Application Note

Energy and Chemicals

Electrolysis Gas Impurity Analysis with the Agilent 990 Micro GC

Using non-backflush Agilent J&W CP-Molsieve 5Å channels to detect oxygen, nitrogen, and hydrogen impurities in electrolyzer gases

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Abstract

This application note demonstrates how oxygen, nitrogen, and hydrogen impurities in electrolyzer gases are analyzed using the Agilent 990 Micro GC equipped with two non-backflush Molsieve 5Å (MS5Å) channels. The two channels are configured with different carrier gases. The first channel uses helium carrier gas for cathode gas analysis. This channel is also used for nitrogen impurity analysis in anode gas. The second channel using argon carrier gas for hydrogen impurity analysis in anode gas. The two-channel configuration enables the system to toggle between analyzing the cathode and anode gas. A single analysis cycle can be finished within 80 seconds. Method precision was tested with response precision less than 1% for target analytes ranging from 10 to 1,000 ppm. The calculated limits of detection (LOD) are below 1 ppm. The retention time (RT) stability of the non-backflush MS5Å channel was evaluated by applying it for lab-made humidified sample analysis. With the effective removal of moisture from the gas sample, oxygen and nitrogen RT shifts were observed less than 5% on the MS5Å channel after around 30,000 injections.

Introduction

Electrolyzer gas is high-purity hydrogen and oxygen produced by splitting water using electricity in an electrolyzer. Hydrogen is created at the cathode and oxygen is generated from the anode. The main impurities in the electrolyzer gas are oxygen, nitrogen, and hydrogen, which can be analyzed using a GC system with a thermal conductivity detector (GC-TCD). Previous application work was published using the 990 Micro GC equipped with two MS5Å channels (backflush type) for this analysis.[1]

In this application note, a solution based on straight (i.e. non-backflush) MS5Å channels is presented. Compared to the backflush MS5Å channel, the straight channel is economical, method development is straightforward, and cycle time is shorter. However, straight Molsieve channels cannot backflush moisture and are less suitable for humid samples. The moisture is known to decrease separation capacity of the column, leading to small shifts in retention time. This may ultimately lead to wrongly identified peaks.

In the water splitting industry, electrolyzer gas typically goes through a dehumidification process before analysis. To assess the feasibility of using the straight MS5Å channel for dehumidified electrolyzer gas analysis, a water absorbing filter is positioned in the sample line to the 990 Micro GC simulating this purification process. A lab-made "wet gas" was then analyzed by micro GC to evaluate the long-term RT stability on the straight MS5Å channels.

Experimental

Chemicals and gases

Standard gases 1 and 2 simulate the cathode and anode gas, respectively. These gases were used in a system performance assessment.

Standard gas 1 was also diluted to four different concentrations for method linearity test. Gas sample information is shown in Table 1. Diluted gas 1 was also used for LOD tests.

Table 1. Standard gas composition.

	Standard Gas 1 (ppmv)	Diluted Gas 1 (ppmv)	Standard Gas 2 (ppmv)	Diluted Gas 2 (ppmv)	Diluted Gas 3 (ppmv)	Diluted Gas 4 (ppmv)
Oxygen	980	9.7	Balance	23.9	49.0	89.1
Nitrogen	1,050	10.4	10.0	25.6	52.5	95.4
Hydrogen	Balance	Balance	10.0	Balance	Balance	Balance

Instrumental

The 990 Micro GC system was equipped with two straight 10 m Agilent J&W CP-Molsieve 5Å channels with RTS. The gas samples can be connected via a multi-position gas selection valve to the two-channel system (Figure 1). Table 2 shows the analytical conditions.

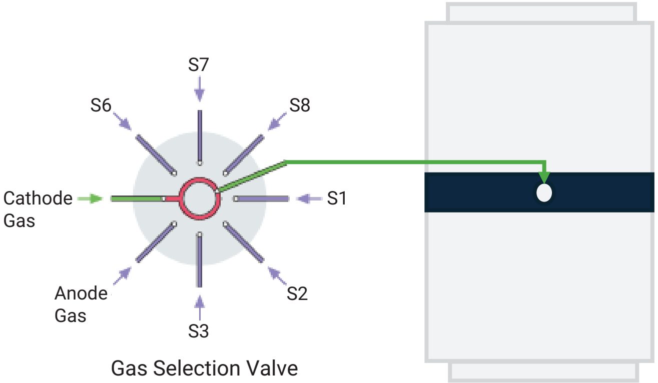

Figure 1. Gas connections for the two-channel Agilent 990 Micro GC system.

Table 2. Test conditions for cathode and anode gas analysis.

