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WAGIHA MAHMOUD
Department of Chemistry, faculty of science, Ain Shams University, Cairo , Egypt.

MOHAMED ABO ALY
Department of Chemistry, faculty of science, Ain Shams University, Cairo , Egypt.

MOHAMED HAMZA
Department of Chemistry, faculty of science, Ain Shams University, Cairo , Egypt.

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NOVEL AND QUICK SENSOR RESPECTIVE FOR SULFATE

WAGIHA H. MAHMOUD*, MOHAMED M. ABO ALY, MOHAMED S.. HAMZA, SABAH M. MOLTAZEM

Department of Chemistry, faculty of science, Ain Shams University, Cairo , Egypt.

Abstract

A sulfate-selective PVC-membrane sensor based on nickel complex of 3, 8-dimethyl 5, 6-benzo- 4, 7-diazadece-3, 7-diene-2, 9-dione (dioxime) as (a novel sensing material) is presented. The Potentiometric behavior of the sensor was independent on the pH of the solution between 4.5 and 7.5 pH. The sensor revealed a linear response towards SO_4^{2-} ion in the range of $5.0\times10^{-7}$to 1.0×10^{-2} M with an anionic slope of -30±0.2 mV per decade. The sensor possesses a satisfactory reproducibility, fast response time, low limit of detection (3×10^{-7}M). The interference of hydrophobic inorganic anions was very low in comparison with the conventional ion-exchanger based electrodes, as shown by the selectivity coefficients determined by the separate solution method (SSM). The selectivity was also good towards the most common univalent and divalent anions. The sensor was used as an indicator electrode in potentiometric titration of sulfate with barium ions and in determination of sulfate in some pharmaceutical products .

Keywords: Sulfate ion-selective sensor ; 3, 8-dimethyl 5, 6-benzo- 4, 7-diazadece-3, 7-diene-2, 9-dione (dioxime); PVC-membrane; Potentiometry

Introduction

The quick determination of minute quantities of ionic species by simple methods in a wide variety of real samples, as well as the growing interest in the host guest chemistry of anions [1] thus a new areas of application have opened up as a result of these improved characteristics and they are of great importance in analytical chemistry. Potentiometric detection based on ion selective electrodes (ISEs) is the simplest of all other analytical techniques and offers great advantages such as speed and ease of preparation and procedures, wide dynamic range often spanning about five decades of ion concentration, and low cost, no sample destruction and short response time. These characteristics have inevitably led to sensors for several ionic species,(2-4) and the list of available sensors has grown substantially over the past decades. Among different anions, the recognition of strongly hydrophilic anions such as SO_4^{2-} by potentiometric methods has shown to be quite difficult [1-4]. Thus, despite the urgent need for selective potentiometric determination of minute amounts sulfate ion in many chemicals, pharmaceutical, environmental and industrial samples, only a few reports on the preparation of SO_4^{2-} ion-selective electrodes are available in the literature [5-9]. None of the solid state sulfate ion-selective electrodes has reported to be satisfactory, due to the lack of adequate selectivities [4].Recently, new sulfate ion-selective electrodes based on a bis-thiourea ionophore [6], a derivative of imidazole [7] and a zwitterionic bis-guanidinium ionophore as a sulfate carrier [8] have been reported. Although, these electrodes show a close Nernstian behavior over a relatively wide concentration range, they suffer from rather strong interferences from such other anions as NO_2^-, NO_3^-, Br^-, I^-, ClO_4^- and SCN^- [6- 8].

In ISEs, selectivity is introduced by the receptor molecules (or ionic carrier) which are generally immobilized in a polymeric membrane matrix, often consisting of high molecular weight poly(vinyl chloride) (PVC) mixed with a plasticizer. The receptor molecule attributes selectivity to the sensor by its strong and selective interactions with the target analyte.

Due to vital importance of sulfate determination in chemical, pharmaceutical, environmental and industrial analyses, we were interested in preparation of a new PVC-based membrane sensor for sulfate ion monitoring in solution. In this paper, we report a highly selective PVC-membrane sulfate ion-selective electrode based on nickel complex of 3, 8-dimethyl 5, 6-benzo- 4, 7-diazadece-3, 7-diene-2, 9-dione (dioxime) as an excellent ionic carrier .

