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CHALCOGENIDE SENSORS FOR COPPER (II) DETECTION IN POLLUTED WATERS

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Sensors based on chalcogenide glasses for copper (II) detections have been studied. Bulk and thin film membranes exhibit a Nernstian slope in a large range of metallic ion concentration. The detection limits are close to 10^{-6} M. Electrochemical characteristics of Ion-Selective Electrodes are presented. Analytical behaviour of Cu-ISEs sensors was fully characterised in term of selectivity in presence of iron (II) species. Since the electrodes are intended to provide in situ and continuous detection of toxics species, the very first measurements have been carried out in waste waters.

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1. Introduction

The detection of heavy metal ions in aqueous solutions represents one important measurement task in the fields of environmental and industrial water analysis. Of the many analytical methods available for the waters analysis, only direct potentiometry with an ISE enables the in situ measurement of the toxic species concentrations. Since more than twenty years, chalcogenide glasses are well investigated [1-4]. One of the most promising applications of these materials is as membranes potentiometric chemical sensors, and multisensor systems, which are recently widely used for process control, environmental monitoring, industrial and sea water analyses [5]. Because of their specific properties such as their high sensitivity, their better selectivity and their excellent durability in acidic and oxidation media, chalcogenide glasses can be considered for the development of electrode for continuous and in situ determination of heavy metal ions in solution [6-8].

Jasinski et al. [9] were the first to use Cu-As-S based sensor for the determination of copper (II) ions in aqueous solutions. Latterly, Cali et al. Started new investigation of this membrane [10] and tested its sensitivity to both copper and sulphide ions. On the other hand, Baker and Trachtenberg [11, 12] were the first to use $Ge_{28}Sb_{12}Se_{60}$ glassy matrix doped with metal impurities for the determination of copper (II) and iron (III) ions in aqueous solution. Driven by these activities, Taillades et al. prepared potentiometric microsensors as well as ISFET devices with a copper-selective thin film by means of RF co-sputtering process [13, 14]. In addition, The sensor properties of the sputtered Cu[Ge-Sb-Se] thin film were studied in both potentiometric measurements and composition analysis [15]. Lately, Mear et al. report some investigations of the sensitive thin layer tested in water site conditions [16]. It is well known that different types of ion-selective chemical sensors are used for the control of the water quality but only a few of them can really be widely applied for selective direct potentiometric measurements in natural media and waste effluents. A large part of them can be used only in laboratory.

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In this paper we study Cu(II)-ISEs based on chalcogenide glasses. Various methods have been used to investigate the selectivity of bulk and thin film devices in the presence of foreign species. The ability of the sensors to provide in-situ monitoring has been checked. The very first measurements of copper (II) selective electrodes in waste waters, which are withdrawn from polluted sites, are presented.

2. Experimental methods

The $Cu_{10}(As_2S_3)_{90}$ sensor was prepared by melting the mixture of copper metal and As_2S_3 glass matrix of high purity at 950 °C for about 24 h in silica tubes evacuated to 10^{-5} Pa and further quenching in water at room temperature. To prepare electrode, a 5 mm diameter disc was cut from the bulk material. The two faces were then polished with a very fine diamond paste. A platinum layer was sputtered on one side and a wire was attached to the later with silver micro-adhesive. The deposition of the thin film was performed in a RF sputtering set-up type Alcatel DION 300. To strike the Ar-plasma the pressure was fixed to 10^{-1} mbar. A RF sputtering power of 30 W was used and the distance target-substrate was equal to 5 cm. The Cu-Ge-Sb-Se target was striking a thin copper fold (a target built by Alfa Aesar, thickness 0.1 mm, purity 99.9975%) onto a 2’’ diameter $Ge_{28}Sb_{12}Se_{60}$ target (Vitron, Gmbh, Germany). The substrate was cleaned microscope slides onto which was deposited a chromium layer of 300 nm in thickness such a metallic connection helped indeed in improving the continuity of the electrochemical chain. It also helped in increasing the adhesion of the film to the substrate. To prepare micro-sensor, a wire was attached with a silver micro adhesive on metallic films. Then, the inner side was coated with an epoxy resin.

