CROATICA CHEMICA ACTA CCACAA 59 (2) 451—462 (1986)

YU ISSN 0011-1643
CCA-1658 UDC 541.257.2
Original Scientific Paper

Investigation of Selectivity of a Sulfide Ion-selective Electrode

Dinko Tuhtar

Institute for fire and explosion protection, Romanijska 10, 71000 Sarajevo, Yugoslavia

Received December 21, 1984

The behaviour of a sulfide ion-selective electrode in the presence of numerous foreign anions was studied by the mixed solution method. The results revealed that in the Nernstian portion of the calibration curve the sulfide ion-selective electrode exhibited a remarkable selectivity, since out of the 32 anions examined only the cyanide ion interfered. However, at $pS > 7.2$ the electrode followed a super-Nernstian response which was, moreover, irregular and irreproducible. This severely limits its use for sulfide determination even in pure sulfide solutions. For all practical purposes the lower limit of sulfide determination by either direct potentiometry or by titration in deaerated and nitrogen-purged solutions appears to be cca 2.0 μg/L.

INTRODUCTION

Sulfide ion is not usually present in appreciable concentration in water owing to the relatively high oxygen content of running water. However, in still water, in the bottom layers, sulfide may be found as a result of the decomposition of organic matter and the bacterial reduction of sulfate.[1] Its higher levels are a good indicator of water pollution from industrial and urban wastewaters.[2] Toxicity of hydrogen sulfide is well known and the maximum allowable limit in most countries is set at about 0.002 mg/L.

Standard methods of water analysis[1] call for the iodometric or methylene blue procedure as a method for quantitative sulfide determination, with sample preparation to remove interfering substances, or to concentrate the sulfide. With the availability of the silver sulfide ion-selective electrode the determination of sulfide and sulfur compounds has been performed[3–10] in a variety of samples. However, some features of the electrode method make routine sulfide ion determination, especially in low concentration range, still a laborious procedure. Thus, the Nernstian response of the electrode varies with its history and time of use,[11] and poor potential reproducibility and a tendency to supersensitivity are generally observed at pS 5—7.[12–14]

$$pS = -\log([S^{2-}]/\text{mol L}^{-1}) = 5 \ldots 7$$

The sulfide ion-selective electrode is therefore, more frequently used for direct potentiometry.[15]

In any analytical work with ion-selective electrodes it is important to have some information on the electrode selectivity. A quantitative measure of interference by foreign ions is provided by the potentiometric selectivity coefficient, $k_{1,2}^{\mathrm{pot}}$, for the measured ion 1, and an interfering ion 2. $k_{1,2}^{\mathrm{pot}}$ is defined by Eq. (1):[16]

$$E = const. + \frac{2.303\ RT}{z_1F} \log (c_1 + k_{1,2}^{\mathrm{pot}}\ (c_2)^{z_1/z_2} + \ldots) \qquad (1)$$

where E is the experimentally measured potential of a cell (in volts), R the gas constant (8.31441 J K^{-1} mol^{-1}), T the thermodynamic temperature, F the Faraday constant (9.648670×10^4 C mol^{-1}), c_1 and c_2 are the concentrations of the measured and interfering ions, z_1 and z_2 the charge numbers of ions 1 and 2, respectively, and the *const.* a term that includes the standard potential of the indicator electrode, E_1°, the reference electrode potential, $E_{\mathrm{ref.}}$, and the liquid junction potential, E_{j}.

Values of $k_{1,2}^{\mathrm{pot}} = 1$ indicate that interfering and measured ions contribute equally to the electrode potential. In such a case it is imposible to speak about a selective electrode. This does not necessarily mean that such electrodes are analytically useless. For example, the determination of water hardness with liquid ion-exchange electrodes is based exactly on this principle, as such electrodes are equally sensitive to most divalent cations in water which make up water hardness. On the other hand, small values of $k_{1,2}^{\mathrm{pot}}$ mean a high specificity to the measured ion , as compared with the interfering ion. Thus, a value of, say, 10^{-4} indicates that the measured ion is detected 10000 times more sensitively than the interfering ion. In practice, the majority of ion-selective electrodes have been found to have potentiometric selectivity coefficients below 1, mostly in the range 10^{-3} to 10^{-6}, and a few measure interfering ions better than the measured one (*i. e.* have $k_{1,2}^{\mathrm{pot}} > 1$).

