Application Note

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Micro GC Analysis of Permanent Gas Impurities in PEM Fuel Cell-Grade Hydrogen

According to SAE J2719, ISO 14687, EN 17124, and ISO 19880-8

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Abstract

A robust solution using the Agilent 990 Micro GC was developed for analyzing selected impurities in Proton Exchange Membrane (PEM) fuel cell-grade hydrogen. Accuracy, precision, and detection levels for helium (He), argon (Ar), oxygen (O_2), nitrogen (N_2), and methane (CH_4) meet requirements as listed in SAE J2719. Even though not listed in SAE J2719, neon (Ne) may also be quantified at low ppm levels. Analysis time with this method is less than five minutes, enabling high throughput for this quality control method.

Introduction

Quality requirements for hydrogen purity vary with application. Proton Exchange Membrane (PEM) fuel cell hydrogen is the application with the most stringent specification. Hydrogen purity specifications for other applications, i.e. residential or industrial use, typically allow for higher levels of specific contaminants.

For PEM fuel cell-grade hydrogen, there are several key methods regulating quality. Some methods may also cover other scopes, but where they pertain to PEM fuel cell-grade hydrogen, they align on specific requirements for purity level and limit concentrations of specific contaminants.

- **SAE J2719** specifies hydrogen fuel quality requirements for PEM fuel cell vehicles, such as hydrogen-powered cars.
- **ISO 14687** specifies minimum quality characteristics of hydrogen fuel for various applications, including residential, commercial, industrial, stationary systems, and vehicular use.
- **EN 17124** specifies the quality characteristics of hydrogen fuel dispensed at hydrogen refueling stations for use in PEM fuel cell vehicle systems.
- **ISO 19880-8** specifies the quality of the gaseous hydrogen at hydrogen distribution facilities and hydrogen fueling stations for PEM fuel cells for road vehicles.

Table 1 lists specific quality control requirements for various specifications. Multiple alternative instrumental solutions are needed for full scope coverage.

Micro GC is a suitable choice of technique for covering analysis of permanent gases in ultra high purity (UHP) hydrogen (oxygen, nitrogen, argon, helium, and methane). The small internal volume of the MEMS-based µTCD in the Agilent 990 Micro GC means that lower detection levels can be achieved when compared to regular TCDs, allowing for detection of contaminants in the single-digit ppm range. Note that ammonia, carbon monoxide, carbon dioxide, and formaldehyde can also be detected with Micro GC; however, additional/different columns might be required. Sensitivity requirements below 1 ppm may require alternate techniques.

Table 1. Quality control requirements.

Component	SAE J2719 (ppm)	DIN EN 17124 (ppm)	ISO 14687 type I/II grade D (ppm)	ISO 19880-8 (ppm)	Technique
Nitrogen (N_2)	300	300	300	300	µGC
Oxygen (O_2)	5	5	5	5	µGC
Argon	300	300	300	300	µGC
Helium	300	300	300	300	µGC
Methane	100	100	100	100	µGC
Total Hydrocarbons	2	2	2	2	GC-FID
Carbon Dioxide (CO_2)	2	2	2	2	GC-Meth-FID
CO	0.2	0.2	0.2	0.2	GC-Meth-FID
Water (H_2O)	–	5	5	5	–
Total Sulphur (S1 eq.)	0.004	0.004	0.004	0.004	GC-SCD
Formaldehyde (HCHO)	0.2	0.2	0.2	0.2	TD-GC-SQ
Formic Acid (HCOOH)	–	–	0.2	0.2	–
Ammonia	0.1	0.1	0.1	0.1	GC-NCD
Total Halogens	0.05	0.05	0.05	0.05	TD-GC-SQ
Particulate	–	1 mg/kg	1 mg/kg	1 mg/kg	–

