Colorimetric Determination of COD(Mn) Using Hydrogen Peroxide

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Iodometric colorimetry is applied for measuring COD(Mn), using hydrogen peroxide as the mediator. It saves time, space, and chemicals without degradation of accuracy. The method can be applied to any digestion method which uses permanganate. The remaining permanganate is reduced by hydrogen peroxide at pH 1-2, where the peroxide is stable. If the silver ion for masking halides remains in the digested mixture, it is made to settle on the reduction by an excess of sodium chloride. The supernatant of digested mixture is transferred to 0.3 M KI in the acetate buffer (pH 5-6) which contains molybdate (catalyst). As the peroxide oxidizes iodide within 2 min, the formed triiodide is colorimetrically measured at 353 nm within 2 h of reaction. Blank increase by air oxidation can be ignored during this time. The method of controlling the pH of the reaction mixture is also described.

The consumption of permanganate by water samples has long been used as a simple and good indicator for organic substances in water including soluble and suspended materials, though it becomes confusing sometimes because of consumption by inorganic materials. There are many methods for COD determination by permanganate.¹⁻¹¹⁾ However, all the methods are composed of two steps; digestion (initial oxidation) of samples by permanganate and determination of the remaining permanganate. Both steps have several methods and their combination adds more. The initial step can be roughly classified into two types; acid and alkaline digestion. The second step has several kinds of titration in an acidic medium usually; using oxalate-ferrous sulfate-permanganate, iodide-thiosulfate, and so on. This step can be expected to proceed in a stoichiometric way. However, the initial digestion cannot be so. This situation often makes it difficult to make the direct comparison of the data obtained by different methods. In this way, the COD is operationally defined by the method, especially in the digestion step. Therefore, we attempted simply to revise the determination of permanganate that remained after digestion in order to reduce the time and effort for titration, but not to change the method of digesting the sample itself. However, we also wish to suggest scaling down the method of oxidizing samples,

considering the high sensitivity in the second step and error sources in each step.

Since official methods in Japan introduced silver ion in the acidic digestion in order to overcome consumption by halides in the sample¹⁻⁸⁾ around 1970, the efforts to apply colorimetry to COD determination have almost ceased, because the precipitation of silver halides made the colorimetry difficult due to their turbidity.^{1-8,9)} Since then, many automated installed instruments and electro-metric titration methods have been introduced.^{10,11)} However, installed meters are not suitable for measuring the COD of samples which are collected from different places, because the sampling site and interval are usually fixed. Automated titration methods are not always quick to operate. A simple and quick method is always desirable, but more especially when many samples are collected from different locations. Since colorimetry is quicker to operate than titration, it can be a suitable method, if the problem caused by precipitation such as that of silver halides is overcome. This problem can be overcome by letting it settle, while excessive silver ion is also made to settle by an introduction of excessive sodium chloride at room temperature. The supernatant can be used for sensitive colorimetry of triiodide, because silver-iodide complexes are much more soluble than silver-chloride complexes, when the medium contains iodide

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Fig. 1. Effect of pH and light condition on the air-oxidation of KI.

Δ Abs is the increase in blank absorbance over 2 h. Open circles are for those under ordinary room light, triangles are for those near fluorescent light, and solid circles for those near UV light.

ion over 0.1 M (Fig. 2). Another problem with iodine colorimetry is the air-oxidation of iodide during measurement. However, this is overcome by controlling the pH of the reaction medium, because iodide is not oxidized by air in a medium whose pH is over 5 (Fig. 1).

The principle of the method is as follows: the remaining permanganate and manganese oxides are reduced by excessive hydrogen peroxide in an acidic condition (pH 1–2), while the silver halides are allowed to settle. The remaining peroxide oxidizes iodide into triiodide, which is finally measured by a colorimeter at the wavelength of 353 nm. The molar absorptivity index is reported to be 26,400.¹⁷⁾ The reactions employed are as follows:

Fig. 2. Solubility of silver halides in molarity.

The number “*n. m*” means $\text{Ag}n\text{X}m$, while X represents halogen such as Cl and I. Solid lines are for those of chlorides, broken ones for iodides, and bold ones for the sum of these. They were calculated from the formation constants.¹⁶⁾

The following reactions were also considered:

The loss due to evaporation on heating has a serious effect on the colorimetry. The correction is also shown in the examples of application.