Selectivity coefficients for most of the commercially available ion-selective electrodes have been determined in the presence of common ions only.[17] Results of these determinations are unfortunately of little practical use as they were performed by different methods of measurement and calculation. Hence, more uniform work in determining and calculating selectivity coefficients data has been called for in many electrode systems.[18] Moreover, the variability of selectivity coefficients with respect to important experimental parameters, such as temperature and the rate of solution stirring, has also been suspected.[19]

The theory of operation of the sulfide ion-selective electrode,[20] as well as accumulated experimental evidence, reveal it to be among the most selective of all the solid-state ion-selective electrodes. Thus, Hseu and Rechnitz[21], Light and Swartz[22] and Bock and Puff[23] found no interference from a large excess of a number of anions. More recently, Radić and Mark[24] examined the effects of eight different anions on the potential response of a »home-made« silver/silver sulfide selective micro-electrode and found no measurable interference. However, in all these experiments the sulfide concentration used was substantially higher than naturally occurring sulfide levels in surface water.

The only seriously interfering anion is the cyanide.[10,25,26] However, there are few data on the behaviour of the sulfide ion-selective electrode in the presence of ions other than the most common ones, and almost none at the very low sulfide concentration levels. In a previous paper,[18] the behaviour of a cyanide ion-selective electrode was examined in the presence of a number of anions. It was shown that the most useful information was extracted from the determination of selectivity coefficients if they were determined following the IUPAC recommendations.[26] In this paper, the behaviour of a sulfide ion-selective electrode in the presence of 32 anions has been studied with a view of determining $k_{S,X}^{pot}$ (X — a foreign anion) where appropriate.

EXPERIMENTAL

Instrumental

Potential differences between the sulfide ion-selective electrode (Orion, model 94-16) and a doble-junction Ag/AgCl reference electrode (Orion, model 90-02, with Orio filling solution in the inner and outer chambers) were measured with an Orion pH/mV digital meter (model 701A). For stirring of the solution a magnetic stirrer, with a piece of styrofoam over it, was used. All measurements were performed at room temperature (293—296 K). During the measurements N_2 gas was bubbled to deaerate the solution.

Chemical

All solutions were prepared from analytical grade reagents of various manufacturers and the boiled deaerated distilled water. The sulfide anti-oxidant buffer (SAOB), containing 2 M NaOH, 0.2 M ascorbic acid and 0.2 M disodium EDTA, was made weekly according to the electrode instruction manual.[27] The sulfide stock solution was prepared by dissolving cca 0.38 g $Na_2S \cdot 9H_2O$ in 500 mL 25% SAOB solution. The exact concentration was determined by titrating 50 mL of the stock solution with 0.01 M Cd^{2+} using the sulfide ion-selective electrode as indicator. Diluted sulfide standards were prepared daily by serial dilution of the stock solution and making up to the mark with 25% SAOB solution. The 0.01 M metal ion (Cd^{2+}, or Pb^{2+}) titrant stock solution was made by dissolving appropriate amounts of metal nitrate or chloride in deionized deaerated water and making up to the mark in a 1 L flask.

Procedure

Interference experiments were carried out by the method of mixed solution.[18,26] The plots *E vs.* pX^{n-} were used as a criterion for interference effects. In an alternative method (28) the foreign anion concentration was kept constant, while that of the sulfide ion varied, resulting in curves *E vs. pS*. On the addition of the buffer the ionic strength of different samples is nearly equal. The activity coefficients can then be incorporated into the E° term of Nernst's equation, thus enabling the substitution of activities by concentration. Hence, pX^{n-} and pS here denote negative concentrations of the foreign and sulfide ions, respectively.

RESULTS AND DISCUSSION

Standardization of Sulfide Solution

Large crystals of $Na_2S \cdot 9H_2O$ were selected and washed with deionized water before weighing. The weighed amounts (0.38 g/500 mL) were intended to give approximately 100 ppm S^{2-} stock solution. The stock solution was standardized by potentiometric titration with 0.01 M metal ion with the sulfide ion-selective electrode as indicator. The obtained concentration was usually much lower than 100 ppm (40—60 ppm), depending on the extent of washing large crystals. Of the metals tried Cd^{2+} gave more stable potential readings, even in the vicinity of the equivalence point, whereas experimental points on titration with Pb^{2+} were poorly reproducible and required longer times for stabilization (Figure 1).