Experimental

Reagents and materials

All chemicals were of analytical reagent grade. Dioctyl phthalate (DOP), dioctyl sebacate (DOS), tetrahydrofuran (THF), and high relative molecular weight PVC were purchased from Aldrich chemical company and used as received. Potassium salts of all anions used (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. Doubly distilled deionized water was used throughout. The chelating agent H_2L was synthesized and purified as described elsewhere [10]. The chloro-nickel complex of this ligand [Ni(HL)]Cl was prepared by the direct reaction of equal quantities of the ligand (solvent used 50% ethyl alcohol and 50% water) and $NiCl_2$ solution (used water as a solvent) of concentration 1x 10^{-2} M. The red precipitate was filtered, washed with water, dried at room temperature and incorporated as electro- active material in the formation of the selective membrane respective for sulfate ions.

Electrode preparation

The general procedure to prepare the PVC membrane was to mix thoroughly 190 mg of powdered PVC, 350 mg of plasticizer DOP or DOS, and 10 mg of the elctroactive [Ni(HL)]Cl. Then, the mixture was dissolved in 5 ml of THF. The resulting clear mixture was evaporated slowly at room temperature for 24 hour until an oily concentrated mixture was obtained. The membrane was sectioned with cork porer (10 mm diameter) a disk (0.1mm) thick was cut from the transparent membrane and glued to PVC tube (using THF) as previously described [11]**.** The tube was then filled with the internal solution (1.0×10^{-3} M K_2SO_4). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} M potassium sulfate solution until a stable potential value was obtained, according to a widely accepted practice. A silver–silver chloride electrode was used as an internal reference electrode

The emf measurements

All emf measurements were carried out with the following assembly:
Ag–AgCl | KCl (3 M) | internal solution, 1.0×10^{-3} M K_2SO_4 | PVC membrane | test solution | Ag–AgCl

All potentiometric measurements were made at 25 ± 1^{o}C with an Orion digital pH /mV using PVC- nickel - 3, 8-dimethyl-1, 5, 6-benzo- 4, 7-diazadece-3, 7-diene-2, 9-diome (dioxim) sulfate membrane sensor in conjunction with an Orion double junction Ag/AgCl reference electrode (Model 90-02) filled with 10 % w/v KNO_3 in the outer compartment. An Orion combination pH electrode (model 91-02) was used for all pH adjustment.

Results and Discussion

The wide uses of ISEs in routine chemical analysis have been accompanied by a search for ionophores that can chemically recognize specific ions and offer either new or improved selectivities for different ions. In the literature, the membranes used in anion selective sensors are based on quaternary ammonium or phosphonium salts [5-8]. In the case of most anion-selective electrodes, there are relatively few examples of the use of ionophores. These include the derivatives of bis-thiourea [6], imidazole [7], cytosine [13] and guanidinium ion [4, 14], as well as different and macrocyclic polyamines [15-18]. Due to low lipophilicily of sulfate ion, the design of a selective ligand for its selective recognition has been a challenging subject [6-8 , 18-20]. Some neutral carriers such as bis-thiourea [12] and imidazole [7] derivatives possessing high enough lipophilicity and specific host–guest interactions with sulfate ion have recently shown to be promising for this purpose.

Identification of the new synthesized Ni-dioxime complex

The structure of the prepared red Ni-dioxime sulfate complex was confirmed Via elemental analysis and electronic spectra. The results obtained was compared with that of the chelating agent under the same conditions. The data of the elemental analysis was tabulated in table 2. this data confirmed the formation of [Ni(HL)]Cl complex. The U.V spectra of that complex is similar to that previously reported for Ni-dimethylglycozimate [22], these results was confirmed by I.R spectra. The υ C=N appear at 1629 in the I.R spectra of the ligand was shifted to 1649 Cm^{-1} in the complex spectra. A new band at 519 Cm^{-1} respective for Ni-N was observed also there are two new bands at 1240 and 1100 Cm^{-1} respective for cyclic skeleton of the complex. The I.R spectra of the prepared membrane was evaluated before and after socking in 10^{-3}M K_2SO_4 solution. The prepared complex was preformed using $NiSO_4$ and the resulted ppt was measured by I.R the spectra give a new band at about 1050 Cm^{-1} indicating the presence sulfate group in the prepared complex.

