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The Oxidation Behavior of Various Organic Compounds on the Determination of Chemical-oxygen Demand by Means of Flow-injection Analysis with Acidic Permanganate

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Forty-five organic compounds have been oxidized with an acidic permanganate solution under various oxidation conditions. In an attempt to determine the standard substance for chemical oxygen demand (COD), their oxidation behavior is analyzed in detail with respect to the reaction temperature and the reaction time by means of flow-injection analysis using ammonium iron(II) sulfate as the internal standard. The compounds used are classified into three groups according to the oxidation values obtained by the standard $\mathrm{COD_{Mn}}$ method. The results show that the compounds with oxidation values of more than 50% are easily oxidized with acidic permanganate, even under relatively mild conditions; those with oxidation values of 5—50% are severely influenced by the reaction temperature and the reaction time, and those with oxidation values of less than 5% are seldom oxidized at below 100 °C or for less than 30 min. As a standard substance for COD, it has been established that a mixture of the compounds has to be properly chosen from the aforementioned three groups according to the oxidation behavior of the water sample. The addition of silver nitrate to the oxidation system accelerates the oxidation reaction with acidic permanganate, whereas that of phosphoric acid suppresses the oxidation of organic compounds.

There is a growing interest on the part of environmental researchers in determining the contribution of organic substances to water pollution. For measurements of the chemical oxygen demand (COD), however, there is no specific substance to be used as a standard. Hence, skillful and complicated procedures have been established based on the standard methods with permanganate ($\mathrm{COD_{Mn}}$)[1,2] and dichromate ($\mathrm{COD_{Cr}}$).[2,3] It is, however, difficult to obtain correct values of COD in water samples, because of the lack of a standard substance for COD.[4] To select a proper standard substance for the COD measurements, therefore, the oxidation behavior of D-glucose[5,6] and lactose[7] has been studied in detail with dichromate and permanganate. Also, the oxidation values of various organic compounds[8–10] have been examined to some extent with the standard method previously established,[1–3] but their oxidation behavior has not yet been determined in detail with regard to the reaction temperature and the reaction time.

Recently, the present authors have developed a useful method, based on flow-injection analysis (FIA),[11] for the simple and continuous determination of COD ($\mathrm{COD_{FIA}}$) using potassium permanganate ($\mathrm{COD_{FIA\cdot Mn}}$)[12–18] or potassium dichromate ($\mathrm{COD_{FIA\cdot Cr}}$).[19] These methods for the COD determination always need a standard substance for COD, so sodium oxalate,[12] D-glucose,[13–19] lactose,[17,18] *etc.* were used to obtain the calibration curves. However, the oxidation behavior of these standards did not always accord with those of various organic pollutants in environmental water samples. Hence, the oxidation behavior with permanganate and dichromate should be investigated further in connection with various fundamental organic compounds in order to design a more complete FIA apparatus for COD measurements.

Therefore, this paper will mainly described the oxidation behavior of forty-five organic compounds as determined by means of the $\mathrm{COD_{FIA\cdot Mn}}$ method developed in this laboratory,[12–18] and the effects of silver nitrate[17] and phosphoric acid,[18] added to the FIA system with acidic permanganate. It will also describe some problems of the present official Japanese method using $\mathrm{COD_{Mn}}$,[2] as considered in view of the oxidation behavior of the organic compounds obtained in this work.

Experimental

Materials. All the reagents used were of an analytical reagent grade except antipyrine, *o*-cresol (guaranteed), disodium dihydrogen ethylenediaminetetraacetate (EDTA), soluble starch (guaranteed), and sodium dodecylbenzesulfonate (DBS; standard for the determination of alkylbenzenesulfonate). These reagents were used as received after dissolution with distilled water. Preparations of potassium permanganate and sulfuric acid solutions were the same as those reported previously.[17]

Apparatus. The FIA apparatus used in this work is basically the same as those used in the previous works,[13–17] as is shown in Fig. 1. To obtain flexible operating conditions, however, it was composed of a double reciprocating micropump (Kyowa-Seimitsu Model KHU-W-52), a sampling valve (Kusano, sampling volume: 20 mm^3), a water bath (Yamato Model BM-41), a spectrophotometer (Shimadzu Model UV-100-01), a quartz tubular flow-through cell (path length: 10 mm, inner volume: 18 mm^3), a multirange recorder (Nippon-Denshi-Kagaku Model U-228), and poly(tetrafluoroethylene) (PTFE) tubings with various inner diameters (i. d.) and lengths.

