

CHEMICAL SENSOR FOR THE DETERMINATION OF TOXIC SPECIES IN SOLUTION

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All solid state ion sensor based on a sensitive chalcogenide glass had been developed. The sensing membrane was characterised using electron microprobe analysis and X-ray photoelectron spectroscopy. The analytical characteristics of CdS-AgI-Ag₂S-As₂S₃ ISE were investigated and compared to the standard method for cadmium determination. The potentiometric measurements in waste waters showed a Nernstian behaviour in a large range of cadmium (II) concentration with short response time. The specific property of this sensor was the ability to detect the sulphide species.

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1. Introduction

The detection of toxic species by means of conventional analytical methods is very complicated and difficult problem. These techniques such as inductive coupled plasma are expensive and require adequate expertise. ISEs on the basis of inorganic sensor membranes are useful analytical instruments in order to determine the concentration of a specific or several components in a liquid test sample [1]. Amorphous chalcogens and chalcogenides form an important class of low-phonon-energy materials transparent in infrared region of spectra [2] with many interesting properties and applications in chemistry, medicine and ecology. This class of materials are promising membrane materials for conventional sensors because of their several advantages. The chalcogenide vitreous material makes the electrodes very robust and they do perform well where most other ion selective electrodes fail [3, 4]. These sensors are simple in construction and special conditions are not required; neither for storage, nor for the surface recovering even after continuous measurements [5, 6]. Due to these advantages chalcogenide materials became preferred membrane materials in ISE for heavy metal ions determination [7-11] instead of their crystalline analogues. Chalcogenide glass-based ISE, have been introduced by Baker and Trachtenberg in the 1970's [12, 13]. A systematic progress in term of studying the physical properties and analytical characteristics and investigating the sensing mechanism has been made [14, 16]. However, anion-selective chalcogenide membranes are less known. Bohnke [17] reported the response of a PbI₂ based sensor in iodide and sulfide solutions. In addition, Vlasov [18] studied the analytical characteristics of the glassy crystalline AgBr-Ag₂S-As₂S₃ alloys and concluded that the sensors showed a high sensitivity to bromide ion. Moreover, Cali investigated the response of Cu-As₂S₃ ISE versus sulfur species [19]. The present paper is devoted to investigations in the field of sensors with chalcogenide glass materials. Cd(II)-ion-selective electrode was created on the base of chalcogenide glass from the CdS-AgI-Ag₂S-As₂S₃ system. Electrochemical parameters of sensor have been checked and compared to a conventional Cd-ISE. The ability of the studied sensor to work on polluted sites had been checked. The very first measurements have been carried out in waste waters withdrawn from polluted sites. The

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potentiometric response of the sensor versus anion concentration in solution has been checked. The analytical parameters of the studied sensor were investigated in terms of sensitivity and reproducibility to sulphide species.

2. Experimental methods

The sensor material 4 CdS-24 AgI-47 Ag₂S-25 As₂S₃ (mol.%) were synthesized by melting the mixture of reagents (99.99 % Aldrich®) at 950 °C for 24 h in silica tubes evacuated to 10⁻⁵ Pa. Ampoule were then quenched. The homogeneity was checked by scanning electron microscopy. The XRD measurements were performed using a SEIFERT diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). An operating voltage of 40 kV and a beam current of 25 mA were selected. The bulk material composition was controlled by EDS and EPMA. A CAMECA SX100 electron probe micro-analyser employing five wavelength-dispersive spectrometers was used for chemical analysis. The experiments were made with a beam intensity of 10 nA and an accelerating voltage of 20 keV. For EPMA measurements the chalcogenide materials were cut in their middle. All the samples were then prepared by grinding with SiC papers and finally by fine polishing with Al₂O₃ suspension. XPS measurements were carried out with a Thermo Electron® spectrometer (model ESCALAB 250) using a focused monochromatised Al K α radiation ($h\nu = 1486.6\text{eV}$). The residual pressure inside the analysis chamber was ca. 5.10⁻⁸ Pa. The spectrometer was calibrated by using the photoemission lines of Au (Au4f_{7/2} = 83.9 eV, with reference to the Fermi level) the Au4f_{7/2} line, the full width at half maximum (FWHM) was 0.86 eV under the recording conditions. The peaks were recorded with constant pass energy of 50 eV. The binding energy scale was calibrated using the C1s line (284.6 eV) from the carbon contamination. Neutralization of the surface charge was performed using low energy flood gun.

