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Analysis and Discussion on the Formula of Classical Monitoring Method for Chemical Oxygen Demand (COD_{Cr})

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Abstract

In this paper, the calculation formula of the classical monitoring method of COD (COD_{Cr}) is deducted and analyzed in detail by analyzing the calculation formula of the method for the classical monitoring of COD_{Cr}, and the difficult points of the COD_{Cr}, calculation formula is discussed, and the general doubts about the existence of this formula are solved in the environment monitoring industry.

Keywords: chemical oxygen demand; Formula of calculation; Parsing; misgivings

1.Introduction

COD (chemical oxygen demand) is one of the comprehensive indicators of water quality, which reflects the degree of contamination of the water with the reducing substances, including organic substances, sulphides, ferrous salts, nitrites, and so on. It is one of that important index to measure the relative content of the organic substances of the body of water, which is one of the key indexes to measure the relative amount of organic substances in the body of water, and the great the amount of chemical oxygen demand, indicating that the water is polluted by organic substances.

The determination method of COD adopts the most common oxidation system with acidic potassium chromate oxidation, acid permanganate oxidation method, ozone and hydroxyl oxide , etc., and some imported online monitoring instruments adopt this oxidation system[1-3].

The development period of our country's environmental monitoring is lagging behind the developed country, so the measurement standard of $K_2Cr_2O_7$ method is converted from the standard of international passage[4]. This standard method is relatively simple; however, there is a lot of questions about the meaning and formula of each parameter in the standard calculation formula; however, it is difficult to find relevant information and answers in the literature, so the calculation formula of COD_{Cr} is deeply analyzed, derived and analyzed.

2. Determination principle and calculation formula of COD_{Cr}

2.1 Determination principle of COD_{Cr}

When $K_2Cr_2O_7$ method is used, its determination principle is as follows：In this experiment, CODCr is determined by the potassium dichromate method, where excess potassium dichromate standard solution is used as oxidant. Reducing substances (mainly organic matter) are oxidized and excess oxidant is titrated using a standard solution of ammonium ferrous sulfate as the reductant and ferroin solution as the indicator. Most compounds, including straight-chain aliphatic compounds can be oxidized by acidic potassium dichromate using a silver sulfate-sulfuric acid reagent as catalyst. COD_{Cr} of water sample is calculated according to the consumption of potassium dichromate standard solution. Chloride ions in water samples can be oxidized by potassium dichromate and generate a precipitate with silver sulfate and effects experimental results.

$$Cr_2O_7^{2-}+6Cl^-+14H^+\rightarrow 2Cr^{3+}+3Cl_2+7H_2O$$

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

Mercury sulfate is used in water samples containing chloride ions to eliminate the interference.

$$Hg^{2+} + 4Cl^- \rightarrow [HgCl_4]^{2-}$$

Water samples with concentrations of chloride ion above 1000 mg/L should be diluted before determination.

2.2 Determination the process of COD_{Cr}

When $K_2Cr_2O_7$ was used, the measurement process was as follows[5]： 20.00 mL of water sample or an appropriate volume of water sample is diluted to 20.00 mL, 10 mL of standard potassium dichromate solution and several boiling chips are placed in the Erlenmeyer flask (250 mL) and the flask is connected to the reflux condenser. 30 mL of silver sulfate-sulfuric acid reagent is added slowly through the condenser to the flask. The mixture solution is gently swirled and refluxed for 2h. In the acid medium - H_2SO_4, $K_2Cr_2O_7$ as oxidant, Ag_2SO_4 as catalyst, can join $HgSO_4$ masking the chloride ion, the boiling point temperature is 148□+2□. After the refluxing, the solution is cooled and the reflux condenser is rinsed with 90 mL of distilled water. The total volume of the resulting solution should not be less than 140 mL. Otherwise, excessive acidity will make the endpoint difficult to detect. Three drops of ferroin indicator solution is added and solution is titrated with standard ferrous ammonium sulfate solution. The volume consumed is recorded after the solution color turns from yellow through blue-green to reddish-brown. A blank consisting of 20.00 mL of distilled water is analyzed following exactly the same procedure as for the water samples. The COD value of water sample was calculated according to the consumption of $(NH_4)_2Fe(SO_4)_2$ solution.

