Application Note

Energy and Chemicals

Agilent

Trusted Answers

Analysis of Trace Carbon Dioxide and Permanent Gas Impurities in Fuel Cell Hydrogen and High-Purity Hydrogen by GC

Achieve low detection limits using an Agilent 8890 GC fitted with a pulsed discharge helium ionization detector (PDHID)

Author

Li, Wan
Agilent Technologies
(Shanghai) Co. Ltd.

Abstract

An Agilent 8890 GC fitted with a plug and play pulsed discharge helium ionization detector (PDHID) was used to detect ppb to low-ppm concentration carbon dioxide, carbon monoxide, methane, argon, oxygen, nitrogen, and other impurities in high-purity hydrogen. The GC method provided low detection limits, good reproducibility, and excellent linearity, meeting the requirements specified in GB/T 3634.2-2011, GB/T 37244-2018, and ISO 14687-2019.

Introduction

China has set a goal of becoming carbon-neutral by 2060. To help achieve the target, the Chinese government is supporting the development of new technologies such as hydrogen energy and hydrogen fuel cells for vehicles, and hydrogen refueling stations. The importance of the hydrogen fuel cell vehicle industry to China is underlined by its inclusion in various strategic plans. The plans include the "National Innovation-Driven Development Strategy Outline", "Made in China 2025", and "Medium and Long-Term Development Plan for the Automobile Industry". To date, many automobile companies around the world have launched fuel cell passenger vehicles, and cities such as Beijing and Shanghai have built a network of hydrogen refueling stations. As hydrogen is increasingly used to power vehicles, strict requirements have been imposed to limit pollution from any impurities in the gas. Specifications for the purity of hydrogen used in other applications are also becoming more stringent. Hydrogen is used in the manufacturing and processing of large-scale integrated circuits (ICs), smelting and processing of high-purity metals, development and production of liquid hydrogen and its derivative products, carrier gas used for precision instruments (chromatographs, etc.), and diluents used in standard gas mixtures. Therefore, hydrogen-purity testing, especially for high-purity hydrogen and ultra-high-purity hydrogen, is fast becoming a critical requirement of various hydrogen producers and industrial users.

Traditional GC methods based on flame ionization detection (FID) with methanizer have a detection limit for carbon monoxide of 50 to 100 ppb, which is above the sensitivity needed for some users of hydrogen. However, a GC fitted with a pulsed discharge helium ionization detector (PDHID) can lower the carbon monoxide detection limit below 50 ppb, which is welcomed by many users in China.

The PDHID uses a pulsed DC discharge in helium as its ionization source. The column effluent, which flows counter to the discharge helium flow, is ionized by photons from the helium discharge. The PDHID is universal except for neon (Ne) which has an ionization potential (IP) of 21.56 eV. The IP is higher than the energy of the He metastable (19.8 eV), leading to low ionization of Ne. The PDHID is a highly sensitive detector with minimal detectable levels (MDLs) to fixed gases in the low ppb range.[1]

In this study, an Agilent 8890 GC fitted with a plug and play PDHID (Valco Instruments Co., Inc.) was used for the simultaneous qualitative and quantitative detection of impurities in high purity hydrogen. Carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), argon (Ar), nitrogen (N_2), and other impurities were measured from a single injection into the GC. The method was evaluated against the requirements for sensitivity, reproducibility, and linearity specified in GB/T 3634.2-2011[2], GB/T 37244-2018[3], and ISO 14687-2019[4].

Experimental

Samples

Details of the hydrogen calibration standard (bought from Air Liquide) are given in Table 1. The standard contained approximately 10 ppm of CO_2, CO, CH_4, Ar, O_2, and N_2. To test the dynamic range and detection limits of the method, an Agilent dynamic dilution system was used to dilute the calibration sample. Ultrahigh purity hydrogen (99.999% grade, Air Liquide) was used as the diluent.

