

## Home Made Ion-selective Electrodes for Education

Raja Ram Pradhananga<sup>1\*</sup>, Lok Kumar Shrestha<sup>1,2</sup>

<sup>1</sup> Central Department of Chemistry, Tribhuvan University, Kirtipur Kathmandu, Nepal.  
Tel: 977-1-4-332034, e-mail: rajaramp@enet.com.np

<sup>2</sup> Graduate School of Environment and Information Sciences, Yokohama National University,  
Tokiwadai 79-7, Hodogaya-ku, Yokohama 240-8501, Japan.

All solid-state ion-selective electrodes (ISEs) based on silver sulphide pressed pellets were fabricated. The electrode was found to be sensitive and selective to  $\text{Ag}^+$  and  $\text{S}^-$  ions, and followed the Nernstian behavior in the concentration of  $1 \times 10^{-1}$  to  $1 \times 10^{-5} \text{M}$  with slope of 31.5 mV and 57.5 mV per decade change in  $\text{S}^-$  and  $\text{Ag}^+$  ion concentrations, respectively. The electrode was used to determine the solubility products of  $\text{Ag}_2\text{CrO}_4$ ,  $\text{AgBrO}_3$ , and  $\text{AgSO}_4$  and the amount of  $\text{H}_2\text{S}$  in the cigarette smoke. The average amount of  $\text{H}_2\text{S}$  per stick of a cigarette was found in the range of 0.0332 to 0.0766 mg. The iodide, bromide, and chloride selective electrodes were also fabricated by incorporating appropriate amount of  $\text{AgI}$ ,  $\text{AgBr}$ , and  $\text{AgCl}$  in silver sulphide. The potentiometric selectivity coefficients of the iodide for bromide ( $K_{\text{I}^-/\text{Br}^-}^{\text{pot}}$ ) and chloride ions ( $K_{\text{I}^-/\text{Cl}^-}^{\text{pot}}$ ) were found to be  $1 \times 10^{-2}$  and  $5 \times 10^{-3}$ , respectively. The  $\text{LaF}_3$  single crystal electrode was used to determine the fluoride ion in fluorinated toothpaste and tea samples. The sensitivity and reliability of these home made ISEs were comparable to the commercial electrodes. Therefore, we believe that the thus prepared electrodes will play a pivoted role in teaching of analysis with ion-selective electrode.

Key words: Ion-selective electrodes, silver sulphide, fluoride, Iodide, hydrogen sulphide

### 1. INTRODUCTION

In the recent years, there has been increasing interest in providing laboratory teaching experiments based on the principle and application of ion-selective electrodes (ISEs). This interest is natural because the ISEs are widely used in industry, pharmaceutical, environmental analysis and fundamental research. Therefore, chemistry graduates should have a clear concept on the principles and techniques of using ISEs. Haber and Kleimenswiz<sup>1</sup> fabricated the first ISE of practical importance from glass membrane in 1909 for the determination of activity of hydrogen ion in aqueous solutions. Glass is an amorphous solid containing complex form of silicates and various ions. By suitable alteration of compositions of glass, the glass membrane electrode selective to monovalent cations like  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ag}^+$  and other ions have been fabricated<sup>ii</sup>. The glass electrode responds only to monovalent cations. The ISEs that would respond to anions and divalent cations need to be fabricated using materials other than glass. In this regard, Frant and Ross<sup>iii</sup> in 1966 presented a europium doped lanthanum fluoride single crystal ISE, which is selective to the fluoride and lanthanum ions. With the advent of  $\text{LaF}_3$  ISE, measurement of activities of fluoride ion in potable waters and other samples becomes as simple as the measurement of hydrogen ion activity with the glass electrode. After the establishment of Orion Research Inc., ISEs for different cations and anions became commercially available and the analysis with ISE progressed very rapidly. Though, many ISEs are commercially available, they are too expensive for

education institutes of underdeveloped countries like Nepal who cannot afford procuring commercial ISEs for the teaching purpose from the meager resources at their disposal. In an effort to make chemistry more interesting and relevant to graduate students and to cope with increasing interest in analysis with the ISEs, we in our laboratory, fabricated inorganic precipitate-based ISEs using simple materials that are available in chemistry laboratory. We have also carried out a number of experiments using these home made ISEs with a purpose of demonstrating using principle and techniques of ISEs. The basic strategy of this study is to present a simple technique of fabrication of all solid-state silver sulphide-based ISEs and present a series of experiments designed to illustrate the principle and techniques of the ISEs for analysis of practical importance.

