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Application of the Flow Injection Analysis Based on Iodometry to the Determination of Ozone Decomposition Rate

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Synopsis. The determination of ozone decomposition rate by flow injection analysis (FIA) was investigated. Under the conditions studied a sampling rate was about 43 samples/h, and the pseudo-first-order kinetic plot of the obtained data showed a good linearity. This FIA method seems to be useful for kinetic measurement of ozone decomposition in water.

Ozone is known as a powerful oxidant, and widely applied to the treatment of drinking water and waste water. In routine water-disinfection application of ozone, residual ozone at 5 minutes after ozone injection is maintained at sub-mg dm^{-3} levels. In order to obtain these residuals, in general, the initial ozone concentration in water is known to be between 0.5 and 4.0 mg dm^{-3}. The decomposition rate of ozone is very important for the achievement of the treatment. The rapid determination of the rate is, therefore, desired.

Ozone in water is commonly determined by iodometry or by photometric detection at 254 nm.$^{1)}$ The former is a standard analytical method for ozone, but it is disadvantageously time-consuming, and requires a large sample volume. The latter is convenient for continuous measurement of ozone, but the sensitivity is not high enough because of the small molar extinction coefficient of ozone in water, and large interference from coexisting substances in sample solutions is unavoidable. Straka et al.$^{2)}$ reported the flow injection analysis (FIA) of residual ozone by employing indigo as a reagent. But this method has a disadvantage of evaluating a negative peak caused by ozone decoloration of the dye, and the background absorption level is very high. In ozone measurement, an automated technique based on iodometry is desirable in order to achieve a continuity between the data obtained by a new method and the known data determined by the standard iodometric method. In this paper, the automated iodometric measurement of ozone by FIA and its application to the rapid determination of the ozone decomposition rate were investigated.

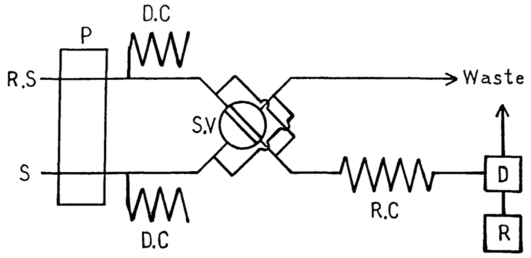

Fig. 1. Schematic flow diagram for ozone analysis. R.S: KI aqueous solution, S: sample solution, P: peristaltic pump (MP-3, Tokyo Rikakikai Co., Ltd.), D.C: damper coil, S.V: sample injection valve (46 μl), R.C: reaction coil (1 mm i.d.), D: detector (Absorbance at 354 nm, UVIDEC-100, Nihon Bunko Co., Ltd.), R: recorder (D2R2M, Ohkura Co., Ltd.).

Experimental

The flow diagram of FIA is shown in Fig. 1. A sample solution was pumped through a flow line by a micro pump. The sample solution(46 μl) was periodically injected into the flow of a reagent solution by rotating a sample injection valve, followed by mixing in a reaction coil, and liberated I_2 was directly measured by photometry at the maximum wavelength 354 nm. The reaction of ozone with I^- is shown as follows: $O_3+2I^-+2H^+ \rightarrow O_2+H_2O+I_2$. The stoichiometry of the ozone–iodide reaction is known to be 1.0 over a wide pH range.$^{3)}$

Results and Discussion

Effect of the Reaction Coil Length. The result is presented in Fig. 2. In this case, the peak width of the FIA signal increased with increasing length of the coil, and therefore the sampling rate decreased from 55 samples/h (40 cm coil) to 45 (300). If the coil was shorter than 40 cm, the reproducibility of the FIA signal was not good. Under these experimental conditions, the coil length was shown to be most suitable in the range of about 40—100 cm.