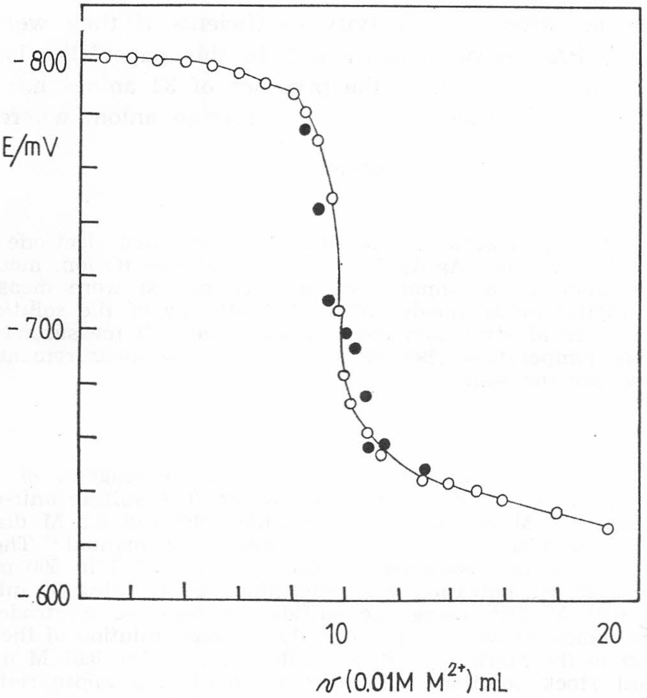

Figure 1. Standardization of sulfide stock solution with 0.010 M M^{2+} (○ Cd^{2+}, ● Pb^{2+}).

Weekly controls of solution concentration gave no appreciable changes in sulfide concentration. Nevertheless, a stock solution was not used more than a week after its preparation.

Interference Effects

An ideally selective ion electrode immersed in a solution of an ion to which it responds would exhibit a constant potential irrespective of the concentration range of foreign ion, X, present in the same solution. In other words, plots *E vs. pX* would give a line parallel to the concentration axis. In this work such plots were constructed from experiments in which the sulfide ion concentration was kept constant ($C(S^{2-}) = 6.2 \times 10^{-7}$; M = 0.02 ppm) while the foreign anion concentration varied from 10^{-7} to 10^{-1} M. An example of this type of plot is given for determination of the sulfide electrode potential in the presence of CrO_4^{2-} ion (Figure 2, $pCrO_4^{2-}$ is negative logarithm of chromate concentration).

The same plots were obtained in the presence of ClO_4^-, ClO_3^-, SCN^-, F^-, PO_4^{3-}, CH_3COO^-, NO_2^-, CO_3^{2-}, BrO_3^-, SO_4^{2-}, Cl^-, Br^-, I^-, $C_6H_5O_7^{3-}$, $C_8H_{11}N_2O_3^-$, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, WO_4^{2-}, N_3^-, $C_4H_4O_6^{2-}$ and SO_3^{2-} indicating an impressive selectivity of the sulfide ion-selective electrode at the sulfide concentration level studied.

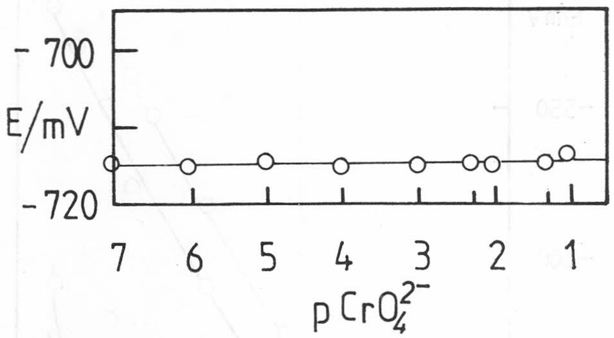

Figure 2. *E vs. pX*$^{n-}$ plot for CrO_4^{2-} ion.

Should an ion exhibit a genuine electrode interference, *i. e.* participate in the electrode reaction, the plots *E vs pX* would curve to potentials corresponding to higher primary ion concentrations (in the case of the sulfide ion-selective electrode towards the more negative potentials). Of the 32 anions examined only the cyanide ion showed such interference, the extent of which depended upon the sulfide concentration (Figure 3).

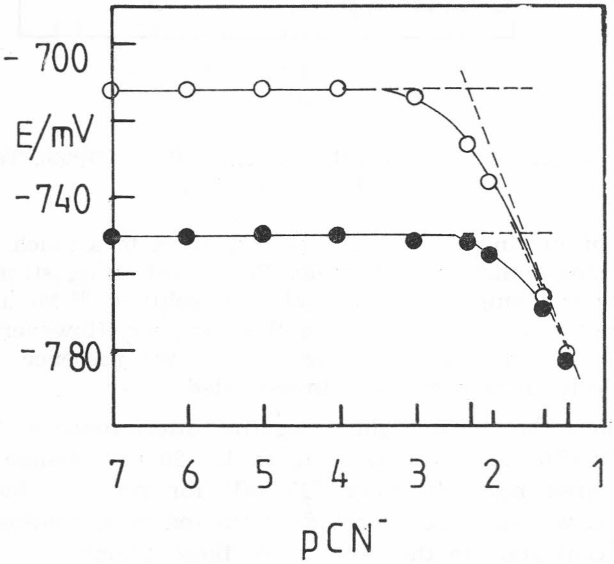

Figure 3. *E vs. pX*$^{n-}$ plot for CN^- ion (○ $C_{S^{2-}}$ = 6.26 × 10^{-7} M, ● $C_{S^{2-}}$ = 9.9 × 10^{-6} M).

