Journal of Education and Practice
ISSN 2222-1735 (Paper) ISSN 2222-288X (Online)
Vol.9, No.22, 2018
www.iiste.org

Analysis and Discussion on the Calculation Formula of the Classical Monitoring Method of the Permanganate Index (I_{Mn})

Jing-Ping Wang Qing-Hua Dong
School of Chemical and Environmental Engineering,Yancheng Teachers University, Jangsu, 224007, China

The research is supported by a Project Funded by the brand professional project form Yancheng teachers college (2016) and the teaching reform and practice of medicinal chemistry (2018YCTUJGY006) and the Flagship Major Development of Jiangsu Higher Education Institutions"(PPZY2015B113)。

Abstract
In this paper, the calculation formula of the classic monitoring method of the permanganate index (I_{Mn}) is analyzed and deduced, the difficult points of the calculation formula are discussed in the process of analysis and derivation, and the common questions about the formula in the environmental monitoring industry are solved.

Keywords Permanganate index; Formula of calculation; Parsing; misgivings

Introduction

Industrial wastewater and domestic sewage discharges contain organic matters and reducing substances, which consume dissolved oxygen (DO), and cause serious threats to the aquatic habitat and domestic water supplies. Permanganate index is to point to in acidic or alkaline medium, with potassium permanganate as oxidant, the amount of consumption by dealing with water, said by oxygen mg/L. Potassium permanganate[1] can be consumed by reducing inorganic substances such as nitrite, ferrite and sulfide in water and organic substances that can be oxidized under such conditions. Therefore, this index is often used as a comprehensive indicator of the contamination of surface water by organics and reduced inorganic substances. In order to avoid secondary contamination of Cr^{6+}, the state of Japan and Germany also used permanganate as an oxidizer to measure the chemical oxygen needs of the wastewater.

I_{Mn} is appropriate for testing water of better quality, such as natural water and potable water. COD_{Cr} with higher oxidizability is more suitable for analyzing complex organic wastewater. However, I_{Mn} is used as the international standard method for chemical oxygen demand[2].

The development period of our environment monitoring work lags behind the developed countries, so the measurement standard of $KMnO_4$ method is converted from the standard of international traffic[3]. For the meaning and formula of the parameters in the standard calculation formula, there are many questions in the environment monitoring worker; however, it is difficult to find relevant data and answers in the existing document and network. Therefore, the calculation formulas of I_{Mn} are deeply analyzed, derived and analyzed.

2. Measurement principle and calculation formula of I_{Mn}

2.1 Measurement principle of I_{Mn}[4]

Its determination principle is adopt by $KMnO_4$ method：In this experiment, the permanganate titration is used to determine the chemical the chemical oxygen demand of water. The sample, containing reducing substances and organic matter is heated to boiling under acidic condition, oxidized with potassium permanganate, and the excess potassium permanganate is titrated with sodium oxalate. Chemical oxygen demand is determined by calculating the amount of potassium permanganate consumed by the difference method.

2.2 The measurement of I_{Mn}

Its measurement process is adopt by $KMnO_4$[5]：The water sample of diluted water sample (100.0 mL) and (1:3) sulfuric acid solution (5.0 mL) are added to an Erlenmeyer flask (250 mL). 10.0 mL of potassium permanganate solution (0.01 mol/L) is accurately added using a pipette. The solution is heated in a boiling water bath for 30 min. 10.0 mL of sodium oxalate solution (0.01 mol/L) is added immediately into the flask. The mixed solution is titrated using standard potassium permanganate solution (0.01 mol/L) to reddish color and the amount of potassium permanganate (V) consumed is recorded.

2.3 The measurement and calculation formula of I_{Mn}

The calculation formula of I_{Mn} in the national standard method is shown in (1) :

$$I_{Mn}\,(O_2，mg/L) = \frac{\{[(10+V_1)K-10]-[(10+V_0)K-10]f\}\times C\times 8\times 1000}{V_3} \tag{1}$$

Where, V_1—volume of potassium permanganate in titration (mL); V_3—volume of water sample (mL); V_0--volume of water blank sample (mL); C—concentration of standard oxalic acid solution; K—correction factor for the potassium permanganate solution (mol/L).