The homogeneity and the amorphous state were checked by scanning electron microscopy (Cambridge 360) and X-ray diffraction (Seifert). Chemical analysis was performed using an energy dispersive spectroscopy probe. X-ray photo-electron spectroscopy (XPS) was used to determine the oxidation state of copper.

The electrode potential was measured with a Minisis high impedance millivoltmeter (Radiometer Tacussel). The external reference electrode was a saturated Ag/AgCl electrode used with a double junction. KNO_3 (10^{-1} M) was used as the supporting electrolyte. Tests solutions in the concentration 10^{-1} – 10^{-4} M were prepared by successive 10-fold dilutions of a 1 M $Cu(NO_3)_2$, $5H_2O$ solutions by the supporting electrolyte. Calibrations were performed in the concentration range 10^{-7} – 10^{-3} M by addition of a known volume of copper (II) nitrate test solutions to 100ml of supporting electrolyte. After calibration sensor was kept in deionised water to limit membrane ageing [6, 10].

The studied sensors were tested in waters taken on polluted sites of Alès in the south of France. Table 1 shows ion concentrations measured by Inductive Coupled Plasma (ICP-MS), pH and redox potential of PZ1, PZ2, PZ3 and PZ4 samples withdrawn from polluted sites. Waste waters were filtered and kept at +4 °C.

Table 1. Ion concentrations (mol.L^{-1}), pH and redox potential of waste waters withdrawn from contaminated sites of Alès (south of France). In sake of clarity the value of concentration X.10^{-n} is written X^{E-n}.

	Pz 1	**Pz 2**	**Pz 3**	**Pz 4**
Al	1.3^{E-6}	***weak***	***weak***	***high***
Cr	2.8^{E-7}	7.5^{E-8}	7.7^{E-8}	1.3^{E-6}
Mn	**9.8^{E-6}**	2^{E-7}	4.9^{E-6}	***high***
Co	1.5^{E-6}	1.3^{E-9}	2.8^{E-8}	6.5^{E-6}

Ni	2.3^{E-6}	2.5^{E-8}	1.6^{E-7}	**1.1^{E-5}**
Cu	**1.2^{E-7}**	**7.4^{E-9}**	**1.5^{E-8}**	**3.7^{E-5}**
Zn	2.7^{E-7}	3.1^{E-8}	3.7^{E-7}	**2.7^{E-4}**
As	2.2^{E-7}	2.5^{E-9}	1.3^{E-8}	**6.8^{E-5}**
Sr	6.8^{E-6}	**1^{E-4}**	**1.1^{E-5}**	5.5^{E-6}
Cd	2.7^{E-8}	1.6^{E-10}	1.6^{E-10}	1.6^{E-6}
Sb	1.6^{E-8}	7.3^{E-11}	9^{E-9}	1.6^{E-7}
Ba	1.5^{E-7}	1.5^{E-7}	2^{E-7}	3.4^{E-8}
Tl	5.7^{E-8}	2.6^{E-12}	2.4^{E-10}	1.4^{E-8}
Pb	1.8^{E-10}	1.1^{E-10}	2.5^{E-10}	2.1^{E-7}
Fe	**1.6^{E-4}**	**2.7^{E-6}**	**5.3^{E-5}**	**4.7^{E-5}**
pH	**7.6**	**6.7**	**7.1**	**2.6**
rH	**310**	**350**	**320**	**597**

3. Results and discussion

SEM observations and X-ray diffraction indicate that $Cu_{10}(As_2S_3)_{90}$ consist in sinnerite crystallites embedded in an amorphous matrix. The conduction of the material is predominantly electronic with a room temperature conductivity close to 10^{-2} $S.cm^{-1}$. XPS measurements indicated an atmospheric oxidation of the sulphur when the sample is in contact with air. At the membrane surface, copper surrounding area is similar to the one observed in Cu_2S. Moreover, As(III) has the same characteristics as in the reference compound As_2S_3. Data obtained by SEM and SIMS indicated that $Cu_x(Ge_{28}Sb_{12}Se_{60})_{1-x}$ layer was homogeneous with a columnar structure and a surface of good quality. Performed EDS analysis showed that the deposited films contained 40 atomic percent of copper, while the relative amount of Ge, Sb and Se was close to the one existing in the target. XPS analysis reveals that copper was present in the film as Cu (I). Cu and Ge are in a selenide environment, type Cu_2Se and $GeSe_2$ respectively. In all the case, the selenium is Se^{2-} type. All these experimental data are in agreement with previous studies [5, 10, 13, 16].