On the other hand, the curving of *E vs pX* plots towards potentials corresponding to lower primary ion concentrations would indicate chemical, rather than electrode interference. Such interferences arise due to a gradual disappearance of the primary ion by processes such as oxidation, reduction, precipitation, complexation *etc.*[29] In the presence of TeO_3^{2-}, IO_3^-, IO_4^-, $Fe(CN)_5NO^{2-}$ and $Cr_2O_7^{2-}$ all the measured electrode potentials were less negative with the rising concentration of these anions (Figure 4).

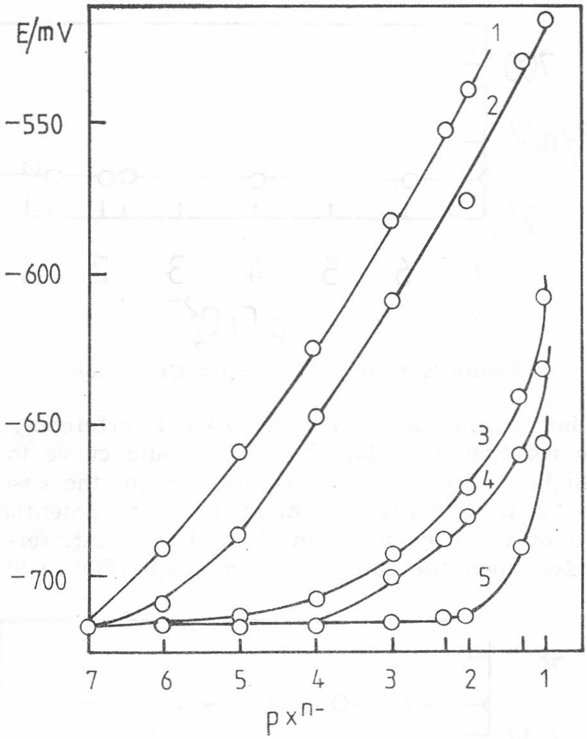

Figure 4. E *vs.* pX^{n-} plots for IO_4^-(1), IO_3^-(2), $[Fe(CN)_5NO]^{2-}$(3), TeO_3^{2-}(4) and $Cr_2O_7^{2-}$(5).

The point of curving of, say IO^-_3, corresponded to a much lower concentration of this anion than, for example, TeO_3^{2-}, reflecting stronger oxidative ability of the former anion in strongly alkaline solutions.[30] Metal ions forming insoluble sulfides would also come into this category. However, since sulfide ion in water cannot normally exist as such in the presence of most metal ions, these interferences were not investigated.

A few anions showed a slightly negative interference at the most concentrated levels (0.01 M), corresponding to 10—20 mV change in respect to the first measured point (E = cca 715 mV for $pX = 7$), indicating some sulfide reduction which, however, could be ignored in evaluating the apparent sulfide ion concentration in the presence of these anions.

The IUPAC recommendations[26] and practice[10,18] call for the electrode selectivity determination by the mixed solution methods, as opposed to the separate solution method. In the mixed solution method foreign ion activity is kept constant, while that of the measured ion is varied over a wide range, covering both the Nernstian and curved portions of the calibration curve E *vs.* pS. To ascertain the detection limit of the sulfide ion-selective electrode calibration experiments were run covering the sulfide ion concentration from $pS = 8.8$ to $pS = 4$. The resulting plot is shown in Figure 5.