Procedure. Both a suitable concentration of potassium permanganate solution (*ca.* 1 mol m^{-3}) and a 10% v/v sulfuric

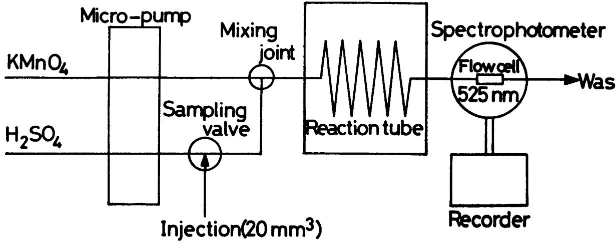

Fig. 1. Schematic diagram of a basic composition of the apparatus for $\mathrm{COD_{FIA}}$.

Table 1. Operating conditions of the FIA apparatus for evaluating oxidation behavior

Parameter	Change in reaction temperature				Change in reaction time			
Temperature of water bath/°C	38	59	79	98	98	98	98	98
Residence time of sample/min	30	30	30	30	2	10	30	45
Flow rate of $KMnO_4$ solution/$cm^3\ min^{-1}$	0.32	0.32	0.32	0.32	0.24	0.48	0.32	0.21
Flow rate of H_2SO_4 solution/$cm^3\ min^{-1}$	0.32	0.32	0.32	0.32	0.24	0.48	0.32	0.21
Flow rate of carrier stream/$cm^3\ min^{-1}$	0.64	0.64	0.64	0.64	0.48	0.96	0.64	0.42
Inner diameter of PTFE reaction tube/mm	1.0	1.0	1.0	1.0	0.5	1.0	1.0	1.0
Length of PTFE reaction tube/m	20	20	20	20	4	10	20	20
Peak height of Mohr's salt[a)]/mm	54.5	61.5	77.0	96.0	169.5	82.5	96.0	98.0
Peak height of water blank[b)]/mm	2.0	1.5	1.0	0.5	6.0	0.5	0.5	0.0

a) Mohr's salt can be completely oxidized in spite of changes in the reaction temperature and time. The flowing and mixing patterns of the sample zones are variable according to the viscosities of the carrier streams, so that peak heights are stably changed to some extent only with a change in the reaction temperature. However, the peak areas of Mohr's salt are almost equal in all FIA systems in this work. b) For the same reason as in a), the peak heights of the water blank are changed according to the peak-broadening phenomena based on the flowing and mixing patterns of their FIA systems.

acid solution are individually pumped up with the micro-pump in a 1 : 1 ratio. The concentrations of the potassium permanganate solution are adjusted to obtain absorbances of about 0.9 at 525 nm when this FIA apparatus system is operated.[17)] Also, the flow rates of the two solutions are constant at the 1 : 1 flow-ratio and are adjusted between the potassium permanganate and sulfuric acid solutions in order to obtain a proper residence time of the injected samples. Twenty-mm^3 portions of sample solutions are continuously injected into the stream of the sulfuric acid solution by means of the sampling valve just before a PTFE mixing joint. The sample is merged with the mixing joint and carrier solutions and then introduced into the PTFE reaction tube. The tube is properly selected from the various PTFE tubings with many inner diameters and lengths in order to minimize the dispersion of the sample zones and to keep a suitable residence time of the samples. The reaction tube is placed in an accurately thermostated water bath to control the oxidation reaction. The reaction mixture is detected by means of a spectrophotometer with a flow cell at 525 nm. The absorbances are continuously recorded with the recorder; the peaks in the recordings are then compared with that of an internal standard substance (Mohr's salt: ammonium iron(II) sulfate). The peak-height ratio of each organic compound (see below) is used to evaluate its oxidation behavior. The operating conditions of the apparatus, such as the temperature of the water bath, the flow rates, the kind of PTFE reaction tube, and the residence time, are given in Table 1.

