

Continuous measurement of copper concentration in aqueous solutions with highly changing physico-chemical parameters

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Abstract. Continuous measurement of heavy metals in waste water without sampling and without adding reagents is one of the main objectives of our work. We propose to adapt the potentiometric technique so as to know the concentration of copper in solutions that reproduce the variations of waste water (T , σ , pC_{Cu}) through multiparameter measurement. We show that the measure can be extended to the hydroxyl complexation by introducing the pH in Nernst's equation. The modelisation and the results are then discussed.

Keywords. Ion Selective Electrode – Copper, heavy metals – water quality – continuous monitoring

Introduction

Laws on the environment are increasingly demanding on the quality of urban and industrial sewage rejected in the environment. One of the priorities is the control of the heavy metals content in sewage. No current solution is well adapted to the continuous monitoring of the concentration in metallic ions within a complex and uncontrolled water medium. Spectrophotometric [1] and amperometric [2] methods, although precise and selective, require sampling and are heavy to implement. Regarding practice, the ISFETs, (ion selective field effect transistor) [3], [4], have not yet fulfilled their theoretical promises. Finally, biosensors are generally hampered by too long a time response [5].

To attempt to remedy to this problem, we propose a solution that, by multiparameter measurement, allows to extend the use of specific electrodes [6] (Copper ISE in our study) to solutions presenting highly changing physico-chemical characteristics. Nernst's equation, generalized by Nickolski and Eisenman [7], shows that the potential of ISEs depends upon the concentration in primary ions and in interferent ions, the ionic strength and the medium's temperature. Our model of response correction rests on a similar law in which the ionic strength is rounded by the measure of the solution's conductivity. Its originality lies in the introduction of the pH which allows a good estimation of the copper concentration even in the presence of hydroxylated forms. The first part introduces the multiparameter measurement device and the experimental set-up used during the experimentation. In a

second part we develop and explain the design of the electrode as well as the organization of the experiment plan on which this study is based. The resulting measures of copper concentration in various situations are summarized in a last part. We especially focus on those observed with strong pH variations.

Equipment and method

Measuring set

The measuring set is constituted of five sensors: a pH-hydrogel electrode with Ag/AgCl integrated reference, a Redox potential electrode, a Cu(II) electrode, a Pt100 temperature probe, a four-poles conductivity probe. They are all placed in a specific circular support (figure 1).

The electrode operating the measurement of copper concentration has to respond to concentrations of 10^{-6} to 10^{-3} mol/dm³. In table I, we present an account of the measure's ranges and precisions.

In order to study the response of the measuring set, we have developed an experimental set-up (figure 2) which simulates physico-chemical variations of a real medium.

The main element is a reactor containing solutions, on which the measuring set is inserted. The latter is fitted with two Teflon[®] pipes connected to a pump and two mini holes enable the injection or the extraction of solutions. The

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Received April, 14, 1999; revised July, 15, 1999; accepted July, 20, 1999.

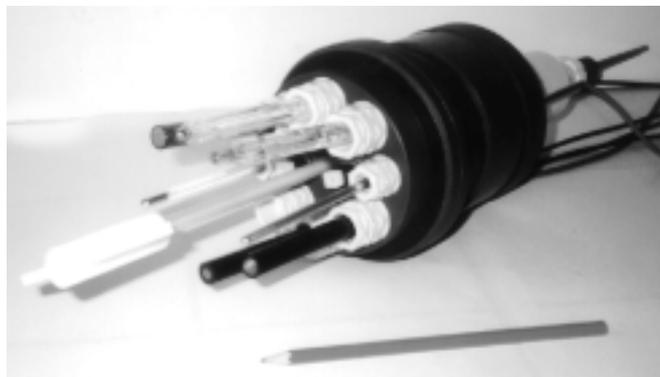


Fig. 1. Measuring set.

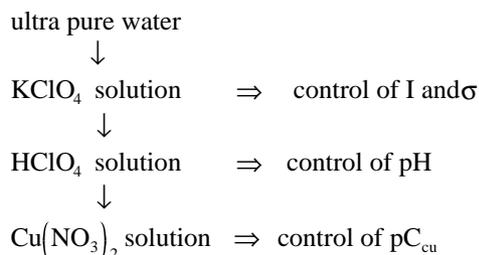
solution' concentrations in the reactor are calculated on the basis of the weight of extracted or injected solutions. The precision is better than 0.05% for mother solutions, than 0.15% for solutions diluted 10 times and than 1% for solutions diluted 100 times.

