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RAPID LABORATORY METHOD FOR THE DETECTION OF CHLORINE IN WATER

The possibility of chlorine detection in water by using of amperometric sensor with dialysis membrane was investigated. The sensor consists of platinum cathode and silver anode, which were immersed in electrolyte whose pH was controlled. The calibration diagrams were constructed for different electrolytes and polarization potentials. The detection limit of 0.1 mg/dm³ was obtained, middle value of sensor sensitivity was approximately 14 nA/mgdm⁻³ and response time was less than 1 s for designed amperometric sensor in laboratory conditions.

All over the world chlorine and chlorine-based compounds are used for drinking water disinfection [1]. During water disinfection, chlorine reacts with organic compounds in water and different disinfection by-products are formed [2,3]. Many toxicological studies have proved that some of these compounds show carcinogenic or mutagenic effects. Due to the necessary presence of chlorine in drinking water, continuous control of its amount is preferable. This imposes the need of developing fast and inexpensive methods for its detection [4]. There are many spectrophotometric and electrochemical methods for chlorine determination. Depending on the nature of the investigated analyte, the nature of the sample and the requested sensitivity and selectivity, different electrochemical sensors may be used for environmental monitoring [5]. Most of these devices are amperometric and potentiometric sensors. By using amperometric sensors [6], one may define the current-solute concentration relationship at a fixed electrode potential, at which oxidation/reduction of the analyte occurs. The current which passes through the electrochemical cell is directly proportional to the analyte concentration.

The aim of this work was to establish the basis for a rapid, inexpensive and reliable laboratory method for chlorine detection.

EXPERIMENTAL

Sensor design

The sensor had a platinum cathode and a silver anode. The Pt cathode was a disc or it consisted of several Pt wires, which were soldered at one end with tin and embedded in epoxide resin. The anode was silver

wire. 2M KCl, saturated KCl, 1.5M LiCl with 1.5M NaCl and gel electrolyte were used as the electrolytes. The acidity of the electrolytes was controlled with potassium hydrogen phthalate buffer (pH 4). A dialysis membrane, manufactured by in "Zdravlje", Leskovac, was used to separate the electrochemical cell from the working solutions. The membrane was placed on the bottom of the sensor body (it was plastic for a sensor with a Pt disc electrode and glassy in the second case). A dialysis membrane was used because it is permeable for electroactive chlorine species [1], which are usually used as disinfection agents. A natural cellulose membrane, used in the experiments, contained OH-groups. The internal diameter of the membrane pores and wall thickness were 200 µm and 8 µm, respectively. The cross section of the sensor with a cathode consisting of several Pt wires is presented, in Fig. 1.

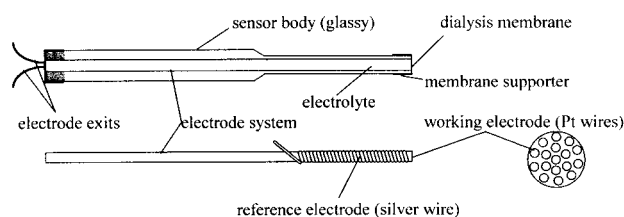


Figure 1. Cross section of the investigated amperometric sensor with a cathode consisting of several Pt wires

Solutions

Chlorine stock solutions (concentration about 10 mg/dm³) were prepared by diluting bleach (concentration of active chlorine 40 g/dm³). The standardization of these solutions was performed with 0.01M thiosulphate solution using starch as an indicator. Working solutions, in the concentration range from 0.1 to 10 mg/dm³, were prepared daily. All the reagents, except bleach, were of analytical grade. Distilled water was used to prepare the working solutions, and

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deionized water (12 M Ω) for sodium–thiosulphate standard solutions.

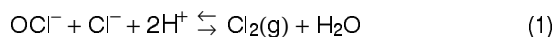
Instrumentation

A Potentiostat PA 2, Polarographic Analyzer RE 541, recorder, Servogor S and VEB MLW magnetic stirrer were used to construct the device.

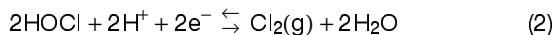
RESULTS AND DISCUSSION

The sensor was immersed into a chlorine solution of known concentration, which was constantly mixed for 20 minutes, and then rinsed and left in distilled water for 5 minutes. The electrode exits were connected to a potentiostat, which was assigned a polarization potential. The scheme of the electrochemical system is shown in Fig. 2. Output signal (current vs. time) was followed as a function of the chlorine concentration, polarization potential and elapsed time since the membrane or electrolyte were replaced.

