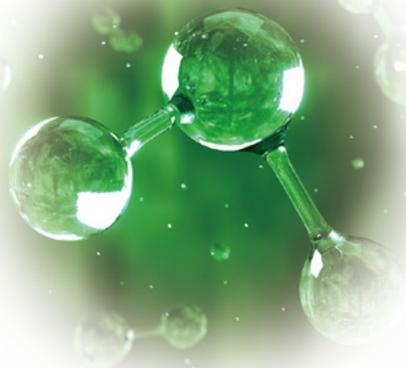


Analytical Solutions for

# Artificial Photosynthesis

— Photocatalyst Characterization and Product Quantification —



# Toward a Carbon Neutral Society



## What's Artificial Photosynthesis

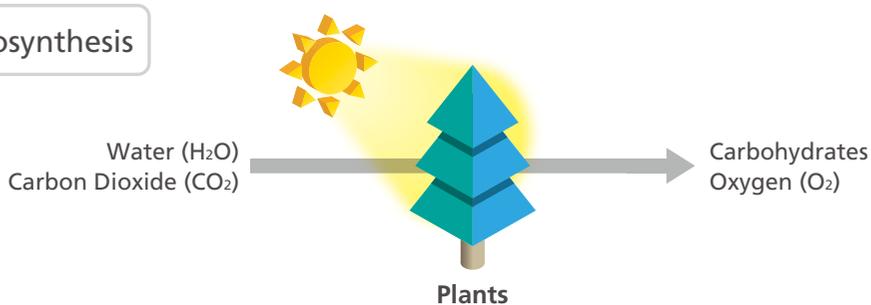
Artificial photosynthesis is a technology that artificially performs photosynthesis using photocatalysts and sunlight. It is expected to be a next-generation renewable energy technology because it can convert light energy into useful compounds. Research is being conducted using artificial photosynthesis to produce "green hydrogen," which is hydrogen that does not emit carbon dioxide during production. It is also possible to generate useful compounds such as carbon monoxide, alcohols, formic acid, and hydrocarbons by reducing carbon dioxide. However, there are significant challenges in terms of cost and efficiency compared to conventional manufacturing processes when it comes to implementing it into society. To achieve the benchmark energy conversion efficiency of 10 % for practical implementation of artificial photosynthesis, it is essential to develop photocatalysts that can effectively utilize sunlight with a wide range of wavelength distributions and construct reaction systems with higher efficiency.

Here, we present a range of analytical techniques that are designed for the evaluation of artificial photosynthesis. Our focus is on three key areas:

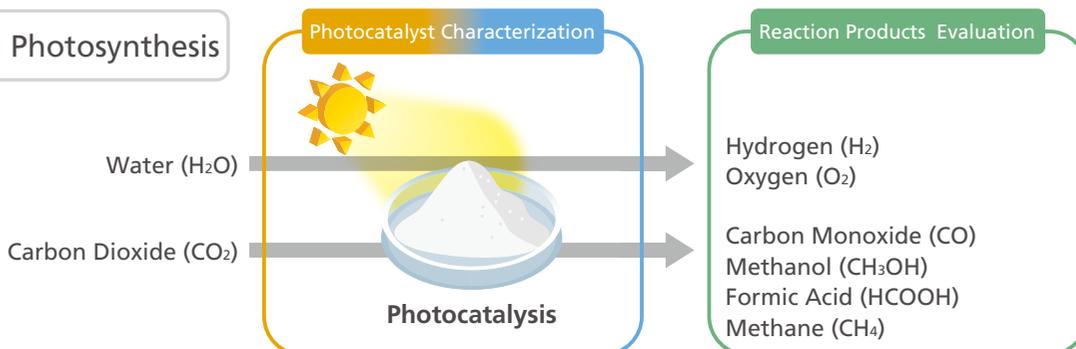
1. Evaluation of Physical Properties
2. Evaluation of Excited State and in situ Measurements
3. Quantification of Reaction Products

Shimadzu Corporation is dedicated to contributing to the realization of artificial photosynthesis technology in society by providing advanced analytical measurement techniques.

### Natural Photosynthesis



### Artificial Photosynthesis



# Analytical Techniques Involved in Artificial Photosynthesis

## Photocatalyst Characterization — Physical Properties —



### Band Gap

Measurement of the Band Gap of Titanium (IV) Oxide

UV-VIS Spectrophotometer P. 4

### Particle Size Distribution

Measurement of the Particle Size Distribution of Titanium (IV) Oxide

Particle Size Analyzer P. 5

## Photocatalyst Characterization — Excited State / in situ Measurement —



### Photoinduced Charge Distribution

Visualization of the Photoinduced Charge Distribution of a Au Nanoparticle Assembly

Scanning Probe Microscope P. 6

### Quantum Yield and Intermediates

Determination of Photoreaction Quantum Yield and Direct Observation of Intermediates in CO<sub>2</sub> Reduction by Artificial Photosynthesis

Photoreaction Evaluation System P. 7

## Reaction Products Evaluation — Quantitative Analysis of Reaction Products —



### Confirmation of Reaction Mechanism

Identification of Reaction Products and Atmospheric Components

Gas Chromatograph Mass Spectrometer P. 9

### Inorganic Gases and Hydrocarbons

Evaluation of a Catalyst Used in the Production of Fuel Cell Hydrogen  
Simultaneous High-Sensitivity Measurements of Carbon Monoxide and Hydrogen  
High-Speed Analyzer for Inorganic Gases and Hydrocarbons  
Inorganic Gases and Hydrocarbons Analysis  
Inorganic Gases and Hydrocarbons Analysis

Transportable Gas Analyzer P. 10  
Gas Chromatograph P. 11  
System Gas Chromatograph P. 12  
Gas Chromatograph P. 13  
Gas Chromatograph Mass Spectrometer P. 14