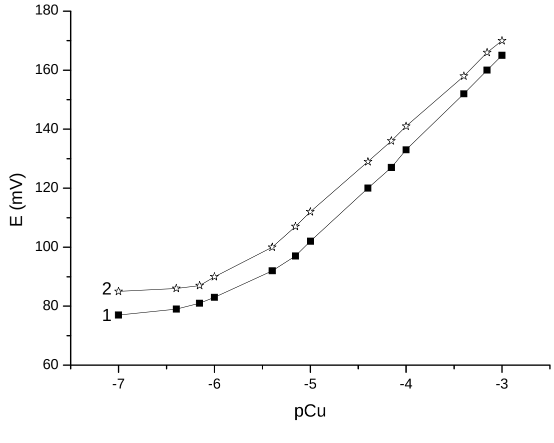


Fig. 1. Typical copper calibration curve of $Cu_{40}(Ge_{28}Sb_{12}Se_{60})_{60}$ [1] and $Cu_{10}(As_2S_3)_{90}$ [2] membranes in a copper (II) nitrate solution.

The electrodes out-put signal in copper (II) nitrate solutions with constant ionic strength (KNO_3; 10^{-1} M) are shown in figure 1. Bulk and thin film membranes were primary soaked in a copper (II) solution in order to activate them. During this conditioning period a “modified surface layer” formation, which is needed for the sensor to get its sensing property, occurs at the membrane surface. In both case, the detection limit is about 10^{-6} M, the slope S is about 30 mV/pCu and corresponds to the theoretical $S_0 = RT/2F$ in the Nernst equation (1). Studied sensors showed fast ion response (less than 10s) and good long term stability over a period of several weeks. An average of about 2 mV per day in absolute potential with time was observed for both devices.

$$E = E_0 + \frac{RT}{nF}\log\left[Cu^{2+}\right] \qquad (1)$$

where,

E_0 is the formal electrode potential;

R is the universal gas constant, equal to 8.314510 $J.K^{-1}.mol^{-1}$;

T is the temperature in Kelvin;

n is the number of electrons transferred in the half-reaction;

F is the Faraday constant (charge per a mole of electrons), equal to 9.6485309×10^4 $C.mol^{-1}$;

$[Cu^{2+}]$ is the concentration of the reducing agent (the oxidized species, Cu^{2+}).

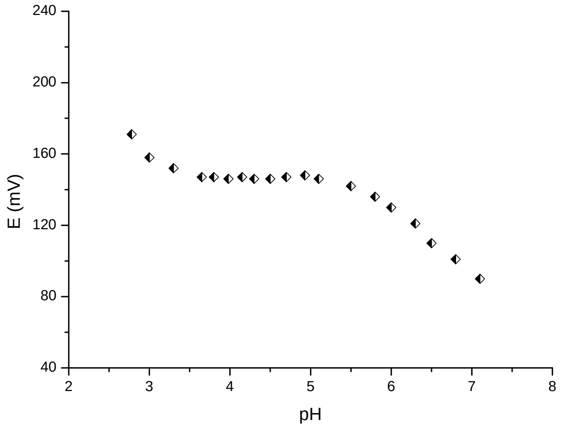
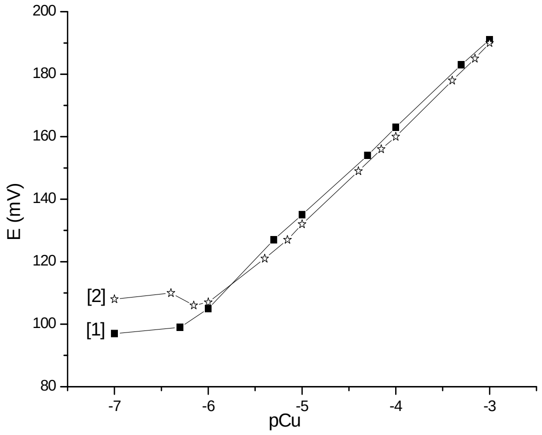
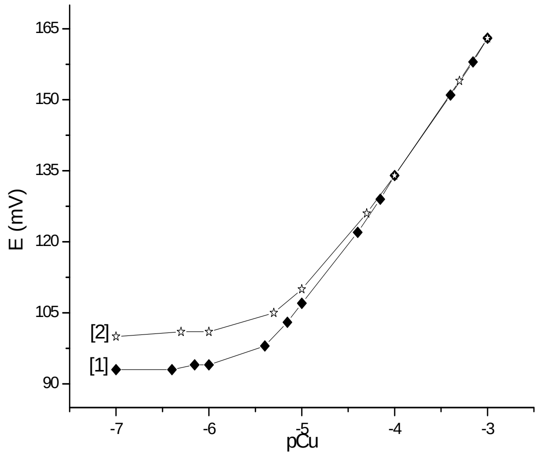