Table 1. Hydrogen samples and the concentration of impurities in the hydrogen samples after each level of dilution.

Calibration Standard Flow (mL/min)	Diluent (H_2) Flow (mL/min)	Dilution Factor	Concentration of the Sample Following a Dilution (ppb)					
			CO_2	CO	CH_4	Ar	O_2	N_2
4.78	0	1	10,100	10,000	10,000	9,900	9,950	9,910
4.78	4.92	2.03	4,977	4,928	4,928	4,879	4,903	4,883
4.78	19.17	5.01	2,016	1,996	1,996	1,976	1,986	1,978
2.84	25.66	10.04	1,006	996	996	987	992	988
2.84	53.96	20.00	502	500	497	492	498	493
2.84	139.16	50.00	202	200	200	198	199	198
2.84	281.66	100.18	101	100	100	99	99	99
1.50	298.50	200.00	51	50	50	50	50	50

Instrumentation

The 8890 GC PDHID was configured as shown in Table 2 and instrument operating conditions are given in Table 3.

Table 2. Agilent 8890 GC-PDHID system configuration.

Valve System	**Valve 1:** 10-port valve **Valves 2 to 4:** 6-port valves **Valve 5:** 6-port sample switching valve **Loop volume:** 0.25 mL Purge chamber uses helium to protect analytical valves 1 to 4.
Analytical Column	Four capillary chromatographic columns **Columns 1 and 2:** PLOT-Q **Columns 3 and 4:** Molsieve
Detector	Pulsed discharge helium ionization detector (PDHID)
Dynamic Dilution System	Pneumatic Control Module (PCM) channel 1 is used for diluent control.

Table 3. Agilent 8890 GC-PDHID operating conditions.

Valves	**Helium purge flow rate:** 2 mL/min Ambient temperature
Column Flow	**Column 1:** Constant pressure, 35 psi (approximately 10 mL/min) **Column 2:** Constant pressure, 30 psi (approximately 10 mL/min) **Column 3:** 30 psi held for 5 min, increased to 40 psi at the rate of 2 PSI/min and held for 16 min **Column 4:** Constant pressure, 15 psi (approximately 10 mL/min)
Column Temperature	Initial temperature at 50 °C, maintained for 5 min, then raised to 120 °C at the rate of 20 °C/min, then maintained for 7.5 min. **Duration:** 16 min
PDHID	150 °C **Helium flow rate:** 32 mL/min
Data Collection Rate	5 Hz

Results and discussion

Chromatogram of hydrogen

A chromatogram of the hydrogen standard containing impurities at the 10 ppm level obtained using the 8890 GC-PDHID is shown in Figure 1A. The figure shows good separation of CO_2, CO, CH_4, Ar, O_2, N_2, and other impurities in hydrogen. Heart-cut and secondary separation methods were used to prevent CO_2 and Ar from being affected by the unpurged H_2 matrix, while enabling the separation of O_2 and Ar in the same run.

The 10 ppm hydrogen standard was diluted by a factor of 200 to obtain a sample with CO_2, CO, CH_4, Ar, O_2, N_2 at a concentration of approximately 50 ppb. Figure 1B shows the chromatogram of the diluted standard, and insets for CO_2, Ar, CH_4, and CO from 10 consecutive injections. Due to the adsorption and temperature programming of the chromatographic column and tubing, it was difficult to determine O_2 at the 50 ppb level, but it was possible to detect 50 ppb CO. Using the helium purge chamber to protect the valve body allowed the PDHID baseline to be reduced to less than 1,000 pA. This low detector baseline level is helpful for the analysis of ppb level impurities in high purity hydrogen.