Characterization of the membrane sensor

Among different membrane compositions tested, membrane with proportion 1% [Ni(HL)]Cl ionic carrier,33% PVC, 66% plasticizer DOP or DOS, offers the best sensitivity as well as the widest linear range, with a Nernstian slope of about -30 mV per decade (Table1). From the (fig 2), it is immediately obvious that the nature and amount of additive did not influence the performance characteristics of the membrane sensor significantly. It can be seen that the two sensors prepared, showed a linear Potentiometric response over a wide concentration range of $5x10^{-7}$− $1x10^{-2}$ M sulfate ions concentration with a slope of −30.04 mV per decade of sulfate ions and a correlation coefficient of 0.9998. The slopes of the calibration graphs is Nernstian compared with the sub-Nernstian or over-Nernstian slopes given by some other sensors [23-25]. The linear range of the sensor response for SO_4^{2-} is about five decades of concentration, which is 1–2 decades greater than those reported for some other sulfate ions electrodes . The limits of detection, defined as the concentration of sulfate ions obtained when extrapolating the linear calibration region to the baseline potential, are given in (fig 2). As can be seen, the sensor showed detection limits of (0.288ppm), which are better than those of most other sulfate sensor. The limits of detection obtained in this work are several orders of magnitude below the sulfate concentration in pharmaceutical samples[15-24,19-21].

The influence of the concentration of internal solution on the potential response of the SO_4^{2-} ion-selective sensor was studied. The K_2SO_4 concentration was changed from 1.0×10^{-7} to 1.0×10^{-2} M and the emf were recorded. It is seen that the variation of the concentration of the internal potassium sulfate solution does not cause any significant difference in the potential response, except for an expected change in the intercept of the resulting Nernstian plots. A 1.0×10^{-3} M concentration of the reference solution is quite appropriate for smooth functioning of the sensor system.

The pH sensitivity of the proposed electrode was examined by obtaining the potential responses of the membrane electrode in 1.0×10^{-3} and 1.0×10^{-4} M sulfate solution at pH 2 -9, and the results are shown in Fig. 3. As seen, the most sensitive potential response is obtained at a pH 4- 7.5. At pH values lower than 4, the sensor seems to respond to proton significantly while at higher pH values, the ionic carrier has presumably a low tendency for sulfate ions.

The response time of the proposed sulfate sensor for step changes in concentration of SO_4^{2-} ion, from low to high concentrations are shown in Fig. 4. As seen, the time for the electrode to reach 90% of the steady response was <15 sec and no change is normally observed up to 5min. Potentional were monitored periodically at fixed concentration and standard deviation of ten identical measurements was 2.0 mV. In term of the life of the PVC membrane sensor, the response stability was observed for over more than 6 months.

The potentiometric selectivity coefficients, describing the preference by the PVC membrane incorporating the ionic carrier for an interfering ion, B, relative to sulfate ion, A, were determined by the separate solution method (SSM), which is recommended by IUPAC [26]. In these method, the selectivity coefficients of sulfate sensor was evaluated graphically at fixed concentration of sulfate ion and interferant as shown in (fig. 5) As it is seen, excellent selectivity coefficients in the order of 10^{-3} and lower are obtained for a large number of inorganic and organic anions indicating insignificant interfering effect of these anions on the sulfate ion determination, by the proposed membrane sensor are given in(Table 3).

A typical selectivity patteran for a series anions showed by the electrode is as follows $SO_4^{2-} > SO_3^{2-} > CO_3^{2-} > S_2O_3^{2-} > HPO_4^{2-} > B_4O_7^{2-} > CH_3COO^- > BrO_3^- > Cl^- > IO_4^- > NO_3^- > HCO_3^- > SCN^- > NO_2^- > ClO_4^-$.

