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Cu^{2+} – SEÇİCİ LİKİT MEMBRAN ELEKTRODUN BAZI ANALİTİK UYGULAMALARI

SOME ANALYTICAL APPLICATIONS OF Cu^{2+} – SELECTIVE LIQUID MEMBRANE ELECTRODE

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SUMMARY

In the present paper, a liquid membrane Cu^{2+} – selective electrode of our construction and a commercial solid membrane Cu^{2+} – selective electrode were used for the determination of sodium sulphide and thioacetamide by potantiometric titration with $CuSO_4$ solution as titrant.

ÖZET

Bu çalışmada, geliştirdiğimiz Cu^{2+} – seçici likit membran elektrot ve ticari solid membran elektrot kullanılarak, standart $CuSO_4$ çözeltisi ile potansiyometrik titrasyonla sodyum sülfür ve tiyoasetamidin tayinleri yapıldı.

INTRODUCTION

The development of sulphide–selective electrodes has made possible selective, highly sensitive and rapid determinations of sulphide ions by means of the direct potentiometric method or potentiometric titration (1 – 3). Determination have usually been made in alkaline solution (1 M or 0,1 M in sodium hydroxide). Pungor et al. (4) have described potentiometric method for the determination of thioacetamide using S^{2-} –selective membrane electrode (Radelkis, Type OP–S–711).

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Baiulescu et al. have determined these compounds by using Cu^{2+} , Hg^{2+} –liquid membrane electrodes consisting of mercury (II), copper complexes dissolved in suitable organic solvents (5,6). Cosofret (7) have determined thioacetamide in alkaline solution by potentiometric titration with a Ag^{+} –selective membrane electrode (the membrane consisted of the Ag^{+} – dithizonate chelate in carbon tetrachloride). An aqueous silver nitrate solution was used as titrant.

The present paper, described the results of a potentiometric precipitation titrations of thioacetamide and sodium sulphide with a Cu^{2+}– selective liquid membrane electrode consisting of Cu^{2+} – dithizonate [$Cu(Dz)_2$], in chloroform. An aqueous copper sulphate solution was used as titrant.

EXPERIMENTAL PART

Apparatus and reagent

The measurements were made with an E 518 Metrohm Herisau potentiometer. A Orion Cu^{2+} – selective 94–29 membrane electrode and Cu^{2+} – liquid membrane were used as the indicator electrode and saturated calomel electrode was used as reference electrode. These electrodes were connected to the sample solution by a saturated KNO_3 bridge. The e.m.f. values were measured at room temperature in stirred solutions. Automatic digital burette E 436 Metrohm Herisau used in titrations. All reagents used were analytical grade. Thioacetamide and sodium sulphide solutions (0,1 M) were prepared by dissolving the appropriate amount of these compounds in 1 M sodium hydroxide solution.

Construction of the Cu^{2+} – selective electrode

The construction of the electrode has been described previously (8–11). This electrode consist of impregnating the support material (a graphite rod, 15 mm long, 6,5 mm diameter, made water reppelent) attached to the end of the teflon tube with the liquid membrane. Liquid exchanger consist of Cu(II) dithizone chelate dissolved in $CHCl_3$. The internal reference electrode was eliminated by using stainless–steel wire introduced into the graphite rod. The electrode was stored in the $[Cu(Dz)_2]$ solution and washed with distilled water between measurements.

RESULTS AND DISCUSSION

Potentiometric titrations of thioacetamide and sodium sulphide solutions (10^{-1} , 10^{-3} M) were estabilished in sodium hydroxide solutions (0,1 , 1 M). $CuSO_4$ solution (10^{-2} M) was used as titrant in every case. The titration curves were shown in Figs. 1 – 2. As seen from the curves it was obtained large potential jump at the equivalance point. For the reverse titration, i.e. $CuSO_4$ with thioacetamide and sodium sulphide dissolved in 1 M sodium hydroxide solution, two potential jumps were observed in Figs. 3 – 4. The first potential jump for both curves correspondes to the precipitation of $Cu(OH)_2$ and the second one to the pecipitation of CuS. For the determination of these compounds, the second one can be used. The titration curves of thioacetamide and sodium sulphide (in 1 M NaOH) obtained by using Cu^{2+}– liquid and solid membrane electrodes are given Figs. 3 – 4. The results obtained by these titrations were statistically compared and values were given in Table 1 and 2. As it seen Table 1 and 2, the difference between standard deviations and mean values are not statistically significant.

