Preliminary studies for investigating the feasibility of using three different compounds recently prepared in our lab to prepare sulphide – selective ionophores

# **Chemical structures**

2







#### 1- Complex compounds formation:

Compounds 1, 2 and 3 were dissolved in ethanol and allowing them to react with various cation solutions to check their ability to form stable complexes. All the three compounds formed complexes with cerium (IV) ions (Yellowish color) while compounds 1 and 3 only formed complexes with copper (II) ion (Blue color). Five complexes were separated.

Precipitates formed: Compound No.

(1) + Cu<sup>2+</sup> blue -----VII
(1) + Ce<sup>4+</sup> pale yellowish -----V
(2) + Ce<sup>4+</sup> yellow -----III
(3) + Ce<sup>4+</sup> pale yellowish-----IV
(3) + Cu<sup>2+</sup> blue -----II

#### **Coated graphite electrodes (CGE)**

A carbon rode of 5 mm diameter and 5 cm length was cleaned by washing with 0.1 M H Cl and ethyl alcohol then dried at 100°C, was dipped to 1 cm in the membrane solution for 2 s according to the IUPAC recommendation. The rode was picked up agains a fan to evaporate the THF leaving the PVC layer coating it. That operation was repeated for (12-17) time to have the proper layer thickness. The rode was fitted into a plastic body and connected to the pH/ion meter from the membrane free end using a copper wire. Let the CGE kept at room temperature for about overnight to complete dryness of the coated membrane. The electrode was finally conditioned for 24 h by soaking in  $1.0 \times 10^{-3}$ M Na<sub>2</sub>S solution.

#### **Potentiometric Measurements**

The electrode potentials were monitored with a PC-EMF16 interface data acquisition board (Lawson Labs, Inc) utilizing a multi-channel at room temperature in stirred solutions, in a galvanic cell of the type:

Ag/AgCl/3 M KCl / sample solution/ ISE-membrane/Graphite with a double-junction reference electrode (Type 6.0729.100, Methrom). The calibration and selectivity measurements were performed in a 100 ml glass beaker. Only the tip of the electrodes were immersed into the sample solution. 50 mL of phosphate buffer (10<sup>-3</sup>M) pH 7.2 was added to 100 mL beaker, and different concentrations of sulphide ions were added from 10<sup>-8</sup>M to 10<sup>-2</sup>M. A calibration curve was plotted logarithm of sulphide against the difference in potential obtained.

#### Calibration of CGE for sulphide anion

CGEs with each of the five complex compounds were prepared, their composition was 15 mg ionophore (4.76%) + 100 mg PVC + 200 mg DOP. The potentiometric response of the electrodes prepared using ionophores I-V toward various anions was measured using multi-channel station. Only reasonable responses have been obtained toward sulphide anion with ionophores (III) , (IV) and (V). Thus, calibration of CGEs prepared using the ionophores I-V was conducted only with different concentrations of sulphide ion.



Fig (1) Calibration of different CGEs using I - V ionophores and NPOE as a plasticizer for sulphide ion concentrations from  $1 \times 10^{-7}$  to  $1 \times 10^{-2}$  mol L<sup>-1</sup> in phosphate buffer pH 6.8.

ionophore	Slope	R <sup>2</sup>	Linear range	Lower D. L.
(I)	-14.4	0.9663	-	-
(II)	-18.9	0.9568	-	-
(III)	-29	0.9324	1 X10 <sup>-4</sup> - 1X10 <sup>-2</sup>	9 X 10 <sup>-5</sup>
(IV)	-29	0.9869	1 X10 <sup>-4</sup> - 1X10 <sup>-2</sup>	5 X 10 <sup>-5</sup>
(V)	-34.5	0.9994	1 X10 <sup>-5</sup> - 1X10 <sup>-2</sup>	7 X 10 <sup>-6</sup>

Table 1Potentiometric response of the different ionophores I-V to sulphide ion

Complex compound V was decided to be used as a promising sulphide ionophore as it offers the best potentiometric performance .