2.3 Determination calculation formula of COD_{Cr}

The calculation formula of CODCr in the t-national standard method is shown in (1) :

$$COD_{Cr}(O_2，mg/L) = \frac{C\times(V_0-V_1)\times 8\times 1000}{V} \quad (1)$$

Where ,c—concentration of the standard ammonium ferrous sulfate solution (mol/L)； V_0-volume of the standard ammonium ferrous sulfate solution used for the blank (mL)； V_1-volume of the standard ammonium ferrous sulfate solution used for water sample (mL)； V-volume of the water sample (mL)； 8-1/2 molar mass of O (g/mL).

3.The industry has questioned the COD_{Cr} formula

For formula (1), the following four questions are often raised by environmental monitoring workers.

First of all questions: the calculation formula is independent of the potassium rechromate of the capacity analysis.

The type of determination and analysis method of COD_{Cr} is capacity analysis, which is a back titration capacity analysis, with $(NH_4)_2Fe(SO_4)_2$ solution titrating remaining $K_2Cr_2O_7$. During the digestion process, the only oxidant is $K_2Cr_2O_7$, the reducing agent is the organic matter in the water sample, and the reducing agent in the titration process is $(NH_4)_2Fe(SO_4)_2$. According to the customary rule of capacity analysis, that is, if the reaction formula of capacity analysis is $xA + yB \rightarrow zC + z'D$, A is the oxidizing agent, the concentration is c_1, the consumption volume is v_1, B is the reducing agent, the concentration is c_2, the consumption volume is v_2, then equation $x c_1 v_1 = y c_2 v_2$ should be used. However, for the only oxidizer $K_2Cr_2O_7$, in this formula, there is no concentration and volume of $K_2Cr_2O_7$ and so on. It seems that this capacity analysis is independent of $K_2Cr_2O_7$, why is this?

Second of all questions：why use 1/2 the molar mass of oxygen？

The equation 8 is explained with respect to 8: "8 is the molar mass (g/mole) of oxygen (1/2 O)", which is half of the molar mass of oxygen, which is very rare, and the smallest unit of chemical reaction is atomic, and the oxygen of 1/2 is not able to participate in the reaction, and why is a molar mass of 1/2 oxygen?

The third of all questions: $K_2Cr_2O_7$ method of determination of COD_{Cr}'s national standard method for determining the concentration of potassium dichromate standard solution is ($1/6\ K_2Cr_2O_7 = 0.2500$ mol/L), why the molar concentration of base unit "$1/6\ K_2Cr_2O_7$" is used?

Fourth all questions: why is the blank deducted in the formula from the volume that consumes ferrous sulfate, and not vice versa?

4.Analysis and discussion of COD_{Cr} formula

4.1 The COD calculation formula is discussed for reasons not related to the potassium chromate recreate.

For question 1, we first explore the chemical reactions of water samples in solution during the process of digestion and titration. The compounds in water samples are: Fe^{2+}, NO^{2-}, sulfide (S^{2-}), organic matter (R), etc., etc. In the process of dissolution, these reducing substances are oxidized, as shown in (2) :

$$Fe^{2+} \rightarrow Fe^{3+}；\ NO^{2-} \rightarrow NO^{3-}；\ S^{2-} \rightarrow SO_2 \rightarrow H_2SO_3\text{(binary weak acid)}$$

$$R \rightarrow R'-OH \rightarrow R''-COOH \rightarrow CO_2 + H_2O$$

(R'、R'' For the different organic substituents)

