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Analysis of water used in boiler and cooling system - Determination of hardness

锅炉用水和冷却水分析方法 硬度的测定

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WARNING -- The strong acids and alkalis used in this Standard are corrosive. Avoid inhalation or contact with skin when using. If splashed on the body, rinse immediately with plenty of water. In severe cases, seek medical attention immediately.

1 Scope

This Standard specifies the determination method for hardness of water used in boiler and cooling system.

This Standard applies to the determination for hardness of water used in boiler and cooling system. The determination range of chrome black T method in this Standard is 0.01mmol/L~5mmol/L. When it exceeds 5mmol/L, the sampling volume can be appropriately reduced. Determine after dilution. The determination range of acid chrome blue K method is 1μmol/L~100μmol/L. The determination range of potentiometric titration is 0.25mmol/L~10mmol/L (both with Ca^{2+} and Mg^{2+} as basic units). This Standard is also applicable to the determination of the hardness of natural water, cooling water, demineralized water and boiler feed water.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

GB/T 601, *Chemical reagent - Preparations of reference titration solutions*

GB/T 603, *Chemical reagent - Preparations of reagent solutions for use in test methods*

GB/T 6682, *Water for analytical laboratory use - Specification and test methods*

3 General

The reagents used in this Standard, unless otherwise specified, shall be of analytically pure. The water used shall comply with the provisions of GB/T 6682. Of which, the determination of constant hardness shall meet the requirements of grade two water. The

4.1.2.6 Disodium ethylenediaminetetraacetic acid standard titration solution I: c (EDTA) is about 0.05mol/L.

4.1.2.7 Disodium ethylenediaminetetraacetic acid standard titration solution II: c(EDTA) is 0.005mol/L. Accurately dilute 10 times with disodium edetate standard titration solution I. This solution is prepared when required.

4.1.2.8 Chrome black T indicator solution: 5g/L.

4.1.3 Test steps

4.1.3.1 Use a pipette to measure 100mL of water sample. Place it in a 250mL Erlenmeyer flask. If the water sample is turbid, it shall be filtered with medium-speed quantitative filter paper before sampling. When the water sample is highly acidic or alkaline, it can be neutralized with sodium hydroxide solution or hydrochloric acid solution. The buffer solution is then added. When the iron in the water sample is greater than 2mg/L, the aluminum is greater than 2mg/L, the copper is greater than 0.01mg/L, and the manganese is greater than 0.1mg/L, it will interfere with the determination. Before adding the indicator, 2mL of L-cysteine hydrochloride solution and 2mL of triethanolamine solution can be used for combined masking to eliminate the interference.

4.1.3.2 Add 5mL of ammonia-ammonium chloride buffer solution. Add two to three drops of chrome black T indicator.

NOTE: For water samples with high carbonate hardness, pre-dilute or add 80%~90% of the required EDTA standard solution before adding the buffer solution (recorded into the titration volume). Otherwise, after the buffer solution is added, the carbonate is precipitated, and the end point is prolonged.

4.1.3.3 Under constant shaking, use disodium ethylenediaminetetraacetic acid standard titration solution I to titrate. When it is near the end point, titrate slowly. When the solution changes from red to pure blue, it is the end point. When the water sample hardness is less than 1mmol/L, disodium edetate standard titration solution II shall be used, or a microburette (device) shall be used.

4.1.3.4 Conduct the blank test at the same time.

4.1.4 Result calculation

The hardness is expressed in molar concentration c_1. The value is expressed in millimoles per liter (mmol/L), calculated according to formula (1):

$$c_1 = \frac{(V_1 - V_0)c \times 10^3}{V} \qquad \cdots\cdots (1)$$

Where,

V_1 - The value of the volume of the standard titration solution of disodium edetate consumed by the titration of the water sample, in milliliters (mL);

V_0 - The value of the volume of the disodium EDTA standard titration solution consumed by the blank test, in milliliters (mL);

c - The exact value of the actual concentration of disodium EDTA standard titration solution, in moles per liter (mol/L);

V - The value of the volume of the water sample measured, in milliliters (mL) (V=100).

4.1.5 Tolerance

Take the arithmetic mean of the parallel determination results as the determination result. When the hardness is greater than 1mmol/L, the absolute difference between the two parallel determination results is not greater than 0.05mmol/L. When the hardness is less than or equal to 1mmol/L, the absolute difference between the two parallel determination results shall not be greater than 0.005mmol/L.

4.2 Acid chrome blue K method

4.2.1 Method summary

In an aqueous solution with a pH of about 10, acid chrome blue K is used as an indicator. Titrate with ethylenediaminetetraacetic acid disodium salt (EDTA) standard titration solution to blue as the end point. Calculate the hardness value according to the volume of EDTA consumed.

When the content of iron, aluminum, copper and manganese in the water sample reaches a certain concentration, there will be interference to the determination. L-cysteine hydrochloride and triethanolamine can be added to jointly mask and eliminate the interference.

