

# Analytical Methods

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Original Papers

**A durable solid contact sulphide sensor based on ceric acrylohydrazide ionophore attached to polyacrylamide with nanomolar detection limit**

Mohammad Nooredeen ABBAS, <sup>\*\*†</sup> Abdel-Latif A. RADWAN<sup>\*</sup> and Galal A. NAWWAR<sup>\*\*</sup>, N.

Zine<sup>\*\*\*</sup> and A. ERRACHID<sup>\*\*\*</sup>

*\*Analytical Lab., Dept. Appl. Org. Chem., National Research Centre, Dokki, Cairo,1231,1 Egypt*

*\*\* Dept. Green Chemistry., National Research Centre, Dokki, Cairo,12311, Egypt*

*\*\*\* Institut des Sciences Analytiques (ISA), Université de Lyon, Université de Claude Bernard Lyon 1, UMR*

*5280, 5 rue de la Doua, 69100 Villeurbanne, France*

---

<sup>†</sup> To whom correspondence should be addressed.

E-mail: [dr.nooreldin@yahoo.com](mailto:dr.nooreldin@yahoo.com)

1  
2  
3  
4 A durable sulphide selective solid-contact sensor based on newly synthesized ceric complex of [N'  
5  
6  
7 Acetyl-2-(benzothiazol-2yl)-3-(3-chloro-5-metyl-4H-pyrazol-4-yl) acrylo hydrazide] (ABPAH)  
8  
9  
10 covalently attached to polyacrylamide (PAA) as ionophore has been developed and potentiometrically  
11  
12  
13 evaluated. The all solid-contact sensor constructed by the application of a thin film of the selective  
14  
15  
16 membrane cocktail onto the surface of a gold electrode, which was pre-coated with conducting  
17  
18  
19 polymer poly (3, 4-ethylenedioxythiophene) (PEDOT) as an ion and electron transducer. The cocktail  
20  
21  
22 composed of poly (butyl methacrylate-co-dodecyl methacrylate) (PBDA) copolymer as a plasticizer-  
23  
24  
25 free matrix and the covalently attached acrylohydrazide ionophore. The sensor containing 12.5% of  
26  
27  
28 the Ce-ABPAH-PAA (ionophore II) showed a Nernstian slope of -29.42 mV/ conc. decade with linear  
29  
30  
31 range of  $1.0 \times 10^{-8}$  -  $1.0 \times 10^{-2}$  mol L<sup>-1</sup> and a detection limit of  $2.0 \times 10^{-9}$  mol L<sup>-1</sup> in sulphide anti-oxidant  
32  
33  
34 buffer (SAOB) solution of a pH value of 13.0. The fast response time of > 10 seconds proposed of the  
35  
36  
37  
38 proposed sulphide sensor allowed its utilization as a detector for the flow injection potentiometric  
39  
40  
41  
42 (FIP) determination of sulphide ions in various water samples.  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

## 1. Introduction

The toxicity of sulphide to different forms of life has been known for a quite long time, while the toxic nature of hydrogen sulphide ( $\text{H}_2\text{S}$ ) has claimed several lives, especially of those working in the sewerage systems. This species also causes serious corrosion of metals as well as concrete sewers because of its biological oxidation to  $\text{H}_2\text{SO}_4$ . Sulphide can be found naturally in well water and can build up in wastewater collection systems due to anaerobic conditions. It can contribute to odour problems in water treatment facilities. The increase in the concentration of this species in water is mainly attributed to the indiscriminate discharge of inadequately treated effluent from several industries into rivers and streams. Similarly, the decomposition of organic matter from industrial wastes, as well as, the bacterial reduction of sulfate results in the release of sulphide into waste water. One of the major users of sulphide is the leather industry, where bulk quantities of sodium sulphide ( $\text{Na}_2\text{S}$ ) used in dehairing hides <sup>1</sup>. The ever increasing concern over the environmental consequences of chemical discharges has required the implementation of robust monitoring systems that facilitate the compositional evaluation of effluent prior to release. Thus, the detection of sulphide has gained significant importance within the analytical community because of the toxicity of this ion<sup>2</sup>. Fortunately, the high reactivity of sulphide has provided a wealth of detection strategies and as such, this anion can also act as a versatile intermediate through which other sulphur based species can be determined <sup>3,4</sup>. Sulphide analysis is well represented in most branches of analytical science emerging from the more classical procedures to span iodimetry<sup>5</sup>, spectrophotometry<sup>6</sup>, chromatography<sup>7</sup>, electrochemistry<sup>8</sup> and combinations thereof <sup>9</sup>. Recently, chemical sensors have been used in many fields of applications, including clinical diagnosis, biomedical analysis and monitoring of environmentally hazardous materials <sup>10</sup>. The lifetime of these sensors and their lower limit of detection are among their most important characteristics. Therefore, increasing efforts are being directed towards the optimum design and operating conditions of long-living sensors. In particular, covalent binding of ionophores to polymeric sensing membranes provides long-term stability by

1  
2  
3 preventing the ionophore from leaching into sample solution, crystallizing or evaporating <sup>11</sup>. In  
4 addition, it can improve the sensor selectivity and detection limit <sup>12</sup>. At the same time, all-solid-state  
5 ion-selective electrodes (ISEs) based on polymeric membranes doped with electrically neutral or  
6 charged ionophores (carriers) have attracted considerable interest since the invention of the so-called  
7 coated-wire electrode (CWE) about 40 years ago<sup>13</sup>. Their further development led to ion-selective  
8 electrodes with a solid internal contact  
9  
10 (SCISEs) <sup>14</sup> that characterized by a well-defined ion-to-electron transduction process between the  
11 ionically conducting ion-selective membrane and the electronically conducting substrate. The notable  
12 progress in sensor technology is manifested in the wide application of ion sensors in environmental  
13 analysis <sup>15</sup>. However, while there a few number of sulphide ISEs were reported in the literature<sup>16-19</sup>,  
14 most of them are insufficiently sensitive or selective<sup>16,18</sup>, with short life time<sup>17</sup> or long response time<sup>19</sup>  
15 to permit accurate measurements of the low levels of sulphide. Moreover, the majority of which are  
16 not usable in strong alkaline media where the sulphide ion dominate in solution and can be directly  
17 measured and only have a limited lifetime. Therefore, the development of durable sulphide sensor  
18 with improved sensitivity and selectivity is still an urgent need. We have previously introduced a solid  
19 contact sulphide sensor based on the ceric complex of ABPAH as a part of E-tongue system<sup>20</sup> for  
20 resolving mixtures of sulphide and perchlorate anions in an un-buffered aqueous solution. However,  
21 in this contribution, we report on long living and a highly selective and sensitive membrane electrode  
22 for the determination of nanomolar concentration of sulphide in various types of water. Finally,  
23 noteworthy we have integrated the excellent potentiometric performance of the developed sensor with  
24 the agreed advantages of the flow injection technique with the high sample throughput and low  
25 sample volume.  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51

## 52. Experimental

53  
54  
55  
56  
57  
58  
59  
60

### 2.1. Materials and reagents

All chemicals used were of analytical grade and doubly distilled water was used throughout all experiments unless otherwise mentioned. O-nitrophenyloctyl ether (NPOE), dioctyl phthalate (DOP), dibutyl phthalate (DBP), dibutyl sebacate (DBS), high relative molecular weight poly (vinylchloride) PVC were purchased from Aldrich. Benzyl dimethyl hexadecyl ammonium chloride (BDMHAC), conducting polymer poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT-PSS) and *N,N*-dimethyl-*p*-phenylene diamine hydrochloride(DMPD) were purchased from Sigma. Cetyl pyridinium chloride (CPC), Cetyltrimethylammonium bromide (CTMAB), oleic acid (OA) and tetrahydrofuran (THF) were obtained from Fluka. The sodium or potassium salts of the anions used were from Merck or Aldrich. A sulphide standard solution ( $0.1 \text{ mol L}^{-1}$ ) was prepared from  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  salt. Here,  $0.1 \text{ mol L}^{-1}$  stock solutions of the various anions used were prepared from their sodium or potassium salts. The corresponding working solutions were freshly prepared by accurate dilution from their stock solution.

Sulphide anti-oxidant buffer (SAOB) <sup>21</sup>: Approximately 60 mL of distilled water was taken in a 100 mL volumetric flask and 8.0 g of NaOH, 3.5 g of ascorbic acid and 6.7 g of  $\text{Na}_2\text{EDTA}$  were added. The solution swirled to dissolve completely and then made up to 100 mL. The color of the freshly prepared alkaline antioxidant reagent ranges from colorless to yellow. This solution was stored in a tightly capped brown glass bottle and discarded when the solution became discolored.

### 2.2. Apparatus

A PC-based EMF-16 high-resolution data logger (Lawson Labs, Inc) was used to record the output signals against Ag/AgCl/Cl double-junction reference electrode (model 6.0729.100, Methrom AG, Herisau, Switzerland). Orion pH-meter model 330 was used for pH measurements. Spectroscopic measurements were carried out using UV/Visible Shimadzu 2040 spectrophotometer. Peristaltic pump 4 channels model Ismatec MCP Cole-Parmer, Tygon tube R-3603 of 0.25mmi.d and Rheodyne injection valve, Model 5060 were used in the FI system. Rotary evaporator model BUCHI, Rota vapor R-215 Switzerland was used during the synthesis of ionophores.