The working solutions (pH=7) contained hypochlorous acid HOCl, the hypochlorite anion OCl⁻ and chlorine. The fraction of OCl⁻ was the largest. All of the chlorine species diffused through the dialysis membrane [1] to the electrolyte inside the sensor (pH=4). In the electrolyte, the OCl⁻ ion participated in reaction (1):



Since HOCl is unstable in acid medium, chlorine evolved according to reaction (2):



After that, chlorine was reduced on the working electrode. In order to reduce practically all the chlorine, which diffused through the dialysis membrane, the working electrode was leaned on the membrane and a thin electrolyte layer was obtained between the membrane and the electrode surface.

Replacement of the dialysis membrane and internal electrolyte was performed every 3–7 days, since the concentration of Cl⁻ ions in the electrolyte increased with time and the potential of the reference electrode varied. Calibration diagrams represented the dependence of current vs. the chlorine concentration. After membrane or electrolyte replacement, the slope of the plot changed. According to the obtained results, represented in Table 1, changes in the daily sensitivities (slope of the calibration diagram) were the least for saturated KCl.

Calibration diagrams for sensors with a Pt disc cathode and a cathode consisting of Pt wires, obtained

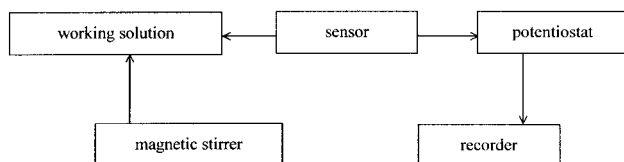


Figure 2. Scheme of the electrochemical system

Table 1. The daily sensitivities of the sensor with a Pt disc cathode for the following electrolytes: a) 2M KCl; b) saturated KCl, c) 1.5M LiCl+1.5M NaCl and d) gel electrolyte at PP=0 mV

Electrolyte	Sensitivity (nA/mg dm ⁻³)			
	a	b	c	d
1 st day	0.57	0.68	0.92	0.52

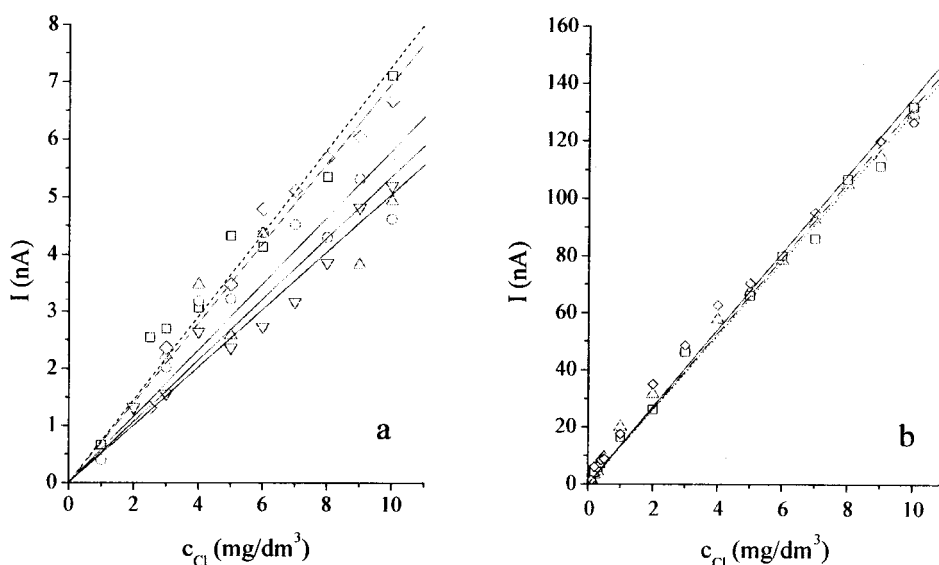


Figure 3. Calibration diagrams for sensors with a disc-shaped Pt cathode (a) and a cathode consisting of several Pt wires (b) obtained at a polarization potential of PP=-100 mV

Table 2. Heights of the output signals for sensors with a disc-shaped cathode (I^A) and a cathode consisting of several Pt wires (I^B); electrolyte: saturated KCl

c_{Cl} (mg/dm ³)	PP (mV)	I^A (nA)	I^B (nA)
0.1	-100	–	1.8
	0	–	1.3
	+100	–	1.5
0.5	-100	–	10.3
	0	–	9.1
	+100	–	8.9
1.0	-100	0.6	20.2
	0	0.6	18.2
	+100	0.6	18.8
5.0	-100	3.8	67.5
	0	3.9	61.1
	+100	3.5	63.8
10.0	-100	7.2	129.6
	0	6.9	121.0
	+100	7.2	117.1

on polarization potential PP = -100 mV for saturated KCl as electrolyte, are represented in Fig. 3. The diagrams (Fig. 3a) show mean values for current intensity vs. chlorine concentration for five membrane replacements. The slope of the plot differed because of the low reproductivity of the sensor assembly. Similar results were obtained for other polarization potentials and electrolytes. The results showed that this sensor might serve for chlorine determination, as long as a calibration diagram was made after every membrane or electrolyte replacement.