### 2. EXPERIMENTAL

#### 2.1 Preparation of $\text{Ag}_2\text{S}$ Membrane Electrode

Passing hydrogen sulphide gas to  $\text{AgNO}_3$  solution till complete precipitation precipitated the  $\text{Ag}_2\text{S}$ . The precipitate was washed thoroughly with hot water, acetone and finally dried at  $110^\circ\text{C}$  for about 6 hrs. The precipitate was pulverized in an agate mortar. About 1g of the precipitate was transferred into KBr-die and evacuated for 5 min and pressed under vacuum for 15 min by applying pressure of  $10 \text{ tons/cm}^2$ . The pellet was removed carefully from the die and silver paste was applied on one side. The pellet was then mounted in a polypropylene tube with the help of Araldite (Ciega-gigy) and back contact was made with a silver

disk in which copper wire is soldered. After the Araldite was completely dried, the electrode was polished on an emery paper and finally in a bottom cloth to a mirror finished.

## 2.2 Preparation of I<sup>-</sup>, Br<sup>-</sup>, and Cl<sup>-</sup> Ion-Selective Membrane Electrodes

Solution of equimolar quantities of Na<sub>2</sub>S and KX were taken in a clean and dry beaker and silver nitrate solution was added to it with vigorous shaking. The co-precipitate thus formed was filtered and Ag<sub>2</sub>S/AgX pellet was prepared, the details on the method of preparation is described elsewhere<sup>iv</sup>.

## 2.3 Determination of Solubility Product

An appropriate amount of sparingly soluble silver salts (AgBrO<sub>3</sub>, Ag<sub>2</sub>CrO<sub>4</sub>, and Ag<sub>2</sub>SO<sub>4</sub>) was taken in a clean and dry 250mL stopper bottle containing pure distilled water or distilled water with known amount of anions in the form of potassium salt and equilibrated for 2-3 hours in a mechanical shaker. The resulting solution was filtered through a Whatman number 40 filter paper. The first 10mL filtrate was rejected and rest was collected in a dry glass vessel. To 100mL of the saturated solution, 2mL of 5M sodium nitrate solution was added as ISAB (Ionic Strength Adjustment Buffer) and the laboratory-made Ag<sub>2</sub>S-ISE was immersed into it and EMF of the cell was determined by coupling it with a saturated calomel electrode at room temperature. The concentration of silver ions was determined from the standard calibration curve and the solubility product (K<sub>sp</sub>) was calculated. The K<sub>sp</sub> is the products of equilibrium concentration of dissociated ions in solution.

The solubility products of these salts are also determined by measuring conductivity of their saturated solution using Systronics digital conductivity meter (Model 304, India) coupled with Systronics conductivity cell (Model CD-10, India).

## 2.4 Determination of H<sub>2</sub>S in Cigarette Smoke

In an artificial cigarette smoker, 50mL of 0.1M NaOH was taken in the gas-washing bottle. A cigarette was attached to the inlet and outlet was connected to a suction pump operated by water supply from a tap. The water supply to the suction pump was turned on and the cigarette was lit. The cigarette smoke bubbles through the NaOH solution. The water flow of the tap was manually adjusted so that it takes about 6-7 minutes to completely puff off the cigarette. The smoke resulting solution contains H<sub>2</sub>S, whose concentration was determined by using Ag<sub>2</sub>S-ISE by standard addition method. Altogether 9 brands of Nepalese cigarette were analyzed to determine the H<sub>2</sub>S content on complete combustion of the cigarette. The details are given elsewhere<sup>v</sup>.

## 2.5 Potentiometric Titration and Determination of Selectivity Coefficients

The Ag<sub>2</sub>S-ISE was used as an indicator electrode for the titration of 50mL of 7.4x10<sup>-3</sup>M Na<sub>2</sub>S with 0.1M AgNO<sub>3</sub>.

The potentiometric selectivity coefficients  $K_{\Gamma\text{Br}^-}^{\text{pot}}$  and

$K_{\Gamma\text{Cl}^-}^{\text{pot}}$  were determined by mixed solution method.

## 2.6 Determination of Fluoride in Toothpaste

Different brands of toothpaste samples were purchased from the local market of Kathmandu valley. About 0.4g of the sample was weighed into a 100mL beaker and 25mL of 1M HClO<sub>4</sub> was added to it. After complete digestion of the sample, the suspension was diluted to 50mL with water. The Orion Fluoride-ISE was immersed in the suspension, coupled with the reference electrode and EMF of the cell was measured using Orion ion meter.