Effect of the KI Concentration of the Reagent Solution. The experimental conditions such as the rea-

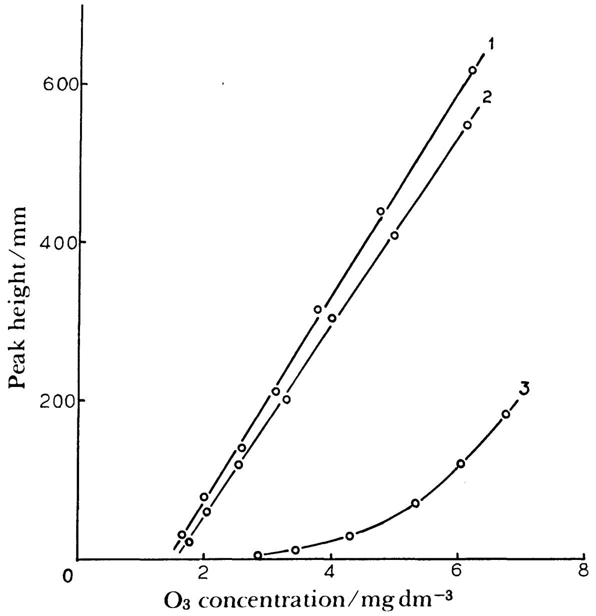

Fig. 2. Effect of reaction coil length on FIA of O_3 at 25 °C. Reagent solution: 5% KI Aqueous solution, reagent flow rate: 1.45 cm^{3}min^{-1}, 1: 40 cm, 2: 100 cm, 3: 300 cm.

gent flow rate, the temperature of the reagent solution and the reaction coil length were 1.45 $cm^3 min^{-1}$, 25 °C and 100 cm respectively. The detection limit (S/N=2.5) and the sampling rate were as follows: 0.1% KI solution, 0.3 $mg dm^{-3}$ (30 samples/h); 1, 0.7 (43); 5, 1.6 (50); 10, 2.5 (60). A suitable KI concentration should be selected by considering the levels of ozone in sample solutions.

Effect of the Reagent Flow Rate. The effect of the flow rate was investigated in the range 1.70—0.55 $cm^3 min^{-1}$. The experimental conditions such as the reagent solution, its temperature and the reaction coil length were 5% KI, 25 °C and 100 cm, respectively. The peak width increased with decreasing flow rate, and hence the sampling rate decreased from 64 samples/h (1.70 $cm^3 min^{-1}$) to 26 (0.55). A desirable flow rate of the reagent solution was shown to be near 1.45 $cm^3 min^{-1}$ or above.

Conditions of FIA. From experimental results, the conditions of the FIA were decided as follows: Reagent solution, 1% KI; reaction coil, 100 cm; reagent flow rate, 1.45 $cm^3 min^{-1}$; temperature of the reagent solution, 25 °C. Under these conditions, dispersion of sample zone was investigated, and a dispersion coefficient (D) was shown to be 30. The obtained calibration curve was confirmed to be linear up to 11.3 $mg dm^{-3}$ O_3, but the upper limit of the linear range could not be evaluated because of the low power of a ozone generator used. When the sample (2.92 $mg dm^{-3}$ O_3) was injected five times, the precision (C.V.) was 0.67%.

Effect of Coexisting Substances. Tap water (2000 cm^3) was aerated at a constant flow rate of 2.8 $dm^3 min^{-1}$ using a G-2 sintered glass filter for 5 h at 50 °C, and residual chlorine was purged. A sample solution was prepared by using 500 cm^3 of chlorine-free tap water, followed by measurement of dissolved ozone by the standard iodometric method and by this FIA. Typical data are shown in Table 1. Minerals, the levels of which were suitable for drinking water, were shown not to interfere the measurement of O_3 by this FIA. Ozone attacks many organic compounds containing carbon-carbon double bonds to result in oxalic acid as a main final oxidation product.[4] Therefore, in the measurement of residual ozone, the effect of oxalic acid should be examined. Experimental data in Table 1 show that the interference of oxalic acid with the O_3 measurement by this FIA is small.