Channel Type	Channel 1: 10 m Agilent J&W-CP Molsieve 5Å Column, Straight*, RTS	Channel 2: 10 m Agilent J&W-CP Molsieve 5Å Column, Straight, RTS
Carrier Gas	Helium	Argon
Column Pressure	250 kPa	250 kPa
Injector Temperature	80 °C	80 °C
Column Temperature	80 °C	80 °C
Injection Time	100 ms	40 ms
Sampling Time	20 s	
Running Time	60 s	

* Straight means a non-backflush-type analytical channel

Results

Chromatograms

Cathode gas/bulk hydrogen: Standard gas 1 simulates cathode gas with trace-level nitrogen and oxygen impurities. This gas was analyzed on MS5Å channel 1 using helium carrier gas. The chromatogram is shown in Figure 2. It took approximately 30 seconds for oxygen impurity to elute off the analytical column. Nitrogen contaminant eluted out within one minute.

Impurities in cathode gas can be as low as single-digit ppm levels. Standard gas 1 was diluted approximately 100 fold to simulate low ppm contaminants and then tested. The corresponding chromatogram (subtracting the diluent gas blank) is shown in Figure 3. The responses of oxygen and nitrogen in the diluted gas 1 are 0.029 and 0.032, around 1/100th of oxygen and nitrogen response from standard gas 1 (2.904 and 3.095), indicating good linearity. The obtained chromatogram showed the two peaks had excellent signal-to-noise ratio at a low ppm level (> 30:1).

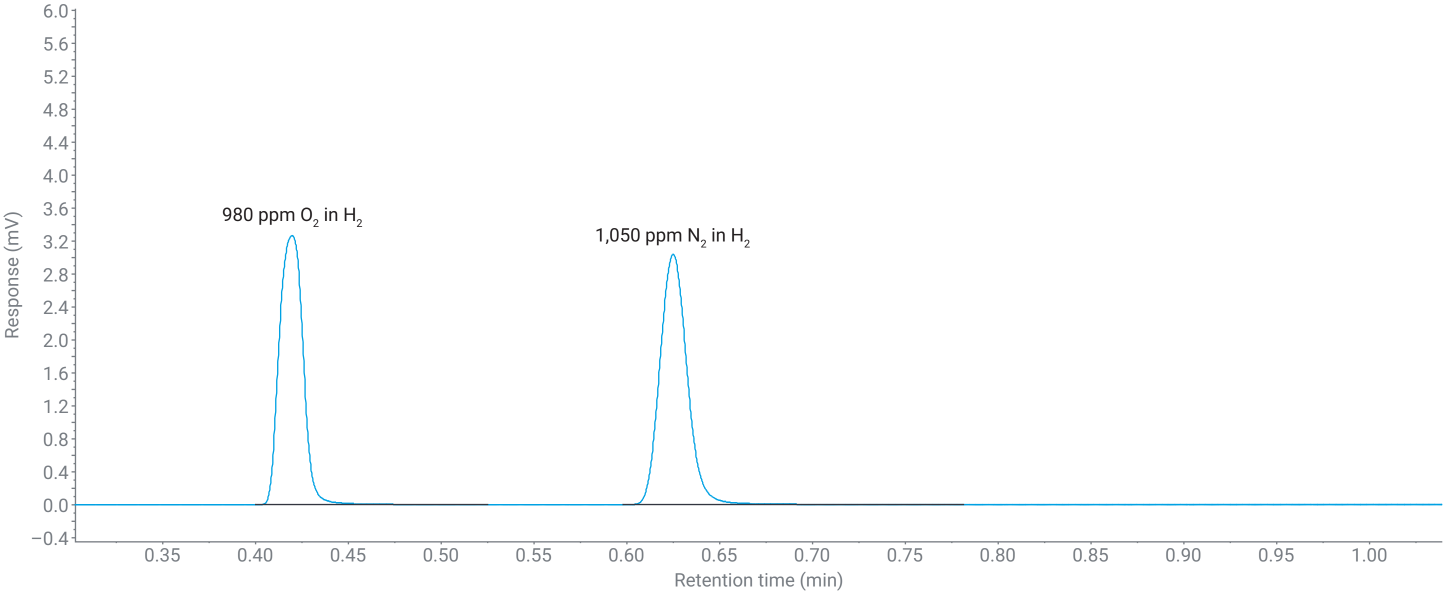

Figure 2. Chromatogram of 1,000 ppm oxygen and nitrogen in hydrogen (cathode gas) on MS5Å channel 1 configured with helium carrier gas.

