

HALOGEN ANALYSIS BY MEMBRANE COVERED POLAROGRAPHIC SENSORS

SHMUEL BEN-YAAKOV

Department of Electrical Engineering, Ben-Gurion University of the Negev, Beer-Sheva (Israel)

(Received 24th April 1978; in revised form 14th August 1978)

ABSTRACT

A membrane covered polarographic sensor was found to be sensitive to dissolved molecular and hydrated halogens. Sensitivity to a given species was found to be dependent on the composition of the membrane. Solid plastic membranes are permeable to dissolved molecular halogens: polyethylene to $\text{Cl}_2(\text{aq})$ and silicone rubber to $\text{I}_2(\text{aq})$. Sensors with a microporous membrane are sensitive to both molecular halogens and associated acids (HOCl and HOBr). The sensitivity threshold for a sensor with a 0.8 mm^2 cathode was found to be better than 1 ppm. A sensor with a dialysis membrane was successfully used to implement an automatic controller for maintaining a constant level of free available chlorine or free available bromine in swimming pool waters.

INTRODUCTION

Polarographic sensors which incorporate a gas permeable membrane to separate the electrochemical cell from the test solution [1] have found wide acceptance in industrial and scientific applications. The main advantage of these sensors, which are presently primarily used for dissolved oxygen analysis [2], is that they allow the isolation of the analyzed solution from the internal electrolyte of the sensor. The composition of the electrolyte of the cell can thus be fixed independently of the tested solution. This has the effect of improving stability of response and enhancing specificity by reducing interferences.

An earlier investigation by Sawyer et al. [3] demonstrated that a membrane covered polarographic sensor responds to Cl_2 , Br_2 , NO_2 , SO_2 , and HCN at partial pressures of 0.01 to 1 atm. Johnson and Edwards [4] investigated the permeability of chlorine and bromine species through microporous membranes (Polypropylene and sulfonic acid fluorocarbon) and demonstrated the feasibility of constructing a membrane covered halogen sensitive sensor. In an earlier paper Johnson [5] reported that Teflon is highly selective to Cl_2 (as compared to HOCl and OCl^-) but that the sensitivity of a polarographic sensor using Teflon membrane is rather low.

The analytical methods presently recommended for chlorine determination are based on colorimetric or amperometric titration [6]. These procedures are less convenient than methods based on a direct reading sensor [7], especially if automatic monitoring and control are desirable. Recently, Kane and Young [8] described various designs of membrane covered sensors and discussed their

application to process control. They have considered the application of a Teflon membrane to chlorine analysis but point out that the low permeability of Teflon to Cl_2 results in a low sensitivity sensor. In the study reported here, the response of a membrane covered sensor to dissolved halogens at ppm levels was investigated for various membrane films.

The primary objective of the present study was to explore the possibility of applying membrane covered polarographic sensor sensitive to both dissolved molecular chlorine $\text{Cl}_2(\text{aq})$ and hypochlorous acid HOCl . These halogen species are the most commonly used disinfecting agents [7]. Determination of these species with an electrochemical sensor can thus be useful in continuous monitoring and controlling water and waste treatment processes.

In the present study we first examined solid (non-porous) plastic membranes. It was found that two of the tested materials were highly permeable to halogens; polyethylene to chlorine and silicone rubber to iodine. The investigation revealed, however, that the transport mechanism was due to diffusion of the molecular halogen through the membrane. Hence, sensitivity to HOCl could be obtained only after acidifying the sample or using other pretreatments as discussed below. It was decided, therefore, to test a porous membrane in which the diffusion of HOCl could take place in the aqueous phase. Dialysis membranes were found to fulfil this requirement. Using this cellulose material, it was possible to construct a membrane covered sensor sensitive to both molecular and hydrated halogens. In this respect our study is complementary to the investigation of Johnson et al. By using a different membrane type we confirm their general conclusions as to the usefulness of microporous membranes for the electrochemical determination of disinfecting power.

EXPERIMENTAL

(a) Polarographic sensor

The sensor (Fig. 1) had a gold cathode and a silver anode. The disc shaped cathode had a surface area of approximately 0.8 mm^2 . Filling solution for chlorine and bromine studies was a pH 4 potassium hydrogen phthalate buffer to which 2 M KCl per liter were added. Filling solution for iodine studies was 5% KBr, 2.5% KI buffered by a pH 4 potassium hydrogen phthalate buffer.

