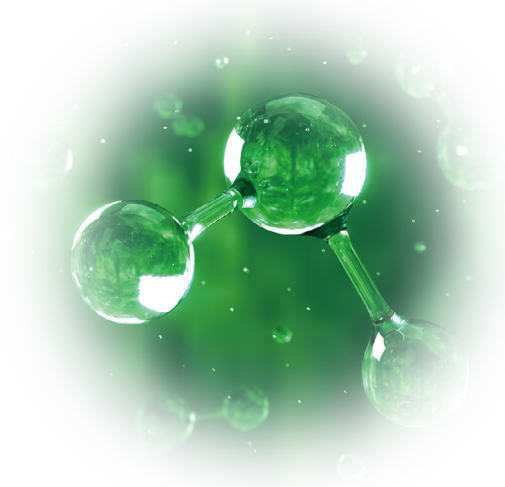


Analytical Solutions for

Artificial Photosynthesis

— Photocatalyst Characterization and Product Quantification —



Toward a Carbon Neutral Society



What's Artificial Photosynthesis

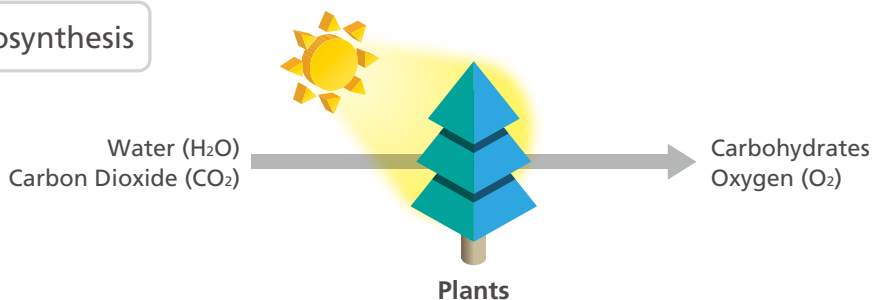
Artificial photosynthesis is a technology that artificially performs photosynthesis using photocatalysts and sunlight. It is expected to be a next-generation renewable energy technology because it can convert light energy into useful compounds. Research is being conducted using artificial photosynthesis 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:

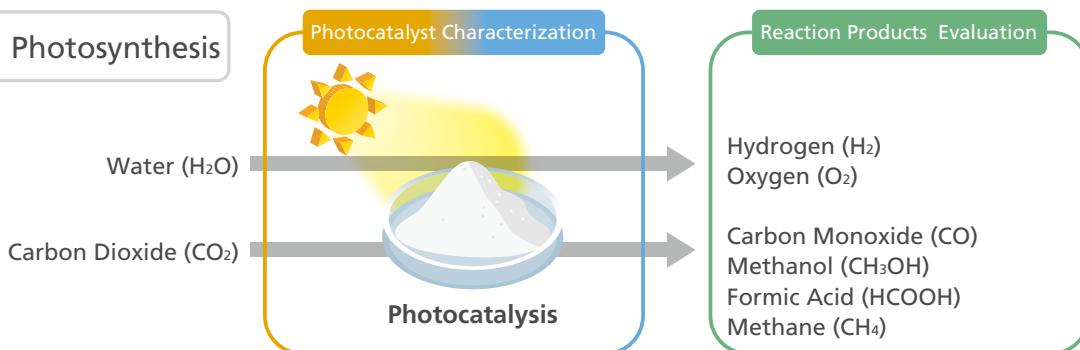
1. Evaluation of Physical Properties
2. Evaluation of Excited State and in situ Measurements
3. Quantification of Reaction Products

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



Artificial Photosynthesis

Analytical Techniques Involved in Artificial Photosynthesis

Photocatalyst Characterization — Physical Properties —



When researching artificial photosynthesis, it is essential to evaluate the physical properties of photocatalysts. This requires conducting a variety of applications, such as determining the band gap of catalysts, evaluating the valence charge of catalyst elements, and measuring the specific surface area and size distribution of catalyst particles. Shimadzu offers multiple instruments to support these analyses.