### 2.3. Synthesis of the ionophore

The ionophore II, ceric ABPAH attached to PAA synthesized in three steps as follows:

#### 1- Preparation of the chelating compound ABPAH :

Benzothiazol-2-ylacetohydrazide and an equimolecular amount of 3-chloro-4-formyl-5-pyrazole refluxed in ethanol containing triethylamine (TEA) (3 drops) for 6 h. The precipitate was formed on hot, and then it was filtered off, and re-crystallized from acetic acid; m.p. 219 – 221 °C; yield 65%  
Anal. Calcd. for  $C_{16}H_{14}ClN_5O_2S$  (375.84): C 51.13%, H 3.75%, Cl 9.43%, N 18.63%, O 8.51%, and S 8.53%, found: C 51.10%, H 3.64%, Cl 9.32%, N 18.58%, O 8.40%, and S 8.44%. IR (KBr) ( $cm^{-1}$ ): 3431.71 (NH), 1619.91 (CN) benzothiazole.  $^1H$ -NMR (DMSO- $d_6$ ) ppm:  $\delta$  2.4 (s, 1H, CH<sub>3</sub>); 7.4 -7.5 (m, 2H, benzothiazole H-5 and H-6); 7.95 – 8.15 (m, 2H, benzothiazole H-4 and H-7); 9.8 (s, 1H, NH); and 12.1 (s 1H, NH).

#### 2- Preparation of ionophore I (free):

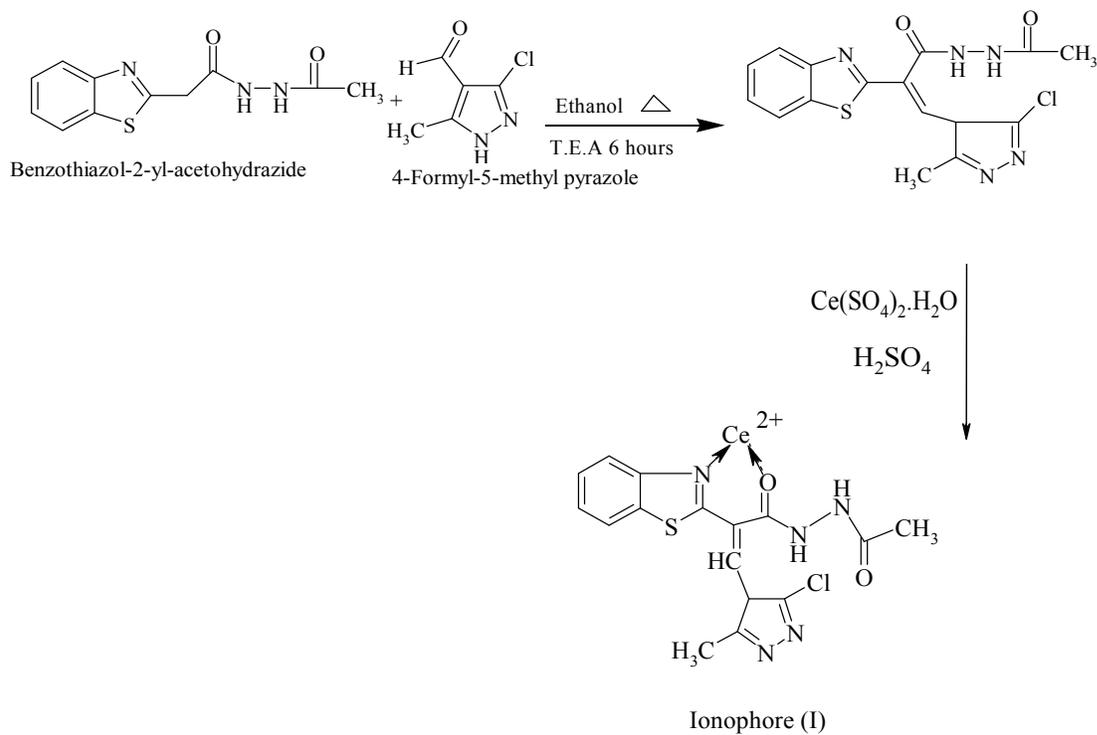
0.01 mole (3.50 g) of Ce (SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O dissolved in 100 mL of 0.01 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> was added dropwise to 0.01 mole (3.75 g) of the chelating compound dissolved in 100 mL of ethanol with continuous stirring. The thus formulated yellow precipitate complex was filtered and washed with water followed by ethanol, then allowed to dry at ambient temperature to obtain ionophore I. IR (KBr) ( $cm^{-1}$ ): 3429 (NH), 1613 (CN) benzothiazole, 1069 (Ce-N-), and 562 (O-Ce). The synthesis of the chelating compound and Ionophore I are shown in Scheme 1.

#### 3- Preparation of ionophore II ( attached) by covalent attachment of ionophore I with PAA

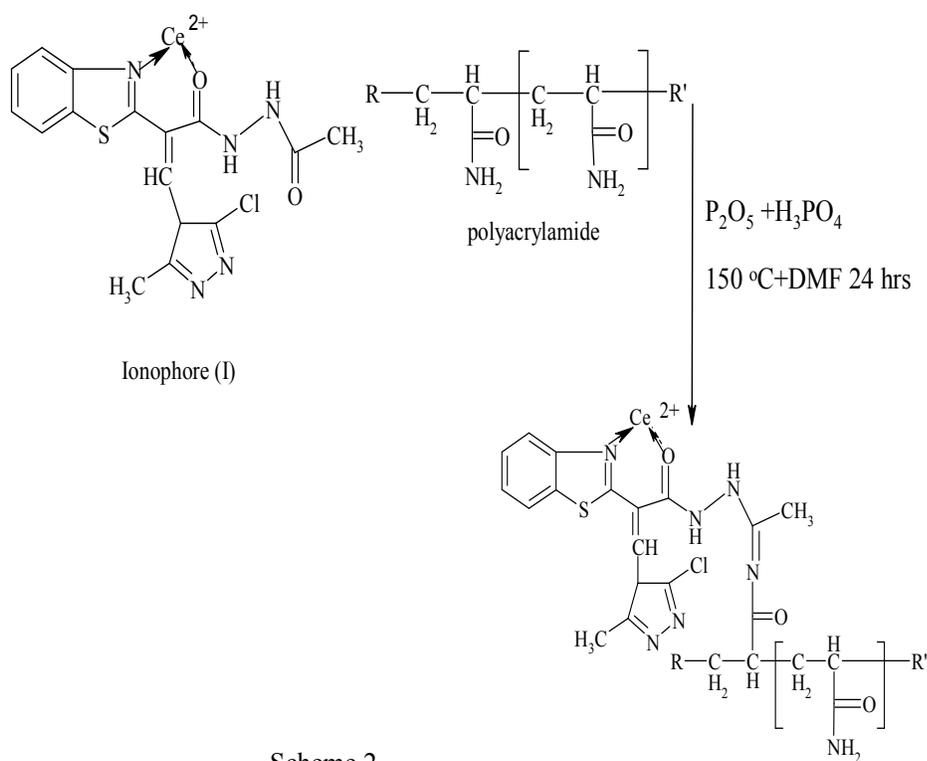
The proper weights of ionophore I and of PAA were mixed in 50 mL of DMF in the presence of P<sub>2</sub>O<sub>5</sub> and H<sub>3</sub>PO<sub>4</sub> as dehydrating agent purged with nitrogen gas for about 6 h. The mixture was refluxed for about 24 h at 140 °C, the yellow precipitate was filtrated and washed with water and ethanol, then allowed to dry at ambient temperature to obtain ionophore II. The ionophore II was synthesized in 10, 20 and 30% ratios of ionophore I with PAA polymer. The prepared Ionophore II that contained 30%

of ionophore I showed the optimum results. IR (KBr) ( $\text{cm}^{-1}$ ): 3434.6 (NH), 1645 (CO)<sub>ionophore</sub>, 1548(CO)<sub>PAA</sub>, 2927.41 ( $\text{CH}_3$ ).

Scheme 2 illustrates the immobilization of ionophore I onto PAA by covalent amide bond formation.



Scheme 1



#### 2.4. Preparation of the membrane

The general procedure for the preparation of PVC membranes was performed by dissolving various amounts of ionophore I with the proper amount of a plasticizer (DBS, DBP, NPOE, or DOP) and PVC in THF. The cocktail was well mixed in a 5.0 mL vial until a clear solution was obtained. At the same time, the general procedure for the preparation of the sensing membranes for all-solid contact

1  
2  
3  
4 electrode was carried out by well mixing appropriate amounts of ionophore II with poly butyl  
5 methacrylate - dodecyl methacrylate (PBDA)<sup>22</sup> as a plasticizer-free copolymer in THF, to obtain  
6 membranes containing 4.76 %, 5.0%, 7.5 %, 10.0%, 12.5%, and 15.0% of ionophore II respectively.  
7  
8 The potentiometric performance of the sensors constructed using the previously prepared membranes  
9  
10 was evaluated using Na<sub>2</sub>S solution at a concentration of 10<sup>-2</sup> mol L<sup>-1</sup> to 10<sup>-9</sup> mol L<sup>-1</sup>, at a pH 13.0 using  
11  
12 SAOB solution.  
13  
14

### 15 16 17 *2.5. Preparation of the sensors* 18 19

20  
21 Coated graphite electrodes (CGEs) were prepared as mentioned in a previous paper<sup>23</sup>. However, for  
22 the construction of solid contact electrodes (SCEs) with gold contact (SC<sub>gold</sub>); a gold wire of 1 cm  
23 length and 0.1 mm diameter was carefully washed with 1 mol·L<sup>-1</sup>H<sub>2</sub>SO<sub>4</sub>, water and acetone, dried,  
24 and attached to a silver wire using conducting silver-epoxy glue (silver epoxy E10-101, Alfa). The  
25 conducting polymer films were casted from an aqueous dispersion of PEDOT/PSS containing FeCl<sub>3</sub>  
26 onto a gold wire. 10 µl of the aqueous dispersion of PEDOT (PSS) was applied to the gold wire and  
27 allowed to dry. In order to make the polymer stable in aqueous solution and prevent excessive  
28 swelling and disintegration, it was ionically crosslinked with a multivalent cation. The cation  
29 solutions were prepared from FeCl<sub>2</sub>/FeCl<sub>3</sub>. The proportion of both cationic species of the redox  
30 couples was 1:1, 0.125 M Fe<sup>2+</sup> and 0.125 M Fe<sup>3+</sup> in solutions. The Au/PEDOT(PSS) electrodes were  
31 immersed in the 0.25 M Fe<sup>2+/3+</sup> crosslinking solution for at least 5 h, the resulting cross-linked  
32 polymer does not contain any iron. The resulting electrodes are referred to as Au/PEDOT(PSS). The  
33 fabricated polymer films possessed low water solubility and allowed for stabilized standard electrode  
34 potential<sup>24</sup>. Finally, the membrane cocktail was applied onto the dry PEDOT/PSS polymer layer  
35 deposited onto a gold electrode. The electrodes were conditioned in a 1×10<sup>-3</sup> mol·L<sup>-1</sup> sulphide solution  
36 for at least 24 h before their first use and kept in such a solution over-night when in use, and stored  
37 dry for longer time. The same method was applied for preparing the graphite solid contact electrodes  
38 (SC<sub>graphite</sub>); however, a spectroscopic-grade graphite rod with 3mm diameter and 10mm long was used  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3 after cleaning as usual.  
4  
5  
6  
7  
8  
9  
10