Experiments

All the chemicals used were of special grades according to JIS or equivalent. The water was deionized after passing through activated charcoal. However, the water for the blank was obtained by distilling deionized water with KMnO_4 and sulfuric acid.

The absorbance (Abs) of permanganate was measured at 525 nm where the molar absorptivity index was about 23×10^3 . The measurement of triiodide was carried out at 353 nm where the index was 264×10^3 . The slit width was 2 nm. The light path of the colorimetric cell was 1 cm. The change in absorbance was recorded by a balancing pen recorder to trace the reaction speed. A combined glass electrode was used to measure the pH of the medium.

Reactivity of KMnO_4 with H_2O_2 (Exp. 1)

The absorbance due to permanganate was recorded when putting 1.22 mM KMnO_4 , 1.66 mM H_2O_2 , and 152 mM buffer (sulfate or phosphate) in a colorimetric cell, letting the reaction proceed.

The time needed for the absorbance of KMnO_4 to become 5% by H_2O_2 was as follows:

pH	6.98	4.92	2.11	1.66	1.06	0.48
time, s	19.5	6.3	5.4	6.6	6.0	1.5 (23°C).

The absorbance became zero within 2 min in all the above cases. No dark color due to MnO_2 was observed in these cases. However, when KMnO_4 was in excess of H_2O_2 , a brown color was observed in the media whose pH was over 3.1.

Reactivity of MnO_2 with H_2O_2 (Exp. 2)

Once MnO_2 was produced on the reduction of KMnO_4 , the manganese dioxide was usually reduced to manganese (II) ion very slowly. However, it was possible to reduce MnO_2 to Mn^{2+} ion by an excessive addition of H_2O_2 in the media of pH 0.5–6.8.

Effect of pH on the Stability of KMnO_4 (Exp. 3)

Media that contained 0.3 mM KMnO_4 in 167 mM buffer (sulfate or phosphate) were kept in the dark for 96 h (19–22°C). The absorbance due to permanganate was measured at 525 nm.

Table 1 shows that the permanganate in media

Table 1. Effect of pH on the stability of permanganate

pH	Time after preparation of the media, h		
	1	17	96
100 × Absorbance (525 nm)			
7.06	70.5	69.3	68.4
4.73	70.5	69.4	68.1
2.07	69.5	70.0	62.4
1.56	70.0	70.1	62.7
1.11	70.3	68.7	62.5
0.70	70.6	67.5	62.6

Table 2. Effect of pH on the stability of H_2O_2

pH	Time after preparing the stock solution, h		
	1	12	105
Reduction of KMnO_4 by H_2O_2 100 × Absorbance (525 nm)			
5.79	95.20	94.08	86.00
4.89	95.30	95.28	68.92
3.89	95.10	95.23	67.58
2.97	95.45	94.88	64.42
2.32	95.10	95.33	67.58
1.84	96.10	95.73	93.33
1.49	93.05	95.48	91.00
1.38	94.95	95.43	93.25
0.90	95.10	95.23	92.08
0.54	94.60	96.23	85.50

with a pH of over 4.7 is more stable than in the acidic medium, as is commonly known. However, its decomposition could be ignored within a day or so over the whole range tested.

Effect of pH on the Stability of H_2O_2 (Exp. 4)

Stock mixture of 52 mM H_2O_2 , 1.6 mM AgNO_3 and 79 μM MnCl_2 in 167 mM buffer (sulfate or acetate) was kept in the dark (18–23°C), and 200 μl of the stock solution was transferred to 10 ml of 0.44 mM KMnO_4 solution (pH 0.5 sulfate buffer). The reduction of absorbance due to MnO_4^- was measured at 525 nm.

Table 2 shows that hydrogen peroxide is stable in an acidic solution, especially over the range of pH 0.9–1.8, as is commonly known. However, the decomposition could be ignored within half a day over the whole range tested.

Effect of pH on the Air-Oxidation of KI (Exp. 5)

One of the problems with iodine colorimetry is the air-oxidation of iodide, because the colorimetry is much more sensitive to this than the

titration. The sensitivity in ordinary titration is thought to be about $2\text{--}3\ \mu\text{M}$ I_3^- with starch indicator, while $0.4\ \mu\text{M}$ I_3^- solution shows 0.01 Abs at 353 nm.¹⁷⁾ If the oxidation can be suppressed, the colorimetric determination of I_3^- will become applicable, because H_2O_2 is known to oxidize KI with molybdate as a catalyst, without the addition of acid.¹²⁾

Aliquots of 57 mM KI in 0.2 M acetate buffer that contained 10 mM ethylenediaminetetraacetate (EDTA) and 10 mM tartrate were kept on the desk under different light conditions; under ordinary room light, 20–30 cm from a 20 W fluorescent light and 20–30 cm from a 15 W UV-light for sterilization. After keeping the aliquots for 2 h at 20–23°C, the absorbance was measured at 353 nm.