### Formic Acid

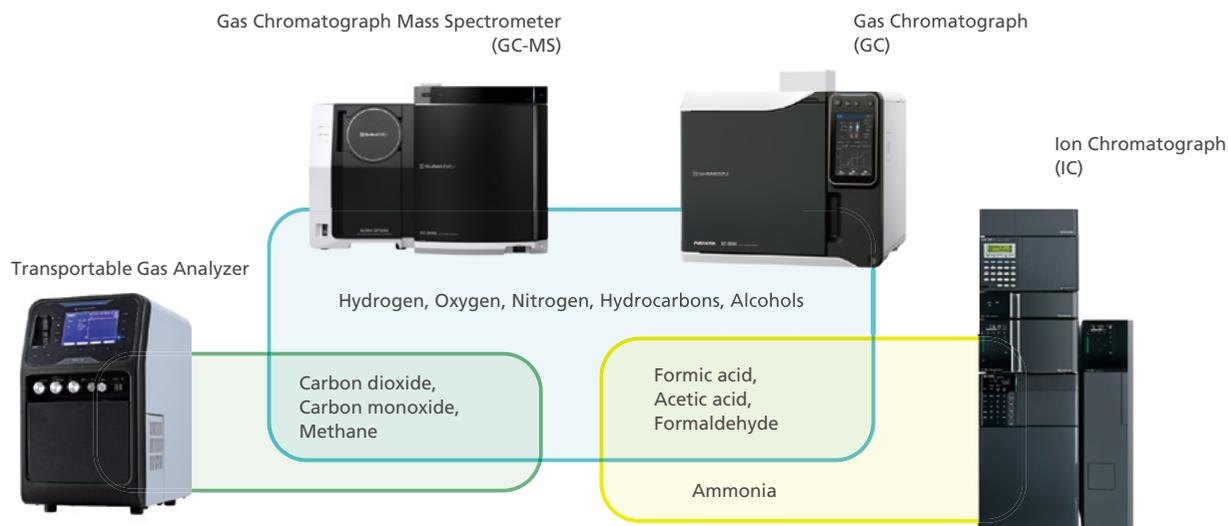
Analysis of Formic and Acetic Acids in Aqueous Solutions  
Formic Acid Analysis

Ion Chromatograph P. 15  
Gas Chromatograph P. 16

### Photocatalytic Hydrogen Generation System

Evaluation of an Iridium Complex-Based Photocatalytic Hydrogen Generation System

Photoreaction Evaluation System P. 17  
Gas Chromatograph



# Measurement of the Band Gap of Titanium (IV) Oxide

Application 

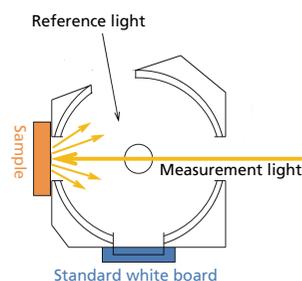
The band gap, which represents the energy required to activate photocatalysts in their excited state, is a fundamental, highly important property of photocatalysts.



- Diffuse reflectance measurement can be performed using an integrating sphere.
- By utilizing a band gap calculation macro, the band gap based on the Tauc plot can be easily determined from the diffuse reflectance spectrum.

## Integrating Sphere

An integrating sphere is a spherical accessory with a highly reflective inner surface made of materials such as barium sulfate. It is designed to scatter and homogenize the incoming light. This allows for accurate detection of transmitted and reflected light from samples with scattering properties, such as solid samples or suspended samples.



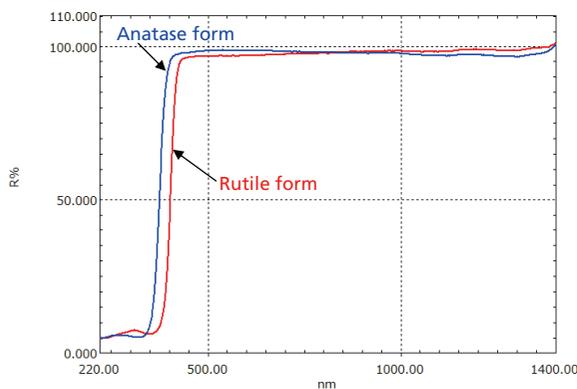
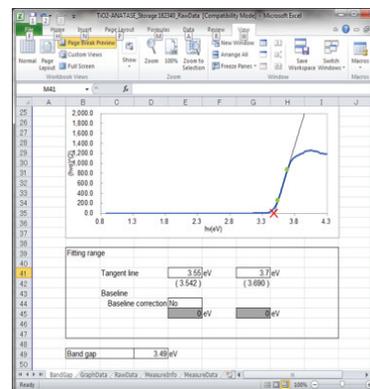
Diffuse Reflectance Measurement



Sample Compressed into Sample Holder

## Measurement Results (Extract)

The difference in band gaps of different crystal forms of titanium dioxide was confirmed by measuring the diffuse reflectance spectra using a UV-visible spectrophotometer and a band gap Excel macro.

Diffuse Reflectance Spectra  
(Red: Rutile form, Blue: Anatase form)

Main Window (Band Gap Calculation)

## UV-VIS Spectrophotometer

This instrument is used to measure the light absorption or emission intensity of chemicals in the ultraviolet-visible region. Typically, the light from the light source is diffracted and measured using a diffraction grating to observe its wavelength dependence. By incorporating an integrating sphere, it is possible to accurately measure powdered samples with scattering properties or substrates coated with catalysts.

Product 

# Measurement of the Particle Size Distribution of Titanium (IV) Oxide

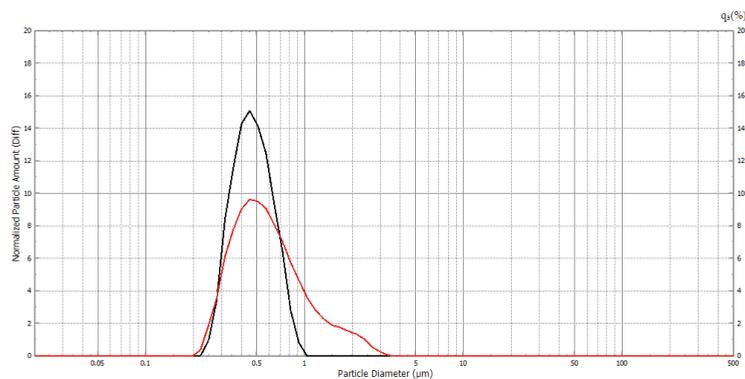
Catalysts classified as heterogeneous systems undergo reactions on their surfaces, so the particle size and reaction efficiency are closely related.



A wide range of particle size distributions, ranging from 7 nm to 800  $\mu\text{m}$ , can be measured for catalyst materials, which are powder samples.

## Measurement Results (Extract)

It was found that the anatase form of titanium (IV) dioxide has less variation in particle size distribution when measuring the particle size distribution of titanium (IV) dioxide with different crystal forms.