#### 11 2.6. Calibration of the sulphide-selective sensor 12 13 14 15

16 The proposed sensors were calibrated by immersion, along with an Ag/AgCl reference electrode, in  
17 a 20-mL beaker containing 9.0 mL SAOB solution of pH 13.0. Then aliquots of a standard sulphide  
18 solution were added successively under continuous stirring to obtain solutions with a sulphide  
19 concentration ranging from  $1 \times 10^{-10}$  to  $1 \times 10^{-2}$  mol L<sup>-1</sup>. The potential was recorded at room  
20 temperature (25°C) using a PC-EMF16 interface data acquisition board after stabilization to  $\pm 0.5$  mV.  
21 A calibration graph was then constructed by plotting the recorded potentials as a function of the  
22 logarithm of the sulphide concentration. The resulting graph was used for subsequent determination of  
23 an unknown sulphide ion concentration using the same procedure.  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33

#### 34 2.7. Sample collection, storage and preservation 35 36

37 Water samples were collected in clean plastic bottles, filled completely and capped tightly. Excessive  
38 agitation or prolonged exposure to air was avoided and immediate analysis was always preferred after  
39 samples were filtered. In case of spectrophotometric analysis, samples with high concentration of  
40 sulphide may inhibit full color development and require proper dilution; however, some loss in  
41 sulphide concentration can occur.  
42  
43  
44  
45  
46  
47  
48  
49

### 50 3. Results and Discussion 51 52 53

54 Three different chelating compounds containing sulphur, nitrogen and oxygen function groups  
55 were synthesized for the first time in our laboratory following a procedure similar to that previously  
56  
57  
58  
59  
60

reported<sup>25</sup>. Fig. 1 shows the structure of the compounds namely:

1) N'-Acetyl-2-(benzothiazol-2-yl)-3-(3-chloro-5-methyl-4H-pyrazol-4-yl) acrylohydrazide

2) 2- Imino-N-(5- methyl-1, 3, 4- thiadiazol-2-yl)-2H-chromene-3-carboxamide

3) 5-(1-phenyldiazo) cyanomethyl -1, 3, 4-oxadiazol (3H)-2-spiro-3-indol-2-(1H)-one

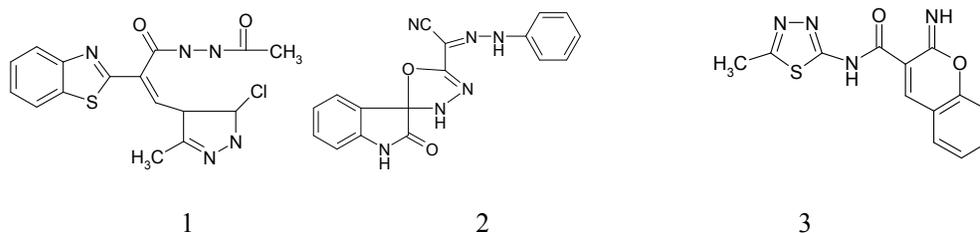
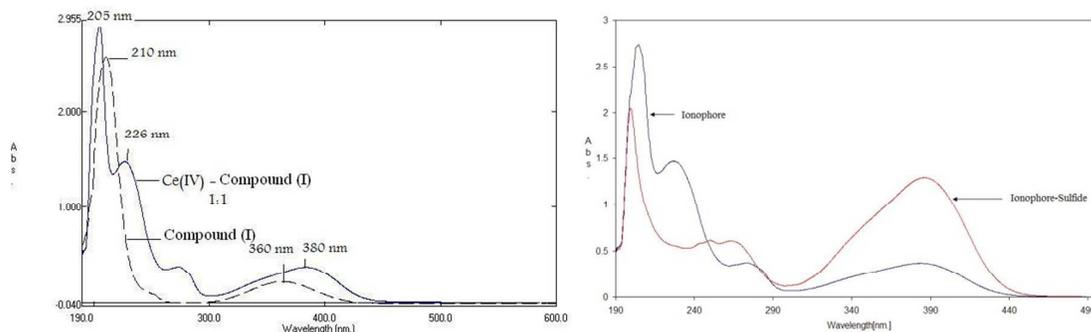


Fig.1 Chemical structure of the chelating compounds

We examined the three compounds for the preparation of some metal chelate that may act as possible ionophore for anion selective sensors. Preliminary experiments were carried out using various cations like  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{La}^{3+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{ZrO}_2^{2+}$ ,  $\text{VO}_2^{2+}$ ,  $\text{In}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$ . The chelating compound is completely soluble in ethanol, while all the used inorganic salts (0.01 M) are soluble in water and still soluble in 50:50 v/v ethanol: water mixed solvent. At mixing equal volumes of the compound and metal salt solutions, the precipitation of the metal complex took place from completely clear solution. Only the addition of copper and ceric solutions to the alcoholic solution of each of the three compounds resulted in the formation of blue and yellow to pale yellowish precipitate respectively. When tried as ionophores, the copper complexes

showed poor response toward various anions and were found to be not interesting at all for further study. At the same time, ceric complexes of compounds, 2 and 3 showed also non interesting response. Therefore, only the detailed synthesis and analysis of compound 1 is given in the experimental part, as compounds 2 and 3 were found uninteresting.

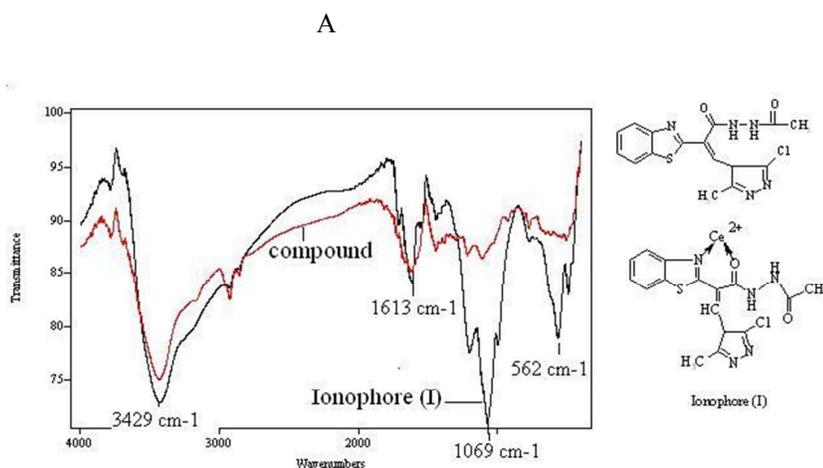


.2 UV-Vis spectra of the chelating compound and its ceric complex (Ionophore I) (a), the Ionophore (I) and its sulphide adduct measured in ethanol-water medium.

The ceric complex of compound 1 has showed a distinctive response toward sulphide ion as clear from Fig. 2, therefore, our study has focused on it. This result agrees with the known high affinity of cerium to sulphur, which has allowed for the potential use of cerium-doped materials in desulphurization<sup>26</sup> of mineral oils and fuels. Additionally, the degradation of the catalytic performance of cerium oxide due to its sulphidation by sulphur diffusion and its strong binding to cerium, even at very low levels of sulphur contaminants, has been reported<sup>27</sup>. The presence of ceric (IV) in the chelate compound still offer two positive charges that may allowed a more suitable circumstances for interaction with sulphide ion compared to the neutral copper (II) complex. When comparing the IR spectra of both compound 1 and ionophore I as shown in Fig. 3 (A), it was found that the peak at  $3429\text{ cm}^{-1}$  for secondary amine -NH- was not changed. This indicates that, the two nitrogen atoms of the secondary amines do not participate in the formation of the complex. A medium

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

strength peak was observed at  $1619\text{ cm}^{-1}$  that corresponds to  $\text{C}=\text{N}$  of the benzothiazole moiety of compound 1 and because the carbonyl group ( $\text{C}=\text{O}$ ) frequency peaks exist at  $1650\text{--}1750\text{ cm}^{-1}$  this peak cannot be assigned for a  $\text{C}=\text{O}$  group. Furthermore, the same peak of the  $\text{C}=\text{N}$  in the ceric complex appeared at  $1613\text{ cm}^{-1}$  with a negative shift of about  $6\text{ cm}^{-1}$  indicated the coordination of the benzothiazole nitrogen to the metal ion<sup>28</sup>. The peak at  $1069\text{ cm}^{-1}$  that may be assigned to  $\text{Ce}-\text{N}$  bond could be explained by the fact that the nitrogen atom of the benzothiazole ring donates a pair of electrons to the metal ion forming a coordinate covalent bond. A new peak was observed at  $562\text{ cm}^{-1}$  that can be assigned to the bond between the oxygen atom in the carbonyl group and cerium atom stretching vibration<sup>29</sup>. Fig. 3.B. shows the IR spectra of ionophore II and PAA amide alone. The peaks in PAA at  $3427\text{ cm}^{-1}$  and  $3392\text{ cm}^{-1}$  has been replaced by a more intense peak at  $3434\text{ cm}^{-1}$  of the  $\text{NH}$  of the ionophore. Instead of the peaks at  $1708\text{ cm}^{-1}$  of  $\text{O}=\text{C}-$  and  $1681\text{ cm}^{-1}$  of Amide ( $\text{O}=\text{C}-\text{NH}_2$ ), two peaks appear at  $1645\text{ cm}^{-1}$  of and  $1548\text{ cm}^{-1}$  imide ( $\text{O}=\text{C}-\text{NH}$ ) indicating the covalent attachment of ionophore I to PAA. Spectrophotometric experiments also confirmed the specific interaction between the sulphide ion and the covalently attached ionophore II. Thus, it represents as an excellent sulphide anion sensory candidate that is convenient for use in a solid contact electrode configuration and it was subjected to further investigation.