Experimental

The method developed covers permanent gases defined in SAE J2719, and by default, also ISO 14687, ISO 19880-8, and EN 17124. The 990 Micro GC system was set up similar to the method described in Agilent application note 5994-2138EN.[1] A 20 m MS5A straight channel on hydrogen carrier gas was used. Table 2 lists experimental conditions for method development. A 20 m molsieve provides sufficient separation for the argon/oxygen peak pair at low-ppm concentrations.[2] For best results, the column was operated at a low temperature of 30 °C. Hydrogen was used as carrier gas to completely mask the bulk hydrogen matrix peak, resulting in separation of the helium and neon baseline[3], while still allowing for a similar sensitivity as with the helium carrier. The hydrogen carrier allows helium (He), argon (Ar), oxygen (O2), nitrogen (N_2), methane (CH_4), and even neon (Ne) to be measured at their required levels. Carbon monoxide (CO) that elutes from the molsieve column is not part of the scope. SAE J2719 requires these to be measured at the sub-ppm level, which is too low for Micro GC. Table 3 lists the composition of calibration gas used. The system was calibrated using single-point calibration.

Table 2. Experimental conditions for the Agilent 990 Micro GC, considering SAE J2719.

Channel Type	20 m MS5A, Straight
Carrier Gas	Hydrogen
Column Pressure	120 kPa
Injector Temperature	50 °C
Column Temperature	30 °C
Injection Time	200 ms
Backflush Time	N/A
Sample Time	Continuous flow

Table 3. Composition of the standard gas for calibration.

Component	Concentration (ppm)
He	277.4
Ar	284.9
O_2	4.637
N_2	298.2
CH_4	98.57
H_2	Balance

Results and discussion

Figure 1 shows chromatograms for the calibration gas, with zoomed sections for He/Ne and Ar/O_2 separation. As can be seen in (A), the He/Ne pair is fully baseline separated at this low column temperature, with the hydrogen bulk peak completely masked by the carrier, as expected. (B) demonstrates that oxygen and argon cannot be 100% baseline-separated, but the achieved separation on a 20 m molsieve is sufficient for quantifying low-ppm oxygen in the presence of 300 ppm argon with acceptable precision.

Recovery and repeatability were determined for the system using the calibration gas. Repeatability was established over eight analytical runs on the same day, by the same analyst. Site precision was derived using an additional set of eight analytical runs, extended over a 20-day measuring period. Recovery was near-perfect at 99–100%, and repeatability was found to be 0.1–0.4% for all components, except for O_2. When considering the low test concentration for oxygen relative to the expected limit of detection, the repeatability of 1.8% found for oxygen is expected statistically. In addition, considering the O_2 presence in air, 1.8% is pretty good for low-level O_2. Site precision was slightly higher than repeatability, 0.2–0.4%, with O_2 at 2.2%. This second precision statement shows long-term stability of the 990 Micro GC. The Method Detection Limit (MDL) was determined according to EPA CFR-2011-40 (10 analytical runs, same day, same analyst, MDL = student t-factor × standard deviation). The MDL, calculated for all components, is below 2 ppm. With an MDL of 0.3 ppm for oxygen (as the most critical component), this solution is suitable, and meets the five ppm limitation listed in SAE J2719. It must be noted that concentrations of helium, argon, nitrogen, and methane in the gas standard are relatively high for using this method of assessing MDL, as it may skew MDL to higher values, but calculated values are indicative of what can be achieved.