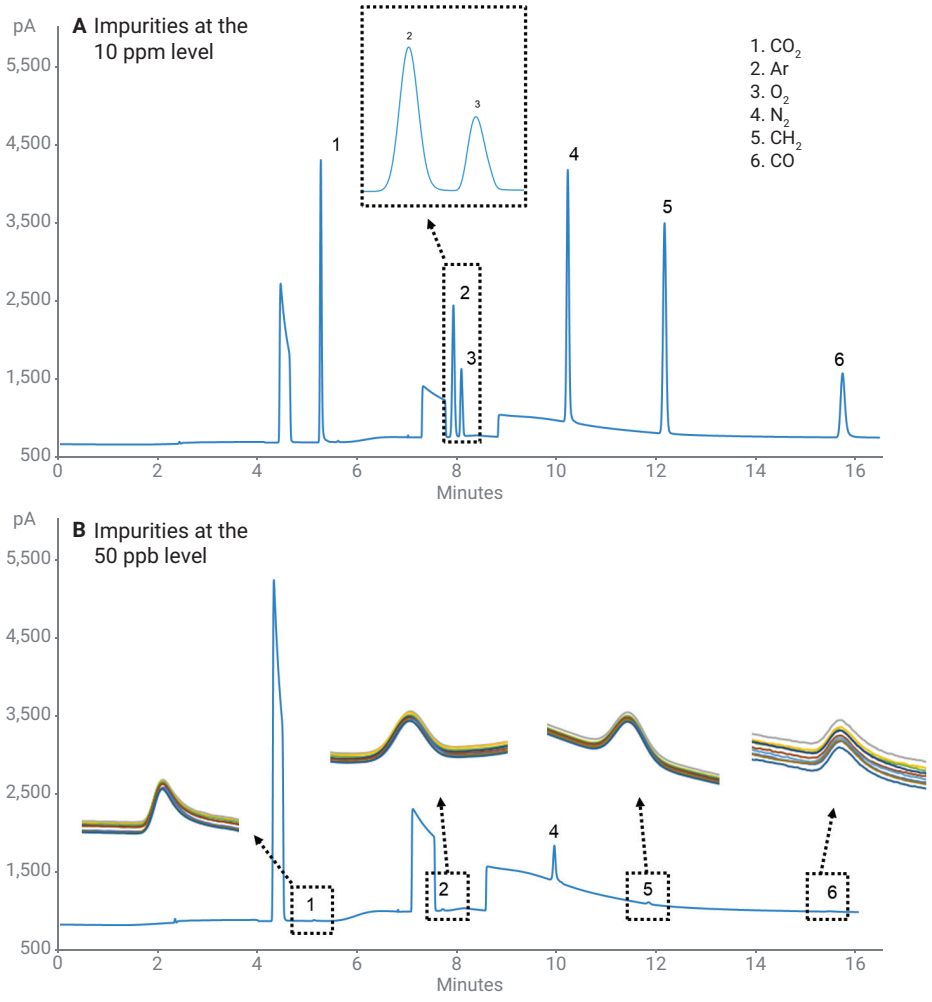

Figure 1. Typical chromatogram obtained from the analysis of impurities at the 10 ppm level (A) and 50 ppb level (B) in high-purity hydrogen using the Agilent 8890 GC-PDHID.

Reproducibility

Table 4 shows the reproducibility results for CO_2, CO, CH_4, Ar, and N_2 obtained by six consecutive injections of samples with a concentration of around 1 ppm and 50 ppb. See Table 1 for the specific concentration of each gas. For the 1 ppm samples, the peak height relative standard deviation (RSD) was below 1% and for the 50 ppb samples, the peak height RSD was below 5%.

Detection limits

The method detection limits (MDLs) in Table 4 were calculated using the 50 ppb sample analysis results, based on signal-to-noise ratio (S/N)=3 criteria. The MDLs of the five impurities were all lower than 20 ppb, meeting the requirements specified in GB/T 3634.2-2011, GB/T 37244-2018, and ISO 14687-2019.

