Thallium(I)-Selective Membrane Potentiometric Sensor Based on Phenyl Disulfide

غشاء الثاليوم (I) الانتقائي المتحسس مجهاديا بالاعتماد
على Phenyl Disulfide

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Abstract:

A thallium(I) selective electrode based on phenyl disulfide as membrane carrier was prepared. The electrode exhibits a near-Nernstian response for Tl^+ ions over a wide concentration range from ($1.0x10^{-5}$-$1.0x10^{-1}$ M) with a slope of 56.9 mV/decade and a limit of detection of $5.6x10^{-6}$ M, and was found to be selective and useable within the pH range (4.0-10.0). The electrode was successfully used as an indicator electrode in potentiometric titration of thallium ions.

الخلاصة :

قطب الثاليوم (I) الانتقائي حضر بالاعتماد على phenyl disulfide كناقل ايوني في غشاء القطب . أظهر القطب استجـابة نيرنستيـة لايونــات Tl^+ ضـمن مدى تراكيز تراوحت بـين (M $1.0x10^{-1}$-$1.0x10^{-5}$) وبميل نيرنستي مقداره 56.9 mV/decade وحد تحسس مقداره M $5.6x10^{-6}$ ، تم إيجاد الانتقائية ومـدى الدالـة الحامضية المناسبة والتي تراوحت ما بين (4.0-10.0) . وتم استعمال القطب بنجاح كقطب دليل في التسحيح الجهدي لايونات الثاليوم .

Keywords: Thallium ion-selective electrode, membrane, Nernstian response.

Introduction:

From the environmental and biological viewpoint, thallium poisoning is still a problem [1]. Thallium(I) is especially toxic in its bivalent compounds, *e.g.* sulfate (Tl_2SO_4) and carbonate (Tl_2CO_3); moreover Tl^+ may substitute for K^+ in activation of some important enzymes, such as pyruvate kinase [2,3]. The fatal dose of thallium(I) and its compounds are very low (level as low as 0.5 mg/100 g of tissue suggests thallium intoxication) [4]. Thus, the direct determination of Tl^+ in biological materials, such as blood and urine are of special interest.Numerous methods have been proposed for the spectrophotometric determination of thallium [5-8], most of which are based on extraction of ion-associates formed by basic dyes and thallium. These methods, however, are time consuming, have poor selectivity and also have the disadvantage of high blank values. Some of the other chromogenic reagents proposed for the determination of thallium are iodoacetic acid and hexamethylenetetramine [9], brilliant green [10]. Other notable methods used for the determination of thallium include ICP-MS [11], AAS [12] and voltammetry [13]. Most of these methods are disadvantageous in terms of cost and the instruments used in routine analysis. Ion-selective electrode (ISE) is one of the most convenient and reliable analytical tools for estimating metal ion [14]. There have been only a few reports concerning thallium(I) liquid-membrane electrodes [15-18].

The thallium(I) selective electrodes based on bis(crown ether)s containing the benzo-15-crown-5, where exhibited the linear range response (10^{-7}-10^{-1} M) with a slope of 58 mV/decade and the electrode response was stable over a wide pH range [19]. Yamashoji *et al.* [20] found that Tl^+-selective PVC membrane electrodes based on dibenzo-20-crown-6 and dibenzo-22-crown-6 show higher selectivities to Tl^+ than that of symmetrical dibenzo-18-crown-6. The electrode based on DB18C6, DB20C6 or DB22C6 showed linear response to the Tl^+ activity over range of (3.2×10^{-5}-1.0×10^{-1} M) with a slope of 59 mV/decade. Masuda *et al.* [21] found that Thallium ion-selective electrode based on PVC and thiacrown ether were given the linear activity range response (10^{-5}-10^{-1} M) with a slope of 55 mV/decade.

In this work, the use of phenyl disulfide (PD) as an ionophore are reported in the construction of a thallium(I)-PVC membrane electrode and studied the characteristic and properties of selective electrode.

Experimental Section:

Materials*:*

Reagent grade *o*-nitrophenyl octyl ether (*o*-NPOE), dibutyl phthalate (DBP), acetophenone (AP), benzyl acetate (BA), phenyl disulfide (PD), tetrahydrofuran (THF) and high relative molecular weight PVC were all obtained from Alderich Chemical Company. The nitrate salts of the cations used (all from Merck) were of the highest purity available. Doubly distilled deionized water was used throughout. The pH adjustments were made by the addition of (1.0 M) HNO_3 and NaOH solutions.

