Agilent

Trusted Answers

Ammonia Analysis in High-Purity Hydrogen for Fuel Cell Vehicles

Using an Agilent 8890 GC/8255 NCD system

Author

Youjuan Zhang
Agilent Technologies
(Shanghai) Co. Ltd.

Abstract

This application note describes an analytical method for the determination of trace ammonia in hydrogen used for fuel cell vehicles. This analysis was conducted with an Agilent 8890 gas chromatography (GC) system, equipped with an Agilent 8255 nitrogen chemiluminescence detector (NCD). Great results have been obtained on this system. The correlation coefficient for ammonia is 0.9986, with repeatability results ranging from 0.66% to 4.76% at different calibration levels. The detection limit for ammonia was 24.2 ppb.

Introduction

The presence of trace impurities in hydrogen gas can affect the performance and lifespan of fuel cell catalysts, making the analysis of trace impurities in hydrogen gas an important issue to be addressed in the development of hydrogen fuel cell vehicles. Ammonia is a significant impurity in hydrogen gas, and the presence of trace amounts of ammonia can affect the performance of the battery, causing irreversible degradation.[1]

Typically, the main methods for analyzing ammonia in hydrogen fuel are Fourier transform infrared spectroscopy (FTIR), ion chromatography (IC), ion-selective electrode method, and the GC/NCD method. The international standards ISO 14687-2019[2] and SAE J2719- 2015[3] mention FTIR and IC for analysis, while GB/T 37244-2018[4] refers to the ion-selective electrode method for the determination of ammonia in hydrogen. Generally, the IC method and the ion-selective electrode method have higher sensitivity, but they require the use of additional solutions to absorb ammonia for analysis. This makes the sample preparation relatively complex. FTIR only requires filling the sample into the gas cell, which simplifies the sample preparation process, but its sensitivity is slightly inferior to the previous two methods.[1] The GC/NCD method is highly selective and is not easily affected by other impurities in the hydrogen gas. It has high sensitivity and can fully meet the quality control requirements of 100 ppb mentioned in the ISO 14687-2019 and GB/T 37244-2018 methods. Moreover, the introduction of samples through the gas sampling valve eliminates the need for any additional pretreatment, simplifying the workflow.

Agilent previously published an application note detailing the analysis of trace amounts of ammonia in ethylene using GC/NCD technology.[5] Based on the hardware configuration of the previous note, this application note details an analysis method for trace amounts of ammonia in hydrogen for fuel cells. This GC/NCD method has high selectivity and sensitivity, and is able to meet the quality control requirements of trace ammonia analysis for the hydrogen fuel cell industry.

Experimental

This study is based on an 8890 GC, equipped with a six-port gas sampling valve and an NCD detector, which is used to complete the analysis of trace ammonia in hydrogen. In order to improve sensitivity, a 2 mL sample loop was installed, and the sample was directly injected into a dedicated ammonia column (Agilent J&W Select Low Ammonia column, part number CP8590) for analysis. The ammonia standard gas (9.9 µmol/mol) was purchased from Zhongce Standards Technology (Chengdu) Co., Ltd. The preparation of calibration standards to a parts-per-billion (ppb) level was carried out using a pneumatic control module (PCM) and a gas blending module (orderable for new instruments as SP-1 8890-0717). This module, which is also called a mini gas blender, operates by continuously merging a calibration gas with a matrix gas stream, thereby achieving the targeted concentration. Figure 1 illustrates the setup for sample dilution, introduction, and analysis. This study employed high-purity hydrogen (99.999% purity) as the dilution gas, and the dilution ratio is calculated based on the flow of the standard gas (F_1) and the flow of matrix (F_2). The dilution formula is as follows:

$$C_2 = C_1 \times \left[\frac{F_1}{F_1 + F_2} \right]$$

where C_2 presents the concentration after dilution, C_1 is the concentration of the original standard gas, F_1 stands for the flow rate of the standard gas, and F_2 indicates the flow rate of the diluent matrix gas.