Linearity

Each calibration standard (Table 1) was injected six times, and the average peak height of the impurities was plotted against its concentration. Linear regression analysis was performed automatically by the instrument software. The calibration curves and linear regression equations are shown in Figure 2. The insets show the concentration range from 50 ppb to 1 ppm for CO, CH_4, CO_2, and Ar, and 100 ppb to 1 ppm for N_2.

Good linearity was obtained in the 50 ppb to 10 ppm concentration range for all impurities, with R^2 correlation coefficients above 0.995. There was also excellent linearity for CO, CH_4, CO_2, and Ar at the 50 ppb to 1 ppm level. The offset at the origin of the N_2 calibration curve suggests a background interference. The interference is likely due to trace levels of the gas in the diluent gas, and a small amount of air infiltration from the sample line. Excluding the results from the 50 ppb standard, good linearity was obtained for N_2 in the 100 ppb to ppm range.

Table 4. Agilent 8890 GC-PDHID reproducibility data and detection limits.

	10 ppm Dilute to 1 ppm Sample				10 ppm Dilute to 50 ppb Sample						
Components	RT (min)	RT RSD	Height (pA)	Height RSD	RT (min)	RT RSD	Height (pA)	Height RSD	S/N	Concentration (ppb)	MDL (S/N=3)
CO_2	5.2697	0.019%	347.22	0.96%	5.2867	0.025%	6.88	1.29%	196.9	54.1	0.8
Ar	7.9233	0.015%	175.81	0.17%	7.9372	0.015%	11.35	0.83%	324.7	53.0	0.5
N_2	10.2213	0.009%	648.82	0.71%	10.2320	0.007%	237.84	0.49%	6808.2	53.1	0.02
CH_4	12.1629	0.008%	294.62	0.22%	12.1709	0.007%	12.43	0.39%	355.7	54.6	0.5
CO	15.7888	0.005%	76.44	0.30%	15.8882	0.016%	2.73	1.93%	78.2	54.6	2.1