Fig. 2. The effect of pH on the response of $Cu_{40}(Ge_{28}Sb_{12}Se_{60})_{60}$ selective electrode.

The effect of the test solution pH on the $Cu_{40}(Ge_{28}Sb_{12}Se_{60})_{60}$ device response was studied in the pH range of 2-8 at 10^{-2} M Cu^{2+} ion concentration. The pH of the measured solution was adjusted by additions of nitric acid or potassium hydroxide. As can be seen in figure 2 the potential of the chalcogenide thin film does not depend on the pH at pH values from 3,5 to 5,5. The decrease in the electrode potential at higher pH is explained with the precipitation of $Cu(OH)_2$ metal hydroxide. The formation of copper hydroxide results in the decrease of copper (II) ion concentration in the measured solution, followed by the drop of the sensor potential. An increase in the values of the electrode potential, which is characteristic for the response in acidic media, is explained by the slow dissolution of the micro sensor membrane or a response to H^+ ion [17, 18]. However, to prevent membrane dissolution, short times measurements can be carried out in acidic media. These results are similar to those reported for $Cu_{10}(As_2S_3)_{90}$ material [10]. The out-put signal of this membrane does not depend on the pH in the range 3-6.



(a)



(b)

Fig. 3. Selectivity of $Cu_{10}(As_2S_3)_{90}$ electrode in a [1] no interfering ion solution and in a [2] 10^{-3} M Fe^{2+} solution (a); Selectivity of $Cu_{40}(Ge_{28}Sb_{12}Se_{60})_{60}$ electrode in a [1] no interfering ion solution and in a [2] 10^{-3} M Fe^{2+} solution (b).

The response of the $Cu_{10}(As_2S_3)_{90}$ and $Cu_{40}(Ge_{28}Sb_{12}Se_{60})_{60}$ electrodes to ions others than Cu^{2+} ions was examined. High selectivity in the presence of alkali and alkaline-earth metal ions was observed, whereas the only heavy-metal ion to interfere significantly with the sensors is Fe^{3+}. The selectivity data are comparable to those already reported for similar bulk and thin film chalcogenide ISE. Since the influence of Iron (II) species on the chalcogenide membrane responses is not well understood, we have chosen to investigate the selectivity of studied sensors in presence of Fe^{2+} ions. First of all, the responses of bulk and thin film materials to iron (II) ions were checked. Test solutions in the concentration range 10^{-1} – 10^{-4} M were prepared by successive dilutions of a 1M $Fe(SO_4)$, $7H_2O$ solution by the KNO_3 (10^{-1} M) supporting electrolyte. Calibrations were performed in the concentration range 10^{-7} – 10^{-3} M by addition of known volume of iron (II) test solutions to 100 ml of electrolyte solution. It is shown that the electrodes out-put signals are flat. Both sensing materials are not sensitive to iron (II) species because they do not give responses to variation in concentration of Fe^{2+} ions.

The total measured potential that result from the presence of interfering species in the test solution is given by Nernst equation which takes into account the selectivity coefficients (2).

$$E = E_0 + \frac{RT}{nF}\log\left[\left[Cu^{2+}\right] + \sum_{j\neq Cu^{2+}} K_{Cu^{2+},j} \times a_j^{\frac{z_{Cu^{2+}}}{z_j}}\right] \qquad (2)$$

Where,
a_j is the concentration of the interfering ion j;
$z_{Cu^{2+}(j)}$ is the charge of the primary ion Cu^{2+}, (the interfering ion j);
$K_{Cu^{2+},j}$ is the selectivity coefficient of the sensor in the presence of foreign ion j.