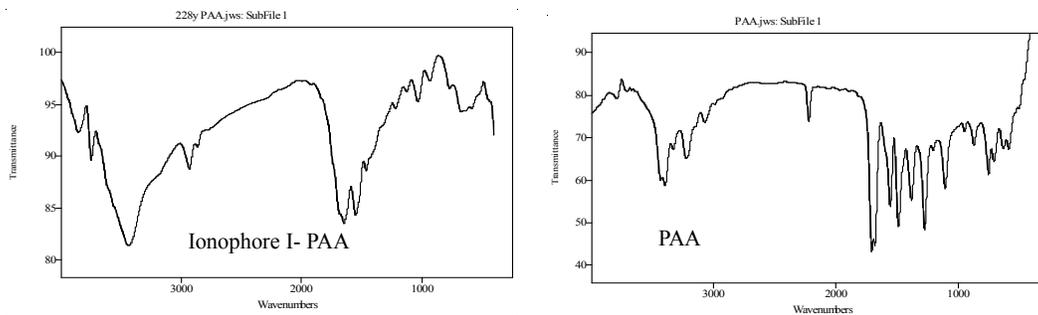


Fig. 3. IR Spectra of , (A) compound 1 and its ceric chelate (ionophore I) and (B) Ionophore I attached to PAA (Ionophore II) and PAA alone.

### 3.1. Optimization of membrane composition

It is now well established that the membrane composition plays a significant role in the potentiometric sensitivity and selectivity for a given ionophore, and its optimization is mandatory. Thus, the effect of the percentage of ionophore on the sensor response has been investigated. Preliminary experiments using CGE configuration showed that 3.84% of ionophore I in a membrane containing 32.75% PVC and 63.59% NPOE as a plasticizer possess the optimum performance with a slope of 29.9 mV/ conc. decade, linear range of  $1 \times 10^{-6}$ -  $1 \times 10^{-2}$  mol. L<sup>-1</sup> and a Lower detection limit (LDL) of  $9 \times 10^{-7}$  mol. L<sup>-1</sup>. Incorporating cationic additives such as CTMAB, CPC, BDHAC or OA with ionophore in the membrane composition of the sensors resulted in no significant improvement of the sensor response. In effect, the additives had worsened its performance. Therefore, no such additives have been considered for further membrane preparations (Supplementary data, CGE). These results were utilized in constructing a series of solid contact sensors with either graphite or gold contacts, but using ionophore II. Data in Table (1) show that, the SC<sub>graphite</sub> electrode No.1 which does not contain ionophore at all (blank) possessed extremely poor potentiometric performance with a slope of 12.99 mV/ concn. decade and R<sup>2</sup> of 0.77. However, the slope and LDL of SC<sub>(graphite)</sub>

1  
2  
3 sulphide selective electrode have improved as the ratio of ionophore II increased in the membrane, till  
4 it reached a ratio of 15 % that correspond to 4.5 % of ionophore I the linear range and the detection  
5 limit has become worse. The optimum composition was of sensor No.6 (SC<sub>graphite</sub>) and No.9 (SC<sub>gold</sub>)  
6 with the 12.5% of ionophore II that corresponded to 3.75 % of ionophore I, agreed with the results  
7 obtained with the CGE sensor. The sensor performance has distinctly improved where a wider linear  
8 range of  $1 \times 10^{-8}$  -  $1 \times 10^{-2}$  mol. L<sup>-1</sup> achieved for both the No.6 (SC<sub>graphite</sub>) and No.9 (SC<sub>gold</sub>) sulphide  
9 sensors. In addition, the sensitivity of sensor considerably improved with a slope of - 32.74 and -  
10 29.42 mV/conc. decades, and a LDL of  $1 \times 10^{-8}$  and  $2 \times 10^{-9}$  mol. L<sup>-1</sup> for the two sensors respectively.  
11 While, the two sensors were developed using the same membrane composition, the preference of gold  
12 as a solid electronic conductor to the graphite one was distinct. In addition to the excellent ion-to-  
13 electron transduction offered by the conducting polymer in the solid contact sensors, the covalent  
14 immobilization of the ionophore to the acrylate polymer has considerably attributed to the  
15 enhancement of the potentiometric performance of the sensor. The effect of immobilization is of  
16 special importance for the sensor design because the covalent attachment of the electroactive  
17 components to membranes seems to be an attractive possibility to obtain durable sensor. It  
18 prevents the leaching of ionophore from the membrane into solution, or its crystallization,  
19 segregation and even precipitation, and hence prevents or minimizes the deterioration of its  
20 sensitivity. The bond between the ionophore and target ion gives different selectivity and  
21 sensitivity toward the other ions. Therefore, ionophores with different binding strengths due  
22 to its fixation to the membrane matrix will improve the sensor selectivity.

23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46 Fig. 4 shows the calibration graphs of the investigated different types of sensors, CGE with  
47 ionophore I (free ionophore), SC<sub>graphite</sub> with ionophore II Attached ionophore) and SC<sub>gold</sub> with both  
48 free and attached ionophores in SAOB. It is obvious that SC<sub>gold</sub> sensor with ionophore II possessed  
49 the best performance over all other types. A slope of -29.4 mV decade<sup>-1</sup> and LDL of  $2.0 \times 10^{-9}$  molL<sup>-1</sup>  
50 was recorded. At the same time, it is clear that the performance of SC<sub>gold</sub> with attached ionophore  
51 was more advantageous to the same sensor type with the free ionophore.  
52  
53  
54  
55  
56  
57  
58  
59  
60

Table 1

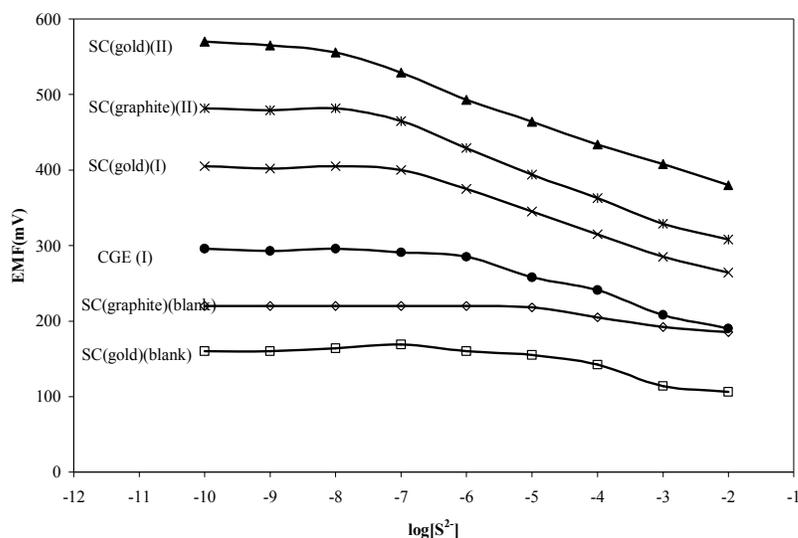


Fig. 4 Calibration graphs of the different types of electrodes with free and attached ionophore in SAOB.

### 3.2. Effect of pH of the sample solution

The sulphide ion ( $S^{2-}$ ) is known to exist only in a strongly alkaline aqueous solution<sup>30</sup>, while in solutions with low pH  $S^{2-}$  combines with a proton to form  $HS^-$ . At  $pH < 7$   $HS^-$  converts to  $H_2S$ <sup>31</sup>. The effect of pH in the response of sulphide selective electrode was studied using CGE and SCEs types at different pH values. The effect of pH on the sensor response was monitored with different samples at pH values of 7.0, 9.0 and using SAOB solution of pH of 13.0. Fig.5 show that the potential of all studied sensors decreased with increasing pH of solution until a value of about 13.0. Afterwards, the slope remained constant at higher pH values. This is in agreement with the fact that almost all sulphide species present in the SAOB solution of pH 13 occurs as the divalent  $S^{2-}$  ion rather than as the monovalent  $HS^-$  that predominate at lower pH values. Data in Table 2 indicates that the sensor contained the free ionophore I possessed the worse potentiometric performance in the SAOB

at pH 13.0 which may be attributed to the leaching of the ionophore at this aggressive medium. However, those sensors which contained Ionophore II, the covalently attached one, proved to be durable and possessed better performance in that harsh medium.

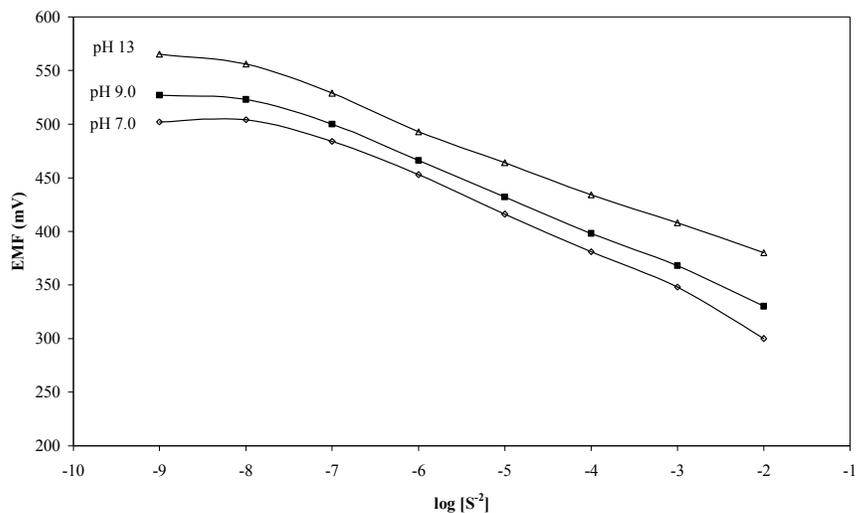


Figure 5. Effect of pH on the calibration of SC<sub>(gold)</sub> sulfide-selective electrode with 12.5% attached ionophore (II) in PBDA membrane at pH 7, 9 and 13.