So the electrode is highly selective towards sulfate over several organic and inorganic anions. In Table 4, the selectivity coefficients of proposed sensor was compared with those reported before (27– 35) . Noteworthy , this is just a gross relative comparison , since the selectivity data have been reported using different experimental method ,as indicated in Table 4 it is clearly indicated that a tremendous enhancement in selectivity behavior of the proposed sensors for SO_4^{2-} ions.

Analytical Application

The proposed membrane sensor was found to work well under laboratory conditions. It is successfully used as an indicator electrode in titration of a sulfate ion solution (1.0×10^{-2} ,1.0×10^{-3},5.0×10^{-3} M) with Ba^{2+} ion (1.0×10^{-2} M) and vice versa. The results of both the titrations are shown in (Fig. 6) indicating that the amount of SO_4^{2-} or Ba^{2+} ions can be accurately determined with the proposed sensor.

The sensor was also applied to the determination of sulfate concentration in some pharmaceutical products using direct potentiometry, as example .Neomycine tablets, Visceralgin tablets, also streptomycin powder injection, the sulfate was determined in this three drugs using the proposed sensor, the results are favorably compared by turbidemetry method as standard method (Table 5)

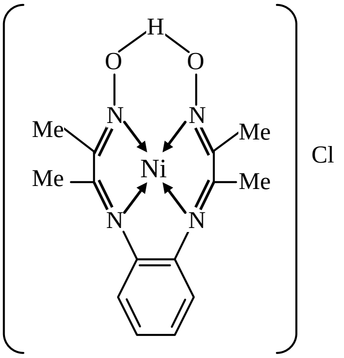

Fig. (1) Structure of Ni dioxime (complex)

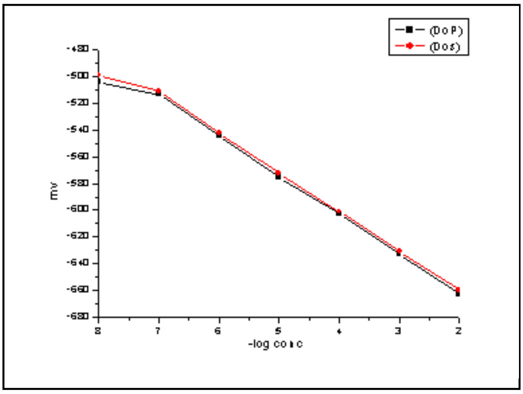

Fig. (2) Potentimetric response curves for the sensor at different plasticizers

Table (1) Response characteristics of the Ni – dioxime –PVC sulfate membrane sensor

Slope, mV/decade	-30.3
Liner concentration range , (M)	5×10^{-7} to 10^{-2}
Lower limit of detection , (M)	3×10^{-7}
Response time , (s)	<15
Working range (pH)	4.5 – 7.5
Intercept , mV	710
Correlation Coefficient , (r)	0.999

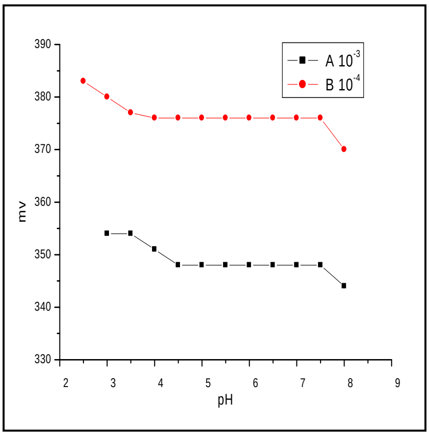

Fig. (3) Effect of pH on the potential response of the proposed sulfate sensor selective electrode .

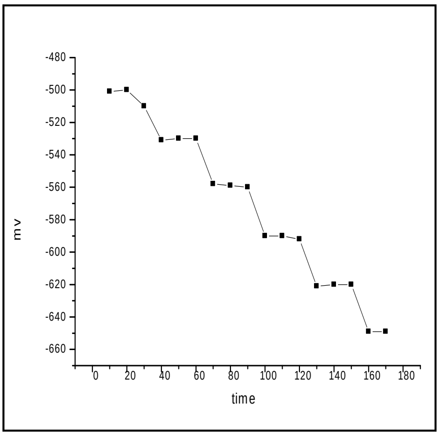

Fig. (4) Dynamic response time of Ni-dimethyl benzo diazadece diene dione membrane electrode for step changes concentration of sulfate from 1 x 10^{-7}-10^{-2} M.

