoxy resin containing MWCNTs and is used as the internal contact and transducer, different mixtures of powdered graphite, MWCNTs, the epoxy resin and hardener were prepared and tested. The best responses were observed when using a CPC of 0.30 g (30% w/w) of epoxy resin, 0.15 (15% w/w) of the hardener, 0.05 g (5% w/w) of MWCNTs and 0.50 g (50% w/w) of powdered graphite. The mixtures were prepared in a THF solvent, which was let to evaporate in open air, for 20-30 min after the completion of the mixing. This aging procedure was visually monitored and once the mixture reached an appropriate viscosity, a freshly polished copper wire (0.5 mm diameter and 15 cm length) was repeatedly dipped into the mixture (about 10 times). This way the wire was effectively covered with the mixture of the CPC, and the system was allowed to rest and dry in open air for 10 hours. Next the so-prepared solid-state contacts were coated with the PVC membrane through being repeatedly dipped into the membrane cocktails (5 times). The PVC-membrane coated devices were next allowed to dry in air for another 24 h. The best ASS-PVC membrane responses were observed for PVC membranes having a composition of 5% w/w of L, 60% w/w of NB, 30% w/w PVC, 2% w/w of RTIL and 3% NaTPB. After drying, the external surface of the ASS-PVC electrodes was conditioned in a 10⁻³ M solution of Hg²⁺ ions.

The procedure for preparing the PVC membrane simply included dissolving a mixture of different amounts of L with appropriate amounts of PVC, plasticizer and IL in tetrahydrofuran (THF), which was thoroughly mixed in a glass dish of 2 cm diameter, and let viscosity due to the evaporation of the THF to yield a rather oily concentrated mixture.



Scheme. 1. Chemical structure of L

2.3. The potentiometric system

The so-prepared ASS-PVC membrane sensors were next used as the indicator electrode in a glass cell. The cell further comprised of an Ag/AgCl double junction reference electrodes (Azar-Electrode Co., Iran) as the external reference electrodes, which was connected to the indicator electrode through an ion analyzer with a 250 pH/mV meter with ± 0.1 mV precision. The cell could hence be represented as:

Cu wire/ASS layer/ion selective PVC membrane | sample solution || Ag-AgCl, KCl (satd.)

All measurements were performed after obtaining a calibration method using several standard solutions.

3. RESULTS AND DISCUSSION

As already mentioned a majority of the potentiometric ion-selective electrodes are of symmetrical (classical) membranes, in which the ion selective membrane is placed between the internal (fixed) and external (sample) solutions. Asymmetrical ion selective electrodes, on the other hand have a different structure. In these devices the internal solution is eliminated and one side of the membrane is actually in contact with a solid phase. The outer surface on the other hand, is in contact with the test solution .

In symmetrical electrodes the inner reference solution serves to help develop a potential gradient across the membrane, but creates some restrictions in terms of the detection limits as well as robustness and miniaturization. Therefore, it has been desirable to eliminate the internal liquid phase. This change, which was successfully implemented in asymmetrical electrodes, paved the way to enhance the applicability range of these sensors to another applications including in-vivo medicinal and biological applications due to the possibility of manufacturing miniaturized devices with improved responses and detection limits.

All-solid-state (ASS) ion-selective polymeric membrane electrodes [8-11], as a category of asymmetric electrodes are of interest due to the above mentioned advantages. In these devices, the use of conductive epoxy supports for the membrane sensors further allows for the construction of all-solid state PVC membrane electrodes, which can take different configurations, apart from miniaturization. These devices can also be used in flow-through systems and flow-injection analyses, specifically due to their improved mechanical stability and robustness.

As their names indicate, in ASS-PVC membrane electrodes, the PVC element composing a suitable and selective ionophore is the heart of the device, and each of its component plays a crucial role in the overall response of the device.

Hence in this work this was carefully studied, and the highlights of the optimization procedure are summarized in Table 1.

Table 1. Optimization of membrane ingredients used in making ASS-PVC membrane sensor

No.	PVC	Plasticizer	RTIL	L	NaTPB	Slope* (mV/decade)
1	30	NB,65	2	3	0	14.9±0.3
2	30	NB,64	2	4	0	16.9±0.4
3	30	NB,63	2	5	0	18.0±0.3
4	30	NB,62	2	6	0	17.9±0.2
5	30	NB,61	2	5	2	27.1±0.5
6	30	NB,60	2	5	3	29.4±0.3
7	30	NB,59	2	5	4	29.3±0.3
8	30	DBP,60	2	5	3	24.1±0.2
9	30	BA,60	2	5	3	24.5±0.3

*The results are based on five replicate measurements.

