Articles

Development of a New Copper(II) Ion-selective Poly(vinyl chloride) Membrane Electrode Based on 2-Mercaptobenzoxazole

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Copper(II) ion-selective PVC membrane electrode based on 2-mercaptobenzoxazole as a new ionophore and *o*-nitrophenyl octyl ether (*o*-NPOE) as plasticizer is proposed. This electrode revealed good selectivity for Cu^{2+} over a wide variety of other metal ions. Effects of experimental parameters such as membrane composition, nature and amount of plasticizer, and concentration of internal solution on the potential response of Cu^{2+} sensor were investigated. The electrode exhibits good response for Cu^{2+} in a wide linear range of 5.0×10^{-6}-1.6×10^{-2} mol/L with a slope of 29.2 ± 2.0 mV/decade. The response time of the sensor is less than 10 s, and the detection limit is 2.0×10^{-6} mol/L. The electrode response was stable in pH range of 4-6. The lifetime of the electrode was about 2 months. The electrode revealed comparatively good selectivities with respect to many alkali, alkaline earth, and transition metal ions.

Key Words : Copper(II) ion-selective electrode, Ion sensor, PVC membrane, Potentiometry, 2-Mercapto-benzoxazole

Introduction

The utility of ion-selective electrodes (ISEs) is being increasingly realised by analytical chemists in view of the rapid growth of industry and technology all over the world as they represent a rapid, accurate and low-cost method of analysis. Moreover, analysis by these electrodes could be non-destructive and adaptable to small sample volumes. ISEs find application in various industrial and biological fields such as ion monitoring and in analysis of sea water, soils, food products, drinking water, industrial effluents, pharmaceutical compounds, etc.[1-12] Due to the vital importance of copper in industry and in many biological systems,[13] and the urgent need for a copper-selective sensor for potentiometric monitoring of Cu^{2+} in different industrial, medicinal and environmental samples, a variety of potential ion-carriers have been used in the construction of copper(II)-selective membrane electrodes. Since the sulfur and nitrogen donor atoms coordinate with transition-metal ions to form metal complexes in these copper sensors, small size thia-crown ethers,[14,15] non-cyclic neutral ionophores,[16,17] cali-xarenes[18] and Schiff bases[19] have been used as ion carriers. In addition, solid-state electrodes based on CuS-Ag_2S are well established.[20] However, most of these copper(II)-selective membranes suffer strong interfering effects from Co^{2+}, Ni^{2+}, Cd^{2+}, Hg^{2+}, and Ag^- ions.
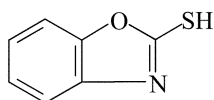

Figure 1. Structure of ionophore.

2-Mercaptobenzoxazole,[21] C_7H_5ONS, (Figure 1), colorless crystals, is insoluble in water, but is soluble in aqueous alkali and common organic solvents; $pka_1 = 6.58$ and $pka_2 = 11.46$. This reagent has been recommended as an extraction photometric reagent for some metal ions such as Os(III) and Ru(III).[22] In this article, we report the use of 2-mercapto-benzoxazole as a good ionophore in construction of a copper(II)-PVC membrane electrode.

Experimental Section

Reagents. High relative molecular weight PVC, *o*-nitrophenyl octyl ether (*o*-NPOE), dimethyl sebacate (DMS), dibutyl phthalate (DBP), tetrahydrofuran (THF), and 2-mercaptobenzoxazole were purchased from Fluka chemical company and used as received. The chloride and nitrate salts of the cations used (all from Merck) were of the highest purity available and used without any further purification except for vaccum drying over P_2O_5. Doubly distilled deionized water was used throughout.

Copper stock solution (2.0×10^{-1} mol/L) was prepared by dissolving an appropriate amount of $CuCl_2 \cdot 2H_2O$ or $Cu(NO_3)_2$ (Merck) in a 100 mL calibrated flask and diluting to the mark with water. The solution was standarized iodometrically.[23] The working solutions were prepared by suitable dilution of the stock solution.