Table 1. Cation concentrations of Pza and Pzb polluted solutions measured by ICP-AES.

	mg.L ⁻¹										μg.L ⁻¹				
	Al	Ba	Ca	Fe	K	Mg	Mn	Na	P	Ti	As	Cd	Co	Pb	Zn
Pza	<0.25	0.19	572	<0.075	11.3	50.8	0.93	10.2	<0.075	<0.025	51	-	-	159	789
Pzb	<0.25	<0.08	738	<0.075	22.4	66.8	1	6.33	<0.075	<0.025	121	184	49	446	38676

Electrochemical characterisation of the sensitive electrodes was performed using high impedance millivoltmeter (Radiometer Tacussel). The external reference electrode was a saturated Ag/AgCl electrode. Calibrations were performed by addition of a known volume of cadmium (II) nitrate test solutions to 100 ml of supporting electrolyte (0.1 M potassium nitrate). After calibration sensor were kept in deionised water to limit membrane ageing. Studied sensor was tested in waste waters taken on contaminated site of Aubry in the north of France. Table 1 presents cation concentrations measured by ICP-AES of Pza and Pzb polluted waters. Waste samples were filtered and kept at +4°C. To investigate the sensing property versus sulphide in solution, test solutions were prepared by successive 10-fold dilutions of 1M Na₂S-9H₂O solution by the supporting electrolyte.

3. Results and discussion

XPS analysis of the surface was undertaken in order to get information on the environment of the different elements of the sensing membrane. The composition for chalcogenide bulk membrane is similar for both surface and core. An oxygen atomic percentage has been found at the surface. No metal oxide is present in the sample. We confirmed the absence of any by-product such as AgO even on the top surface of the material. XPS measurements indicated that cadmium was present in the membrane as Cd(+II). It is shown that sulphur and silver are S(-II) and Ag(+I)

type respectively. Experimental data indicated that CdS, AgI, Ag₂S and As₂S₃ coexist at the membrane surface. The chemical composition of the membrane was checked by EDS. If it discards the foreign elements (O and C), EDS data show that the relative amount of all elements was close to the theoretical composition of the glassy matrix. Secondary, EPMA analysis was aimed at completing EDS analysis. It is demonstrated that the composition was constant throughout the depth of the bulk device. We did not identify any secondary phases using electron probe micro-analysis. The average contents of Cd, S, Ag, I and As are 1.16, 38.66, 38.13, 7.94 and 14.11. On the whole the data obtained by EPMA indicated that bulk membrane was homogeneous and was poorly contaminated.

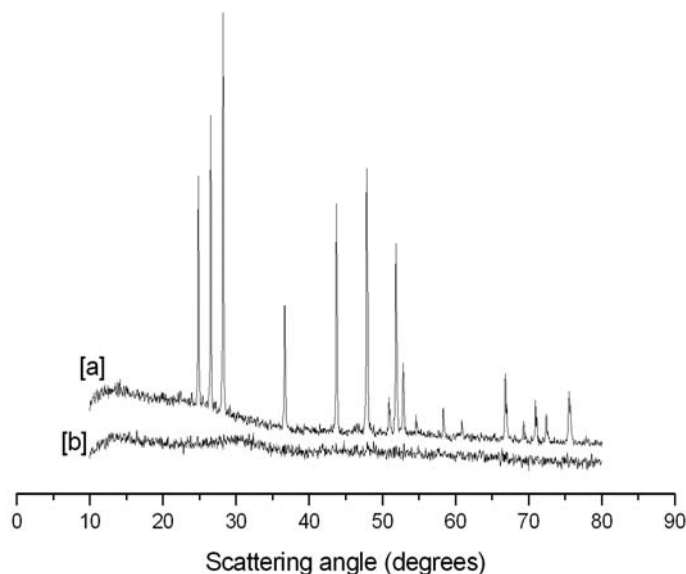


Fig. 1. X-ray diffraction patterns of CdS starting powder [a] and CdS-AgI-Ag₂S-As₂S₃ sensing membrane [b].