Particle Size Distribution of Titanium (IV) Oxide  
(Red: Rutile form, Black: Anatase form)

## Laser Diffraction Particle Size Analyzer

This device covers a measurement range of 7 nm to 800  $\mu\text{m}$ , allowing for particle size evaluation of nano-sized particles. It enables particle size evaluation in wet measurements, where the sample powder is dispersed in a liquid, as well as dispersion state evaluation in high-concentration measurements without the need for dilution using a high-concentration measurement unit.



Product

## Dynamic Particle Image Analysis System

For image analysis, it is possible to analyze one particle out of a group of 10,000 particles. This enables capabilities such as "particle image analysis," "particle shape analysis," "particle size distribution measurement," "foreign object detection," and "particle number concentration measurement." This makes it possible to detect large particles and foreign objects in liquid dispersions containing nanoparticles.



Product

# Visualization of the Photoinduced Charge Distribution of a Au Nanoparticle Assembly

Application 

In heterogeneous catalysis, chemical bonding occurs between the catalyst surface and the reactants. Since chemical bonding involves electron exchange, understanding the electronic state of the catalyst, particularly the electronic state at the surface, is crucial for understanding catalytic activity.



- By using Kelvin Probe Force Microscopy (KPFM) measurements, it is possible to simultaneously obtain information about the shape and surface potential of a photocatalyst.
- By performing measurements while illuminating with light, it is possible to visualize the surface potential of a photocatalyst in its excited state.

## Light Irradiation Unit

By incorporating a light irradiation unit into the SPM (Scanning Probe Microscope), it becomes easy to measure the surface potential distribution in the excited state. By measuring the band gap of the catalyst using a UV-Vis spectrophotometer beforehand, it is possible to select the appropriate irradiation wavelength.

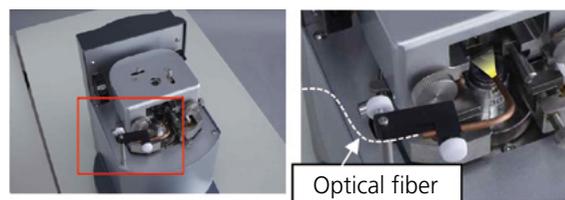
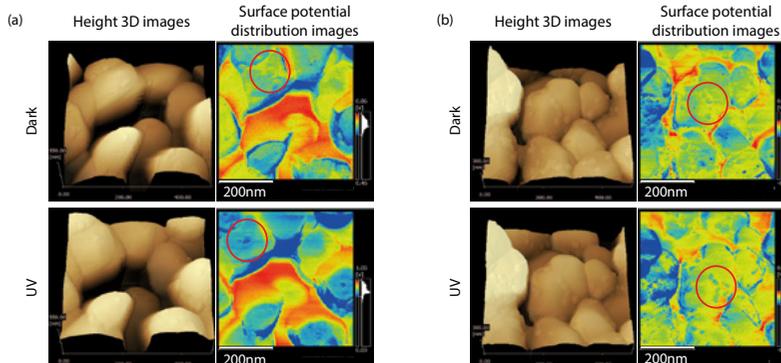


Image of Measurement Using a Light Irradiation Unit

## Measurement Results (Extract)

In comparison with the top row (without UV irradiation), a condition in which the relative potential of the AuNP is lower than that of the TiO<sub>2</sub> surface can be seen in the bottom row (under UV irradiation).



(Left) Height Images and (Right) Surface Potential Distribution Images  
(a) Without Streptavidin Interaction, (b) With Streptavidin Interaction

## Scanning Probe Microscope (SPM) Atomic Force Microscope (AFM)

Scanning Probe Microscopy (SPM) is a general term used for microscopes that employ a small probe (tip) to scan the surface of a sample, allowing for the observation of the sample's three-dimensional shape and local properties at high magnification. In KPFM measurements, an alternating voltage is applied to a conductive cantilever, enabling the detection of the electric force between the sample surface and the cantilever. This facilitates the measurement of the sample's surface potential. By conducting measurements while simultaneously illuminating the sample with light, it becomes possible to examine the distribution of surface potential in the excited state. This capability greatly contributes to the functional evaluation of supported catalysts.

Product 

# Determination of Photoreaction Quantum Yield and Direct Observation of Intermediates in CO<sub>2</sub> Reduction by Artificial Photosynthesis

Application 

In advancing the practical implementation of artificial photosynthesis, one of the challenges is the low reaction efficiency. By investigating the photoreaction quantum yield, which is one of the indicators of photochemical efficiency, it becomes possible to contribute to the development of more efficient artificial photosynthesis systems.



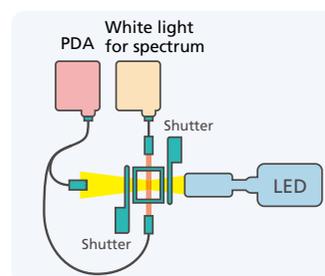
- It is possible to measure the photoreaction quantum yield easily, without the need for complex calibration of light intensity or preparation of chemical actinometers.
- By simultaneously measuring the absorption spectrum while illuminating, it is possible to observe intermediates during the photoreaction.

## Photoreaction Quantum Yield

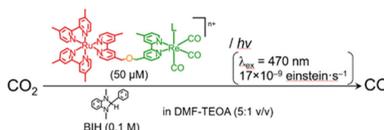
The value that indicates the reaction efficiency of photocatalysts and artificial photosynthesis is the quantum yield. In homogeneous catalysis, the ratio of the number of generated molecules to the number of absorbed photons, known as the internal quantum yield, is used. In heterogeneous catalysis, it is often difficult to estimate the number of absorbed photons, so the external (apparent) quantum yield, which evaluates the ratio of the number of generated molecules to the number of incident photons, is sometimes used.

## Materials and Methods

In this study, the photoreaction quantum yield in the carbon dioxide reduction reaction was measured using a Ru-Re supramolecular photocatalyst. The Lightway system, comprising a calibrated LED light source and a spectrophotometer, enabled accurate determination of the number of absorbed photons. The generated carbon monoxide was quantified using gas chromatography (GC) analysis. The results demonstrate the high quantum yield achieved by the Ru-Re photocatalyst, contributing to the development of efficient carbon dioxide conversion technologies.