### 3.3. Response time and lifetime

For analytical applications, the response time of a sensor is of critical importance. The average time required for the sensor to reach a steady potential response within  $\pm 1$  mV of the final equilibrium value after successive immersion of a series of S<sup>2-</sup> solutions, each having a 10-fold difference in concentration was investigated. The response time of the PBDA-based membrane sensor was  $< 12$  s for SC<sub>graphite</sub> and  $< 10$  s for SC<sub>gold</sub> electrodes over the studied linear concentration range. The equilibrium potentials essentially remained constant for over 5 min  $\pm 0.64$  min. Fig.6 shows the

dynamic response of SC<sub>gold</sub> electrode.

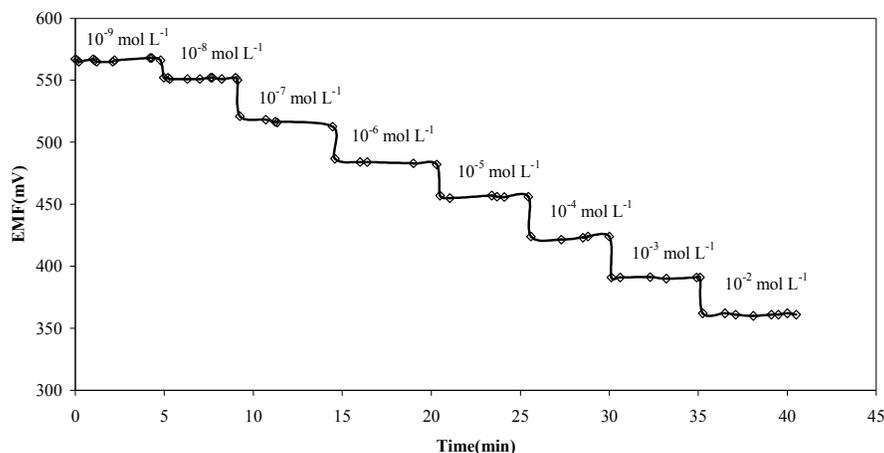


Fig.6 Dynamic response of the proposed SC<sub>gold</sub> sulphide sensor with ionophore II (attached) for change in the concentration of sulphide ions from  $7.0 \times 10^{-9}$  –  $1.0 \times 10^{-2}$  M.

The SC<sub>graphite</sub> sensors proved to be usable for at least 4 months while the SC<sub>gold</sub> one could be used for at least 6 months without any measurable divergence in their response. However, CGE with ionophore I was usable only for approximately one month. This may have been due to the leaching of the free ionophore from the membrane in the aggressive basic medium that was previously mentioned.

Table 2.

### 3.4. Sensor selectivity

Table 3

The potentiometric selectivity coefficients, which reflect the relative response of a sensor for the primary ion over other ions, present in solution, is perhaps the most important characteristics of an ion selective electrode<sup>32, 33</sup>. The potential selectivity of the proposed S<sup>2-</sup> ion-selective sensor to 14

1  
2  
3  
4 common anions were investigated by separate solution method (SSM) <sup>34</sup> and fixed interference  
5  
6 method (FIM) <sup>35</sup> using SC<sub>gold</sub> and SC<sub>graphite</sub> with free and attached ionophores. The FIM and SSM are  
7  
8 recommended for electrodes that exhibit a Nernstian response both to primary and interfering ions, the  
9  
10 FIM can always be used to determine a minimum primary ion concentration level at which the effect  
11  
12 of interference can be neglected. The actual conditions of the FIM match the conditions under which  
13  
14 the electrodes were used. Data in Table 3 shows clearly that solid contact sulphide sensors No. 6 and  
15  
16 No.9 with membranes containing Ionophore II possess remarkable selectivity for S<sup>2-</sup> over all studied  
17  
18 anions compared to the sensor No.1 i.e. CGE. At the sample of pH 13 it is unlikely that heavy metal  
19  
20 cations are still existing in solution. It is also noteworthy that the results show that when comparing  
21  
22 PVC and PBDA as suitable matrices for the membrane, the later resulted on improving the slope of  
23  
24 the sensor toward the Nernstian value. The data reveals also that sensors with the attached ionophore  
25  
26 are superior to those with the free one in terms of selectivity. It is interesting to note that the observed  
27  
28 selectivity pattern (i.e. S<sup>2-</sup>>Cl>F>I>Br>NO<sub>2</sub><sup>-</sup>>NO<sub>3</sub><sup>-</sup>>IO<sub>3</sub><sup>-</sup>>ClO<sub>4</sub><sup>-</sup>>AcO>SO<sub>4</sub><sup>2-</sup>>SO<sub>3</sub><sup>2-</sup>>S<sub>2</sub>O<sub>3</sub><sup>2-</sup>  
29  
30 >Citrate<sup>3-</sup>>PO<sub>4</sub><sup>3-</sup>) significantly differs from the so-called Hofmeister selectivity sequence (i.e.,  
31  
32 selectivity based solely on lipophilicity of anions). The performance characteristic of the different  
33  
34 prepared sulphide sensors is summarized in Table 4, A comparison of the proposed SC<sub>gold</sub> sensor No.  
35  
36 9 with some of the previously reported sulphide sensors in addition to the commercially available  
37  
38 sulphide electrode from Orion Company is given in Table 5.  
39  
40  
41  
42  
43

44 Table 4& Table 5.  
45  
46  
47  
48  
49

### 50 3.5. Aqueous layer formation test for solid contact sensor 51 52 53

54 The degradation in sensor response with solid-contact ion selective electrodes (SCISEs) has been  
55  
56 proved to be associated with the existence of a water layer between the membrane and the solid  
57  
58  
59  
60

1  
2  
3  
4 contact, which behaves unintentionally as an electrolyte reservoir that re-equilibrates on every change  
5  
6 in a sample composition <sup>36</sup>. However, the use of a water-repellent poly (methyl methacrylate)/ poly  
7  
8 (decyl methacrylate) (PMMA/ PDMA) copolymer as the ion-sensing membrane, along with a  
9  
10 hydrophobic poly(3-octylthiophene 2,5-diyl) (POT) solid contact as the ion-to-electron transducer, is  
11  
12 an excellent strategy for avoiding the detrimental water layer formed at the buried interface of SCISEs  
13  
14 <sup>37</sup>. The proposed SC<sub>gold</sub> sensor with 12.5 % of ABPAH-PAA ionophore in plasticizer-free PBDA  
15  
16 copolymer that was applied onto a gold electrode pre-coated with the hydrophobic conducting  
17  
18 polymer poly(3,4-ethylenedioxythiophene) (PEDOT) as an ion and electron transducer has been  
19  
20 examined for the formation of aqueous layer between the polymer coating and the gold conductor. In  
21  
22 the potential vs. time plot, shown in Fig. 7, the dashed trace indicates the expected potential response  
23  
24 with an undesirable aqueous layer between the ion-selective membrane and its solid contact. The  
25  
26 continuous trace indicates the obtained actual potential response of SC<sub>gold</sub> sulphide sensor. It is clear  
27  
28 that there is no aqueous layer between the ion-selective membrane and its SC as there was the no  
29  
30 potential similar to the dashed trace of the ill-contact sensor. It is also, noteworthy, that Data from  
31  
32 Table 3 shows that when comparing PVC and PBDA as suitable matrices for the membrane, the latter  
33  
34 resulted on improving the slope of the sensor toward the Nernstian value.  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

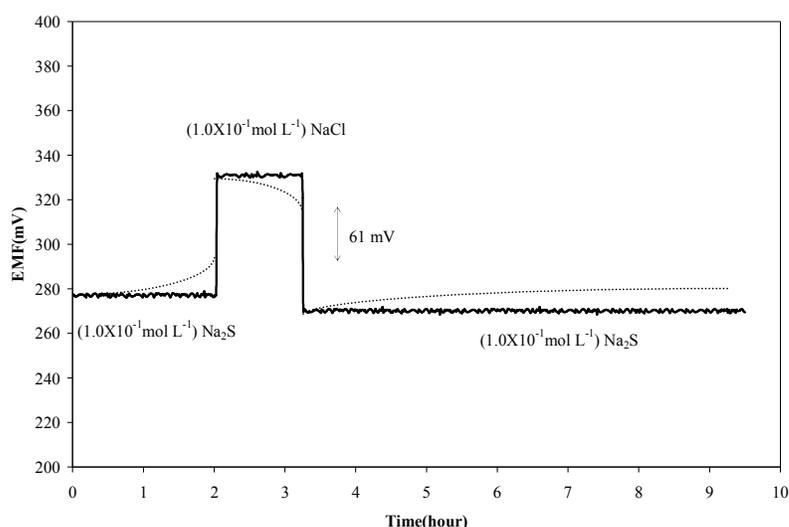
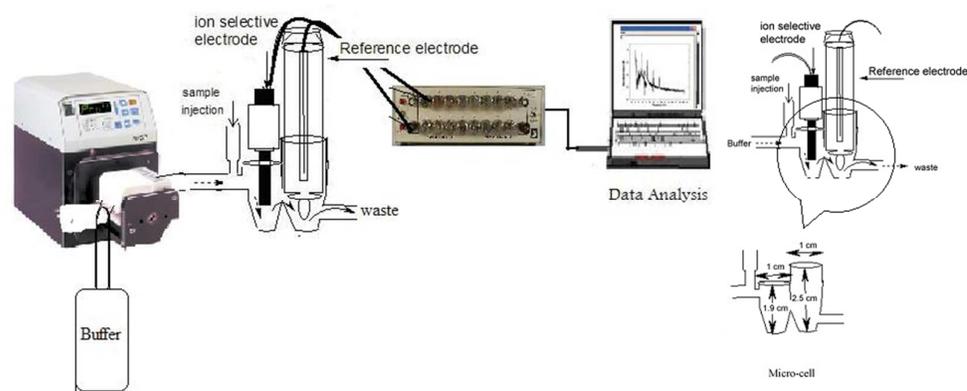