Figure 1 shows that the air-oxidation of KI can be ignored in media of a pH above 5, though the oxidation speed was much more variable in media with a pH below 5.

Increasing concentration of KI enhanced the air-oxidation, when 16–253 mM KI in 0.15 M citrate buffer (pH 3.3) was tested at 26°C. However, air-oxidation was not observed for over 2 h even in 307 mM KI solution (acetate buffer of pH 5) that was continuously exposed to UV-light in a colorimetric cell (28°C).

Effect of Chelators on the Oxidation of KI by H_2O_2 (Exp. 6)

Iodometry is usually carried out in acidic conditions. However, it was possible to measure H_2O_2 colorimetrically as I_3^- in KI solution without the addition of acid, when 49 mM ammonium molybdate was employed as a catalyst.¹²⁾ Nitrite

is known to catalyze the oxidation of iodide by air and to be broken by azide or sulfamate before the addition of iodide. Ferric and cupric ions are also known to oxidize the iodide. For the former, it is suggested in JIS K0101^{1,2)} and K 0102^{3,4)} that fluoride should be added before the iodometric titration in order to make ferric fluoride complexes. However, ferric ion also forms a complex with pyrophosphate,¹³⁾ which does not erode glass. Cupric ion also forms firm complexes with picolinate,¹³⁾ which has hitherto been thought not to be consumed by other metals. Tartrate was also recommended in order to suppress the problems with iodometry by forming complexes.¹⁵⁾

The effect of chelators on the oxidation speed of KI by H_2O_2 was tested by employing either 25 mM tartrate, 4 mM pyrophosphate, 1.2 mM nicotinate (β picolinate) or deionized water (as control) in 0.24 M acetate buffer that contained 0.12 M KI and 0.003% sodium azide. The concentration of oxidants, mainly hydrogen peroxide, was about 55 μN , and all the concentration shown above was that in the reaction mixture that was put in a colorimetric cell. Finally ammonium molybdate was added to bring the concentration to 49 mM. The absorbance due to I_3^- was measured at 353 nm and recorded until it reached a plateau (27–28°C). The time needed to reach the plateau was read after the addition of molybdate. The pH of the reaction mixture was measured after recording the absorbance.

Table 3 shows that picolinate and pyrophosphate were possible chelators, while tartrate hindered the reaction in this pH range. Sodium hypochlorite was found to be a suitable standard

Table 3. Effect of chelators on the oxidation speed of KI by H_2O_2 (27–28°C)

Chelator	DW* ¹	Tartrate	Picolinate	Pyrophosphate	
Buffer	Time to reach the plateau, s				
A	<15	2880	36	48	<1500* ²
B	20	1800	48	54	
C	105	1440	96	138	<1700* ²
D	105	1800	78	144	24* ³
pH					
A	4.72	5.02	4.99	5.10	5.08* ²
B	—	5.26	5.22	5.34	
C	5.63	5.65	5.60	5.79	5.79* ²
D	5.62	5.64	5.55	5.78	5.77* ³

*¹ Same volume of deionized water was added instead of the chelator.

*² Oxidation by KIO_3 instead of H_2O_2 .

*³ Oxidation by NaClO instead of H_2O_2 .

Table 4. Evaporation during the boil when the deionized water was put in a 18 ϕ test tube

Time of boiling, min	30	60
Initial volume, ml	Evaporation, mg	($m \pm sd, n$)* ¹
Covered with aluminum foil* ²		
5.0	80 $\pm$ 44.2, 10	112 $\pm$ 32.5, 13
10.0	77 $\pm$ 58.3, 10	118 $\pm$ 31.4, 9
Without any cover		
5.0	907 $\pm$ 210.6, 10	1641 $\pm$ 230.2, 10
10.0	1040 $\pm$ 235.3, 10	2087 $\pm$ 289.6, 9

*¹ m , mean; sd , standard deviation; n , the number of observation.*² A single layer of aluminum foil covered the opening of tube.

for colorimetry in this pH range, where potassium iodate reacted very slowly in spite of the ease of preparation of its standard solution.