Calculation of Peak-height Ratio. To symbolize the extent of oxidation for various fundamental organic compounds, the idea of the peak-height ratio is used for each organic compound in this work. The peak height of a certain organic compound is widely changed when the operating conditions are changed in the apparatus, according to the parameters in Table 1. Hence, ammonium iron(II) sulfate, which is readily and quantitatively oxidized with potassium permanganate, even at room temperature, is used as the internal standard substance to obtain a standardized peak value. The calculation of the peak-height ratio is as follows;

$$\textit{Peak-height ratio} = \frac{H_{\text{organic compound}}(\text{mm}) - H_{\text{blank}}(\text{mm})}{H_{\text{Mohr's salt}}(\text{mm}) - H_{\text{blank}}(\text{mm})}, \quad (1)$$

where H is the peak height using 20-mm^3 portions of organic compounds or an ammonium iron(II) sulfate solution as 200 mg-COD_{Mn} dm^{-3} and 20 mm^3 of distilled water (blank) in the recordings.

Results and Discussion

Choice of Organic Compounds. From the previous papers,[5—10)] forty-five organic compounds were chosen and classified into three groups according to their oxidation values with acidic permanganate by means of the standard COD_{Mn} method.[2)] Fifteen of the forty-five compounds (Group 1 in Table 2), all of which showed oxidation values of more than 50% in comparison with the theoretical oxidation values (COD_{Th}) of the compounds,[8)] were first examined in order to evaluate their oxidation behavior with permanganate at various reaction temperatures and reaction times. Fourteen compounds (Group 2 in Table 2), all of which showed oxidation values of from 5 to 50% in comparison with the COD_{Th} values, were then examined. Sixteen compounds (Group 3 in Table 2), which showed oxidation values of less than 5%, were also examined. Almost all the organic compounds are adjusted to 200 mg-COD_{Mn} dm^{-3} solutions according to their own oxidation values by means of the standard COD_{Mn} method in use, but several compounds showing oxidation values of less than 1% were prepared to make them as close to 200 mg-COD_{Mn} dm^{-3} as possible.

Oxidation Behavior of Group 1. In the ten organic compounds in Group 1, the effect of the reaction temperature was examined in order to evaluate their oxidation behavior at a residence time of 30 min; the results are shown in Figs. 2a and 2b. The effect of the reaction time on the oxidation behavior (reaction temperature: 98 °C) is also shown in Figs. 2c and 2d. The organic compounds used in Group 1 have turned out to be easily oxidizable. Figures 2a and 2b show that the oxidation reactions with acidic permanganate easily occurred at a relatively low temperature and were seldom changed in the temperature range between 80 and 100 °C except soluble starch, lactose, and glycine. As for the reaction time (Figs. 2c and 2d), the oxidation with permanganate at 98 °C occurred at a relatively short residence time (2—10 min), so that almost all the values of the peak-height ratio were apparently constant, even with a change in residence time.

TABLE 2. CLASSIFICATION OF FORTY-FIVE ORGANIC COMPOUNDS USED

Group 1[a]	Group 2[a]	Group 3[a]
Sodium oxalate (1)	Acetaldehyde (1)	Ethyl acetate (1)
Citric acid (2)	Ethanol (2)	1-Propanol (2)
EDTA (3)	1-Butanol (3)	Urea (3)
Saccharose (4)	Methanol (4)	DBS (4)
Starch, soluble (5)	Acetic acid (5)	Butyric acid (5)
Glycerol (6)	1-Propanol (6)	Acetone (6)
o-Cresol (7)	Formic acid (7)	Pyridine (7)
Aniline (8)	Lactic acid (8)	Benzoic acid (8)
D-Glucose (9)	L-Glutamic acid (9)	Glycine (9)
Lactose (10)	Propionic acid (10)	Valeric acid (10)
Tartaric acid	Isobutyric acid	Isovaleric acid
Malic acid	Formaldehyde	Diethyl ether
Phenol	2-Butanol	2-Propanol
Salicylic acid	L-Cystine	Isobutyl acetate
Antipyrine		*β*-Alanine
		L-Methionine