It was found that a plasticizer/PVC ratio of about 2.0 led to the best responses, and consequently, for all the membrane compositions mentioned in this table the amount of PVC is taken to be constant and equals 30%wt. The other vital component of the membranes is the water-immiscible organic solvent, which enhances the mobility of the free and complexed ionophores through the polymeric membrane phase. This, so-called, plasticizer should have a low vapor-pressure, be compatible with PVC and the other membrane components, and have no functional groups which can undergo protonation reactions. Some conventional plasticizers with a variety of dielectric constants include dibutyl phthalate (DBP with DC of 6.4), nitrobenzene (NB with DC of 35.7) and benzylacetate (BA with DC of about 5.7) were hence used in preparation of the sensing membrane, and the results showed that NB-

containing membranes have better responses. This could be attributed to the fact that due to the polarity of Hg^{2+} this rather polar plasticizer facilitates the extraction of mercury ion into the organic phase of the membrane. This is further enhanced by the incorporation of some ionic additive, which also reduces the Ohmic resistance of the membrane.

More recent works have shown that the use of water-immiscible room temperature ionic liquids (RTILs) helps further optimize the response of the sensors with PVC membranes. Due to their ionic nature and liquid phase, these RTILs can act as the ionic additive (reducing the Ohmic resistance of the membrane), in addition to improving the ion-exchange properties of the membrane.

The effect of the ionophore on the response of the electrode is undeniable [12-18]. Based on the membrane concentration-sensor response changes in the table membrane no. 6, showing the best Nernstian slope (29.4 ± 0.3 mV/decade) was selected for further studies.

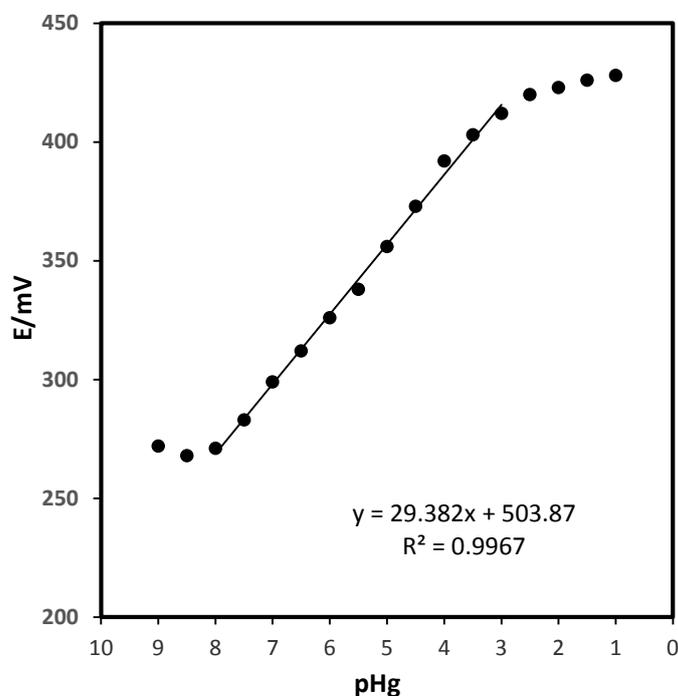


Fig. 1. Calibration curve of Hg ASS PVC membrane sensor; the results are based on 5 replicate measurements.

To evaluate the other properties of the optimal sensor, the potential response of the electrochemical cell was recorded at different concentrations of the Hg^{2+} ion (from 1.0×10^{-8} - 1.0×10^{-1} M), and the potential vs. $-\log [\text{Hg}^{2+}]$ curve was plotted (Figure 1). The linear part of this curve indicates the linear range of the sensor, where a Nernstian response is observed. In conventional PVC membrane sensors, the linear range does not transcend 10^{-6} M, apart from some exceptions. In the case of ASS-PVC membrane sensors however, much lower detection limits have been observed [10,11].

On the other hand, due to the saturation of the active sites of the electrode surface which originates from the smaller electrode surface, the upper limit of detection is usually limited and was found to be in the range of 10^{-3} M, in the case of the case of the current work. The slope of the linear section of the calibration curve, which ranged from 1.0×10^{-8} to 1.0×10^{-3} M was 29.4 mV/decade of the Hg^{2+} concentration, which is in very good agreement with a Nernstian behavior. The standard deviation of the measurements based on five replicate tests was calculated to ± 0.3 mV. Further extrapolation of the two linear segments of the lower part of the calibration curve, proved the detection limit of the ASS-PVC electrode to be 3.2×10^{-9} M.