Effect of Iodide Concentration on Discoloration (Exp. 7)

Since iodine is volatile, the decrease in absorbance was continuously recorded over 2 h by keeping iodine (triiodide) solution in a colorimetric cell with no cover. The iodine was produced by putting hydrogen peroxide into different concentrations of potassium iodide. The solution was buffered by 0.25 M acetate at pH 5 (28°C).

The decrease in absorbance was about 4%/h (120 mM KI), 2%/h (228 mM) and 0.7%/h (307 mM), probably due to the evaporation of iodine, though it was said that 241 mM (4%) KI could effectively suppress the evaporation during titration.¹⁵⁾

Amount of Evaporation during Heating (Exp. 8)

The colorimetric data directly depend upon the concentration of the substance in question, and the titrimetric data upon the total amount in the titration vessel. This situation makes evaporation during heating have a serious effect on the colorimetric data. Heating is usually carried out in a boiling water bath for 15–60 min by keeping the water in the bath boiling.

Either 5.0 or 10.0 ml of deionized water was put in 18 ϕ test tubes. Half of the tubes were firmly covered with a single layer of aluminum foil on the mouth. The other were not covered at all. All of them were placed in a boiling water bath, and the water level of the bath during the time was kept higher than that in the tubes. Halves of both covered and uncovered tubes were placed in a boiling water bath for 30 min, and the others for 60 min. After withdrawal from the bath, they were immediately cooled in cold

water, and water droplets which had attached to the outer surface of the tubes were wiped off. the weight loss during heating was measured to the nearest mg, this being shown in Table 4.

Table 4 shows the large amount of loss due to evaporation when no cover was applied. However, the loss from covered tubes was found to be fairly small: about 1.2% from 10 ml of water even after 1 h boiling. The variation was also small. This can be corrected in calculations. Since no methods suggest the use of capped (or sealed) vessels for digestion, we did not try them.

Discussion

Although the experimental condition described above was not steady or consistent, the result will help us to construct the procedure for measuring COD by colorimetry. There are many methods of determining COD, defined as the consumption of potassium permanganate by samples. However, all of them are composed of two steps: initial oxidation of samples by permanganate and determination of the remaining permanganate. There are two kinds of initial oxidation; acid and alkaline digestion. The acidity usually ranges from 0.33 to 1.13 N in the former case.^{1-7,9)} and the alkalinity from 0.04 to 0.37 N^{1,3-9)} in the latter, ignoring what is brought in by the sample. These conditions are created by the addition of either sulfuric acid or sodium hydroxide. The other chemicals used in this step are strong acid salts, and the pH of the salt solution is almost neutral. Therefore, it is usually enough to consider the acid or the base for controlling the pH of the medium in which hydrogen peroxide reacts with either permanganate or iodide.

Hydrogen peroxide is a convenient mediator, because it can work as both reductant and oxidant. It is stable in the acid condition (pH 1–2, Table 2), and can reduce both permanganate and

manganese oxides in the range of pH 0.5–6.7 (Exps. 1 and 2). It can also oxidize iodide even in the range of pH 5–6 (Table 3), where the air-oxidation of iodide can be avoided (Fig. 1). Therefore, a little excess of peroxide is allowed in order to reduce the remaining permanganate in the medium of pH 1–2, while the remaining silver can be made to settle down by means of sodium chloride if necessary. For this purpose, sulfate buffer can be used, since its second dissociation constant (K_a) is around 0.01 ($pK_a \approx 2^*$). Recording the pH curve when Na_2SO_4 was titrated by sulfuric acid, the molar ratio of $[\text{Na}]/[\text{sulfate}]$ which brought the pH of the medium to 1.7 was found to be 1.63 in 0.2 M sulfate solution and 1.75 in 0.5 M sulfate solution. The hydrogen supplied by the sulfuric acid contributes to making H^+ and HSO_4^- . These data can be used for controlling the pH of media where permanganate oxidizes peroxide. However, we have to be much more careful about the concentration and the volume of acid and base; for example the real concentration of (1+2) sulfuric acid is 13.48 N⁽¹⁰⁾ instead of 12 N. Similarly 0.25 M acetate buffer (pH 5.6) was found to have a molar ratio of $[\text{Na}]/[\text{acetate}]$ of 0.9.

