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Effect of Dimethylsulfoxide as a Masking Agent for Chlorine in the Selective Determination of Aqueous Chlorine Dioxide

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For the selective determination of aqueous chlorine dioxide(ClO_2) in the mixed solution with chlorine, dimethylsulfoxide(DMSO) was used as a masking agent for chlorine. In spectrophotometric and iodometric determination of ClO_2, a large excess of DMSO did not affect on ClO_2, but it completely depressed the interference from chlorine.

Selective determination of aqueous ClO_2 are often interfered from other oxychlorines with various degrees. In most cases, chlorine(Cl_2, HClO and ClO^-) is the most common and serious interfering substance,1-6) because a useful and practical masking agent for chlorine has rarely been known. The authors have been investigating the determination of ClO_2 using a voltammetric membrane electrode.7) In these investigations, we have observed that DMSO selectively affects on chlorine without any effects on ClO_2. In this paper, the effect of DMSO as a masking agent for chlorine is discussed.

Aqueous solutions of ClO_2 and Cl_2 were prepared by absorption of gaseous ClO_2 and Cl_2 generated by acidification of $NaClO_2$ and NaClO solutions, respectively. These solutions were shielded from light and kept in a refrigerator. ClO_2 and Cl_2 in stock solutions were standardized by iodometric titration just before use.

In spectrophotometric determination of aqueous ClO_2, chlorine is the only interfering chlorine substance. At the absorption maximum wavelength of ClO_2(357 nm), absorbance of Cl_2 is much smaller than that of ClO_2, but a large excess of Cl_2 would give a serious error. To decrease the interference from chlorine, sulfamic acid has been added to a mixed solution of ClO_2 and Cl_2.3) Sulfamic acid selectively reacts with Cl_2 to form chlorosulfamic acid which is less interfering than Cl_2. But chlorosulfamic acid also shows a small absorbance at 357 nm.

DMSO is superior to sulfamic acid as a masking agent for chlorine in spectrophotometry. As shown in Fig.1(A), absorption of Cl_2 disappears in the presence of DMSO, and the spectrum of a mixed solution of Cl_2 and DMSO agrees with that of DMSO. The same result was obtained for 1 mM (1 mM = 1×10^{-3} moldm^{-3}) NaClO. The pHs of solutions of 5 mM Cl_2 and 1 mM NaClO were 3.1, and 11.5, respectively, and these values did not change by the addition of 50 mM DMSO. These results suggest that DMSO selectively reacts with chlorine in wide pH range and it converts chlorine to a compound not absorbing at around the wavelength used to determine ClO_2. On the other hand, as shown in Fig.1(B), the spectrum of ClO_2 showed no change in its absorption maximum nor its absorbance by the addition of DMSO in the concentration of 100 times. It did not change 2 h after preparation.

Effect of DMSO on iodometric titration of these oxychlorines were also studied. Iodometric titration has been used as a standard method to determine ClO_2, chlorine, chlorite and chlorate in their mixed solution under

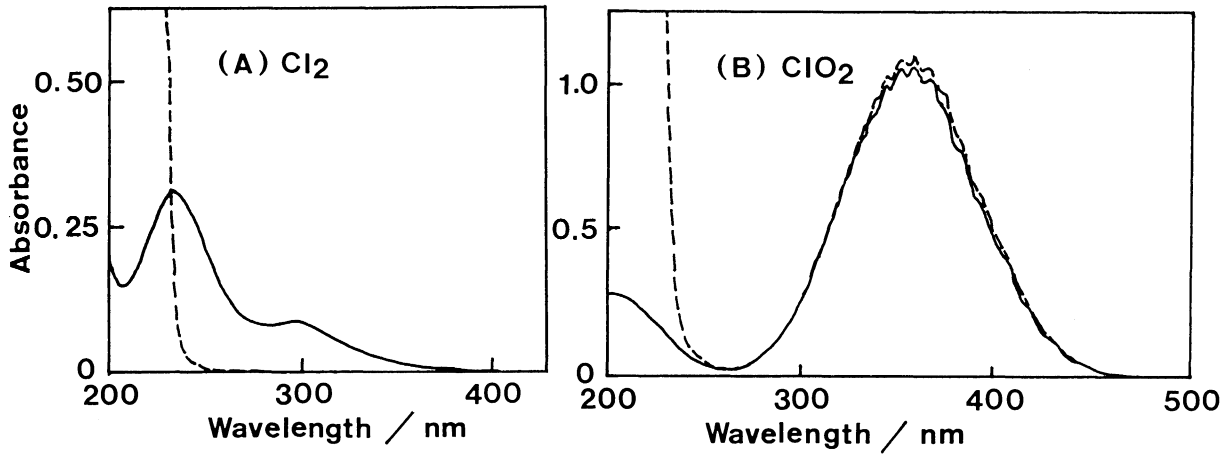

Fig.1. Spectra of of Cl_2 and ClO_2 in the absence(———) or the presence(– – – –)of DMSO
Concentration of each compound : (A) Cl_2 = 5 mM, DMSO = 50 mM ;
(B) ClO_2 = 1 mM, DMSO = 100 mM.

strict control of reaction pH.[1,2] Sulfamic acid can not be used as a masking agent for chlorine in iodomerty, because chlorosulfamic acid also interferes with the determination of ClO_2.