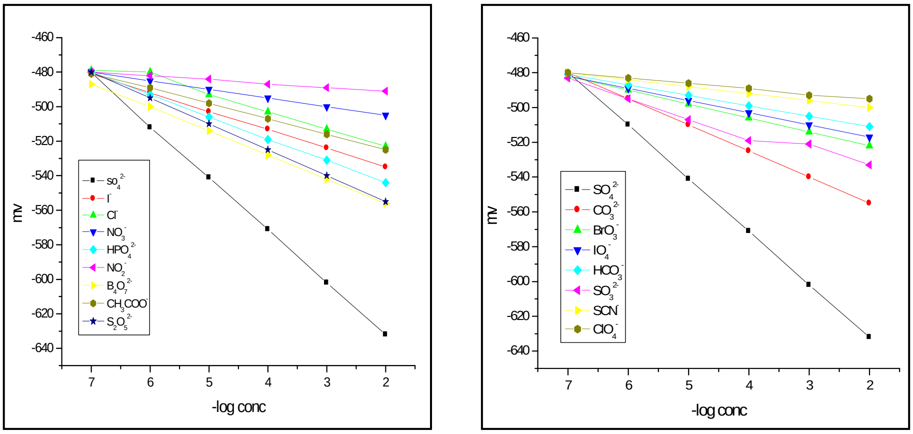

Fig. (5). Potential response of sulfate PVC membrane sensor based on Ni – dioxime for various ions .

Table (2) Elemental analysis of Ni- dioxime complex .

Sample		C %	H %	N %
Ni-complex	Calculated	44.7	4.81	15.9
Ni-complex	Found	43.8	4.64	17.29

Table.(3) Selectivity coefficients for Ni-dioxime PVC- sulphate membarane sensor.

Interferent , I	$K^{pot}_{SO4^{2-},B}$
I^-	2.71×10^{-3}
Cl^-	8.57×10^{-4}
IO_4^-	7.35×10^{-4}
ClO_4^-	1.99×10^{-4}
BrO_3^-	1.07×10^{-3}
$B_4O_7^-$	2.15×10^{-3}
SO_3^{2-}	8.51×10^{-3}
$S_2O_3^{2-}$	5.84×10^{-3}
CO_3^{2-}	7.94×10^{-3}
HCO_3^-	4.64×10^{-4}
NO_2^-	1.35×10^{-4}
NO_3^-	5.01×10^{-4}
SCN^-	$2.92 \times 10^{-4.}$
HPO_4^-	4.29×10^{-3}
CH_3COO^-	1.16×10^{-3}

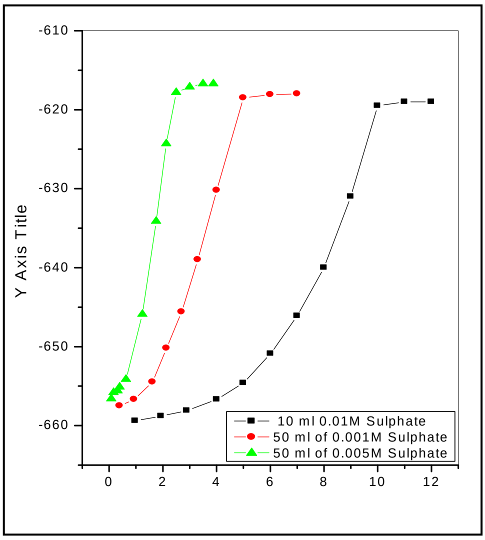

Fig. (6) Potentiometric titration curves for different concentration of sulfate solution, 1.0 x 10^{-2} M of Ba^{2+} (barium Nitrate).

Table (4) .Comparison of the selectivity coefficients of different electrodes .