In addition to chemical analysis, morphological characterisation of the sample had been carried out. The material was investigated after fracture of sample. A homogeneous micro structure is observed. No pore and abnormal grains were found in all fields of view of SEM observation. The membrane does not present any defects and secondary phases. This result is in agreement with the data obtained by EPMA measurements. X-ray diffraction measurement was undertaken in order to identify crystalline phases. Fig. 1 shows the XRD patterns of the sensing membrane and starting material. X-ray data indicated no diffraction peaks confirming the amorphous character of the bulk material. To prepare electrodes, disc having few mm in thickness and a diameter of ten mm were cut from the ingot. The two faces were prepared by grinding with SiC papers and by fine polishing with Al₂O₃ suspension. A metallic layer was sputtered on one side and a wire was attached with a silver micro adhesive. Then the inner side was coated with and epoxy resin to produce a Cd(II)-ISE. Potentiometric measurements were performed on bulk membranes using silver or platinum as a metallic connection. The potentiometric response of sensors built with a platinum layer was less stable than that of sensors elaborated with a silver thin film. It is known that electrons and ions need to be exchanged at the interface metal/membrane in order to insure stable potentials. The fact that a stable potential is observed when a Ag electrode is used shows the presence of a non-null electronic conduction for the sensing device and the existence of an excellent ionic exchange at the interface Ag⁺/Ag which is not obviously the case for the interface Ag⁺/Pt. More generally an ionic bridge is not essential if the sensitive membrane is a mixed conductor and the metal of the electrode is properly chosen [20, 21]. The experimental results reported below only concern sensors built with a metallic silver contact.

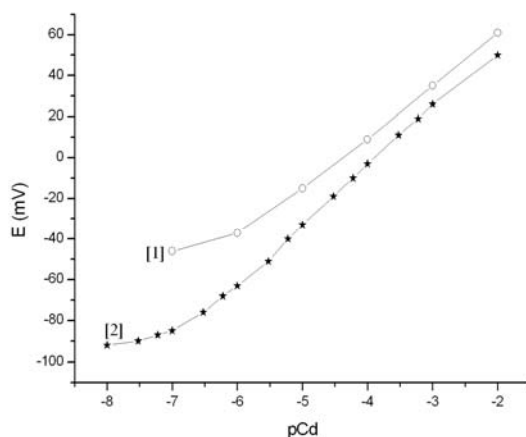


Fig. 2. Potentiometric responses of Elit 8241 electrode [1] and bulk membrane [2].

The electrochemical measurements versus Cd^{2+} were also taken with a standard method, i.e. a potentiometric titration with cadmium-selective electrode (Elit 8241 Nico 2000 Ltd). Figure 2 shows calibration curves of both bulk membrane and Elit 8241 electrode. Experimental data show a good adjustment between data from the reference method and those from the $\text{CdS-AgI-Ag}_2\text{S-As}_2\text{S}_3$ sensor. Because of the limit of sensitivity of the standard method the comparison cannot be extended beyond the concentration 10^{-6}M . As shown in figure 2, the limit of detection of the bulk membrane is close to 10^{-7}M . The sensor potentiometric response obeyed the Nernst law (1):

$$EMF = K + \frac{RT}{zF} \log[\text{Cd}^{2+}] \quad (1)$$

Where, EMF is the electromotive force (the observed potential at zero current). K is a constant potential contribution that often includes the liquid-junction potential at the reference electrode. $[\text{Cd}^{2+}]$ is the sample activity for the ion Cd^{2+} with charge z and R, T and F are the gas constant, absolute temperature and Faraday constant respectively. We note that the fresh built membrane exhibits super-Nernstian slope at low Cd^{2+} ion concentration. However, after conditioning the membrane in a $\text{Cd}(\text{NO}_3)_2$ solution the sensor characteristics became stable.