In this paper, iodometric titration was carried out at around pH 2 adjusted by the addition of 1.8 M H_2SO_4 solution. At this pH, both of ClO_2 and chlorine are reduced to chloride by iodide. The reaction of Cl_2 and DMSO was very fast, but that of NaClO and DMSO seemed to proceed slowly. Therefore, all solutions tested were stood for 10 min before titration.

Table 1 indicates that the oxidation of iodide does not occur in a mixed solution of DMSO and Cl_2 or NaClO. But for ClO_2, the consumption of 50 mM $Na_2S_2O_3$ solution did not change by the addition of DMSO. A mixed solution of ClO_2 and Cl_2 shows a larger consumption than that of ClO_2 solution, but by the addition of DMSO, it decreased to the same level to ClO_2 solution. Therefore, it was confirmed that, in iodometric titration, DMSO does not disturb the determination of ClO_2, but it completely masks chlorine.

As described above, by the reaction with DMSO, chlorine would be converted into a compound which does not absorb in an UV range and does not oxidize iodide.

The reaction products of DMSO and chlorine have been investigated by ion chromatographic analysis with conductivity detection. Apparatus and analytical conditions were as follows: ion chromatograph, a DIONEX 4500i with an anion membrane suppressor DIONEX AMMS-II ; columns, DIONEX AG-4A +AS-4A; eluent, 1.7 mM $NaHCO_3$ - 1.8 mM Na_2CO_3; flow rate, 1.0 ml/min; suppressor solution, 12.5 mM H_2SO_4. In these conditions, hypochlorite ion or ClO_2 can not be detected by conductometry.

Table 2 summarizes concentrations of recovered chloride ion in the solutions of Cl_2 and NaClO in the absence or the presence of DMSO or Na_2SO_3. The concentration of chloride ion obtained by the injection of Cl_2 solution markedly elevated in the presence of DMSO, and it was equal to that of chloride solution injected after the reduction of Cl_2 with Na_2SO_3. NaClO gave the same result as Cl_2. The peak height of chloride obtained by the injection of NaCl solution was not affected by the addition of DMSO or Na_2SO_3.

These results suggest DMSO would reduce chlorine to chloride ion similarly to Na_2SO_3. As described in Table 2, in the presence of DMSO, one mole of Cl_2 or NaClO which originally contained equal mole of NaCl

Table 1. Effect of DMSO on iodometric titration of oxychlorines

Oxychlorine [a)] (10.0 ml)	$Na_2S_2O_3$ consumption / ml [b)] Control	 + 500 mM DMSO
ClO_2	23.69 ± 0.33	23.74 ± 0.21
Cl_2	8.04 ± 0.23	0.01 ± 0.01
NaClO	10.12 ± 0.07	0.04 ± 0.01
$ClO_2 + Cl_2$	32.82 ± 0.41	23.60 ± 0.28

a) Concentration of each oxychlorine was about 50 mM.

b) $Na_2S_2O_3$ consumption is shown as mean ± standard deviation of five times titrations.

was recovered as two moles of chloride ion. An intermediate, such as adduct of a chlorine atom to DMSO, or oxidization product of DMSO may be present in the mixed solution of DMSO and chlorine, but they do not affect on analysis of ClO_2 in spectrophotometry nor in iodometry.

Such compounds as oxalate, malonate, and thioacetamide have been used as masking agents for chlorine in the selective determination of ClO_2,[2,8)] but they also react with ClO_2 more or less. Thus, the use of these agents has been limited in a kinetic-based analytical method.

On the contrary, DMSO reacts with only chlorine and does not interfere with the determination of ClO_2. Moreover, DMSO freely dissolves in water, and it does not need a large excess concentration to chlorine as shown in Table 2. These characteristics of DMSO would be very favorable as a masking agent for chlorine in the analysis of ClO_2 using various methods.

The effect of DMSO on other oxychlorines will be reported elsewhere.

Table 2. Changes of the concentration of recovered chloride ion in Cl_2 and NaClO by the addition of DMSO or Na_2SO_3

Compound (0.1 mM)	Recovered chloride / mM Control	 + DMSO	 + Na_2SO_3
Cl_2	0.12	0.21	0.20
NaClO	0.11	0.19	0.19

a) Concentrations of DMSO and Na_2SO_3 were 0.5 mM, respectively.

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