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NATIONAL STANDARD OF THE PEOPLE'S REPUBLIC OF CHINA

GB/T 44244-2024

Hydrogen for proton exchange membrane fuel cell vehicles - Determination of carbon monoxide and carbon dioxide - Gas chromatography method

质子交换膜燃料电池汽车用氢气 一氧化碳、二氧化碳的测定 气相色谱法

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1 Scope

GB/T 44244-2024 gives the gas chromatographic determination of carbon monoxide and carbon dioxide in hydrogen for proton exchange membrane fuel cell vehicles. Carbon monoxide is the classic poison of the platinum anode: fractions of a part per million adsorb on the catalyst and block the hydrogen from reaching it, and the loss of performance accumulates over the fuelling life of the stack rather than appearing at once, which is why the fuel specification sets a limit at 0.2 micromoles per mole and why measuring at that level in a hydrogen matrix is difficult. The standard describes the principle, the reagents and materials, the instruments and equipment, the test procedures, the processing of the data, the precision and accuracy, the quality assurance and control, and the test report, with informative annexes giving typical chromatograph gas flows and operating conditions and typical precision values. It took effect on 1 November 2024.

This document describes the principle, reagents and materials, instruments and equipment, test procedures, test data processing, precision and accuracy, quality assurance and control, and test report for the determination of carbon monoxide and carbon dioxide content in hydrogen for proton exchange membrane fuel cell vehicles using gas chromatography-helium ionization detector. This document is applicable to the determination of carbon monoxide and carbon dioxide content in hydrogen for proton

exchange membrane fuel cell vehicles. The determination of carbon monoxide and carbon dioxide content in hydrogen for other purposes shall be carried out in accordance with the scope specified in this document. The measurement range of carbon monoxide is 0.05 μmol/mol~10.0 μmol/mol. The measurement range of carbon dioxide is 0.05 μmol/mol~10.0 μmol/mol.

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 43306, Gas analysis -- Sampling guidelines

GB/T 44244, Hydrogen for proton exchange membrane fuel cell vehicles -- Determination of carbon monoxide and carbon dioxide -- Gas chromatography method

JJF 1342, General Requirements for the Competence of Reference Material Producers

3 Terms and definitions

There are no terms or definitions that require definition in this document.

4 Principle

The specimen is introduced into a gas chromatograph equipped with three valves and three columns. By adjusting the opening and closing time of the three six-way valves, the direction of the carrier gas flowing through the chromatographic column can be changed at different time points, and a large amount of hydrogen in the sample is discharged through the first chromatographic column in sequence. Carbon dioxide is separated by the second chromatographic column and detected by a helium ionization detector. Carbon monoxide is separated by the third chromatographic column and detected by a helium ionization detector. Quantification is performed using the external standard method.

5.1 Gas

5.1.1 Carrier gas. helium, with a purity of not less than 99.9999%.

5.1.2 Detector discharge area gas, valve drive gas, valve protection gas, and protection gas for electronic flow control components. helium, with a purity of not less than 99.999%.

5.2 Gas reference materials

5.2.1 The qualifications of the production (development) institutions of gas reference materials shall comply with the requirements of JJF 1342.Users shall give priority to the use of certified gas reference materials. The nominal value of gas reference materials shall be 3

significant figures.

5.2.2 It is advisable to prepare at least 2 groups of carbon monoxide and carbon dioxide gas reference materials with different content levels. The balance gas is hydrogen. One of them is used as a standard sample for daily calibration. The target value shall be the same or similar to the carbon monoxide and carbon dioxide technical indicator limit required by GB/T 37244 or other hydrogen applications. The remaining content level reference materials can be used as quality control samples.

6.1 Gas chromatography system

6.1.1 Composition of gas chromatography system The gas chromatograph is equipped with a helium ionization detector. See Figure A.1 in Annex A for a typical gas flow diagram.

6.1.2 Chromatographic columns Use a chromatographic column with divinylbenzene and styrene copolymer as the stationary phase to determine carbon dioxide. Use a chromatographic column with molecular sieve as the stationary phase to analyze carbon monoxide. Other equivalent chromatographic columns can also be used. See A.2 for typical chromatographic column parameters that meet the analysis requirements of this method.

6.1.3 Detector The technical indicators of the helium ionization detector shall at least meet the following requirements. - Linear range greater than 105; - Minimum detection amount as low as 10-12 g.

6.2 Sampling gas cylinder Sampling gas cylinders shall comply with the requirements of GB/T 44244 and GB/T 43306.

7 Test procedures

7.1 Sampling The sampling of hydrogen for proton exchange membrane fuel cells shall comply with the provisions of GB/T 44244.

7.2 Operating conditions Typical gas chromatograph operating conditions are shown in Table A.1.

7.3 Detector stability According to the instrument manual, introduce a certain flow of helium into the detector. Wait until the detector response value stabilizes within the normal measurement allowable range. The lower the response value, the higher the purity of the helium, and the better the cleanliness and sealing of the system.

7.4 Sample injection

7.4.1 General requirements The connection between the gas cylinder and the gas chromatograph inlet shall follow the principle of small gas contact area and short connection distance. Needle valve shall be used as gas flow regulating valve. Stainless steel pipe shall be used for connecting pipeline. The injection method and injection pressure

of the calibration sample and the sample shall be consistent.

7.4.2 Injection method pen the outlet valve of the sample or calibration gas cylinder. Purge the injection system including the sample loop in one of the following two ways. - Continuous purge method. During the test sequence of a specimen, keep the outlet valve of the gas cylinder open. Continuously purge the sampling system with a certain flow of gas. The gas flow rate shall be stabilized at a fixed value of 80 mL/min~100 mL/min. - Intermittent purge method. Purge the injection system with a stable gas flow for at least 2 min. Close the outlet valve of the gas cylinder. After 2 s~5 s, start the analysis process immediately. Introduce the gas sample in the quantitative loop into the chromatographic column. The gas flow rate shall be stable at a fixed value of 80 mL/min~100 mL/min. NOTE. Connect a flow meter to the outlet of the sample purge pipeline to observe the gas flow.

7.5 Analysis of calibration samples Perform 5 initial measurements on the calibration gas reference material. Continue the measurement until the carbon monoxide and carbon dioxide response values do not drift in one direction during the continuous measurement process, and the difference between the results of two consecutive measurements meets the repeatability requirement. Take the average value as the quantitative basis. The typical chromatogram is shown in Figure A.2.Calibration analysis shall be performed on the day of sample analysis.

7.6 Sample analysis Use the same analytical conditions as the calibration samples to perform 5 initial measurements on the sample. Continue the measurement until the difference between the results of 2 consecutive measurements meets the repeatability requirement. Take the average value as the peak area of the sample measurement. The sample shall be tested within 7 d after collection. The storage of the sample shall be carried out in accordance with the provisions of GB/T 34525.