Preparation of PVC membrane. The general procedure to prepare the PVC membrane was to mix thoroughly 32.4 mg of powdered PVC, 64.6 mg of *o*-NPOE as solvent mediator and 3.0 mg of 2-mercaptobenzoxazole as iono-phore. The mixture was dissolved in 1.5 mL of THF. A pyrex tube (3-mm i.d.) was dipped into the mixture for ~10s

so that a nontransparent membrane of ~0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for ~6 h. Then it was filled with internal filling solution (1.0×10^{-2} mol/L $CuCl_2 \cdot 2H_2O$). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-2} mol/L solution of copper chloride. A silver/ silver chloride coated wire was used as an internal reference electrode.
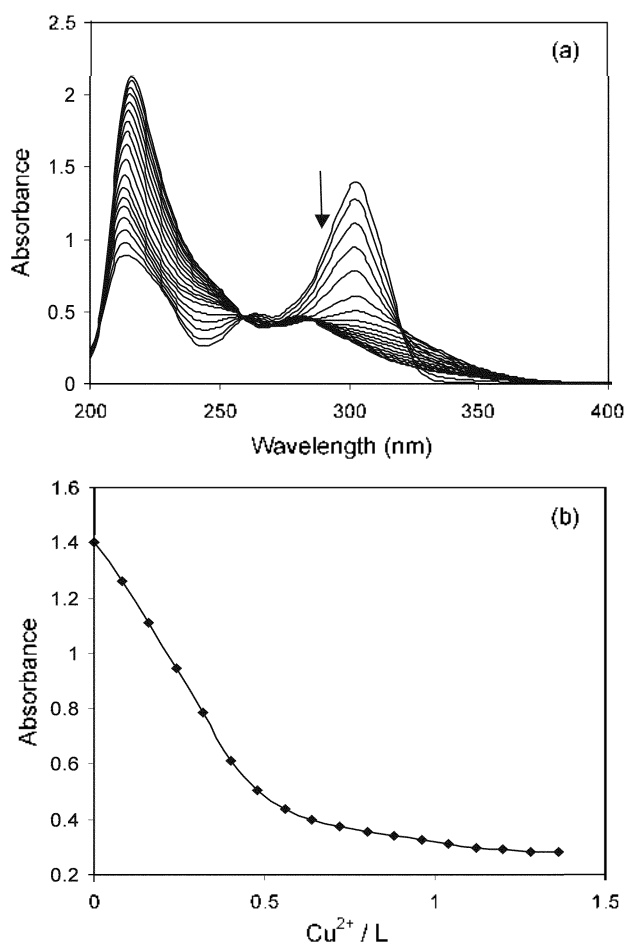
Electrode potential measurement. All emf measurements were carried out with the following assembly:

Ag-AgCl | 1.0×10^{-2} mol/L $CuCl_2 \cdot 2H_2O$ | PVC membrane | test solution | Hg-Hg_2Cl_2, KCl (satd.)

A Metrohm digital research pH meter (Model 624) was used for potential measurements at 25.0 ± 0.1 °C. The emf observations were made relative to a double-junction saturated calomel electrode (SCE, Philips) with the chamber filled with a potassium nitrate solution. Activities were calculated according to the Debye-Huckel equation.
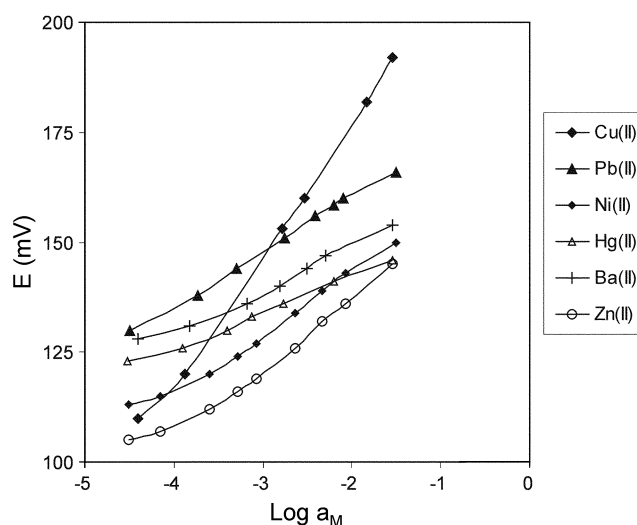
Results and Discussion

Ligands for use as ionophore in a Cu^{2+} ion-selective

electrode should fulfill certain conditions. They should be selective for Cu^{2+} over other metal ions. They should have rapid exchange kinetics and should be sufficiently lipophilic to prevent leachhing of the ligand into the aqueous solutions surrounding the membrane electrode. The existence of a donating nitrogen atom as well as $-SH$ group in 2-mercaptobenzoxazole was expected to increase both the stability and selectivity of its copper complex over other metal ions, especially alkali and alkaline earth cations. The spectrophotometric studies (Figure 2a) in acetonitril solution revealed that 2-mercaptobenzoxazole as a chelating agent can form a fairly stable complex with a 2 : 1 stoichiometry with Cu^{2+} ion (Figure 2b). In the other hand,since the membrane components are generally dissolved in the organic polymer phase, their leaching into the sample must be kept as low as possible, the presence of benzo-ring in skeleton of ligand (in neutral media) prevent leaching of this ionophore into the aqueous solutions.