The dynamic response time of a sensor, which is defined as the time required by the sensor to achieve values within ± 1 mV of the final equilibrium potential [19-22], after successive immersions in the sample solutions, was evaluated for the electrode and it was revealed that using a series of Hg^{2+} solutions with concentrations ranging from 1.0×10^{-8} to 1.0×10^{-3} M, the average response time was about 14 seconds. The results are depicted in Figure 2.

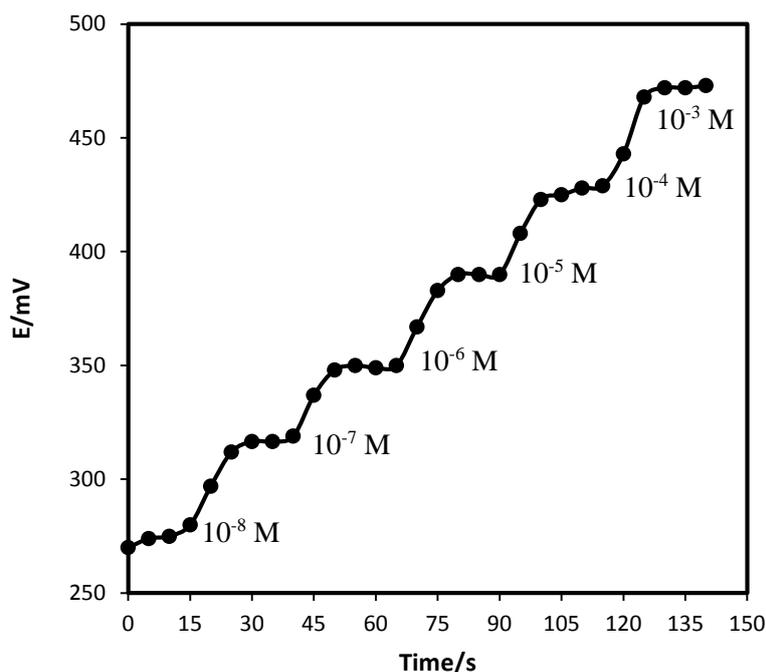


Fig. 2. Dynamic response time of the Hg ASS PVC membrane sensor

To evaluate the effect of pH of the test solutions on the sensor responses, the potential readings were made using a specific concentration of the Hg^{2+} (1.0×10^{-5} M) while changing the pH from 1.0 to 10.0 using concentrated NaOH or HCl solutions (Figure 3), which helped avoid significant changes in the concentration of the Hg^{2+} solution upon changing the pH. The results revealed that the potential is free from the changes of pH in the range of 3.0 to 5.0

Below 3, relatively significant fluctuations in the potential vs. pH behavior was observed due to the protonation of the ionophore, while the fluctuations above 5 were attributed to the formation of $\text{Hg}(\text{OH})^+$ or $\text{Hg}(\text{OH})_2$ species which decrease the concentration of Hg^{2+} ions in the aqueous test solution [23-25].

