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# Construction and Evaluation of a Solid-State Iodide Selective Electrode

*A chemical instrumentation laboratory experiment*

The ion-selective electrodes (ISE) have been a subject of major interest during the recent years within all the areas of chemical research. In spite of the fast increasing numbers of research articles, reviews, and monographs dealing with the development and applications of the ISE, less attention has been given on the teaching of this topic. Brief chapters on the theory of various types of ISE have appeared in some modern textbooks of analytical chemistry and chemical instrumentation. Compared with other branches of chemical instrumentation, articles describing student laboratory experiments on the construction and applications of several types of ISE are very limited (1–7). Survey articles published recently show that it is important for the students of chemistry and related sciences to participate in ISE laboratory experiments (8) because of their increasing use for analysis, process and control measurements (9).

The present article describes a laboratory experiment, designed for our chemical instrumentation course, to introduce the students to the methodology of the fabrication and evaluation of an ISE. The experiment is based on the construction of a crystalline homogeneous membrane electrode (solid-state type) employing an AgI/Ag<sub>2</sub>S coprecipitate pellet-sensing membrane. For the preparation of the electroactive material by simultaneous precipitation of silver iodide and silver sulfide, two different procedures can be applied using sodium sulfide (10) or thioacetamide (11, 12) as precipitating agents. The sensing membranes, prepared by pressing in a KBr-die, are sealed into the end of a prefabricated electrode body. The assembled electrode in combination with the appropriate external reference electrode shows Nernstian response to iodide ions. The electrode response curve which covers more than three decades of iodide concentration range, is obtained by a modified "liter beaker technique" (13), under a background of constant ionic strength. The graphically determined electrode slope is compared to the theoretical  $2.303 RT \times 10^3 / Z_A F$  mV/decade (59.16 mV/decade for the monovalent ions at 25°C) according to the Nernst equation (14):

$$E = \text{constant} \pm \frac{2.303 RT}{z_A F} \log a_A \quad (1)$$

The electrode selectivity to other ions, such as bromide ions, is also studied and the potentiometric selectivity coefficient  $k_{A,B}^{\text{pot}}$  as defined by the modified Nernst equation (14):

$$E = \text{constant} \pm \frac{2.303 RT}{z_A F} \log [a_A + k_{A,B}^{\text{pot}} (a_B) z_A / z_B] \quad (2)$$

is determined. A fixed interference method (mixed solution method) (15) is utilized for the estimation of  $k_{A,B}^{\text{pot}}$ , based on emf measurements in a solution of constant level of interfering ion, by a series of additions of known amounts of the primary ion. The plot of the measured emf values versus  $-\log C_A$ , allows the calculation of the  $k_{A,B}^{\text{pot}}$ , using the equation (14):

$$k_{A,B}^{\text{pot}} = \frac{a_A}{(a_B)^{z_A/z_B}} \quad (3)$$

where  $a_B$  is the constant background activity of the interfering ion B and  $a_A$  the primary ion activity, which corresponds to

the point where the difference in potential between the curve and the extrapolation of the Nernstian response line is 18 mV (15).

The experimental value of  $k_{A,B}^{\text{pot}}$  is compared to the theoretically predicted from the solubility products of the AgA and AgB using the relation (15, 16)

$$k_{A,B}^{\text{pot}} = \frac{K_{\text{sp}}(\text{AgA})}{K_{\text{sp}}(\text{AgB})} \quad (4)$$

## Experimental

### Chemicals

All chemical reagents utilized in this experiment are of analytical grade without further purification.

### Equipment

The emf measurements of the constructed electrode in combination with a double junction reference electrode (Orion, model 90-02-00), can be made by an analog or digital pH/mV meter with relative accuracy of  $\pm 0.1$  mV (e.g., Corning, model 12, or Orion, model 801 or 701). An evacuated KBr-type pellet die (13 mm diameter) together with a hydraulic bench press is needed for the preparation of the pellet-sensing membrane. This attachment usually accompanies every IR instrument available in laboratories. The following equipments and materials are also required: electric rotary vacuum pump, magnetic stirrer, continuously adjustable microliter pipets (recommended ranges of 5–50  $\mu\text{l}$  and 50–250  $\mu\text{l}$ ), volumetric transfer pipets (1, 2, 5, 10 and 100 ml capacity) and various pieces of plastic tubing, rubber tubing, BNC connectors, silver wire etc., as described below.

