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Determination of calcium and magnesium in industrial circulating cooling water and scale -- Atomic absorption spectrometric method

工业循环冷却水及水垢中钙、镁的测定

原子吸收光谱法

(ISO 7980:1986, Water quality -- Determination of calcium and magnesium -- Atomic absorption spectrometric method, NEQ)

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Determination of calcium and magnesium in industrial circulating cooling water and scale -- Atomic absorption spectrometric method

1 Scope

This document specifies the determination method of the content of calcium and magnesium in industrial circulating cooling water and the content of calcium and magnesium in the scale of the boiler water system or circulating water system - atomic absorption spectrometry.

This document is applicable to the determination of calcium content of 0.5 mg/L~75 mg/L and magnesium content of 0.1 mg/L to 50 mg/L in industrial circulating cooling water; it is applicable to the determination of calcium content ≥0.005% and magnesium content ≥0.005% in scale.

This document is also applicable to the determination of calcium and magnesium content in the scale of various other industrial water, raw water, and water systems, as well as calcium content in phosphorus-zinc pre-film solution for industrial circulating refrigeration.

2 Normative references

The following documents are essential to the application of this document. For the dated documents, only the versions with the dates indicated are applicable to this document; for the undated documents, only the latest version (including all the amendments) is applicable to this standard.

GB/T 602 Chemical reagent -- Preparations of standard solutions for impurity

GB/T 4470 Analytical spectroscopic methods. Flame emission, atomic absorption and atomic fluorescence. Vocabulary

GB/T 6682-2008 Water for analytical laboratory use -- Specification and test methods

DL/T 1151.2 Analytical methods of scale and corrosion products in power plants. Part 2: Sampling and dissolving method for scale and corrosion products

HG/T 3530 Industrial circulating cooling water. Sampling and production for sludge and corrosion products

3 Terms and definitions

Terms and definitions defined in GB/T 4470 are applicable to this document.

4 Principles

The sample is sprayed into air-acetylene flame or nitrous oxide-acetylene flame by atomization, calcium and magnesium are pyrolyzed into ground state atoms; take calcium resonance line 422.7 nm and magnesium resonance line 285.2 nm as analytical lines to measure their absorbances, respectively. When using the air-acetylene flame to measure calcium and magnesium, adding strontium chloride or lanthanum chloride can inhibit the interference of water treatment chemicals and various coexisting elements in water (see Appendix A). When using the nitrous oxide-acetylene flame to measure calcium and magnesium, add cesium chloride to suppress interference.

5 Reagents or materials

Warning: The acetylene gas specified in this document is flammable and explosive when mixed with air; nitrous oxide is harmful to the human body; pay attention to safety in use, prevent leakage, and operate in strict accordance with the specifications. Strong acids are caustic, so pay attention when using them; handle them with care; if being splashed by them, rinse with plenty of water; avoid inhalation or skin contact.

Unless otherwise specified, the reagents used in this document are analytical grade only. See GB 6819 for the requirements for acetylene gas used in the test. The standard solution for impurity used in the test shall be prepared in accordance with the provisions of GB/T 602 unless other provisions are specified.

5.1 Water: it shall be grade 2 specified in GB/T 6682-2008.

5.2 Hydrochloric acid.

5.3 Nitric acid.

5.4 Perchloric acid.

5.5 Hydrochloric acid solution: 1+1.

5.6 Hydrochloric acid solution: 1+99.

5.7 Nitric acid solution: 1+99.

min~10 min before measurement can be performed.

8 Preparation of samples

8.1 Collection of water sample and preparation of sample solutions

Collect a certain amount of water sample from the flowing water to be tested; immediately, add the hydrochloric acid solution (5.5) to acidify the water sample to pH ≈1 [generally, add 2.0 mL of hydrochloric acid solution (5.5) per 100 mL of water sample] to prepare a sample solution, and record the volume of the collected water sample and the volume of the added hydrochloric acid solution (5.5). The collected and acidified water sample shall be clear and transparent, otherwise, it shall be filtered with medium-speed quantitative filter paper. The sample solution is sealed and stored in the sampling container and can be placed stably for 14 days.

8.2 Preparation of scale sample and sample solutions

8.2.1 Collect and prepare scale sample according to the requirements of HG/T 3530 or DL/T 1151.2, and then dissolve the scale sample according to the steps of 8.2.2 or 8.2.3. to prepare the scale sample solution.