Apparatus:

All potentiometric measurements were carried out with the following assembly:

Ag | AgCl(satd.) | KCl(satd.) | internal solution (1.0×10^{-1} M $TlNO_3$) | PVC membrane | test solution | KCl(satd.) | Hg_2Cl_2(satd.) | Hg

A pH-inolab 720 pH/mV meter was used for the potential and the pH measurements.

Preparation of Membrane and Electrodes:

The general procedure to prepare the PVC membrane was to mix thoroughly 3.0 mg of ionophore (PD), 60 mg of plasticizer *o*-NPOE, 30 mg of powdered PVC and 5.0 mg of $TlNO_3$ in 6 mL of THF. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A pyrex tube (8-10 mm o.d.) was dipped into the mixture for about 5 s so that a nontransparent 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 12 h. The tube was then filled with internal filling solution (0.1 M $TlNO_3$). The electrode was finally conditioned by soaking in 0.1 M $TlNO_3$ solution for 24 h. A silver/ silver chloride wire was used as an internal reference electrode, it is shown in Figure 1.

Selectivity:

The selectivity coefficient ($K_{Tl,J}$) of the electrode towards different cationic species (J^{+n}) was determined using the mixed solution method [22]. The mixed solution method was used according to the following equation:

$$K_{Tl,J}^{Pot} a_J^{1/Zj} = a_{Tl}(anti \log \frac{E_2 - E_1}{RT/F}) - a_{Tl}$$

where E_1 is the potential of a known volume of solution containing Tl^+ ions at an activity of a_{Tl}, and E_2 is the potential of the Tl^+ solution with a known volume of interfering ions at activity of a_{Tl}.

Precision [18]:

The mean, is the numerical average obtained by dividing the sum of the individual measurements by the number of measurements.

$$\overline{X} = \frac{\sum X_i}{n}$$

The absolute standard deviation, S.D. describes the spread of individual measurements about the mean and is given as:

$$S.D. = \frac{\sum \left(X_i - \overline{X}\right)^2}{n-1}$$

The relative standard deviation, R.S.D. is reported.

$$R.S.D. = \frac{S.D.}{n} \times 100$$

Results and Discussion:

Phenyl disulfide (PD) it is shown in Figure 2. The ionophore used to construct a membrane for potentiometric measurements should be selective for the metal ion (Tl) over other metal ions, should show rapid exchange kineties, and should be sufficiently liophilic to the ligand into the solution surrounding the membrane electrode. It is well known that the sensitivity and selectivity of the ion-selective sensors not only depend on the nature of ionophore used, but also significantly on the membrane composition and the properties of plasticizers [23-27]. Thus, the influences of the membrane composition, the nature and amount of plasticizer on the potential response of the Tl^+ sensor were investigated; the results are summarized in (Table 1). Several plasticizers including DBP, *o*-NPOE, AP and BA, which are often used with PVC membrane electrodes, were evaluated. Since the nature of plasticizer influences the dielectric constant of the membrane phase, the mobility of the inophore molecules and the state of ligands [28], it is expected to play an important role in determining the ionselective characteristics. As it is seen from Table 1, among different plasticizers examined, *o*-NPOE results in the best sensitivity, it is shown in Figure 3. The dependence of the electrode response (slope and detection limit) on the amount of carrier was also examined and is shown in Figure 4. In the case of the carrier-type ionselective electrodes, the mechanism of the electrode response depends mainly on the extraction equilibrium in the vicinity of the interface between the membrane and aqueous layer [29]. In spite of these considerations, a carrier content of 3.0 mg was chosen as the optimum condition (No. 4, Table 1), because the surface condition of the PVC membrane deteriorated as a result of decreasing and increasing the carrier content (1.0 and 4.0 mg, respectively). The plasticizer/PVC ratio of 1.0-3.0 were examined. The membranes prepared with a plasticizer/PVC ratio of about 2.0 were found to have the best sensitivity [30], with a slope of 56.9 mV per decade over a wide concentration range (Figure 5).

The concentration range, the slope and detection limit:

The emf response of the proposed Tl^+ sensor (prepared under optimal membrane ingredients) indicate a rectilinear range from 1.0×10^{-5}-1.0×10^{-1} M. The slope of the calibration curve were 56.9 mV/decade. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration curve, was 5.6×10^{-6} M.