### Preparation of Membrane Material

The membrane material is prepared by coprecipitation of silver iodide and silver sulfide in a 1:1 molar ratio. An amount of 19.9 g of KI is dissolved in 100 ml of a solution of 1 M Na<sub>2</sub>S and then 100 ml of 3 M AgNO<sub>3</sub> solution is added slowly under vigorous stirring into the Na<sub>2</sub>S-KI mixture (10). An alternate procedure can also be used for the coprecipitate preparation, which assures a homogeneous precipitation (11, 12). In a 500-ml beaker containing 100 ml of 1 M CH<sub>3</sub>CSNH<sub>2</sub> and 100 ml of 1 M KI, drops of 5 M NaOH solution are added to adjust the pH to between 8–9. The beaker is placed in a boiling water bath, and 80 ml of 3 M AgNO<sub>3</sub> solution are added slowly with stirring. The stirring is continued for 10–15 min after the addition of AgNO<sub>3</sub>. The mixture of AgI/Ag<sub>2</sub>S coprecipitate obtained from both preparations is then treated the same way. First, it is washed thoroughly by decantation with hot water 5–6 times, then filtered, washed twice with acetone, and dried overnight at 105°C. The dried coprecipitate is pulverized in a mortar and kept dry in a dessicator.

To save time, the AgI/Ag<sub>2</sub>S coprecipitate should be prepared in advance for the students. Electrodes made with membranes prepared from both coprecipitate preparations show almost the same behavior, except those from thioacetamide preparation, which exhibit slightly slower response in low concentrations.

### Preparation of the Pellet-Sensing Membrane

An amount (0.7–1 g) of AgI/Ag<sub>2</sub>S coprecipitate is transferred into the KBr-die and is evacuated for 4–5 min by the rotary vacuum pump. The material is then pressed under the vacuum for 10–15 min, applying a pressure of 8–9 tons/cm<sup>2</sup>. The pellet is removed carefully from the die and is inspected to insure that it is free from cracks and pits. The above mentioned amount of coprecipitate gives pellets of about 1 mm thick. If the laboratory section time permits, the students can convince themselves that pellets having small cracks and pits, when used for the electrode construction, show a poorer performance.

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### Assembly of the Electrode Body

The electrode body is constructed using easily available materials and consists of three main parts, which can be assembled very easily by the students. These parts, shown in Figure 1, are (1) A male BNC connector (type UG-88/U) (with a 6–8 cm long silver wire soldered on it to be used as internal reference electrode (17), which is mounted at the one end of (2) a 10-cm long piece of stiff polypropylene (PP) tubing (10 mm O.D.) and is held in place by (3) a piece of rubber tubing. A 2–3-mm diameter side hole must be opened on the PP tubing, close to the BNC connector, to serve for the electrode filling with the internal electrolyte. Tubes of 3 cm long are cut from 1/2-in. Bel-Art polypropylene tubing connectors of T or Y form, which are used for the mounting of the membrane. All these parts should be available and prefabricated in advance for the students.

The prepared pellet-sensing membrane is sealed on the polished end of the 3 cm long polypropylene tube using an appropriate amount of Araldite® Rapid epoxy resin glue. The tube with the sealed pellet is laid aside for 15–20 min to allow the glue to harden. The tube is adapted firmly by slow and gentle rotation at the free end of the 10-cm long polypropylene tubing. The assembled electrode is finally filled through the side hole with the  $10^{-3}M$   $AgNO_3$  internal reference solution (17). Before their use the newly constructed electrodes must be checked for leaks. A coaxial cable from a useless glass electrode attached to a female BNC connector can be used for the electrode connection to the pH/mV meter.

