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

(ISO 6878:2004, Water quality - Determination of phosphorus - Ammonium molybdate spectrometric method, NEQ)

锅炉用水和冷却水分析方法 磷酸盐的测定

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

Warming: The strong acid and strong base which are used in this document are corrosive. Avoid inhalation or contact with the skin during use. If it splashes on the body, use plenty of water to rinse it immediately. If serious, seek medical advice immediately.

1 Scope

This document describes methods for the determination of orthophosphate, total inorganic phosphate, and total phosphate content in water used in boiler and cooling system: ammonium molybdate spectrophotometric method and continuous flow-ammonium molybdate spectrophotometric method.

This document applies to the determination of orthophosphate, total inorganic phosphate, and total phosphate content in water used in boiler and cooling system. The measurement range of the ammonium molybdate spectrophotometric method is 0.05 mg/L ~ 50 mg/L (based on PO_4^{3-}); the measurement range of the continuous flow-ammonium molybdate spectrophotometric method is 0.1 mg/L ~ 50 mg/L (based on PO_4^{3-}).

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the version corresponding to that date is applicable to this document; for undated references, the latest version (including all amendments) is applicable to this document.

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

3 Terms and definitions

No terms and definitions need to be defined in this document.

4 Ammonium molybdate spectrophotometric method

4.1 Determination of orthophosphate content

4.1.1 Method summary

In the presence of acidic media and antimonic salts, orthophosphate reacts with ammonium molybdate solution to produce yellow phosphomolybdenum heteropoly acid. Use ascorbic acid to reduce it to phosphomolybdenum blue, and measure it by the spectrophotometric method at a wavelength of 710 nm.

The reaction formula is:

$$12(NH_4)_2MoO_4 + H_2PO_4^- + 24H^+ \xrightarrow{KSbOC_4H_4O_6} [H_2PMo_{12}O_{40}]^- + 24NH_4^+ + 12H_2O$$

$$[H_2PMo_{12}O_{40}]^- \xrightarrow{C_6H_8O_6} H_3PO_4 \cdot 10MoO_3 \cdot Mo_2O_5$$

4.1.2 Reagents or materials

Unless otherwise specified, only use analytical reagents or above.

4.1.2.1 Water: GB/T 6682-2008, grade 3.

4.1.2.2 Ascorbic acid solution: 100 g/L. Store it in brown bottles at 4 °C, valid for 14 days.

4.1.2.3 Ammonium molybdate solution: 26 g/L. Weigh 13 g of ammonium molybdate and 0.35 g of potassium antimony tartrate ($KSbOC_4H_4O_6 \cdot 1/2H_2O$); dissolve in 200 mL of water; add 230 mL of sulfuric acid solution (1+1); mix well; cool and use water to dilute to 500 mL; shake well. Store it in brown bottles, valid for 2 months.

4.1.2.4 Phosphate standard stock solution (based on PO_4^{3-}): 500 mg/L. Weigh 0.716 5 g of potassium dihydrogen phosphate that has been dried to a constant weight at 100 °C ~ 105 °C, accurate to 0.2 mg; dissolve in about 500 mL of water; transfer to a 1 000 mL volumetric flask; use water to dilute to the mark; shake well.

4.1.2.5 Phosphate standard solution (based on PO_4^{3-}): 20 mg/L. Pipette 20.00 mL of phosphate standard stock solution into a 500 mL volumetric flask; use water to dilute to the mark; shake well. Formulate this solution when needed.

4.1.3 Instruments and apparatuses

Spectrophotometer: Equipped with an absorption cell with a thickness of 1 cm.

4.1.4 Test procedure

4.1.4.1 Preparation of sample

Filter the water sample collected on site through medium-speed filter paper and collect into clean and dry glass bottles for subsequent analysis. Operate things to note during the test according to Appendix A. See Appendix B for the interference judgment and elimination of coexisting ions in the sample.

4.3.2.3 Potassium persulfate solution: 40 g/L. Store in brown bottles, valid for 14 days.

4.3.2.4 Other reagents: Same as 4.1.2.

4.3.3 Instruments and apparatuses

Spectrophotometer: Equipped with an absorption cell with a thickness of 1 cm.

