

Gas monitoring systems and calorimeters for hydrogen-containing natural gas applications

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Abstract. This study proposes semi-custom-made gas monitoring systems that combine our existing gas detection alarms and calorimeters to support decarbonization technologies. These systems require no catalytic combustion or separate columns, and the use of physical sensors eliminates the need for frequent cleaning or recalibration. Even with preprocessing, the unit remains compact and ensures straightforward maintenance. Application examples include monitoring hydrogen-containing natural gas, analyzing ammonia synthesis and decomposition, evaluating methanation, and assessing steel-mill by-product gases.

1 Background

The global trend toward decarbonization to mitigate climate change is accelerating, and green energy is gaining significant attention. Among the various green energy sources, hydrogen has emerged as one of the most promising options, and its utilization is currently being demonstrated worldwide. With this shift, the demand for gas calorimetry is increasing. While several calorimeters are available for natural gas, there are very few devices capable of measuring hydrogen-containing natural gas in real-time with high accuracy.

2 Calorimeter principle

We developed the calorific value determining device OHC-800, as shown in Figure 1. The calorific value of a gas can be determined using the correlation among its speed of sound (measured by a sonic sensor), its refractive index (measured by an optical sensor), and the calorific value itself.



Fig. 1. OHC-800 calorimeter.

For gases composed mainly of paraffinic hydrocarbons, each sensor can accurately measure calorific value. However, when the gas contains components with low calorific value (e.g., CO, N₂, CO₂),

these introduce measurement errors. By combining the signals from both sensors, these errors can be canceled.

2.1 Sonic sensor

The sonic sensor determines the speed of sound through precise time-of-flight measurements, using a pair of piezoelectric elements—one for transmission and one for reception—positioned at opposite ends of the gas cell, as shown in Figure 2.

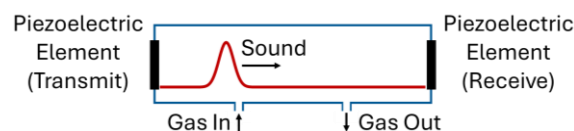


Fig. 2. Sonic sensor image.

Figure 3 illustrates the relationship between the speed of sound and the calorific value of various gases. The straight line connecting the ■ marks represents the function Q_{sonic} , which describes the correlation between calorific value and speed of sound in mixtures composed of paraffinic hydrocarbons.

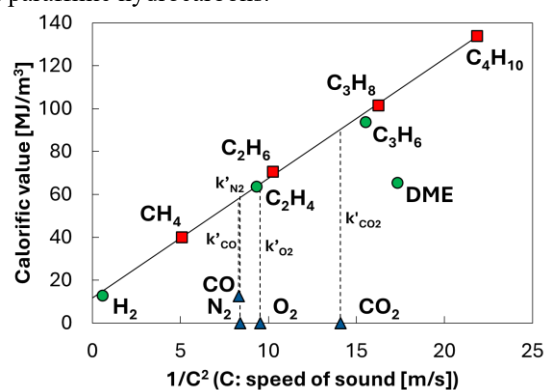


Fig. 3. Speed of sound vs. calorific value.

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2.2 Optical sensor

The optical sensor measures the refractive index by detecting interferometric fringe shifts. The device comprises two gas chambers: one filled with a reference gas—typically air or N₂—and the other with the measurement gas, as shown in Figure 4.

Light emitted from an LED is split into two paths, passes through both chambers, and is then recombined before reaching the camera. The phase shift arising from the difference between the two gases generates an interferometric fringe shift, which is captured by the camera.

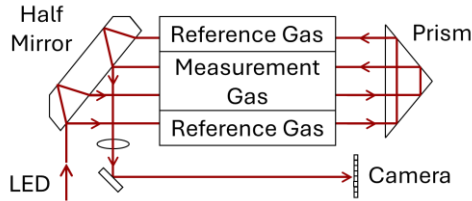


Fig. 4. Optical sensor image.

Figure 5 illustrates the relationship between refractive index and calorific value of various gases. The straight line connecting the ■ marks represents the function Q_{opt} , which describes the correlation between calorific value and refractive index in mixtures composed of paraffinic hydrocarbons.

