Simultaneous Spectrophotometric Determination of Ozone and Hydrogen Peroxide

Kenta Kitsuka,*[1,2] Ahmad M. Mohammad,[2,3] Mohamed Ismail Awad,[2,3] Kazuhiro Kaneda,[1]
Mineo Ikematsu,[1] Masahiro Iseki,[1] Katsuhiko Mushiake,[1] and Takeo Ohsaka[2]
[1]*Human Ecology Research Center, Sanyo Electric Co., Ltd., 1-1-1 Sakata, Oizumi, Ora-gun, Gunma 370-0596*
[2]*Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama 226-8502*
[3]*Chemistry Department, Faculty of Science, Cairo University, P. O. 12613-Giza, Egypt*

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A simple, rapid, and highly selective spectrophotometric method for the simultaneous analysis of ozone (O_3) and hydrogen peroxide (H_2O_2) is proposed. On the basis of the large difference in the reaction rates of O_3 and H_2O_2 with I^-, a changed absorbance corresponding to the reactions of the two species with I^- was observed. This method enables a highly selective simultaneous analysis of O_3 and H_2O_2 in their coexistence.

Advanced oxidation processes (AOPs) have become of great interest as alternatives to treatment of drinking water and municipal waste water. One of the most common AOPs involves adding H_2O_2 to ozonated water[1] to produce the so-called peroxone, as represented by eq 1.

$$H_2O_2 + 2O_3 \rightarrow 2OH + 3O_2 \quad (1)$$

The produced hydroxyl radical is an extremely powerful oxidant, capable of breaking down almost all organic substrates. The simultaneous analysis of an O_3–H_2O_2 mixture is crucial for remedial use of AOPs. A suitable method for the analysis of the two oxidants should have a high selectivity to avoid their mutual disturbing reactions. The analysis of O_3 is often achieved by spectrophotometric method using indigo,[2] chemiluminescence method[3] and a direct UV measurement.[4] However, these methods cannot be used for the simultaneous analysis of the two species in their coexistence. Recently, our group has developed a new potentiometry-based simultaneous analysis of O_3 and H_2O_2.[3] However, while highly accurate this system is technically complicated. In this study, a simple and rapid spectrophotometric approach is proposed for the simultaneous determination of O_3 and H_2O_2. This analysis is based on the change in absorbance caused by the oxidation of I^- to I_3^- by O_3 and H_2O_2. The oxidation reactions of I^- by O_3 and H_2O_2 are represented as follows:

$$O_3 + 3I^- + 2H^+ \rightarrow O_2 + I_3^- + H_2O \quad (2)$$

$$H_2O_2 + 3I^- + 2H^+ \rightarrow 2H_2O + I_3^- \quad (3)$$

It is known that the rate of oxidation of I^- (the rate of I_3^- production) with O_3 (eq 2) is much faster than that with H_2O_2 (eq 3).[3] This difference in reactivity was used to quantitatively determine the concentrations of these two species in their coexistence from the change in absorbance of I_3^- at 352 nm ($\varepsilon = 27600\,M^{-1}\,cm^{-1}$)[5] with time.

All solutions were prepared using deionized water (Milli-Q, Millipore), and all the chemicals were of analytical grade. The H_2O_2 solutions of appropriate concentrations were prepared from a stock solution (31%). The concentration of the H_2O_2 was determined by volumetric titration using a standard solution of potassium permanganate ($KMnO_4$), the concentration of which was determined by titration with a solution of sodium oxalate (NaOCOCOONa) of a known concentration. The ozonated water was produced by an ozonizer (Toyota Auto Body Co., Ltd.), and its concentration was determined by using its UV absorbance at 254 nm ($\varepsilon = 3000\,M^{-1}\,cm^{-1}$). In the absorbance measurements, a spectrophotometer (JASCO V-560) was used. A standard solution of potassium iodide (KI, 0.06 M) was maintained at pH 7.0 by 0.1 M phosphate buffer. Ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (abbreviated as Mo^{VI}) was purchased from Kanto Chemicals Co., Inc.