We used Midgley equation [19] and the fixed interference method to determine the selectivity coefficient $K_{Cu^{2+},Fe^{2+}}$. The out-put signal was then measured with solutions of constant concentration of Fe^{2+} ion (10^{-3} M) and a varying activity of the Cu^{2+} ion. Figure 3 show typical copper calibration curves in the presence of iron (II) ion. After investigations, measurements without foreign species were performed in order to check the Nernstian membranes behaviour. It can be seen from the curves that the sensors give a Nernstian response to Cu^{2+} ion in a 10^{-3} Fe^{2+} solution. According to Midgley equation, the value of $K_{Cu^{2+},Fe^{2+}}$ is close to 10^{-4} for both Cu-ISEs. This value seems interesting, since the lower the coefficient, the smaller is the influence of the interfering ion. However, the selectivity limit occurs in a 10^{-2} M Fe^{2+} solution. It is clearly evident that high selectivity is observed in solution with low concentration of iron (II) species. Moreover, studied membranes are not suitable for the detection of Cu^{2+} ion in solution with high concentration (>10^{-3} M) of Fe^{2+} ion.

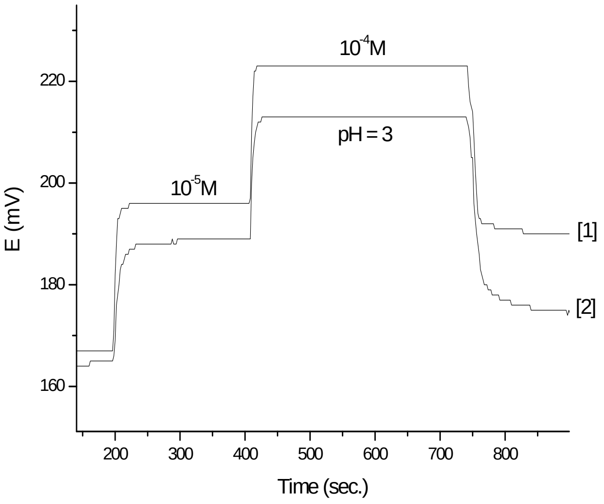
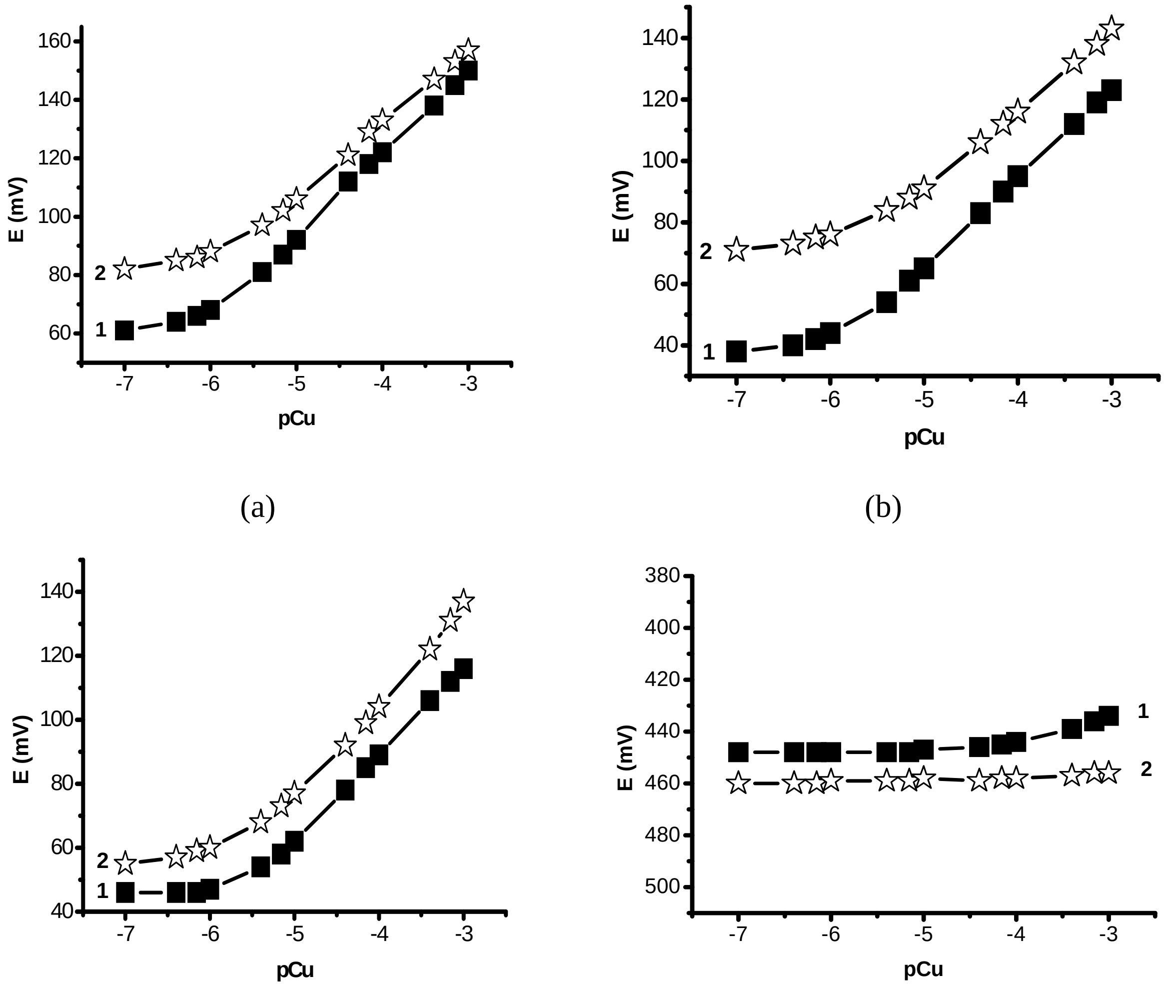