In the acidic digestion, chloride in the sample, as an example of halides, is oxidized into chlorine on the consumption of permanganate. So silver ion is often used to mask halides in the sample so as not to oxidize them. There remains the silver ion, which will disturb the colorimetry of iodine due to the precipitation of silver iodide. This problem can be overcome by converting it to silver chloride before colorimetry. The chloride easily settles when kept still or being centrifuged. If it adheres strictly to the methods,^{1-9,11)} the concentration of remaining Ag^+ ion is estimated to range from 0–140 (very rarely 535) mM in the digested mixture. Even if the analyst uses more silver than is prescribed, the large solubility of sodium chloride will help us to avoid any large dilution of sample. The soluble Ag including complexes will be less than 10 μM in this step and will remain soluble in 0.3 M KI solution as is seen in Fig. 2. The supernatant can be diluted for colorimetry, because triiodide has a large molar absorptivity index.¹⁷⁾

The dilution ratio is expected to be 6.5–59.1 (353 nm) or 1.7–15.1 (400 nm) in the acid digestion.^{1-7,9,17)} In the alkaline digestion methods, on the other hand, the ratio is 10.5–17.1 (353

nm) or 2.7–4.4 (400 nm),^{1,3-9,17)} though no silver is added in these cases. Five to ten ml of sample is usually enough to put into a colorimetric cell. This means that the volume of digested mixture can be reduced to a few milliliters. Then the digestion can be carried out in a test tube and many tubes can be boiled at the same time, which will save time, space, and chemicals. The small-scale method will reduce variance too, because variance within a single boiling was smaller than that between boilings. In our undergraduate students' test (COD_{OH} of JIS K0102-1786⁽¹⁾), for example, the coefficients of variation (CV) in blank titer (10 ml) were 0.34% within a single boiling and 2.5% between boilings (significantly larger at 0.5%). Yagi *et al.*⁽¹¹⁾ have also said that the largest variation source was the boiling process for digestion. The CV of a single glass transfer pipette, on the other hand, was found to be (0.05) 0.01–0.1 (0.2)% in the size of 1–100 ml by a similar test to the above. That of a 50–500 μl -sized constriction pipettes (Lang-Levy type) was less than 1% (0.1–1%). However, air-spaced adjustable pipettes had about two times larger CV than the constriction pipette, and were often biased. Therefore, the increase in volumetric error associated with scaling down is not thought to be so serious in the overall error, even if we employ a 1/10-scaled official method. The small sample will reduce the error caused by the precipitation of suspended materials by shortening the sampling time. However, we have to give careful consideration to the evaporation during boiling in that case (Table 4).

The air-oxidation of iodide can be ignored in media of pH above 5 (Fig. 1), in which hydrogen peroxide can complete the oxidation of iodide to triiodide within a short time (Table 3). As acetate has pK_a of 4.65,⁽¹³⁾ it can make a good pH-buffer. In this pH range it is not necessary to consider other anions that have a similar dissociation constant, as the sample had already been acidified; most of the carbonate has been expelled out by the acidification to reduce manganese by hydrogen peroxide. The amount of excessive acid that will be carried in is estimated to be 0.7–72 mN from the dilution ratio that is calculated from the absorbance.¹⁻⁹⁾ Even if $\text{pH} = pK_a$, a 72 mN addition of acid will considerably change the pH of 0.25 M acetate buffer, because the buffer capacity is 144 mN/pH at that pH. Therefore, it is better to add an equivalent amount of base,

* pK_a or pX refers to $-\log_{10} K_a$ or $-\log_{10} X$, respectively

such as sodium hydroxide, to the buffer in advance in order to neutralize the excess acid.

The concentration of KI has also influence on the color development of triiodide. It has been said that a concentration above 0.1 M is enough to develop the color fully.¹²⁾ Awtrey and Connick¹⁷⁾ gave the formation constant of triiodide at 1 and 39°C and also the molar absorptance indexes of iodine and triiodide. Using the constants, the concentration of KI that made the difference in absorbance between the temperatures less than 1% was computed to be 0.15 M, above which the difference was reduced. It is said that iodine evaporates so easily that the transformation to triiodide is a remedy for it by increasing the concentration of iodide: 4% (241 mM) KI solution was recommended for the iodometric titration.¹⁵⁾ However, 307 mM KI solution could suppress the decrease in absorbance to 0.7%/h at 28°C, while a 2%/h decrease was observed in 228 mM KI solution (Exp. 7). Fortunately, the air-oxidation of iodide could be ignored at this concentration (pH 5). Therefore, 0.3 M KI is considered suitable in this case.