a) Number in parenthesis denotes those compounds in Groups 1, 2, and 3 in Figs. 2, 3, and 4 respectively.

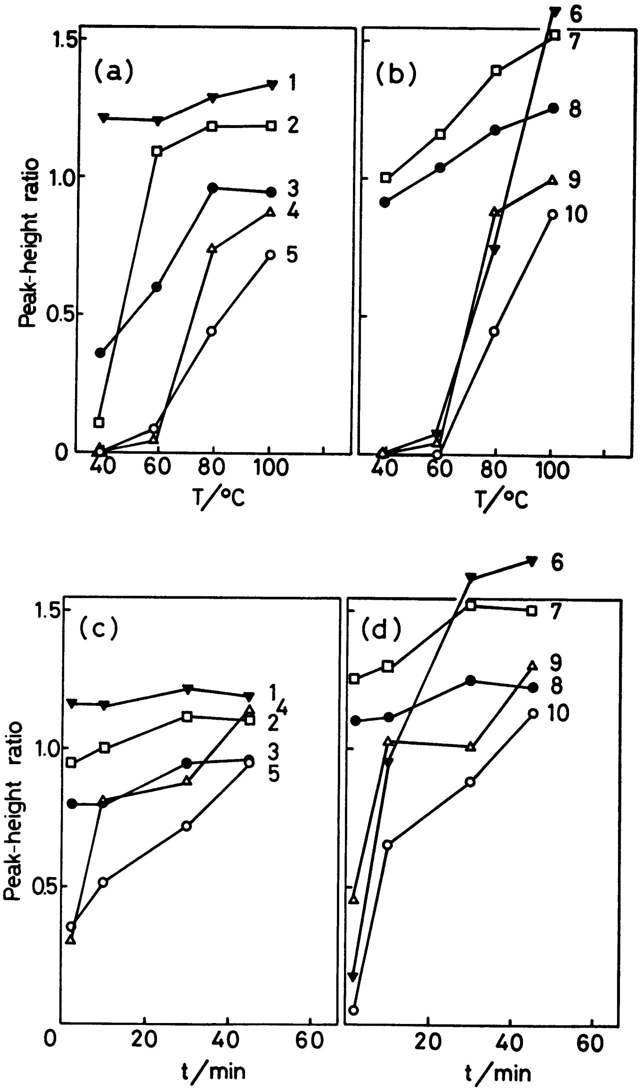

Fig. 2a—d. Effect of the reaction temperature (a, b) and the reaction time (c, d) on oxidation behavior of Group 1.
(a) and (b): Change in reaction temperature for a residence time of 30 min, (c) and (d): change in reaction time at a reaction temperature of 98 °C, 1: sodium oxalate, 2: citric acid, 3: EDTA, 4: saccharose, 5: soluble starch, 6: glycerol, 7: *o*-cresol, 8: aniline, 9: D-glucose, 10: lactose.