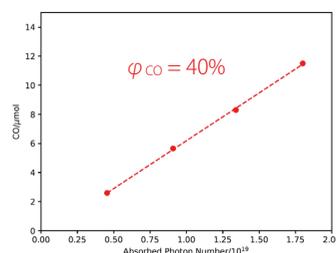
Ru-Re Supramolecular Complex Photocatalyst



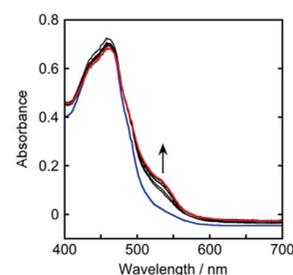
Optical Construction of Lightway

## Measurement Results (Extract)

It was found that the photoreaction quantum yield measured this time is 40%. Additionally, the presence of an intermediate species with absorption at 530 nm was confirmed in the carbon dioxide reduction reaction process.



Relationship of CO Formation and Absorbed Photon Number



Time-Dependent Change of Absorption Spectrum

## Photoreaction Evaluation System

Our system allows for simultaneous measurement of absorption spectra while irradiating with monochromatic LED light. With accurate calibration of the irradiation intensity, it can be utilized for measuring the number of absorbed photons in photocatalysts and determining the quantum yield, which represents the efficiency of photon utilization. The unique design incorporates essential elements for software-guided operation and real-time monitoring, enabling easy and straightforward measurements.

Product 

## ~Evaluating the Efficiency of Artificial Photosynthesis~

In the implementation of artificial photosynthesis, "conversion efficiency" is a crucial indicator. However, there can be challenges in interpretation due to the different metrics and definitions used. In this column, we introduce several indicators commonly used to assess the conversion efficiency of artificial photosynthesis.

### ○ Photoreaction Quantum Yield

- Apparent Quantum Yield

$$\Phi \text{ Product} = \frac{\text{The amount of product (mol)}}{\text{The number of photons irradiated (einstein)}}$$

- Internal Quantum Yield

$$\Phi \text{ Product} = \frac{\text{The amount of product (mol)}}{\text{The number of photons absorbed (einstein)}}$$

There are two main concepts for the photoreaction quantum yield of a photochemical reaction: the apparent quantum yield, which is calculated by dividing the number of photons irradiated by the system, and the internal quantum yield, which evaluates the contribution of absorbed photons to the reaction. The apparent quantum yield is a measure that combines the absorption rate of photons and the reaction efficiency, and it can be influenced by factors, such as the concentration of the samples, that affect the absorption rate. On the other hand, the internal quantum yield is an indicator that strongly reflects the mechanism after excitation by light, as it evaluates the contribution of absorbed photons to the reaction. In practical applications, the apparent quantum yield is often used in artificial photosynthetic systems using heterogeneous catalysts that make it difficult to estimate the number of absorbed photons. In contrast, in artificial photosynthetic systems using homogeneous photocatalysts, where the number of absorbed photons in the system can be relatively easily estimated, it is possible to determine the internal quantum yield.

In the above definition, the maximum value of the internal quantum yield varies depending on the reaction system. For example, in the reduction reaction of  $\text{H}_2\text{O}$ , where two  $\text{H}^+$  ions are reduced to obtain one  $\text{H}_2$  molecule, the maximum value of the quantum yield is 50 % for a one-photon, one-electron transfer case. Therefore, there are cases where the quantum yield is defined and measured using the number of electrons used in the reaction instead of the quantity of the product, in order to achieve a theoretical maximum value of 100 % regardless of the reaction system.

- Internal Quantum Yield (based on the number of electrons)

$$\Phi \text{ Product} = \frac{\text{The number of electrons used in the reaction (mol)}}{\text{The number of photons absorbed (einstein)}}$$

### ○ Solar Energy Conversion Efficiency

$$\eta_{\text{sun}} = \frac{\text{The total energy of the product}}{\text{The energy of the irradiated pseudo-solar light}}$$

In some cases, the solar energy conversion efficiency, which is a similar but distinct measure from the apparent quantum yield, is used. It is measured using pseudo-solar light, such as AM1.5, which is designed to have a wavelength distribution and intensity equivalent to natural sunlight. In quantum yield measurements, monochromatic light sources are typically used, so the solar energy conversion efficiency can be considered a more practical evaluation metric. However, similar to the apparent quantum yield, the changes in absorption rate in the system also contribute to the results, so it is necessary to use an appropriate evaluation metric depending on the purpose. One example of solar energy conversion efficiency is STH (Solar to Hydrogen), which is used in artificial photosynthesis for hydrogen production.

- STH (Solar to Hydrogen)

$$\text{STH} = \frac{\text{The Gibbs energy of the generated H}_2 \text{ molecule}}{\text{The energy of the irradiated pseudo-solar light}}$$

# Identification of Reaction Products and Atmospheric Components

Application 

Products of the carbon dioxide reduction reaction may also be present in the atmosphere and should be distinguished from those resulting from the experimental system.

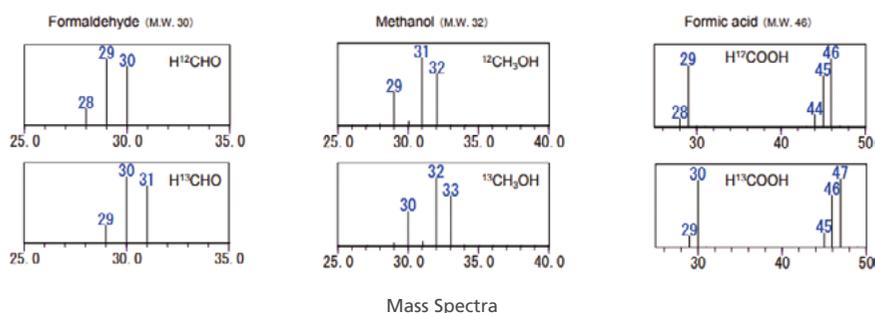


- By utilizing a mass spectrometer (MS), isotope-based labeling experiments can be performed.
- It is easy to determine whether a compound is generated from an experimental system or from contamination from the environment.

## Measurement Results (Extract)

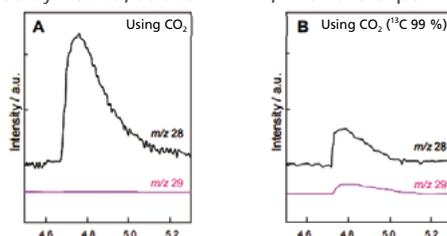
To confirm that the reaction was with carbon dioxide in the experimental system rather than in the environment, we used  $^{13}\text{C}$ , a stable isotope with low natural abundance. The reduction reaction using  $^{13}\text{C}$  isotope-labeled carbon dioxide and the reaction using non-labeled carbon dioxide were compared.