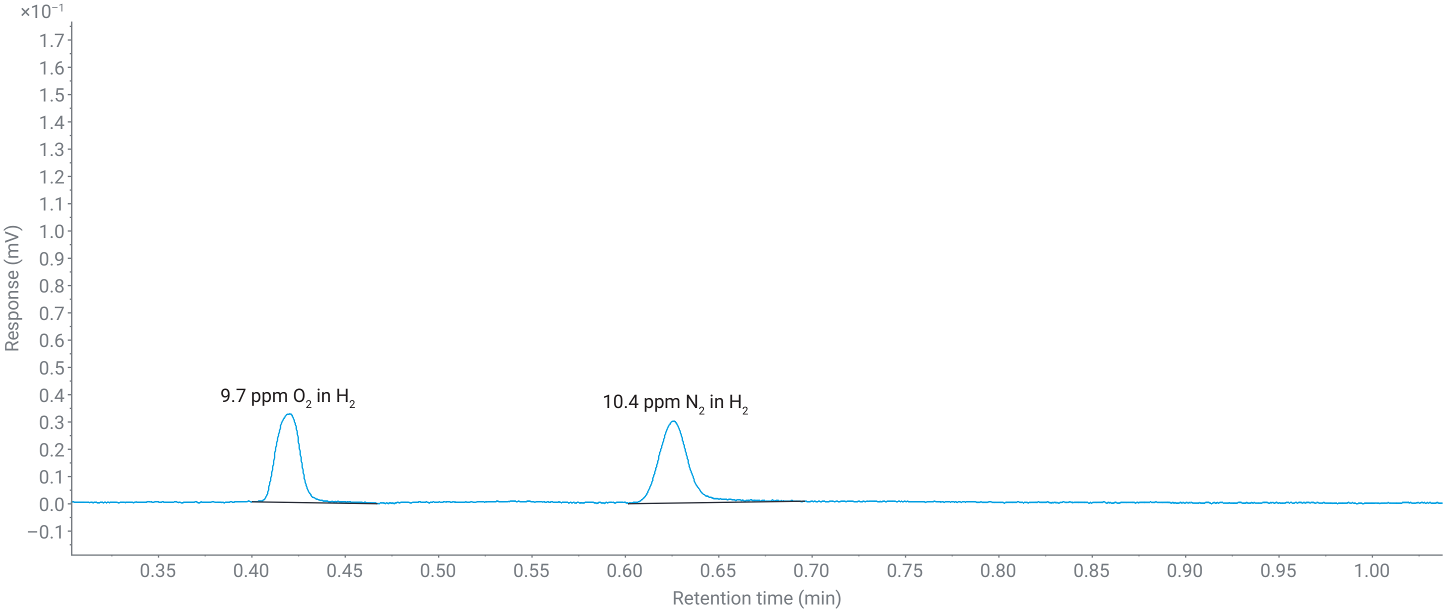

Figure 3. Chromatogram of 10 ppm oxygen and nitrogen in hydrogen on MS5Å channel 1. The chromatogram was generated by subtracting the diluent gas (hydrogen) blank.

Anode gas/bulk oxygen: Standard gas 2 simulates anode gas with trace level hydrogen and nitrogen impurities. The test standard is injected into two MS5Å channels simultaneously. The nitrogen contaminant is analyzed on channel 1 (Figure 4A). Nitrogen (10 ppm) eluted on the peak tail of bulk oxygen. The quality limit of nitrogen in electrolyzer gas is generally no less than 100 ppm, which can be easily detected by the straight MS5Å channel.

The hydrogen impurity in oxygen is analyzed on channel 2 (Figure 4B). The peak of 10 ppm hydrogen is very sharp and symmetrical on channel 2 using argon carrier gas, indicating good sensitivity.

The described two-channel system is used for sequential analysis of cathode and anode gases. It is necessary to purge the sample flow path each time the sample is switched for accurate results. If a parallel analysis of the two gas streams is needed, a three-channel system equipped with two sample inlets is recommended. In this configuration, one sample inlet and one MS5Å channel is dedicated to cathode gas analysis, and the other inlet and the remaining two MS5Å channels are for anode gas analysis.