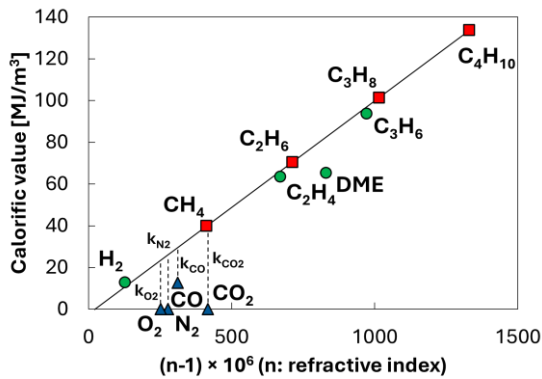


Fig. 5. Refractive index vs. calorific value.

2.3 Opt-sonic calculation

The ratio of calorific values measured by the sonic sensor and the optical sensor remains approximately constant for most interfering gases (e.g., CO, N₂, CO₂), as summarized in Table 1. This characteristic allows the measurement errors introduced by these interfering gases to be effectively canceled when the outputs of both sensors are combined.

Table 1. Error factor of two sensors.

Gas	Optical Sensor	Sonic Sensor	Ratio
CO ₂	$k_{CO_2} = 40.52$ MJ	$k'_{CO_2} = 89.84$ MJ	2.21
CO	$k_{CO} = 17.14$ MJ	$k'_{CO} = 45.24$ MJ	2.63
N ₂	$k_{N_2} = 26.19$ MJ	$k'_{N_2} = 58.18$ MJ	2.22
O ₂	$k_{O_2} = 23.60$ MJ	$k'_{O_2} = 64.56$ MJ	2.75
DME	$k_{DME} = 17.32$ MJ	$k'_{DME} = 42.43$ MJ	2.45

Let the true calorific value of a natural gas, including interfering gases, be represented by Q . Then:

$$Q = Q_{opt} - (k_{CO_2}x_{CO_2} + k_{CO}x_{CO} + k_{N_2}x_{N_2} + k_{O_2}x_{O_2}) \quad (1)$$

$$Q = Q_{sonic} - (k'_{CO_2}x_{CO_2} + k'_{CO}x_{CO} + k'_{N_2}x_{N_2} + k'_{O_2}x_{O_2}) \quad (2)$$

where:

- x_i denotes the volume fraction of each interfering gas component.
- k_i and k'_i represent the error coefficients corresponding to the influence of each component.

Although these coefficients differ for each gas, their ratio—denoted as α —remains nearly constant:

$$k_{CO_2} \approx \alpha \cdot k'_{CO_2}, k_{CO} \approx \alpha \cdot k'_{CO}, k_{N_2} \approx \alpha \cdot k'_{N_2}, k_{O_2} \approx \alpha \cdot k'_{O_2} \quad (3)$$

Using equation (3), the opt-sonic calculation formula is obtained:

$$Q = Q_{opt} - \frac{(Q_{opt} - Q_{sonic})}{1 - \alpha} \quad (4)$$

Figure 6 illustrates the correlation between calorific values calculated from equation (4) and the actual values. All data points align along a straight line with a slope of 1, confirming that accurate calorific values can be obtained—even when the natural gas contains interfering components—by combining Q_{opt} and Q_{sonic} .

The same approach can also be applied to determine the specific gravity of natural gas, providing a unified method for characterizing gas properties.

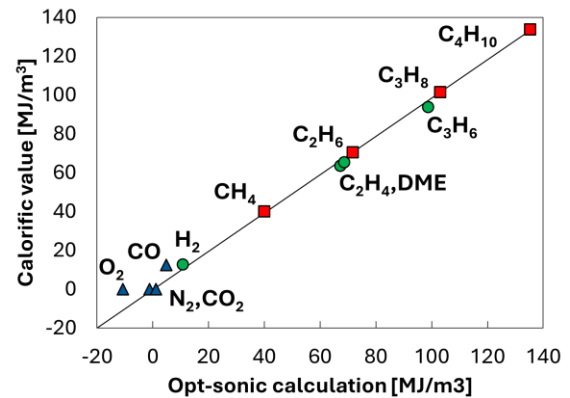


Fig. 6. Opt-sonic calculation results.

3 H₂-containing natural gas application

The opt-sonic calculation method is applicable not only to natural gas but also to hydrogen-containing natural gas mixtures. We propose several approaches for determining both the calorific value and the hydrogen concentration within such blended gases.