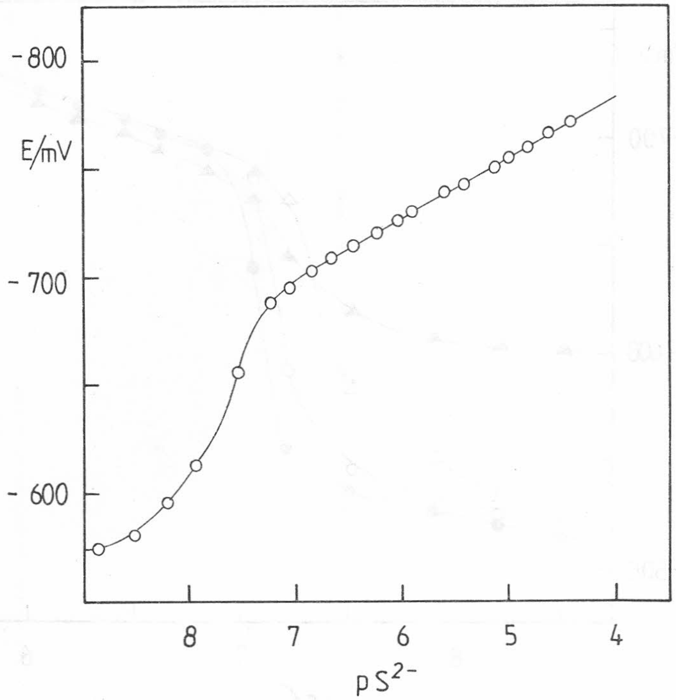

Figure 5. Calibration plot E vs. pS^{2-}.

While the Nernstian portion of the calibration curve (from $pS = 7.2$ downwards) remained constant and fairly reproducible over a length of time, the super-Nernstian portion was poorly reproducible since it was changing from day to day. The electrode responded rapidly (cca 5 min) once in the region of Nernstian response, while longer response times (up to 20 min) were measured in the super-Nernstian region. A family of calibration curves in the region $pS = 8.5$ to $pS = 6.0$ is shown in Figure 6.

Of course, such deviations from the Nernstian behaviour of the electrode do not enable the application of the IUPAC method for selectivtiy coefficient evaluation. Furthermore, certain anions which showed no effect on the basis of E vs. pX^{n-} plots often showed strong interference in the region of the super-Nernstian response, in comparison with the calibration curve for the pure sulfide solution recorded on the same day. Examples of plots for SO_4^{2-}, $Fe(CN)_6^{4-}$, Cl^-, $C_8H_{11}N_2O_3^-$, PO_4^{3-} and $C_6H_5O_7^{3-}$ are given in Figure 7.

Attempts to reproduce these plots failed, even if the runs were repeated one just after another. Moreover, after some experiments even the limit of the Nernstian response changed toward the larger sulfide concentration, although in the majority of experiments it stayed around $pS = 7.2$. Electrode performance was restored by polishing the surface with an abrasive strip. Standard electrode potential ($E = 730 \ldots 735$ mV), calculated according to Crombie *et al.*[13], remained fairly constant over the course of this study.

Midgley[31] interpreted non-ideal calibrations of ion-selective electrodes as arising from several causes, such as the presence of the determinand in

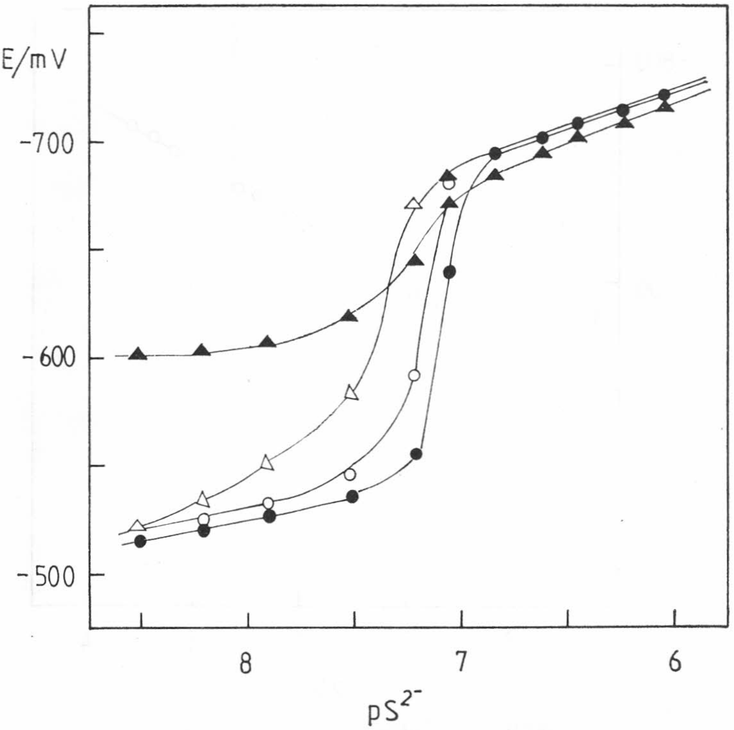

Figure 6. Calibration plots E *vs.* pS^{2-} recorded on different days in June 1983 (▲) 6 June, (△) 23 June, (●) 27 June, (○) 29 June.

reagents added to a sample solution, the presence of interfering species and the solubility of the electrode membrane, provided that the electrode is operating reversibly and conforms to a particular mechanism. It appears that none of the above causes can completely explain the deviations in the potential of the sulfide ion-selective electrode in low concentration range, as the electrode in this range in most cases does not operate reversibly.