(b) Solutions

All reagents were analytical grade. Stock solutions of chlorine were prepared by diluting a NaOCl solution (11% available free chlorine) a hundred fold. Stock solutions of bromine were prepared by dissolving 1 g of liquid Br_2 in 1 l of double distilled water. Stock solutions for iodine were prepared by dissolving 1 g iodine in 100 ml of 2.5% KI solution. Working solutions were prepared by further dilution with distilled water. Each set of measurements was carried out with the same stock solution that had been left at least overnight to stabilize. pH was adjusted by addition of 1 M HCl.

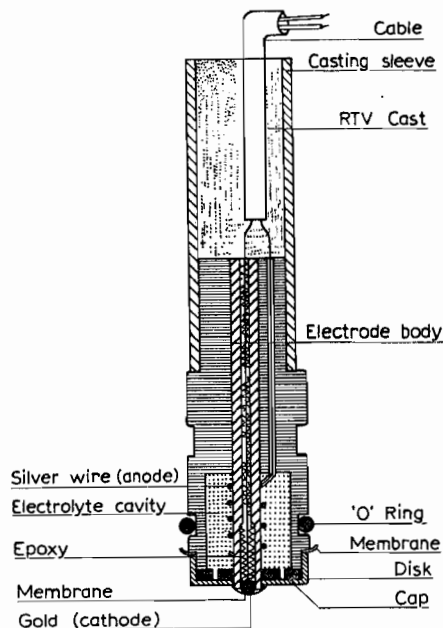


Fig. 1. Cross section of the sensor used in the study.

(c) Instrumentation

The sensor's output was fed to a current-to-voltage converter built around a CMOS operational amplifier (RCA Type CA3130). The sensor's response was monitored by a digital voltmeter connected to the output of the operational amplifier. Standard electronic test instruments were used as voltage sources, power supplied, digital voltmeters, etc. pH determinations were carried out with a glass combination electrode (Metrohm type EA120) connected to a Metrohm type E560B pH meter.

(d) Analytical procedure

All experiments were carried out in 100 ml beakers and conducted at room temperature ($25 \pm 2^\circ\text{C}$). During measurement, the sensor's head was immersed in solution which was stirred by a Teflon coated magnetic bar. pH was adjusted by HCl addition and halogen concentration was varied by pipeting stock or diluted solutions. All glassware was soaked with the working solution for at least 1 h prior to measurement.

Temperature dependence of the sensor's response was determined by controlling the temperature of a pH adjusted sample with a water bath. Once the temperature was stabilized, stock solution was added and the output of the sensor monitored.

RESULTS AND DISCUSSION

Three film membranes were studied: polyethylene ($7 \mu\text{m}$ thick), silicone rubber ($30 \mu\text{m}$ thick) and a dialysis membrane ($20 \mu\text{m}$ thick when dry). The first