Anion	Ref 32	Ref 33	Ref 34	Ref 35	This Work
Br	3.2×10^{-3}	6.9×10^{-3}	7.9×10^{-3}	7.9×10^{-4}	--
CO_3^{2-}	6.3×10^{-3}	4.0×10^{-3}	3.3×10^{-3}	3.2×10^{-4}	$7.94x10^{-3}$
Cl^-	4.0×10^{-3}	4.9×10^{-3}	5.8×10^{-3}	5.0×10^{-4}	8.57×10^{-4}
CN^-	1.5×10^{-2}	4.0×10^{-3}	3.5×10^{-4}	--	--
I^-	1.6×10^{-2}	8.0×10^{-3}	2.7×10^{-4}	--	2.7×10^{-3}
NO_3^-	6.2×10^{-3}	5.0×10^{-3}	3.4×10^{-3}	2.4×10^{-4}	5.01×10^{-4}
NO_2^-	1.0×10^{-2}	9.9×10^{-4}	7.2×10^{-2}	5.3×10^{-5}	1.35×10^{-4}
SO_3^{2-}	1.2×10^{-3}	7.9×10^{-2}	8.7×10^{-3}	4.9×10^{-3}	8.51×10^{-3}
SCN^-	7.9×10^{-2}	1.0×10^{-4}	3.4×10^{4}	7.8×10^{-4}	2.98×10^{-4}
ClO_4^-	3.1×10^{-2}	4.0×10^{-3}	3.6×10^{-4}	9.0×10^{-4}	1.99×10^{-4}
CH_3COO^-	6.3×10^{-3}	3.1×10^{-3}	--	1.6×10^{-3}	1.16×10^{-3}
HPO_4^{2-}	--	--	--	4.0×10^{-5}	4.29×10^{-3}

Table (5) Determination of sulfate in some pharmaceutical formalastion using potintiomtric method & turbidemetrey method .

Sample & sours	Conc. mg/L potentiometry	Recovery,%	Conc. mg/L turbidemetrey	Recovery,%
Visceralgine , sedico pharmaceutical . Co	2.9±0.3 mg/L	96.6%	3.1±0.4 mg/L	103.3%
Streptomycine , nileco .for farm & chimical lnd	394.3±0.4 mg/L	99.5%	395±0.5 mg/L	99.7%
Neomycine , Memphisco . for pharm chimical lnd	94.9±0.2mg\L	97.8%	95.5±0.3 mg/L	98.4%

References

1. F. P. SCHMIDTCHEN AND M. BERGER, *Chem. Rev.* 97 (1997), pp. 1609–1646.
2. P. BÜHLMANN, E. PRETSCH AND E. BAKKER, *Chem. Rev.* 98 (1998), pp. 1593–1687.
3. M. M. G. ANTONISSE AND D.N. REINHOUDT, *Electroanalysis* 11 (1999), pp. 1035–1048.
4. E. BAKKER, P. BÜHLMANN AND E. PRETSCH, *Electroanalysis* 11 (1999), pp. 915–927
5. D. MIDGLEY, *Ion-Sel. Electrode Rev.* 8 (1986), pp. 3–54.
6. S. NISHIZAWA, P. BÜHLMANN, K.P. XIAO and Y. UMEZAWA, *Anal. Chim. Acta* 358 (1998), pp. 35–44
7. Z.-Q. LI, G.-D. LIU, L.-M. YUAN, G.-L. SHEN AND R.-Q. YU, *Anal. Chim. Acta* 382 (1999), pp. 165–170.
8. M. FIBBIOLI, M. BERGER, F.P. SCHMIDTCHEN AND E. PRETSCH, *Anal. Chem.* 72 (2000), pp. 156–160.
9. M. SHAMSIPUR, G. KHAYATION AND S. TANGESTANINEJAD, *Electroanalysis* 11 (1999), pp. 1340–1344.
10. M. R. GANJALI, L.NAJI, T.POURSABERI, M.TAGHIZADEH, H.pirelahi, Myosefi, A. yequnesh-fall , M. shmsi pur Talanta 58 (2002) 359
11. V.WUTHIER, H. V. PHAM, R. ZŰNI, D.WELTI, R.J.J. FANK, A. BEZEGH, D.AMMAN, E.PERISH, W. SIMON, Amal-Chem.56(1984) 535.
12. M. SHAMSIPUR, S. ROUHANI, A. MOHAJERI, M. R. GANJALI AND P. RASHIDI-RANJBAR, *Anal. Chim. Acta* 418 (2000), pp. 197–203.

