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Application News

No.G283

Gas Chromatography

Trace Impurity Analysis of Hydrogen Fuel in Fuel Cell Vehicle-Related Fields

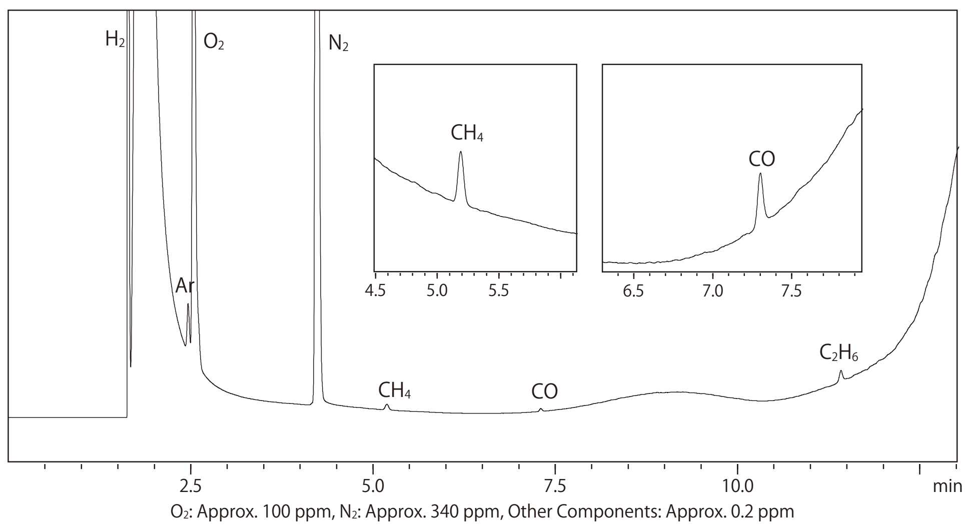
With the development of fuel cell technology for electricity generation using hydrogen (H) as fuel, attention is turning to household fuel cell systems and fuel cell vehicles. However, one of the problems associated with fuel cells in their current state is the presence of carbon monoxide (CO) in the hydrogen fuel used in the fuel cells. Carbon monoxide adversely affects the performance of the catalyst used in the battery. This phenomenon is referred to as "catalyst poisoning," and therefore necessitates the use of high-purity hydrogen fuel. The international standard (ISO 14687-2) pertaining to hydrogen fuel for fuel cell vehicles, which went into effect in 2012, specifies that, in addition to a maximum concentration of 0.2 ppm carbon monoxide in the hydrogen, maximum concentrations are also specified for oxygen (O) and carbon dioxide (CO_2) as well as hydrocarbons. In the past, analysis of impurities in hydrogen conventionally required a complex system including multiple detectors and columns, which from the standpoint of cost and maintenance, posed a significant hurdle.
The barrier discharge ionization detector (BID) is a new, universal detector that can detect almost all components, except helium (He, used as the plasma gas) and neon (Ne), with higher sensitivity than that obtained using TCD and FID detectors. This Application News introduces an example of high-sensitivity analysis of carbon monoxide in hydrogen and simultaneous analysis of impurities in hydrogen using the Tracera high-sensitivity gas chromatograph equipped with a BID detector.

■ High-Sensitivity Analysis of Carbon Monoxide Using the Rt-Msieve 5A Column

Molecular sieve 5A columns offer good separation of air components and carbon monoxide, and area suitable type of column for the analysis of carbon monoxide.
First, a standard gas was diluted with hydrogen to adjust the concentration of each component (excluding air components) to about 0.2 ppm, and measurement of the gas was then conducted using the Rt-Msieve 5A column.
The chromatogram is shown in Fig. 1, and the analytical conditions are shown in Table 1. The lower limit of detection (S/N=3) of carbon monoxide was then calculated as 0.032 ppm.

Table 1 Analytical Conditions for Trace Impurities in Hydrogen (Rt-Msieve 5A column)

Model	: Tracera (GC-2010 Plus + BID-2010 Plus)
Column	: RESTEK Rt-Msieve 5A (30 m × 0.53 mm I.D., df = 50 µm) with Particle Trap 2.5 m
Column Temp.	: 35 ˚C (2.5 min) → 20 ˚C/min → 250 ˚C → 15 ˚C/min → 270 ˚C (3.42 min)
Inj. Mode	: Split 1:7
Carrier Gas Controller	: Constant linear velocity mode (He)
Linear Velocity	: 45 cm/sec
Det. Temp.	: 280 ˚C
Discharge Gas	: 50 mL/min (He)
Inj. Volume	: 3 mL



	S/N
Methane (CH_4)	38
Carbon monoxide (CO)	19
Ethane (C_2H_6)	74

Fig. 1 Chromatogram of Trace Impurities in Hydrogen (Rt-Msieve 5A Column)

Simultaneous Analysis of Impurities in Hydrogen Using the Micropacked ST Column

As carbon dioxide does not elute with the Rt-Msieve 5A column, a different system is required for analysis when carbon dioxide is among the target substances. The Micropacked ST column supports separation of inorganic gasses, including carbon dioxide and lower hydrocarbons, making it suitable for simultaneous analysis of impurities in hydrogen gas.
A standard gas was diluted with hydrogen to adjust the component concentrations (other than air components) to about 0.2 ppm, and this gas was analyzed using the Micropacked ST column.
The resultant chromatogram is shown in Fig. 2, and the analytical conditions are shown in Table 2. The lower limit of detection of carbon monoxide was calculated as 0.078 ppm (S/N=3). Though not as good as those obtained with the Rt-Msieve 5A column, the results include detection of the maximum concentration stipulated by ISO 14687-2.