Such super-sensitivity of the sulfide ion-selective electrode was noted earlier.[10] Explanations for these deviations were offered ranging from the deviation of Ag_2S membrane crystal from stoichiometry,[11] the solubility of the membrane material[12] to the effects of preparation procedures[11,32] and problems of easy sulfide oxidation in alkaline solutions[13]. Gulens and Ikeda[14] examined effects of membrane surface heterogenity on the sensitivity of the sulfide ion electrode. The super-Nernstian response observed at low sulfide concentration was attributed to the measurement of mixed potentials arising as the result of several factors, such as the porosity of electrode surface, kinetics of surface reactions, localized corrosion reactions and the influence of redox reactions.

However, the most important factor, deduced from scanning electron microscopy of the electrode surface, turned out to be the appearance of metal silver and films of Ag_2S or Ag_2O at the membrane surface. This accounted for the difference in the limit of Nernstian response for various sulfide ion-

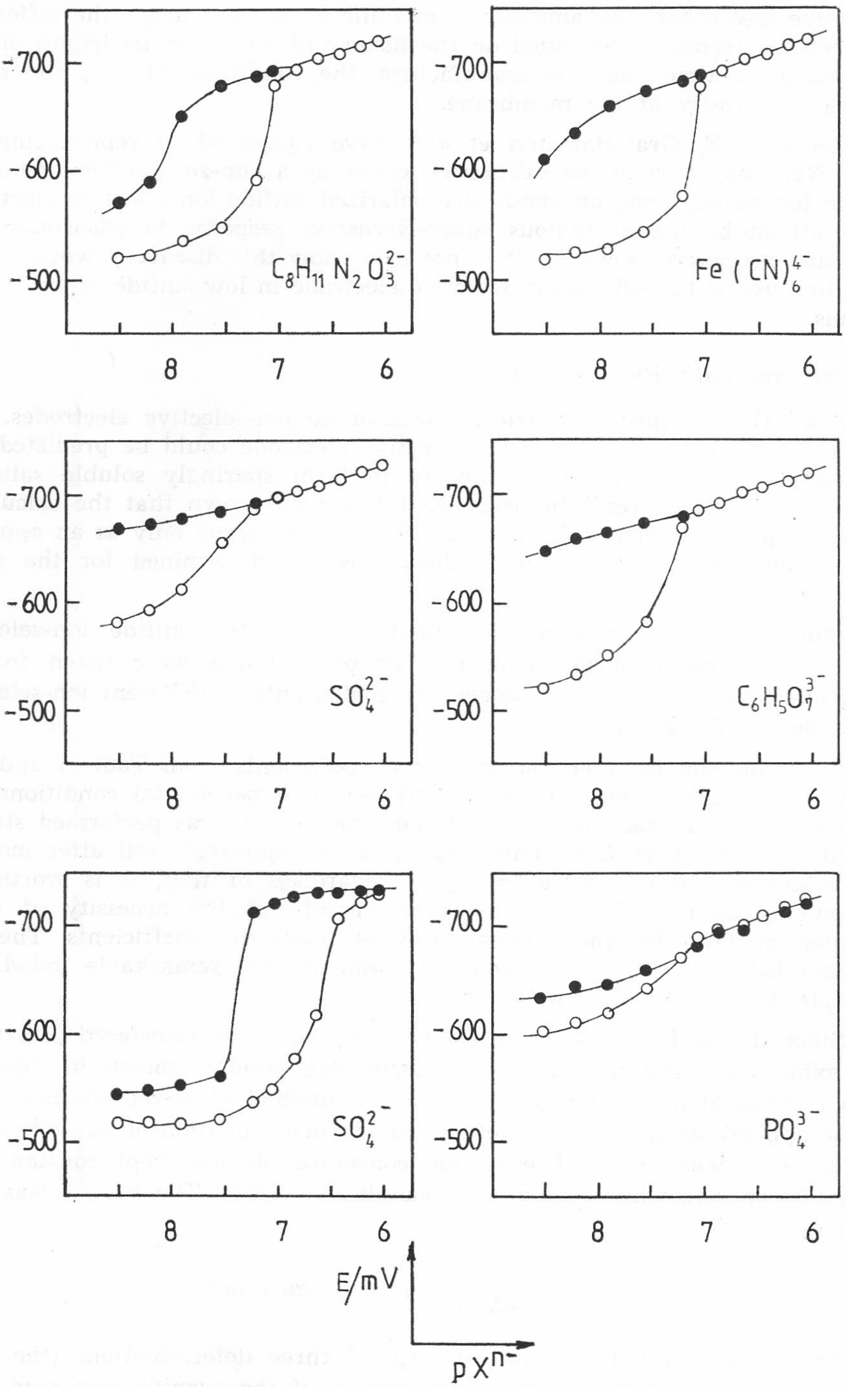

Figure 7. *E vs.* pX^{n-} plots (●) for $C_8H_{11}N_2O_3^{2-}$ ($C = 0.01$ M), $Fe(CN)_6^{4-}$ ($C = 10^{-5}$ M), SO_4^{2-} ($C = 0.05$ M), PO_4^{3-} ($C = 0.005$ M) and again SO_4^{2-} ($C = 0.005$ M) in the super--Nernstian region of the calibration curve *E vs.* pS^{2-} (○).