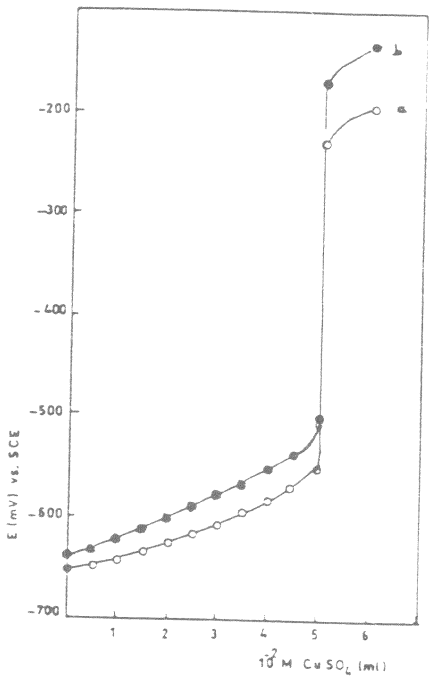

Fig. – 1: Potentiometric titration curves of 10^{-3} M thioacetamide in 1 M sodium hydroxide with 10^{-2} M $CuSO_4$.
(a) Cu^{2+}–selective liquid membrane electrode.
(b) Cu^{2+}–selective solid membrane electrode.

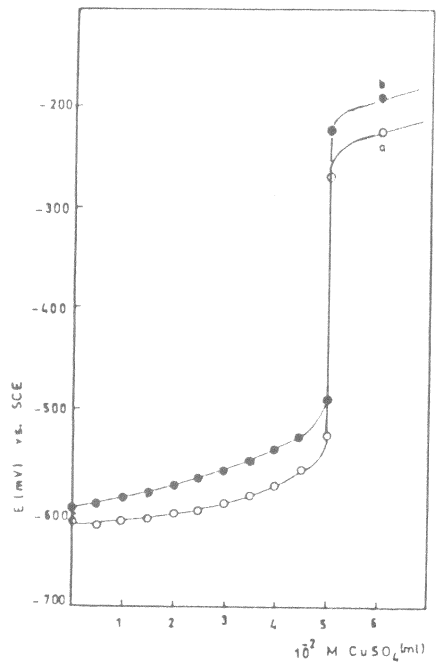

Fig. – 2 : Potentiometric titration curves of 10^{-3} M sodium sulphide in 1 M sodium hydroxide with 10^{-2} M $CuSO_4$.
(a) Cu^{2+}–selective liquid membrane electrode.
(b) Cu^{2+} – selective solid membrane electrode.

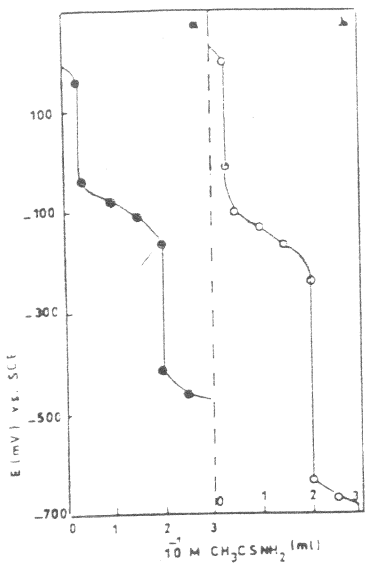

Fig. – 3 : Potentiometric titration curves of 10^{-2} M $CuSO_4$ with 10^{-1} M thioacetamide (in 1 M NaOH).
(a) Cu^{2+}–selective liquid membrane electrode.
(b) Cu^{2+}–selective solid membrane electrode.