The  $^{13}\text{C}$ -labeled and non-labeled compounds have the same retention time and cannot be distinguished by GC alone, but using MS enabled identification because the mass spectrum of  $^{13}\text{C}$ -labeled compounds is shifted by 1 in  $m/z$ .



In the chromatograms below, the black one is from non-labeled carbon monoxide from the atmosphere, and the pink one is from labeled carbon monoxide from the experimental system.

If you use non-labeled carbon dioxide, you cannot tell the two apart, as shown in A, but the products from the experimental system can be confirmed by  $m/z$  29, as shown in B, with the experiment using labeled-carbon monoxide.



Extracted Ion Chromatograms, Measuring Carbon Monoxide in Gas Phase Samples Generated by a Reaction Using Non-Labeled / Labeled Carbon Dioxide

\*These data were obtained using GCMS-QP2010 Ultra.

## Gas Chromatograph Mass Spectrometer

GC/MS analysis can be performed with higher selectivity than GC. Even if peaks overlap they can be separated by mass, allowing labeling experiments using stable isotopes. The mass spectrometer is equipped with a contamination-resistant ion optical system, which keeps the frequency of maintenance to a minimum while also enabling highly reliable measurements to be performed for an extended period.

Product 

# Evaluation of a Catalyst Used in the Production of Fuel Cell Hydrogen

Application 

It is important to monitor gas generation over time to assess changes in catalytic capacity and the degree of degradation.

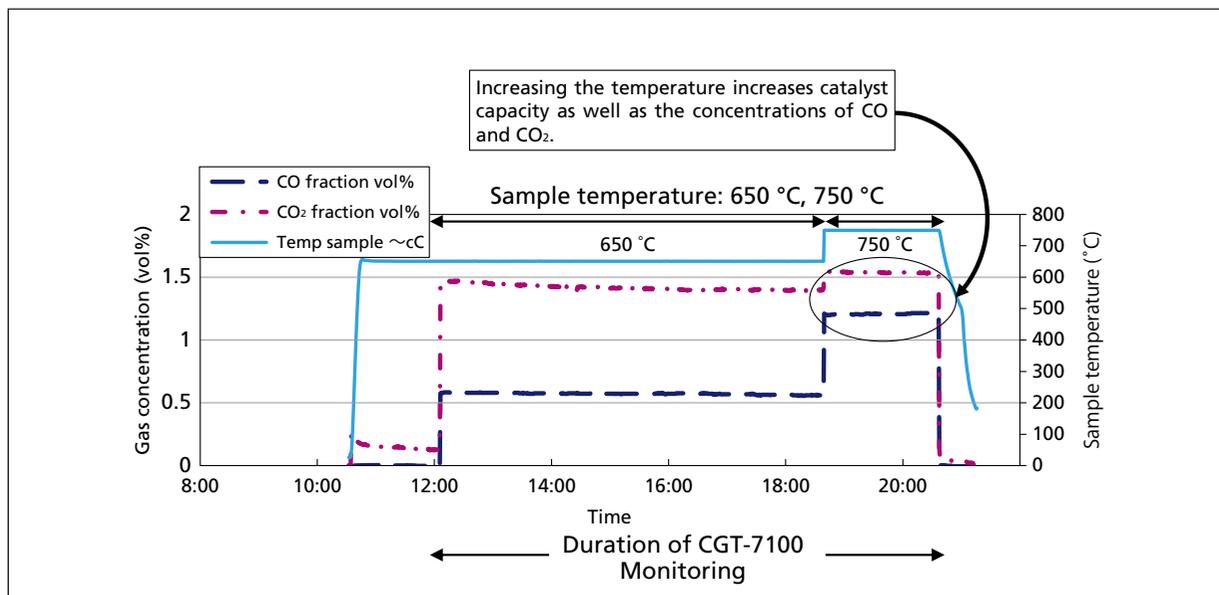


- Real-time measurement of carbon monoxide, carbon dioxide, and methane can be performed by simply introducing sample gas into the measurement gas inlet.
- It has outstanding stability and is a perfect solution for on-site measurements.

## Measurement Results (Extract)

To evaluate a catalyst used for hydrogen gas production (steam reforming), changes in the concentration of product components, such as carbon monoxide and carbon dioxide, are monitored, followed by an assessment of the catalyst performance and how catalyst degradation is affected by different reaction temperatures.

A single experiment was performed over a period of between 6 and 10 hours, during which time the change in carbon monoxide and carbon dioxide concentration was monitored continuously. It shows that increasing the temperature of the catalyst increases its reforming capacity.



Transition of Gas Concentration

## Transportable Gas Analyzer

With all the pretreatment units required for measurement built-in, such as the pump, filter, and dehumidifier, gas concentration can be measured in real-time by simply introducing sample gas into the measurement gas inlet.

The system can be equipped with a detection unit for up to two components of carbon monoxide, carbon dioxide, and methane. It uses the ratio photometric non-dispersive infrared absorption method, which offers superior stability, making it ideal for on-site measurements.

Product 

# Simultaneous High-Sensitivity Measurements of Carbon Monoxide and Hydrogen

[Application](#)

In a photochemical carbon dioxide reduction utilizing a photocatalyst, efficiency can be evaluated by quantifying carbon monoxide and hydrogen.



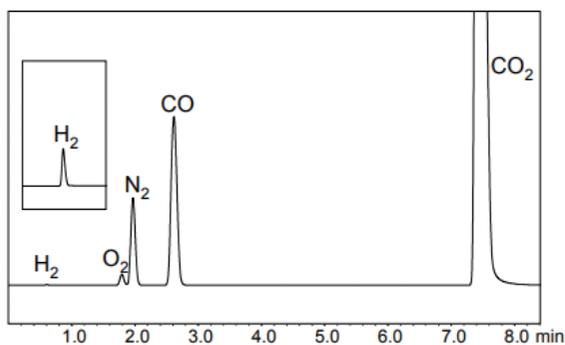
benefits

- The Barrier discharge Ionization Detector (BID) can provide simultaneous high-sensitivity measurements of carbon monoxide and hydrogen.
- Almost all components can be detected in addition to the target component in a single measurement.