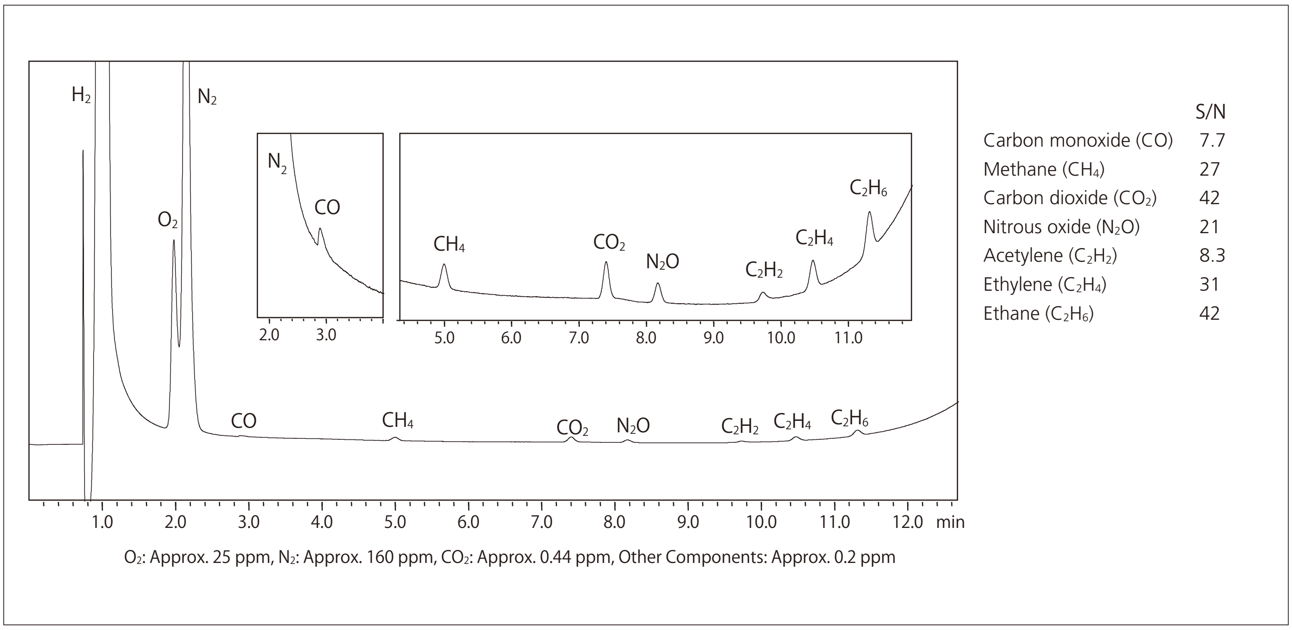
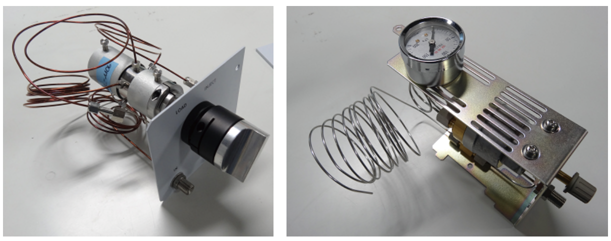


Fig. 2 Chromatogram of Simultaneous Analysis of Impurities in Hydrogen (Micropacked ST Column)

Table 2 Analytical Conditions for Simultaneous Analysis of Impurities in Hydrogen (Micropacked ST Column)

Model	: Tracera (GC-2010 Plus + BID-2010 Plus)
Column	: Micropacked ST (2 m × 1 mm I.D.)
Column Temp.	: 35 ˚C (2.5 min) → 20 ˚C/min → 250 ˚C → 15 ˚C/min → 265 ˚C (3 min)
Inj. Mode	: Split 1:4
Carrier Gas Controller	: Pressure mode (He)
Pressure Program	: 226.8 kPa (2.5 min) - 15 kPa/min - 400 kPa (3.2 min)
Det. Temp.	: 280 ˚C
Discharge Gas	: 50 mL/min (He)
Inj. Volume	: 3 mL



Valve Unit　　Manual Flow Controller for Purge

Fig. 3 MGS-2010 Gas Sampler

In this analysis, the MGS-2010 gas sampler was used for the introduction of gas into the instrument; the column was connected using the SPLITTER-INJ (P/N: 221-76252-41).
The MGS-2010 is a manual gas sampler for the Tracera (GC-2010 Plus). A purge mechanism is included to reduce the leakage of peripheral air into the system. The SPLITTER-INJ refers to a special injection unit that permits split injection of the sample without requiring that it pass through the standard split/splitless injection unit.
Using the MGS-2010 for sample gas injection together with the SPLITTER-INJ unit, it is possible to quantitatively analyze trace level air components, including Oxygen (O_2), Nitrogen (N_2), etc., with high accuracy.

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