

Determination of ClO_2 Using ClO_2 Selective Electrode

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A voltammetric membrane electrode is applied to the measurement of ClO_2 . The electrode can detect ClO_2 below 10 ppb in aqueous solution, and linearly responds to ClO_2 ranging in concentration from 20 ppb to 100 ppm.

As an alternative of chlorine, ClO_2 has attracted much attention in water treatment.^{1, 2)} In Japan, ClO_2 has recently been permitted to be used as a disinfectant for pool water, and it has been proposed to limit the residual level of ClO_2 in pool water to 0.4 ppm. Therefore, it is an important requisite to determine a low level of ClO_2 routinely.

The authors have previously reported a simple, selective and sensitive analysis of ClO_2 using a voltammetric membrane electrode (ClO_2 electrode).^{3, 4)} It consists of a gold working electrode, a silver counter electrode, and a gas permiable membrane ($8\mu\text{m}$ thick) made of polymeric tetrafluoroethylene. A mixed solution of 0.1 M KCl and 0.1 M HCl is used as a supporting electrolyte. An applied potential on the working electrode vs. the counter electrode is maintained at 300 mV. The electrochemical reactions on the working and the counter electrodes are as follows.⁵⁾

working electrode : $\text{ClO}_2 + 4\text{H}^+ + 5\text{e}^- \rightarrow \text{Cl}^- + 2\text{H}_2\text{O}$

counter electrode : $\text{Ag} + \text{Cl}^- \rightarrow \text{AgCl} + \text{e}^-$

A commercial model of this electrode can be purchased from TOA Electronics Ltd. as a TOA CLO-20.

In this paper, characteristics of this electrode are described.

A stock solution of ClO_2 was prepared by absorption of ClO_2 gas in water, which was generated by acidification of NaClO_2 solution. Standardization of ClO_2 was carried out by iodometric titration just before use. The electrode response was calibrated with 100 ppm ClO_2 solution. The electrode was set in a flask filled with a standardized

analyse and to standardize ClO_2 .^{8,9)} The electrode responses and absorbances of ClO_2 in the range of 1 to 65 ppm have a good linear relationship, and its coefficient of correlation is 0.9998. By spectrophotometry, the determination of ClO_2 below 1 ppm (0.015 mM) would be difficult because of its poor sensitivity. The electrode method is sensitive to two orders of magnitude over the spectrophotometry.

Table 1 shows the electrode responses of several inorganic ions without or with 1 ppm ClO_2 . Chloride, bromide, nitrate, phosphate, sulfate, chlorate, sodium, potassium, magnesium at concentration of 1000 ppm showed no response to the electrode and no interference on the determination of ClO_2 . Recoveries of ClO_2 in mixed solutions with these ions ranged from 95.0 to 101.3%. These results suggest that ClO_2 in a solution with high ionic strength such as sea water or industrial waste water could be determined using this electrode.

On the other hand, ClO_2 electrode responds to chlorite and chlorine. The mixed solutions of ClO_2 and chlorite or chlorine show combined values of each response. Nevertheless, the response of the electrode to chlorite is estimated to be below 0.01% of ClO_2 at the same concentration, therefore, chlorite would not give a serious error. On the contrary, the electrode shows considerable response to chlorine.

Table 1. Electrode responses of various inorganic ions

Ionic specie ^{a)} (Conc./ppm)	Electrode response/ppm		Recovery of ClO_2 /%
	without ClO_2	with ClO_2	
—	0.005	1.017	100.0
Cl^- (1000)	0.006	0.989	97.1
Br^- (1000)	0.004	0.973	95.8
NO_3^- (1000)	0.004	1.002	98.6
HPO_4^{2-} (1000)	0.004	0.968	95.3
SO_4^{2-} (1000)	0.003	0.974	95.9
ClO_2^- (1000)	0.071	1.064	97.6
ClO_3^- (1000)	0.003	1.028	101.3
Na^+ (1000)	0.004	0.991	97.5
K^+ (1000)	0.004	0.973	95.8
Mg^{2+} (1000)	0.005	1.023	100.6
Ca^{2+} (1000)	0.003	0.964	95.0
Cl_2 (100)	1.068	2.008	92.9

a) All anions were sodium salts, and cations were chloride salts.

ClO_2 solution or a test solution stirred at a constant rate. The flask was shielded from light with aluminium foil and capped with an O-ring made from silicon gum. Between runs, the electrode was kept polarized and stored in purified water. All measurements were carried out at room temperature. Under the conditions, the electrode achieved a 90% response within 20 seconds.