Fig.7 Aqueous layer formation test: typical trace of solid contact sulphide-selective electrode when

1  
2  
3 the sample solution is changed from  $1.0 \times 10^{-1} \text{ mol L}^{-1} \text{ Na}_2\text{S}$  to  $1 \times 10^{-1} \text{ mol L}^{-1}$  of NaCl then again  
4  
5  $1.0 \times 10^{-1} \text{ mol L}^{-1} \text{ Na}_2\text{S}$ . Before the experiment, the electrode was conditioned in  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  of  
6  
7  $\text{Na}_2\text{S}$  for 24 h.  
8  
9

### 10 11 12 3.6. Flow injection analysis (FIA)

13  
14  
15 We have integrated the excellent potentiometric performance of the developed sensors with the  
16  
17 agreed advantages of the flow injection technique with the high sample throughput and low sample  
18  
19 volume. FIA determination of sulphide was successfully performed using the proposed  $\text{SC}_{\text{gold}}$  and  
20  
21  $\text{SC}_{\text{graphite}}$  sulphide selective electrodes as suitable detectors in conjunction with a homemade flow-cell  
22  
23 and pH 13.0 SAOB solution as a carrier. A schematic diagram of the flow injection manifold is shown  
24  
25 in Fig. 8. The parameters of the FIA method were optimized to obtain the best signal sensitivity and  
26  
27 sampling rate under low dispersion conditions. The geometry of the flow-cell limited the sample  
28  
29 dispersion, which allowed for optimum sensitivity and fast response of the sensor.  
30  
31  
32



52 Fig. 8: Schematic diagram of the flow injection manifold and the homemade micro flow-cell .  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4  
5  
6 The effects of sample injection volume (50–500  $\mu\text{l}$ ) and carrier flow rate (5–20  $\text{ml}/\text{min}$ ) were  
7 examined. A high sample volume yielded high peak heights, long residence times and low sample  
8 throughput. Applying a constant injection volume, the residence time of the sample was inversely  
9 proportional to the flow rate, a sample volume of 100  $\mu\text{l}$  was found to be the optimum. The  
10 dependency of the peak heights and peak width (and time to recover the base line) with flow rate was  
11 studied using the electrode response in a  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  solution of sulphide ion. Fig 9 shows that as  
12 the flow rate increased, the peaks became narrower and increased in height to a near plateau at a flow  
13 rate of 15  $\text{ml min}^{-1}$  for  $\text{SC}_{\text{graphite}}$  and 12  $\text{mL min}^{-1}$  for  $\text{SC}_{\text{gold}}$ . However, the peak height decreased  
14 considerably at flow rates higher than 15  $\text{mL min}^{-1}$ . Thus, a flow rate of 15  $\text{mL min}^{-1}$  was selected as  
15 an optimum value for further studies using  $\text{SC}_{\text{graphite}}$  and 12  $\text{mL min}^{-1}$  for  $\text{SC}_{\text{gold}}$ . The optimum  
16 conditions revealed a residence time of  $T=51 \text{ s}$  ( $T$ , the time span from injection until the appearance of  
17 the maximum signal) and a travel time of  $t=3 \text{ s}$  ( $t$ , the time elapsed from injection to the start of the  
18 signal). A return time of  $T'=30 \text{ s}$  ( $T'$ , the time span between the appearance of the maximum signal and  
19 the return to baseline) and a baseline-to-baseline time of  $\Delta T=81 \text{ s}$  ( $\Delta T$  or peak width, the interval  
20 between the start of the signal and its return to the baseline) has been also obtained. These results  
21 proved that the proposed sensor possesses a very fast response toward sulphide ions and can be  
22 rapidly washed, allowing for a sampling rate of at least 40 samples / h. At flow rates higher than 15  
23  $\text{mL}/\text{min}$ , the response deteriorates rapidly. Fig.10 (a) shows the triplicate peaks obtained from the FI  
24 system using the proposed  $\text{SC}_{\text{gold}}$  sensor under optimal experimental conditions for varying  
25 concentrations of  $\text{S}^{2-}$  solutions in the range of  $1.0 \times 10^{-8}$  to  $1.0 \times 10^{-2} \text{ mol L}^{-1}$ .  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

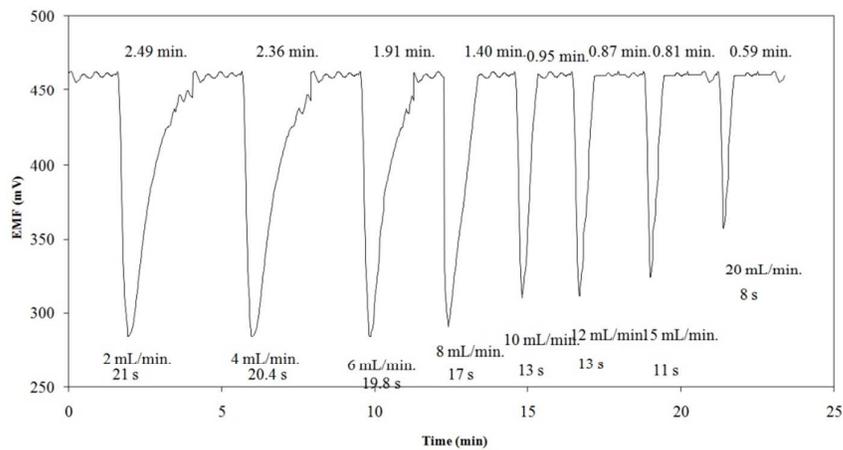
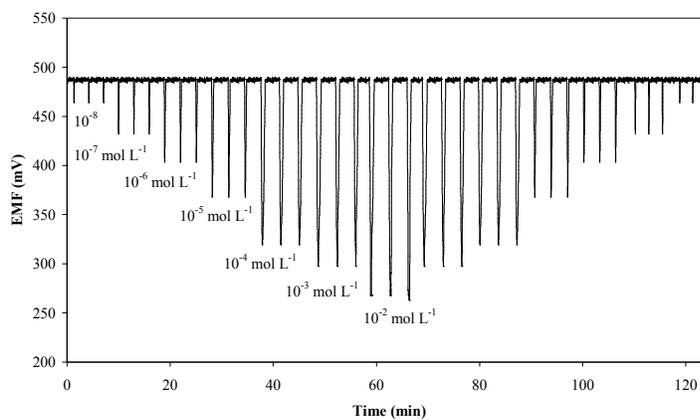
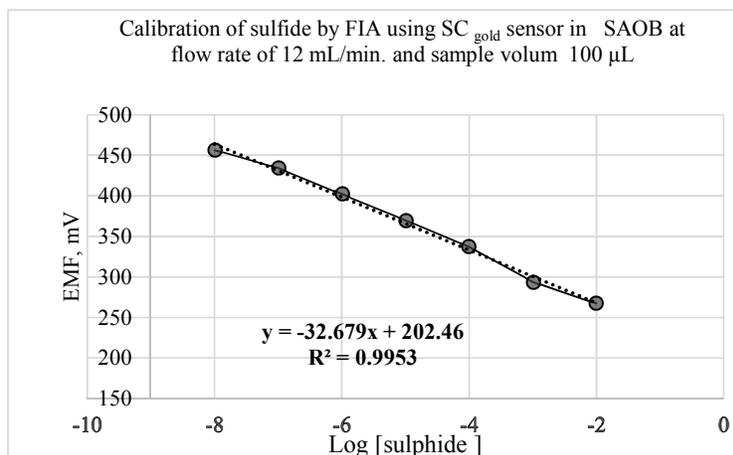


Fig. 9. Effect of flow rate using  $SC_{\text{gold}}$  sensor  $10^{-3} \text{ mol L}^{-1}$  of sulfide  $150 \mu\text{L}$  in SAOB, pH 13



(a)



(b)

Fig.10. (a) Triplicate peaks obtained from the FI system using the proposed  $SC_{\text{gold}}$  sensor with flow rate of 12 mL min<sup>-1</sup> and a sample volume of 100  $\mu$ L in SAOB medium for varying concentrations of S<sup>2-</sup> solutions in the range of  $1.0 \times 10^{-8}$  to  $1.0 \times 10^{-2}$  mol L<sup>-1</sup>. (b) The calibration line of the solid contact sulphide sensor ( $SC_{\text{g}}$ ) under the same conditions.

### 3.7. Application of the proposed sensor for the determination of sulphide in various environmental samples

The proposed solid contact sulphide sensor in a FIP analysis performs well under laboratory conditions. A quantitative recovery of sulphide in samples collected from leather tannery at Ain El-Sera, Glucose and Starch factory at Helwan City and the Nile River at ~500 m from the Glucose and Starch factory have been achieved using FI potentiometric methods. Also underground water from Ain Helwan about 1 Km from Iron and Steel industries, and wastewater at NRC, and from the main drainage tube samples. The results were compared to those obtained by the methylene blue spectrophotometric method<sup>37</sup>. However, the spectrophotometric method cannot be applied for the determination of sulphide in tannery samples, which contain high concentrations of chromium due to the dark color of the sample. This was not the case with the potentiometric method. Data in Table 6 shows the results of the analysis for various samples with the FIP using the proposed sensor compared to the results using the standard spectrophotometric method. The statistical Student's t-test and the F-tests were selected for this purpose. Considering as null hypothesis that the two methods agree, a paired two-tail test for 5% level of significance gave calculated t values below the tabulated one, therefore accepting the null hypothesis. The comparison of variances attained for each sample was made by the F-test using the same assumptions as for the Student's t-test, and the calculated values were always below the critical F-value, thus confirming the null hypothesis.