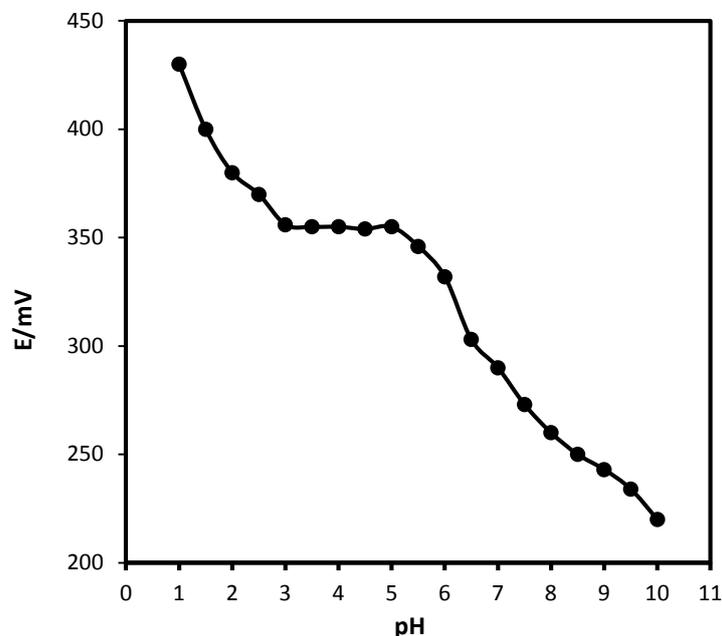


Fig. 3. pH effect on potential response of the Hg ASS PVC membrane sensor

The lifetime of the sensor was also estimated using the calibration curves, acquired through the periodical application of a standard solution and calculation of its response slope, using three electrodes. To acquire these data the three electrodes were employed for 1 hour per day for 12 weeks. After a period of 10 weeks, a slight gradual decrease in the slope and an increase in the detection limit were observed [23-31]. This is generally attributed to the loss of the plasticizer, the ionophore, or the ionic additives from the polymeric film due to leaching into the sample solution after extensive use of the devices. Using RTILs in the composition of the membrane causes a longer lifetime of the sensor. ASS PVC membrane sensors show a longer life-time than traditional PVC membrane sensors.

Selectivity, which describes an ion-selective electrode's specificity toward the target ion in the presence of interfering ions, is the most important characteristic of such devices. The potentiometric selectivity coefficients of the ASS-PVC were evaluated by the matched potential method (MPM) [32,33], and the resulting values are shown in Table 2. Note that all selectivity coefficients indicate that the interferences have a negligible influence on the performance of the electrode assembly.

To evaluate the repeatability of the experiment, 3 standard synthetic samples were measured by calibration method. The RSD values obtained for the ASS-PVC membrane were

2.55, 2.70 and 3.10%. The RSD values for the intra- and inter-day assays in the cited formulations performed in the same laboratory by the two analysts did not exceed 4.0% .

Table 2. Selectivity coefficients of interfering cations for Hg²⁺ ASS PVC membrane sensor

Cation	Selectivity Coefficients
Na ⁺	2.7×10 ⁻⁶
K ⁺	2.5×10 ⁻⁶
Mg ²⁺	7.5×10 ⁻⁶
Ca ²⁺	9.1×10 ⁻⁶
Cu ²⁺	7.5×10 ⁻⁴
Cd ²⁺	9.5×10 ⁻⁵
Pb ²⁺	2.1×10 ⁻⁴
Ag ⁺	4.5×10 ⁻⁵
Fe ³⁺	8.4×10 ⁻⁵
Ni ²⁺	3.6×10 ⁻⁵

Table 3. Results of mercury analysis in waste water samples

Sample	Found by the sensor* (ppm)	Found by ICP-OES (ppm)
Sample 1	1.7±0.1	1.8±0.1
Sample 2	2.5±0.2	2.4±0.1
Sample 3	3.9±0.1	4.0±0.1

* The results are based on five replicate measurements.

To assess the applicability of the proposed sensor to real samples, the concentration of Hg²⁺ in some industrial wastewater samples were analyzed. The samples were collected and acidified with HNO₃, and each sample was analyzed three times using the proposed mercury sensor by calibration method. The samples were also analyzed through inductively coupled plasma optical emission spectrometry (ICP-OES) as a reference method. The results are given in Table 3, which shows that the amount of mercury recovered with the help of the sensor are in good agreement with reference method.

4. CONCLUSIONS

An all-solid-state potentiometric PVC membrane sensor was constructed for fast and simple determination of mercury ions in waste water samples. The solid contact as an effective transducer was made based on graphite, MWCNT, epoxy resin on a copper wire. A thin layer PVC membrane coated on the surface of the transducer composed of 30% PVC, 60% NB, 2% ionic liquid, 3% NaTPB and 5% ionophore L. The sensor showed a dynamic linear range of the sensor is 1.0×10⁻⁸-1.0×10⁻³ M of the mercury concentration and a

detection limit of 3.2×10^{-9} M. The proposed sensor was successfully applied in determination of mercury ions in some water samples.