Oxidation Behavior of Group 2. Of ten organic compounds in Group 2, the effects of the reaction temperature (residence time: 30 min) and the reaction time (reaction temperature: 98 °C) are shown in Figs. 3a and 3b, and Figs. 3c and 3d, respectively. The compounds in Group 2 are considered oxidizable in the middle region of many of the organic compounds used in this work. Of the reaction temperature, all the compounds except acetaldehyde, acetic acid, and propionic acid gave an almost linear relationship, obtained by means of the increases in the peak-height ratio values with increases in the reaction temperature, as is shown in Figs. 3a and 3b. From Figs. 3c and 3d, it was found that the residence time severely affected methanol, ethanol, 1-propanol, 1-butanol, formic acid, and glutamic acid, but not acetaldehyde, lactic acid, acetic acid, and propionic acid. Also, the peak-height-ratio values of acetic and propionic acids were found to be very small in the absence of silver salt. Acetaldehyde, ethanol, 1-propanol, 1-butanol, and formic acid gave very large peak-height-ratio values of more than 1.5 in this work. Therefore, the values in Figs. 3a—d were plotted on a reduced scale of from 1 to 2 or 4.

Oxidation Behavior of Group 3. Of ten organic compounds in Group 3, the effects of the reaction temperature and the reaction time were also examined in a similar way (Figs. 4a—d). The compounds in Group 3 were generally considered to be difficult to oxidize by the use of an acidic permanganate solution. As for the effect of the reaction temperature on oxidation behavior, all the compounds in Figs. 4a and 4b gave exponential increases in the peak-height-ratio value when the reaction temperature increased. Therefore, the compounds in Group 3 were found to be much less oxidizable than those in Groups 1 and 2 in the low-temperature region. Of course, the former were further oxidized by acidic permanganate at a temperature of more than 100 °C, since the slopes of the oxidation-behavior curves were very abrupt between the reaction temperature and the peak-height ratio. As for the reaction time, almost all the compounds except butyric acid and glycine gave abruptly sloped relationships between the reaction time and the peak-height ratio at 98 °C, as is shown in Figs. 4c and 4d. In Figs. 4a—d, however, ethyl acetate, 2-propanol, and acetone gave outstandingly large peak-height-ratio values of more than 1.5, so those values in these figures had to be plotted on a reduced scale of from 1 to 4 or 8. Moreover, the peak-height-ratio values of butyric acid, glycine, and valeric acid showed oxidation behavior typical of much less oxidizable compounds when an acidic permanganate solution was used at more or less than 100 °C in the absence of silver salt.

