Arabian Journal of Chemistry (2012) **5**, 201–205

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Asymmetric Schiff base as carrier in PVC membrane electrodes for manganese (II) ions

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Received 26 July 2010; accepted 30 August 2010
Available online 7 September 2010

KEYWORDS

Manganese;
Ion-selective electrode;
PVC membrane;
Schiff base;
Potentiometry

Abstract Manganese(II) complex of (E)-2-(hydroxyl-5-methoxybenzylideneamino) phenol was synthesized and used as a suitable Mn(II) – selective membrane in PVC matrix. The plasticized membrane sensor exhibits a nersian response for Mn(II) ions over a wide concentration range of 6×10^{-6}–2×10^{-2} M with slope of 29 ± 1 mV per decade. It has a response time of <11 s and can be used for 2 months without any measurable divergence in potential. The response of the proposed sensor is independent of pH between 4 and 9.5. The proposed sensor shows a fairly good discriminating ability towards Mn(II) in comparison with some hard and soft metals. The electrode was used in the determination of Mn(II) in aqueous solutions and as an indicator electrode in potentiometer titration of manganese ions against EDTA.

1. Introduction

In recent decades many intensive studies have been introduced on the design and synthesis of highly selective ion-carrier as sensory molecules in the fabrication of ion-selective electrodes. There are many examples about the selective affinity of Schiff's bases toward metal ions, and hence their application in the construction of ion-selective electrodes (ISEs) Sadeghi et al., 2006; Mashhadizadeh et al., 2002; Gupta et al., 2007; Farhadi et al., 2004. Manganese is the twelfth most abundant element and the third most abundant transition element (exceeded only by iron and titanium). The most stable oxidation state of manganese is Mn(II), and in the group oxidation state of Mn(VII) it is even more strongly oxidizing than Cr(VI). Manganese liberates hydrogen from water and dissolves readily in dilute

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Peer review under responsibility of King Saud University.
doi:10.1016/j.arabjc.2010.08.013

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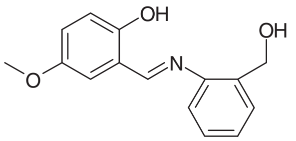

Figure 1 Structure of ionophor (E)-2-(hydroxyl-5-methoxybenzylideneamino) phenol (HMP).

aqueous acids to form manganese(II) salts. With a non-metal it is not very reactive at ambient temperatures but frequently reacts vigorously when heated (Greenwood and Earnshaw, 1985). The major uses of manganese are in the iron and steel industries. Manganese dioxide is used quite extensively in alkaline batteries, and in the glass, paints, and drying industries. Other compounds of manganese are used as driers for paints, varnishes, oils, fertilizers, disinfectants, and as anti-clock compounds for internal combustion engines (Singh, 2005). Manganese is the essential trace element that has a complex role in many body functions. This element is toxic at higher levels for organisms and plants. In humans, chronic manganese poisoning affects the central nervous system (Kendyzler and Turker, 2002; Malvankar and Shinde, 1991). Therefore, it is important from analytical point of view to develop sensitive, selective and economical method for the determination of the trace amounts of manganese (Wang and Lu, 1995; Afzali et al., 2008; Shamspur and Mostafavi, 2009; Mashhadizadeh et al., 2007).

The Schiff base derived from salicylaldehyde (salens) polydentate ligands are known to form very stable complexes with transition metal ions (Ochiai, 1973; Tajmir-Riahi, 1983; Arena et al., 1986; Calligaris et al., 1987; Martell and Sawyer, 1988; Atwood, 1997; Shamsipur, 2009). The resulting salen complexes have attracted increasing attention, mainly due to their peculiar properties (Calligaris et al., 1987; Atwood, 1997) and their reactivity mainly in the area of binding small molecules (Martell and Sawyer, 1988). Chelating agents with moderate coordination sites like nitrogen seem to generate great affinity toward moderate metal ions such as Cu(II). Schiff bases are ligands containing mixed O, N-donor atoms, which have high bonding affinities with some metal ions such as Cu(II), Cd(II), and Pb(II) . . . ions.

The aim of this work is to use an asymmetrical tridentate Schiff base ligand E)-2-(hydroxyl-5-methoxybenzylideneamino) phenol (Fig. 1) as an active material in PVC matrix for the fabrication of Mn(II) – selective sensor.