3 The environment monitor has a question of the existence of an I_{Mn} 's computing formula

For formula (1), there are three common problems in environmental monitoring:
Question I: when the potassium permanganate and sodium oxalate are formulated, c (1/5KMnO$_4$) = 0.01 mol/L, C (1/2 Na$_2$C$_2$O$_4$) = 0.0100mol/L, why are the solutions of the molar concentration of the base unit 1/5 KMnO$_4$ and 1/2 Na$_2$C$_2$O$_4$ prepared?
Question 2: the correction factor of potassium permanganate solution concentration k= 10/V$_2$, how to get this formula?
Question3: how is the formula (1) derived and how does it correspond to the measurement principle?

4 Analysis and discussion on the calculation formula of I_{Mn}

4.1 Study on the reason of preparation of special concentration solution

For question 1, it is necessary to start from the reaction of potassium permanganate and oxalic acid. Potassium permanganate is a strong oxidizer, and oxalic acid is a strong reducing agent, and the oxidation-reduction reaction takes place under the acidic condition, as shown in (2) :

$$2MnO_4^- + 5C_2O_4^{2-} + 10H^+ \xrightarrow{70-80^0C} 2Mn^{2+} + 10CO_2 + 8H_2O \qquad (2)$$

Even for every fifth mole of potassium permanganate, half a mole of oxalic acid (potassium permanganate, 1/5n ~1/2n) is consumed. Formula (3) can be obtained:

$$1/5C_{MnO_4^-} \times V_{MnO_4^-} = 1/2C_{C_2O_4^{2-}} \times V_{C_2O_4^{2-}} \qquad (3)$$

According to the conversion relationship between the amount and concentration of substances in different basic units, $C_{KMnO_4} = 5C_{1/5KMnO_4}$，$C_{Na_2C_2O_2} = 2C_{1/2Na_2C_2O_2}$ formula (4) can be obtained:

$$C_{1/5MnO_4^-} \times V_{MnO_4^-} = C_{1/2C_2O_4^{2-}} \times V_{C_2O_4^{2-}} \qquad (4)$$

It was found that molar concentration of 1/5 KMnO$_4$ and 1/2 Na$_2$C$_2$O$_4$ was selete in the preparation of potassium permanganate and sodium oxalate solution, so that the 1:1 reaction of oxalic acid and potassium permanganate could be realized, which greatly facilitate the calculation of the result.

4.2 Discussion on the origin of KMnO$_4$ solution concentration correction formula

For question two, it can also be explained based on the analysis of 3.1, and when you calibrate the concentration of potassium permanganate, the formula for the oxidation reduction is the same as (4), and formula (5) can be obtained:

$$C_{1/5MnO_4^-(actual)} = K \times C_{1/5MnO_4^-(theory)} = C_{1/2C_2O_4^{2-}} \times V_{C_2O_4^{2-}} / V_{MnO_4^-} \qquad (5)$$

$C_{1/5MnO_4^-(theory)} = 0.01mol/L$，$C_{1/2C_2O_4^{2-}} = 0.01mol/L$ ，$V_{C_2O_4^{2-}} = 10.00ml$

The simplified formula (6) and (7) can be obtained:

$$K = 10V_{MnO_4^-} = 10V_2 \qquad (6)$$

$$C_{1/5MnO_4^-(actual)} = KC_{1/2C_2O_4^{2-}} \qquad (7)$$

Where (7) is the formula for calculating the correction coefficient of KMnO$_4$ solution concentration.

4.3 The derivation of the calculation formula of I_{Mn}

To derive the calculation formula of the I_{Mn} of permanganate index, the numerical results of I_{Mn} were calculated as "O$_2$, mg/L". Second, since the I_{Mn} determination process is complex, it is necessary to define the analysis flow for each step, and the chemical reaction flow of I_{Mn} is shown in figure (1):