Nitrite is often found in samples. It is oxidized by the permanganate only in hot or warm acidic conditions, and it unfortunately catalyzes the air-oxidation of iodide.¹⁵⁾ Therefore, it may be contained in the alkaline-digested sample. Azide and urea have been said to destroy nitrite.¹⁸⁾ Since azide does this quickly, it is usually used in order to avoid the interference. According to Alsterberg,¹⁸⁾ however, it reduces iodine in neutral or acetic acid solutions, while urea does not, although it destroys nitrite very slowly. They are not suitable for our method. However, sulfamic acid ($pK_a \approx 1$)¹⁹⁾ can also destroy nitrite very quickly in the following way:

Since it did not disturb the oxidation of hydrogen peroxide by permanganate, it was considered to be a good remedy for nitrite in our method, though it was not so stable because of its hydrolysis into ammonium bisulfate.

Iron and copper are also often or sometimes found in samples. By digestion, they are already oxidized before iodometry. Ferric and cupric ions are known to interfere with iodometry by oxidizing iodide, though the dilution before colorimetry is favorable for reducing the interference. Considering the molar absorptance index of triiodide, if $[\text{Fe}^{3+}] < 10 \text{ nM}$ and $[\text{Cu}^{2+}] < 10 \text{ nM}$, the

interference can be ignored. EDTA is a good chelator for masking them. However, Fe-EDTA has been said to have a large absorption peak in the UV-region.¹⁴⁾ If the chelator is not specific, so much of it will be consumed in forming complexes with other metals that more chelator has to be used.

Acetate that is used as pH-buffer can also be a chelator, and this is used in high concentrations. Using the formation and dissociation constants given by Ringbom,¹³⁾ either 10 mM Fe³⁺ or 1 mM Cu²⁺ is thought not to interfere with the colorimetry in 0.25 M acetate buffer of pH 5–6, if no other metals compete with them. It is thought that the competition with Ca²⁺, Mg²⁺ and Mn²⁺ can be ignored. The acetate buffer is usually thought to be sufficient for carrying out the colorimetry without any problems from ferric or cupric ion, as is discussed in the next paragraph.

Pyrophosphate is a salt of tetraprotonic acid. It has a large formation constant and a very small solubility product with Fe³⁺. However, the precipitation of ferric and cupric ions at pH 1–2 is not thought to be possible because of its small dissociation constants. Although it effectively masks Fe³⁺ at pH 5–6 in its 1 mM solution, Ca²⁺ is thought to be competitive in the case of a seawater sample. Nicotinate has pK_a of 5.23 and a large formation constant with Cu²⁺; a slightly larger concentration of nicotinate than cupric ion can easily reduce cupric ion to 10 nM. However, Mn²⁺ in a few mM can compete with it in the nicotinate solution. Tartrate is also a good chelator, but it retards the oxidation speed of iodide (Table 3).

Awtrey and Connick¹⁷⁾ gave the molar absorptance indexes of triiodide and iodine at 353 nm, and the formation constants for triiodide at 1 and 39°C. The overall molar absorptance index was computed from the data as 26,343 (1°C) and 26,218 (39°C) when 0.3 M KI was employed. Since the mean was 26,281, 76.101 μN triiodide (iodine) is equivalent to 1 Abs/ppm O/cm; 0.6088. This can be used in the computation. However, if another wave length is forced to use, sodium hypochlorite can be a good standard for drawing the calibration line (Table 3). The 0.1 N solution was said to be very stable when kept in a dark and cool place.¹⁵⁾ The reaction is as follows:

However, this standard has to be calibrated with other standards, such as iodate.

The data on evaporation loss during boiling (Table 4) tell us the importance in covering the mouth of the tube and in employing a large volume of sample. When we employ a 18 ϕ test tube for digestion, a sample of *ca.* 10 ml can be used with its correction. Five ml sample, on the other hand, will introduce a large error because of evaporation. However, with the method that involves heating the digestion vessels directly on a flame it is very difficult to correct the loss. In that case, we have to employ tubes that have a mark at a certain volume to which redistilled water should be added after digestion.