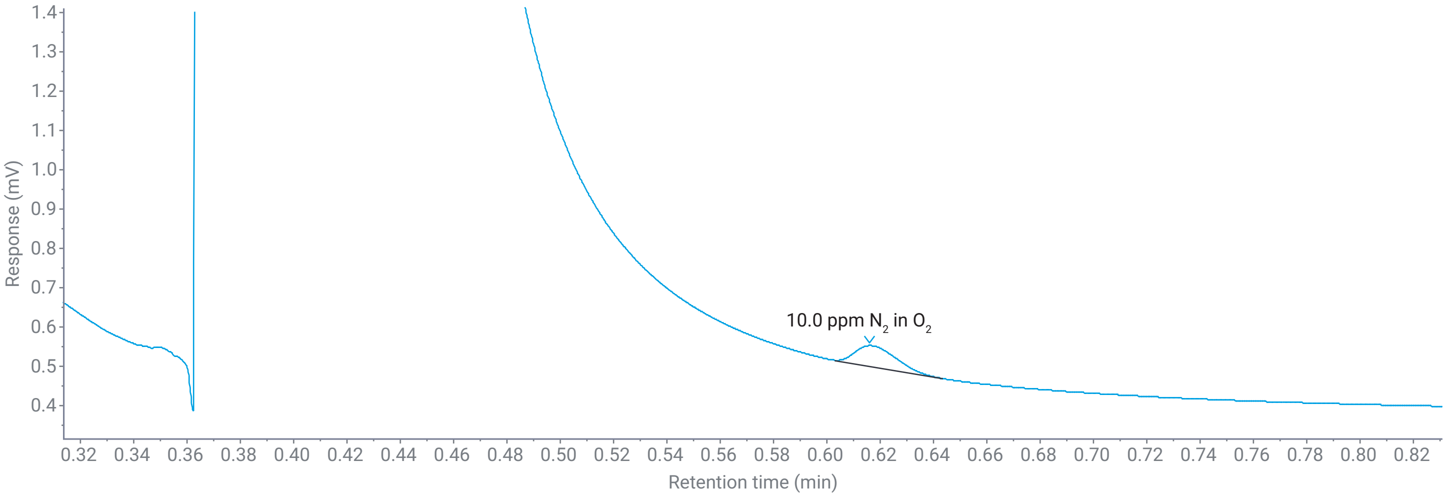

Figure 4A. Chromatogram of 10 ppm nitrogen in oxygen (anode gas) on MS5Å channel 1 using helium carrier gas.

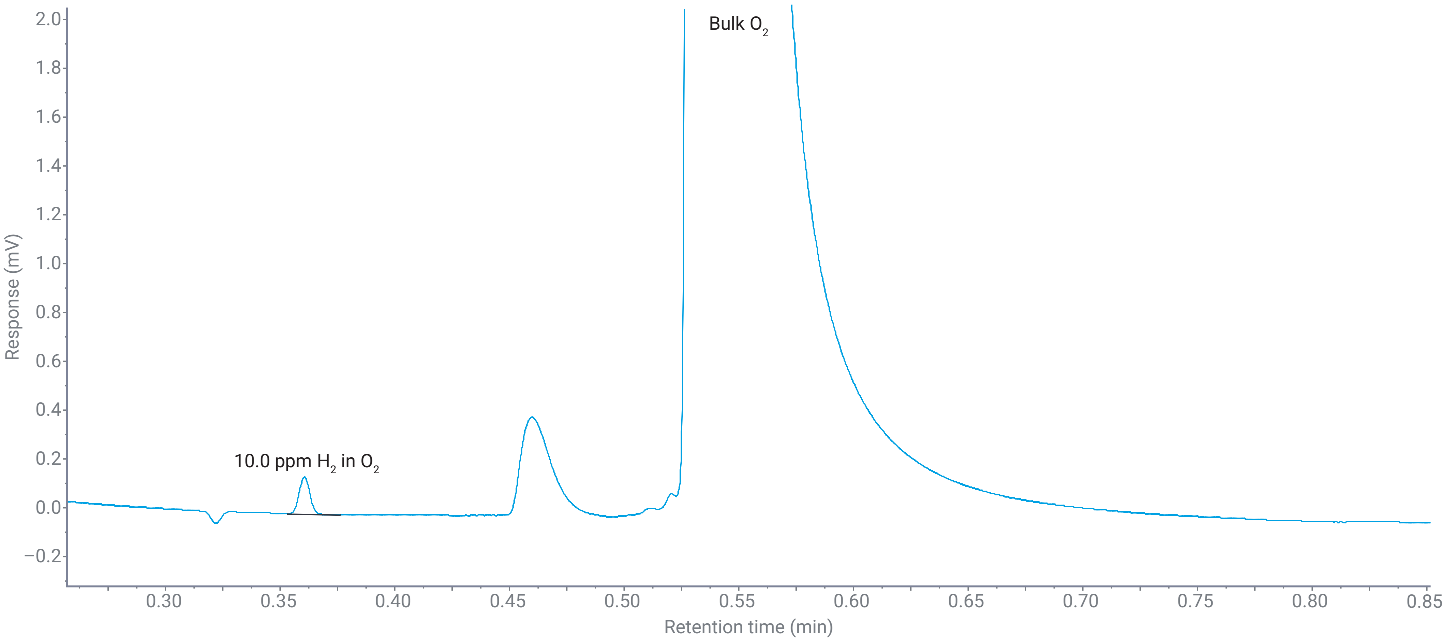

Figure 4B. Chromatogram of 10 ppm hydrogen in oxygen (anode gas) on MS5Å channel 2 using argon carrier gas.

