Application Note

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Electrolysis Gas Impurity Analysis Using the Agilent 990 Micro GC Configured with Backflush MS5Å Channels

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Abstract

This work demonstrates how the oxygen, nitrogen, and hydrogen impurities in electrolyzed gases are analyzed using the Agilent 990 Micro GC equipped with two Molsieve 5Å (MS5A) column channels configured with different carrier gases. In this experiment, the nitrogen and oxygen impurity in bulk hydrogen were analyzed on the MS5Å channel using helium carrier gas. The hydrogen and nitrogen impurity in bulk oxygen were analyzed on two MS5Å channels simultaneously. The method precision and limits of detection (LODs) were evaluated.

Introduction

Water electrolysis is the process of splitting water molecules into hydrogen and oxygen gases using an electric current. It consists of two electrodes, an anode and a cathode, separated by an electrolyte. When an electric current is passed through the water, hydrogen gas is generated at the cathode, while oxygen gas is released at the anode. This process can be powered by renewable sources of electricity, such as wind or solar, making it a sustainable method for green hydrogen production. By analyzing the composition of the gases produced, operators can ensure the efficiency and effectiveness of the electrolysis system. If any errors or deviations from the expected values are detected, they can be quickly corrected. This real-time feedback enables process optimization, leading to increased efficiency and hydrogen yield.

Additionally, maintaining purity levels is crucial for the successful utilization of green hydrogen in various applications, such as fuel cells and industrial processes. The main impurities in hydrogen generated by electrolysis include oxygen, nitrogen, carbon monoxide, carbon dioxide, etc. Among these impurities, oxygen and nitrogen are usually no less than single digit ppm level and can be detected by a GC-TCD system. Similarly, the main impurities in oxygen are trace-level hydrogen and nitrogen which can also be analyzed by GC-TCD.

The 990 GC features a fast gas analysis based on a short and highly efficient capillary column using isothermal separation mode and sensitive μ-TCD detection. It is suitable for electrolysis process control and final product impurities analysis.

Experimental

The 990 Micro GC system was equipped with two 10 m Agilent J&W CP-Molsieve 5Å channels. The backflush type channels were used to backflush the remaining moisture and other contaminants out of the precolumn so they would not enter the MS5Å analytical column. One MS5Å channel was configured with helium carrier gas for trace oxygen and nitrogen analysis and the other channel was run under argon carrier gas for trace hydrogen analysis. Table 1 shows the experimental conditions.

Note: the backflush time may vary on different Molsieve channels. The backflush time applied here can be used as a starting point for further optimization on each channel. The 10 m J&W CP-Molsieve 5Å backflush channel with retention time stability (RTS) option can be considered for extended RT stability.

Three cylinders of standard gas were used for system performance assessment. Gases no.1 and no. 3 were also used for detection limit test. The gas compositions are shown in Table 2.

Table 1. Test conditions for the O_2-H_2-N_2-mixture.

Channel Type	Channel 1: 10 m Agilent J&W CP-Molsieve 5Å Column, 1 m Backflush	Channel 2: 10 m Agilent J&W CP-Molsieve 5Å Column, 1 m Backflush
Carrier Gas	Argon	Helium
Column Pressure	150 KPa	150 KPa
Injector Temperature	80 °C	80 °C
Column Temperature	50 °C	50 °C
Injection Time	40 ms	100 ms
Backflush Time	7.0 s	6.8 s
Invert Signal	On	Off
Sampling Time	20 s	
Run Time	90 s	

Table 2. Standard gas composition.

Gas	Standard Gas No. 1	Standard Gas No. 2	Standard Gas No. 3
O_2	10.5 ppm	980 ppm	Balance
N_2	9.9 ppm	1,050 ppm	10.0 ppm
H_2	Balance	Balance	10.0 ppm

Results and discussion

Separation and chromatograms

Standard gases no. 1 and no. 2 contain different concentrations of oxygen and nitrogen in the hydrogen balance gas. The two standard gases cover the general oxygen and nitrogen concentration range in the hydrogen generated during the electrolysis process. The chromatograms of the two standard gases on the MS5Å channel using helium carrier gas are shown in Figures 1 and 2. It takes approximately one minute for nitrogen to elute off the column. The response factors of nitrogen in a hydrogen matrix under 10 ppm and 1,050 ppm were calculated as 1.51 and 1.54 $\mu v \times s \cdot ppm^{-1}$. The consistency of nitrogen response factors under concentrations with two orders of magnitude difference showed good linearity of the µ-TCD. In real application, if the analysis is performed on an established process, a single point calibration approach can be used based on the good linearity of µ-TCD. Under such a scenario, it is suggested to calibrate the system with a gas concentration close to expected concentrations in the sample streams.