In preliminary experiments, the ionophore was used as a neutral carrier to prepare PVC membrane ion-selective sensors for a wide variety of metal ions, including alkaline earth, transition and heavy metal ions. The slope, correlation coefficient, and linear range of some of them are shown in Figure 3 and Table 1. As seen, with the exception of Cu^{2+}, in

Figure 2. (a) UV-visible spectra of 1×10^{-4} mol/L of 2-mercaptopbenzoxazole in acetonitril and various concentration of Cu^{2+} 1×10^{-3} mol/L, (b) Mole ratio plot.

Figure 3. Potential response of variuos ion-selective electrodes based on $Loga_M^{n+}$ cations: Cu^{2+}, Pb^{2+}, Ni^{2-}, Hg^{2-}, Ba^{2-}, Zn^{2+}.

Table 1. Potential response of various metal ion-selective electrodes

Cations	Slope (mV/decade)	R^2	Interval of linear response (mol/L)
Cu^{2+}	30.4	0.994	$3.9 \times 10^{-5} - 2.9 \times 10^{-2}$
Ag^+	28.0	0.980	$6.3 \times 10^{-5} - 3.3 \times 10^{-3}$
Hg^{2-}	7.56	0.966	$7.1 \times 10^{-5} - 3.2 \times 10^{-3}$
Ba^{2+}	9.96	0.967	$3.6 \times 10^{-5} - 4.5 \times 10^{-3}$
Mg^{2-}	12.2	0.994	$5.8 \times 10^{-5} - 5.5 \times 10^{-3}$
Pb^{2-}	12.6	0.995	$3.2 \times 10^{-5} - 6.3 \times 10^{-3}$
Ni^{2+}	10.0	0.953	$5.0 \times 10^{-5} - 8.1 \times 10^{-3}$
Co^{2+}	7.20	0.980	$6.9 \times 10^{-5} - 8.5 \times 10^{-3}$

Table 2. Optimization of membrane ingredients

No.	Composition%					Slope (mV/decade)	R^2
	PVC	o-NPOE	DBP	DMS	Ionophore		
1	32.8	66.0	–	–	1.2	26.6	0.996
2	32.8	65.5	–	–	1.7	31.5	0.990
3	32.5	65.1	–	–	2.4	30.65	0.995
4	32.4	64.6	–	–	3.0	29.5	0.998
5	32.1	64.3	–	–	3.6	31.2	0.995
6	32.0	64.9	–	–	4.1	31.0	0.994
7	31.6	63.1	–	–	5.3	27.9	0.995
8	31.3	62.7	–	–	6.0	27.0	0.996
9	32.4	–	64.6	–	3.0	22.0	0.995
10	32.4	–	–	64.6	3.0	18.7	0.989

all other cases, the slopes are much lower than expected Nernstian slope.

It is well known that the sensitivity, linearity and selectivity obtained for a given ionophore depends significantly on the membrane composition. Since the selectivity of carrier–based ISEs are highly influenced by the membrane solvent nature (plasticizer)[1,5,24] it is expected to play a fundamental role in specifying the selective electrode characteristics. It has been assumed that this influence is due to the polarity of the plasticizer, which can be estimated from the interaction of charged species with a continuum of given dielectric constant,[5] So, several solvent mediators such as o-NPOE, DMS, and DBP, which are often used in PVC-membrane electrodes, were evaluated and the results are summarized in the Table 2. Among these plasticizers, o-NPOE provided faster, more stable and sensitive response in the concentration range of 5.0×10^{-6}–1.6×10^{-2} mol/L of Cu(II) ion.