Some of these approaches utilize techniques that combine multiple gas sensors with a programmable logic controller (PLC). By leveraging our extensive sensor lineup, it is possible to measure multiple parameters of mixed gases by integrating different sensors into a unified system. We refer to this integrated solution as the Real-Time Gas Monitoring System (RTGMS).

3.1 Measurement of calorific value

The OHC-800 calorimeter was certified as OIML R140 Class A in 2023. The instrument is applicable to both natural gas and hydrogen-containing natural gas, covering a calorific value range of 30.1–47.3 MJ/m³. The certified working ranges for each gas component are summarized in Table 2.

Table 2. Working range of OIML-certified OHC-800.

Component	Working range [mol%]	
	Natural gas	Natural gas + H ₂
CH ₄	70–100	67–100
C ₂ H ₆	0–15	0–15
C ₃ H ₈	0–5	0–9
C ₄ ⁺	C ₄ ⁺ shall be converted to the equivalent CH ₄ + C ₃ H ₈ mixture; the result must fall within their concentration ranges.	
N ₂	0–20	0–10
CO ₂	0–5	0–6
H ₂	0	0–20
CV [MJ/m ³]	30–47.5	

The OHC-800 enables continuous calorific value measurement of natural gas and mixtures containing up to 20 mol% hydrogen. The system provides a measurement-data update interval of 0.25 s, a 90% response time below 5 s, and a measurement uncertainty within ±0.5%, as shown in Figure 7. These performance characteristics exceed those achievable with conventional calorimeters and gas chromatographs, particularly in applications requiring rapid response and real-time monitoring.

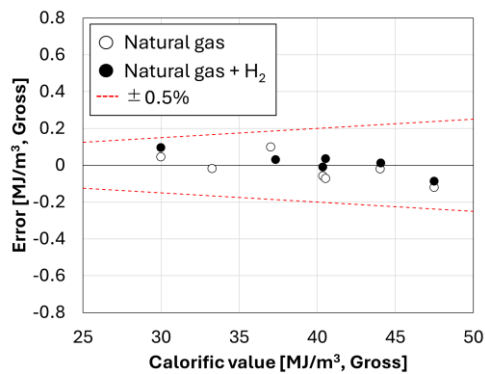


Fig. 7. Measurement results of OIML-certified OHC-800.

3.2 Measurement of added H₂ proportion

If the measurement of natural gas prior to hydrogen addition is possible, the RTGMS extends the effective working range for hydrogen in calorific value measurement up to 100 vol% and enables the proportion of added hydrogen to be measured.

In this method, calorific value and refractive index of the original natural gas are first measured using the OHC-800 before hydrogen is added. After hydrogen addition, the refractive index of the resulting mixture is measured using the FI-900, which is equipped solely

with an optical sensor. The calorific value and hydrogen concentration of the mixture are then calculated by a PLC, as shown in Figure 8. The specific gravity of the mixture can also be determined using the same approach.

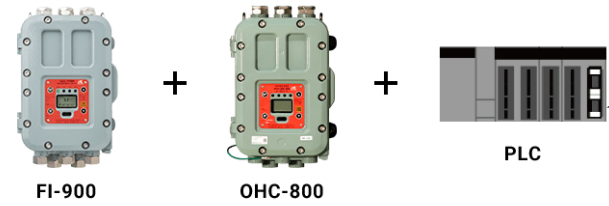


Fig.8. RTGMS for H₂ + natural gas measurement.

Table 3 presents the measurement and calculation results for hydrogen concentration, calorific value, and specific gravity when hydrogen was incrementally added to natural gas using this system. The theoretical hydrogen addition rate corresponds to the ideal volumetric mixing ratio. The results show that the calculated values closely match the theoretical values, demonstrating that the system provides highly consistent and reliable measurement.

Table 3. Measurement results for H₂ added natural gas.