## 2.7 Determination of Fluoride in Tea

Different brands of tea samples (both CTC tea and leaf tea) were purchased from the local market of Kathmandu valley. About 1g of tea sample was weighed into a 100mL beaker and 25mL of 1M HClO<sub>4</sub> was added to it, stirred well and left for 30 min. The mixture was diluted to 50mL with water, stirred, decanted and the clean tea infusion was used for the measurement.

## 2.8 Determination of Fluoride in Water

Different water samples (Ground, Tap, Rain, and Mineral water) were collected randomly from different parts of Kathmandu valley. 50mL of water sample prepared in 0.5M HClO<sub>4</sub> was taken in a 100mL beaker and the fluoride content was determined using the Fluoride-ISE.

## 3. RESULTS AND DISCUSSION

### 3.1 Determination of Solubility Product

The home made silver ISE is characterized by measuring the EMF of the cell as a function of silver ion concentration and the plot of EMF of the cell vs. Ag<sup>+</sup> is shown in Fig. 1. The equilibrium potential is attained with a minute. The plot is linear from silver ion concentration 10<sup>-1</sup> to 10<sup>-6</sup>M, with slope 57.5mV per decade change in silver ion concentration at 25°C, which is in agreement with the previous work<sup>v</sup>.

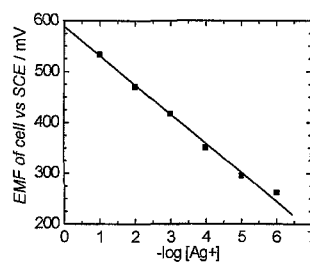


Fig. 1: Cell EMF as a function of  $-\log [\text{Ag}^+]$

The solubility products of Ag<sub>2</sub>CrO<sub>4</sub>, AgBrO<sub>3</sub>, and Ag<sub>2</sub>SO<sub>4</sub> were determined by determining the equilibrium [Ag<sup>+</sup>] in their saturated solutions using Ag-ISE. The results obtained at 25°C are presented in Table 1.

Table 1: Solubility products of different sparingly soluble silver salts

Salts	K <sub>sp</sub> /ISE	K <sub>sp</sub> /conductimetry	K <sub>sp</sub> /literature
AgBrO <sub>3</sub>	6.00±0.23×10 <sup>-5</sup>	8.04×10 <sup>-5</sup>	5.77×10 <sup>-5</sup>
AgCrO <sub>4</sub>	1.67±0.69×10 <sup>-12</sup>	1.50×10 <sup>-12</sup>	1.2×10 <sup>-12</sup>
Ag <sub>2</sub> SO <sub>4</sub>	6.43±1.49×10 <sup>-6</sup>	2.45×10 <sup>-5</sup>	1.4×10 <sup>-5</sup>

As can be seen from the Table 1, the solubility products determined by home made ISE is comparable to the values determined by the conductivity or other methods. Thus, it can be said that the home-made ISE can be used

as an analytical tool for the determination of silver ion concentration in different samples.

### 3.2 Determination of H<sub>2</sub>S in Cigarette Smoke

More than 3000 constituents have been identified in tobacco<sup>vi</sup>. Hydrogen sulphide is one of the toxic components present in cigarette smoke. The amount of H<sub>2</sub>S in cigarette is so low that the sulphide content cannot be determined by direct potentiometry or potentiometric titration method. Therefore, standard addition method with modified Gran's plot, which is shown in Fig. 2, is utilized to determine the H<sub>2</sub>S in the cigarette smoke<sup>vii</sup>.

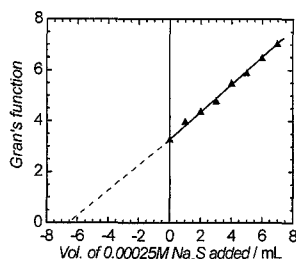


Fig. 2: Modified Gran's plot for the determination of H<sub>2</sub>S in cigarette smoke.

One stick of cigarette on complete combustion produces on an average 0.03 to 0.07mg of H<sub>2</sub>S, which is equal to 1 to 2 cc of H<sub>2</sub>S at ambient temperature and pressure. The amount of H<sub>2</sub>S gas produced by complete combustion of 1 stick of Nepalese cigarette lies in the same level of other international brands.

### 3.3 Direct Potentiometry Study

Response of Ag<sub>2</sub>S-AgI ISE to I<sup>-</sup>: The plot of EMF of cell with Ag<sub>2</sub>S-AgI membrane as an indicator electrode as a function of iodide-concentration is presented in Fig. 3.

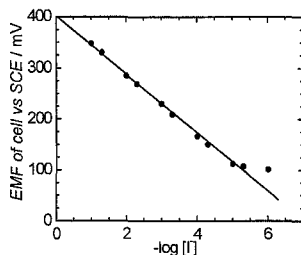


Fig. 3: Cell EMF as a function of  $-\log [I^-]$

The points are the experimental values and the line is the line of best fit computed from regression analysis.