-selective electrodes. The amounts of metallic silver, and hence the difference in electrode response, depended on the history of electrode, its length of use, the length of time since its manufacture, the conditions of use, and differences in porosity of the membrane.

Recently, E. Graf-Harsanyi *et al.*[33] have succeeded in reproducing the super-Nernstian part of the calibration curve by a non-zero current potentiometric technique, using an anodically polarized sulfide ion-selective electrode. They attributed the anomalous super-Nernstian response to adsorption and oxidation processes. However, it is not clear how this discovery would affect a routine use of the sulfide ion-selective electrode in low sulfide concentration regions.

Comparison with Published Data

Similarly to other homogeneous membrane ion-selective electrodes, ions that interfere with the sulfide ion-selective electrode could be predicted and calculated on the basis of the ability to form sparingly soluble salts, or undissociated complexes.[10] In practice, it has been shown that the calculated values of potentiometric selectivity coefficients can serve only as an approximation, and that more reliable values must be determined for the given conditions.[10,18]

Published data on selectivity coefficients of the sulfide ion-selective electrode are collected in Table I. Most of the data were taken from a comprehensive compilation of selectivity coefficients of different ion-selective electrodes by Pungor *et al.*[17]

A comparison between the published coefficients from Table I and this work is not possible due to vast differences in experimental conditions and electrode types. In fact, none of the published works was performed strictly according to the IUPAC recommendation which appeared well after most of the values in Table I were reported. Regardless of that, it is worthy to inspect the data in Table I since they point out the necessity of using aceepted methods for the determination of selectivity coefficients. The differences between k^{pot} or one and the same ion are remarkable inded. For example, $k_{\text{S,Cl}}{}^{\text{pot}}$ varies from 10^{-3} to 3×10^{-31}.

Since it was found in this work that only CN^- ion interfered (Figure 3). *i. e.* exhibited a genuine electrode interference (anions, shown in Figure 4 caused chemical interference), and since the method of mixed solution could not be applied, an alternative method for the determination of $k_{\text{S,CN}}{}^{\text{pot}}$, shown in Figure 3, was used.[28] The sulfide concentration was kept constant (see Figure 3 caption), while that of the cyanide ion varied. The $k_{\text{S,CN}}{}^{\text{pot}}$ was then calculated as:[15]

$$k^{\text{pot}}_{\text{S,CN}} = \frac{C_{\text{S}^{2-}}}{(C_{\text{CN}^-})^2} = (3.20 \pm 0.60) \times 10^{-2}$$

The calculated value is the average of three determinations (the third one is not shown in Figure 3). Concentration of the cyanide was read from the intercept of the two straight lines of the graph $E = f(pCN^-)$ in Figure 3.

The calculated value obtained in this way is close to that reported by Clears[34] (the method of determination and experimental conditions unavailable to the author of this work).

CONCLUSION

Sulfide ion-selective electrode exhibits an exceptionally high selectivity in the Nernstian portion of the calibration curve E *vs* pS, *e. g.* at $pS \leq 7.2$. Of the 32 anions examined only the cyanide showed an electrode interference. A few anions caused chemical interference, resulting in the lowering of sulfide concentration, *i. e.* increasing measured potentials. At $pS > 7.2$ the electrode exhibits a super-Nernstian response. In this concentration range the electrode is not selective any more since the reproducibility of potential measurements is poor, even for pure sulfide solutions. Therefore, any measurement of sulfide concentration by direct potentiometry, or by titration, in this concentration range, is of very limited use.

Acknowledgment. — The author thanks R. Furtula for carrying out some of the potentiometric measurements, and the Republic Hydrometeorologycal Institute, Sarajevo for making these investigations possible.

This work was supported by the Self-Management Council for Scientific Research of SR Bosnia and Herzegovina under Contract No. 0412-3259-1/80.