The solvent polymeric membranes used in ion sensors are usually based on a matrix about 33%(w/w) of PVC and 66% of a membrane solvent.[24,25,26] In general, the thickness and hardness of the membrane depend upon the amount of PVC used. Therfore, the membranes with a o-NPOE/PVC ratio of 2 were prepared. From the data given in this Table 2 indicate that the best sensitivity (Nernstian slope) and regression coefficient is obtained for membrane number of 4 with PVC/ o-NPOE/ionophore of 32.4%/64.6%/3.0%.

Since, the variation of the concentration of the internal solution does not cause any significant difference in the potential response of the electrode, except for an expected change in the intercept of the resulting Nernstian plots, a 1.0 $\times 10^{-2}$ mol/L concentration of $CuCl_2 \cdot 2H_2O$ was used as an internal solution .

The influence of pH for 1.0×10^{-4} mol/L Cu^{2-} on the potential response of the membrane sensor was tested in the pH range 1.5-8.0 and results are shown in Figure 4. As seen the potential remained constant from pH 4.0-6.0. The observed drift at lower and higher pH values could be due to the protonation of the ion carrier and formation of some hydroxy complexes of Cu^{2-} ion in solution, respectively.

Optimum conditioning time for the ion-selective electrode in a 1.0×10^{-2} mol/L copper chloride solution is 24 h. It then
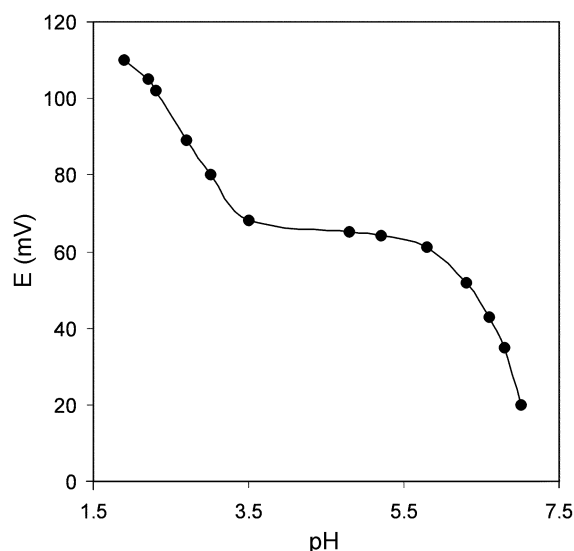
Figure 4. Effect of pH of test solution on the potential response of the ion-selective electrode in 1×10^{-4} mol/L of Cu^{2+}.

generates stable potentials when placed in contact with Cu^{2-} solutions. For analytical applications, the response time of a membrane sensor is an important factor. The static response time of the electrode, tested by measuring the average required to achieve a potential within ± 1 mV of the final steady-state potential upon successive immersion of a series of Cu^{2+} ion, each having a tenfold difference in concentration, was within < 10 s for Cu^{2+} concentrations < 1.0 × 10^{-3} mol/L. Reproducibility of electrode was examined by using six similar constructed electrodes under the optimum conditions. The results showed good reproducibility for proposed electrode. For instance, the slopes observed were 29.1 ± 2.0 mV per decade and the standard deviation of 10 identical potential measurements (at 1.0 × 10^{-3} mol/L) was ± 0.2 mV. The long-term stability of the electrode was studied by periodically re-calibrating in standard solutions
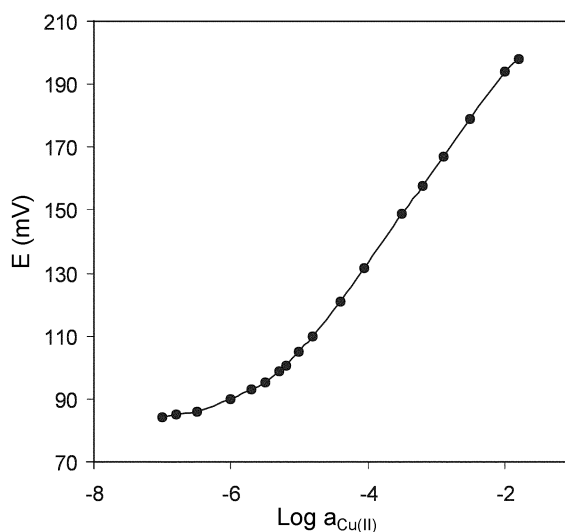
Figure 5. Calibration plot for the proposed Cu^{2+}-selective electrode.