The liquid temperature is feedback-controlled by a cryostat which lets a liquid flow within the double wall of the reactor. The quality of the regulation is $0.03^{\circ}\text{C}/72$ hours with a static error of 0.5°C .

The solutions in the reactor are made homogeneous by an agitator the speed of which is set on 140 tr/min. This speed is the best compromise between the homogenisation quickness, vortex, air bubbles or whirlwinds creation and the reactor's time response in terms of temperature.

Procedure

Solutions and means to control physico-chemical parameters within the framework of our experimentations are presented below.



Instrumentation

The different probes are connected to electronic conditioner which digitises information. An acquisition (PC) and processing of data system has been developed under HP-VEE. It samples the data from the electronic conditioner through of an RS 232C multiplexor with a period of 10 s.

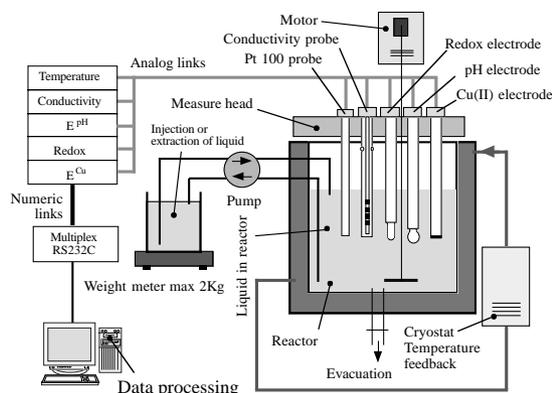


Fig. 2. Experimental set-up.

Table I. Measure ranges and precisions.

Parameters	Range	Accuracy
temperature $^{\circ}\text{C}$	5	35 $\pm 0.1^{\circ}\text{C}$
conductivity $\mu\text{S}/\text{cm}$	0	4000 $\pm 5\%$ of the measure
pH	3	10 ± 0.1 unit of pH
redox mV	-2000	2000 ± 10 mV
pC_{Cu}	6	3 not specified

The characteristics of the conductivitymeter and the precision millivoltmeter are summed up in table II.

Response study

Elaboration of the model

Our purpose is to modify Nernst's equation so as to show the influence of temperature, activity coefficient and pH.

Table II. Characteristics of the conductivitymeter and millivoltmeter.

Millivoltmeter	Range: -2 to 2V
PHM 220	Resolution: 0.1mV
Radiometer	Accuracy: +/-0.1mV
Analytical	$Z_e > 2.10^{12} \Omega$
	$I_e < 0.5 \text{ pA}$ at 25°C
Conductivitymeter	Resolution: 1/4000 of full scale
CDM210	Accuracy: 0.2% of read value
Radiometer	Freq: 2.93 kHz
Analytical	Range: 0 to 4000 $\mu\text{S}/\text{cm}$

$$E_{Cu} = E_0 + 2.3 \frac{RT}{nF} \log \left[(Cu^{2+}) + a_0 \right] \quad (1)$$

E_{Cu} is the potential of the copper specific probe
 T is the temperature in Kelvin
 (Cu^{2+}) is the activity of free copper ion
 a_0 is the detection limit of activity

We set as hypothesis that hydroxyl forms are a majority in our medium following the equation of mass below [8]:

$$|Cu^{2+}|_{tot} = |Cu^{2+}| + |CuOH^+| + |Cu(OH)_2| \quad (2)$$

$|X|$ is the concentration of X species.

(X) is the activity of X species.