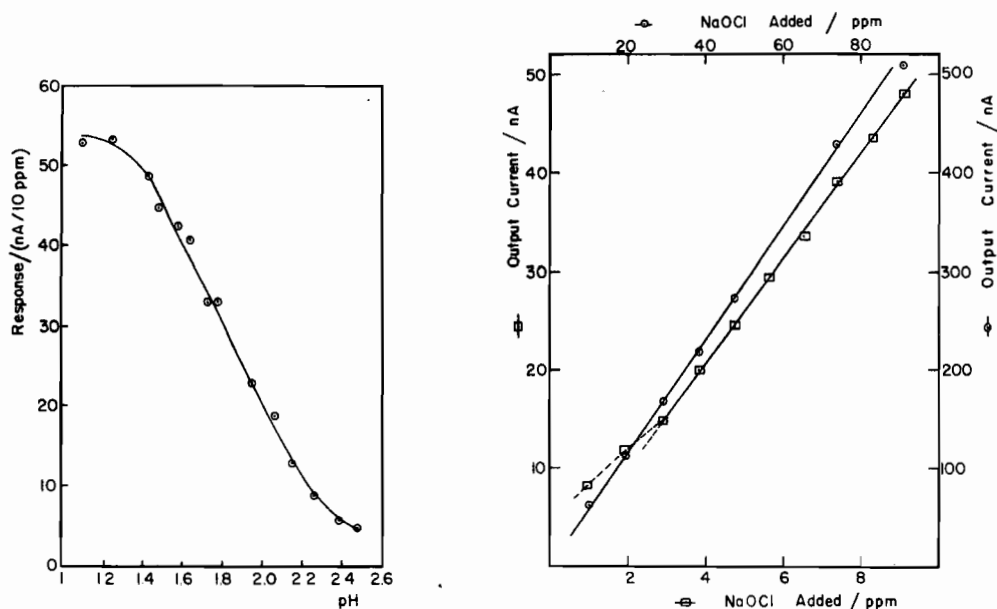


Fig. 2. Sensor's response to addition of a fixed amount of NaOCl (to make 10 ppm available chlorine) as a function of pH. pH was adjusted by HCl. Membrane: polyethylene.

Fig. 3. Linearity of response to NaOCl addition at pH 1.5. Deviation between high and low concentration curves is partially due to instrumental error and partially due to instability of chlorine solutions used for titration. Membrane: polyethylene.

two have a solid, non-porous structure whereas the dialysis membrane (Union Carbide, Ill., U.S.A.) is reported to have 2.4 nm diameter pores. It was found that each plastic membrane was highly permeable to one particular halogen: polyethylene to chlorine, and silicone rubber to iodine. The porous dialysis membrane was found to have high permeability to chlorine, bromine and iodine. The results reported here are given only for high sensitivity membrane halogen combination.

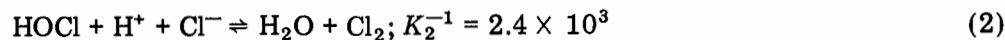
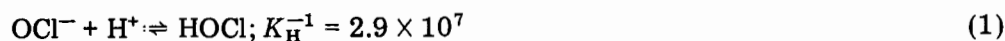
Polyethylene membrane: high sensitivity to chlorine

Output current, for a given chlorine concentration, was found to be constant to within 5% over the polarization potential range of ± 150 mV. All reported results are for a polarization potential of 0 V.

The response of the sensor was found to be pH dependent (Fig. 2). Low response was obtained for pH levels above pH 3. For a given pH, the response was found to be linear with chlorine concentration (Fig. 3) over the range 3 ppm to 100 ppm. The non-linearity of the response below 3 ppm (Fig. 3) is probably an experimental error as the sensor did not fully recover from a previous high chlorine content solution. The sensitivity of the sensor was found to be approximately $5 \mu\text{A ppm}^{-1}$ of sodium hypochlorite added or about $0.62 \mu\text{A ppm}^{-1}$ per 1 cm^2 of cathode area. Dark current was about ± 2 nA, setting the

sensitivity limit of the tested sensor to 0.3 ppm of hypochlorite added.

The pH dependence of the response of the sensor (Fig. 2) suggests that, as in the case of a Teflon membrane [7,8], a sensor with polyethylene is mainly sensitive to free dissolved $\text{Cl}_2(\text{aq})$. At low pH, hypochlorite and H^+ association will produce hypochlorous acid which will subsequently react with HCl to produce free dissolved chlorine [9,10]:



Since the solutions were acidified with HCl, reaction (2) can be rewritten in the form (assuming activity coefficient of unity):

$$[\text{Cl}_2]/[\text{HOCl}] = 2.4 \times 10^3 \times 10^{-2 \text{pH}} \quad (3)$$

It is thus evident that at low pH most of the chlorine is present in the form of dissolved molecular chlorine (Cl_2) and the data (Fig. 2) seem to support the assumption that chlorine transport through a polyethylene film is achieved by diffusion of free chlorine. This assumption can be further substantiated by calculating the expected pH dependence of the response and comparing it to the experimentally determined one. At any given pH, chlorine is distributed among the various species according to reactions (1) and (2). By simple algebraic manipulation the two reactions can be combined to yield the relationship:

$$[\text{Cl}_2] = \frac{[\text{NaOCl}]_{\text{T}}}{1 + K_2/10^{-2\text{pH}} + K_2K_{\text{H}}/10^{-3\text{pH}}} \quad (4)$$