A 100 μL of H_2O_2 was mixed with 3 mL of potassium buffer solution (pH 7.0) containing 0.6 mM KI in a quartz cell (light path: 1 cm), and then the measurement was started immediately. Figure 1 curves a–c show the time dependence of absorbance for I_3^- liberated from the oxidation of I^- by (a) 1, (b) 0.1, and (c) 0.01 mM H_2O_2 at 24 °C. It is clear that the absorbance change due to the reaction of I^- and H_2O_2 is slow and does not reach a steady state over the studied time range (ca. 5 min). The each absorbance for I_3^- was not measured continuously but every 30 s to prevent I_3^- from being decomposed by the light at the measurement.

It has been previously reported that the reaction rate of H_2O_2 and I^- in acid solutions is accelerated by adding Mo^{VI} catalyst[3,6] in which Mo^{VI} reacts with H_2O_2 to form a peroxo complex which in the next step oxidizes I^- to I_3^-.

To investigate the influence of Mo^{VI} catalyst on the kinetics of I^- and H_2O_2 reaction, Mo^{VI} catalyst (100 μL, 10 mM) was added to the 3 mL of KI-containing potassium buffer solution ([KI] = 0.6 mM, pH 7.0) before mixing with 100 μL of H_2O_2. The time dependence of absorbance for I_3^- in the reactions using H_2O_2 of concentrations (a′) 1.0, (b′) 0.10, and (c′) 0.010 mM at 24 °C is illustrated in Figure 1 curves a′–c′. In this case, the absorbance quickly increased and reached its constant value. The leveling off of the absorbance, indicating the completion of the reaction, was obtained after ≈120 s.

The accuracy of the present method was veryfied by comparing the obtained results with those obtained using the conventioinal titration method. The typical results are given in Table 1 indicating that the present spectrophotometric method is comparable with the titration method.

The oxidation of I^- by O_3 is instantaneous, while its oxidation by H_2O_2 is very slow. On the basis of the large difference in the rate constants of both reactions, the individual responses of O_3 and H_2O_2, when coexist in a mixture, toward the I^- oxidation can easily be discriminated.

A mixture of ozonated water (500 mL) and H_2O_2 (10 mL, 1 mM) was prepared, and 100 μL of this solution was mixed with

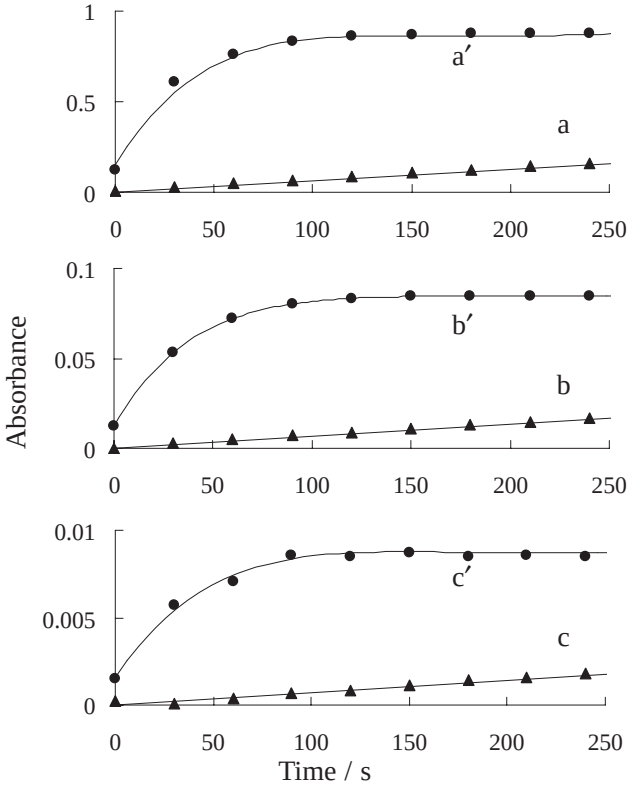

Figure 1. Absorbance–time curves at $\lambda = 352$ nm for I_3^- liberated from the oxidation of I^- by (a, a′) 1.0, (b, b′) 0.10, and (c, c′) 0.010 mM H_2O_2, 100 μL H_2O_2 of was injected in 3 mL of phosphate buffer (pH 7.0, 0.1 M) containing 0.06 M KI at 24 °C. In the case of (a′), (b′), and (c′), Mo^{VI} catalyst (10 mM, 100 μL) was previously added to 3 mL of phosphate buffer solution KI before 100 μL of H_2O_2 was injected.