### The Electrode Response Curve

Into a 250-ml beaker are pipetted 100.0 ml of deionized water and then 2.0 ml of 5 M ionic strength  $NaNO_3$  adjuster (18) are added. After the immersion of the electrode pair, the solution is stirred at a proper steady rate to avoid splashing and bubbling. Then, known amounts of 0.1000 M KI standard solution are added, and the emf measurements are taken when a steady state potential is established after each addition. The additions of KI solution are made, so that the iodide should cover a range of concentrations from  $5 \times 10^{-6}$  to  $5 \times 10^{-3}M$ . The electrode response curve is constructed by plotting the measured emf values versus  $-\log C_{I^-}$  ( $C_{I^-}$  = iodide concentration) on a graph paper. The final iodide concentration  $C_{I^-}$  in the solution after each addition, can be calculated by the equation

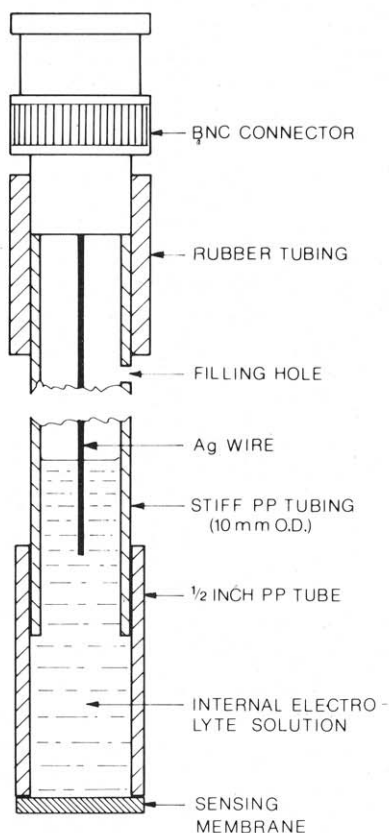


Figure 1. Schematic diagram showing the constructed iodide ISE and the assembled parts.

Table 1. Typical Student Measurements with an Assembled Iodide ISE for the Preparation of the Response Curve <sup>a</sup>

Addition of 0.1 M KI (ml)	Total Volume of KI additions (ml)	Iodide concentration $C_{I^-}(M)$	$-\log C_{I^-}$	E (mV)
0.005	0.005	$4.9 \times 10^{-6}$	5.31	-108.2
0.005	0.010	$9.8 \times 10^{-6}$	5.01	-125.9
0.010	0.020	$2.0 \times 10^{-5}$	4.70	-144.8
0.030	0.050	$4.9 \times 10^{-5}$	4.31	-168.8
0.050	0.100	$9.8 \times 10^{-5}$	4.01	-188.1
0.100	0.200	$1.96 \times 10^{-4}$	3.71	-206.4
0.300	0.500	$4.88 \times 10^{-4}$	3.31	-231.2
0.500	1.00	$9.71 \times 10^{-4}$	3.01	-249.7
1.00	2.00	$1.92 \times 10^{-3}$	2.72	-266.7
5.00	7.00	$6.42 \times 10^{-3}$	2.19	-298.9

<sup>a</sup> Slope:  $-61.4$  mV/decade, Correl. Coeff.: 0.9997.

Table 2. Typical Student Measurements with an Assembled Iodide ISE for the Estimation of the  $k_{I,Br}^{pot}$

Additions of 0.1 M KI (ml)	Total volume of KI additions (ml)	Iodide concentration, $C_{I^-}(M)$	$-\log C_{I^-}$	E, (mV)
0.005	0.005	$4.8 \times 10^{-6}$	5.32	-163.2
0.005	0.010	$9.5 \times 10^{-6}$	5.02	-164.8
0.005	0.015	$1.4 \times 10^{-5}$	4.84	-167.7
0.005	0.020	$1.9 \times 10^{-5}$	4.72	-170.4
0.030	0.050	$4.8 \times 10^{-5}$	4.32	-179.1
0.050	0.100	$9.5 \times 10^{-5}$	4.02	-194.8
0.100	0.200	$1.90 \times 10^{-4}$	3.72	-210.1
0.300	0.500	$4.74 \times 10^{-4}$	3.32	-233.4
0.500	1.00	$9.43 \times 10^{-4}$	3.02	-249.0
1.00	2.00	$1.87 \times 10^{-3}$	2.73	-266.2
5.00	7.00	$4.54 \times 10^{-3}$	2.34	-295.7