2. Experimental

2.1. Apparatus

All potentiometric measurements were made at 25.0 ± 0.1 °C with a pH/mV meter (Zag Chimi, Iran) using proposed sensor in conjunction with a double junction Ag/AgCl (Azar electrode, Iran) as reference electrode.

2.2. Reagents and solutions

Analytical reagent grade chemicals and doubly distilled water were used for preparing all aqueos solutions. High molecular weight polyvinyl chloride powder (PVC), dioctyl phthalate (DOP), dibutyl phthalate (DBP), dimethylsebacate (DMS), and tetrahydrofuran (THF) were obtained from Aldrich company. Sodium tetraphenylborate (NaTPB) and o-nitrophenyloctyl ether (NPOE) were obtained from Fluka. Salts of metal nitrates were of the highest purity available from Merck (Darmstadt, Germany) and were used as received.

2.3. Synthesis

(E)-2-(hydroxyl-5-methoxybenzylideneamino) phenol (HMP) was prepared by the standard method (22). A mixture of 2-hydroxy-5-mehoxybenzaldehyde (0.001 mol, 0.152 g) and 2-amino benzyl alcohol (0.001 mol, 0.123 g) was mixed. The resulting mixture was boiled under reflux for 2 h and the solution was concentrated and allowed to cool at room temperature for 48 h. The yellow solid obtained was filtered, washed with cooled methanol, and recrystalized from ethanol–chloroform (1:1), m.p.:120–121 °C. Yield:69% IR (KBR) (υ_{max} (cm^{-1})):1616 and 3100–3416 (OH).

Anal calcd for $_{15}H_{15}NO_3$ (257.29):C, 70.02%; H, 5.88%; N, 5.44% found: C, 69.9%; H, 5.9%; N, 5.35%.

^{1}HNMR (400 MHz, DMSO solutions); 3.71 (1H, s, OH), 3.89 (3H, s, CH3), 4.63 (2H, s, CH2), 5.41 (1H, s, OH), 6.83–7.34 (7H, m, 7CH), 8.61 (1H, s, CH).

^{13}CNMR (400 MHz, DMSO solutions):118.1, 132.4, 148.2, 153.3, 154.5 (5c), 111.5, 116.9, 117.4, 121.6, 120.3, 128.4, 132.6 (7ch), 59.7 (CH2), 52.4 (CH3), 158.6 (C=N).

2.4. Electrode preparation

The procedure to prepare the PVC membrane was to mix the powdered PVC, the plasticizer, the ionophore HMP and the

Table 1 Optimization of membrane ingredients.

No.	Composition (w/w)%			NaTPB	Slope (mV/dec)	Dynamic range (M)
	PVC HMP	Plasticizer				
1	31.5	62.4, DBP	3.1	3.2	19	1.0×10^{-5}–1×10^{-3}
2	31.25	62.5, DOP	3.12	3.12	6.10	1.0×10^{-6}–3.0×10^{-4}
3	29.8	61.9, DBP	5.1	3.3	9	1.0×10^{-5}–1.0×10^{-3}
4	83.3	0	8.30	8.30	0.95	1.0×10^{-6}–1.0×10^{-3}
5	29	61.9, DOP	0	4.1	21	2.0×10^{-6}–1.0×10^{-2}
6	30	67, NPOE	3	0	10.9	2.0×10^{-5}–1.0×10^{-3}
7	36.3	52.9, DBP	4.3	6.5	16	2.0×10^{-6}–5.0×10^{-3}
8	28.6	62.4, DBP	5.2	3.7	28.6	6.0×10^{-6}–2.0×10^{-2}

additive NaTPB dissolved in 3 ml of THF as the compositions shown in the Table 1.

The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was then allowed to evaporate at room temperature until an oily concentrated mixture was obtained. A Pyrex or Teflon tube (3–5 mm i.d. on top) was dipped into the mixture for about 11 s so that transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 1 h. The tube was then filled with internal filling solution(1×10^{-2} (M) $Mn(NO_3)_2 \cdot 4H_2O$); the electrode was finally conditioned for 24 h by stoking in a 1×10^{-2} M solution of manganese nitrate. A silver/silver chloride electrode was used as an internal reference electrode. The ratio of various ingredients, concentration of equilibrating solution and time of conditioning was optimized to provide membrane, which resulted in reproducible, and potentials with relatively little noise.