Table 3. Selectivity coefficients of various interfering ions

Interfering ion	$k_{Cu^{2+}}^{Pot}$,	Interfering ion	$k_{Cu^{2+}}^{Pot}$,
Na⁻	1.2×10^{-3}	Pb²⁺	6.4×10^{-2}
K⁻	8.0×10^{-3}	Zn²⁻	4.6×10^{-2}
Mg²⁻	2.0×10^{-2}	Cd²⁺	6.3×10^{-2}
Ba²⁺	1.3×10^{-2}	Ni²⁻	7.4×10^{-1}
Sr²⁺	2.3×10^{-2}	Li⁻	6.0×10^{-3}
Co²⁻	2.2×10^{-2}	Cs¹	5.0×10^{-2}

and calculating the response slope. The slope of the electrode responses was reproducible over a period of at least 2 month. Therefore the proposed electrode can be used for 2 month without a considerable change in its response characteristics towards Cu²⁺.

The potential response of the optimized electrode, to varying concentration of Cu²⁻ ions, was examined. The calibration plot is shown in Figure 5, which indicates a linear range of $5.0 \times 10^{-6} - 1.6 \times 10^{-2}$ mol/L with a Nernstian slope of 29.1 ± 2.0 mV per decade of Cu²⁻ activity. The practical limit of detection was 2.0×10^{-6} mol/L as determined from the intersection of the two extrapolated segments of the calibration graph based on recommended procedure by IUPAC.[27,28]

In addition to the Nernstian behavior, linear range and detection limit, the selectivity of the membrane sensor for Cu²⁺ ions over other metal cations is also of fundamental importance. Thus, the selectivity of the membrane electrode was tested by its potential response measurements in the presence of a wide variety of cations including alkali, alkaline earth, transition and heavy metal ions. The selectivity coefficients, $k_{Cu^{2+}}^{Pot}$, were evaluated graphically by the mixed solution method[1,29,30] from potential measurements on solutions containing a fixed concentration of Cu²⁺ (5.0×10^{-4} mol/L) and varying amounts of the interfering

Figure 6. Potentiometric titration curve of 10 mL of 1.0×10^{-2} mol/L of Cu²⁺ solution with 1.0×10^{-1} mol/L EDTA. at pH 5, using the proposed sensor as an indicator electrode.

ions (Mⁿ⁺) according to the Eq. (1):

$$K_{Cu^{2+}}^{Pot} \cdot a_M^{2/n} = a_{Cu^{2+}} \{\exp[(E_2 - E_1)F/RT]\} - a_{Cu^{2+}} \tag{1}$$

Where E_1 and E_2 are the electrode potentials for the solution of Cu²⁻ ions alone and for the solution containing interfering ions and copper ions, respectively. According to Eq. (1), the $k_{Cu^{2+}}^{Pot}$, values for diverse cations can be evaluated from the slope of the linear graph $a_{Cu}\{\exp[(E_2-E_1)F/RT]\}-a_{Cu}$ against $a_M^{2/n}$. The resulting values are summarized in Table 3. As can be seen, for most of the diverse ions used, the selectivity coefficients are in the order of 10^{-2} or smaller except Ni²⁻ ions that have interfering effect on the potential response of the Cu²⁻ membrane electrode.

The applicability of the proposed sensor was checked by its use as an indicator electrode for the titration of 10 mL 1.0 $\times 10^{-3}$ mol/L Cu²⁻ solution with 0.01 mol/L EDTA and the result is shown in Figure 6. A very good inflection point, showing perfect stoichiometry, is observed in the titration plot. As seen, the amount of copper ion in solution can be accurately determined with the electrode.