In the second case (Fig. 3b), the sensor sensitivity was improved by using several Pt wires embeded in epoxide resin as the cathode. Saturated KCl was used as the electrolyte in order to reduce the potential drop. The slope of the calibration diagrams did not alter significantly upon membrane and electrolyte replacement and better reproductivity of its assembly was achieved. The heights of the output signal for both sensors with saturated KCl as the electrolyte, are given in Table 2.

The calibration diagrams were linear in the concentration range from 1 to 10 mg/dm³ for the first and from 0.1 to 10 mg/dm³ for the second sensor, at all polarization potentials. The mean values of the first sensor sensitivities varied between 0.4 and 0.8 nA/mgdm⁻³, depending on the used electrolyte, and for the second amounted to approximately 14 nA/mgdm⁻³. These values are shown in Table 3. The detection limits amounted to 1 and 0.1 mg/dm³ for the first and for the second sensor, respectively. The response time was less than 1s.

Table 3. Dependence of the sensor sensitivities (S) on the polarization potential (PP)

Cathode shape	Electrolyte	PP (mV)	S (nA/mg dm ⁻³)	
disc	2M KCl	-100	0.53	
		+100	0.80	
		0	0.41	
	saturated KCl	-100	0.70	
		+100	0.81	
		0	0.58	
	LiCl+NaCl	+100	0.78	
		gel electrolyte	-100	0.29
			0	0.52
wires	saturated KCl	-100	13.2	
		+100	15.2	
		0	14.5	

CONCLUSION

The detection limits of the designed amperometric sensor with a Pt disc or Pt wires embedded in epoxide resin as the cathode, a Ag anode and a dialysis membrane for chlorine detection in water, observed under laboratory conditions were 1 mg/dm³ in the first and 0.1 mg/dm³ in the second case, respectively. The obtained sensitivities in the second case were good enough to apply described method for the rapid, inexpensive and reliable determination of chlorine in laboratory conditions.

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IZVOD

BRZA LABORATORIJSKA METODA ZA ODREĐIVANJE HLORA U VODI

(Naučni rad)

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U poslednjoj deceniji se poklanja sve veća pažnja razvoju hemijskih i biohemijskih senzora, koji omogućavaju da se merenja velikog broja neorganskih i organskih zagađivača vrše na terenu umesto u laboratorijama, što skraćuje vreme potrebno za analizu, snižava cenu analize, a obezbeđuje veću pouzdanost.

Ispitana je mogućnost metode za brzo određivanje hlora u vodi pomoću amperometrijskog senzora sa membranom za dijalizu. Kao katoda korišćene su Pt disk elektroda i elektroda sastavljena od nekoliko Pt žica zatopljenih u epoksidnu smolu, a kao anoda Ag žica. Na osnovu eksperimentalnih rezultata konstruisani su kalibracioni dijagrami za različite elektrolite (2M KCl, zasićeni KCl, 1,5M LiCl sa 1,5M NaCl i gel elektrolit) i različite polarizacione potencijale (-100, 0 i +100 mV). Kalibracioni dijagrami su linearni u opsegu koncentracija 0,1 do 10 mg/dm³. Određeni su granica detekcije, osetljivost i vreme odgovora senzora u laboratorijskim uslovima. Granica detekcije amperometrijskog senzora sa Pt disk elektrodom iznosila je 1 mg/dm³, dok je za drugi senzor bila 0,1 mg/dm³. Utvrđeno je da osetljivost senzora sa radnom elektrodom u obliku diska iznosi 0,7 nA/ppm, a za senzor sa radnom elektrodom sastavljenom od nekoliko Pt žica zatopljenih u epoksidnu smolu 14 nA/ppm. U oba slučaja je kao elektrolit korišćen zasićeni KCl. Vreme odgovora senzora je kraće od 1s.

Postignuta osetljivost u slučaju senzora sa radnom elektrodom sastavljenom od nekoliko Pt žica zatopljenih u epoksidnu smolu je dovoljno visoka za primenu opisanog metoda za brzo, jeftino i pouzdano određivanje hlora u laboratorijskim uslovima.

Ključne reči: Amperometrijski senzor • Membrana za dijalizu • Određivanje hlora • Voda •

Key words: Amperometric sensor • Dialysis membrane • Detection of chlorine • Water •