4.3.4 Test procedure

Transfer an appropriate volume of sample (4.1.4.1) to a 100 mL Erlenmeyer flask by referring to Table 1; add water to approximately 40 mL. Add 1.0 mL of sulfuric acid solution and 5.0 mL of potassium persulfate solution; place it on an electric furnace to maintain a slight boil for about 30 minutes for digestion. When boiling, add water regularly to keep the solution volume at 25 mL ~ 30 mL. After cooling, use sodium hydroxide solution to adjust the pH to 3 ~ 10 and transfer to a 50 mL volumetric flask. Add 2.0 mL of ammonium molybdate solution and 1.0 mL of ascorbic acid solution; use water to dilute to the mark; shake well; leave at room temperature for 10 minutes. Use a spectrophotometer to measure the absorbance at a wavelength of 710 nm with a 1 cm absorption cell and a blank as a reference.

Note: Other digestion methods, such as microwave digestion, can also be used.

4.3.5 Result calculation

4.3.5.1 The total phosphate (based on PO_4^{3-}) content ρ_3 is expressed in terms of mass concentration, in milligrams per liter (mg/L), and is calculated according to Formula (3):

$$\rho_3 = \frac{m}{V} \quad \cdots\cdots\cdots\cdots (3)$$

Where:

m – the mass of PO_4^{3-} found from the calibration curve (4.1.4.2) or calculated from the regression equation, in micrograms (μg);

V – the volume of the sample transferred, in milliliters (mL).

Express the calculation result to two digits after the decimal point.

4.3.5.2 The organophosphate (based on PO_4^{3-}) content ρ_4 is expressed in terms of mass concentration, in milligrams per liter (mg/L), and is calculated according to Formula (4):

$$\rho_4 = \rho_3 - \rho_2 \quad \cdots\cdots\cdots\cdots (4)$$

Adjust the instrument according to the instrument instruction manual to achieve optimal usage conditions. After starting up, first replace the reagent with water to check the tightness of the entire analysis flow path and the smoothness of the liquid flow. After the baseline stabilizes (about 20 minutes), the system begins to take the reagent package. After the baseline stabilizes again, proceed to the measurement of total phosphate according to 5.4.3 ~ 5.4.4. When measuring orthophosphate, use water instead of potassium persulfate solution; turn off the hydrolysis heating and UV digestion functions of the total phosphate analysis module for measurement. When measuring total inorganic phosphate, use water instead of potassium persulfate solution, and turn off the UV digestion function of the total phosphate analysis module for measurement.

5.4.2 Preparation of calibration solutions

Respectively pipette 0.00 mL (blank), 0.50 mL, 1.00 mL, 2.00 mL, 3.00 mL, 4.00 mL, 5.00 mL, 6.00 mL and 7.00 mL of phosphate standard solution into nine 50 mL volumetric flasks, corresponding to the PO_4^{3-} mass concentrations of 0.00 mg/L, 0.50 mg/L, 1.00 mg/L, 2.00 mg/L, 3.00 mg/L, 4.00 mg/L, 5.00 mg/L, 6.00 mg/L and 7.00 mg/L.

5.4.3 Drawing of calibration curve

Add an appropriate amount of phosphate standard series solution (larger than the instrument's liquid absorption capacity) to the sample cup; use the injector to sample and measure in sequence according to the program. Draw a calibration curve with the measured signal value as the ordinate and the corresponding mass concentration of PO_4^{3-} (mg/L) as the abscissa.

5.4.4 Determination

Measure the sample (4.1.4.1) using the blank as a reference under the same conditions as for drawing the calibration curve. If the phosphate content in the sample exceeds the range of the calibration curve, it shall be measured after dilution.

Note: When using a continuous flow analyzer for measurement, the type and concentration of the solution in the required reagent package, the flow and flow rate of the reagent, and the range of the calibration curve will vary depending on the model of the instrument. The user shall choose the best test conditions according to the instrument model.