Fig. 4. The profiles of electrodes potential depending on the time and the varying Cu^{2+} concentration.

The fluctuations in heavy metal concentration can be closely related to the pumping cycles observed in polluted sites [5]. The profiles of electrodes potential depending on the time and the varying Cu^{2+} concentration have been studied (figure 4). As a matter of fact, sensors potential increase (i.e the Cu^{2+} concentration increase) by addition of a know volume of Cu (II) test solutions to supporting electrolyte. In addition, a decrease of copper concentration by $Cu(OH)_2$ formation at higher pH induce a decrease of sensor potential. The sensor was then found to return reversibly to the original lower potential. These results indicated the good sensitivity of the sensors to primary ions.



(a) (b)

(d) (c)

Fig. 5. Potentiometric response of [1] $Cu_{40}(Ge_{28}Sb_{12}Se_{60})_{60}$ and [2] $Cu_{10}(As_2S_3)_{90}$ sensors versus Cu^{2+} ion (at pH = 3) in PZ1 (a); PZ2 (b); PZ3 (c) and PZ4 waste waters.

In order to check the ability of studied sensors to provide in-situ and continuous monitoring, potentiometric measurements have been carried out in solutions withdrawn from infected sites. To avoid $Cu(OH)_2$ metal hydroxide formation the pH was adjusted to 3 by addition of KOH. Figure 5 presents corresponding calibration curves. $Cu_{10}(As_2S_3)_{90}$ and $Cu_{40}(Ge_{28}Sb_{12}Se_{60})_{60}$ electrodes exhibit Nernstian behaviours in polluted samples. Since good selectivity of chalcogenide glass based sensor is observed in presence of alkali and alkaline-earth ion, the high concentrations of strontium ion in PZ1, PZ2 and PZ3 solutions did not influence membranes responses. The electrode performed well in contaminated solutions in spite of high manganese ion concentration. This observation is in agreement with low interference of Mn (II) ion on the sensing systems response [10]. However, due to the strong ions concentration and the high redox potential, the membranes responses are flat in PZ4 polluted water. These worse out-put signals are explained with the strong alteration of the sensors surface observed by SEM after soaking in this later polluted sample.

4. Conclusions

Chalcogenide glass membranes for copper (II) detection have been studied. Sensors give a Nernstian response to metallic ions in a great range of pH after a needed conditioning period. Cu-ISEs show good selectivity to Cu^{2+} ion in presence of iron (II) species. However, the selectivity limit occurs at higher concentration of Fe^{2+} ion. The very first calibrations in polluted waters have shown the ability of the sensors to work in waste waters under suitable conditions.

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