Added H ₂ [%]		CV [MJ/m ³]		Specific Gravity	
Theo.	Meas.	Theo.	Meas.	Theo.	Meas.
0	0.0	45.40	45.33	0.647	0.645
10	9.3	42.13	42.27	0.589	0.591
20	19.1	38.86	39.08	0.531	0.534
30	29.2	35.60	35.81	0.473	0.476
40	39.4	32.34	32.49	0.416	0.417
50	49.5	29.08	29.20	0.358	0.359
60	60.1	25.82	25.76	0.300	0.298
70	70.2	22.56	22.48	0.243	0.241
80	80.2	19.31	19.20	0.185	0.181
90	89.9	16.05	16.04	0.127	0.127
100	99.5	12.79	12.94	0.070	0.072

3.3 Measurement of H₂ concentration

The RTGMS—consisting of thermal conductivity type hydrogen sensors, the OHC-800, and a PLC—enables an extension of the measurable range to 60 vol% hydrogen for calorific value determination and up to 100 vol% for hydrogen concentration measurement. In this method, the difference in output from the thermal conductivity sensor at two distinct sensor temperatures is utilized. As shown in Figure 9, the sensor output remains essentially zero for the major components of natural gas, except for N₂ and CO₂.

The influence of N₂ and CO₂ can be corrected using the OHC-800, as expressed in equation (5):

$$x_{H2} = \Delta I - a \times (Q_{opt} - Q_{sonic}) \quad (5)$$

where:

- x_{H2} denotes the volume fraction of hydrogen gas.
- ΔI represents the difference in thermal conductivity sensor output at two sensor temperatures.
- a is a constant representing the correction factor for N₂ and CO₂ induced errors.

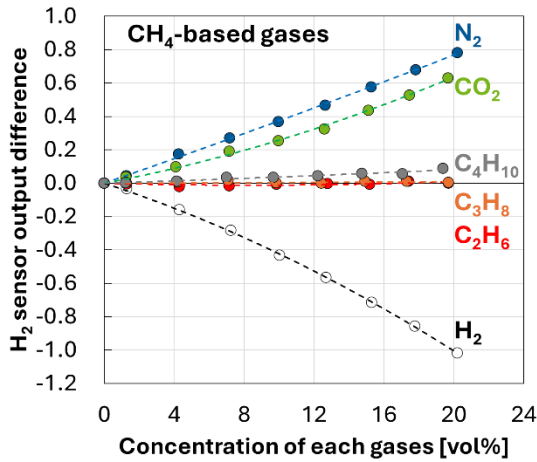


Fig. 9. H₂ sensor output vs. gas concentration.

Measurements were conducted using several natural gas compositions, as summarized in Table 4. Hydrogen was added to each natural gas sample in the range of 0 to 100 vol%, and both the hydrogen concentration and calorific value were evaluated. As shown in Figure 10, the system achieved measurement errors within $\pm 0.5\%$ for calorific value and within ± 1.0 vol% for hydrogen concentration, demonstrating high measurement accuracy across the entire hydrogen addition range.

Table 4. Composition of measured natural gas.

Composition [vol%]						CV [MJ/m ³]
CH ₄	C ₂ H ₆	C ₃ H ₈	i-C ₄ H ₁₀	N ₂	CO ₂	
80	10	2	1	5	2	42.32
90	2	1	0	5	2	38.35
90	4	2	0	3	1	40.77
83	10	3	0	3	1	43.19
90	4	2	1	3	0	42.10
82	10	4	1	3	0	45.14
90	6	3	1	0	0	44.52
85	10	5	0	0	0	46.33

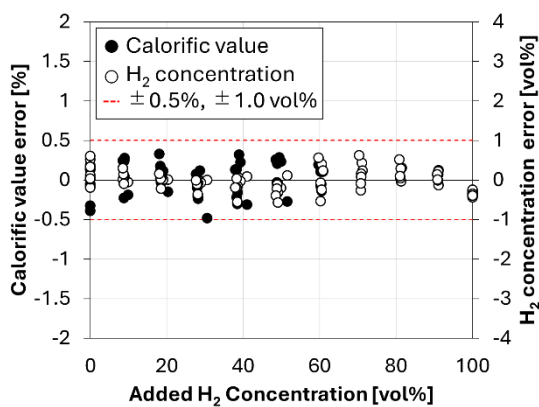


Fig. 10. Measurement results of H₂ added natural gas.

4 Other applications

4.1 Ammonia synthesis and decomposition

Ammonia is considered an essential energy source for carbon neutrality, contributing to decarbonization across various sectors. As a result, there is a growing demand

to accelerate its rapid social implementation. Compared with the direct transport of hydrogen, ammonia offers significant advantages in terms of safety, storage density, and feasibility for large-scale, long-distance transportation. For these reasons, technologies for ammonia decomposition systems have been developed by several research groups, under the assumption that ammonia will be transported to ports near industrial facilities and subsequently decomposed into H₂ and N₂.