Table 6

#### 4. Conclusions

A long living sulphide selective solid-state sensor was developed for the FIP determination of sulphide concentration in environmental samples. The sensor that contains ceric- ABPAH ionophore covalently attached to PAA performs with high efficiency in strong alkaline solutions allowing a direct measurement of the actual concentration of sulphide ions without need for correction. Moreover, the proposed sensor possesses high sensitivity with nanomolar detection limits for the sulphide ion. The sensor possesses quite high selectivity, being free from interference for all common anions and compared to all previously report sulphide-selective ion sensors can provide considerable accuracy for sulphide determination.

#### Acknowledgements

Authors thank the Egyptian STDF and NATO **Project Title: Novel Electrochemical Nano-Sensors for Toxic Ions Detection** Project Number: CBP.NUKR.SFP 984173 for financially supporting this work.

#### 5. References

- [1] A. D. Covington, *“Tanning Chemistry: The Science of Leather”*. **2009**, RSC, Cambridge, UK.
- [2] P. Patnaik, *“A Comprehensive Guide to the Hazardous Properties of Chemical Substances”*. **3<sup>rd</sup> ed.** **2007**, Wiley, New York.
- [3] M. Garcia-Calzada, G. Marban, A.B. Fuertes, *Anal. Chim. Acta* **1999**, *380*, 39.
- [4] N. Batina, I. Ciglencecki, B. Cosovic, *Anal. Chim. Acta* **1992**, *267*, 157.
- [5] A. I. Vogel, J. Mendham *“A Text Book of Quantitative Inorganic Analysis”* 6th Ed. **2000**, Pearson

Education Asia, Delhi, India.

- [6] M. Barzegar, A. Jabbari, M. Esmaeili, *Bull. Korean Chem. Soc.* **2003**, *24*, 1261.
- [7] D. Tang, P. H. Santschi, *J. Chromato. A*, **2000**, *883*, 305.
- [8] D. Giovanelli, N. S. Lawrence, L. L. Jiang, T. G. J. Jones, R. G. Compton, *Sens. Actuat. B: Chemical* **2003**, *88*, 320.
- [9] W. Wardencki, *J. Chromatography. A* **1998**, *793*, 1.
- [10] E. Pretsch, *Trends in Analytical Chemistry* **2007**, *26*, 46.
- [11] S. Daunert, L. G. Bachas, *Anal. Chem.* **1990**, *62*, 1428.
- [12] M. Püntener, T. Vigassy, E. Bakker, A. Ceresa, E. Pretsch, *Anal. Chim. Acta* **2004**, *503*, 187.
- [13] R. W. Cattrall, H. Freiser, *Anal. Chem.* **1971**, *43*, 1905.
- [14] A. Michalska, *Electroanalysis*, **2012**, *24*, 1253 – 1265
- [15] R. De Marco, G. Clarke, B. Pejčić, *Electroanalysis* **2007**, *19*, 1987.
- [16] Y. L. Ma, A. Galal, H. Zimmer, H. B. Mark Jr., Z. F. Huang, P. L. Bishop, *Anal. Chim. Acta* **1994**, *289*, 21.
- [17] N. F. Atta, A. Galal, H. B. Mark Jr., T. Yu, P. L. Bishop, *Talanta* **1998**, *47*, 987.
- [18] C. Cali, G. Taillades, A. Pradel, M. Ribes, *Sens. Actuat. B* **2001**, *76*, 560.
- [19] S. S. M. Hassan, S. A. M. Marzouk, H. E. M. Sayour, *Anal. Chim. Acta*, **2002**, *466*, 47.
- [20] D. Wilson, M. N. Abbas, A. L. A. Radwan, M. Del Valle, *Sensors* **2011**, *11*, 3214.
- [21] M. G. Glaister, G. J. Moody, T. Nash, J. D. R. Thomas, *Anal. Chim. Acta* **1984**, *165*, 281.
- [22] Y. Qin, S. Peper, E. Bakker, *Electroanalysis* **2002**, *14*, 1375.
- [23] M. N. Abbas, A. A. Radwan, *Talanta* **2008**, *74*, 1113.
- [24] M. Vázquez, P. Danielsson, J. Bobacka, A. Lewenstam and A. Ivaska, *Sensors and Actuators B: Chemical* **2004**, *97*, 182.
- [25] S. M. A. Yakout, Y. A. Allam, G. A. Nawwar, *Heteroatom Chem.* **1999**, *10*, 1.
- [26] T. Fuping, W. Weicheng, J. I. Zongxuan, Y. Yongxing, C. Tianxi, L. Can, *Chinese J. Catalysis* **2005**, *9*, 734.

- 1  
2  
3  
4 [27] Z. Lu, J. Kullgren, Z. Yang, K. Hermansson, *J. Phys. Chem. C*, **2012**, *116*, 8417.  
5  
6 [28] K. B. Gudasi, S. A. Patil, R. S. Vadavi, R. V. Shenoy, M. S. Patil, *J. Serb. Chem. Soc.* **2006**, *71*  
7  
8 529.  
9  
10 [29] B. H. Stuart, “*Infrared Spectroscopy: Fundamentals and Applications*”, **2004**, John Wiley &  
11  
12 Sons, Lt, West Sussex, England  
13  
14 [30] B. Meyer, K. Ward, K. Koshlap, L. Peter, *Inorg. Chem.* **1983**, *22*, 2345.  
15  
16 [31] N. N. Greenwood, A. Earnshaw, “*Chemistry of the elements*” 2nd Edn. **1997**, Elsevier  
17  
18 Butterworth-Heinemann, Oxford.  
19  
20 [32] Y. Umezawa, “*CRC Handbook of Ion-Selective Electrodes*”, **1990**, CRC Press, Boca Raton, FL.,  
21  
22 [33] P. L. Bailey, “*Analysis with Ion-Selective Electrodes*”, **1996**, Heyden, London.,  
23  
24 [34] G. G. Guibault, R. A. Durst, M. S. Frant, H. Freiser, E. H. Hansen, T. S. Light, E. Pungor, G.  
25  
26 Rechnitz, N.M. Rice, T. J. Rohm, W. Simon, J.D.R. Thomas, *Pure Appl. Chem.* **1976**, *48*, 127.  
27  
28 [35] Y. Umezawa, K. Umezawa, H. Sato, *Pure & Appl. Chem.* **1995**, *67*, 507.  
29  
30 [36] E. Bakker, E. Pretsch, *TrAC*, **2005**, *24*, 199.  
31  
32 [37] J. Veder, R. De Marco, G. Clarke, R. Chester, A. Nelson, K. Prince, E. Pretsch, E. Bakker, *Anal.*  
33  
34 *Chem.* **2008**, *80*, 6731.  
35  
36 [38] J. D. Cline, *Limnology and Oceanography* **1968**, *14*, 454.  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

E. No.	Ionophore II, %	Equivalent to / or Ionophore I, %	Slope mV / decade	R <sup>2</sup>	Linear range Mol. L <sup>-1</sup>	LDL Mol. L <sup>-1</sup>
0	Blank	0.00	-12.99	0.7712	--	--
1	----	3.75	-24.00	0.9915	1.0X10 <sup>-6</sup> – 3.0X10 <sup>-3</sup>	7.0X10 <sup>-7</sup>
2	-----	3.75	-28.00	0.9976	7.0X10 <sup>-7</sup> – 1.0X10 <sup>-2</sup>	1.0X10 <sup>-7</sup>
3	5.0	1.5	-25.7	0.9722	2.0X10 <sup>-5</sup> – 1.0X10 <sup>-3</sup>	8.0X10 <sup>-6</sup>
4	7.5	2.25	-27.6	0.9925	1.0X10 <sup>-6</sup> – 1.0X10 <sup>-2</sup>	4.0X10 <sup>-7</sup>
5	10.0	3.00	-30.37	0.9942	1.0X10 <sup>-7</sup> – 1.0X10 <sup>-2</sup>	6.0X10 <sup>-8</sup>
6	12.5	3.75	-32.74	0.9982	7.0X10 <sup>-8</sup> – 1.0X10 <sup>-2</sup>	1.0X10 <sup>-8</sup>
7	15.0	4.5	-35.25	0.9745	2.0X10 <sup>-6</sup> – 5.0X10 <sup>-4</sup>	2.0X10 <sup>-7</sup>
8*	10.0	3.00	-28.6	0.9979	8.0X10 <sup>-8</sup> – 1.0X10 <sup>-2</sup>	3.0X10 <sup>-8</sup>
9*	12.5	3.75	-29.42	0.9974	1.0X10 <sup>-8</sup> – 1.0X10 <sup>-2</sup>	2.0X10 <sup>-9</sup>
10*	15.0	4.50	-35.6	0.9706	5.0X10 <sup>-7</sup> – 3.0X10 <sup>-4</sup>	1.0X10 <sup>-7</sup>

Table 1. Effect of the percentage of ionophore II in the membrane on the potentiometric response of

SC<sub>graphite</sub> and SC<sub>gold</sub> sulphide sensor at pH 13

-All solid contact electrodes contain PEDOT, PBDA and ionophore II.

\*All are of SC<sub>graphite</sub> type except electrodes No.: 8 - 10 are SC<sub>gold</sub> type.

- For solid contact sensors the % of ionophore I contained in ionophore II is given for comparison.

-Electrode No. 1 = CGE / ionophore I / PVC / NOPE

-Electrode No.2= SC<sub>gold</sub> / ionophore I

Table 2. Effect of pH on response of the proposed sulfide selective electrodes using CGE with free ionophore(I),  $SC_{(graphite)}$  and  $SC_{(gold)}$  configurations with attached ionophore (II) at pH 13.0 using SAOB solution.