Repeatability

Method precision was evaluated based on 15 injections of standard gases 1 and 2, and diluted gas 1. Results summarized in Table 3 show a typical peak area repeatability of < 0.1% at higher concentrations, and up to 1% when at the 10 ppm level.

Table 3. RT and response repeatability of the target analytes (n = 15).

Matrix Gas Type	Hydrogen				Oxygen	
Target Analytes	O_2	N_2	O_2	N_2	N_2	H_2
Nominal Concentration (ppmv)	9.7	10.4	980	1,050	10.0	10.0
Area (mv×s)	0.027	0.032	2.839	3.105	0.037	0.049
Area %RSD	0.531	0.934	0.013	0.047	1.048	0.323
RT (min)	0.420	0.626	0.420	0.625	0.615	0.361
RT %RSD	0.024	0.007	0.006	0.005	0.008	0.006

Linearity

The method linearity is assessed for oxygen and nitrogen from 10 to 1000 ppm based on their typical concentration range in cathode gas.

Standard gas 1 was diluted to different concentrations. The calibration curve showed excellent linearity with R^2 greater than 0.9999 for both compounds (Figures 5A and 5B). There was not an appropriate standard gas for the linearity test of hydrogen in oxygen. Based on the TCD mechanism and the linearity results of oxygen and nitrogen, the described method is expected to deliver equivalent linearity performance for hydrogen impurity.

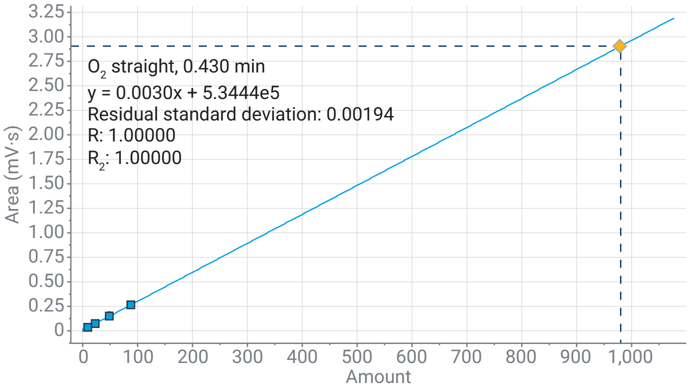

Figure 5A. Calibration curve of oxygen in cathode gas (10 to 1,000 ppm), $R^2 > 0.9999$.

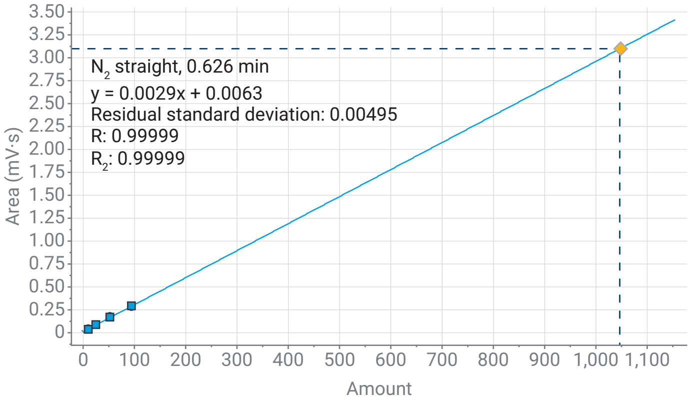

Figure 5B. Calibration curve of nitrogen in cathode gas (10 to 1,000 ppm), $R^2 > 0.9999$.

Limit of detection

The calculated LODs of hydrogen/nitrogen in oxygen and oxygen/nitrogen in hydrogen are shown in Table 4. All LODs are calculated to be < 1 ppm. Both channels perform similarly and are sensitive enough for target impurities measurement in the electrolyzer gas. The LOD test sample is diluted gas 1.

Equation 1.

$$LOD = t_{(n-1,\, 0.99)} \times S$$

Where:

t: t value at n-1 degrees of freedom under a confidence level of 99%, t = 2.998

n-1: The degree of freedom

S: The standard deviation of n replicate analyses

Table 4. The calculated LOD results on the straight MS5Å channels (n = 8).