References

1. Ammann, D.; Morf, W. E.; Anker, P.; Meier, P. C.; Pretsch, E.; Simon, W. *Ion-Selective Electrode Rev.* **1983**, 5, 3.
2. Arnold, M. A.; Meyerhoff, M. E. *Crit. Rev. Anal. Chem.* **1988**, 20, 149.
3. Janata, J.; Josowics, M.; Vanysek, P.; Devancy, D. M. *Anal. Chem.* **1998**, 70, 179 R.
4. Bühlmann, P.; Pretsch, E.; Bakker, E. *Chem. Rev.* **1998**, 98, 1593.
5. Bakker, E.; Bühlmann, P.; Pretsch, E. *Chem. Rev.* **1997**, 97, 3083.
6. Antonisse, M. M. G.; Reinhoudt, D. N. *Electroanalysis* **1999**, 11, 1035.
7. Aamrani, F. El; Garcia-Raurich, J.; Sastre, A.; Beyer, L.; Florido, A. *Anal. Chim. Acta* **1999**, 402, 129.
8. Fathi, M. R.; Darviche, F.; Ganjali, M. R. *Anal. Lett.* **2000**, 30, 1025.
9. Mousavi, M. F.; Sahari, S.; Alizadeh, N.; Shamsipur, M. *Anal. Chim. Acta* **2000**, 414, 189.
10. Shamsipur, M.; Rouhani, S.; Ganjali, M. R.; Eshghi, H.; Sharghi, H. *Sens. Actuat. B* **1999**, 59, 30.
11. Shamsipur, M.; Yousefi, M.; Ganjali, M. R. *Anal. Chem.* **2000**, 72, 2391.
12. Rouhollahi, A.; Shamsipur, M. *Anal. Chem.* **1999**, 71, 1350.
13. Greenwood, N. N.; Earnshow, A. *Chemistry of Elements*; Pergamon Press: New York, 1984.
14. Kamata, S.; Yamasaki, Y.; Higo, M.; Bhale, A.; Fukamaga, Y. *Analyst* **1988**, 113, 45.
15. Casabo, J.; Mestres, L.; Escriche, L.; Texidor, F.; Perez-Jimenez, C. *J. Chem. Soc. Dalton Trans.* **1991**, 1969.
16. Abbaspour, A.; Kamyabi, M. A. *Anal. Chim. Acta* **2002**, 455, 225.
17. Kamata, S.; Murata, H.; Kubo, Y.; Bhale, A. *Analyst* **1989**, 114, 1029.
18. Cobben, P. L. H. M.; Egberink, R. J. M.; Bomer, J. G.; Bergveld, P.; Verboom, W.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1992**, 114, 10573.
19. Alizadeh, N.; Ershad, S.; Naeimi, H.; Sharghi, H.; Shamsipur, M.
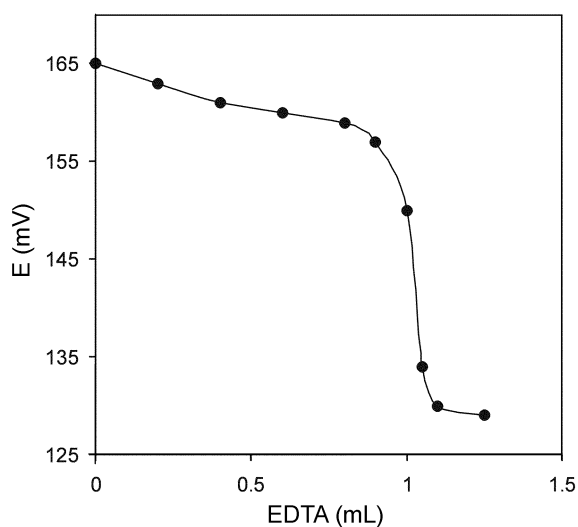
Fresenius J. Anal. Chem. **1999**, *365*, 511.

20. Framt, M. *Analyst* **1990**, *119*, 2293.
21. Van Allan, J. A.; Deacon, B. D. *Org. Synth.* **1963**, *IV*, 569.
22. Lonakina, L. N.; Ignateva, T. I.; Busev, A. I. *Zh. Anal. Kim.* **1978**, *11*, 527.
23. Vogel, A. I. *A Testbook of Quantitative Inorganic Analysis*, 3rd ed; Longman: London, 1961.
24. Tavakkoli, N.; Shamsipur, M. *Anal. Lett.* **1996**, *29*, 2269.
25. Craggs, A.; Moody, G. J.; Thomas, J. D. R. *J. Chem. Edu.* **1974**,

51, 541.

26. Moody, G. J.; Oke, R. B.; Thomas, J. D. R. *Analyst* **1970**, *95*, 910.
27. Umezawa, Y. *Anal. Chem.* **1982**, *54*, 1198.
28. Guilbault, G. G; Durst, R. A.; Freiser, H. *Pure Appl. Chem.* **1976**, *48*, 127.
29. Umezawa, Y.; Umezawa, K.; Sato, H. *Pure Appl. Chem.* **1995**, *67*, 507.
30. Bakker, E. *Electroanalysis* **1997**, *9*, 7.