No.	Electrode type	slope	$R^2$	Linear range ( $mol L^{-1}$ )	LDL ( $mol L^{-1}$ )
1	CGE, (I)	-24.00	0.9915	$1.0 \times 10^{-6} - 2.0 \times 10^{-3}$	$7.0 \times 10^{-7}$
6	$SC_{(graphite)}$ , (II)	-30.70	0.9936	$1.0 \times 10^{-7} - 3.0 \times 10^{-3}$	$6.0 \times 10^{-8}$
9	$SC_{(gold)}$ , (II)	-29.42	0.9972	$2.0 \times 10^{-8} - 1.0 \times 10^{-2}$	$7.0 \times 10^{-9}$

Table3. Selectivity coefficients  $\log K_{A,B}^{pot}$  &  $\log k_{A,B}^{pot}$  for the  $SC_{(graphite)}$  electrode No. 6 and  $SC_{(gold)}$  electrode No.9 sulphide sensor with free and attached ionophores measured using SSM and FIM respectively.

Interfering ion	$SC_{(graphite)free}$ SSM	$SC_{(graphite)free}$ FIM	$SC_{(graphite)attached}$ SSM	$SC_{(graphite)attached}$ FIM	$SC_{(gold)free}$ SSM	$SC_{(gold)free}$ FIM	SC (gold)attached- SSM	SC (gold)attached- FIM
Chloride	-2.11	-2.01	-3.03	-2.21	-2.37	-2.17	-3.17	-2.26
Fluoride	-3.16	-3.01	-3.60	-3.45	-3.47	-3.50	-3.84	-3.52
Iodide	-2.65	-2.40	-3.63	-2.39	-3.28	-2.44	-3.88	-2.45
Bromide	-3.68	-3.61	-4.14	-3.90	-4.01	-3.80	-4.25	-3.98
Nitrite	-3.14	-3.11	-3.48	-3.20	-3.47	-3.25	-3.61	-3.30
Nitrate	-3.55	-3.40	-3.74	-3.60	-3.69	-3.52	-3.88	-3.63
Iodate	-3.02	-2.88	-4.08	-3.18	-3.47	-3.16	-4.45	-3.24
Perchlorate	-3.35	-3.12	-3.93	-3.20	-3.54	-3.18	-4.18	-3.25
Acetate	-3.74	-2.72	-4.73	-3.05	-4.65	-2.90	-4.93	-3.15
Sulfate	-3.28	-3.05	-4.05	-3.44	-3.89	-3.35	-4.22	-3.66
Sulfite	-3.13	-3.00	-3.52	-3.20	-3.35	-3.18	-3.61	-3.27
Thiosulfate	-3.56	-3.32	-3.69	-3.52	-3.61	-3.40	-3.72	-3.67
Citrate	-3.52	-2.67	-4.27	-3.10	-4.18	-3.03	-4.38	-3.18
phosphate	-4.89	-4.47	-5.34	-4.81	-5.19	-4.75	-5.97	-4.82

Table 4. Performance characteristics of CG,  $SC_{(graphite)}$  and  $SC_{(gold)}$  sulphide selective electrodes using I (free) and II (attached) ionophores and plasticizer-free PBDA.

Electrode No.	1	2	6	9
Characteristics	CG (I)	$SC_{(gold)}$ (I)	$SC_{(graphite)}$ (II)	$SC_{(gold)}$ (II)
Lower detection limit, mol. L <sup>-1</sup>	$7 \times 10^{-7}$	$1 \times 10^{-7}$	$1 \times 10^{-8}$	$2 \times 10^{-9}$
Limit of quantification	$1 \times 10^{-6}$	$1 \times 10^{-6}$	$1 \times 10^{-7}$	$1 \times 10^{-8}$
Linear range, Mol. L <sup>-1</sup>	$1 \times 10^{-6}$ - $3 \times 10^{-3}$	$7 \times 10^{-7}$ - $1 \times 10^{-2}$	$7 \times 10^{-8}$ - $1 \times 10^{-2}$	$1 \times 10^{-8}$ - $1 \times 10^{-2}$
Slope, mV / decade	-24.0	-28.00	-32.7	-29.42
Response time, (s)	20	20	12	<10
Working pH	12	12	12	12
Life Time, (month)	1	1	4	6

Table 5. Comparison between some solid contact sulphide selective sensors and the proposed sensor

Parameter	R =17	R=18	Orion model 9616BNWP	Present work
Electro-active component	Poly(3-methylthiophene) and poly(dibenzo-18-crown-6)	Cu <sub>10</sub> -(AS <sub>2</sub> S <sub>3</sub> ) <sub>90</sub> alloy	Ag <sub>2</sub> S	Ceric complex of ABPAH *
Detection limit (mol L <sup>-1</sup> )	2.0 X10 <sup>-9</sup>	2.0 X10 <sup>-6</sup>	9.0X10 <sup>-8</sup>	1.0X10 <sup>-9</sup>
Linear range (mol L <sup>-1</sup> )	1.0X10 <sup>-7</sup> - 1.0X10 <sup>-2</sup>	2.0X10 <sup>-6</sup> - 1.0X10 <sup>-2</sup>	1.0X10 <sup>-7</sup> - 1.0	1.0X10 <sup>-8</sup> - 1.0X10 <sup>-2</sup>
Slope, (mV/ decade)	-35.7	-55.0	- 26 ± 3	-29.42
pH	1-13	3-7	13 – 14	13
Response time S	< 60	-	< 10	< 10
Interference	-	Br <sup>-</sup> , Cu (II)	Ag(I) & Hg(II) ( very high )	Not found
Measured species	HS <sup>-</sup>	HS <sup>-</sup>	S <sup>2-</sup>	S <sup>2-</sup>
Life time	3 days	>3 months	-	>6months

\*Ceric complex of [N'-Acetyl-2-(benzothiazol-2yl)-3-(3-chloro-5-metyl-4H-pyrazol-4-yl) acrylohydrazide] -covalently attached to polyacrylamide.

Table 6: Determination of sulphide ion in various environmental samples using the proposed solid contact sensor with attached ionophore

Type of Sample	FIA mg/L <sup>a</sup>	Spectrophotometry mg/L <sup>a</sup>	t- test	F-test
Pretannery solution <sup>b</sup>	250.73 ± 0.21	252.47± 0.49	0.015	0.302
Tannery solution <sup>b</sup> (containing chromium)	15.47 ± 0.25	-- --		
Ain – El sera lake (2 Km from Tannery industry)	80.33 ± 0.15	82.43 ± 0.70	0.031	0.090
Glucose and starch Company (Helwan City)	5.30 ± 0.26	6.13 ± 0.47	0.072	0.477
Nile River (~500 m from Glucose and Starch company)	1.40 ± 0.20	1.83 ± 0.31	0.120	0.600
Underground water from Ain Helwan about 1 Km from iron & and steel industries	15.47 ± 0.25	16.70 ± 0.72	0.085	0.217
Waste water from NRC main drainage tube.	123.6 ± 0.26	125.97 ± 0.21	0.0004	0.765
<sup>a</sup> (Average found concentration of three measurements, mean ±S.D.) <sup>b</sup> (Ain El-Sera leaser industry)				

**Figure Captions**

Fig.1 Chemical structure of the chelating compounds

Fig.2 UV-Vis spectra of the chelating compound and its ceric complex (Ionophore I) (a), the Ionophore (I) and its sulphide adduct measured in ethanol-water medium.

Fig. 3 IR Spectra of , (A) compound 1 and its ceric chelate (ionophore I) and (B) Ionophore I attached to PAA (Ionophore II) and PAA alone.

Fig.4 Calibration graphs of the different types of electrodes with free and attached ionophore in SOAB.

Figure 5. Effect of pH on the calibration of  $SC_{(gold)}$  sulfide-selective electrode with 12.5% attached ionophore (II) in PBDA membrane at pH 7, 9 and 13.

Fig.6 Dynamic response of the proposed  $SC_{gold}$  sulphide sensor with ionophore II (attached) for change in concentration of sulphide ions from  $7.0 \times 10^{-9}$  –  $1.0 \times 10^{-2}$  M.

Fig.7 Aqueous layer formation test: typical trace of solid contact sulphide-selective electrode when the sample solution is changed from  $1.0 \times 10^{-1}$  mol L<sup>-1</sup> Na<sub>2</sub>S to  $1 \times 10^{-1}$  mol L<sup>-1</sup> NaCl then again  $1.0 \times 10^{-1}$  mol L<sup>-1</sup> Na<sub>2</sub>S. Before the experiment the electrode was conditioned in  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> Na<sub>2</sub>S for 24 h.

Fig. 8 Schematic diagram of the flow injection manifold and homemade mini flow-cell .

solution, flow rate 12 mL min<sup>-1</sup>, volume 100 μL, SAOB medium, and coated gold electrode.

Fig.9 Effect of flow rate using  $SC_{gold}$  sensor  $10^{-3}$  mol L<sup>-1</sup> of sulfide 150 μL in SAOB, pH13

Fig.10. (a) Triplicate peaks obtained from the FI system using the proposed  $SC_{gold}$  sensor with flow rate of 12 mL min<sup>-1</sup> and a sample volume of 100 μL in SAOB medium for varying concentrations of

1  
2  
3 S<sup>2-</sup> solutions in the range of  $1.0 \times 10^{-8}$  to  $1.0 \times 10^{-2}$  mol L<sup>-1</sup>. (b) The calibration line of the solid contact  
4  
5 sulphide sensor (SC<sub>g</sub>) under the same conditions.  
6  
7  
8

9 Manuscript ID: AN-ART-03-2013-000532

10 Title: A durable solid contact sulphide sensor based on ceric acrylohydrazide ionophore attached to  
11 polyacrylamide with nanomolar detection limit

12 Authors: Abbas, Mohammed

13 Date Submitted: 16-Mar-2013  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60