13. S. AMEMIYA, P. BÜHLMANN, K. TOHDA AND Y. UMEZAWA, *Anal. Chim. Acta* 341 (1997), pp. 129–139.

14. R. S. HUTCHINS, P. BANSAL, P. MOLINA, H. ALAJARIN, A. VIDAL AND L.G. BACHAS, *Anal. Chem.* 69 (1997), pp. 1273–1275.

15. M. KATAOKA, R. NAGANAWA, K. ODASHIMA, Y. UMEZAWA, E. KIMURA AND T. KOIKE, *Anal. Lett.* 22 (1989), pp. 1089–1105.

16. R. NAGANAWA, H. RADECKA, M. KATAOKA, K. TOHDA, K. ODASHIMA, Y. UMEZAWA, E. KIMURA AND T. KOIKE, *Electroanalysis* 5 (1993), pp. 731–738.

17. C. M. CAREY AND W. B. RIGGAN, *Anal. Chem.* 66 (1994), pp. 3587–3591.

18. H. STEPHAN, K. GLOE, P. SCHIESSL AND F.P. SCHMIDTCHEN, *Supramol. Chem.* 5 (1995), pp. 273–280.

19. M. BERGER AND F. P. SCHMIDTCHEN, *J. Am. Chem. Soc.* 118 (1996), pp. 8947–8948.

20. E. BAKKER, P. BÜHLMANN AND E. PRETSCH, *Chem. Rev.* 97 (1997), pp. 3083–3132

21. S. K. NOROV, M. T. GULAMVA, A. F. ZHUKOV, G. H. NOROVA AND Y. G. MEMEDOVA, *Zh. Anal. Khim.* 43 (1988), pp. 986–991.

22. A. UGUR, B. MERCIEMK, M. ALZER, AND NSAHIN, TR metal chemistry 25 (2000) 421.

23. M. FAAL-RASTGAR, M. S. THESIS, Tehran University, Tehran, Iran, 27 (1995) 219.

24. M. FARNIA, A. KAKANEJADIFAR, S. KARIMI AND L.J. TODARO, *J. Chem. & Chem. Eng.* 12 (1993), pp. 57–62.

25. S. KAMATA, A. BHALE, Y. FUKUNAGA AND A. MURATA, *Anal. Chem.* 60 (1988), pp. 2464–2467.

26. IUPAC, IPURE and Applied chemistry , 74 (2002), 923 .

27. S.NISHIZ AWA, P.BUHIMANN, K.P.XIAO, Y. UMEZAWA, Anel Chim. Acta 35 (1998) 358.

28. Z. Q. LI, G.D.LIU, L. M.DUAN, G.L.SHEN, R.Q.YU, Anal.Chim. Acto 165 (1999) 382.

29. M. FIBBIOLI, M.BERGER, F.SCHMIDTCHEN, E. Pretsch Anal.Chem, 72 (2000) 156.

30. M. J. BERROCAL, A. CRUZ, I.H.A. BADER, L. G. BACHAS, Anal. Chem., 72 (2000) 5295.

31. M. MORIGI, E. SCAVETTA, M. BERRETTONI, M. GIORGETTI, D TONELLI, Anal. Chim. Acta, 439 (2001) 265.

32. M. SHAMSIPUR, M. YOUSEFI, M. HOSSEINI, M. R.GANJALI, H. SHARGHI, H. Naemi, Anal. Chem., 73 (2001) 2869.

33. M. SHAMSIPUR, M. YOUSEEFI, M. HOSSEINI, M.R. GANJALI, T POURSABERI , AND M.FAAL-RASTGAR, Sens. Actuators, 82 (2002) 105 .

34. M. R.GANJAALI, L. NAJI, T. POURSABERI, M. TAGHIZADEH, HPIRELAHI, M. YOUSEFI, A. YEGANEH-FAAL, AND M. SHAMSIPUR, Talanta 58 (2002) 359.

35. M. GANJALI, M. POURJAVID, AND M. SHAMSIBUR, Analytical sciences 319 (2000) 203.