The EMF of the cell follows the following equation

$$E = -0.3980 - 0.057 \log [I^-] \quad (1)$$

The electrode shows linearity in the  $E$  vs.  $-\log [I^-]$  plot from  $10^{-1}$  to  $5 \times 10^{-6}$  M. The slope is found to be 57.0 mV and intercept 398.0 mV with coefficient of determinant 0.9798. The observed standard electrode potential (-398 mV) is more negative than the theoretical standard electrode potential (-150 mV) of the second kind. This is because the standard electrode potential of all solid state ISEs with apparently the same sensitive material, can differ significantly from the electrodes of second kind, because of the electronic conductor-salt interfacial potential. In all experiments, the potential drifts were relatively small, which did not affect the calibration curve.

It was found that when Ag<sub>2</sub>S-AgI membrane soaked for a long time (24 hrs) in  $10^{-2}$  M KI solution, the electrode lost its Nernstian behavior, but showed satisfactory potential response after the membrane was repolished. The exposed surface of the Ag<sub>2</sub>S-AgI membrane slightly tanned. This may be due to leaching of AgI via the formation of soluble iodide complex  $K[AgI_2]$ . The experimental slope of -57 mV per decade change in ion concentration is slightly less than the theoretical value; however, it agrees with the values cited in literature 53 mV to 59 mV.

### 3.4 Potentiometric Titration

The applicability of Ag<sub>2</sub>S-AgI electrode is tested as an indicator electrode for the potentiometric titration of Na<sub>2</sub>S and KI separately with 0.1 M AgNO<sub>3</sub>. A typical potentiometric curve obtained from the titration of 50 mL of Na<sub>2</sub>S with the 0.1 M AgNO<sub>3</sub> is shown in Fig. 4. At the equivalent point, there was a large EMF change of about 484 mV, which corresponds to 99% of sulphide ion titrated and coincides with the theoretical equivalent point.

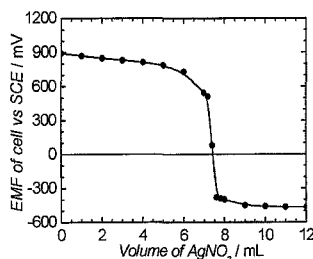


Fig. 4: Titration of 50 mL of  $7.4 \times 10^{-3}$  M Na<sub>2</sub>S with 0.1 M AgNO<sub>3</sub>

### 3.5 Selectivity Coefficient Determination

In case where an electrode is responding to more than one ion where an electrode can be described by semi-empirical equation given by Nikolsky-Eisemann.

$$E = E^0 \pm \frac{RT}{n_A F} \ln(a_A + \sum K_{A,B}^{pot} (a_B)^{n_A/n_B}) \quad (2)$$

Where  $a_A$  and  $a_B$  are the activities of main and the interfering ions having charges  $n_A$  and  $n_B$ , respectively.

$E^0$  is the standard electrode potential and  $K_{A,B}^{pot}$  is the selectivity coefficient, which describes the relative sensitivity to the interfering ion in comparison to the main ion. In the present study, a mixed solution method is used to determine the selectivity of Ag<sub>2</sub>S-AgI electrode containing iodide ion as the main ion and bromide and chloride ions as interfering ions. Following the standard method, the selectivity coefficient is found to be  $K_{I,Br}^{pot} = 1 \times 10^{-2}$  and  $K_{I,Cl}^{pot} = 5 \times 10^{-3}$ . These results show that response of laboratory made electrode to iodide ion is not adversely affected by the presence of bromide and chloride ions. This is well explained by the solubility product of AgI, which is much less than that of the AgBr and AgCl.

### 3.6 Fluoride in Toothpaste

Fluoride in 7 different brands of toothpaste is determined using 0.5 M HClO<sub>4</sub> as TISAB. The electrode system during the measurement is, Ag/AgCl(s)/Cl<sup>-</sup>(0.1 M), F<sup>-</sup>(0.1 M)/LaF<sub>3</sub> crystal/test

solution/KCl(satd.), Hg<sub>2</sub>Cl<sub>2</sub>/Hg. The results obtained for triplicate analysis are shown in Table 2. The table shows that the amount of fluoride in toothpaste differs depending on their brands. Each brand should contain 1000 ppm of available fluoride as specified in the packet of the toothpaste. However, in some of the toothpastes, much less amount of fluoride is observed, which is in our opinion cannot be due to the experimental errors. The low values may be due to the loss of fluoride during the storage. An appreciable amount of fluoride may be lost from the toothpaste with the period of time. Furthermore, different brands have used different abrasive materials and other constituents. In fact, the rate and extent of loss is reported to be dependent on abrasive materials and other constituents of the toothpaste.