8.2.2 Use the electric heating method to dissolve the scale sample, and operate according to the following requirements:

a) Weigh about 0.2 g~0.3 g of the prepared scale sample, and the weight shall be accurate to 0.1 mg; place it in a 250 mL glass beaker.

b) Add a small amount of water to the beaker to fully wet the scale sample; slowly add 15 mL of hydrochloric acid and 5 mL of nitric acid, cover with a watch glass, and shake well; slowly heat and boil the solution on an electric hot plate or adjustable electric furnace for 20 min. If there is still brown or tan residue, add 10 mL of hydrochloric acid and boil until the solution is clear.

c) Remove the beaker, add 10 mL of perchloric acid after the solution cools slightly, then heat until thick white smoke begins to emit; remove the watch glass slightly, and continue to slowly heat for 15 min~20 min; must not evaporate the solution to dryness.

d) Remove the beaker, add 10 mL of the nitric acid solution while it is still hot, and stir well to dissolve the salts on the wall of the beaker.

e) If the scale sample is completely dissolved, transfer the solution to a 100 mL volumetric flask; use a pipette to absorb the nitric acid solution to wash the inner wall of the beaker (no less than 3 times), and collect the washing solution in the 100 mL volumetric flask; add nitric acid solution to dilute to the Scale, and shake well; it is the scale sample solution. If the dissolved solution contains white suspended solids, filter it with medium-speed quantitative filter paper; wash the beaker wall, the precipitation attached to the wall, and filter paper with the nitric acid solution (about 10 mL each time) several times; wash them no less than 5 times; collect the filtrate and the washing solution in a volumetric flask, add nitric acid solution to dilute to the Scale, and shake well; it is the scale sample solution.

8.2.3 Use microwave digestion to dissolve scale sample, and operate according to the following requirements:

a) Weigh 0.2 g~0.3 g of the prepared scale sample, and the weight shall be accurate to 0.1 mg; put it into the digestion inner tank of the microwave digestion apparatus, add a few drops of water to wet it, and slowly add 6 mL hydrochloric acid and 2 mL nitric acid; shake the digestion inner tank, and let the gas run out (if a large amount of gas is generated, the inner tank can be pre-digested at 100 °C for 20 min on the electric hot plate, and then add the same proportion of digestion solution to about 10 mL); cover the tank tightly and put it into the vessel. Put the digestion vessel into the microwave digestion apparatus, and digest the scale sample according to the instrument instructions.

b) After the digestion is completed, transfer the solution in the tank to a 250 mL glass beaker, wash the digestion tank and the lid with a small amount of nitric acid solution, and pour the washing solution into the beaker together; add 10 mL perchloric acid; place the beaker on an electric hot plate or adjustable electric furnace, and slowly heat until white smoke emits for 15 min~20 min; do not evaporate the solution to dryness; remove the beaker from the electric hot plate or adjustable electric furnace, add 10 mL of the nitric acid solution while it is still hot, and stir well to dissolve the salts on the wall of the beaker.

c) If the scale sample is completely dissolved, transfer the solution to a 100 mL volumetric flask, use a pipette to suck the nitric acid solution to wash the inner wall of the beaker (no less than 3 times), and collect the washing solution in the 100 mL volumetric flask; add nitric acid solution to dilute to the Scale, and shake well; it is the scale sample solution. If the dissolved solution contains white suspended solids, filter it with medium-speed quantitative filter paper; wash the beaker wall, the precipitate attached to the wall, and the filter paper with the nitric acid solution (about 10 mL each time) several times; wash them no less than 5 times; collect the filtrate and the washing solution in the volumetric flask, add nitric acid solution to dilute to the Scale, and shake well; it is the scale sample solution.

8.2.4 Except for not adding the scale sample, follow the same operation as preparation of the scale sample solution in 8.2.2 or 8.2.3 to prepare the blank solution.

zero-setting with the reagent blank, and respectively measure the absorbances of the blank solution and the scale sample solution after dilution; then, obtain the corresponding calcium content (mg/L) from the calcium calibration curve. If the calcium content is lower than the detection limit or exceeds the range of the calibration curve, the dilution factor can be adjusted and then re-measured.

9.2 Determination of the content of magnesium

9.2.1 Drawing of the magnesium calibration curve

Accurately pipette 0.00 mL (blank), 0.50 mL, 1.00 mL, 2.00 mL, and 3.00 mL of magnesium standard solution II into 50 mL volumetric flasks respectively, and add 5.0 mL strontium chloride solution or 2.0 mL lanthanum chloride solution (if using nitrous oxide-acetylene flame, then add 5.0 mL cesium chloride solution); dilute to the Scale with the hydrochloric acid solution (5.6), and shake well. The mass concentrations of magnesium in this series of calibration solutions are 0.00 mg/L, 0.10 mg/L, 0.20 mg/L, 0.40 mg/L, and 0.60 mg/L, respectively. Under the best working conditions of the instrument, at the wavelength of 285.2 nm, carry out zero-setting with the reagent blank and then measure the absorbance. Taking the measured absorbance as the ordinate and the corresponding magnesium content (mg/L) as the abscissa, draw the calibration curve or calculate the regression equation. The linear correlation coefficient of the calibration curve shall be greater than 0.999, otherwise, it shall be redrawn.

9.2.2 Determination of water sample

Pipette an appropriate volume of the acidified sample solution (8.1) accurately, put it into a 50 mL volumetric flask, and add 5.0 mL of strontium chloride solution or 2.0 mL lanthanum chloride solution (if using nitrous oxide-acetylene flame, then add 5.0 mL cesium chloride solution); dilute to the Scale with the hydrochloric acid solution (5.6), and shake well. According to the same instrument conditions as that is in the preparation of the calibration curve, carry out zero-setting with the reagent blank and measure the absorbance; then, obtain the corresponding magnesium content (mg/L) from the magnesium calibration curve. If the magnesium content is lower than the detection limit or exceeds the range of the calibration curve, the dilution factor can be adjusted and then re-measured.