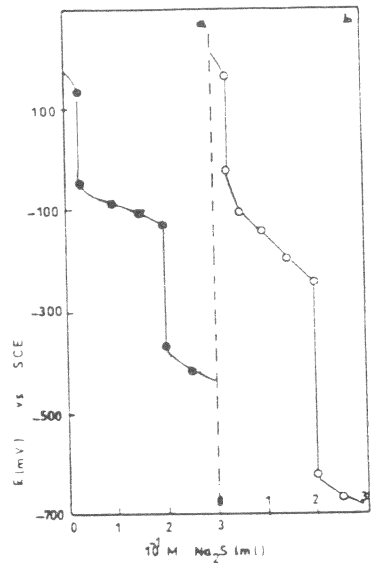

Fig. – 4 : Potentiometric titration curves of 10^{-2} M $CuSO_4$ with 10^{-1} M Na_2S (in 1 M NaOH).
(a) Cu^{2+}–selective liquid membrane electrode.
(b) Cu^{2+} –selective solid membrane electrode.

Table – 1 : Potentiometric determination of sodium sulphide and thioacetamide with the Cu^{2+} –selective membrane electrodes.

Titrated compound (mg)	Satistical value	x	y
Na_2S	N	5	5
	$\overline{X}$	38.87	38.64
	S	0.316	0.522
	$Sx100/\overline{X}$	0.812	1.350
CH_3CSNH_2	N	5	5
	$\overline{X}$	37.36	37.38
	S	0.409	0.288
	$Sx100/\overline{X}$	1.094	0.770

x = Cu^{2+} – selevtive liquid membrane electrode ; y = Cu^{2+} – selective solid membrane electrode ; N = Number of determinations; X = Mean value ; S = Standart deviation ; $Sx100/\overline{X}$ = Relative standart deviation.

Table – 2 : Statistical comparision of Cu^{2+} –liquid and solid membrane electrodes by using t– and –F tests.

Compound	$t_{x,y}$ (cal.)	$t_5^{0.05}$: 2.77	$F_{x,y}$ (cal.)	$F_5^{0.05}$: 6.39
Na_2S	0.756		2.751	
CH_3CSNH_2	0.080		2.036	

x : Cu^{2+} – selective liquid membrane electrode.

y : Cu^{2+} – selective solid membrane electrode (Orion 94 – 29 type).

REFERENCES

1. Tong–Ming Hsen and Rechnitz, R.A. : *Anal. Chem.*, **40,** 1054, (1968).
2. Light, T.S. and Swartz, J.L. : *Anal. Lett.*, **1,** 825, (1968).
3. Brand, M.J. and Rechnitz, G.A. : *Anal. Chem.*, **42,** 478, (1970).
4. Papay, M.K., Toth, K., Izvekov and E. Pungor : *Anal. Chim. Acta,* **64,** 409, (1973).
5. Baiulescu, G.E. and Cosofret, V.V. : *Rev. Chim. (Bucharest),* **27,** 158, (1976).
6. Cosofret, V.V. : *Ibid.*, **27,** 240, (1976).
7. Cosofret, V.V. : *Ibid.*, **25,** 836, (1974).
8. Růžička, J., Tjell, J.C. : *Anal. Chim. Acta,* **51,** 1, (1970).
9. Burdin, M.M.A., Mesplede, J., Porthault, M. : *C.R. Acad. Sc., Paris,* t 276, Serie C–65, (1973).
10. Kocaoba, S. : Master Thesis, Yıldız University, Faculty of Science and Lit., Chem. Dept., İstanbul (1991).
11. Baiulescu, G.E., Kandemir, G.K., Ionescu, M.S., Cristescu, C. : *Talanta,* **32,** 295, (1985).

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