As a result of these oxidation-behavior studies,

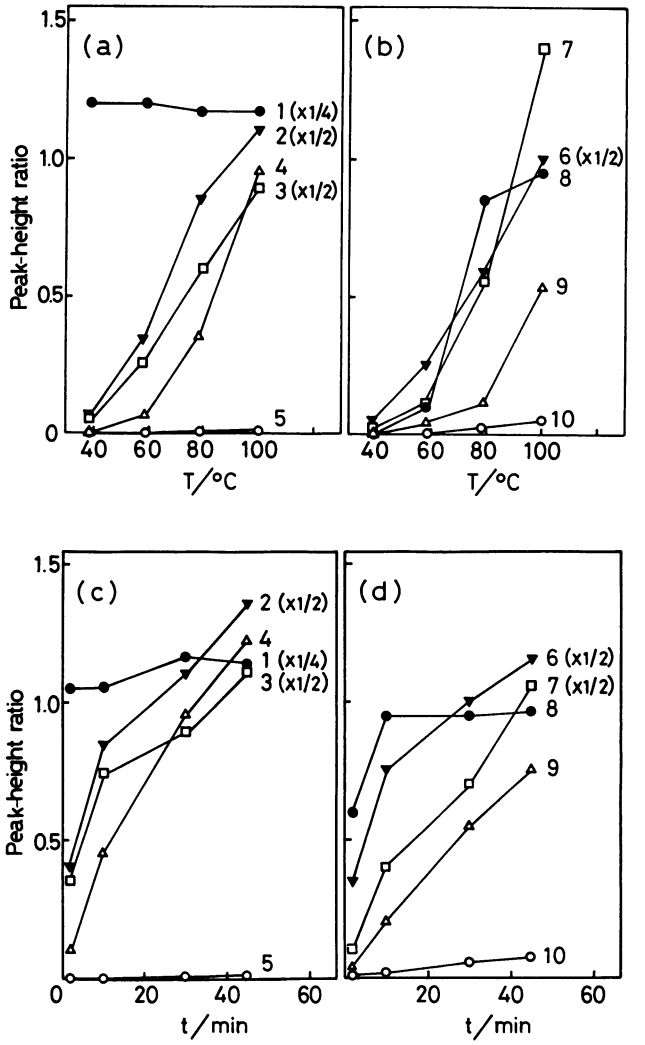

Fig. 3a—d. Effect of the reaction temperature (a, b) and the reaction time (c, d) on oxidation behavior of Group 2.
(a) and (b): Change in reaction temperature for a residence time of 30 min, (c) and (d): change in reaction time at a reaction temperature of 98 °C, 1: acetaldehyde, 2: ethanol, 3: 1-butanol, 4: methanol, 5: acetic acid, 6: 1-propanol, 7: formic acid, 8: lactic acid, 9: L-glutamic acid, 10: propionic acid.

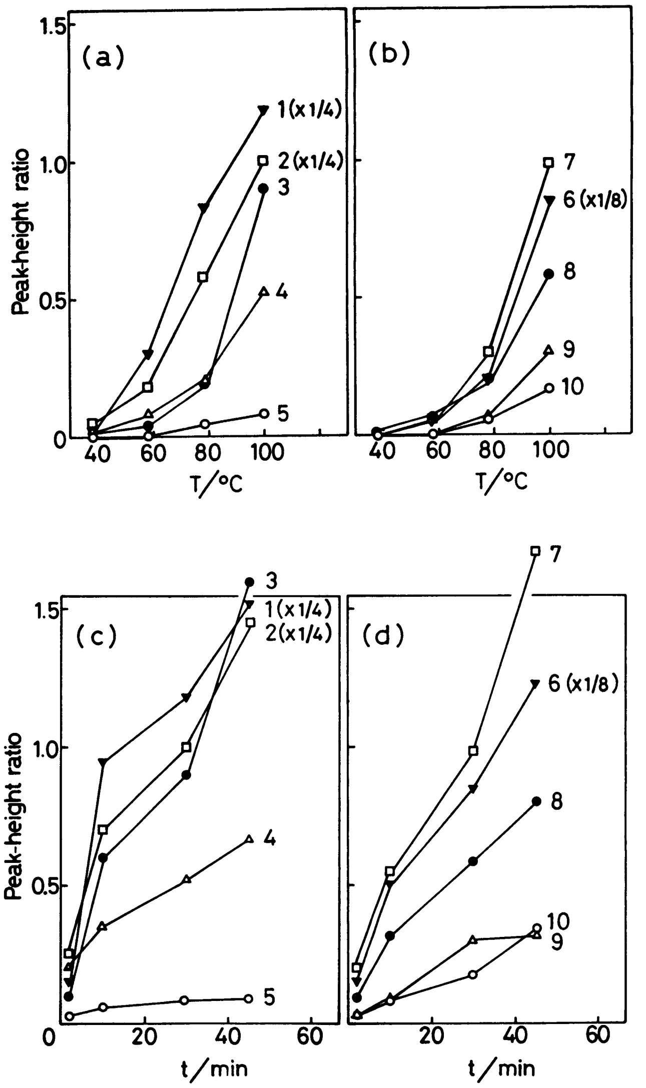

Fig. 4a—d. Effect of the reaction temperature (a, b) and the reaction time (c, d) on oxidation behavior of Group 3.
(a) and (b): Change in reaction temperature for a residence time of 30 min, (c) and (d): change in reaction time at a reaction temperature of 98 °C, 1: ethyl acetate, 2: 1-propanol, 3: urea, 4: DBS, 5: butyric acid, 6: acetone, 7: pyridine, 8: benzoic acid, 9: glycine, 10: valeric acid.