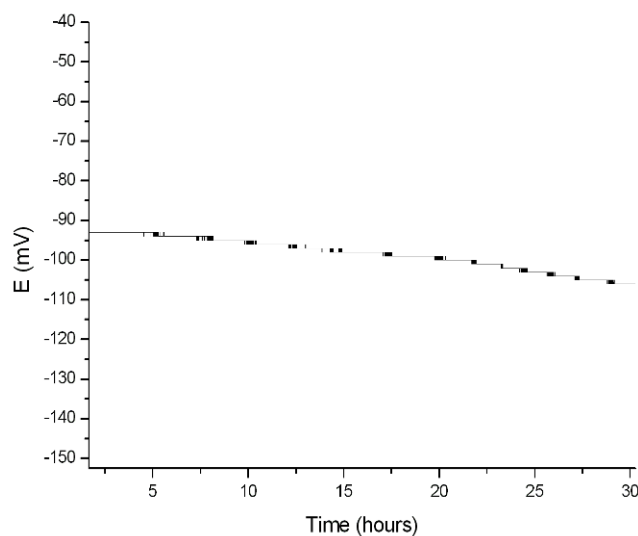


Fig. 3. Potentiometric response of the chalcogenide sensor in a solution containing 10^{-4}M Cd^{2+} ions versus time.

XPS analysis clearly shows that the chemical composition of the membrane surface is modified as soon as the membrane is soaked in cadmium (II) solution. These results point out for the presence of a “modified layer” needed for the sensor to get its sensing property. Studied electrode showed fast Cd^{2+} ion response (less than 20s). The potential of the chalcogenide glass-based sensor was found to be independent of change in pH in the range of 4 – 8. The selective electrode showed good long term stability over the period of several weeks. However, as shown in figure 3 a slight drift of about 9mV per day in absolute potential with time was observed. The selectivity of the sensor against several interfering ions as tested. High selectivity in the presence of alkali and alkaline-earth metal ions was observed, whereas the sensing device is not suitable for the detection of Cd^{2+} ion in solution containing Cu^{2+} . Exposure to cadmium (II) nitrate solution caused some millivolts change in the initial out-put signal and a slight degradation of the sensitivity behaviour. The reversibility of the Cd-ISE had been study. The sensor is sensitive to fluctuations in primary ion concentrations.

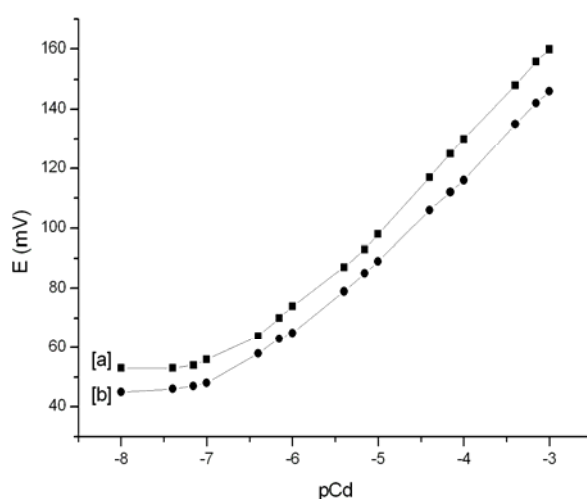


Fig. 4. Sensor out-put signal in Pza [a] and Pzb [b] samples.

It is well known that various kinds of chemical sensors are used for in-situ monitoring but only few of them can be applied for direct measurements in waste effluents. Selectivity of the majority of sensors is often poor when the determined species are present in solution simultaneously in comparable concentrations. This situation usually becomes more dramatic due to commonly low levels of concentration of heavy metals. Our goal was to check the electrochemical behaviour of the sensing devices in polluted solution. Figure 4 depicts electrode potential in waste samples containing significant amounts of calcium magnesium and zinc. The sensing material exhibits high sensitivity to cadmium in both waste samples. These results are in agreement with the good selectivity of the chalcogenide glass based sensor in presence of alkali and alkaline-earth species. Measurements in waste waters show a good reproducibility and long term stability and allow the monitoring of cadmium (II) concentrations. Since more than twenty years, chalcogenide glasses are well investigated. These materials have been mainly used for the development of ion-selective electrodes for the determination of metal cation in solution. However, anion-selective chalcogenide electrodes are less known. The potentiometric method using a conventional silver sulphide electrode is commonly used for the determination of sulphide in solution.