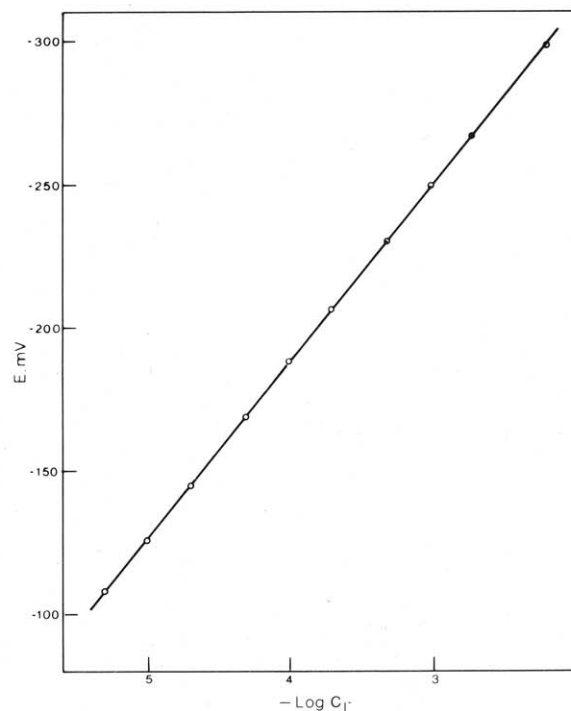


Figure 2. Student response curve for an assembled iodide ISE.

$$C_{I^-} = \frac{0.1000 \left( \frac{\text{mmol}}{\text{ml}} \right) \times V_T(\text{ml})}{100.0(\text{ml}) + V_T(\text{ml})} \quad (5)$$

where  $V_T$  is the total volume (ml) of 0.1 M KI solution added.

Typical student data obtained by this procedure are shown in Table 1 and Figure 2. The slope of the linear part of the curve on Figure 2, which is a measure for the Nernstian behavior of the constructed electrode, is calculated graphically from the plot or by a simple least-squares routine.

### The Estimation of the $k_{I,Br}^{pot}$

Into a 250-ml beaker containing 100.0 ml of deionized water are added 5.0 ml of 2 M KBr solution. The resulting 0.095 M bromide concentration provides the required constant background level of interfering ion and serves also as an ionic strength adjuster. After the immersion of the electrode pair and the adjustment of the stirring rate, additions of known amounts of 0.100 M KI standard solution are made. The final concentration  $C_{I^-}$  of the iodide after each addition, is calculated from eqn. (5). The measured emf values are plotted against the  $-\log C_{I^-}$  on a graph paper.

The calculation of the  $k_{I,Br}^{pot}$  is based on eqn. (3), but in the present experiment, the activities in the eqn. (3) can be replaced by the concentrations without significant error. This is true because for the applied experimental conditions all measurements are made under a constant background of ionic strength (18). Typical student data obtained by this procedure and the corresponding curve for the estimation of the  $k_{I,Br}^{pot}$  are shown in the Table 2 and Figure 3, respectively.

### Conclusion

The experiment should be performed by the students working in pairs or triads in a 3-hr laboratory section. It requires minimum input from the instructor if the students have already some previous experience with potentiometric measurements.

The proposed experiment has been tested successfully for six semesters during a chemical instrumentation course. The average value of the obtained response slopes from 12 electrodes, constructed by the students during a one-semester period, was  $-59.9 \pm 1.8$  mV, while the average of the  $k_{I,Br}^{pot}$  estimated values was  $(1.7 \pm 0.3) \times 10^{-3}$ . The response time of the constructed electrodes was less than 1 min, even in low concentrations of iodide ions. Slightly longer response times have been observed only during the  $k_{I,Br}^{pot}$  estimation procedure, because of the high bromide concentration present.