Impurities in Hydrogen		Impurities in Oxygen	
Component	LOD (ppmv)	Component	LOD (ppmv)
Oxygen	0.34	Nitrogen	0.31
Nitrogen	0.34	Hydrogen	0.1

Long-term RT stability

The MS5Å channel is very sensitive to moisture. If the moisture in samples enters the MS5Å column and accumulates, column retention will gradually decrease. When the compound peak shifts out of the preset RT window in the data processing method, peak identification fails. Typically, thousands of accurate identifications of high-moisture samples can be made with the RT window for identification set at 5%. When RT does shift out of that window, "baking" the MS5Å column at elevated temperature will normally recover retention behavior.

During electrolyzer gas production, the gas generated from electrolysis process will go through a purification procedure to remove most of the moisture before impurity analysis.

To understand how long a non-backflushed MS5Å channel can operate in a realistic environment (until a column bake-out is needed), we connected a water filter (CP17971) in the sample line preceding the 990 Micro GC to simulate the water purification process. We then analyzed a lab-made wet hydrogen stream with humidity between 50% to 80%.

An Agilent J&W PoraPLOT U channel was used to evaluate water content after the filter (Figure 6). No water peak was detected in the sample after the water filter, demonstrating effective simulation of the moisture purification process. The "dried" hydrogen was then analyzed continuously, and its retention time stability was monitored over time.

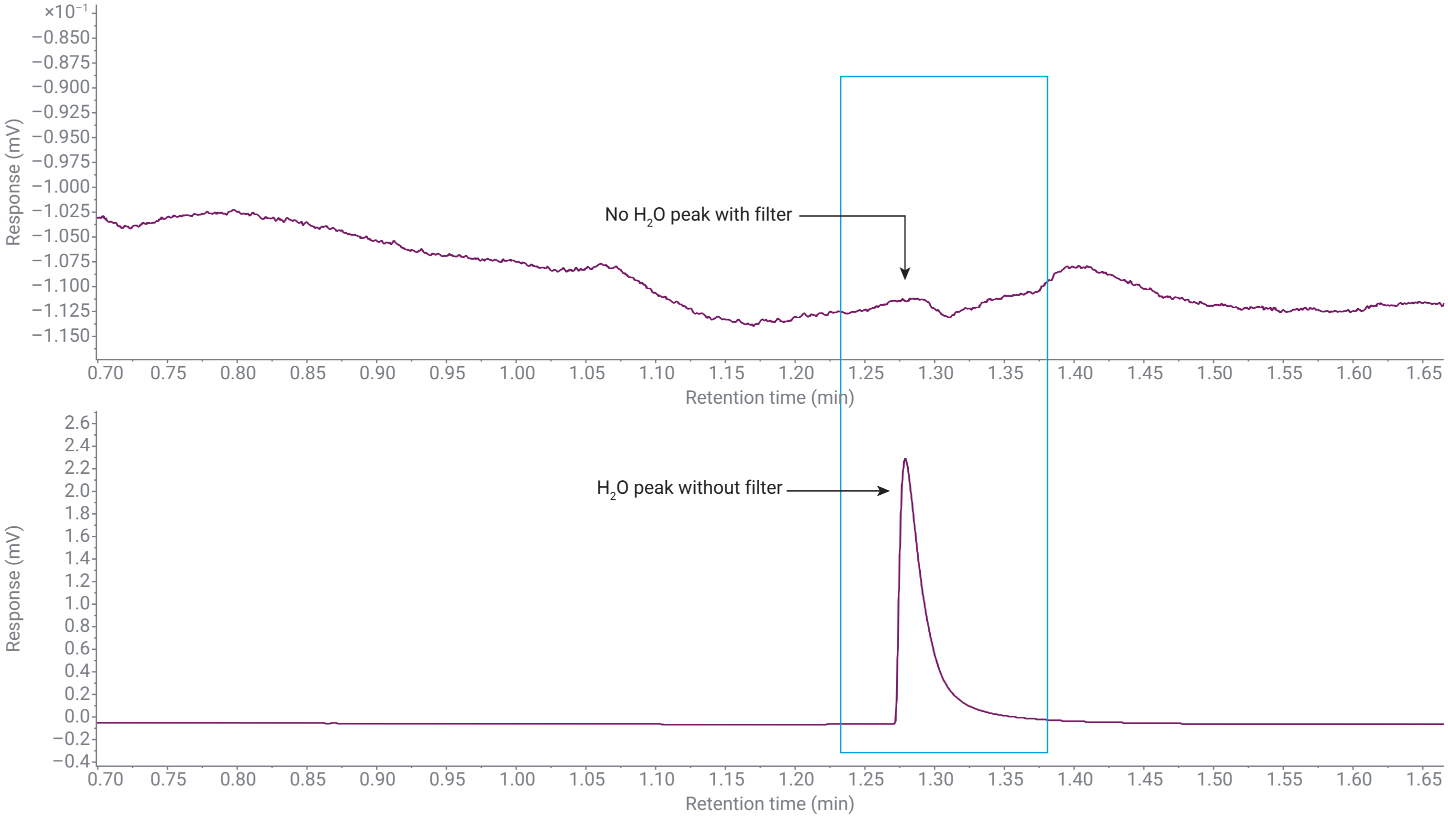

Figure 6. Chromatograms of the humidified hydrogen on PPU channel before and after the water filter.