The effect of internal solution:

The influence of the concentration of internal solution on the potential response of the Tl^+ ion-selective electrode was studied. The $TlNO_3$ concentration was changed from 1.0×10^{-3} to 1.0×10^{-1} M and the emf-pTl plot was obtained. It was found that the variation of the concentration of

internal solution does not any significant difference in the electrode's potential response, except for an expected change in the intercept of the resulting near-Nernstein plots. A 0.1 M concentration of the reference solution is quite appropriate for smooth functioning of the system (Figure 6).

Response time and stability:
Optimum conditioning time for the membrane sensor in a 0.1 M $TlNO_3$ solution is 24 h. It then generate stable potentials when placed in contact with Tl^+ solutions. The response time measured was less than 10 s for Tl^+ concentrations $1.0x10^{-2}$ M. It is noteworthy that the equilibrium potentials essentially remained constant for more than 5 min, after which only a very small divergence within the resolution of the pH meter was recorded the membrane sensor prepared could be used for at least 3 months without any measurable divergence.

The effect of pH:
The pH dependence of the electrode was studied for the pH range 1-12. The results indicate the working range of the electrode to be between pH (4-10), Figure 7. Above pH 10 the measured potential decreased, due to the effect of the hydroxyl ion, (TlOH) may be formed. At lower pH values the electrode responds to H^+ ions.

Selectivity:
The important parameter of many potentiometric ion is response to the primary ion in the presence of the other ions presence in solution, which is expressed in terms of the potentiometric selectivity constant ($K_{Tl,J}$). The values obtained for selectivity coefficients by the mixed solutions method with a mixed concentration of interference metal ion (J^{+n}) with an activity of aqueous 0.1 M solution of $TlNO_3$, are given in (Table 2). It can be seen from these values that the electrode is characterized by a high selectivity towards thallium ions with respect to alkali, alkaline earth, transition and heavy metal ions [21].

Analytical Application:
The proposed thallium membrane electrode was found to work well under laboratory conditions. It was successfully applied to the titration of a Tl^+ ion solution with sodium iodide. During the titration no pH or ionic strength adjustments were made. All titration were performed with 0.01 M of $TlNO_3$ in 50 mL of sample solution with 0.1 M of NaI. A typical titration curve is shown in Figure 8. The other titrants led to similar titration curves, the steepness of the potential jump being inversely dependent on the solubility product, as usual. As shown, the amount of Tl^+ ions in solution can be accurately determined with the electrode.

Conclusion:
A PVC-membrane electrode for Tl^+ ions based on (PD) as ionophore, was investigated. The optimized formulation of the membrane (*i.e*. 3.0 mg PD, 30 mg PVC, 60 mg *o*-NPOE, 5.0 mg $TlNO_3$) resulted in a linear concentration range of $1.0x10^{-5}-1.0x10^{-1}$ M with a slope of 56.9 mV/decade and a limit of detection of $5.6x10^{-6}$ M. The fast response time, wide linear range, fair selectivity coefficients and long lifetime of the proposed sensor are advantageous over most of the reported Tl^+ ion-selective electrodes. The proposed electrode can be used successfully as a sensor in potentiometric titrations.
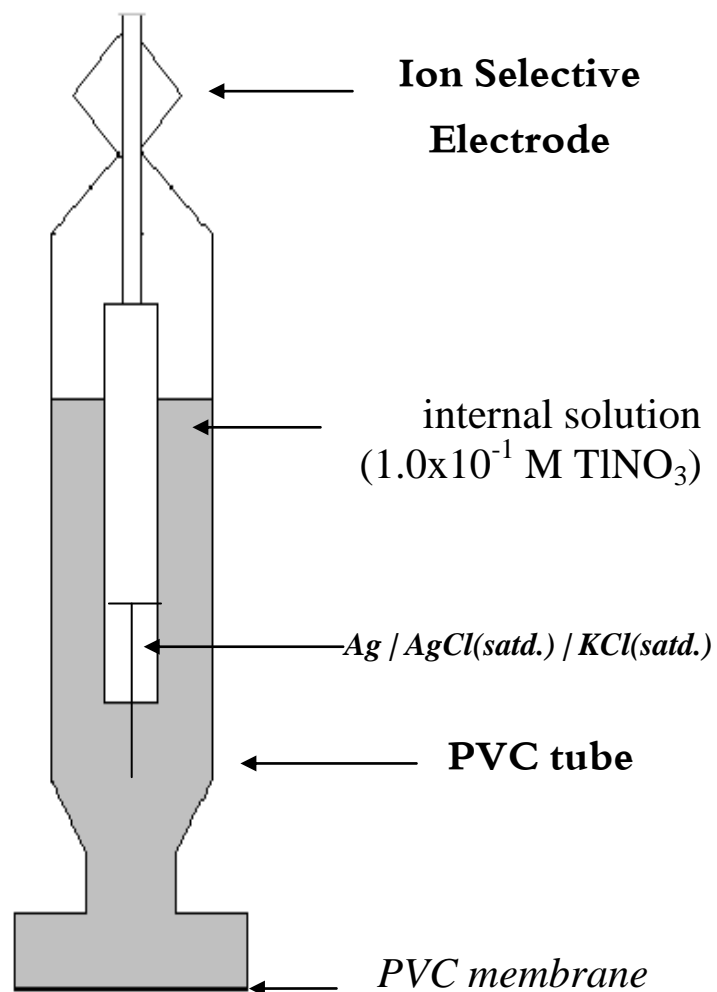
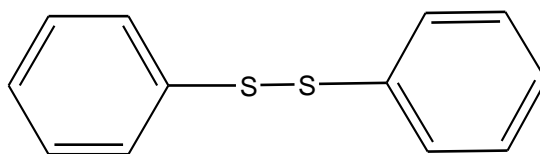**Figure 1. Structure of Thallium(I)-Selective electrode**