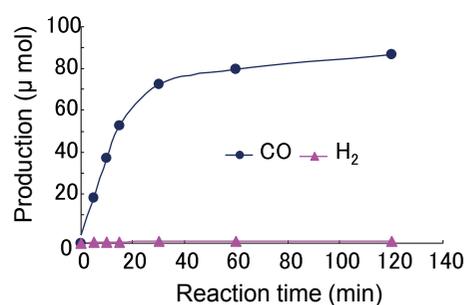
## Measurement Results (Extract)

Carbon monoxide and hydrogen, generated in a photochemical carbon dioxide reduction utilizing a photocatalyst, were simultaneously measured. It was confirmed that carbon monoxide production increased sharply for the first 30 minutes of reaction time, after which it shifted to a more gradual increase.

BID can detect all components eluted from the column, thus enabling acquisition of a variety of information, as well as the target component measurements.



Chromatogram of Substances Generated in a Reduction



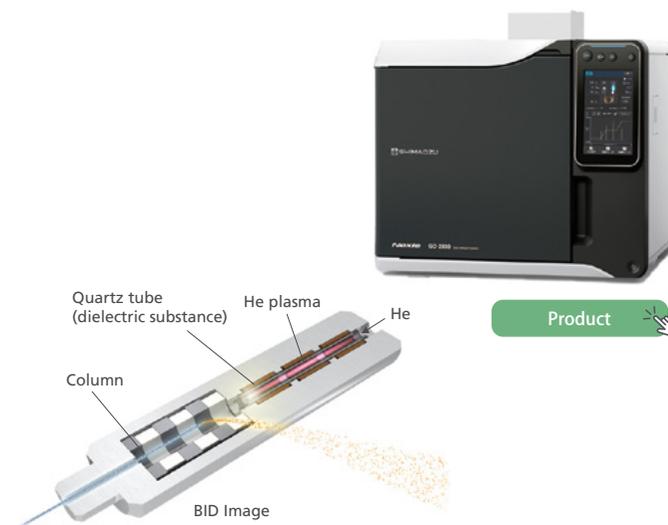
CO and H<sub>2</sub> Production Versus Reaction Time

Data from Dr. Hitoshi Ishida and Dr. Yusuke Kuramochi, Department of Chemistry, School of Science, Kitasato University; PRESTO, Japan Science and Technology Agency

## Gas Chromatograph

GC allows for the qualitative and quantitative determination of vaporizable components in gas and liquid samples. With a BID, almost all components except helium and neon can be analyzed with high sensitivity.

Shimadzu's proprietary technology has been adopted for the BID, which incorporates ionization via a new dielectric barrier discharge plasma. It is more sensitive than conventional detectors, can detect components that are difficult to detect by FID, TCD and other all-purpose detectors, and retains long-term stability.



# High-Speed Analyzer for Inorganic Gases and Hydrocarbons

Application 

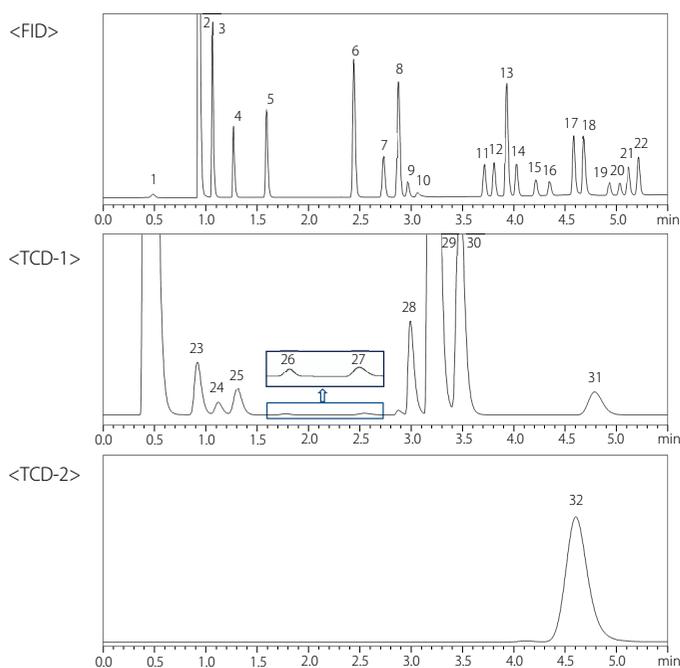
A shorter analysis time enables comparison of various catalysts and reaction conditions.



Inorganic gases, hydrocarbons C3 through/to C5, and hydrogen sulfide can be analyzed in less than half the time required by conventional methods using an application-specific GC system.

## Measurement Results (Extract)

The analysis of inorganic gases, hydrocarbons C3 through/to C5, and hydrogen sulfide was performed in less than 6 minutes using a high-speed refinery gas analyzer with four valves, eight columns, and three detectors.



Chromatograms

&lt;FID&gt;

1: C6+	12: 1-Butene
2: Methane	13: i-Butene
3: Ethane	14: cis-2-Butene
4: Ethylene	15: Isopentane
5: Propane	16: n-Pentane
6: Propylene	17: 1,3-Butadien
7: Isobutane	18: Methylacetylene
8: n-Butane	19: trans-2 Pentene
9: Propadien	20: 2-Methyl-2-butene
10: Acetylene	21: 1-Pentene
11: trans-2-Butene	22: cis-2-Pentene

&lt;TCD1&gt;

23: Carbon dioxide
24: Ethylene
25: Ethane
26: Acetylene
27: Hydrogen Sulfide
28: Oxygen
29: Nitrogen
30: Methane
31: Carbon monoxide

&lt;TCD2&gt;

32: Hydrogen
--------------

Measured Compounds

\*These data were obtained using a Refinery Gas Analysis System.

## Application Specific GC Systems

System GC is a customized gas chromatograph system for reaction gas research to which a sample introduction section, valves, etc., are added to match the operating environment. A large valve oven can be mounted on the GC, eliminating the need for extra space. Shimadzu offers a large System GC lineup to meet a wide range of application requirements.

Product 

# Inorganic Gases and Hydrocarbons Analysis Using GC

[Application](#)

In addition to carbon monoxide and hydrogen, inorganic gases and hydrocarbons are important analytes in artificial photosynthetic reactions.