where $[\text{NaOCl}]_{\text{T}}$ is the total hypochlorite added. At pH levels below pH 3, the last term in the denominator can be neglected and the response of the sensor (assuming it is sensitive only to Cl_2) should follow the function:

$$(1 + K_2 \times 10^{2\text{pH}})^{-1} \quad (5)$$

When the data are plotted against this function (Fig. 4) one obtains a slightly curved line. This non-linearity can probably be attributed to kinetic effects and to the dependence of activity coefficients on ionic strength [11]. If dissolved free chlorine is diffusing preferentially through the membrane, chlorine will be depleted from the solution layer adjacent to the membrane surface. Unfortunately, the magnitude of the kinetic effect can not be calculated due to the lack of relevant thermodynamic data.

The present data reveal that the permeability of polyethylene to chlorine is much higher than the permeability of Teflon. Johnson [7] reported that the sensitivity of a platinum electrode (Beckman No. 39281) equipped with a 1 mil Teflon membrane was $0.014 \mu\text{A ppm}^{-1}$ of Cl_2 . Since the area of the Beckman No. 39281 is about 1 cm^2 , the sensitivity per cathode area was $0.014 \mu\text{A ppm}^{-1} \text{ cm}^{-2}$. The thickness of polyethylene membrane used in this study was $0.7 \mu\text{m}$ and the cathode area 0.8 mm^2 . The sensitivity for 1 mil thick polyethylene membrane is calculated to be $0.172 \mu\text{A ppm}^{-1} \text{ cm}^{-2}$, i.e. more than ten times as sensitive as a sensor with a Teflon membrane.

The temperature dependence of the response was found to be exponential

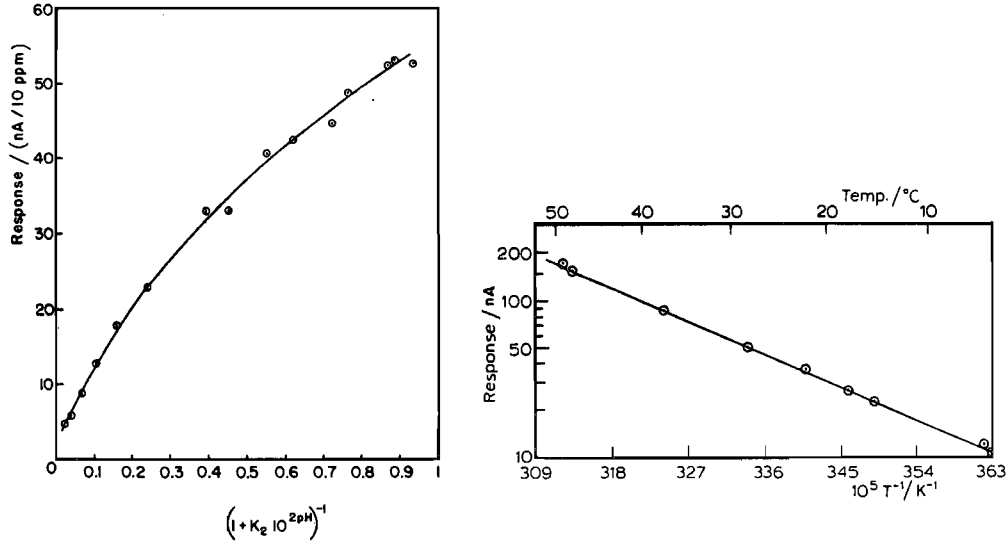


Fig. 4. Experimental (Y axis) versus theoretically expected response (X axis) assuming that the sensor responds to free dissolved chlorine $\text{Cl}_2(\text{aq})$. Same data points as in Fig. 2.