2.5. *Emf measurements*

All emf measurements were carried out with the following cell assembly:

Ag/AgCl | internal solution (1×10^{-2} (M), $Mn(NO_3)_2$) | PVC membrane | test solution | Ag–AgCl.

All measurements were carried out in a 50 ml double-walled glass cell, with constant magnetic stirring of the test solution. Activities were calculated according to debye–huckel procedure (Kamata et al., 1988).

3. Results and discussion

3.1. *Preliminary experiments*

The structure of the compound examined as a carrier to prepare PVC membrane electrodes for a number of metal ions including alkali, alkaline earth and transition metal ions is presented in Fig. 1. The key ingredient of such plasticized PVC membrane is the incorporated carrier that defines the selectivity of the electrodes via selective complex formation with the cation of interest. Due to its sufficient insolubility in water and the presence of donating nitrogen and oxygen atoms in its structure HMP ligand was expected to act as a suitable ion-carrier in the PVC membranes with respect to special transition and heavy metal ions of proper size and charge. Thus, in preliminary experiments, it was used as a neutral carrier to prepare PVC-based membrane electrodes for a variety of metal ions. Characterization of the selectivity of Mn(II) sensor over other metal ions is shown in Fig. 2. It is seen that the membrane electrode responds to manganese(II) with near Nernstian slope and a wide concentration range while other metal ions show poor response. Therefore, the ligand (HMP) was selected as a suitable sensor material for Mn(II)-ion in PVC matrix. The potential response of the most sensitive electrodes is prepared under the same experimental conditions (except for 24 h conditioning in a 0.01 M of the corresponding cations).

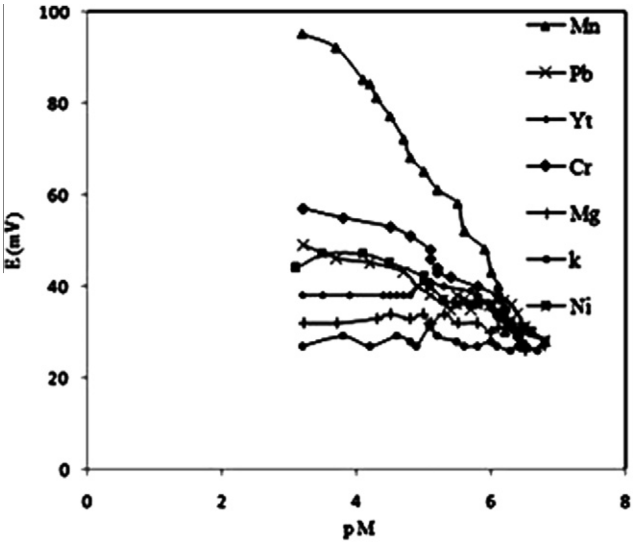

Figure 2 Potential response of various ion-selective electrodes based on HMP ligand. Conditions: membrane ingredients, 5.2% ionophore, 28.6% PVC, 62.4% DBP, and 3.7% NaTPB; internal solution, 1 × 10−2 M of each cation used. The electrodes have been conditioned in 1×10^{-2} M of the corresponding cation for 24 h.

As it can be seen, among different tested cations, Mn(II) with the most sensitive response seems to be suitably determined with the PVC membrane based on HMP and the emf responses obtained for all other cation-selective electrodes are much lower than those of the predictor by the Nernst equation. This is probably due to both the selective behavior of the ionophore against Mn(II) in comparison to some other metal ions and the rapid exchange kinetics of the resulting HMP–Mn(II) complexes.

3.2. *Effect of membrane composition*

Besides the critical role of the nature of the ion-carrier in preparing membrane-selective electrodes, some important features of the PVC membrane, such as the amount of ionophore, nature of solvent mediator, plasticizer/PVC ratio, and, especially the nature of additives used, are known to significantly influence the sensitivity and selectivity (Javanbakht et al., 1999, 2000; Shamsipur et al., 1999, 2000, 2001, 2002; Ganjali et al., 2000a,b; Fakhari et al., 1997). It is well known that the sensitivity and selectivity obtained for a given ion-selective electrode depends not only on the nature of ionophore used, but also significantly on the membrane composition and the properties of the plasticizer employed. Thus, the influences of the membrane composition and the nature of plasticizer on the response characteristics of Mn(II) ion-selective electrode based on HMP were investigated and the results are summarized in Table 1. The nature and amount of plasticizer on the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligand largely affect the response characteristics of ion-selective electrodes.