4.2.2 Reagents or materials

4.2.2.1 Water: GB/T 6682, grade one.

4.2.2.2 Borax buffer solution: Weigh 40g of borax ($Na_2B_4O_7 \cdot 10H_2O$). Add 10g of sodium hydroxide. Dissolve in water and dilute to 1L. Store in plastic bottles.

4.2.2.3 Disodium ethylenediaminetetraacetic acid standard titration solution: c(EDTA) is about 0.005mol/L. Same as 4.1.2.7.

4.2.2.4 Acid chrome blue K indicator solution: 5g/L. Weigh 0.5g of acid chrome blue K ($C_{16}H_9O_{12}N_2S_3Na_3$) and 4.5g of hydroxylamine hydrochloride. Grind well in a mortar. Add 10mL of borax buffer solution. Dissolve in 40mL of water. Use 95% ethanol to dilute to 100mL. Store in brown bottles for later use. The storage time is one month.

result. The absolute difference between the two parallel determination results is not more than 1.0μmol/L.

5 Potentiometric titration method

5.1 Method summary

Use automatic potentiometric titrator and calcium electrode to measure. Use disodium ethylenediaminetetraacetic acid (EDTA) standard titration solution to titrate calcium and magnesium ions. When the titration reaches a complete jump curve, the instrument automatically recognizes the stoichiometric point (that is, the jump point). Hardness is calculated from the volume of standard titration solution consumed at the jump point.

When the content of copper and manganese in the water sample reaches a certain concentration, there will be interference to the determination. L-cysteine hydrochloride and triethanolamine can be added to jointly mask and eliminate the interference.

5.2 Reagents or materials

5.2.1 Disodium ethylenediaminetetraacetic acid standard titration solution: c(EDTA) is about 0.05mol/L. When the hardness of the water sample is less than 1mmol/L, the standard titration solution of c(EDTA) 0.005mol/L is used.

5.2.2 Other reagents are the same as 4.1.2.

5.3 Instruments and equipment

5.3.1 Automatic potentiometric titrator.

5.3.2 Calcium ion electrode.

5.4 Test steps

5.4.1 Take an appropriate amount of water sample in the measuring cup. If the water sample is turbid, it shall be filtered with medium-speed quantitative filter paper before sampling. Add 5mL of ammonia-ammonium chloride buffer solution. When the water sample is highly acidic or alkaline, it can be neutralized with sodium hydroxide solution or hydrochloric acid solution. It is then added with buffer solution. When the copper and manganese in the water sample are greater than 0.2mg/L, it will interfere with the determination. Before the determination, 2mL of L-cysteine hydrochloride solution and 2mL of triethanolamine solution can be used for joint masking to eliminate the interference.

5.4.2 Place the measuring cup on the titration stand. Insert the calcium ion electrode. Turn on the instrument and the stirrer. Use disodium edetate standard titration solution to titrate. Stop the titration when the titration reaches a complete jump curve.

Annex A

(normative)

Adjustment of ammonia-ammonium chloride buffer solution

A.1 Method summary

Use chrome black T as indicator. To improve the sensitivity of endpoint indication, a certain amount of ethylenediaminetetraacetic acid (EDTA) disodium magnesium salt shall be added to the buffer solution. To avoid the unequal amount of EDTA and magnesium ions, and the hardness substances in the ammonia water used in the preparation, it is necessary to adjust the ammonia-ammonium chloride buffer solution after preparation, so as to avoid the hardness in the buffer solution or excessive EDTA, which will bring errors to the determination results.

A.2 Reagents or materials

A.2.1 Magnesium standard solution: 0.010mol/L. Weigh 0.6159g of magnesium sulfate heptahydrate (excellent pure). Dissolve it in water. Transfer it to a 250mL volumetric flask. Dilute to the scale mark. Shake well. Or use commercially available magnesium (Mg^{2+}) standard solution to accurately dilute.

A.2.2 Disodium ethylenediaminetetraacetic acid standard titration solution: c(EDTA) is about 0.01mol/L.

A.2.3 Other reagents: Same as 4.1.2.

A.3 Test steps

A.3.1 Use a pipette to measure 10.00mL of the prepared ammonia-ammonium chloride buffer solution in the Erlenmeyer flask. Add 90mL of water. Add two to three drops of chrome black T indicator solution.

A.3.2 After adding the indicator solution, if the solution turns red, it indicates that there are hardness substances in the buffer solution. Use disodium edetate standard titration solution to titrate until it changes from red to pure blue. Then according to the consumption of disodium edetate standard titration solution and the amount of buffer solution to be adjusted, calculate the volume of disodium edetate standard titration solution to be added (for example, prepare 1000mL of buffer solution. 0.10mL of standard titration solution of disodium edetate is consumed during the test, then 9.90mL of the EDTA disodium standard titration solution needs to be added to the remaining 990mL of buffer solution).

A.3.3 After adding the indicator solution, if the solution turns blue, there may be two

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