$|Cu^{2+}|$ is the concentration of free copper ions

From the equilibrium equations, we express the two equilibrium constants K_1 and K_2 by supposing that they do not vary in the temperature domain.

$$K_1 = \frac{|CuOH^+|}{\gamma_1 \gamma_2 |Cu^{2+}| |OH^-|} \quad (3)$$

$$K_2 = \frac{|Cu(OH)_2|}{K_1 \gamma_1^2 \gamma_2 |Cu^{2+}| |OH^-|^2} \quad (4)$$

γ_1 is the activity coefficient of ion OH^-

γ_2 is the activity coefficient of ion Cu^{2+}

It must be considered the activity coefficient for $CuOH^+$ and $Cu(OH)_2$ is equal to 1. The concentration of $CuOH^+$ is very low and $Cu(OH)_2$ is a neutral form and principally in a separate phase.

(Cu^{2+}) is effectively measured by Cu ISE and $|Cu^{2+}|_{tot}$ is the quantity of copper we expect to measure.

From the equation of mass (2) and the equilibrium equations, we express the relation between $|Cu^{2+}|_{tot}$ and (Cu^{2+})

$$|Cu^{2+}|_{tot} = \frac{(Cu^{2+})}{\gamma_2} \left[1 + K_1 \gamma_1 \gamma_2 |OH^-| + K_1 K_2 \gamma_1^2 \gamma_2 |OH^-|^2 \right]$$

The ionic equilibrium of water is given by:

$$K_e = (H^+) (OH^-)$$

With $pH = -\log(H^+)$, we obtain:

$$(Cu^{2+}) = \frac{\gamma_2 |Cu^{2+}|_{tot}}{1 + K_e K_1 \gamma_2 10^{pH} + K_e^2 K_1 K_2 \gamma_2 10^{2pH}} \quad (5)$$

From equations (1) and (5) we can write:

$$E_{Cu} = b_0 + b_1 T \cdot \log(\gamma_2 A + b_4) \quad (6)$$

$$\text{with } A = \frac{|Cu^{2+}|_{tot}}{\left[1 + b_2 \gamma_2 10^{pH} + b_3 \gamma_2 10^{2pH} \right]}$$

The coefficients b_0 to b_4 are the parameters to identify.

The coefficient γ_2 is calculated from the ionic strength I of the solution and we propose to estimate this ionic strength from the measure of conductivity, corrected in temperature.

$$I = \frac{1}{2} \sum_i C_i z_i^2 = 7.910^{-6} \frac{\sigma_{mes} + 0.55(T_{ref} - T_{mes})}{1 + 0.017(T_{ref} - T_{mes})} \quad (7)$$

where C_i is the concentration of species i

z_i is the valence of species i

σ is the measured conductivity in $\mu S \cdot cm^{-1}$

With this equation, we can get considering the Debye-Hückel's law:

$$\gamma_2 = 10^{\frac{Bz_i^2 \sqrt{I}}{1 + D\sqrt{I}}} \approx 10^{-2\sqrt{I}} \quad (8)$$

(in the concentration range considered here)

Experimental plan

The experimental plan includes 108 measures in relation with conductivity, pH, temperature, Cu^{2+} concentration according to figure 3.

Values of concentration are linearized by the change of variable $pC = -\log(C)$.

Data from the experiment plan are represented in figure 4. They show that the hypothesis of the hydroxyl complexation is to be considered and there is no risk to have reduced form of copper. For this reason it is not necessary to include the Redox potential in calculations.

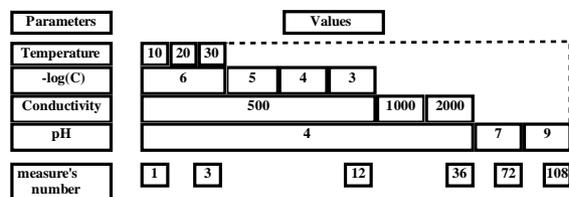


Fig. 3. Experimental plan.

Results of the modelisation

From the experimental plan, we have identified coefficients b_0 to b_4 (equation 6) by the gradient method [9]. We get:

$$\begin{aligned} b_0 &= 2.369 \cdot 10^2 \text{ mV} \\ b_1 &= 8.85 \cdot 10^{-2} \text{ mV.K}^{-1} \\ b_2 &= -1.197 \cdot 10^{-6.8} \text{ mol.kg}^{-1} \\ b_3 &= 1.6617 \cdot 10^{-13} \text{ mol.kg}^{-1} \\ b_4 &= 2 \cdot 10^{-6} \end{aligned}$$

The quality of the identification is shown in the dispersion diagram of the statistical data (figure 5).