Band Gap

Measurement of the Band Gap of Titanium (IV) Oxide

[UV-Vis Spectrophotometer](#) P. 5

Particle Size Distribution

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

[Particle Size Analyzer](#) P. 6

Photocatalyst Characterization — Excited State / in situ Measurement —



It is extremely important to evaluate how photocatalysts function in their active state. In situ measurement refers to a method that simulates the actual usage environment. In catalyst research, it refers to measuring catalysts under real-world operating conditions or in a simulated version of that environment. These in situ measurements help clarify the functions of photocatalysts and provide valuable information that leads to more efficient development of photocatalysts.

Photoinduced Charge Distribution

Visualization of the Photoinduced Charge Distribution of a Au Nanoparticle Assembly

[Scanning Probe Microscope](#) P. 7

Quantum Yield and Intermediates

Determination of Photoreaction Quantum Yield and Direct Observation of Intermediates in CO₂ Reduction by Artificial Photosynthesis

[Photoreaction Evaluation System](#) P. 8

Evaluating the Oxidative Activity of a Photoredox Catalyst Using Methylene Blue

[Photoreaction Evaluation System](#) P. 9

Column:

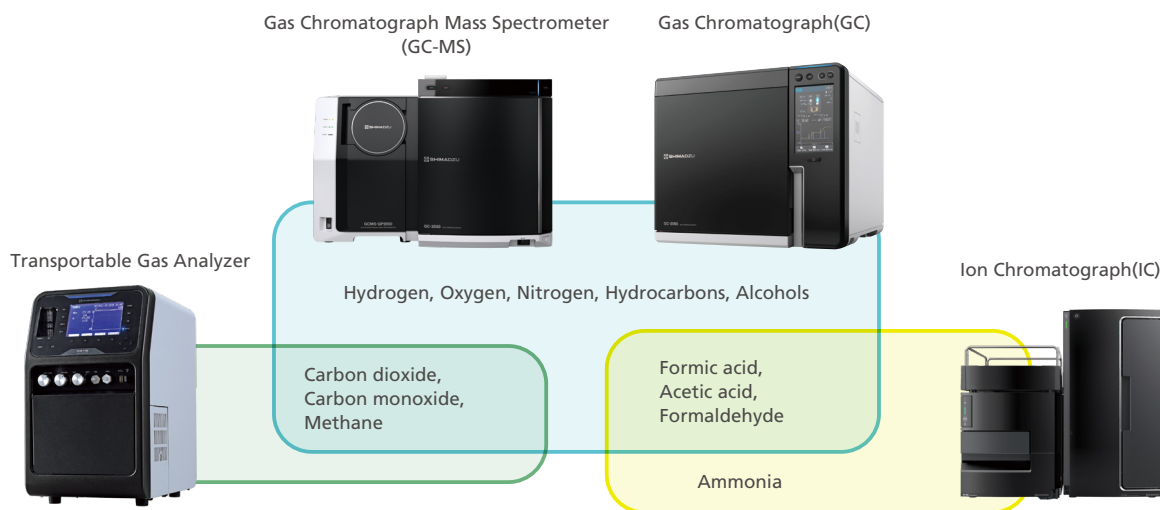
Evaluating the Efficiency of Artificial Photosynthesis

P. 10

Reaction Products Evaluation

Quantitative Analysis of Catalytic Products

The reaction efficiency of photocatalysts can be evaluated by quantifying the products generated during artificial photosynthesis reactions. Here, we introduce methods for the quantitative analysis of hydrogen produced by water splitting, carbon monoxide generated by CO₂ reduction, alcohols, formic acid, hydrocarbons, and other products.