Table 2: Fluoride content in different brands of toothpaste.

Sample	Mean fluoride (ppm)	SD	RSD
TP1	919	±23	±2.5
TP2	652	±8	±1.5
TP3	764	±21	±2.7
TP4	765	±22	±2.9
TP5	381	±2	±0.5
TP6	941	±10	±1.0
TP7	577	±21	±3.6

The values obtained for all the brands are reproducible with the relative standard deviation of ±5%. This strongly supports the precision of the obtained data and reliability of method of analysis.

### 3.7 Fluoride in Tea

The general method of fluoride determination in tea sample are to boil certain amount of tea in water for 3-5 min and after cooling the amount of fluoride is determined in the tea infusion by adjusting fixed ionic strength and pH, which is achieved by the addition of required amount of TISAB (total ionic strength adjustment buffer). The validity and reliability of such method is checked by recovery test method. For this purpose, 100µg of the pure fluoride is added to the tea sample and analyses are made triplicate. The results of recovery test are shown in Table 3.

Table 3: Recovery test for fluoride in tea sample

Sample	Fluoride added (µg)	Fluoride found (µg)	%Recovery
1.	100	105	105
2.	100	102	102
3.	100	109	109

The percentage recovery is found to be 105.3±2.9. Therefore, the test strongly supports the reliability of the method. The amount of fluoride obtained for 7 different brands of CTC tea and 2 different brands of leaf tea samples is shown in Table 4. The values obtained are the results of triplicate analyses. The symbol '\*' is given to the leaf tea samples, while others are CTC tea.

Table 4: Fluoride content in different brands of tea

Sample	Mean fluoride	SD	RSD
Tea1	95	±3	±3.1%
Tea2	133	±2	±1.5%
Tea3	153	±3	±2.0%
Tea4	106	±2	±1.9%
Tea5	90	±1	±1.2%
Tea6	84	±2	±2.3%
Tea7	71	±1	±1.4%
*Tea8	<DL	...	...
*Tea9	56	±1	±1.8%

	(µg/gm)	(µg/gm)	
Tea1	95	±3	±3.1%
Tea2	133	±2	±1.5%
Tea3	153	±3	±2.0%
Tea4	106	±2	±1.9%
Tea5	90	±1	±1.2%
Tea6	84	±2	±2.3%
Tea7	71	±1	±1.4%
*Tea8	<DL	...	...
*Tea9	56	±1	±1.8%

The table shows that the amount of fluoride in tea samples depends on their brands; different brands have different fluoride content. It has found that the fluoride content in the tea depends on the nature of soil, water and geographical environment of plantation area, reason of collection of tealeaves, maturity of tealeaves, and other constituents. The samples presently investigated are originally produced in different places. Therefore, the different values obtained for different brands are not surprising. Previous studies have shown that the fluoride content in the tea can reach up to 445µg. The table 4 shows that the amount of fluoride found in different brands of tea available in the local market of Kathmandu valley varies from 56 to 153 µg/gm. The higher fluoride content in CTC tea compared to the leaf tea might be due to the geographical differences of their production. However, we cannot avoid the possibility of fluoride leaching in tea infusions, which increases with decrease in the size of the tea grains. The values obtained are reproducible within the relative standard deviation of ±5%.

### 4. CONCLUSION

The laboratory made Ag<sub>2</sub>S-AgI solid-state electrode is found to be comparable with the commercial electrodes and the analysis with the direct potentiometry is sufficiently precise and reproducible. Furthermore, the electrode excellently works as an indicator electrode in the potentiometric titrations. The quick response of the electrode suggests that continuous monitoring of the I<sup>-</sup>, S<sup>2-</sup>, and Ag<sup>+</sup> ion activities in aqueous solutions with the present electrode would be feasible.

Due to the extravagant cost of commercial ISE, it is rather difficult to provide commercial ISE to educational institutes of third world countries. The low cost and ease of fabrication of present home made ISEs gives an opportunity to learn the analysis with ISEs even by the students of underdeveloped countries, who cannot afford procuring high cost commercial ISE. The home made ISEs have been successfully used in the central department of chemistry, Tribhuvan University, Nepal, in their regular practical classes. This success has opened the possibility of introducing analysis with ISEs even to the students of higher secondary level. This will certainly have a positive impact on education on electro-analytical technique. However, the long term stability and applicability of electrodes containing more than one interfering ions needs further investigation.

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