During titration, the reducing agent is $(NH_4)_2Fe(SO_4)_2$, which is ionized as follows :$(NH_4)_2Fe(SO_4)_2 \rightarrow Fe^{2+} + NH_4^{+} + 2SO_4^{2-}$. When the reaction occurs, ferrous ions are oxidized to iron ions:$Fe^{2+} \rightarrow Fe^{3+}$。In addition to ionizing the oxidizing agent $K_2Cr_2O_7$, a balance as shown in (2) exists in the aqueous solution:

$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2H^{+} + 2CrO_4^{2-} \quad [k = 1.2 \times 10^{14}] \quad (2)$$

Although equilibrium moves to the right under acidic conditions and the equilibrium constant k is large, CrO_4^{2-} actually exists. Therefore, the digestion reaction in the digestion process is extremely complicated, and the ion species and morphologies involved in the reaction are numerous, especially organics, which can not write the whole reaction equation.

Then, this capacity balance will be calculated. Next, we look at the definition of COD in the national standard method: COD refers to the concentration of oxygen in oxygen, which is the concentration of oxygen corresponding to the dichromate consumed by the solubility substance and suspended substance in the water sample under the conditions of the oxidation treatment of potassium dichromate. The last three words in this definition are extremely critical in terms of oxygen, and we have eyes on "oxygen," since the digestion reaction is difficult to write the fact that the reaction is reversed in reality, and that the residual $K_2Cr_2O_7$ is titrated in $(NH_4)_2Fe(SO_4)_2$ during the titration, and the result is calculated as an oxygen meter, in order to characterize the usage of $(NH_4)_2Fe(SO_4)_2$, we attempt to view the oxidizing agent as "O" for the case of the digestion reaction. If the oxidant is oxygen, the reaction equation is shown in (3) :

$$Fe^{2+} + [O] \rightarrow 2Fe^{3+} + [O]^{2-} \qquad (3)$$

Where, [O] denotes that oxygen is free state, that is, the combined price is zero, $[O]^{2-}$ denotes that the combined price of oxygen is negative bivalent. Equation (3) is obtained, which is suddenly enlightened. According to the calculation rules of capacity analysis, equation (4) can be obtained:

$$n(O)=1/2n(Fe^{2+}) =(1/ 2) \times c(Fe^{2+})\times v(Fe^{2+}) \qquad (4)$$

Where, n is the quantity of matter, the same as below; The calculation of mass m(O) of oxygen is shown in equation (5) :

$$m(O)= n(O) \times M(O) = (1/ 2) \times c(Fe^{2+})\times v(Fe^{2+})\times 16 = 8\times c(Fe^{2+})\times v(Fe^{2+}) \quad (5)$$

The calculation formula of COD can be obtained after the above analysis, as shown in equation (6) :

$$COD = m(O)/v(\text{water sample})= 8c(Fe^{2+})+v(Fe^{2+})/v(\text{water sample}) \qquad (6)$$

This calculation formula is consistent with the national standard method. Therefore, there is no relevant parameter of $K_2Cr_2O_7$ in the calculation formula.

4.2 Discussion on the origin of "molar mass of 1/2 oxygen" parameter in the calculation formula of COD

The parameter "8" appears in formula (6), which is the origin of the parameter "8" of "oxygen (1/2O) molar mass (g/mol)" in formula (1).

4.3 An analysis of the cause of the concentration of a substance with a base unit of 1/6 $K_2Cr_2O_7$ was selected

It is difficult to write down that oxidized reduction reaction equation of oxidizing in the whole reaction system, and we will look at the oxidized $(NH_4)_2Fe(SO_4)_2$ and the reduce $K_2Cr_2O_7$, which can derive the ion reaction equation (7) according to the digestion reaction:

$$Fe^{2+}+1/3Cr^{6+}\rightarrow 1/3Cr^{3+}+ Fe^{3+} \qquad (7)$$

That is, corresponding to the quantitative relationship shown in(8) :

$$Fe^{2+}\sim 1/3Cr^{6+}\sim 1/6\ K_2Cr_2O_7 \qquad (8)$$

The answer to the third question has been revealed that each mole of $(NH_4)_2Fe(SO_4)_2$ requires a one-sixth mole of $K_2Cr_2O_7$, which is used in a molar concentration of 1/6 $K_2Cr_2O_7$ for ease of calculation.

