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Standard test method for fluorine, chlorine and sulfur in petroleum products - Combustion-ion chromatography

石油产品中氟、氯和硫含量的测定 燃烧-离子色谱法

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Warning -- The personnel using this document should have practical experience in formal laboratory work. The use of this document may involve certain hazardous materials, equipment and operations. This document does not point out all possible safety issues. The user is responsible for taking appropriate safety and health measures and ensuring compliance with the conditions stipulated by relevant national laws and regulations.

1 Scope

This Standard specifies the test method that uses combustion-ion chromatography to determine fluorine, chlorine and sulfur content in petroleum products, interference, instruments and equipment, reagents and materials, sampling, preparation, calibration, test procedures, calculation of results, expression of results, as well as precision and deviation.

This Standard is applicable to the determination of fluorine, chlorine and sulfur content in petroleum products of which the boiling point range is 30°C~380°C and the determination range is 0.30mg/kg~15.00mg/kg, including gasoline, ethanol gasoline, naphtha, distillate, jet fuel, diesel, biodiesel blended fuel. This method can be also used for the samples outside this range, but the precision has not been determined.

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 1884, *Petroleum and liquid petroleum product - Determination of density - Hydrometer method*

GB/T 1885, *Petroleum measurement tables*

GB/T 4756, *Method for manual sampling of petroleum liquids*

6.2.7 Humidification device: a certain flow rate of primary water (7.1) can be passed into the high-temperature combustion tube to obtain a high-temperature hydrolysis environment.

6.3 Absorption unit

6.3.1 Connecting pipe: It is used to connect the high-temperature combustion pipe and the absorption pipe. There shall be pipelines for the water inlet and the water outlet. After the specimen is completely burned in the high-temperature combustion tube, the instrument automatically flushes the connecting pipe with grade one water (7.1) and transfers all to the absorption pipe (6.3.2).

6.3.2 Absorption tube: At least containing 10mL of absorption solution. During the sample combustion process, the absorption liquid in the tube continuously absorbs gas and all liquids to ensure that all combustion products (HX and SO_x) are absorbed. After the combustion is over, the volume can be automatically adjusted to the required volume. A quantitative absorption solution can be automatically injected into the ion chromatography instrument through the quantitative loop.

6.3.3 After the absorption liquid is injected into the ion chromatography instrument, and before the next specimen is burned, use grade one water (7.1) to rinse the connecting tube and absorption tube, so as to minimize the contamination of the previous sample.

6.4 Ion chromatography unit

6.4.1 Pump: transport eluent.

6.4.2 Continuous eluent generator (optional): the device that can automatically prepare and purify eluent, including electrolytic eluent generator method and automatic quantitative tube method. Without reducing the precision and accuracy of the method, other continuous eluent generators can be used.

6.4.3 Anion pre-concentration column (optional): mainly play a role in pre-concentrating anions and eliminating matrix effect. If a pre-concentration column is installed, then the remaining hydrogen peroxide can be removed before the absorption liquid is injected into the guard column and the separation column, so as to eliminate the potential interference to the fluoride ion chromatographic peak resolution.

6.4.4 Guard column: protect the separation column from contamination by strongly retained components. At the same time, a better separation effect can be obtained.

6.4.5 Separation column: anion exchange column, which can make the anion

7.11 Absorbent: Take 0.7mL of 30% hydrogen peroxide (7.7) in a 2000mL volumetric flask. Use grade one water (7.1) to dilute to the scale mark. The purpose of adding hydrogen peroxide to the absorption solution is to convert all the SO_x in the gas to be measured into SO_4^{2-}. If the sulfur content in the sample is not determined, hydrogen peroxide cannot be added to the absorption solution. Use grade one water (7.1) as absorbent.

NOTE 1: Under the premise of meeting the precision of the method, other concentrations of absorbents can also be used.

NOTE 2: When the sulfur content in the sample is less than 15mg/kg, hydrogen peroxide may not be added. Select according to the determination situation of the instrument. When the difference in the area count of the sulfur peak obtained with and without hydrogen peroxide in the absorbent is less than 5%, hydrogen peroxide may not be added to the absorbent.

7.12 Quality control (QC) samples: stable, representative samples or use standard working solutions (9.2.2), used to verify the accuracy of the entire test process, see Chapter 14.