Table 1 illustrates the instrument conditions. Table 2 shows the concentrations of ammonia prepared at six calibration levels using the gas blending module.
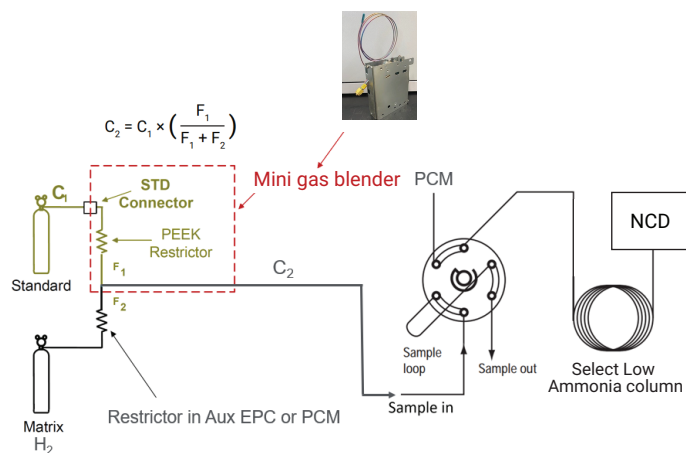

Figure 1. Schematic illustration of the Agilent 8890 GC/8255 NCD system.

Table 1. GC conditions.

Parameter	Value
Agilent 8890 GC	
Sample Introduction	6-port GSV; valve box temperature: 50 °C
Sample Loop	2 mL
Column	Select Low Ammonia (p/n CP8590)
Carrier Gas	Helium, 10 mL/min, constant flow
Oven Program	40 °C (2 min), 25 °C/min to 150 °C (2 min)
Agilent 8255 NCD	
Burner Temperature	900 °C
Base Temperature	280 °C
H_2 Flow	3 mL/min
Oxidizer Flow (O_2)	12 mL/min
O_3 Generator Flow	37.31 mL/min
Burner Pressure	131 Torr
Reaction Cell Pressure	4.4 Torr
Data Rate	5 Hz

Table 2. Dilution table (starting standard gas at 9.9 μmol/mol with hydrogen as the balance gas).

Standard Gas Flow (mL/min)	PCM (H_2) Flow (mL/min)	Final Concentration (ppb)
1	266	37.1
1	199	49.5
1	124	79.2
1	99	99
2	98	198
4	76	495

The flow rates mentioned in Table 2 are actual flow rates measured by an Agilent flow meter (part number: G6691A).

Results and discussion

In analyzing trace ammonia, it is critically important to passivate the entire sample flow path including the sample loop, connecting tubes, and regulator. When analyzing a hydrogen sample for the first time, or if the system has been idle for a long period, the loop and tubing are filled with air. Therefore, a purging process is necessary. It is crucial to completely replace air with the sample before proceeding with the analysis. It also should be noted that the system requires some time to reach a state of equilibrium before running samples if it has been idle for a few days. Therefore, the first two or three runs need to be discarded because the retention time and peak area may fluctuate. Once the instrument is well balanced, the subsequent results will be very stable.

Figure 2 shows the chromatogram of ammonia at different concentrations. Due to the unique properties of ammonia, it was found that there is a certain degree of tailing, even on this dedicated ammonia column at ppb level. Therefore, it is very important to set appropriate integration parameters when performing quantitative analysis. The ammonia elutes after 4 minutes, indicating that this column has good retention capacity for the target substance.