5.5 Calculation of results

The phosphate (based on PO_4^{3-}) content ρ is expressed in terms of mass concentration, in milligrams per liter (mg/L), and is calculated according to Formula (5):

$$\rho = \rho_0 f \qquad \cdots\cdots (5)$$

Appendix A

(Normative)

Things to note during the test

A.1 Filtration of water sample

The water sample shall be filtered within 4 hours after collection, and the filtration time shall not exceed 10 minutes. If the temperature of the water sample is lower than room temperature, the sample shall be brought to room temperature before filtering. The first 10 mL of filtrate shall be discarded during filtration.

A.2 Cleaning of glassware

Before use, all glassware shall be soaked in hydrochloric acid solution (1+4) or nitric acid solution (1+4) for more than 12 hours, and then washed thoroughly with water.

Regularly use sodium hydroxide solution (80 g/L) to wash the absorption cell or detector, and then rinse thoroughly with water to remove colored complex deposits attached to the glassware.

A.3 Calibration of absorption cell

Before the test, the absorption cell shall be calibrated to eliminate differences between different absorption cells.

A.4 Decomposition of organophosphorus substance

In the presence of a large amount of organic matter, the decomposition effect of potassium persulfate is poor, and nitric acid and perchloric acid shall be used to decompose organic matter. The operation is as follows: accurately pipette a certain volume of sample; add 2 mL of nitric acid and 1 mL of perchloric acid; heat on an adjustable electric furnace until brown vapor no longer comes out and white crystals appear. After cooling, add water and heat slightly until a clear and transparent solution is obtained. Use sodium hydroxide solution (80 g/L) to adjust the pH to 7 ~ 9.

A.5 Processing and storage of water sample

To ensure that the water sample does not change, it is best to measure it immediately after taking the sample. If the measurement cannot be carried out immediately, adjust the pH to less than 2 with sulfuric acid and store it in a glass bottle at 4 °C.

Appendix C

(Normative)

Continuous flow analyzer system performance check

C.1 Reagents or materials

C.1.1 Phosphate standard solution: 50 mg/L, same as 5.2.9.

C.1.2 Sodium pyrophosphate standard stock solution: 500 mg/L (based on PO_4^{3-}). Weigh 1.173 8 g of sodium pyrophosphate decahydrate; dissolve it in an appropriate amount of water; transfer it to a 1 000 mL volumetric flask; use water to dilute it to the mark; shake well. Store at 4 °C, valid for 3 months.

C.1.3 Sodium pyrophosphate standard solution: 2.50 mg/L (based on PO_4^{3-}). Pipette 10.00 mL of sodium pyrophosphate standard stock solution into a 100 mL volumetric flask; use water to dilute to the mark; shake well. Pipette 5.00 mL of the above solution into a 100 mL volumetric flask; use water to dilute to the mark; shake well. Formulate this solution when needed.

C.1.4 Pyridoxal-5-phosphate standard stock solution: 500 mg/L (based on PO_4^{3-}). Weigh 0.279 1 g of pyridoxal 5-phosphate; dissolve it in an appropriate amount of water; transfer it to a 200 mL volumetric flask; use water to dilute to the mark; shake well; store in a brown glass bottle. Store at 4 °C, valid for 3 months.

C.1.5 Pyridoxal-5-phosphate standard solution: 2.50 mg/L (based on PO_4^{3-}). Pipette 10.00 mL of pyridoxal-5-phosphate standard stock solution into a 100 mL volumetric flask; use water to dilute to the mark; shake well. Pipette 5.00 mL of the above solution into a 100 mL volumetric flask; use water to dilute to the mark; shake well. Formulate this solution when needed.

C.2 Performance check

Use sodium pyrophosphate standard solution to verify the hydrolysis efficiency of the method, and use pyridoxal-5-phosphate standard solution to verify the digestion efficiency of the method. Generally, the test is performed once every 2 weeks. Parallelly measure sodium pyrophosphate standard solution (when measuring orthophosphate or total inorganic phosphate) or pyridoxal-5-phosphate standard solution (when measuring total phosphate) and phosphate standard solution; calculate the hydrolysis or digestion efficiency R according to Formula (C.1), where R shall be greater than 90%.

$$R = \frac{\rho_r}{\rho_s} \times 100\% \qquad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (C.1)$$

------ The End ------