The RTGMS, consisting of the OHC-800 and a PLC, enables continuous monitoring of gas composition during ammonia synthesis and decomposition processes. Gas mixtures composed of NH₃, H₂, and N₂ exhibit a triangular correlation between refractive index and specific gravity, as shown in Figure 11. Using the refractive index and specific gravity coordinates from the OHC-800, the PLC calculates the concentrations of NH₃, H₂, and N₂ in real time.

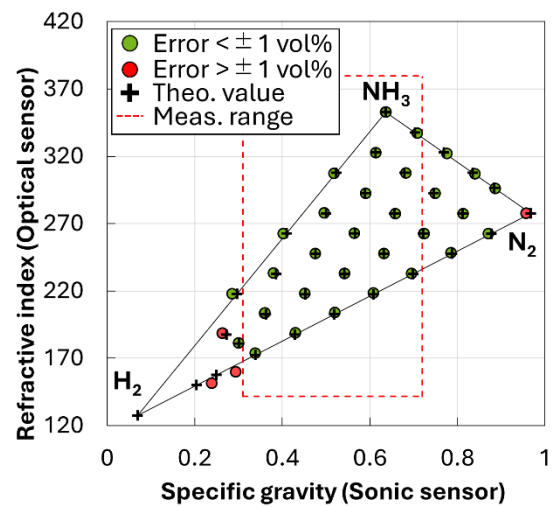


Fig. 11. Refractive index vs. specific gravity.

Figure 12 illustrates the measurement performance of the system for NH₃, H₂, and N₂ mixtures with a specific gravity range of 0.31–0.72, achieving an accuracy of $\pm 1.0\%$ under calibrated conditions. For applications requiring higher N₂ concentrations, an alternative configuration supports a specific gravity range of 0.43–0.97. Multiple RTGMS units have already been deployed in operational ammonia synthesis and decomposition facilities, demonstrating the system's applicability and stability under real-world process conditions.

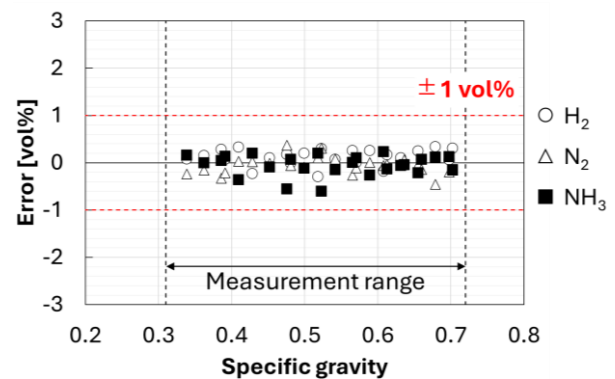


Fig. 12. Measurement results of NH₃, H₂, N₂ concentrations.

4.2 Methanation

Methanation is a process in which CH₄ is synthesized from H₂ and CO₂, and it is increasingly recognized as a key technology for producing carbon-neutral city gas. Using the same analytical approach described in the previous section for ammonia synthesis and decomposition analysis, the RTGMS, consisting of the OHC-800 and a PLC, enables real-time monitoring of CH₄, H₂, and CO₂ concentrations within a specific gravity range of 0.31–0.72, as well as the calorific value, throughout the methanation reaction.

Figure 13 illustrates an example of system performance, showing the behavior of calorific value and calculated gas composition when the mixture was alternately varied from pure methane (CH₄ 99.9995 vol%) to a mixture of CH₄: 90 vol%, H₂: 5 vol%, and CO₂: 5 vol%.

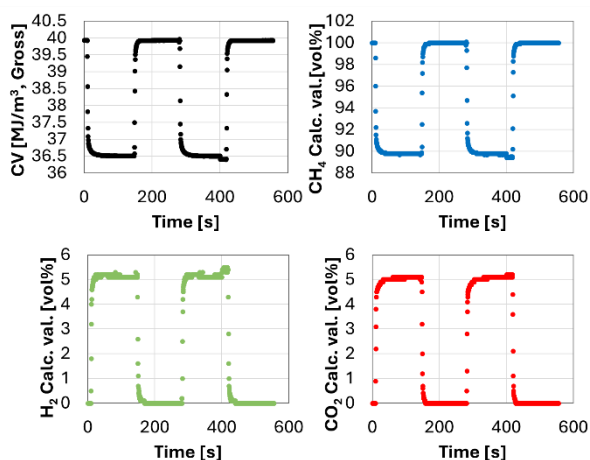


Fig. 13. Methanation gas measurement results.