Fig. 5. Temperature dependence of response. Membrane: polyethylene.

with respect to $1/T$ (Fig. 5). It can thus be expressed as:

$$R = R_0 \exp(-B/T) \quad (6)$$

where R is the response at a given temperature T (K), and R_0 and B are constants. R_0 and B are found experimentally to be 3.67 A and $5.4 \times 10^3 \text{ K}$, respectively. The linearity and temperature dependence of the response are as expected for a sensor based on gas diffusion through a membrane [12,13]. In practical applications, the temperature effect can be compensated by a thermistor which exhibits a complementary temperature dependence [14], i.e.:

$$R = R_0 \exp(\beta/T) \quad (7)$$

In fact, automatic temperature compensation can be achieved by replacing the feedback resistor of an operational amplifier current-to-voltage converter with a thermistor chosen to comply with the relationship:

$$B = \beta \quad (8)$$

Response time of membrane covered sensors is a function of the membrane diffusivity and thickness [13]. For a $7 \mu\text{m}$ polyethylene membrane, the time taken to reach 90% of the final value is about 5 s (Fig. 6). The response time is thus comparable to the one reported for a Teflon membrane [8].

Silicone rubber membrane: high sensitivity to iodine

Unlike the case of chlorine, response to iodine was found to be practically independent of pH in the range pH 7 to pH 2. This should be expected assum-

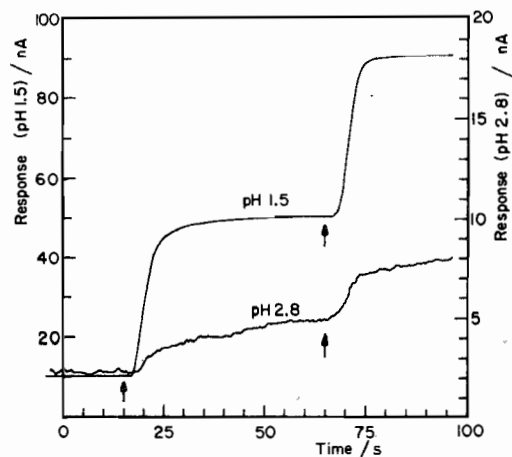


Fig. 6. Response time of sensor to addition of NaOCl at two pH levels. Arrows indicate time of NaOCl injection. Membrane: polyethylene.

ing, as before, that the mechanism of transport is by diffusion of molecular iodine. The equilibrium constant for the reaction:



is 2×10^{-3} [10]. Hence, under the present experimental conditions (pH 7 to pH 2), the reaction is driven to the left so that practically all iodine was present in molecular form over the indicated pH range.

The response of the sensor with 30 μm silicone rubber membrane was found to be linear (Fig. 7) and about $0.024 \mu\text{A ppm}^{-1}$, i.e. the relative sensitivity was about $3 \mu\text{A ppm}^{-1} \text{cm}^{-2}$ for the 30 μm thick membrane. The dark current of

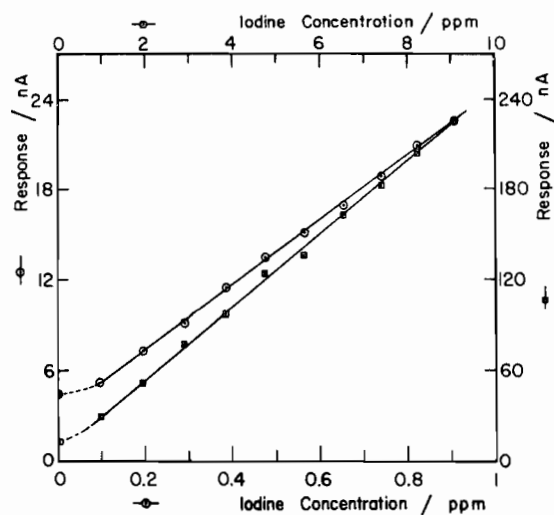


Fig. 7. Linearity of response to $I_2(\text{aq})$ addition at pH 4. A 2 nA base current is reached when the sensor is left for at least half an hour in blank solution. Membrane: silicone rubber.

the electrode was about 3 nA which corresponds to a detection threshold of about 0.1 ppm for the present sensor. The response time to reach 90% of final reading was found to be approximately 10 min, considerably slower than the response to chlorine for a polyethylene covered sensor. This should be attributed to the fact that the membrane was such thicker (30 μm) than the polyethylene membrane.