As it can be seen in Table 1, among the three different plasticizers often used with PVC membrane electrodes including NPOE, DOP and DBP the best calibration parameter and mechanical characteristics of the membranes were observed in the case of DBP; hence this plasticizer was used in further studies. This indicates that the solvent medium of DBP is probably recognized in providing the best complexation environment between manganese ions and carrier. The results obtained indicate that the best performance was observed with the membrane electrode No.8, comprising the percent ratio

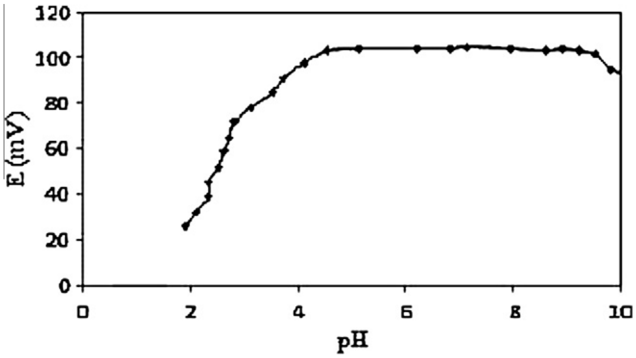

Figure 3 Effect of pH of test solutions on the response of Mn(II) selective electrode based HMP ligand.

as 28.6:62.4:5.2:3.7 for PVC:DBP:HMP:NaTPB constituents, respectively.

3.3. *Effect of pH on the potential response of the electrode*

The pH dependence of the electrode was tested over the pH range of 1.5–10 at a 1.0×10^{-3} M Mn(II) ion concentration (Fig. 3). It is clear from Fig. 3 that the potentials are fairly constant in the pH range of 4.0–9.5 and the same may be taken as the working pH range of the sensor.

At low pH values the donor atoms in the chelating ionophore are probably protonated, and unable to complex readily with Mn(II). The sharp change in the potentials at higher pH values may be due to the hydrolysis of the Mn(II) ions to form manganese hydroxide.

3.4. *Influence of the inner filling solution concentration and condition time*

The proposed electrode was also used at different concentrations of the internal reference solution from 1.0×10^{-2} to 1.0×10^{-5} M. Functioning of the membrane sensor with reference solutions of various $Mn(NO_3)_2$ concentration found only a slight effect on the potential response of the electrode. A 1.0×10^{-2} M concentration of the reference solution is the solution found to be quite appropriate for smooth functioning of the system. Optimum conditioning time for the membrane electrode in a 0.01 M manganese nitrate solution is 24 h. It then generates stable potentials when placed in contact with Mn(II) solutions.

3.5. *Performance of the proposed electrode*

We measured the average time required for the Mn(II) ion-selective electrode to reach a potential within ± 1 mV of the final equilibrium value after successive immersion in a series of manganese ion solution, each having a 10-fold difference in concentration. The static response time of the membrane electrode obtained was ~11 s and the potentials stayed constant for ~9 min, after only a very slow divergence within the months without any measurable change in response time, slope, or detection limit. The performance characteristics of the membrane remained unchanged when the potentials recorded either from low to high concentrations or vice versa. This means that the response was rapid and reversible. The membrane electrode prepared could be used for about 2 months without observing any change in response characteristics (week-to-week tested). The standard deviation of ten replicate measurements with one membrane within 6 weeks was 5.0%. The membranes were stored in 0.01 M Mn(II) solution or were dry when not in use. If the membrane was stored dry, it must be conditioned in a 0.01 M manganese nitrate solution for 24 h.

To evaluate reproducibility of this electrode, a series of membranes (five) with similar composition (No. 8) were prepared and the response of these electrodes to Mn(II) ion concentration was tested. The results showed that the average of slopes, detection limits and linear dynamic ranges were 28.6 ± 1 mV/decade, $3.0(\pm 0.2) \times 10^{-6}$ M and $2.0(\pm 0.2) \times 10^{-2}$ to $6.0(\pm 0.3) \times 10^{-6}$ M), respectively. The standard deviation of measurements of 1.0×10^{-5} M to Mn(II) solution with these five electrodes was ± 1.5. The standard deviation of 10 replicate measurements was ± 0.5 mV.