4.4 The analysis of the blank deductions in the formula

The COD_{Cr} assay was performed by titration:The reaction of potassium dichromate with organic compounds：

backflow $\boldsymbol{2Cr_2O_7^{2-}}$（excessive）$\boldsymbol{+3C+16H^+\rightarrow 4Cr^{3+}+3CO_2+8H_2O}$ （9）

Measurement of excess: the excess potassium dichromate is titrated with ferrous ammonium sulfate until all of the excess oxidizing agent has been reduced to Cr^{3+}.

titration $\boldsymbol{Cr_2O_7^{2-}}$（residue）$\boldsymbol{+6Fe^{2+}+14H^+\rightarrow 2Cr^{3+}+6Fe^{3+}+7H_2O}$ （10）

In the case where the excess amount of the potassium dichromate standard solution is added and the reducing substance represented by the organic material in the wastewater is used as a catalyst in the process of the silver sulfuric acid, the reaction is conducted at the high temperature under reflux at the high temperature, and in this case, all the organic substances in the waste water are totally reacted, the remaining unreacted potassium dichromate is completely reacted, and the quantity of the reacted potassium dichromate is to be cooled, which is known as the amount of the potassium dichromate substance which is reacted and the amount of the potassium dichromate substance which is reacted is the amount which is known to be the amount of potassium dichromate that is needed to react with the waste water, which is a method for the analytical method of reflux titration.

The titration reaction equation（10）shows that:

$$1molCr_2O_7^{2-} \approx 6molFe^{2+} \qquad 6n_{Cr_2O_7^{2-}} = n_{Fe^{2+}} \qquad (11)$$

From the back titration（9）and（10）:

$$n_{Cr_2O_7^{2-}(reaction)} = n_{Cr_2O_7^{2-}(excessive)} - n_{Cr_2O_7 2-(residue)} \qquad (12)$$

In addition, in the measurement, the interference caused by the other components in the test component is to be blanked simultaneously, then the amount of organic substance in the waste water is the quantity of potassium chromate consumed after deducting the blank quantity:

$$n_{Cr_2O_7^{2-}} = n_{Cr_2O_7^{2-}(wasterwater)(reaction)} - n_{Cr_2O_7^{2-}(blank)\ (reaction)}$$

$$=[n_{Cr_2O_7^{2-}(excessive)} - \mathrm{n}_{\mathrm{Cr}_2O_7 2\text{-}(residue)}]_{(wasterwater)} - [n_{Cr_2O_7^{2-}(excessive)} - \mathrm{n}_{\mathrm{Cr}_2O_7 2\text{-}(residue)}]_{(blank)} \quad (13)$$

In addition, the amount of potassium dichromate in both blank and waste water was added to a certain amount.

$$n_{Cr_2O_7^{2-}(excessive)(wastewater)} = n_{Cr_2O_7^{2-}(excessive)(blank)} \quad (14)$$

Then:

$$n_{Cr_2O_7^{2-}} = \mathrm{n}_{\mathrm{Cr}_2O_7^{2-}(wasterwater)} - \mathrm{n}_{\mathrm{Cr}_2O_7^{2-}(blank)}$$

$$= \mathrm{n}_{\mathrm{Cr}_2O_7^{2-}(residue)(blank)} - \mathrm{n}_{\mathrm{Cr}_2O_7^{2-}(residue)(wasterwater)} \quad (15)$$