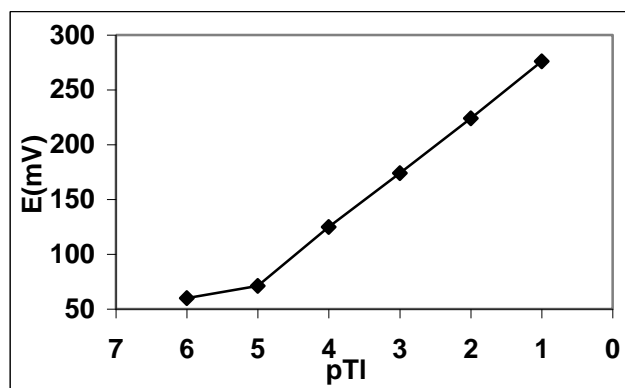**Figure 2. Structure of Phenyl Disulfide (PD)**

Figure 3. Calibration Curve of Structure of thallium(I) selective electrode
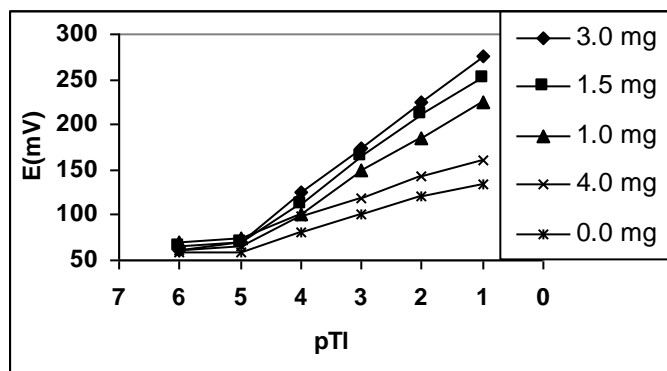
Figure 4. Effect of the content of (PD) on the response of the membrane
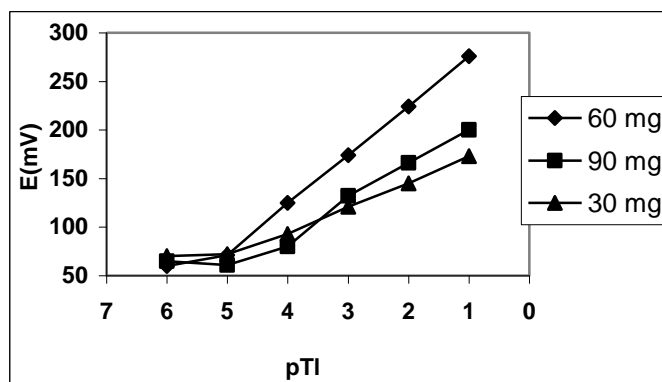