Applications

The data and consideration described above are only concerned with the procedure after digestion. A very brief description of the applications is given below. However, as there are too many versions of the method, it is impossible to describe the procedures for all of them. Here, those for COD_{Mn} and COD_{OH} in JIS K 0102⁴⁾ are taken as examples to show how to apply colorimetry; there is no modification in digestion, except for scaling down the method. If a sample with a very low COD is desired for measuring with greater precision, the dilution ratio in the iodine development and the buffer concentration have to be changed.

We assume that the sample has a chlorinity of less than or equal to ordinary seawater and that colorimetry is carried out at 353 nm (76.10 μ M I₃⁻/Abs). We also assume that all the volumetric apparatuses are accurate and that all the concentrations of reagents are correct.

COD_{Mn} (JIS K0102-17-1968)

The following assumptions are adopted: the chlorinity is less than 20‰ and the error in the estimation is less than 10%.

Reagents

- A. (1+2) H₂SO₄
- B. 25 mN KMnO₄
- C. Ag₂SO₄ powder: 4.95 g/g Cl instead of 4.5 g/g Cl (prescribed in the original method) and less than 0.9 g/sample is used
- D. NaCl/NaOH: 114 mm NaCl, 626 mm Na₂SO₄ and 796 mm NaOH
- E. 11 mN H₂O₂ in 1 mm H₂SO₄
- F. 420 mm KI in 350 mm acetate buffer which contains 350 mm acetic acid and 345 mm NaOH

G. 340 μ M (NH₄)₆Mo₇O₂₄

Procedure

Put 10.0 ml of sample in a 18 ϕ test tube, add 1.0 ml of reagent A, 1.0 ml of reagent B and an appropriate amount of reagent C. Mix well to dissolve reagent C. Firmly cover the tube with a piece of aluminum foil. Keep the covered tubes in a boiling water bath for 30 min. After cooling down the tubes, mix well, transfer 5.0 ml of the supernatant to a 18 ϕ tube, add 5.0 ml of reagent D and 1.0 ml of reagent E. Mix well and let the precipitation settle down overnight. After transferring 1.0 ml of the supernatant to a 18 ϕ tube, mix 5.0 ml of reagent F and 1.0 ml of reagent G well. Put the tubes in a dark place for 2–5 min and measure the absorbance with a 1 cm quartz cell at 353 nm within 2 h. Blank is also treated as above.

Computation

$$\text{COD, ppm} = 0.6088 \times 11.92 / 10 \times 11/5 \times 7 \times (a-b) \\ = 11.176 \times (a-b)$$

a: Sample absorbance; the difference in absorbance between the colored sample and discolored sample that is obtained by mixing a drop of 10–15 mN sodium thiosulfate in the cell, if you suspect turbidity in the sample.

b: Blank absorbance.

Since the addition of *x*g of silver sulfate increases the volume by *ca.* *x*/2 ml, 11.92 should be changed to be (11.92 + *x*/2) in that case.

COD_{OH} (JIS K0102-19-1986)

Reagents

- A. 10% NaOH
- B. 10 mN KMnO₄
- C. H₂O₂: 21 mN H₂O₂, 20 mm NH₂SO₃H, 1751 mm Na₂SO₄, and 740 mm H₂SO₄
- D. 342 mm KI in 285 mm acetate buffer which contains 285 mm acetic acid and 264 mm NaOH
- E. 1.84 mm (NH₄)₆Mo₇O₂₄

Procedure

Put 10.0 ml of sample in a 18 ϕ test tube, add 200 μ l of reagent A and 2.0 ml of reagent B. Mix well. Firmly cover the tube with a piece of aluminum foil. Keep the covered tubes in a boiling water bath for 20 min. After cooling down the tubes, mix 1.0 ml of reagent C well. Transfer 500 μ l of the supernatant to a 18 ϕ tube, mix 5.0 ml of reagent D and 200 μ l of reagent E

well. Put the tubes in a dark place for 2–5 min and measure the absorbance with a 1 cm quartz cells at 353 nm within 2 h. Blank is also treated as above.

Computation

$$\text{COD, ppm} = 0.6088 \times 13.12/10 \times 5.7/0.5 \times (a-b) \\ = 9.106 \times (a-b)$$

a: Sample absorbance; the difference in absorbance between the colored sample and discolored sample that is obtained by mixing a drop of 10–15 mN sodium thiosulfate in the cell, if you suspect turbidity in the sample.

b: Blank absorbance.

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*1 The page shown is that of Jpn. edition.

*2 The previous version (1966) did not employ the Ag-addition.