Table 1. Comparison of the titration and spectrophotometric methods for measuring H_2O_2

	H_2O_2/mM		
Titration method	1.0 ± 0.1	0.10 ± 0.01	0.010 ± 0.001
Spectrophotometric method	1.02 ± 0.05	0.098 ± 0.005	0.0120 ± 0.0006

3 mL of KI-containing phosphate buffer ([KI] = 0.06 mM, pH 7.0) with and without injecting 10 mM Mo^{VI} catalyst. Figure 2 shows the absorbance–time curves at $\lambda = 352$ nm of 0.06 M KI-containing 0.1 M phosphate buffer solutions after (a) O_3 solution and (b) and (c) $O_3 + H_2O_2$ mixture were injected at 24 °C. The absorbance changes are ascribed to the formation of I_3^- by the oxidation of I^- by O_3 or $O_3 + H_2O_2$.

In the case of curve a, a constant absorbance was obtained immediately after the KI-containing phosphate buffer solution was mixed with O_3 solution, indicating that the oxidation of I^- by O_3 took place quickly and was actually completed within the solution mixing time (ca. several minutes). The O_3 concentration (0.0191 mM) was estimated from the observed absorbance change was found to be in good agreement with that (0.0195 mM) determined by directly measuring the absorption spectrum of O_3. In addition, the absorbance was found not to change for 10 min after the beginning of the reaction between O_3 and I^-, indicating that the decomposition of the liberated I_3^- by light irradiation during the absorbance measurement is

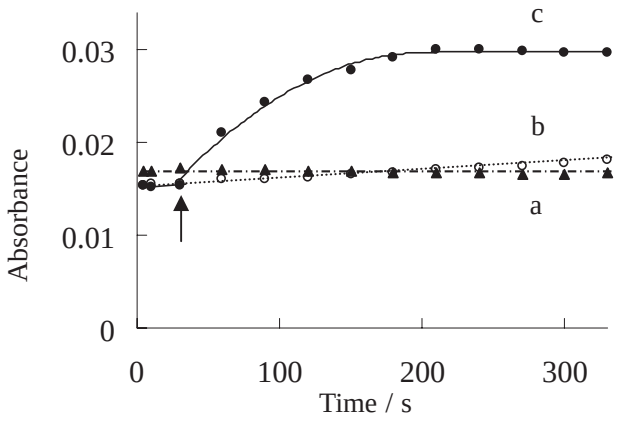

Figure 2. Absorbance–time curves at $\lambda = 352$ nm of 0.06 M KI-containing 0.1 M phosphate buffer solutions (pH 7.0) after (a) O_3 solution and (b) and (c) $O_3 + H_2O_2$ mixture were injected at 24 °C. In the case of (c) Mo^{VI} catalyst was added at the point denoted by an arrow to the phosphate buffer solution and the absorbance of Mo^{VI} at 352 nm was subtracted from the observed absorbance.

Table 2. Comparison of the titration, direct UV and spectrophotometric method for measuring H_2O_2 and O_3 in their coexistence

H_2O_2/mM		O_3/mM	
Titration method	0.017 ± 0.002	Direct UV method	0.0177 ± 0.0009
Spectrophotometric method	0.0172 ± 0.0009	Spectrophotometric method	0.0172 ± 0.0009

negligible. Curve b indicates that the reaction of O_3 and I^- was completed before the start of the reaction between H_2O_2 and I^-. The latter reaction showed a very slow change of absorbance, and the absorbance change did not reach a constant plateau, i.e., the reaction was not completed within the time scale of the present measurement (several minutes). In curve c, the Mo^{VI} catalyst was injected 30 s after the start of measurement. The change in absorbance showed a clear step-wise response from the point of adding the Mo^{VI} catalyst. We found that the concentrations of O_3 and H_2O_2 determined from the observed absorption changes are in excellent agreement with those determined by directly measuring O_3 absorption spectrum and by a titration technique, respectively (Table 2).

A new spectrophotometric method was developed for the simultaneous analysis of O_3 and H_2O_2 in their coexistence with high accuracy and selectivity. The successful fractional analysis of O_3–H_2O_2 mixture, which is based on the difference in their reactivities with iodide, is a continuation in the simultaneous analysis of different binary mixtures including peroxyacetic acid (PAA)–H_2O_2[7,8] and HClO–H_2O_2[9] mixtures by the same idea. Further studies are currently under way to investigate pH effect on the analysis and its detection limit and sensitivity.

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