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Ethylene and Propylene for Industrial Use – Determination of Trace Carbon Monoxide, Carbon Dioxide and Acetylene – Gas Chromatographic Method

工业用乙烯、丙烯中微量一氧化碳、二氧化碳和乙炔的测定 气相色谱法

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Ethylene and Propylene for Industrial Use – Determination of Trace Carbon Monoxide, Carbon Dioxide and Acetylene – Gas Chromatographic Method

1 Scope

This Standard specifies a gas chromatographic method for the determination of trace carbon monoxide, carbon dioxide and acetylene in ethylene and propylene for industrial use.

This Standard applies to the determination of carbon monoxide with content no less than 1mL/m^3, carbon dioxide with content no less than 5mL/m^3, and acetylene with content no less than 1mL/m^3 in ethylene and propylene.

This Standard is not intended to address all safety issues related to its use. It is the user's responsibility to take appropriate safety and health measures to ensure compliance with the relevant state regulations.

2 Normative References

The provisions in following documents become the provisions of this Standard through reference in this Standard. For dated references, the subsequent amendments (excluding corrigendum) or revisions do not apply to this Standard, however, parties who reach an agreement based on this Standard are encouraged to study if the latest versions of these documents are applicable. For undated references, the latest edition of the referenced document applies.

GB/T 3723 Sampling of Chemical Products for Industrial Use – Safety in Sampling (GB/T 3723-1999, idt ISO 3165:1976)

GB/T 8170 Rules of Rounding off for Numerical Values & Expression and Judgement of Limiting Values

GB/T 13289 Ethylene for Industrial Use - Sampling in the Liquid and the Gaseous Phase (GB/T 13289-1991, neq ISO 7382:1986)

GB/T 13290 Propylene and Butadiene for Industrial Use - Sampling in the Liquid Phase (GB/T 13290-1991, neq ISO 8563:1987)

concentrated sulfuric acid; then it is treated with 50% lye, pyrogallic acid-based solution, and then the calcium chloride and phosphorus pentoxide to purify and dry. After the air in the container is exhausted, it can be collected, and the purity is over 99%.

4.4.4 Carbon dioxide: commercial carbon dioxide with a purity (volume fraction) greater than 99%, pure carbon dioxide can also be prepared by the following method: use the carbonate sodium to react with dilute hydrochloric acid, and obtain it after drying with concentrated sulfuric acid. The purity can reach over 99%.

4.4.5 Acetylene: the purity (volume fraction) is greater than 99%. It may use the commercial acetylene with a purity of more than 99%, and pure acetylene can also be prepared by the following method: take tens of grams of calcium carbide; put it into a 500mL three-necked flask; pour an appropriate amount of water into the separatory funnel on the three-necked flask; and add dropwise to the three-necked flask. The produced acetylene needs to be purified by 20% (mass fraction) sodium hydroxide solution and 20% (mass fraction) chromic anhydride solution. After the air in the container is exhausted, it can be collected. The purity of acetylene can reach over 99%.

4.5 Standard sample

Carbon monoxide, carbon dioxide or acetylene standard samples can be purchased from the market for the certified standard samples or self-prepared. If the base gas is nitrogen or ethylene (4.4.1), it shall not contain carbon monoxide, carbon dioxide or acetylene; otherwise, it shall be corrected. The content of carbon monoxide, carbon dioxide or acetylene in the standard sample shall be close to the concentration in the sample to be tested.

5 Instruments

5.1 Gas chromatograph: equipped with a ten-port valve sample-injecting device (quantitative tube volume of 1 mL ~ 3 mL), a backflushing device, a split sample-injecting system and a flame ionization detector (FID); and the dual gas path gas chromatography that can be operated under the conditions of Tables 1 or 3. The determination of carbon monoxide and carbon dioxide also needs to be equipped with a nickel reformer catalytic hydrogenation device. The peak height produced by the instrument for the minimum detection concentration of impurities specified in this Standard shall be at least twice the noise. The ten-port valve connection and backflushing device of the instrument are shown in Figures 1 and 2. Other sample-injecting and backflushing devices that meet the separation and quantification effects of this Standard may also be used.

the determination of acetylene are shown in Table 3; and the typical chromatograms are shown in Figures 5 and 6. Other chromatographic columns and analytical conditions that give equivalent separation and quantification may also be used.

5.3 Nickel reformer: The nickel reformer is a device that converts carbon monoxide and carbon dioxide into methane by catalytic hydrogenation; and consists of a nickel catalytic hydrogenation column and a heating device. The recommended operating conditions of the nickel catalytic hydrogenation column are shown in Table 2 (the operating conditions of the packed column and capillary column are the same).

The nickel catalytic hydrogenation column is prepared as follows: Weigh 200g of nickel nitrate and dissolve it in 90mL of distilled water; add 80g of 6201 chromatographic carrier or other suitable carriers; boil for (5~10) min; cool off; filter; and place the carrier in an evaporating dish. Dry at 105 ℃; and then placed on an electric furnace to heat slowly (shall be in a fume hood) until the reddish-brown nitrogen dioxide is exhausted. After burning at 450℃ for 7 h under nitrogen-injecting state; cool off; and obtain a nickel oxide catalyst. Put it into a clean and dry stainless steel column tube; and inject hydrogen gas (flow rate is about 50 mL/min) at 350 ℃ ~ 380 ℃ for 4 h to reduce it to nickel catalyst and it can be used. The prepared nickel catalytic hydrogenation column shall be sealed and stored to prevent the activity of the catalyst from being reduced after contact with air and water.

NOTE: Standard samples shall be used to check the reactivity of the nickel catalytic hydrogenation column regularly.

5.4 Recording device: electronic integrator or chromatographic data processing device.

Take the gas sample with the same injection volume as the standard sample; inject it into the chromatograph by the gas sample-injecting valve; repeat the measurement twice; record the peak area of carbon monoxide, carbon dioxide or acetylene; and compare it with the corresponding external standard peak area.

NOTE: When injecting liquid propylene sample, measures shall be taken to ensure that the liquid propylene is completely vaporized. It can also be vaporized by means of a flash evaporating injector or a water bath.

8 Presentation of Analysis Results

8.1 Calculation

8.1.1 The content, φ_i, of carbon monoxide, carbon dioxide or acetylene, measured in milliliters per cubic meter (mL/m^3), shall be calculated according to Formula (1):

$$\varphi_i = \varphi_s \times \frac{A_i}{A_s} \qquad \cdots\cdots (1)$$

Where:

φ_s - the content of carbon monoxide, carbon dioxide or acetylene in the standard sample, in milliliters per cubic meter (mL/m^3);

A_i - the peak area of carbon monoxide, carbon dioxide or acetylene in the tested sample;

A_s - the peak area of carbon monoxide, carbon dioxide or acetylene in the standard sample.

8.2 Presentation of results

8.2.1 The numerical value of the analysis result shall be rounded off according to the provisions of GB/T 8170; and the arithmetic mean of the results of two repeated determinations shall be taken to represent the analysis result.

8.2.2 Report the content of carbon monoxide, carbon dioxide or acetylene, and accurate to $1mL/m^3$.

9 Precision

9.1 Repeatability

In the same laboratory, the absolute difference between the two independent test results obtained by the same operator using the same equipment, according to the same test method, and testing the same test object independently of each other in a short period of time shall not exceed the values listed in Table 4. The given repeatability limit (r) is premised on the condition

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