## **Effect of plasticizers:**

Several plasticizers including DOP ( $\varepsilon = 5.0$ ,  $\varepsilon$  is the dielectric constant), DBS ( $\varepsilon$  =4.50), DBP ( $\varepsilon$  =6.42) and o-NPOE ( $\varepsilon$  = 24) which are often used with coated graphite electrode, were evaluated and the results are included in the table (1). Dissolving 15 mg of Ce(IV)-228Y [ionophore(V)] in 200 mg of plasticizer , 100 mg PVC, and using THF as a solvent. Plot the recorded EMF using different concentrations of sulphide ions  $10^{-8} - 10^{-2}$  M in phosphate buffer ( $10^{-3}$ M) pH 7.2, log[S<sup>-2</sup>] CGE 15 mg ionophore (V) + 100 mg PVC + 200 mg plasticizer

Table 2 Effect of plasticizer on response of sulphide-selective electrode with ionophore V

	slope	R <sup>2</sup>	Linear range	LDL
NPOE	-32.93	0.9667	3X10-6-1X10-2	5X10-7
DBS	-40.30	0.9335	7X10-6-4X10-3	4X10-6
DOP	-37.50	0.9603	6X10 <sup>-6</sup> -1X10 <sup>-2</sup>	8X10 <sup>-7</sup>
DBP	-37.55	0.9336	6X10 <sup>-6</sup> -1X10 <sup>-2</sup>	2X10-6



Fig. 2 Effect of plasticizer on the response of CGEs containing ionophore (V) 4.76% in phosphate buffer pH 7.2 and.

Among the four different plasticizers used, NPOE resulted in a best Nernstian slope and linear working range for the electrode, as clearly seen from Figure (1). DBS plasticizer give super Nernistian response -40.3, while DBP and DOP give the same slope -37.5 but DOP has detection limit higher than DBP, and NPOE has best detection limit and slope than the other plasticizers.

### Effect of ionophore ratio

The calibration measurements were performed in a 100 ml glass beaker. Only the tips of the electrodes were immersed into the sample solution. 50 mL of phosphate buffer (10<sup>-3</sup>M) pH 7.2 was added to 100 mL beaker, and different concentrations of sulphide ions were added from  $10^{-8}$ M to  $10^{-2}$ M with continuous stirring, the potential was recorded after stabilization to  $\pm 0.5$  mV. A calibration curve was then constructed by plotting the recorded potential (EMF, mV) versus logarithm of sulphide (log[S<sup>-2</sup>]) The electrode were kept in  $1.0 \times 10^{-3}$ M Na<sub>2</sub>S solution before its first use and stored in  $1.0 \times 10^{-3}$ M Na<sub>2</sub>S solution. Membranes containing 5, 10, 12, 15, and 20 mg ionophore (V) (1.64%, 3.22%, 3.8%, 4.76%, and 6.25%) and 100 mg PVC + 200 mg NPOE were prepared and its response was evaluated using  $10^{-8}$  M to $10^{-2}$  M Na<sub>2</sub>S solution, using phosphate buffer ( $10^{-3}$ M) pH 7.2, CGE

Table 3 Effect of ionophore V ratio on of the calibration of sulphide – selective CGEs at different sulphide ion concentrations.

Ionophore ratio	Slope	R <sup>2</sup>	Linear range	L. D. L.
Blank	-12.99	0.7712		
1.64%	-25.58	0.8795	1X10 <sup>-5</sup> - 1X10 <sup>-2</sup>	8X10-6
3.22%	-29.15	0.9644	1X10 <sup>-5</sup> - 1X10 <sup>-2</sup>	4X10-6
3.84%	-30.05	0.9698	4X10 <sup>-6</sup> - 1X10 <sup>-2</sup>	8X10-7
4.76%	-32.93	0.9667	3X10 <sup>-6</sup> - 1X10 <sup>-2</sup>	5X10-7
6.25%	-35.08	0.9788	8X10 <sup>-7</sup> - 1X10 <sup>-2</sup>	1X10-7

The above table shows that, if the ratio of ionophore is increased the slope and lower detection limit are increased.



Fig. 3 Effect of ionophore ratio on response of sulphide ions using ionophore V by CGE in phosphate buffer pH 7.2.



Fig.4.Calibration graphs for CGE with membranes containing ionophore II, two different cationic additives (two concentrations each) and without neither ionophores nor additives.



Micro-cell

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Fig.5. FTIR spectrum of polyacrylic acid amide (PAA).