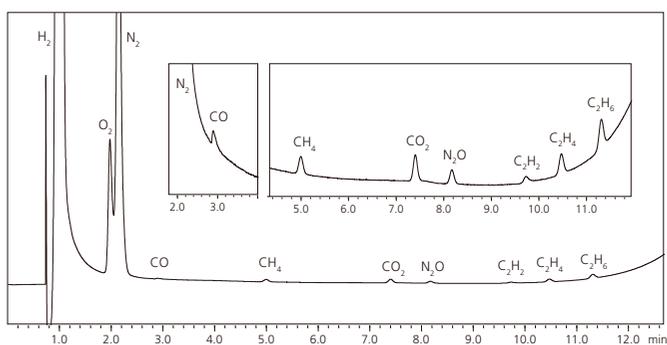
benefits

- High-sensitivity analysis of inorganic gases and hydrocarbons can be performed using the barrier discharge ionization detector (BID).
- Good reproducibility can be obtained by using a gas sampler.

## Measurement Results (Extract)

This is an example of the analysis of inorganic gases and hydrocarbons produced by photocatalytic carbon dioxide reduction reaction by GC with a BID.

In this analysis, a manual gas sampler was used for the introduction of gas into the instrument. A purge mechanism is included to reduce the leakage of peripheral air into the system, which makes it possible to quantitatively analyze trace levels in organic gases with high accuracy.



Chromatogram of Simultaneous Analysis of Impurities in Hydrogen

	S/N
Carbon monoxide (CO)	7.7
Methane (CH <sub>4</sub> )	27
Carbon dioxide (CO <sub>2</sub> )	42
Nitrous oxide (N <sub>2</sub> O)	21
Acetylene (C <sub>2</sub> H <sub>2</sub> )	8.3
Ethylene (C <sub>2</sub> H <sub>4</sub> )	31
Ethane (C <sub>2</sub> H <sub>6</sub> )	42

## Related Applications with Other Detectors and Pretreatment Equipment

### ■ Packed Column Analysis of Inorganic Gases Using TCD

Packed columns and TCDs can also be used to analyze inorganic gases.

[Application](#)

### ■ Analysis of Hydrogen and Methane Dissolved in a Liquid Solution

Autosampler for liquid injection was used to measure the amount of inorganic gases in a liquid solution.

[Application](#)

## Gas Chromatograph

GC allows for the qualitative and quantitative determination of vaporizable components in gas and liquid samples. With a BID, almost all components except helium and neon can be analyzed with high sensitivity. A gas-tight syringe and a gas sampler can be utilized for gas analysis. A purge mechanism is included to reduce the leakage of peripheral air into the system, which helps to analyze gases with high accuracy.



Valve Unit

Manual Flow Controller for Purge

Gas Sampler

[Product](#)

# Inorganic Gases and Hydrocarbons Analysis Using GC-MS

Application 

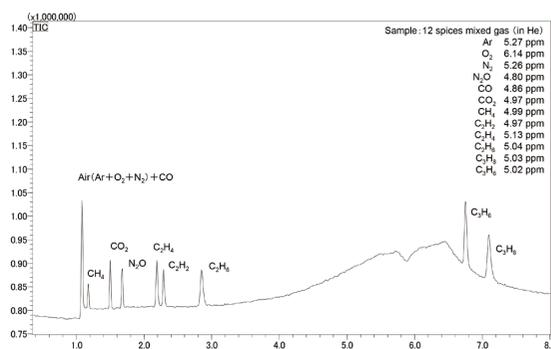
It is important to comprehensively examine unintentionally generated inorganic gases and hydrocarbons.



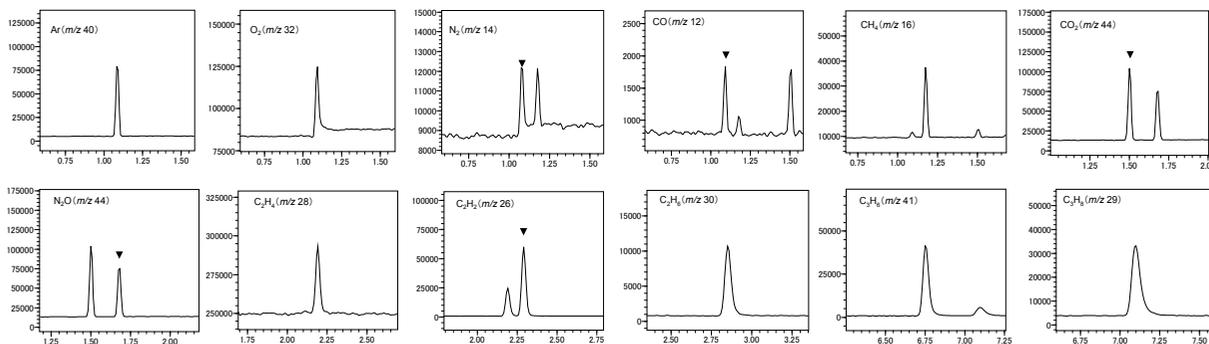
- GC-MS enables qualitative analysis without the use of standard samples.
- By selecting ions, it is possible to analyze components that cannot be separated in the chromatogram obtained by GC analysis.

## Measurement Results (Extract)

In gas analysis, baseline fluctuations are caused due to air components and moisture, but stable and highly sensitive analysis is possible by selecting the appropriate ion ( $m/z$ ) for each compound. Good reproducibility can be obtained by using a gas sampler as on the previous page.



Total Ion Current Chromatogram of Standard Gas Containing 5ppm of Each Component in He



Mass Chromatograms for Respective Components

\*These data were obtained using GCMS-QP2010 Ultra.

## Gas Chromatograph Mass Spectrometer

GC-MS combines the advantages of a gas chromatograph (GC) and a mass spectrometer (MS). Peaks can be identified from mass spectra, so you do not need to prepare standard gases. Even components near the atmospheric components or moisture peaks can be detected. The mass spectrometer is equipped with a contamination-resistant ion optical system, which keeps the frequency of maintenance to a minimum while also enabling highly reliable measurements to be performed for an extended period.

Product 

# Analysis of Formic and Acetic Acids in Aqueous Solutions Using an Ion Chromatograph

[Application](#)

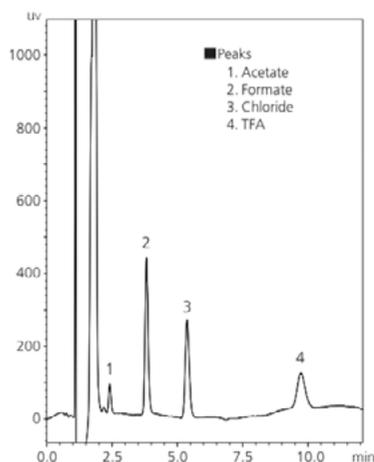
The measurement of formic and acetic acid is important to evaluate the efficiency of carbon dioxide reduction reactions.