As detailed in the ISO 14687-2019, SAE J2719-2015, and GB/T 37244-2018 methods, the concentration of ammonia impurities in hydrogen for fuel cells should not exceed 100 ppb. In this work, the linearity of trace-level ammonia was studied by testing six different concentrations ranging from 37.1 to 495 ppb. As shown in Figure 3, the analysis led to an R^2 value of 0.9986 for ammonia. The response factor (RF) was also calculated at each level of calibration. The RF %RSD was 15.54%, as shown in Table 3.
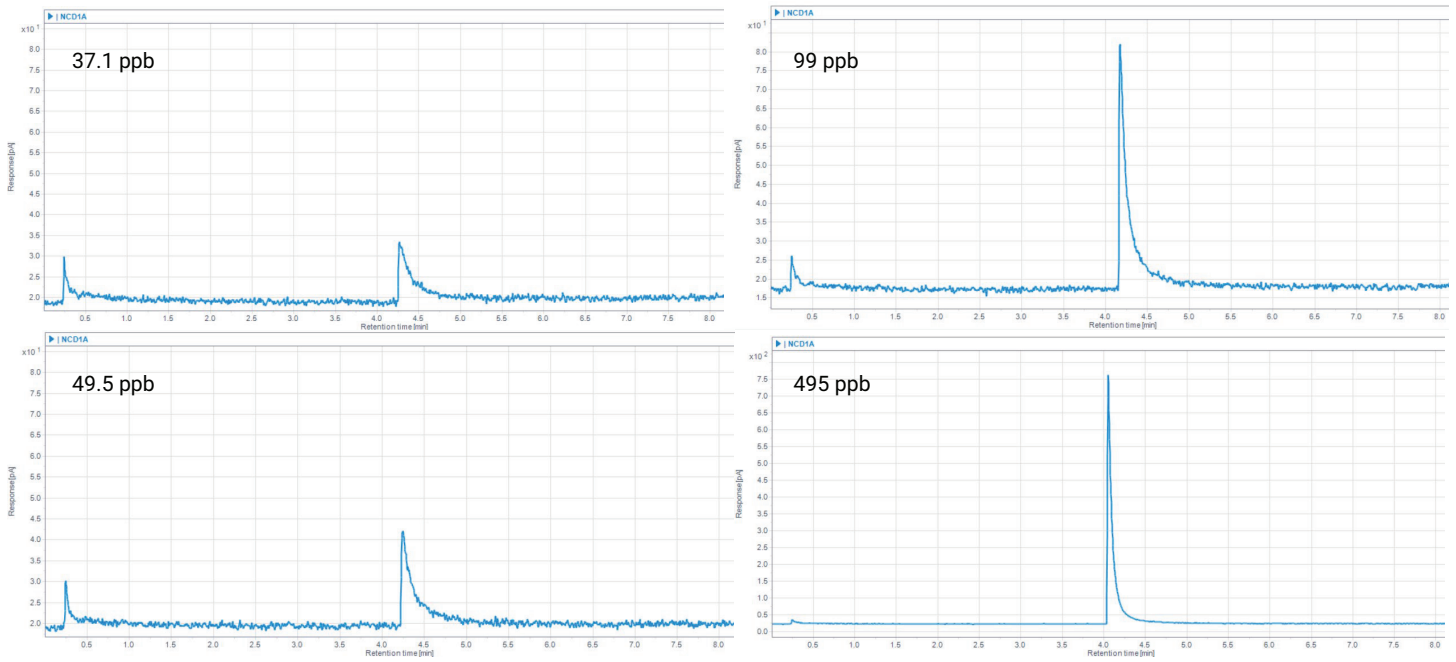
Figure 2. NCD signal of ammonia at the concentration of 37.1, 49.5, 99, and 495 ppb.
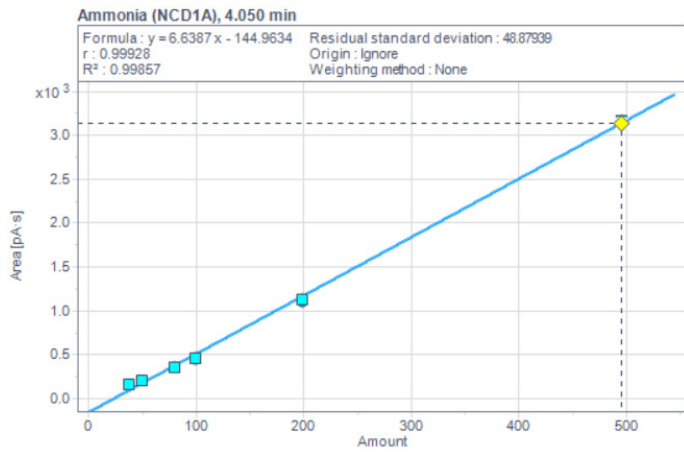

Figure 3. Calibration curve of ammonia.

Table 3. Calibration levels and RF %RSD of ammonia.

	L1	L2	L3	L4	L5	L6
Concentration (ppb)	37.1	49.5	79.2	99	198	495
Average Area	162.88	209.52	363.37	460.85	1,128.75	3,163.34
RF	0.228	0.236	0.218	0.215	0.175	0.156
RF %RSD	15.54%					

The evaluation of repeatability was conducted by determining the relative standard deviation (RSD) of the area from eight consecutive injections. This procedure was replicated at each calibration level. Figure 4 is an overlapped chromatogram of eight runs of ammonia with a concentration of 49.5 ppb. Although there is tailing of the peak shape, each run of the chromatogram overlaps very well. The excellent reproducibility of retention time and peak area indicates that this system is highly suitable for ammonia analysis, and it provides a good foundation for the accurate quantification of the real sample. Figure 5 lists the results of the %RSD

of the peak area for eight runs at each concentration level. As the concentration decreases, the value of the %RSD correspondingly increases, which is consistent with our expectations. None of the results exceed 4.76%, which also indicates the excellent inertness and reliability of the system.

