ICS 27.010
CCS F19

NATIONAL STANDARD OF THE PEOPLE'S REPUBLIC OF CHINA

GB/T 44238-2024

Hydrogen for proton exchange membrane fuel cell vehicles - Determination of helium, argon, nitrogen and hydrocarbons - Gas chromatography

质子交换膜燃料电池汽车用氢气 氦、氩、氮和烃类的测定 气相色谱法

Issued on: July 24, 2024 **Implemented on: November 1, 2024**

Issued by: State Administration for Market Regulation;
Standardization Administration of the PRC

Table of Contents

1 Scope

GB/T 44238-2024 specifies the determination of helium, argon, nitrogen and hydrocarbons in the hydrogen used by fuel cell vehicles, by gas chromatography. These are the inert and near-inert impurities: they do not poison the catalyst the way sulfur or carbon monoxide do, but they dilute the fuel and accumulate in the anode of a dead-ended stack, so they are limited in the fuel specification and they have to be measured. Doing so at the required levels is not trivial, because the analyte is a trace in a matrix of hydrogen, which is the worst possible carrier for thermal conductivity detection. The standard covers the principle, the interferences, the reagents and the calibration gases, the apparatus and the recommended chromatographic conditions and detectors, the introduction of the sample, the calibration, the analytical procedure, the calculation of results, the precision and the limit of quantification for each analyte. It works with the sampling standard GB/T 44262. For a hydrogen supplier, a filling station operator or a laboratory in China, this is the prescribed method.

This document describes the principle, reagents and materials, instruments and equipment, samples, test procedures, test data processing, precision and accuracy, quality assurance

and control, and test report for the determination of helium, argon, nitrogen and hydrocarbon components in hydrogen for proton exchange membrane fuel cell vehicles using gas chromatography-thermal conductivity detector/flame ionization detector method. This document is applicable to the determination of the content of helium, argon, nitrogen and hydrocarbon components in hydrogen for proton exchange membrane fuel cell vehicles. The determination of the content of helium, argon, nitrogen and hydrocarbon components in hydrogen for other purposes within the content range specified in this document shall be carried out as a reference. The measurement range of various components in this document is. helium. 10.0 μmol/mol~600.0 μmol/mol; argon. 5.0 μmol/mol~300.0 μmol/mol; nitrogen. 5.0 μmol/mol~300.0 μmol /mol; methane (C1) in hydrocarbons. 0.10 μmol/mol~200.0 μmol/mol; C2~C6 components and toluene in hydrocarbons. 0.10 μmol/mol~2.0 μmol/mol. NOTE. Hydrocarbons in this document refer to hydrocarbons that may be present in hydrogen, including alkanes, alkenes, alkynes and aromatics.

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 44262, Technical requirements for sampling of hydrogen for proton exchange membrane fuel cell vehicles

JJF 1342, General Requirements for Reference Material Producers

3 Terms and definitions

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

4 Principle

Use a gas chromatograph equipped with a thermal conductivity detector and a flame ionization detector. The specimen is divided into two paths through the injection line. One path enters the quantitative loop connected to the ten-way valve. By adjusting the opening and closing time of the valve, the non-target components are back-flushed and vented through the pre-separation column, and the target components helium, argon and nitrogen are separated through the molecular sieve column and detected by the thermal conductivity detector. The other path of the specimen enters the quantitative loop connected to the six-way valve, the aluminum oxide chromatographic column and the flame ionization detector to achieve the separation and detection of hydrocarbon components. The external standard method is used for quantification.

5.1 Gas

5.1.1 Carrier gas and fuel gas. hydrogen, with a purity of not less than 99.999%. The contents of helium, argon and nitrogen in hydrogen shall all be less than 1 μmol/mol. It is advisable to use hydrogen produced by a hydrogen generator.

5.1.2 Tail gas. nitrogen, with a purity of not less than 99.999%.

5.1.3 Combustion-supporting gas. Air, dry air that meets the requirements for use of gas chromatograph. An air generator with a purifier can be used.

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 The recommended gas reference substances shall include the following components. helium, argon, nitrogen, methane, ethane, propane, n-butane, n-pentane, n-hexane, benzene, toluene, and the balance gas is hydrogen. The preparation scheme can also be designed according to the needs.

5.2.3 It is recommended to prepare at least 2 gas reference substances with different content levels. One of them is used as a sample for routine calibration. The target value shall be the same or similar to the technical indicator limit of the corresponding component in GB/T 37244 or other purposes of hydrogen. The other content level reference substances can be used as quality control samples.

6.1 Gas chromatography system

6.1.1 Composition of gas chromatography system The system consists of a gas chromatograph equipped with a valve injection component, a split/splitless injection port, a thermal conductivity detector and a flame ionization detector. It can also be composed of two gas chromatographs equipped with a thermal conductivity detector and a flame ionization detector respectively. The typical gas chromatograph gas flow is shown in Figure A.1 in Annex A.

6.1.2 Chromatographic columns

6.1.2.1 A chromatographic column with a stationary phase of bonded polystyrene-divinylbenzene is selected as a pre-separation column to separate helium, oxygen/argon/nitrogen components from non-target components. Other equivalent chromatographic columns may also be used. A chromatographic column with a stationary phase of molecular sieve is selected as a separation column for helium, argon, oxygen, and

nitrogen components. The resolution of argon and oxygen components shall be no less than

2.Other equivalent chromatographic columns may also be used.

6.1.2.2 A chromatographic column with aluminum oxide as the stationary phase is selected as the hydrocarbon component separation column. Other equivalent chromatographic columns may also be used.

6.1.2.3 Typical chromatographic columns that meet the analysis requirements of this method are shown in A.2.

6.1.3 Thermal conductivity detector (TCD) Use TCD to detect helium, argon and nitrogen components. The technical indicators of the detector shall meet the following requirements. - The dynamic linear range is greater than 104; - The sensitivity not less than 10000 mV·mL/mg.

6.1.4 Flame ionization detector (FID) Use FID to detect hydrocarbon components. The technical specifications of the detector shall meet the following requirements. - The dynamic linear range is greater than 107; - The minimum detection limit is less than

6.2 Sampling gas cylinders Sampling gas cylinders shall comply with the requirements of GB/T 44262 and GB/T 43306.

7 Test steps

7.1 Sampling The sampling of hydrogen for proton exchange membrane fuel cells shall comply with the requirements of GB/T 44262.

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

7.3 Blank analysis Use hydrogen that meets the requirements of

5.1.1 as a blank sample and test until the baseline signal is stable. The blank value signal is lower than the lower limit of determination of the target compound.

7.4 Sampling

7.4.1 General requirements The connection between the gas cylinder and the gas chromatograph inlet shall be based on 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 calibration sample and sample shall be consistent.

7.4.2 Sample injection method Open the outlet valve of the sample or calibration gas cylinder. Purge the injection system including the sample loop in one of the following two