although the COD_{Mn} values[2] of the eight organic compounds with large peak-height-ratio values in Groups 2 and 3 were precisely adjusted to 200 mg dm^{-3}, the peak-height-ratio values were inconceivably large in comparison with those of the ammonium iron(II) sulfate used as the internal standard. Accordingly, it is noteworthy that organic compounds with small oxidation values[8] really had quite large COD_{Mn} values. Consequently, organic compounds with relatively low boiling points (*e.g.*, acetaldehyde, methanol, ethanol, propanols, butanols, formic acid, acetone, and ethyl acetate) potentially exhibit amazingly high peak-height-ratio values in this closed-flow injection system with acidic permanganate,[12–18] even when the permanganate values are precisely measured after digestion with acidic permanganate at about 100°C by means of the manual-titration method.[1,2] It was, therefore, considered that these organic compounds almost evaporated from the opened Erlenmeyer flask when the mixed solution was heated with a boiling-water bath in the official Japanese method for COD_{Mn}.[2]

Oxidation Behavior of Actual Waste Waters. As for actual waste water samples (*ca.* 200 mg-COD_{Mn} dm^{-3}) from civil sewage, the chemical industry, the food industry, the textile industry, and university laboratories, their oxidation behavior was also investigated with this useful methodology; the results are shown in Figs. 5a and 5b. Figure 5a shows the results on the reaction temperature obtained for the five samples at a residence time of 30 min. Figure 5a shows that waste waters from the food and textile industries gave almost linear increases in the peak-height-ratio values when the reaction temperature increased, while civil sewage and waste water from the chemical industry reacted with acidic permanganate beyond 80 °C, but not up to 60 °C. Figure 5b also shows the effect of the reaction time at 98 °C for the same samples. The civil-sewage sample gave almost constant peak-height-ratio values for more than 30 minutes' residence time, while the waste water from the chemical industry showed a linear increase with an increase in the reaction time. Waste water from the food and textile industries gave constant peak-height-ratio values between 10 and 30 min of reaction time and then proceeded to a new oxidation step for more than 30 min. As is shown in both Figs. 5a and 5b, waste water from university laboratories gave very large peak-height-ratio values which were far beyond 1.0, so it was considered that the water sample contained some volatile organic compounds, such as methanol, ethanol, or acetone. However, it should be noted that the oxidation behavior on the samples used in this work was not found in each sample of the waste water of the same industrial groups, but was particular to their own waste-water samples.

As for a standard substance for COD measurements, it can, therefore, be considered that oxidation behavior of the series of samples has to be first examined with regard to the effects of the reaction temperature and the time with acidic permanganate; an optimum substance (single or mixture) is then chosen according to these oxidation-behavior studies. Of course, the correlation between $\mathrm{COD_{FIA\cdot Mn}}$ and standard $\mathrm{COD_{Mn}}$ methods shall also be considered whenever the substance chosen is used as a standard for $\mathrm{COD_{FIA\cdot Mn}}$ measurement.

Effect on the Addition of Silver Nitrate or Phosphoric Acid. Table 3 shows the results of the additions of silver nitrate or phosphoric acid to a sulfuric acid stream when the reaction temperature and reaction time of the present FIA system were 98 °C and 30 min respectively. With waste-water samples, the peak-height-ratio values increased when 0.05% silver nitrate was added to a carrier solution containing 5% sulfuric acid and potassium permanganate, whereas they decreased when 10% phosphoric acid was added to the carrier solution, as is shown in Table 3. Of the organic substances used in this work, D-glucose, citric acid, ethanol, *o*-cresol, *etc.* were not affected by the addition of silver nitrate or phosphoric acid. However, lactose, starch, glycine, urea, 1-butanol, benzoic acid, *etc.* obviously showed the same phenomena as waste-water samples. These results prove the catalytic effect of silver(I) salt and the formation of manganese(III) phosphate. These effects on oxidation behavior with acidic permanganate are important for deciding on a standard substance for measuring the $\mathrm{COD_{FIA\cdot Mn}}$ values in a series of waste-water samples.