Dialysis membrane: high sensitivity to electroactive halogen species

Unlike the case of plastic membranes, both molecular and hydrated halogen will diffuse through the dialysis membrane. This was evident from the fact that the response to NaOCl addition was independent, within the experimental uncertainty, of pH for the range pH 2 to pH 7. Above pH 8 the response decrease indicating that the sensor is insensitive to OCl^- . The response was again linear with concentration (Fig. 8), with a sensitivity of about $0.006 \mu\text{A ppm}^{-1}$ of NaOCl added or about $0.75 \mu\text{A ppm}^{-1} \text{cm}^{-2}$, for chlorine. Sensitivity to bromine was found to be about 5 times higher: approximately $3.75 \mu\text{A ppm}^{-1} \text{cm}^{-2}$. The sensitivity threshold for chlorine and bromine were found to be approximately 0.1 ppm and 0.02 ppm, respectively.

The temperature dependence of the response when using a dialysis membrane was again found to be exponential with respect to $1/T$ (Fig. 9). Permeability of the dialysis membrane to molecular and hydrated chlorine and bromine, is less sensitive to temperature than the permeability of polyethylene to Cl_2 (Fig. 5). In the latter case, the response increases by about 10 fold when temperature is varied from 10°C to 50°C . This is compared to a 3.5-fold

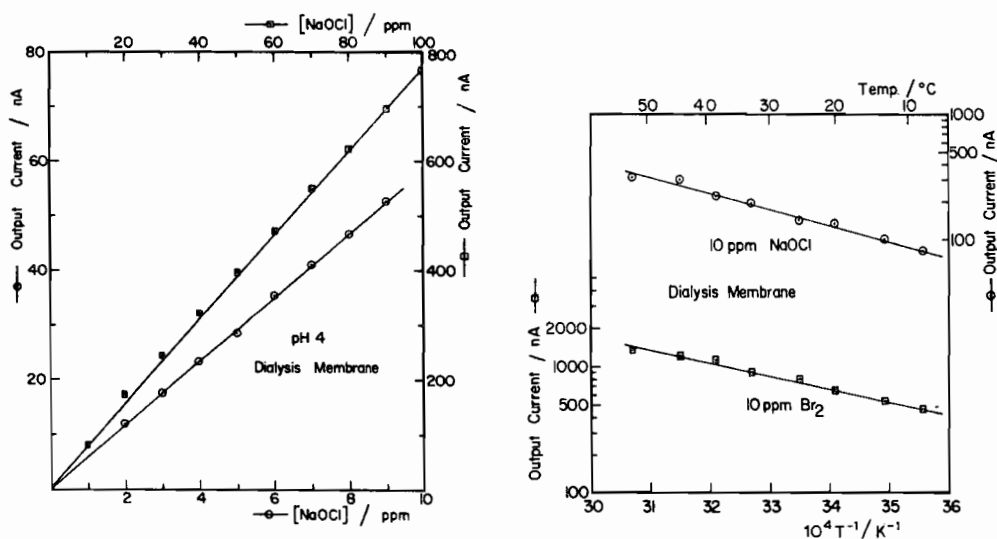


Fig. 8. Linearity of response to NaOCl addition at pH 4. Membrane: dialysis membrane.

Fig. 9. Temperature dependence of response to HOCl and HOBr, pH 4. Membrane: Dialysis membrane.

increase in response for the dialysis membrane for the same temperature range.

Sensitivity of the sensor with a dialysis membrane to the hydrated halogen should probably be attributed to the fact that diffusion, in this case, is primarily through the micropores. Unlike the case of solid plastic membranes, the micropores provide an aqueous phase path between the tested solution and the cathode surface. In this respect the cathode is exposed to the tested solution and can react with any one of the dissolved species. The function of the microporous membrane is to prevent direct mixing between the internal electrolyte and the tested solution. The Ag/AgCl anode is thus kept in a solution of constant composition which helps to maintain a constant half cell potential, independent of the composition of the tested solution. Other functions of the membrane are to protect the cathode physically from silt and dirt in solution and to control the rate of diffusion of the electroactive species. This reduces the sensitivity of the sensor to the rate of flow of the tested solution past the cathode [13].

To fulfil its function as indicated above, the microporous membrane should be hydrophilic to enable the penetration of solution into the pores. Attempts to use porous Teflon membrane were unsuccessful due to the hydrophobic nature of this material.