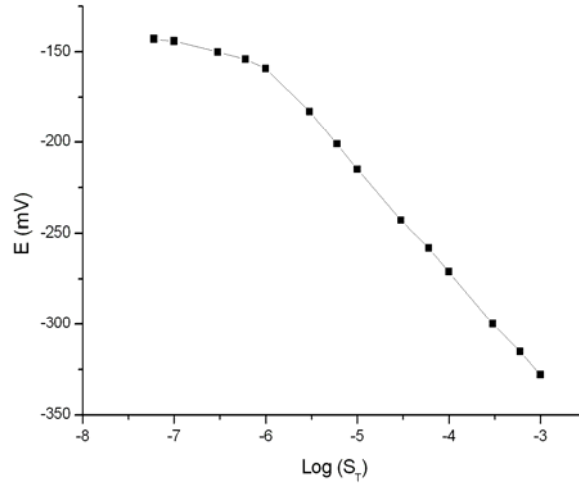
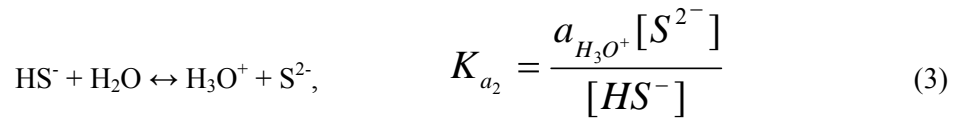
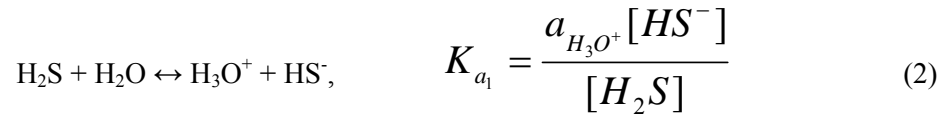


Fig. 5. Potentiometric response of the chalcogenide based sensor versus total sulphide concentration.

The analytical characteristics of CdS-AgI-Ag₂S-As₂S₃ electrode were investigated in term of sensitivity and reproducibility to sulphide species in solution. The total sulphide concentration in solution can be expressed as $S_T = [S^{2-}] + [HS^-] + [H_2S]$. According to the dissociation equilibrium of hydrogen sulphide:



The concentrations of the species can be expressed:

$$[S^{2-}] = \frac{S_T}{(1 + (a_{H_3O^+} / K_{a_1}) + ((a_{H_3O^+})^2 / K_{a_2}))} \quad (4)$$

$$[HS^-] = \frac{S_T}{(1 + (K_{a_1} / a_{H_3O^+}) + (a_{H_3O^+} / K_{a_2}))} \quad (5)$$

$$[H_2S] = \frac{S_T}{(1 + (K_{a_1} K_{a_2} / (a_{H_3O^+})^2) + (K_{a_2} / a_{H_3O^+}))} \quad (6)$$

With $pK_{a_1} = 7.0$ and $pK_{a_2} = 13.9$.

The first series of electrochemical measurements was based on the S_T variation using test solutions at $pH = 7$. As shown in figure 5 the calibrations of the bulk membrane displayed quasi-

Nernstian slopes of 58 mV/pST, which corresponds to the exchange of one electron. The sensor was tested continuously during more than one month. It remained sensitive for such a long period of time and showed high long term stability. The electrochemical behaviour of the sensing device indicated high sensitivity to total sulphide concentration with a detection limit close to 6×10^{-7} M. The second set of electrochemical measurements was based on pH modification with constant S_T . Calibrations were performed in solutions containing 10^{-2} M total sulphide. The pH of the solution was monitored by adding HCl (1M). A linear variation of potential is observed in the pH range 3-7 while the variation is nearly constant for $\text{pH} > 7$. For a given S_T , the HS^- concentration increases linearly versus pH ranging from 3 to 7 to finally reach a nearly constant value over $\text{pH} = 7$. Then, the membrane seems to be sensitive to HS^- species. These results are in agreement with the slope of calibration curve observed in figure 5.

4. Conclusions

Chalcogenide glass based on the system $\text{CdS-AgI-Ag}_2\text{S-As}_2\text{S}_3$ has been studied. The sensor electrochemical behaviour versus Cd^{2+} ion has been validated with a standard method. The very first measurements in polluted waters are promising and allow the monitoring of cadmium (II) concentrations. Moreover, the studied sensor is sensitive to sulphide concentration. The composition was constant throughout the depth of the bulk material and no abnormal morphology and secondary phases was observed.

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