3.6. *Selectivity*

The potentiometric selectivity coefficients of the electrode ($K^{pot}_{Mn^{2+}, B}$), toward different cationic species were determined by IUPAC recommended-matched potential method (Javanbakht et al., 1999) at a 1.0×10^{-2} M concentration of interfering ions. The resulting selectivity coefficients which are summarized in Table 2, indicate that the sensor is selective

Table 2 Selectivity coefficients of various interfering ions for Mn(II) ion-selective electrode based on HMP.

Interfere ion (B)	$-\mathrm{Log}\ K^{pot}_{Mn^{2+}, B}$	$K^{pot}_{Mn^{2+}, B}$
Yt(II)	1.8	1.6×10^{-2}
Pb(II)	2.2	6.6×10^{-3}
Ni(II)	1.6	2.5×10^{-2}
Cr(III)	3.1	7.9×10^{-4}
Zn(II)	2.7	2.0×10^{-3}
Fe(II)	1.6	2.5×10^{-2}
K(I)	2.3	5.0×10^{-3}
Ca(II)	1.7	1.8×10^{-2}
Co(III)	2.4	4.0×10^{-3}
Cu(II)	1.2	6.30×10^{-2}

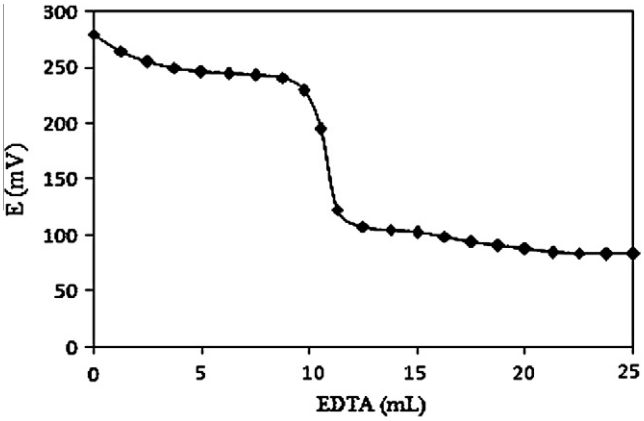

Figure 4 Potentiometric titration curve of 100 ml of 1.0×10^{-3} M $Mn(NO_3)_2$ solution with 1.0×10^{-2} M EDTA using the proposed membrane sensor as an indicator electrode.

Table 3 Comparison of the proposed ion selective sensor with the existing sensors.

Ref. no.	Work ing concentration range (M)	Slope (mV/decade of activity)	pH	Response time	Lifetime (days)
Gupta et al. (2007)	5.0×10^{-6}–1.0×10^{-1}	30.0	3.0–6.5	10 s	75
Mashhadizadeh et al. (2007)	4.0×10^{-7}–1.8×10^{-2}	30.1	4.5–7.5	~10 s	60
Agarwala and Chattopadhyaya (1989)	1.0×10^{-6}–1.0×10^{-1}	NM	2.3–8.8	35 s	NM
Singh et al. (2005)	1.25×10^{-5}–1.0×10^{-1} M	29.5	3.0–8.0	20 s	120
Proposed sensor	6×10^{-6}–2×10^{-2}	29.0	4.0–9.5	11 s	60

NM = not mentioned.

for Mn(II) ion in the presence of interfering ions. As can be seen for most ions used $K^{pot}_{Mn^{2+},B}$ values were of the order of 10^{-2} or smaller, indicating that they would not significantly disturb the functioning of the Mn(II) ion-selective electrode.

Hence, these cations are not expected to interfere with the functioning of the proposed Mn(II)-selective sensor even at high concentration levels. The practical utility of the proposed membrane sensor was tested by its use as an indicator electrode for titration of 100 ml of 1.0×10^{-3} M, Mn(II) ions with a 1.0×10^{-2} M, EDTA solution and results were shown in Fig. 4. As it is seen, the amount of manganese ions in solution can be accurately determined with the electrode.

4. Conclusion

A new PVC membrane electrode for Mn(II) ions based on HMP as ionophore was investigated. The use of the new N–O Schiff's base HMP provides the best response characteristics with Nernstian behavior over a wide concentration range of (2×10^{-2}–6×10^{-6}) and a fast response time of < 11 s. The sensor works well in a pH 4.0–9.5. Consequently, the proposed sensor is on the one hand, superior to the existing sensors in terms of response time and lifetime and on the other hand, comparable with regard to other parameters such as slope, pH range, concentration range and selectivity (Table 3).