REFERENCES

1. *Standard Methods for the Examination of Water and Wastewater,* 15 ed., American Public Health Association, Washington, D. C., 1980, p. 442.
2. R. E. Train: *Quality Criteria for Water,* Castle House Publications, London, 1979, p. 213.
3. D. Weiss, *Chem. Listy* **68** (1974) 528.
4. E. Mor, V. Scotto, G. Marcenaro, and G. Albiso, *Anal. Chim. Acta* **75** (1975) 159.
5. E. W. Baumann, *Anal. Chem.* **46** (1974) 1345.
6. B. L. Wilson, R. R. Schwarzer, C. O. Chukunye, and J. Cyrous, *Microchim. J.* **26** (1971) 402.
7. G. P. Morie, *Tobacco* **173** (1971) 34.
8. E. J. Green and D. Schnitker, *Marine Chem.* **2** (1974) 111.
9. *ORION Guide to Ion Analysis,* Orion Research Inc., Cambridge, Mass., 1983, p. 41.
10. J. Vesely, D. Weiss, and K. Štulik, *Analysis with Ion-Selective Electrodes,* Ellis Horwood, Chichester, Sussex, England, 1978, p. 157.
11. J. Vesely, O. J. Jansen, and B. Nicolaisen, *Anal. Chim. Acta* **62** (1972) 1.
12. W. E. Morf, G. Kahr, and W. Simon, *Anal. Chem.* **46** (1974) 1538.
13. D. J. Crombie, G. J. Moody, and J. D. R. Thomas, *Anal. Chim. Acta* **80** (1975) 1.
14. J. Gulens and B. Ikeda, *Anal. Chem.* **50** (1978) 782.
15. Nj. Radić and M. Milušić, *Anal. Letters* **13** (1980) 1013.
16. G. F. Fricke, *Anal. Chem.* **52** (1980) 259R.
17. E. Pungor, K. Toth, and A. Hrabeczy-Pal, *Pure Appl. Chem.* **51** (1979) 1915.
18. D. Tuhtar, *Anal. Chem.* **55** (1983) 2205.
19. A. Hulanicki and A. Lewenstan, *Talanta* **29** (1982) 671.
20. K. Cammann, *Working with Ion-Selective Electrodes,* Springer-Verlag, Berlin, 1979, pp. 61—65.
21. T. M. Hseu and G. A. Rechnitz, *Anal. Chem.* **40** (1968) 1054.
22. T. S. Light and J. L. Swartz, *Anal. Lett.* **1** (1968) 825.
23. R. Bock and H. J. Puff, *Z. Anal. Chem.* **240** (1968) 381.
24. Nj. Radić and H. B. Mark, Jr., *Croat. Chem. Acta* **58** (1985) 179.

25. J. Koryta and K. Štulik, *Ion-Selective Electrodes,* 2nd ed., Cambridge University Press, Cambridge, 1983, p. 137.
26. IUPAC Analytical Chemistry Division, *Pure Appl. Chem.* **48** (1976) 129.
27. *Instruction Manual, Sulfide Ion Electrode, Silver Ion Electrode, Model 94—16,* Orion Research Inc., Cambridge, Mass., 1977.
28. G. J. Moody and J. D. R. Thomas, *Selective Ion-Sensitive Electrodes,* Merrow, Watford, 1971, p. 16.
29. D. Midgley and K. Torrance, *Potentiometric Water Analysis,* J. Wiley & Sons, Chichester, 1979.
30. Ju Lurie, *Handbook of Analytical Chemistry,* Mir Publishers, Moscow, 1978, p. 306.
31. D. Midgley, *Anal. Chem.* **49** (1977) 1211.
32. M. Mascini and A. Liberti, *Anal. Chim. Acta* **51** (1970) 231.
33. E. Graf-Harsanyi, K. Toth, and E. Pungor, *10th Scientific Session on Environmental Analysis,* Sombathely, Hungary, 3—5 Oct., 1983.
34. J. T. Clerc, G. Kahr, E. Pretsch, R. P. Scholer, and H. R. Wuhrmann, *Chimia* **26** (1972) 287.

SAŽETAK

Selektivnost sulfidne ion-selektivne elektrode

D. Tuhtar

Motrilo se ponašanje sulfidne ion-selektivne elektrode u nazočnosti brojnih stranih iona. U Nernstovu području kalibracijske krivulje elektroda je vrlo selektivna (od 32 iskušana aniona jedini se cijanidni ion pokazao smetnjom). No, pri nižim koncentracijama sulfida ($pS > 7{,}2$), gdje odziv elektrode biva veći od teorijskoga, javljaju se nepredvidive fluktuacije koje onemogućuju rad čak i u čistim otopinama. Utvrđeno je da, za sve praktičke svrhe, donja odrediva granica koncentracije sulfidnih iona leži blizu 2 µg/L, bez obzira na to provodi li se određivanje izravnim potenciometrijskim mjerenjem ili pak titracijom.