From (11) into:

$$n_{Cr_2O_7^{2-}} = \frac{1}{6}\mathrm{n}_{Fe^{2+}} = \frac{1}{6}(C_{Fe^{2+}}V_{\mathrm{Fe}^{2+}(residue)(blank)} - C_{Fe^{2+}}V_{\mathrm{Fe}^{2+}(residue)(wasterwater)}) \quad (16)$$

Here, $V_{\mathrm{Fe}^{2+}(residue)(blank)}$ 1 and $V_{\mathrm{Fe}^{2+}(residue)(wasterwater)}$ are ammonium ferrous sulfate consumed in titration equation (10), which can be abbreviated as $V_{\mathrm{Fe}^{2+}(blank)}$ and $V_{\mathrm{Fe}^{2+}(wasterwater)}$, namely:

$$n_{Cr_2O_7^{2-}} = \frac{1}{6}\mathrm{n}_{Fe^{2+}} = \frac{1}{6}(C_{Fe^{2+}}V_{\mathrm{Fe}^{2+}(blank)} - C_{Fe^{2+}}V_{\mathrm{Fe}^{2+}(wasterwater)}) \quad (17)$$

Next, the idea of chemical oxygen needs, the actual chemical requirement is the amount of oxygen that the organic contaminant would need to have a full oxidation reaction.

$$C_{(organicmatter)} + O_2 \rightarrow CO_2 \quad (18)$$

In the natural state, however, the equation (18) is long, so that the complete oxidation of organic substances is achieved by the artificial regulation of the total oxidation of the organic pollutants by the strong oxidizer, the potassium chromate, in the acidic, high-temperature, silver sulfuric acid catalyst, and the organic pollutants are expressed as C（carbon）, while the final product of the organic matter is expressed as CO_2, see (10), so the chemical oxygen demand is the quantity of oxidizing agent consumed by the reducing substance in the 1 L water sample under certain conditions, expressed as mg/L of oxygen.

Although it's oxidized by the dichromate, but the final expression is still the quantity of O_2, it's:

$$Cr_2O_7^{2-} + 6e = 2Cr^{3+} \quad (19)$$

$$O_2 - 4e = 2H_2O \quad (20)$$

$$2molCr_2O_7^{2-} \approx 3molO_2 \quad (21)$$

$$3n_{Cr_2O_7^{2-}} = 2n_{O_2} \quad (22)$$

Expression of conversion into chemical requirements:

$$\mathrm{n}_{O_2} = \frac{3}{2}n_{Cr_2O_7^{2-}} = \frac{m_{O_2}}{M_{O_2}} / V_{watersample} \quad (23)$$

$$CODcr\ (O_2,\ mg/L) = \frac{3}{2} \times \mathrm{n}_{Cr_2O_7^{2-}} \times 1000 \times M_{O_2} \times \frac{1}{V_{watersample}} \quad (24)$$

$$
\begin{aligned}
CODcr（O_2,\ mg/L）&= \frac{3}{2}\times \mathrm{n}_{Cr_2O_7^{2-}} \times 1000\times M_{O_2}\times\frac{1}{V_{watersample}}\\
&= \frac{3}{2}\times\frac{1}{6}\mathrm{n}_{Fe^{2+}}\times 1000\times M_{O_2}\times\frac{1}{V_{watersample}}\\
&= \frac{1}{4}\times \mathrm{n}_{Fe^{2+}}\times 1000\times 32\times\frac{1}{V_{watersample}}\\
&= \frac{(V_{blank}-V_{wasterwater})\times C_{Fe^{2+}}\times 8\times 1000}{V_{watersample}}
\end{aligned}
\qquad (25)
$$

Put (11) into (24)

Shorthand for：

$$CODcr（O_2,\ mg/L）=\frac{(V_0-V_1)\times C\times 8\times 1000}{V} \qquad (26)$$

Conclusion: after analysis, it is concluded that equations 26 and equations 1 are in complete agreement26 and 1 are in full agreement.

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