The calculated results for each composition remained within an error margin of approximately ±2%, and the system exhibited a 90% response time of roughly 20 s. As shown in Figure 14, multiple RTGMS units have already been deployed in operational methanation facilities, as well as in the ammonia synthesis and decomposition facilities described in the previous section.



Fig. 14. OHC-800 deployed in a methanation plant.

4.3 Steel-mill by-product gas

The Japanese steel industry is recognized for achieving the highest level of energy efficiency worldwide in both converter and electric-furnace steelmaking, with comprehensive energy-saving measures already in place.

In February 2021, the *Basic Policy for the Japanese Steel Industry Regarding Japan's Carbon Neutrality by 2050* was formulated, outlining strategies to further reduce CO₂ emissions across the entire supply chain. These strategies emphasize two primary value propositions:

1. the provision of high-performance steel products and solutions that contribute to CO₂ reduction across society, and
2. the realization of carbon-neutral steel through decarbonization of the steelmaking process.

To monitor the composition of steelmaking by-product gases, the RTGMS—comprising the OHC-800, CO and CO₂ infrared detectors (both from our product lineup), and a PLC—is employed. This system enables real-time calculation of gas compositions containing CO, CO₂, CH₄, H₂, and N₂.



Fig. 15. CO and CO₂ detectors.

Figure 16 shows the relationship between the calculated and theoretical concentrations of each component in mixture gases prepared by blending the cylinder gases listed in Table 5 at various mixing ratios. These cylinder gases simulate typical COG (coke oven gas), BFG (blast furnace gas), and LDG (converter furnace gas). The theoretical values represent ideal volumetric mixing ratios, and the calculated composition values exhibit errors within ±2%, demonstrating the high accuracy of the system.

Table 5. Composition of cylinder gases.

	Composition [mol%]				
	CO	CO ₂	CH ₄	H ₂	N ₂
COG	7.5	3.5	27.3	56.4	5.3
BFG	22.0	20.4	0.0	2.5	55.1
LDG	58.5	18.5	0.0	1.5	21.5

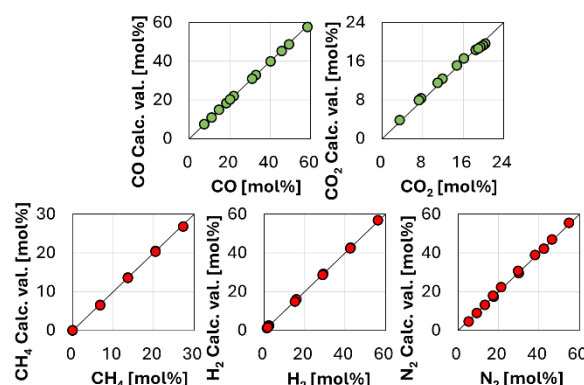


Fig. 16. Measurement results of steel-mill by-product gases.

5 Conclusion

The OHC-800's dual-sensor opt-sonic calculation method provides a robust and maintenance-friendly approach for precise and rapid calorific value determination in complex gas streams. Its capability for continuous, real-time measurement supports a wide range of industrial operations and enables the reliable utilization of hydrogen-containing natural gas. These features facilitate timely decision-making in the energy, chemical, and environmental monitoring sectors, contributing to safer and more efficient industrial processes.

Furthermore, our company has responded to the increasing demand driven by the global trend toward carbon neutrality through the development of the RTGMS, which leverages our long-standing expertise in gas sensing technology. The case studies presented in this paper represent only a portion of the system's potential applications. With our diverse sensor lineup, RTGMS can deliver customized solutions tailored to on-site requirements. In addition to monitoring gas composition, calorific value, and specific gravity, the system enables real-time measurement of compression factors, methane number, combustion rate, and other critical parameters.

We will continue to advance and promote this integrated monitoring platform—combining the continuous measurement capabilities of detectors with the high accuracy of analyzers—to support a broad range of industrial markets and contribute to the transition toward carbon-neutral operations.