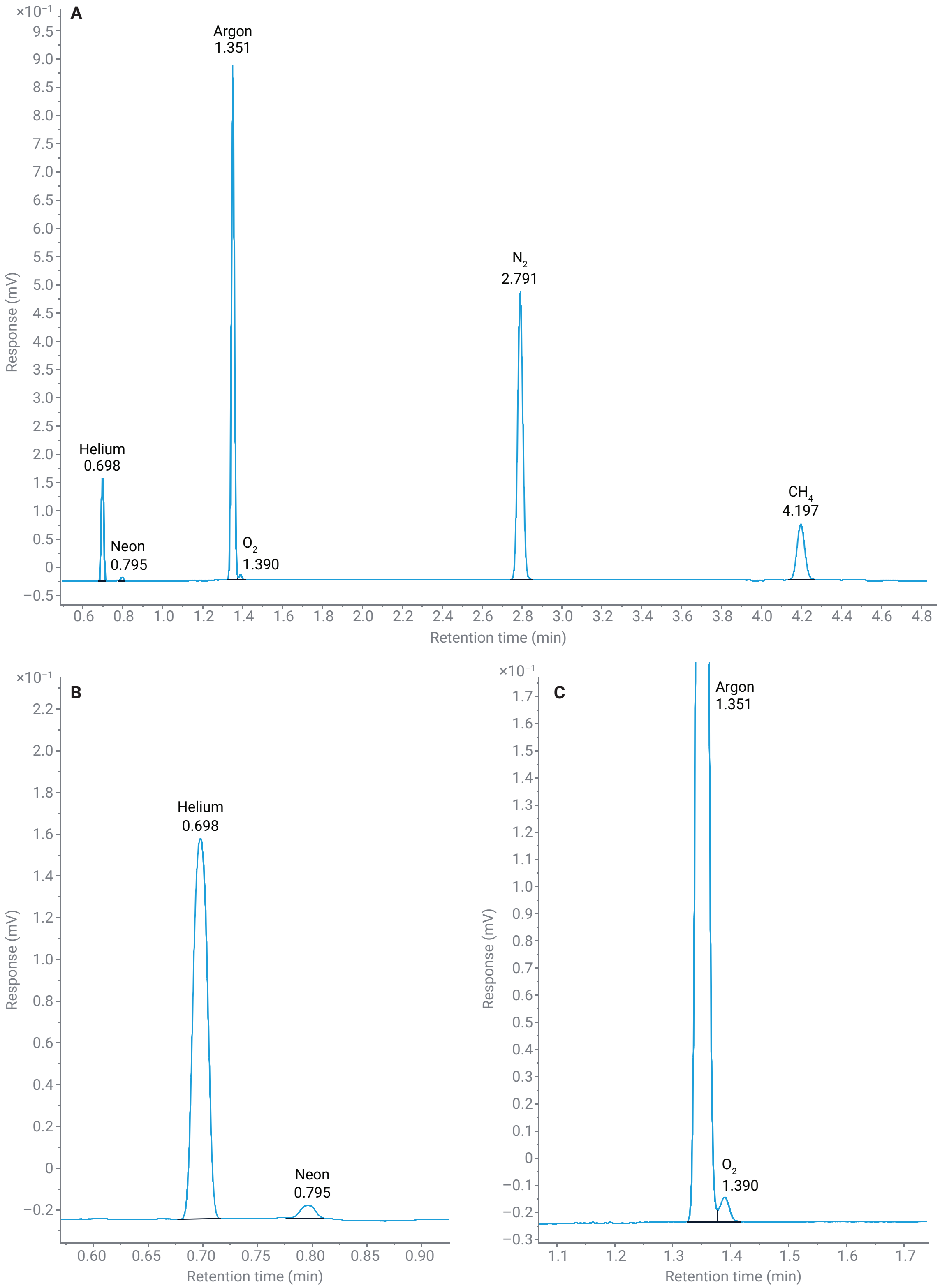

Figure 1. (A) Chromatogram of hydrogen calibration gas with five 300 ppm contaminants on a 20 m MS5A channel. Zoomed sections for (B) helium/neon, and (C) argon/oxygen.

Table 4. Summary of method validation results.

Component	Cert. Conc. (ppm)	Recovery (%)	MDL (ppm)	Repeatabilty (%)	Site Precision (%)	Spec. Limit (ppm)*
He	277.4	99.9	1.6	0.12	0.23	300
Ar	284.9	99.8	0.3	0.04	0.31	300
O_2	4.637	98.6	0.3	1.80	2.2	5
N_2	298.2	100.1	0.8	0.19	0.27	300
Methane	98.57	99.6	1.8	0.40	0.37	100

* SAE J2719

Conclusion

The Agilent 990 Micro GC setup, described with a single 20 m straight molsieve column running hydrogen carrier gas is capable of meeting the hydrogen quality requirement in SAE J2719 and other comparable UHP hydrogen methods for select permanent gases (He, Ar, O_2, N_2, CH_4). The critical component, oxygen, can reliably be measured below the required five ppm level. Precision and accuracy are excellent for all components, and with a short runtime of five minutes, this analytical option can deliver 10–12 runs per hour. Detection of other components listed in SAE J2719, i.e. ammonia or CO/CO_2, will require different equipment.

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