TABLE 3. EFFECT OF ADDITION OF SILVER NITRATE OR PHOSPHORIC ACID ON THE DETERMINATION OF PEAK-HEICHT-RATIO VALUES
(98 °C × 30 min)

Sample	Peak-height-ratio value		
	Reaction medium (5% H_2SO_4)	Reaction medium (5% H_2SO_4 0.05% $AgNO_3$)	Reaction medium (5% H_2SO_4 10% H_3PO_4)
Waste water from			
Chemical industry	0.60	0.93	0.49
Textile industry	0.49	0.54	0.45
Food industry	0.73	0.92	0.85
University lab.	1.45	1.62	1.37
Civil sewage	0.80	0.78	0.60
D-Glucose	1.29	1.34	1.39
Lactose	1.04	1.13	0.82
Starch, soluble	0.73	0.77	0.52
Citric acid	1.18	0.96	1.04
Glycine	0.31	0.46	0.04
Urea	0.89	0.69	0.51
Ethanol	2.18	2.03	2.42
1-Butanol	1.76	1.91	1.68
o-Cresol	1.55	1.30	1.32
Benzoic acid	0.58	1.36	0.68

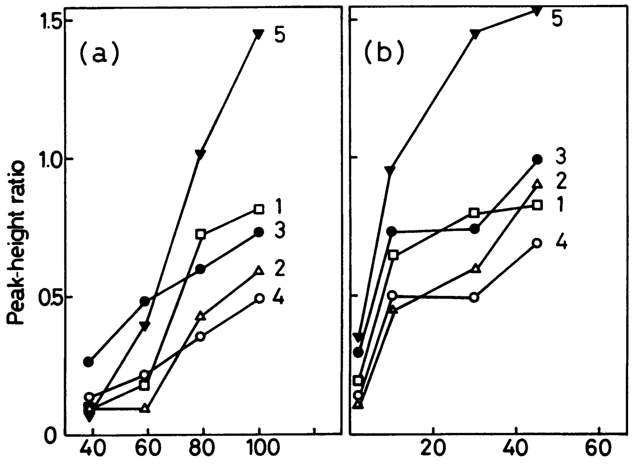

Fig. 5a—b. Effect of the reaction temperature (a) and the reaction time (b) on oxidation behavior of actual waste waters.
(a): Change in reaction temperature for a residence time of 30 min, (b): change in reaction time at a reaction temperature of 98 °C, 1: civil sewage, 2: waste water from the chemical industry, 3: waste water from the food industry, 4: waste water from the textile industry, 5: waste water from university laboratories.

Conclusion

The present study fundamentally proves various aspects of the oxidation behavior of common organic substances with an acidic permanganate solution with reference to COD measurements based on the value of the permanganate consumed. By applying a continuous $\mathrm{COD_{FIA\cdot Mn}}$ analyzer[18] to the monitoring of industrial and municipal waste water, a standard substance containing one or a mixture of organic substances can easily be found out from Groups 1, 2, and 3 after the oxidation behavior of each waste water sample has been analyzed in detail.

Besides, this paper has provided concomitant useful suggestions for preparing a standard substance for the official COD_{Mn} method now being studied in the Japanese Ministry of International Trade and Industry.[20]

This work has also established the orders of oxidizability to sugars, alcohols, carboxylic acids, and benzene derivatives for reference in considering oxidation behavior. The oxidizability to sugars is in this order: D-glucose>saccharose>lactose≈starch; that to alcohols is in this order: ethanol>1-propanol≈2-butanol≳1-butanol>2-propanol≳methanol; that to carboxyl acids is in this order: formic acid>isovaleric acid≳valeric acid>isobutyric acid≈butyric acid>propionic acid>acetic acid, and that to benzene derivatives is in this order: *o*-cresol>phenol>salicylic acid≳aniline≫benzoic acid≈dodecylbenzenesulfonic acid. These results show that the activity of the α-hydrogen in alcohols and carboxylic acids may affect their oxidation behavior.

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