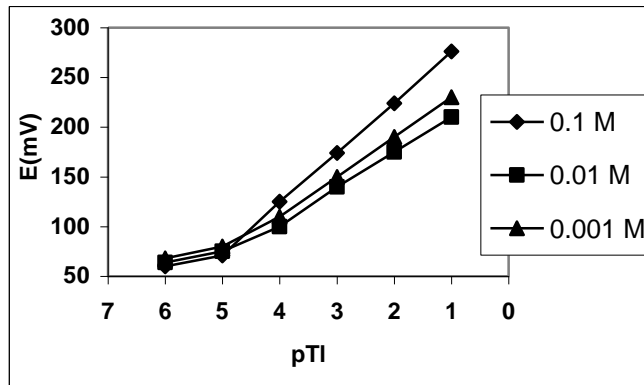**Figure 5. Effect of the content of (*o*-NPOE) on the response of the membrane**

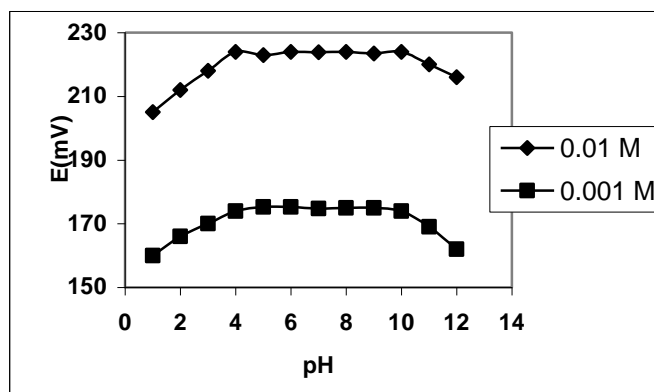**Figure 6. Effect of the internal solution on the response of the membrane**

Figure 7. Effect of pH on the response of thallium(I) selective electrode based on (PD)
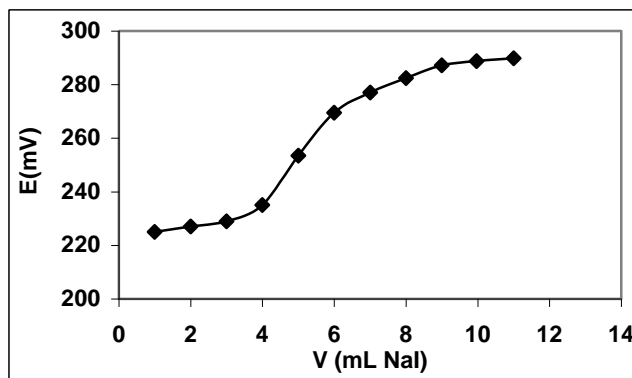
Figure 8. Titration of Tl^+ (0.01 M) in 50 mL of aqueous solution with (0.1 M) NaI using the thallium(I) selective electrode

Table 1. Optimization of the membrane ingredients

No.	Composition (mg)						Slope
	PD	PVC	*o*-NPOE	BA	AP	DBP	mV/decade
1	0.0	30	60	-	-	-	25.3
2	1.0	30	60	-	-	-	49.7
3	1.5	30	60	-	-	-	52.8
4	3.0	30	60	-	-	-	56.9
5	4.0	30	60	-	-	-	34.0
6	3.0	30	30	-	-	-	21.7
7	3.0	30	90	-	-	-	30.1
8	3.0	30	-	60	-	-	13.5
9	3.0	30	-	-	60	-	24.5
10	3.0	30	-	-	-	60	47.2
11	1.5	30	-	60	-	-	11.2
12	1.5	30	-	-	60	-	23.9
13	1.5	30	-	-	-	60	46.3
14	3.0	30	60	-	-	-	21.8
15	3.0	30	60	-	-	-	41.9

Table 2. Selectivity coefficients of various interfering ions

Interfering ion	Log $K_{Tl,J}$	Interfering ion	Log $K_{Tl,J}$
H^+	-2.12	Ba^{+2}	-2.66
Li^+	-2.08	Fe^{+2}	-2.37
Na^+	-3.10	Co^{+2}	-1.11
K^+	-1.31	Ni^{+2}	-2.54
Cs^+	-2.20	Cu^{+2}	-2.57
Ag^+	-1.36	Zn^{+2}	-1.55
NH_4^+	-1.10	Cd^{+2}	-0.92
Mg^{+2}	-2.50	Hg^{+2}	-0.08
Ca^{+2}	-2.82	Pb^{+2}	-3.34