References

Afzali, D., Mostafavi, A., 2008. J. AOAC Int. 91, 1430–1434.

Agarwala, V., Chattopadhyaya, M.C., 1989. Anal. Lett. 22, 1451–1457.

Arena, F., Floriana, C., Chiesi-Villa, A., Guastini, C., 1986. Inorg. Chem. 25, 4589–4596.

Atwood, D.A., 1997. Coord. Chem. Rev. 165, 267–296.

Calligaris, M., Randaccio, R., 1987. In: Wilkinson, G., Gillard, R.D. (Eds.), Comprehensive Coordination Chemistry, vol. 2. McCleverty, London (chap. 20).

Fakhari, A.R., Ganjali, M.R., Shamsipur, M., 1997. Anal. Chem. 69, 3693–3696.

Farhadi, K., Maleki, R., Yamchi, R.H., Sharghi, H., Shamsipur, M., 2004. Anal. Sci. 20, 805–809.

Ganjali, M.R., Fathi, M.R., Pirelahi, H., 2000a. Electroanalysis 12, 1138–1142.

Ganjali, M.R., Hosseini, M., Javanbakht, M., Hashemi, O.R., 2000b. Anal. Lett. 33, 3139–3159.

Greenwood, N.N., Earnshaw, A., 1985. Chemistry of the Elements. Pergamon Press, New York, NY.

Gupta, V.K., Jain, A.K., Maheshwari, G., 2007. Talanta 72, 49–53.

Javanbakht, M., Ganjali, M.R., Eshghi, H., Sharghi, H., Shamsipur, M., 1999. Electroanalysis 11, 81–84.

Javanbakht, M., Shabani-Kia, A., Darvich, M.R., Ganjali, M.R., Shamsipur, M., 2000. Anal. Chim. Acta 408, 75–81.

Kamata, S., Bhale, A., Fukunaga, Y., Murata, A., 1988. Anal. Chem. 60, 2464–2467.

Kendyzler, E., Turker, A., 2002. Anal. Sci. 18, 917–921.

Malvankar, P.L., Shinde, V.M., 1991. Analyst 116, 1081–1084.

Martell, A.E., Sawyer, O.T., 1988. Oxygen Complexes and Oxygen Activation by Transition Metals. Plenum Press, New York.

Mashhadizadeh, M.H., Mostafavi, A., Razavi, R., Shamsipur, M., 2002. Sens. Actuators B Chemical 86, 222–228.

Mashhadizadeh, M.H., Pour Taheri, E., Sheikhshoaie, I., 2007. Talanta 72, 1088–1092.

Ochiai, E.I., 1973. J. Chem. Educ. 50, 610–611.

Sadeghi, S., Fathi, F., Esmaeili, A.A., Naeimi, H., 2006. Sens. Actuators B Chemical 114, 928–935.

Shamsipur, M., Shirmardi Dezaki, A., Akhond, M., Sharghi, H., Paziraee, Z., Alizadeh, A., 2009. J. Hazard. Mater. 172, 566–573.

Shamsipur, M., Rouhani, S., Ganjali, M.R., Eshghi, H., Sharghi, H., 1999. Sens. Actuators B 59, 30–34.

Shamsipur, M., Yousefi, M., Ganjali, M.R., 2000. Anal. Chem. 72, 2391–2394.

Shamsipur, M., Ganjali, M.R., Rouhollahi, A., 2001. Anal. Sci. 17, 935–938.

Shamsipur, M., Yousefi, M., Hosseini, M., Ganjali, M.R., 2002. Anal. Chem. 74, 5538–5543.

Shamspur, T., Mostafavi, A., 2009. J. Hazard. Mater. 168, 1543–1553.

V.P. Singh, Metal Toxicity and Tolerance in Plant and Animals, New Delhi, 2005, pp. 28.

Singh, A.K., Saxena, P., Panwar, A., 2005. Sens. Actuators B 110, 377–381.

Tajmir-Riahi, H.A., 1983. Polyhedron 2, 723–726.

Wang, J., Lu, J., 1995. Talanta 42, 331–335.