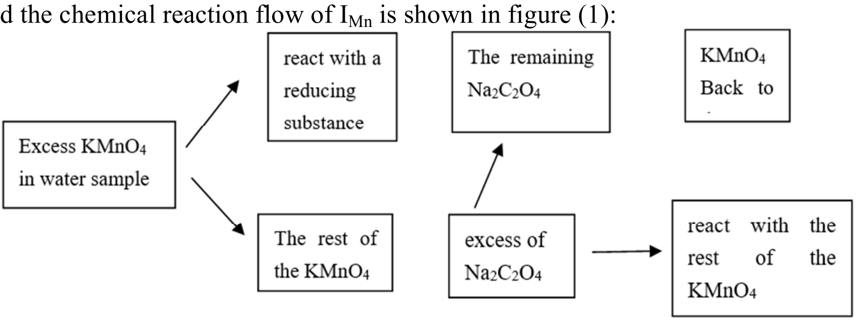

Fig. 1 Analysis flow chart of permanganate index

①Standard sodium oxalate solution was used to calibrate the potassium permanganate solution at 10.00ml (8), and the relat and the relationship between potassium permanganate and standard sodium oxalate solution was shown in (9).

$$2KMnO_4 + 5H_2C_2O_{4\,(standard)} + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2 \qquad \text{（8）}$$

$$1/2n_{MnO_4^-} = 1/5n_{C_2O_4^{2-}(standard)} \qquad 1/2C_{MnO_4^-} \times V_{MnO_4^-} = 1/5C_{C_2O_4^{2-}(standard)} \times V_{C_2O_4^{2-}(standard)}$$

$$C_{MnO_4^-} = 2/5C_{C_2O_4^{2-}(standard)} \times V_{C_2O_4^{2-}(standard)} / V_{MnO_4^-(standard)}$$

$$= 2/5C_{C_2O_4^{2-}} \times 10.00 / V_{MnO_4^-} = 2/5C_{C_2O_4^{2-}} \times K \qquad (9)$$

②An excess of potassium permanganate solution was added to oxidize certain organic and reductive substances in the water sample

The reaction between potassium permanganate and organic matter in the determination process is shown in (10), and the relationship between potassium permanganate and organic matter is shown in (11).

$$4KMnO_{4(excess)} + 6H_2SO_4 + 5C \rightarrow 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5CO_2 \qquad (10)$$

$$1/4n_{KMnO_4\ (reduction)} = 1/5n_C \qquad (11)$$

③The remaining potassium permanganate was reacted and reduced with an excess of sodium oxalate 10.00 ml

The reaction between potassium permanganate and oxalic acid is shown in (12), and the relationship between the reactive potassium permanganate and the residual potassium permanganate is shown in (13).The relationship between residual potassium permanganate and excessive sodium oxalate is shown in 14.

$$2KMnO_{4\,(remaining)} + 5H_2C_2O_{4\,(excess)} + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2 \qquad (12)$$

$$n_{KMnO_4\ (reduction)} = n_{KMnO_4(excess)} - n_{KMnO_4(remaining)} \qquad \text{（13）}$$

$$= C_{KMnO_4} \times 10.00 - C_{KMnO_4} \times V_{KMnO_4(remaining)}$$

$$1/2n_{MnO_4^-(remaining)} = 1/5n_{C_2O_4^{2-}(reactor)} = 1/5(n_{C_2O_4^{2-}(excess)} - n_{C_2O_4^{2-}(remaining)}) \qquad \text{（14）}$$

④The excess sodium oxalate was then added back in standard solution of potassium permanganate

The reaction between potassium permanganate and oxalic acid is shown in (15), and the relationship between the dropping potassium permanganate and the remaining sodium oxalate is shown in (16).

$$2KMnO_{4\,(titration)} + 5H_2C_2O_{4\,(excess)} + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10C \qquad \text{（15）}$$

$$1/2n_{MnO_4^-(titration)} = 1/5(n_{C_2O_4^{2-}(excess)} \qquad \text{（16）}$$

Substitute (14) - (16) into (13) and you get (17).