Table 3. The Precision of 1×10^{-4} M of $TlNO_3$

No.	X_i mV	$(X_i - \overline{X})$	$(X_i - X)^2$
1	125	-0.28	0.0784
2	125	-0.28	0.0784
3	124	-1.28	1.6384
4	126	0.72	0.5184
5	126	0.72	0.5184
6	125	-0.28	0.0784
7	126	0.72	0.5184
$\sum X_i = 877$ $\overline{X} = 125.28$			$\sum (X_i - \overline{X})^2 = 1.712$
	S.D = 0.534		R.S.D = 0.426%

References:

1.Moeschlin, S. *Clin. Toxicol*. **1980**, *17*, 133.

2.Britten, J. S.; Blank, M. *Biochim. Biophys. Acta* **1968**, *159*, 160.

3.Kayne, F. J. *Arch. Biochem. Biophys*. **1971**, *143*, 232.

4.Park, K. S.; Jung, S. O.; Kim, J. S. *Bull. Korean Chem. Soc*. **2000**, *21*, 909.

5.Marczenko, Z. *Separation and Spectrophotometric Determination of Elements*, Ellis Horwood Ltd., Chichester, London, **1986**, 569.

6.Gregorowicz, Z.; Ciba, J. *Talanta* **1981,** *28***,** 805.

7.Fogg, A. G.; Burgess, C.; Burns, D. T. *Talanta* **1971,** *18*, 1175.

8.Sager, M.; Tolg, G. *Mikrochim. Acta II*, **1982,** 1, 231.

9.Mihajlovic, D.; Sta, T. *Fresenius J. Anal. Chem.* **1996,** 356, 371.

10. Agarwal, N.; Patel, K. S. *Analusis* **1991,** *19*, 134.

11.　 Medek, P.; Pavlickova, J.; Zbiral, J.; Cizmarova, E.; Kuban, V. *Int. J. Environ. Anal. Chem.* **2001,** *81,* 207.

12. Zendelovska, D.; Sta, T. *Anal. Sci.* **2001,** *17,* 425.

13. Lu, T. H.; Sun, I. W. *Electroanal.* **1998,** *10,*1052.

14. Saleh, M. B. *J. Electroanal. Chem*. **1998**, *448*, 33.

15. Coetzee, C. J.; Basson, A. J. *Anal. Chim. Acta* **1973**, *64*, 300.

16. Szeczepaniak, W.; Ren, K. *Anal. Chim. Acta* **1976**, *82*, 37.

17. Coetzee, C. J.; Basson, A.J. *Anal. Chim. Acta* **1977**, *92*, 399.

18. Coetzee, C. J. *Talanta* **1985**, *32*, 821.

19. Tamura, H.; Kimura, K.; Shono, T. *J. Electroanal. Chem*. **1980**, *115*, 115.

20. Yamashoji, Y.; Tanaka, M.; Nagamune, S.; Ouchi, M.; Hakushi, T.; Shono, T. *Anal. Sci*. **1991**, *7*, 485.

21. Masuda, Y.; Yakabe, K.; Shibutani, Y.; Shono, T. *Anal. Sci*. **1994**, *10*, 491.

22. Umezawa, Y.; Umezawa, K.; Sato, H. *Pure Appl. Chem*. **1994**, 66, 391.

23. Shamsipur, M.; Khayatian, G. *J. Incl. Phenom*. **2001**, *39*, 109.

24. Tavakkoli, N.; Shamsipur, M. *Anal. Lett*. **1996**, *29*, 2269.

25. Mashhadizadeh, M. H.; Shamsipur, M. *Anal. Chim. Acta* **1999**, *381*, 111.

26. Bakker, E.; Buhlmann, D.; Pretsch, E. *Chem. Rev*. **1997**, *97*, 3083.

27. Fakhari, A. R.; Ganjali, M. R.; Shamsipur, M. *Anal. Chem*. **1997**, *69*, 3693.

28. Yang, X.; Kumar, N.; Chi, H.; Hibbert, D. B. *Electroanalysis* **1997**, *9*, 549.

29. Eyle, E.; Rechnitz, G. A. *Anal. Chem*. **1971**, *43*, 1090.

30. Schaller, U.; Bakker, E.; Spichiger, U. E.; Pretsch, E. *Anal. Chem*. **1994**, *60*, 391.