The chromatograms of the 1st, 10,000th, 20,000th, and 29,200th runs are shown in Figure 7. Oxygen RT shifted from 0.429 to 0.423 minutes with the relative RT change of 1.4% (Figure 8). Nitrogen RT shifted from 0.665 to 0.640 minutes, with a relative RT change of 3.8%. The change in both RTs is within the preset 5% window (the bracket at the peak top representing the identification window), which means no identification was missed. Thirty thousand runs with an 80-second cycle time is the equivalent of running continuously for approximately one month under the effective purification procedure before a column baking step is needed as a maintenance step.

The capacity of the water filter (which functioned using an adsorbent-based mechanism) used in this work is 7.2 g. While the filter is not suitable for large-scale and long-term purification of bulk wet electrolyzer gases, it is clearly effective in removing moisture in the sample line pre-analysis.

To further protect the straight MS5Å channel, larger filters and/or additional water removal devices like semi-permeable tubing (which uses a different mechanism compared to water adsorbents) may also be considered to further extend the operational time of a straight MS5Å channel. Note that adding larger filters will likely add a slight dilution-delay effect to the result. The porous nature of bed filters typically makes this effect even more pronounced, meaning that these larger filters are less suited to situations where concentrations change rapidly.

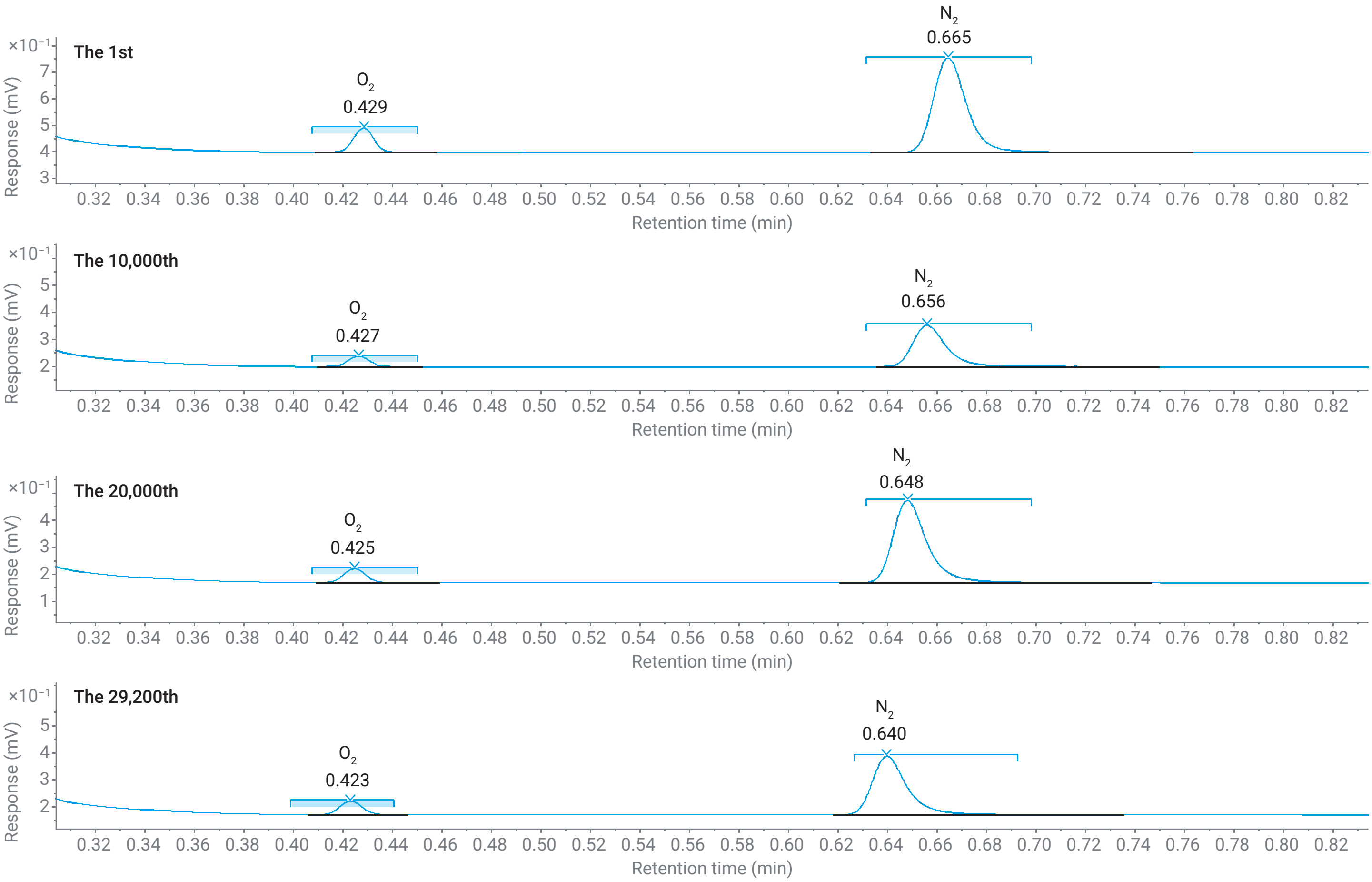