Application to the Determination of Ozone Decomposition Rate. The decomposition rate of ozone in chlorine-free tap water was measured by this FIA. A sample solution was prepared using 500 cm^3 chlorine-free tap water obtained in the same way as described above. Immediately after the completion of ozone injection, the measurement of ozone by this FIA was started. Typical FIA signals obtained in the experiment are presented in Fig. 3. The pseudo-first-order kinetic plot of the obtained data shows a good linearity (n, 6; γ, −0.994; α, 0.001). Therefore, the decomposition of O_3 in this experiment was shown to be first order with respect to O_3. The kinetic plots are shown in Fig. 4. In these cases, the first half-lives of O_3 were 8.7 and 5.8 min, when the initial concentrations of O_3

Table 1. Determination of Ozone in Water

Sample	FIA/$mg dm^{-3}$	Iodometry/$mg dm^{-3}$
Tap water[a)]	1.34	1.34
	2.05	2.00
	2.88	2.95
Oxalic acid Solution[b)]	3.14	3.00
	4.16	4.19
	5.10	4.90

a) Ozone was injected into chlorine-free tap water. b) Ozone was injected into 361 $mg dm^{-3}$ oxalic acid–water.

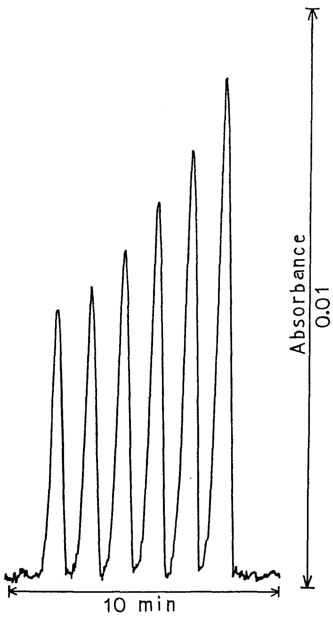

Fig. 3. Typical FIA signals obtained for measurement of O_3 in chlorine-free tap water. Initial concn of O_3: 2.5 $mg dm^{-3}$, pH of the sample solution: 7.9.

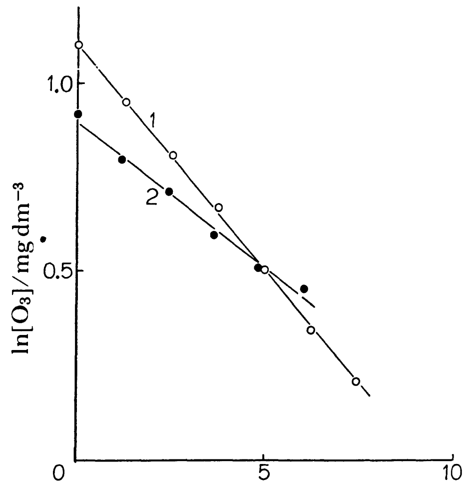

Fig. 4. Pseud-first-order plot for decomposition of ozone in chlorine-free tap water at 25 °C. 1, Initial concn of O_3: 3.0 $mg dm^{-3}$, $\log[O_3]=1.10-0.119 \cdot t$ (n:7, γ:−0.999, α:0.001). 2, Initial concn of O_3: 2.5 $mg dm^{-3}$, $\log[O_3]=0.895-0.0774 \cdot t$ (n:6, γ:−0.994, α:0.001).

were 2.5 and 3.0 mg dm^{-3}, respectively. Horie and coworkers[5] reported on the half-life of O_3 in water which was processed by coagulation and filtration without chlorine treatment, where the half-lives were 8, 15, and 30 min at 20 °C for the initial concentrations of 2.0, 1.0, and 0.5 mg dm^{-3}, respectively. Half-life measured in this experiment was a reasonable value compared with these results. From these results, this FIA can be applied to the automated measurement of the decomposition rate of O_3 in water. If necessary, the sampling rate and the sensitivity of this FIA can be controlled by slight modifications of the KI concentration and reaction coil.

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