Comparison of Characteristics of Instruments Used to Analyze Gases Generated from Catalytic and Other Reactions

Gas Chromatograph/FTIR Spectrometer/Portable Gas Analyzer

P. 11

Gas Analysis Solutions

Evaluation of a Catalyst Used in the Production of Fuel Cell Hydrogen
 Simultaneous High-Sensitivity Measurements of Carbon Monoxide and Hydrogen
 GC Analysis of Inorganic Gases and Hydrocarbons Using an Automatic Gas Injector
 GC-MS Analysis of Inorganic Gases and Hydrocarbons Using an Automatic Gas Injector
 Automatic High-Speed Analysis Using FluxEdge
 High-Speed Analyzer for Inorganic Gases and Hydrocarbons

Transportable Gas Analyzer P. 13
 Gas Chromatograph P. 14
 Gas Chromatograph P. 15
 Gas Chromatograph Mass Spectrometer P. 16
 FluxEdge GC System P. 17
 Application Specific GC System P. 18

Analysis of CO₂ Reduction Products

Analysis of Gases from CO₂ Reduction
 Simultaneous High-Sensitivity Analysis of CO, CO₂ and CH₄ Using a Jetanizer
 Simultaneous Multi-Component Analysis Using a Polyarc System
 Analysis of Formic and Acetic Acids in Aqueous Solutions Using an Ion Chromatograph
 High-Sensitivity GC-FID (Jetanizer) Analysis of Formic Acid in Methanol Solution
 Identification of Reaction Products and Atmospheric Components

Gas Chromatograph P. 19
 Gas Chromatograph P. 20
 Gas Chromatograph P. 21
 Ion Chromatograph P. 22
 Gas Chromatograph P. 23
 Gas Chromatograph Mass Spectrometer P. 24

In situ Measurement with Quantitative Analysis of Products

Photoreaction quantum yield, which refers to how efficiently photons are utilized, is commonly used as to evaluate the energy conversion efficiency of artificial photosynthesis systems. Calculating the photoreaction quantum yield requires determining both the number of absorbed photons, measured with the Lightway system, and the amount of hydrogen produced, measured by GC. Together, these instruments provide researchers with a more complete evaluation of the reaction efficiency of hydrogen generation systems.

Photocatalytic Hydrogen Generation System

Evaluation of an Iridium Complex-Based Photocatalytic Hydrogen Generation System

Photoreaction Evaluation System
 Gas Chromatograph

P. 25

Measurement of the Band Gap of Titanium (IV) Oxide

Application 

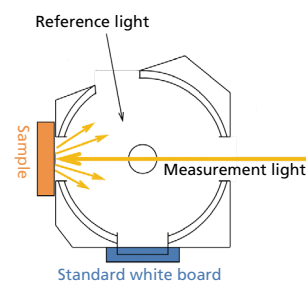
The band gap, which represents the energy required to activate photocatalysts in their excited state, is a fundamental, highly important property of photocatalysts.



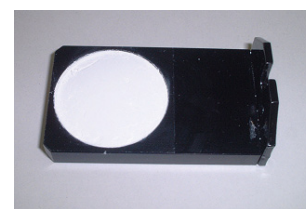
- Diffuse reflectance measurement can be performed using an integrating sphere.
- By utilizing a band gap calculation macro, the band gap based on the Tauc plot can be easily determined from the diffuse reflectance spectrum.

Integrating Sphere

Integrating spheres have a spherical interior coated with a highly reflective, light-scattering material such as barium sulfate. They uniformly scatter incoming (measurement) light. This allows for accurate detection of transmitted and reflected light from samples with scattering properties, such as solid samples or suspended samples.