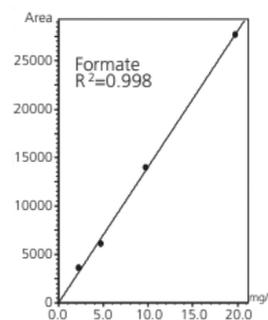
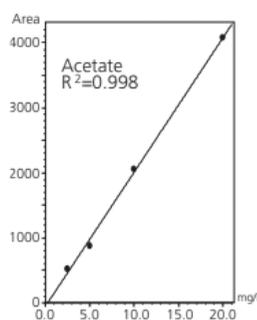
- Formic acid and acetic acid in aqueous solutions can be detected.
- Shimadzu's unique post-column buffering method enables highly sensitive analysis, even of samples with many contaminants.

## Measurement Results (Extract)

It is recommended to use an ion chromatograph to analyze formic acid and acetic acid in aqueous solutions. Good reproducibility and linearity were obtained in the range of 2.5 to 20 mg/mL.



Chromatogram of a Four-Anion Standard Mixture



Linearity of Calibration Curves of Acetate (left) and Formate (right)

## Related Application

### ■ Analysis of Organic Acids Using Post-Column pH Buffering Organic Acid Analysis

[Application](#)

Even an analyte containing many contaminants can be analyzed with high sensitivity using Shimadzu's unique post-column buffering method.

## Ion Chromatograph

IC allows for the separation of components dissolved in liquid samples as well as the qualitative and quantitative determination of them.

When you analyze samples with many contaminants, it is recommended to use an organic acid analysis system with options to detect the target compounds with high selectivity, such as Shimadzu's unique post-column buffering and dual column oven.


[Product](#)

# Formic Acid Analysis Using GC

[Application](#)

Gas chromatography is useful when the carbon dioxide reduction reaction product can be dissolved in an organic solvent.



- The Barrier discharge Ionization Detector (BID) can detect formic acid, which is difficult to detect with general-purpose detectors.
- Phosphoric acid treatment of the glass insert and column allows the detection of low-concentration formic acid peaks.

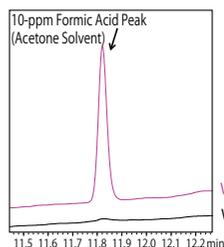
## Measurement Results (Extract)

In contrast to a general-purpose flame ionization detector (FID), a barrier discharge ionization detector (BID), a selective high-sensitivity detector, can be used to detect formic acid.

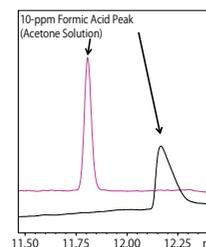
To measure formic acid at low concentrations, we applied the phosphoric acid treatment to the glass insert and the column to suppress adsorption. Peak detection was not achieved using an untreated glass insert, while detection with good sensitivity was achieved using a glass insert that had been pretreated with phosphoric acid. Furthermore, formic acid peak tailing was evident when an untreated column was used, but the comparative results confirmed that the peak shape was sharper following phosphoric acid treatment of the column.



Glass Insert  
Phosphoric Acid Treatment



Effectiveness of Glass Insert Phosphoric Acid Treatment in Low-Concentration Formic Acid Analysis



Comparison of Formic Acid Peak Shapes Before and After Column Phosphoric Acid Treatment

## Related Applications

### ■ High-Sensitivity Analysis of Formic Acid Using GC-BID

To remove the electrolyte in sample using a cation exchange cartridge, you can obtain results with good repeatability.

[Application](#)

### ■ Analysis of Formic Acid and Formaldehyde Using GC-MS

[Application](#)

## Gas Chromatograph

GC allows for the qualitative and quantitative determination of vaporizable components in gas and liquid samples. With a BID, almost any component except helium and neon can be analyzed with high sensitivity. This system is easy to maintain, as inserts and columns can be replaced without the use of tools.


[Product](#)

# Evaluation of an Iridium Complex-Based Photocatalytic Hydrogen Generation System

Application 

In artificial photosynthesis research, efficiency is assessed by analyzing the quantity of light absorbed by the system and the amount of product generated. This serves as a crucial evaluation metric in the pursuit of high-efficiency artificial photosynthetic systems.



- Photoreaction quantum yield, which is essential for evaluating the efficiency of artificial photosynthesis, can be accurately measured.
- Hydrogen can be detected by a gas chromatograph with a thermal conductivity detector (TCD), using argon as the carrier gas.

## Measurement Results (Extract)

Accurate quantum yield can be calculated from the number of absorbed photons measured by Lightway and the number of generated hydrogen molecules measured by GC. This confirms excellent linearity between the number of absorbed photons and the number of generated hydrogen molecules.

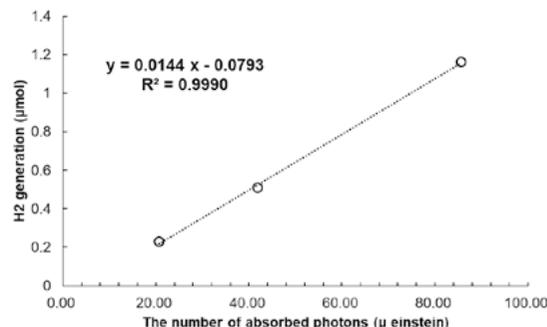


Measurement of the Number of Absorbed Photons by Photoreaction Evaluation System

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Hydrogen Quantitation by Gas Chromatograph



Relationship between Number of Absorbed Photons and Number of Generated Hydrogen Molecules

## Photoreaction Evaluation System

The absorption spectrum is measured while irradiating monochromatic LED light. Due to accurate calibration of the irradiation light intensity, it can be utilized for measuring the number of absorbed photons in photocatalysis and the quantum yield of photon utilization, which is the efficiency of the photoreaction. It features a unique design with navigation functionality for software-guided operation and real-time monitoring, enabling easy measurements.

Product 

## Gas Chromatograph

Using a TCD, it is possible to qualitatively and quantitatively analyze the vaporized components in gas and liquid samples. Hydrogen detection using argon as the carrier gas can be achieved without the need for helium gas or a BID.

Product 



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