REFERENCE

- [1] H. J. M. Bowen, Environmental chemistry of the elements, London, Academic Press, (1979).
- [2] L.R. Drennan-Harris, S. Wongwilawan, and J. F. Tyson, J. Anal. At. Spectrom. 28 (2013) 259.
- [3] National Library of medicine, Hazardous Substances Data Bank (HSDB) (1996).
- [4] [online] EPA Method 1631. Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, (www.epa.gov/nerlesd1/factsheets/mpt.pdf.) Mercury Preservation Techniques.
- [5] E. Kopysc, K. Pyrzynska, S. Garbos, and E. Bulska, Anal. Sci. 6 (2000) 1309.
- [6] P. Shetty, and N. A. Shetty, Indian J. Chem. Technol. 11 (2004) 163.
- [7] M. R. Ganjali, P. Norouzi, T. Alizadeh, M. Salavati-Niasari, Bull. Korean Chem. Soc. 28 (2007) 68.
- [8] I. Isildak, Turk. J. Chem. 24 (2000) 389.
- [9] I. Isildak, A. Asan, Talanta, 48 (1999) 967.
- [10] B. Kemer, M. Ozdemir, Turk. J. Chem., 32 (2008) 521.
- [11] P. Kumar, D. Kim, M. H. Hyun, M. Won, Y. Shim, Electroanalysis, 25 (2013) 1864.
- [12] L. Hajiaghbabaei, A. Sharafi, S. Suzangarzadeh, and F. Faridbod, Anal. Bioanal. Electrochem.5 (2013) 481.
- [13] F. Faridbod, M. R. Ganjali, B. Larijani, P. Norouzi, S. Riahi and F. S. Mirnaghi, Sensors 7 (2007) 3119.
- [14] H. A. Zamani, M. Nekoei, M. Mohammadhosseini and M. R. Ganjali, Mater. Sci. Eng. C 30 (2010) 480.
- [15] M. R. Ganjali, M. Qomi, A. Daftari, P. Norouzi, M. Salavati-Niasari and M. Rabbani, Sen. Actuators B 98 (2004) 92.
- [16] H. A. Zamani, G. Rajabzadeh and M. R. Ganjali, Sensor Lett. 7 (2009) 114.
- [17] H. A. Zamani, M. R. Ganjali, P. Norouzi and M. Adib, Sensor Lett. 5 (2007) 522.
- [18] H. A. Zamani, M. R. Ganjali, and M. Adib, Sensor Lett. 6 (2006) 345.
- [19] M. R. Ganjali, P. Norouzi, M. Adib and A. Ahmadalinezhad, Anal. Lett. 39 (2006), 1075.
- [20] M. Shamsipur, S. Rouhani, H. Shaghi, M. R. Ganjali and H. Eshghi, Anal. Chem. 71 (1999) 4938.
- [21] M. R. Ganjali, Z. Memari, F. Faridbod and P. Norouzi, Int. J. Electrochem. Sci. 3 (2008) 1169.
- [22] H. A. Zamani, M. R. Ganjali, P. Norouzi and S. Meghdadi, Anal. Lett. 41 (2008) 902.

- [23] H. A. Zamani, M. Rohani, A. Zangeneh-Asadabadi, M. S. Zabihi, M. R. Ganjali and M. Salavati-Niasari, *Mater. Sci. Eng. C* 30 (2010) 917.
- [24] M. R. Ganjali, M. Rezapour, M. R. Pourjavid and S. Haghgoo, *Anal. Sci.* 20 (2004), 1007.
- [25] L. Hajiaghababaei, S. Kazemi, and A. R. Badiei, *Anal. Bioanal. Electrochem.* 4 (2012) 246.
- [26] M. R. Ganjali, H. A. Zamani, P. Norouzi, M. Adib and M. Accedy, *Acta Chim Slov* 52 (2005) 309.
- [27] V. K. Gupta, S. Jain, and U. Khurana, *Electroanalysis* 9 (1997) 478.
- [28] V. K. Gupta, A. K. Singh, and B. Gupta, *Anal. Chim. Acta.* 583 (2007) 340.
- [29] H. A. Zamani, M. R. Ganjali and M. J. Pooyamanesh, *J. Brazil Chem. Soc.* 17 (2006) 149.
- [30] H. A. Zamani, M. Masrournia, M. Rostame-Faroge, M. R. Ganjali and H. Behmadi, *Sensor Lett.* 6 (2008), 759.
- [31] H. A. Zamani, G. Rajabzadeh, M. Masrornia, A. Dejbord, M. R. Ganjali and N. Seifi, *Desalination* 249 (2009) 560.
- [32] M. R. Ganjali, P. Norouzi, and M. Rezapour, *Encyclopedia of Sensors*, American Scientific Publisher (ASP), Los Angeles, 8 (2006) pp. 197.
- [33] Y. Umezawa, K. Umezawa, and H. Sato, *Pure. Appl. Chem.* 67 (1995) 507.

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