

HJ

INDUSTRY STANDARD OF THE PEOPLE'S REPUBLIC OF CHINA

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Water quality - Determination of the chemical oxygen demand - Dichromate method

水质 化学需氧量的测定 重铬酸盐法

(English Translation)

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1 Scope

This Standard specifies the dichromate method for determining chemical oxygen demand in water.

This Standard applies to the determination of chemical oxygen demand in surface water, domestic sewage and industrial wastewater. This Standard does not apply to the determination of chemical oxygen demand in water, of which the chloride concentration is greater than 1000 mg/L (after dilution).

When the sampling volume is 10.0 ml, the detection-limit of this method is 4 mg/L, and the lower limit of determination is 16 mg/L. The upper limit of determination of undiluted water samples is 700 mg/L; when the limit is exceeded, the determination shall be made after dilution.

2 Normative references

This Standard refers to the terms of the following documents. For undated references, the valid edition applies to this Standard.

GB 11896, Water quality - Determination of chloride - Silver nitrate titration method

GB 17378.4, The specification for marine monitoring - Part 4: Seawater analysis

HJ 506, Water quality - Determination of dissolved oxygen - Electrochemical probe method

HJ/T 91, Technical specifications requirements for monitoring of surface water and waste water

3 Terms and definitions

The following terms and definitions are applicable to this Standard.

6.1 Sulfuric acid (H_2SO_4), $\rho = 1.84 \text{ g/ml}$, guaranteed reagent.

6.2 Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$): primary reagent; take an appropriate amount of potassium dichromate and dry in a 105°C oven to constant weight.

6.3 Silver sulfate (Ag_2SO_4).

6.4 Mercury sulfate (HgSO_4).

6.5 Ammonium ferrous sulfate ($[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$).

6.6 Potassium hydrogen phthalate ($\text{KC}_8\text{H}_5\text{O}_4$).

6.7 Ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$).

6.8 Sulfuric acid solution: 1+9 (V/V).

6.9 Potassium dichromate standard solution

6.9.1

Potassium dichromate standard solution $c(\text{K}_2\text{Cr}_2\text{O}_7) = 0.250 \text{ mol/L}$.

Accurately weigh 12.258 g of potassium dichromate (6.2); dissolve it in water; fix-volume to 1000 ml.

6.9.2

Potassium dichromate standard solution $c(\text{K}_2\text{Cr}_2\text{O}_7) = 0.0250 \text{ mol/L}$.

Dilute the potassium dichromate standard solution (6.9.1) 10 times.

6.10 Silver sulfate-sulfuric acid solution.

Weigh 10 g of silver sulfate (6.3); add it to 1 L of sulfuric acid (6.1); leave it for 1 ~ 2 day(s) to dissolve it; shake it well; shake carefully before use.

6.11 Mercury sulfate solution, $\rho = 100 \text{ g/L}$.

Weigh 10 g of mercury sulfate (6.4); dissolve in 100 ml of sulfuric acid solution (6.8); mix it

well.

6.12 Ammonium ferrous sulfate standard solution

6.12.1

Ammonium ferrous sulfate standard solution, $c[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}] \sim 0.05 \text{ mol/L}$.

Weigh 19.5 g of ammonium ferrous sulfate (6.5) to dissolve in water; add 10 ml of sulfuric acid (6.1); dilute to 1000 ml after the solution is cooled.

7.1 Reflux device: All-glass reflux device for 250 ml conical flask with grinding

mouth. Water-cooled or air-cooled all-glass reflux device can be selected. Other equivalent condensation reflux devices are also applicable.

7.2 Heating device: electric furnace or other equivalent digestion device.

7.3 Analytical balance: sensitivity of 0.0001 g.

7.4 Acid burette: 25 ml or 50 ml.

7.5 Instruments and apparatuses that are commonly used in general laboratories.

8 Sample

Collect and store water samples in accordance with the relevant regulations of

HJ/T 91. The volume of the collected water sample shall not be less than 100 ml.

The collected water samples shall be placed in glass bottles and analyzed as soon as possible. If it cannot be analyzed immediately, sulfuric acid (6.1) shall be added until $\text{pH} < 2$; store it at 4°C for less than 5 days.

9.1.1 Sample determination

Take 10.0 ml of water sample into the conical flask; add 5.00 ml of mercury sulfate solution (6.11), potassium dichromate standard solution (6.9.2) and several explosive boiling-proof glass beads (6.15) in order; shake well. Add mercury sulfate solution (6.11) at a mass ratio of $m[\text{HgSO}_4]:m[\text{Cl}]$

$] \geq 20:1$; the maximum addition is 2 ml.

Connect the conical flask to the lower end of the condenser of the reflux device (7.1); slowly add 15 ml of silver sulfate-sulfuric acid solution (6.10) from the upper end of the condenser to prevent the escape of low-boiling organics; rotate the conical flask to mix evenly. Since the solution begins to boil, maintain a slight boiling reflux for 2 h. In the case of a

water-cooled device, condensate shall be introduced before adding the silver sulfate-sulfuric acid solution (6.10).

mg/L, 7 mg/L, 9 mg/L, and 19 mg/L, respectively; the reproducibility limits R are 6 mg/L, 8 mg/L, 13 mg/L, and 47 mg/L, respectively.

Seven laboratories measure actual water samples, of which the chemical oxygen demand concentration is 16 mg/L~3.65x10

4 mg/L, in a variety of industries, including surface water, domestic sewage, sewage treatment plant wastewater, pharmaceutical wastewater, textile wastewater, printing and dyeing wastewater, papermaking wastewater, pesticide-containing wastewater and smelting wastewater. The obtained results: the relative standard deviation of the samples whose chemical oxygen demand concentration is 16 mg/L ~ 95 mg/L is 1.3%~11%; the relative standard deviation of the samples whose chemical oxygen demand concentration is 108 mg/L ~ 250 mg/L is 0.4%~6.2%;

the relative standard deviation of the samples whose chemical oxygen demand concentration is 340 mg/L~3.65x10

4 mg/L is 0.3%~5.1%.

11.2 Accuracy

Seven laboratories measure the certified standard samples, of which the chemical oxygen demand concentrations are 28.9 ± 2 mg/L, 74.2 ± 4.9 mg/L, and

208 ± 10 mg/L; the relative errors are -2.8%~1.6%, -5.8%~3.5% and -

0.9%~2.4%, respectively. The final relative errors are $0.43\% \pm 4.2\%$,

$0.14\% \pm 5.8\%$, and $1.2\% \pm 2.2\%$.

12.1 Blank test

For each batch of samples, at least perform two blank tests.

12.2 Precision control

Each batch of samples shall have 10% of parallel samples. If the number of samples is less than 10, make at least one parallel sample. The relative deviation of parallel samples does not exceed $\pm 10\%$.

12.3 Accuracy control

During the determination of each batch of samples, a certified standard sample or quality control sample shall be analyzed. The measurement value shall be within the guaranteed