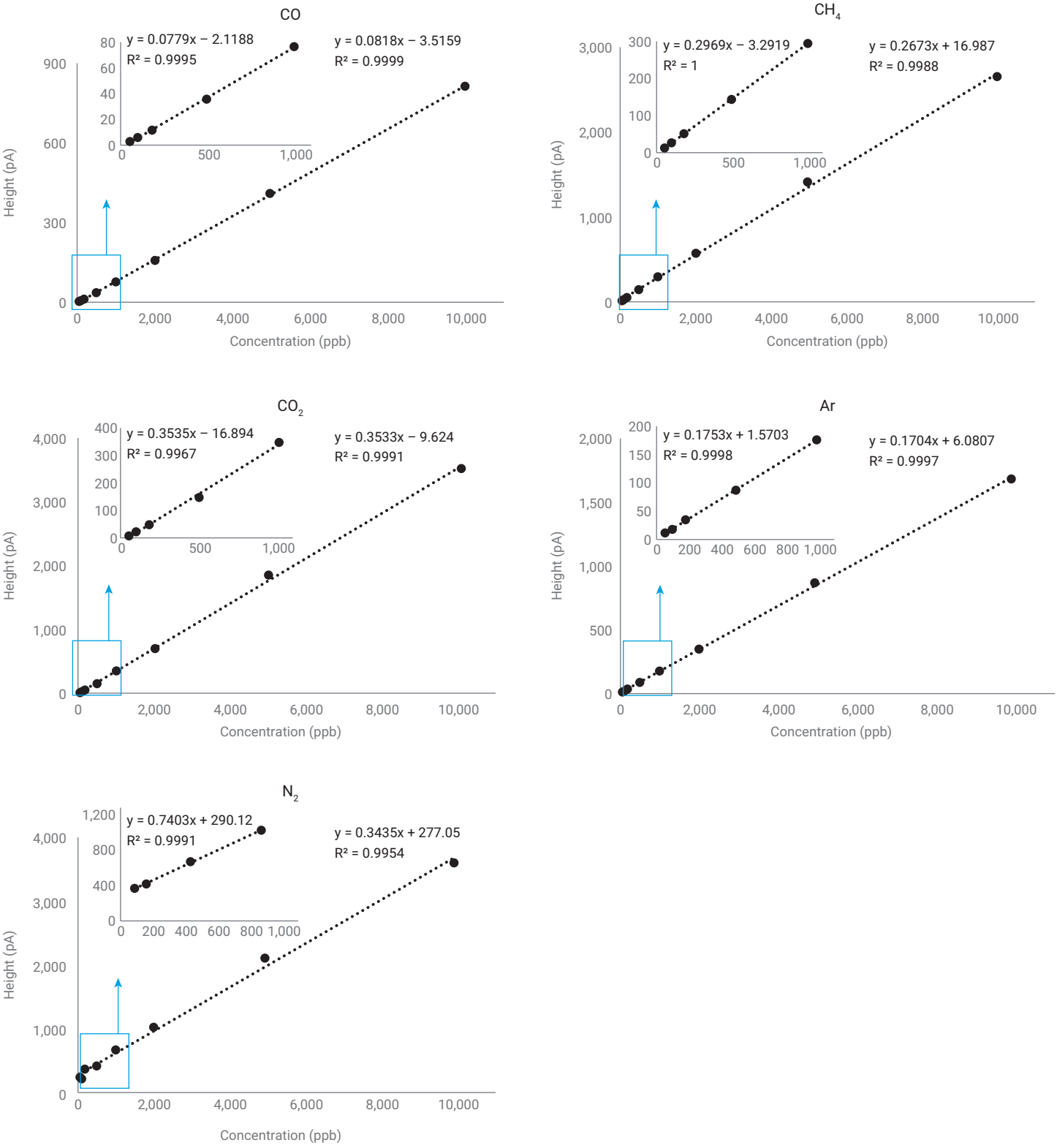

Figure 2. Linearity of each impurity in the range of 50 ppb to 10 ppm.

Conclusion

The Agilent 8890 GC fitted with a pulsed discharge helium ionization detector (PDHID) was used successfully for the analysis of trace impurities in high-purity hydrogen. Qualitative and quantitative detection of CO_2, CO, CH_4, Ar, O_2, and N_2 were be achieved in the same run from one injection. Using heart-cutting, the matrix effects of hydrogen were reduced, enabling baseline separation of Ar, O_2 and CO_2. Separation of O_2 and Ar was also achieved without the need for cryogenic conditions.

The detection limit of each impurity was less than 20 ppb, meeting the requirements of GB/T 3634.2-2011, GB/T 37244-2018, and ISO 14687-2019 standards. Also, good linearity (R^2 >0.995) was achieved for CO, CH_4, CO_2, and Ar in the concentration range of 50 ppb to 10 ppm and for N_2 from 100 ppb to 10 ppm.

The helium purge chamber prevented air leaking into the GC system from the valve connection points, ensuring the baseline level of the PDHID to be kept under 1,000 pA. Maintaining a low baseline is helpful for the analysis of real samples containing impurities below the ppb level.

The GC method enables producers and users of high purity hydrogen to test for a range of impurities, potentially reducing pollution from fuel-hydrogen, or improving yields and performances of ICs or gas mixes.

References

1. Pulsed Discharge Detector Model D-3-I-8890 Instruction Manual, Valco Instruments Co. Inc. VICI publication, accessed December 2021, https://www.vici.com/support/manuals/d3_hp_8890.pdf
2. GB/T 3634.2-2011 Hydrogen. Part 2: Pure hydrogen, high pure hydrogen and ultrapure hydrogen
3. GB/T 37244-2018 Fuel specification for proton exchange membrane fuel cell vehicles—Hydrogen
4. ISO 14687-2019 Hydrogen fuel quality–Product specification

www.agilent.com/chem

DE67222349

Printed in the USA, December 23, 2021
5994-4415EN

Agilent
Trusted Answers