Standard gas no. 3 contained 10 ppm hydrogen and nitrogen in oxygen. This sample was used to demonstrate the hydrogen and nitrogen impurity analysis in the oxygen stream from the anode. The trace hydrogen analysis was performed on the MS5Å channel using argon carrier gas because the thermal conductivity of hydrogen is close to that of helium. As a result, 10 ppm hydrogen cannot be detected if using helium carrier gas.[1] The hydrogen peak eluting before the bulk oxygen peak showed good signal when injection time was set at 40 ms (Figure 3).

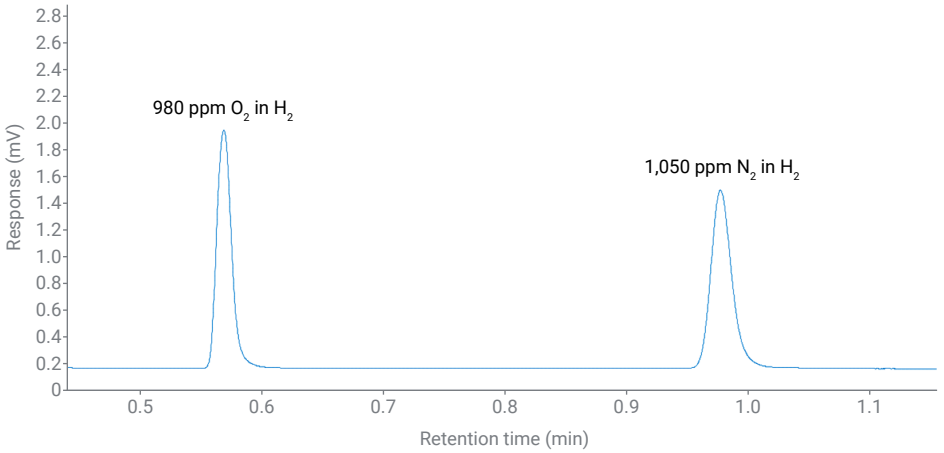

Figure 1. The chromatogram of 1,000 ppm oxygen and nitrogen in hydrogen (channel 2 using helium carrier gas).

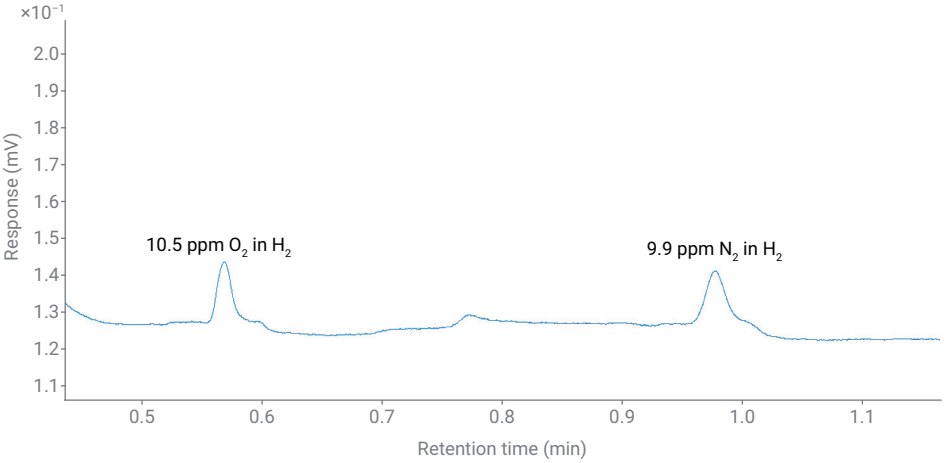

Figure 2. The chromatogram of 10 ppm oxygen and nitrogen in hydrogen (channel 2 using helium carrier gas).

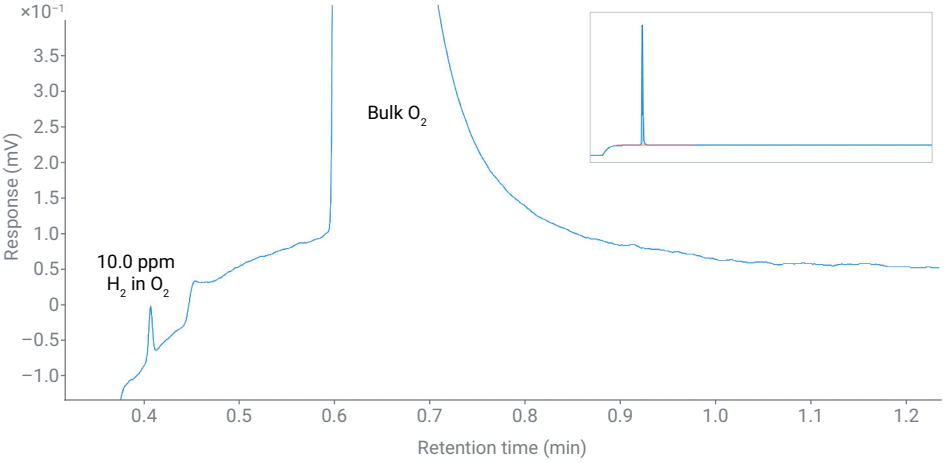

Figure 3. The chromatogram of 10 ppm hydrogen in oxygen (channel 1 using argon carrier gas).