7.13 Quartz wool.

7.14 Carrier gas: argon or helium, with a purity of not less than 99.99%.

NOTE: Purification device can be used to remove impurities, such as: molecular sieve to remove moisture. Use activated carbon or other materials with the same function to adsorb hydrocarbon compounds.

7.15 Oxygen: used as combustion gas, with a purity of not less than 99.75%.

7.16 Nitrogen (optional): access to the eluent tank to prevent air from entering or generating bubbles. The purity is not less than 99.99%.

8 Sampling

8.1 Conduct sampling according to GB/T 4756 and GB/T 27867 methods. Samples containing volatile components shall be opened before the determination of the sample container. The samples shall be analyzed as soon as possible after taking out the samples to avoid the loss and contamination of the measured elements.

8.2 After the sample is collected in the container, if it is not used immediately, the sample shall be thoroughly mixed in the container before analysis.

NOTE: Because there are light components in the sample, pay attention to safety when mixing.

and burned. If carbon deposits are found in the sample boat, the residence time of the sample boat in the combustion furnace shall be increased. If carbon deposits are found at the end of the high-temperature combustion tube, slow down the sampling speed of the sample boat or increase the residence time of the sample boat at the front end of the high-temperature combustion tube. It can also take these two measures at the same time. Remove the carbon deposits on the parts according to the requirements of the instrument manual. Reassemble the instrument.

10.5 After the standard working solution analysis is completed, the sample boat is pulled back to the refrigeration module (6.2.3). The sample boat shall stay on the refrigeration module for at least 100s, or longer. Allow the sample boat to cool down completely. Then proceed to the next standard working solution test.

11 Test steps

11.1 Prepare samples according to Chapter 8.

11.2 Use a syringe to inject a quantitative sample, such as 100μL, into the sample boat. According to the determination conditions of the analytical standard working solution, determine the specimen in the same way to get the chromatogram of the specimen. Integrate the chromatographic peaks of fluorine, chlorine and sulfur elements to obtain the chromatographic peak area of each element. In order to reduce the errors caused by combustion efficiency and absorption efficiency, the conditions of the specimen analysis shall be consistent with the conditions of the analysis standard working solution.

11.3 After analyzing the specimen, check the high-temperature combustion tube and the various components in the flow path through which the gas passes for carbon deposits to ensure that the specimen is completely oxidized and burned. If carbon deposits are found in the sample boat, the residence time of the sample boat in the combustion furnace shall be increased. If carbon deposits are found at the end of the high-temperature combustion tube, slow down the sampling speed of the sample boat or increase the residence time of the sample boat at the front end of the high-temperature combustion tube. It can also take these two measures at the same time. Remove the carbon deposits on the parts according to the requirements of the instrument manual. Reassemble the instrument.

11.4 After the sample analysis is completed, the sample boat is pulled back to the refrigeration module (6.2.3). The sample boat shall stay on the refrigeration module for at least 100s, or longer. After the sample boat can be completely cooled, proceed to the next specimen test. This step is especially important for specimens with a low initial boiling point.

(g/cm^3).

13 Result expression

Take the arithmetic average of the two repeated determinations as the determination result, in milligrams per kilogram (mg/kg). The result is retained to 0.01mg/kg.

14 Quality control

14.1 After each startup, the QC sample (7.12) shall be determined at least once before analysis.

14.2 If the laboratory has established quality control and quality assurance procedures, it can be used to confirm the reliability of the determination results.

14.3 If the laboratory has not established quality control and quality assurance procedures, it can refer to NB/SH/T 0843 as the evaluation system.

15 Precision and deviation

15.1 Precision

15.1.1 Overview

The precision is obtained through collaborative experiments conducted by 6 laboratories on 22 samples, including: gasoline, ethanol gasoline, diesel, naphtha, distillate oil, jet fuel, diesel, biodiesel blended fuel. Refer to GB/T 6683 to determine it through statistical analysis results between laboratories. Judge the reliability of the test results according to 15.1.2 and 15.1.3 (95% confidence level).

NOTE: If the specimens containing volatile components are not properly stored, it will affect the measurement results.

15.1.2 Repeatability (r)

The same operator, in the same laboratory, uses the same instrument to continuously measure the same specimen. The difference between the two test results shall not exceed the repeatability limit of the method in Table 3. See Table 4 for typical repeatability values of samples at different concentrations.

15.1.3 Reproducibility (R)

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