This model gives a sensitivity of $-26.39 \text{ mV / decade}$ at 25°C . The error in the pC restitution is estimated by calculating the ratio between the standard deviation of the model's error and its sensitivity (standard deviation of pC = 0.34 decade).

Our observations show that the pH seems to be the parameter influencing the Cu ISE response most. We are going to confront our model to a copper pollution with strong pH variations.

Measure results

Presentation

The purpose here is to test our model with strong pH variations that can be met in case of pollution by sewage containing copper. Experimental conditions are specified in table III.

Results

For the different tests, we present graphs where we describe the concentration's values for the model, according to the pH value and the conductivity is fixed to $500 \mu\text{S.cm}^{-1}$.

Discussion

All the curves show that values provided by the model are exploitable but tend to overestimate the real concentration.

- pC = 3 (figure 6).
Below, our model overestimates the concentration with an error smaller than 0.5 decade.
Beyond pH 7, pC is underestimated while keeping an error smaller than 0.75 decade. At pH 7, we notice that the error is minimal and equals 0.04 decade.
- pC = 4 (figure 7).
The model overestimates the concentration with an error of at most 1 decade at pH 9.
- pC = 5 (figure 8).
Below, the restitution error remains little, smaller than 0.3 dec. Beyond pH 6.4, the model gives a concentration above the real value, which nevertheless remains exploitable.

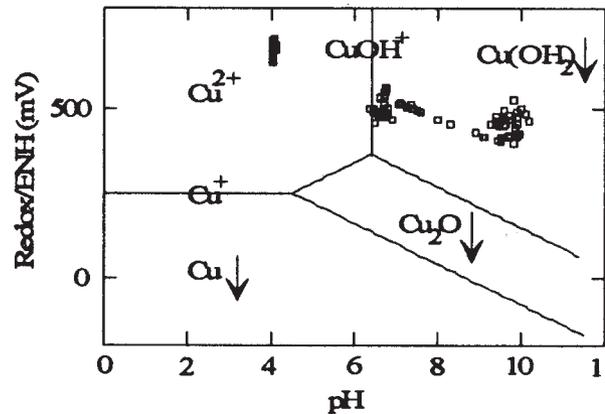


Fig. 4. Measured values in the pH-Redox plane.

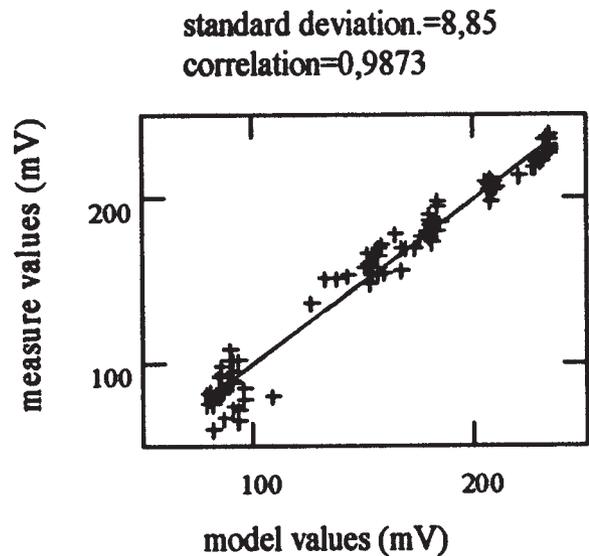


Fig. 5. Dispersion diagram.

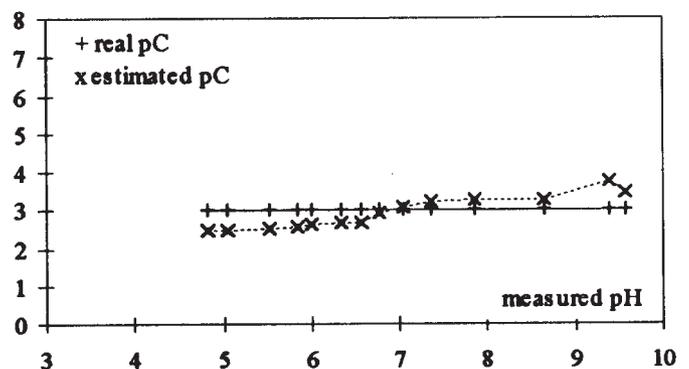


Fig. 6. pC estimated in test 1.