In this study, the method detection limit (MDL) was evaluated by performing eight consecutive runs of standard gas at a concentration of 37.1 ppb. The concentration of ammonia was calculated using a linear equation, followed by the calculation of the standard deviation and multiplication by 3 to determine the MDL. The calculated MDL was 24.2 ppb.
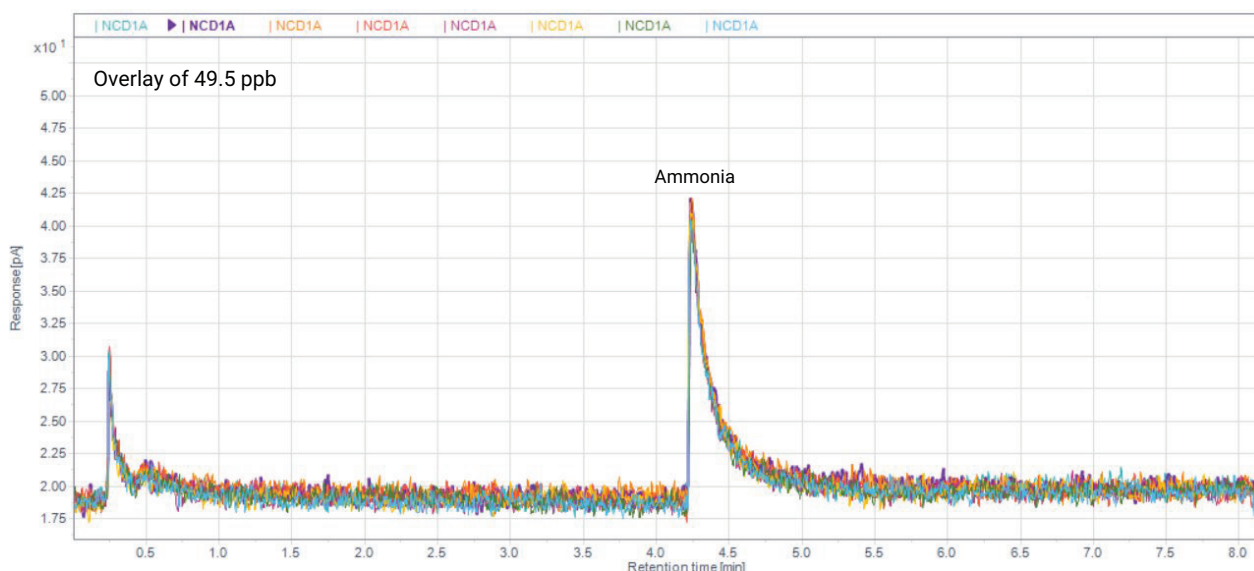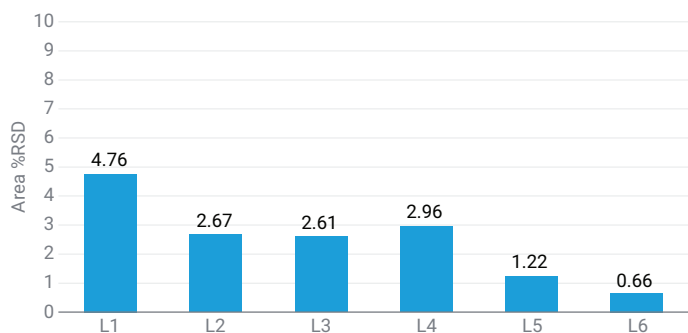

Figure 4. Overlay of 49.5 ppb of ammonia.

Figure 5. Response precision of eight consecutive runs at each concentration level for ammonia.

Conclusion

The Agilent 8890 gas chromatograph, equipped with an Agilent J&W Select Low Ammonia column and the Agilent 8255 nitrogen chemiluminescence detector, is a simple and robust way to analyze trace ammonia in hydrogen for fuel cells. Excellent sensitivity, repeatability, and linearity are shown in this study, indicating the excellent inertness and reliability of the whole system. This analytical method fully meets the quality control measurement requirements for ammonia impurities in hydrogen gas, as detailed in ISO 14687-2019 and GB/T 37244-2018 methods.

References

1. Xu, C.; Xu, G. Analysis Technology of Trace Impurities in Hydrogen for Hydrogen Fuel Cell Vehicles. *Chemical Industry and Engineering Progress* **2021**, *40(2)*, 688–702. DOI: 10.16085/j.issn.1000-6613.2020-0690.

2. ISO 14687-2019 Hydrogen Fuel Quality — Product Specification

3. SAE J2719-2015 Hydrogen Fuel Quality for Fuel Cell Vehicles

4. GB/T 37244-2018 Fuel Specification for Proton Exchange Membrane Fuel Cell Vehicles — Hydrogen

5. Beard, K. Trace Analysis of Ammonia in Ethylene by Gas Chromatography and Nitrogen Chemiluminescence Detection *Agilent Technologies application note*, publication number 5991-8061EN, **2017**

www.agilent.com

Agilent

Trusted Answers