The nitrogen impurity in oxygen should be analyzed on the MS5Å channel using helium carrier gas. As displayed in Figure 4, 10 ppm nitrogen eluted on the peak tail of oxygen. An injection time of 100 ms, instead of 40 ms, was used for trace-level nitrogen analysis in oxygen for better signal-to-noise ratio and response precision.

Repeatability

The method precision was evaluated based on 15 injections of standard gases No.1, 2, and 3. The statistical results showed area %RSD at 10 ppm concentration level was less than 3% (Table 3). As expected, 1,000 ppm of oxygen and nitrogen demonstrated much better response precision (< 0.1%) because their higher absolute response was less influenced by the peak integration variance. Such high precision demonstrates precise pneumatic control of the 990 Micro GC and stable response of its µ-TCD.

Limit of detection

The LODs of hydrogen, oxygen, and nitrogen were calculated according to Equation 1. Each compound had LOD below 1 ppm. The corresponding LOQs were in the range of 1.0 to 3.0 ppm, which guaranteed the accurate quantitation of oxygen, nitrogen, and hydrogen impurities in bulk hydrogen or bulk oxygen generated from the electrolysis process.

Equation 1.

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

t = t value at n − 1 degrees of freedom under a confidence level of 99%

n − 1 = the degree of freedom

S = the standard deviation of measured concentration in n replicate analyses

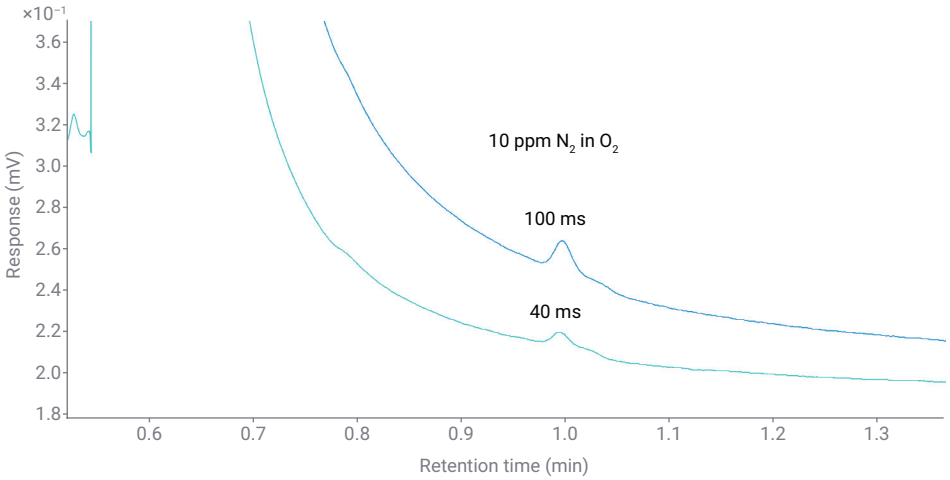

Figure 4. The chromatograms of 10 ppm nitrogen in oxygen (channel 2 using helium carrier gas) and the nitrogen peak showing the signal-to-noise improvement resulting from the longer injection time.

Table 3. RT and response repeatability of 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 (ppm)	10.5	9.91	980	1050	10.0	10.0
Area (mv × s)	0.013	0.015	1.519	1.62	0.016	0.02
Area %RSD	1.13	1.353	0.035	0.034	1.7	2.3
RT (min)	0.569	0.977	0.569	0.976	0.99	0.407
RT %RSD	0.033	0.033	0.009	0.005	0.021	0.012

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

Component	Measured Concentration (ppm)	Standard Deviation (ppm)	LOD (ppm)	LOQ* (ppm)
Impurity in Hydrogen				
Oxygen	10.48	0.12	0.36	1.20
Nitrogen	9.81	0.14	0.42	1.40
Impurity in Oxygen				
Nitrogen	10.00	0.23	0.69	2.30
Hydrogen	10.04	0.19	0.57	1.90

* LOQ = 3.3 × LOD

Conclusion

The Agilent 990 Micro GC configured with two MS5Å backflush channels was used for the electrolyzed gases impurity analysis. The trace-level oxygen and nitrogen contaminants in bulk hydrogen were analyzed on a single MS5Å channel using helium carrier gas. The hydrogen and nitrogen contaminants in oxygen were analyzed on two MS5Å channels using argon and helium carrier gas respectively.

The system response precision at low ppm level was less than 3% for all components. The calculated LOQs were in the range of 1 to 3 ppm, which ensured sensitive detection of the three targeted impurities in electrolyzed gases.

A single analysis was completed within 90 seconds including the sampling time. The fast analysis speed provided near real-time feedback to the electrolysis process and made the quality control of the gas products more efficient.

Reference

1. Hydrogen Detection with a TCD using Mixed Carrier Gas on the Agilent Micro GC, *Agilent Technologies application note*, publication number 5991-3199EN, **2013**.

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