As shown in Fig. 1, the electrode responds linearly to ClO_2 in the range of 20 ppb to 100 ppm. Below 20 ppb, ClO_2 found by the electrode was less than added, but the electrode could detect 2 ppb ClO_2 . A voltammetric membrane electrode using three electrode system has been reported by Kolar and Mancy,⁵⁾ but our two electrode system is more sensitive than that by two orders of magnitude. Our electrode is not so sensitive compared to several others described in literature,^{6, 7)} but applicable enough to monitor ClO_2 in pool water. Its wide dynamic range would be useful for direct determination of ClO_2 , which is favorable to determine ClO_2 at the site of use. Means \pm standard deviations of responses for 1.0 and 100 ppm of ClO_2 from five measurements were 0.98 ± 0.02 and 102.7 ± 0.6 ppm, and their coefficients of variations were 2.0 and 0.6%, respectively.

Accuracy of ClO_2 electrode method was investigated by comparison with spectrophotometric method. A maximum absorbance at 357 nm of ClO_2 (its molar absorption coefficient is $1250 \text{ M}^{-1}\text{cm}^{-1}$) has been used to

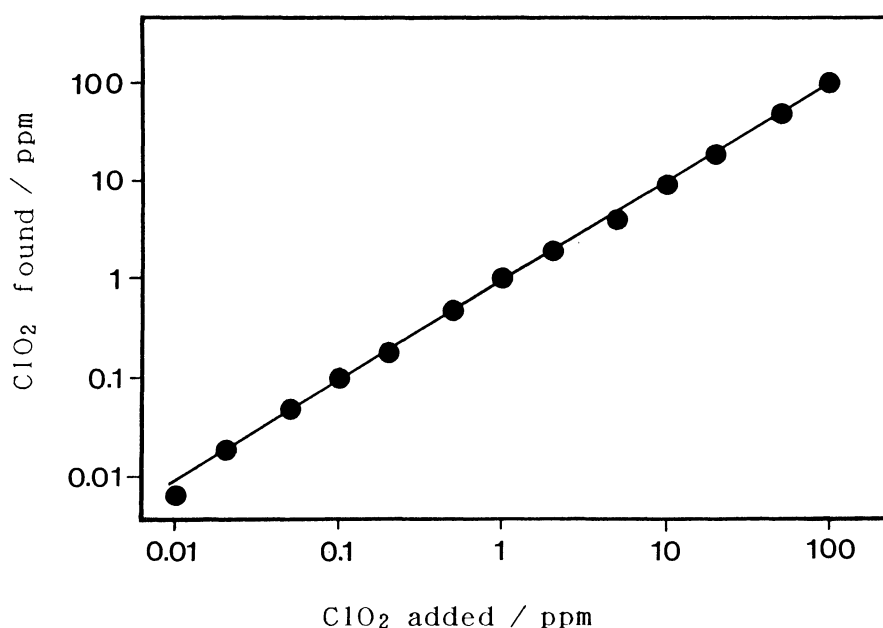


Fig. 1. Calibration curve for ClO_2 .

The response of 100 ppm chlorine corresponds to 1 ppm ClO_2 . The attempt to decrease interference from chlorine will be reported in our following report.

The ClO_2 electrode described here is portable and its operation is very simple. It is sensitive enough to measure ClO_2 at sub-ppm levels, and is not effected by inorganic ions commonly found in natural water. Moreover, it does not need any other reagents. These advantages would make the electrode method suitable for practical use in the determination of ClO_2 in fields, and for the automated monitoring of ClO_2 .

References

- 1) E. M. Aieta and J. D. Berg, *J. Am. Water Works Assoc.*, **78**, 62 (1986).
- 2) B. W. Lykins, Jr. and M. H. Griese, *J. Am. Water Works Assoc.*, **78**, 88 (1986).
- 3) E. Furuya, R. Motohashi, T. Taguchi, M. Ishida, and K. Oikawa, *Proc. of 38th Symp. of The Jpn. Soc. for Anal. Chem., Sendai, Jpn.*, 1989, 199.
- 4) E. Furuya, R. Motohasi, and K. Oikawa, *Proc. of 38th Symp. of The Jpn. Soc. for Anal. Chem., Sendai, Jpn.*, 1989, 245.
- 5) R. Dormand-Herrera and K. H. Mancy, *Anal. Lett.*, **13**, 561 (1980).
- 6) T. Watanabe, C. Lin, S. Chen, Y. Yoshimura, K. Uchiyama, K. Ohsawa, K. Imaeda, Y. Ohtani, and K. Tamura, *Bunseki Kagaku*, **40**, 373 (1991).
- 7) K. Imaeda, T. Watanabe, M. Tanaka, Y. Yoshimura, K. Uchiyama, and K. Ohsawa, *Bunseki Kagaku*, **39**, T121 (1990).
- 8) W. J. Masschlelein, "Chlorine Dioxide: Chemistry and Environmental Impact of Oxychlorine Compounds," Ann Arbor Science, MI (1979).
- 9) J. J. Kolar and B. O. Lindgren, *Tappi J.*, **67**, 89 (1984).

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