Additional experiments with the electrode described above, can be designed in order to expose the students to other problems concerning the ISE's use. Such experiments are (1) Study of the electrode response time. Our experience is that the electrode constructed above shows almost the same response time compared to ones commercially available. Conventional techniques can be used for the study of this characteristic (14, 15). Small variation on the quality of the prepared electrodes can be observed, depending on the technical skills of each individual student. (2) Effect of the sensing surface condition on the electrode performance. The students can improve the performance of the prepared electrodes in terms of sensitivity and response time, by polishing and treating the sensing surface with a fine diamond paste and silicone oil (19). Finally, the students in another laboratory section can use the electrode to learn other analytical techniques, to study interferences, to perform potentiometric titrations, and to carry out kinetic methods of analysis.

In conclusion, it should be pointed out that the construction and evaluation of an ISE in combination with extensive class

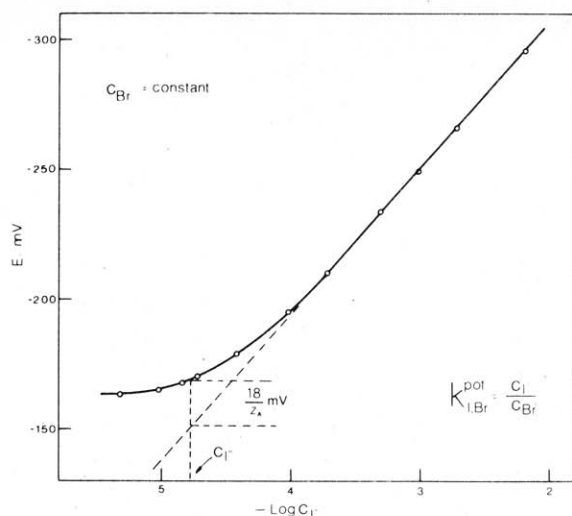


Figure 3. Typical curve obtained by the students for the  $k_{I,Br}^{pot}$  estimation.

lectures on the ISE topic helps the students significantly to understand the function and the abilities of these analytical devices and to feel more comfortable handling them.

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### Literature Cited

- (1) Covington, A. K. and Thain, J., *J. CHEM. EDUC.*, **49**, 554 (1972).
- (2) Lamb, R. E., Natusch, D. F. S., O'Reilly, J. E., and Watkins, N., *J. CHEM. EDUC.*, **50**, 432 (1973).
- (3) Craggs, A., Moody, G. J., and Thomas, J. D. R., *J. CHEM. EDUC.*, **51**, 541 (1974).
- (4) Wilcox, Jr., F., *J. CHEM. EDUC.*, **52**, 123 (1975).
- (5) Light, T. S. and Cappuccino, C. C., *J. CHEM. EDUC.*, **52**, 247 (1975).
- (6) Lloyd, B. N., O'Brien, F. L., and Wilson, W. D., *J. CHEM. EDUC.*, **53**, 328 (1976).
- (7) Fricke, G. H. and Kantz, M. J., *J. CHEM. EDUC.*, **54**, 517 (1977).
- (8) Pickral, G. M., *J. CHEM. EDUC.*, **53**, 182 (1976).
- (9) *Research and Development*, **2**, 26 (1977).
- (10) Czaban, J. D. and Rechnitz, G. A., *Anal. Chem.*, **45**, 471 (1973).
- (11) Hansen, E. H., Lamm, G. G. and Růžicka, J., *Anal. Chim. Acta*, **59**, 403 (1972).
- (12) Heijne, G. J. M., Van Der Linden, W. E., and Den Boef, G., *Anal. Chim. Acta*, **89**, 287 (1977).
- (13) Orion Research Inc., *Newsletter* **2**, 42 (1970).
- (14) IUPAC, "Compendium of Analytical Nomenclature," Pergamon Press, Oxford, 1978, Chap. 21.
- (15) Bailey, P. L., "Analysis with Ion-Selective Electrodes," Heyden and Son, London, 1976.
- (16) Morf, W. E., Kahr, G., and Simon, W., *Anal. Chem.*, **46**, 1538 (1974).
- (17) Mascini, M. and Liberti, A., *Anal. Chim. Acta*, **51**, 231 (1970).
- (18) Camman, K., "Working with Ion-Selective Electrodes," Springer-Verlag, New York, 1979.
- (19) Johansson, G. and Edström, K., *Talanta*, **19**, 1623 (1972).