9.2.3 Determination of scale sample

Accurately pipette appropriate volumes of the scale sample solution (8.2.2 or 8.2.3) and the blank solution (8.2.4) respectively, and place them in a 50 mL volumetric flask. (Select an appropriate dilution factor according to the source of the scale sample and the type of scale. Generally, the scale sample mainly composed of calcium and magnesium scale is diluted about 50 times to 200 times; the scale sample mainly composed of iron oxide scale is diluted about 10 times to 50 times. Adopt the same dilution factor to dilute the blank solution and the scale sample solution.) Add 5.0 mL strontium chloride solution or 2.0 mL lanthanum chloride solution (if using nitrous oxide-acetylene flame, then add 5.0 mL cesium chloride solution), dilute with the hydrochloric acid solution (5.6) to the Scale, and shake well. According to the same instrument conditions as that is in the preparation of the calibration curve, carry out zero-setting with the reagent blank, and respectively measure the absorbances of the blank solution and the scale sample solution after dilution; then, obtain the corresponding magnesium content (mg/L) from the magnesium calibration curve. If the magnesium content is lower than the detection limit or exceeds the range of the calibration curve, the dilution factor can be adjusted and then re-measured.

10 Calculation of results

10.1 Calculation of calcium and magnesium content in water sample

The content of calcium and magnesium is expressed by mass concentration ρ and in milligram per liter (mg/L), calculated according to formula (1):

$$\rho = \rho_1 f \frac{V_1}{V} \qquad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

Where:

ρ_1 --- The value of calcium and magnesium content obtained from the calibration curves of calcium and magnesium, in milligrams per liter (mg/L);

f --- The ratio of the acidulated sample volume (mL) to the volume of the collected water sample (mL) (see 8.1);

V_1 --- The value of the constant volume of the sample solution after dilution during measurement, in milliliters (mL) (V_1=50);

V --- The value of the volume of the collected sample solution during dilution, in milliliters (mL).

The calculation results shall be rounded to two decimal places.

10.2 Calculation of calcium and magnesium content in scale sample

The content of calcium and magnesium is expressed by mass fraction w, and the value is expressed in %; calculate it according to formula (2):

$$w = \frac{(\rho_1 - \rho_0) V_T V_1 \times 10^{-3}}{1\,000 m_0 V} \times 100 \qquad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

Appendix A

(Informative)

Elimination of the interference of water treatment chemicals and coexisting elements in water

A.1 Interference in calcium measurement

Calcium is one of the easily interfered elements in atomic absorption analysis. In industrial circulating cooling water, there are usually some coexisting inorganic ions and the added water treatment chemicals; When there are still some ions, such as Al^{3+}, Si, SO_4^{2-}, PO_4^{3-}, in the water, the sensitivity of the calcium determination will be reduced. After the addition of strontium chloride or lanthanum chloride, the following ions and agents will not interfere with the determination when their concentrations are less than or equal to the following specified values:

a) Inorganic ions in water: Fe^{2+} 50 mg/L; Al^{3+} 50 mg/L; Mg^{2+} 80 mg/L; Si 60 mg/L; Na^+ 500 mg/L; K^+ 50 mg/L; Cl^- 500 mg/L; SO_4^{2-} 100 mg/L; Cu^{2+} 20 mg/L; PO_4^{3-} 60 mg/L; Zn^{2+} 50 mg/L.

b) Water treatment chemicals: polyol phosphonate 10 mg/L; sodium hexametaphosphate 10 mg/L; sodium polyacrylate 10 mg/L; polyacrylic acid 10 mg/L; acrylic acid-acrylate copolymer 10 mg/L; tripolyphosphoric acid Sodium 10 mg/L; HEDP 20 mg/L; EDTMPS 10 mg/L; ATMP 10 mg/L; polyquaternium 100 mg/L; mercaptobenzothiazole 3 mg/L; benzotriazole 3 mg/L.

A.2 Interference in magnesium measurement

Magnesium is an alkaline earth metal with a low ionization potential and is prone to ionization interference in flames. In circulating cooling water, there are usually some coexisting inorganic ions and added water treatment chemicals. When there are some ions, such as Al^{3+}, Si, PO_4^{3-}, Fe^{2+}, they will form difficult-to-dissociate compounds with magnesium, and the sensitivity of the magnesium will be reduced. After the addition of a release agent, such as lanthanum chloride or strontium chloride, it will form stable compounds with the ions; then, magnesium will be released from the compounds of interfering elements. The following ions and agents will not interfere with the determination when their concentrations are less than or equal to the following specified values:

a) Inorganic ions in water: Al^{3+} 50 mg/L; Fe^{2+} 50 mg/L; Si 40 mg/L; Na^+ 500 mg/L; K^+ 50 mg/L; Cl^- 500 mg/L; SO_4^{2-} 100 mg/L; Cu^{2+} 20 mg/L; PO_4^{3-} 60 mg/L; Zn^{2+} 50 mg/L.

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