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ENVIRONMENTAL PROTECTION INDUSTRY STANDARD

OF THE PEOPLE'S REPUBLIC OF CHINA

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High-chlorine wastewater - Determination of chemical oxygen demand - Chlorine emendation method

高氯废水 化学需氧量的测定

氯气校正法

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High-chlorine wastewater - Determination of chemical oxygen demand - Chlorine emendation method

1 Scope

This method applies to the determination of chemical oxygen demand (COD) in high-chlorine wastewater with a chloride ion content of less than 20 000 mg/L. The detection limit of the method is 30 mg/L. It applies to the determination of COD in wastewater from oil fields, coastal refineries, oil depots, chlor-alkali plants, and deep-sea discharge wastewater.

2 References

The following document contains the provisions which, through reference in this Standard, become the provisions of this Standard, and have the same effect as this standard.

GB 11914-89 Water quality - Determination of the chemical oxygen demand - Dichromate method

When the above standard is revised, the latest version shall be used.

3 Definitions

3.1 High-chlorine wastewater

It refers to wastewater with chloride ion content greater than 1 000 mg/L.

3.2 Apparent COD

It refers to the corresponding mass concentration of oxygen converted from the amount of potassium dichromate consumed by the water sample under certain conditions.

3.3 Chloride ion emendation value

It refers to the mass concentration of oxygen corresponding to the chlorine generated by the oxidized chloride ions in the water sample.

Meet the requirements of 4.5.1 in GB 11914-89.

5.8 Ammonium ferrous sulfate [$(NH_4)_2Fe(SO_4)_2$] standard titration solution

Meet the requirements of 4.6 in GB 11914-89.

5.9 Sodium thiosulfate ($Na_2S_2O_3$) standard titration solution

5.9.1 Sodium thiosulfate standard titration solution of which the concentration is $c(Na_2S_2O_3) \approx 0.05$ mol/L

WEIGH 12.4 g of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in water that is freshly boiled and covered for cooling, ADD 1.0 g of anhydrous sodium carbonate (Na_2CO_3), TRANSFER to a 1000 ml brown volumetric flask, DILUTE to the mark with water, and SHAKE well. After standing for one week, CALIBRATE its exact concentration. If the solution becomes cloudy, it must be filtered.

5.9.2 Calibration method

In a 250 ml iodine volumetric flask, ADD 1.0 g of potassium iodide (KI) and 50 ml of water, ADD 5.00 ml of potassium dichromate standard solution (6.7), SHAKE until completely dissolved, ADD 5 ml of sulfuric acid solution (6.3), and immediately PLUG with a plug and SHAKE well. After placing in the dark place for 5 min, TITRATE with sodium thiosulfate standard titration solution to be calibrated until the solution is light yellow, ADD 1 ml of starch solution, and CONTINUE titration until the blue color just disappears, which is the end point. RECORD the amount of sodium thiosulfate standard titration solution consumed. MAKE a blank titration at the same time.

5.9.3 Calculation of the concentration of sodium thiosulfate standard titration solution:

$$c(Na_2S_2O_3) = \frac{0.2500 \times 5.00}{V_1 - V_2}$$

where: V_1 - the volume of sodium thiosulfate standard titration solution consumed in the titration of potassium dichromate standard solution, ml;

V_2 - the volume of sodium thiosulfate standard titration solution consumed in the titration of blank solution, ml.

5.10 Starch solution (1 g/100 ml)

WEIGH 1.0 g of soluble starch, MAKE a paste with a small amount of water, slowly POUR 100 ml of boiling water, continue to BOIL until the solution is clear, and STORE in a reagent bottle after cooling. Prepare before use.

8 Steps

8.1 PIPETTE 20.0 ml of water sample (or take an appropriate amount of water sample and add water to 20.0 ml) in a 500 ml inline conical flask. According to the chloride ion concentration in the water sample, ADD different volumes of mercury sulfate solution (5.5) according to the ratio of $HgSO_4$: Cl^- = 10: 1 (see Table 1 for details), and SHAKE well. ADD 10.0 ml of potassium dichromate standard solution (5.7) and 3 ~ 5 bumping-proof glass beads (5.13).

8.2 When determining a batch of water samples with different chloride ion concentrations at the same time, in order to reduce the number of determinations of blank value, they can be appropriately grouped according to the level of chloride ion concentration. The amount of mercury sulfate added is determined by the highest chloride ion concentration in the group, and the ratio is $HgSO_4$: Cl^- = 7.5: 1.

8.3 CONNECT the inline conical flask to the lower end of the condensing tube, and CONNECT the condensate. Slowly ADD silver sulfate-sulfuric acid solution (5.6) from the upper end of the condensing tube through a funnel (see Table 1 for the added volume), and continuously ROTATE the inline conical flask to make them mix uniformly.

8.4 ADD 20.0 ml of sodium hydroxide solution (5.11) to the absorption bottle, and DILUTE to 200 ml with water.

8.5 CONNECT the device according to Figure 1, and INSERT the outlet tube under the liquid surface of the absorption bottle.

8.6 PASS IN nitrogen (5 ~ 10 ml/min), HEAT, and REFLUX for 2 h after the solution boils. After stopping heating, INCREASE the nitrogen flow (30 ~ 40 ml/min), taking care not to suck the solution back. Continue to PASS IN nitrogen for 30 ~ 40 min.

8.7 REMOVE the absorption bottle, COOL to room temperature; ADD 1.0 g of potassium iodide, and then ADD 7.0 ml sulfuric acid (5.4) to adjust the pH of the solution to about 3 ~ 2; LEAVE it for 10 min; TITRATE to light yellow with sodium thiosulfate standard titration solution; ADD starch indicator to continue to titrate until the blue just disappears, which is the end point. RECORD the milliliters V_3 of sodium thiosulfate standard titration solution consumed.

8.8 After the inline conical flask is cooled, ADD a certain amount of water from the upper end of the condensing tube. See Table 1 for the amount of water added. REMOVE the inline conical flask. After the solution is cooled to room temperature, ADD 3 drops of 1,10-phenanthroline indicator solution (5.12), and TITRATE with ammonium ferrous sulfate standard titration solution (5.8) until

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