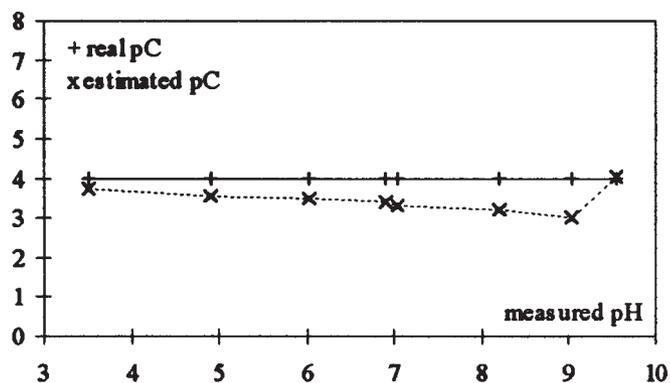


Fig. 7. pC estimated in test 2.

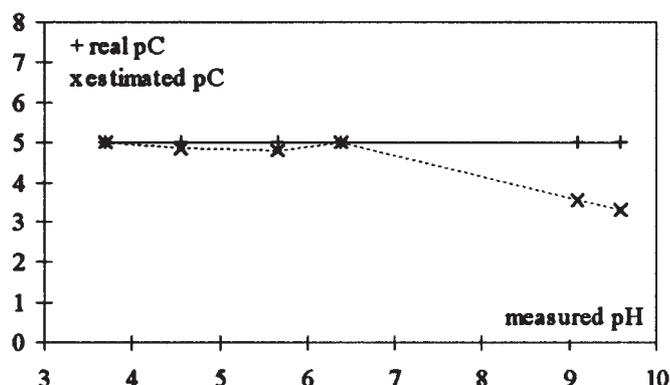


Fig. 8. pC estimated in test 3.

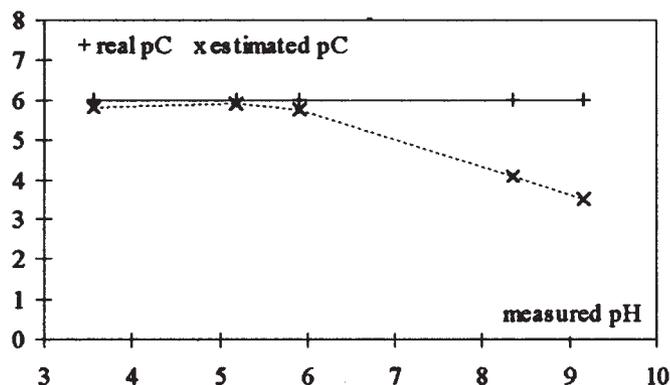


Fig. 9. pC estimated in test 4.

- pC = 6 (figure 9).

Below pH 6, the model gives values very close to the real ones (error < 0.2 decade). By extrapolation, the error at pH 7 is estimated to be 0.6 decade and beyond pH 8, values are highly overestimated (error > 1 decade).

Conclusion

We have tested the feasibility of continuous measurement of the copper concentration in a solution presenting highly changing physico-chemical characteristics, principally in terms of acidity and salinity. This measurement is possible thanks to the association of a Cu ISE, a pH electrode, a temperature sensor and a conductivity probe. The non linear model of correction is inspired from Nernst's generalized law. It merges the measures of 4 parameters and gives a concentration value with an error smaller than 0.5 pC in the 10^{-6} to 10^{-3} mol/dm³ range, for pH from 4.0 to 9.0 and for the conductivity from 400 to 2300 $\mu\text{S}\cdot\text{cm}^{-1}$. The contemplated follow-up is an extension of this method to the detection of a whole heavy metal group. In this perspective, we will have to modify the model so as to take account of correlations and interference problems between the different ions and influential parameters such as Redox potential for values below 250 mV/ENH, frequently observed in sewage water.

Finally the method is not a precise analysis but it could be used as an indication of concentration level for heavy metals in sewage water. This approach is sufficient to manage a process of treatment.

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