$$n_{MnO_4^-(reduction)} = n_{KMnO_4(excess)} - n_{KMnO_4(remaining)}$$

$$= C_{KMnO_4} \times 10.00 - C_{KMnO_4} \times V_{KMnO_4(remaining)}$$

$$= C_{MnO_4^-} \times 10.00 - [2/5(n_{C_2O_4^{2-}(excess)} - n_{C_2O_4^{2-}(remaining)})]$$

$$= 2/5C_{C_2O_4^{2-}} \times 10.00 \times K - 2/5C_{C_2O_4^{2-}} \times 10.00 + 2/5 \times 5/2 \times C_{KMnO_4} V_{KMnO_4(titration)}$$

$$= 2/5C_{C_2O_4^{2-}} \times 10.00 \times K - 2/5C_{C_2O_4^{2-}} \times 10.00 + C_{KMnO_4} \times V_{KMnO_4(titration)}$$

$$= 2/5C_{C_2O_4^{2-}} \times 10.00 \times K - 2/5C_{C_2O_4^{2-}} \times 10.00 + 2/5C_{C_2O_4^{2-}} \times K \times V_{KMnO_4(titration)}$$

$$= 2/5C_{C_2O_4^{2-}} \times [10.00 \times K - 10.00 + K \times V_{KMnO_4(titration)}]$$

$$= 2/5C_{C_2O_4^{2-}} \times [(10.00 + V_{KMnO_4(titration)}) \times K - 10.00] \qquad \text{（17）}$$

⑤Think of oxidants as O_2.,

The reaction between $Na_2C_2O_4$ and oxygen is shown in (18) :

$$2C_2O_4^{2-} + O_2 + 4H^+ \rightarrow 4CO_2 + 2H_2O \qquad (18)$$

Between (18) and (11), there is a relationship between oxygen and sodium oxalate and potassium permanganate (19) and (20).

$$n_{o_2} = 1/2n_{Na_2C_2O_4} = 5/4n_{KMnO_4} = 1/4n_{1/2Na_2C_2O_4} \qquad (19)$$

$$n_{o_2} = 5/4n_{KMnO_4} = 5/4 \times \{2/5 \times 1/2 \times c_{1/2Na_2C_2O_4} \times [(10.00 + V_{KMnO_4(titration)}) \times K - 10.00]\}$$

$$= 1/4 \times C_{1/2Na_2C_2O_4} \times [(10.00 + V_{KMnO_4(titration)}) \times K - 10.00]\} \qquad \text{（20）}$$

Then, it can be calculated that when the oxidant is identified as "O_2", the concentration of the oxygen substance is shown in (21).

$$m_{o_2} = n_{O_2} \times M_{O_2} = 1/4 \times c_{1/2Na_2C_2O_4} \times [(10.00 + V_{KMnO_4(titration)}) \times K - 10.00] \times 32$$

$$= C_{1/2Na_2C_2O_4} \times [(10.00 + V_{KMnO_4(\text{titration})}) \times K - 10.00] \times 8 \qquad （21）$$

The I_{Mn} as follows:

$$I_{Mn}(O_2, mg/L) = \frac{m_{o_2}}{V_{（\text{watersample}）}} \times 1000 = \frac{[(10 + V_{KMnO_4(\text{titration})})K - 10] \times C_{1/2Na_2C_2O_4} \times 8 \times 1000}{V_{\text{watersample}}} \qquad （22）$$

Dilute with distilled water before measurement. Then blank test shall be conducted simultaneously. The calculation formula of permanganate index is (23):

$$I_{Mn}(O_2, mg/L) = \frac{\{[(10 + V_1)K - 10] - [(10 + V_0) \times K - 10]\} \times f \times C \times 8 \times 1000}{V_3} \qquad (23)$$

Where, V_1—volume of potassium permanganate in titration (mL);V_0—volume of blank water sample (mL);V_3--volume of water blank sample (mL);C—concentration of standard oxalic acid solution;K—correction factor for the potassium permanganate solution (mol/L); *f* is the proportion of distilled water in diluted water sample.

References

[1] Ying Liu , Zhong-mu Zhou, Qian Zou , He Gao.**(2017)**. The Calibration of COD Detector Using Permanganate Titration Method. *Journal of measurement and testing technology,* 44(2):71-72.

[2] Bing-qiao Cao. **(2015)**.Progress of determination methods of COD in environmental water sample. Hubei Forestry Science and Technology, 44(2):36-39.

[3] Si-yuan Luo. (2017). Uncertainty assessment of chemical oxygen demand in surface water by potassium dichromate method . Journal of environmental science, 36(12):97-100.

[4] ISO 8467-1986，Water quality -- Determination of permanganate index [s] . witzerland: ISO，1986

[5] GB 11892-89，Water quality , Determination of permanganate index[s].