Figure 7. Oxygen and nitrogen RT change over the course of approximately 30,000 runs using the straight MS5Å channel for the lab-made hydrogen analysis.

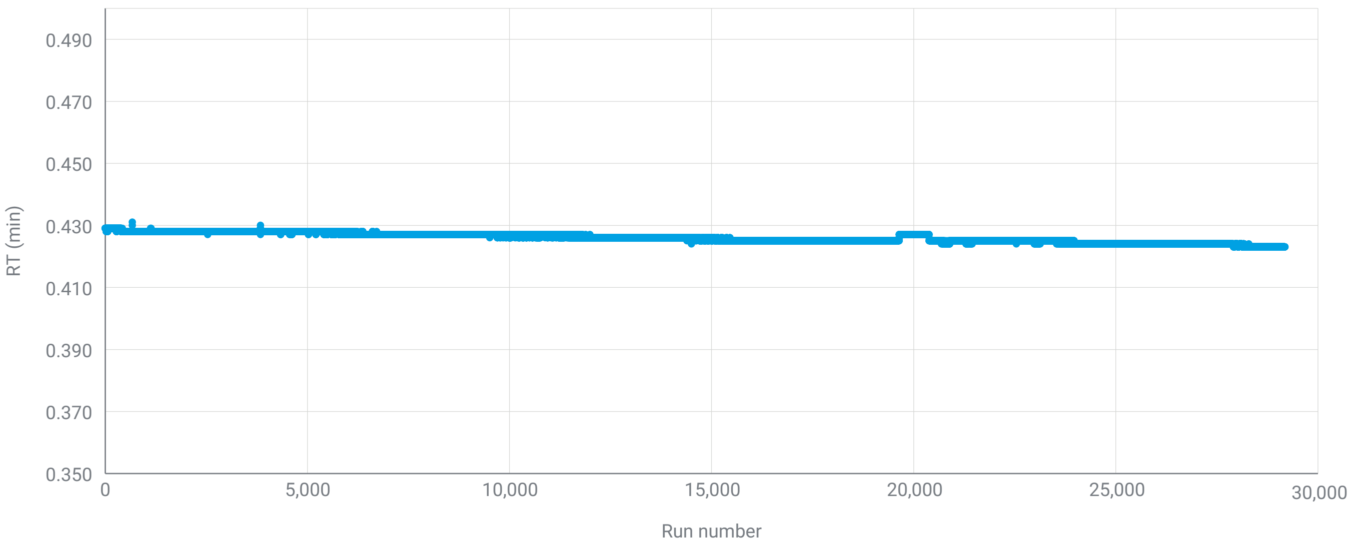

Figure 8. Oxygen RT plot over the course of approximately 30,000 runs.

Conclusion

An Agilent 990 Micro GC configured with two straight MS5Å channels was used in electrolyzer gas impurity analysis. Method quantitation precision was typically < 1% for all test components even at low ppm concentrations. Impurities LODs were found below 1 ppm, which guarantees accurate and sensitive detection of hydrogen, nitrogen, and oxygen contaminants in electrolyzer gases.

Compared to the backflush channel-based solution, the straight-channel solution is easier to use (no backflush time optimization is needed). Analysis speed is faster (80 seconds compared to 90 seconds) and the ownership cost is lower. Without backflush capability, this solution must work with an effective moisture removal procedure for effective 24/7 monitoring of the electrolysis process. This method is very suitable for process control of low-moisture-containing electrolyzer gases like hydrogen used in PEM fuel cells.

Reference

1. Electrolysis Gas Impurity Analysis Using the Agilent 990 Micro GC Configured with Backflush MS5Å Channels. *Agilent Technologies application note*, publication number 5994-8802EN, **2025**.

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DE-014852

Printed in the USA, May 20, 2026
5994-9165EN

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