The sensitivity of the sensor with a dialysis membrane to hyperchlorous and hyperbromous acid could make it useful in monitoring and controlling water and waste treatment processes. The base current, i.e., the sensitivity threshold, of the sensor used in this study was about 0.5 nA which corresponds to approximately 0.1 ppm free available chlorine or 0.02 ppm free available bromine. The sensor is thus sufficiently sensitive for monitoring water and waste treatment [15]. To test its applicability, the sensor was used to construct an ON/OFF controller intended for automatic control of swimming pool feeders for chlorine (chlorinators) and bromine (brominators).

Chlorine and bromine are used for disinfecting swimming pool waters. Health authority regulations require that the level of free available chlorine or free available bromine be maintained at about 0.5 and 0.3 ppm, respectively [15].

The sensitivity of the present sensor seems, therefore, suitable for directly monitoring the level of free available chlorine or free available bromine in swimming pool waters. Automatic control of chlorinators or brominators was implemented by controlling the feeder (Ronen Ltd., Nir Zvi, Israel) with a solenoid valve. The amplified signal of the sensor was fed to a comparator which in turn activated relay, controlling the solenoid valve, whenever the concentration dropped below a pre-determined level.

The automatic system was tested in swimming pools using both bromine and chlorine treatment. The sensor was located at the input to the water circulating pump and the injector was located at the recirculating water inlet to the pool. The sensor was serviced once every two weeks at which time it was wiped clean and the internal solution and membrane were replaced. Using this system the free available chlorine/bromine was automatically maintained as tested by a commercial chlorine/bromine test kits used by the swimming pool operators. Similar systems are now being manufactured commercially (MBK Ltd., Beer-Sheva, Israel).

CONCLUSIONS

A membrane covered polarographic sensor is sensitive to better than ppm levels to both dissolved molecular and hydrated halogens. The sensitivity obtained with the present sensor is sufficient for monitoring and controlling processes such as water and waste treatment. An automatic controller for treatment of swimming pool waters was successfully constructed using a sensor covered with a dialysis membrane. The system was found to meet the health authorities requirements in maintaining a constant disinfectant level in the water.

ACKNOWLEDGEMENTS

I wish to thank Mr. Y. Sanadagi for assisting me during the experimental phase of the research. The study was supported by a research grant provided by the Ben-Gurion University of the Negev.

REFERENCES

- 1 L.C. Clark, Jr., R. Wold, D. Granger and F. Taylor, *J. Appl. Physiol.*, 6 (1953) 189.
- 2 J.P. Hoare, *The Electrochemistry of Oxygen*, Interscience, New York, 1968.
- 3 D.T. Sawyer, R.S. George and R.C. Rhodes, *Anal. Chem.*, 31 (1959) 2.
- 4 J.D. Johnson and J.W. Edwards, Paper No. 32-2, Amer. Water Works Assoc., 95th Ann. Conf. Proc., Minneapolis, June 1975.
- 5 J.D. Johnson, Proc. National Symp. Quality Standards for Natural Waters, The University of Michigan, Ann Arbor, Mich., 1966, p. 265.
- 6 A.S.T.M. Standards, Part 23, Water; Atmospheric Analysis, A.S.T.M., Philadelphia, Pa., 1972.
- 7 J.D. Johnson, Proc. Conf. on the Environ Impact of Water Chlorination, Oak Ridge National Laboratory, U.S.A., EPA, 1975, p.43.
- 8 P.O. Kane and J.M. Young, *J. Electroanal. Chem.*, 75 (1975) 255.
- 9 F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 2nd edn. 1966.
- 10 E.J. Laubusch, Physical and chemical properties of chlorine in J.J. Sconce (Ed.), *Chlorine, its Manufacture Properties and Use*, Reinhold, New York, 1962.
- 11 H.S. Harned and B.B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold, New York, 3rd edn., 1958.
- 12 A. Lebovits, *Modern Plastics*, 43 (1966) 139.
- 13 K.H. Mancy, D.A. Okun and C.N. Reilley, *J. Electroanal. Chem.*, 4 (1962) 65.
- 14 Fenwal Electronics, *Thermistor Manual*, Fenwal Electronics Inc., Farmingham, Mass.
- 15 J.A. Salvato, Jr., *Environmental Engineering and Sanitation*, Wiley-Interscience, New York, 2nd ed., 1972.