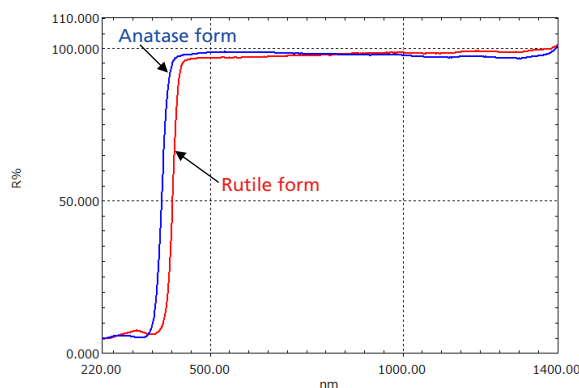
Diffuse Reflectance Measurement



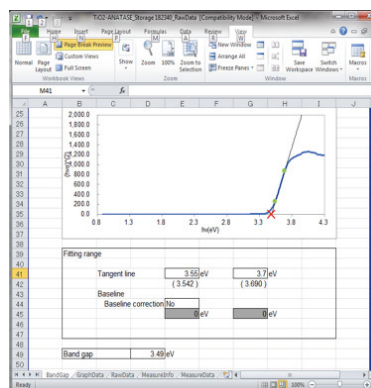
Sample Compressed into Sample Holder

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

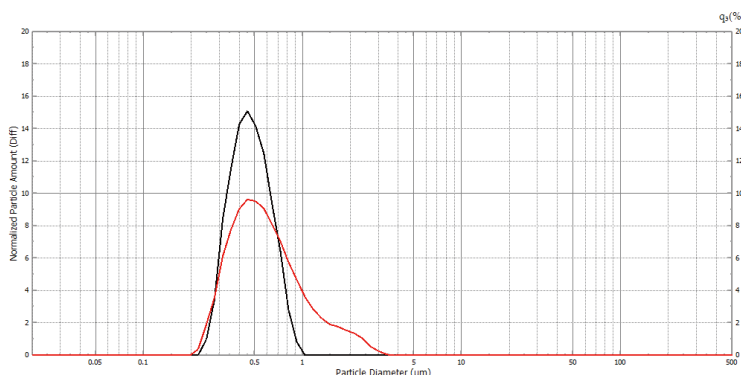
Catalysts classified as heterogeneous systems undergo reactions on their surfaces, so the particle size and reaction efficiency are closely related.



A wide range of particle size distributions, ranging from 7 nm to 800 μm , 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 μm , 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.

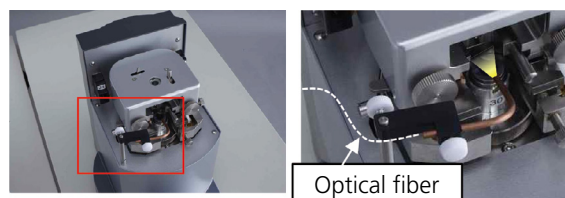
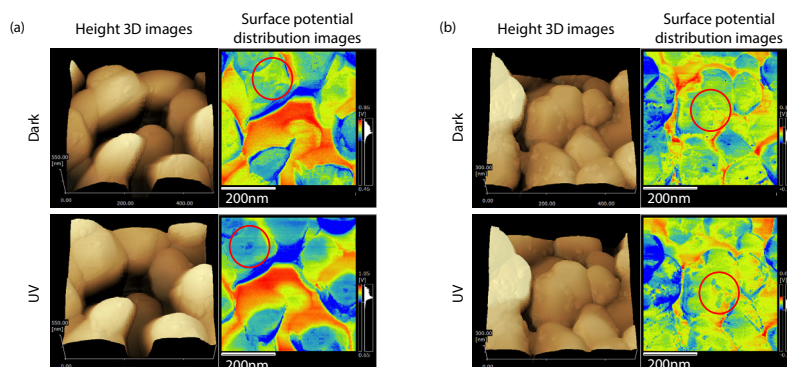


Image of Measurement Using a Light Irradiation Unit

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 TiO₂ 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 CO₂ 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.



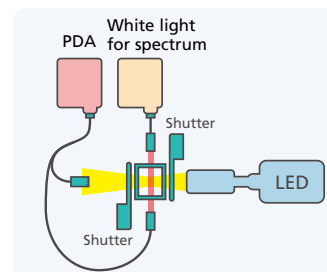
- It is possible to measure the photoreaction quantum yield easily, without the need for complex calibration of light intensity or preparation of chemical actinometers.
- By simultaneously measuring the absorption spectrum while illuminating, it is possible to observe intermediates during the photoreaction.

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.

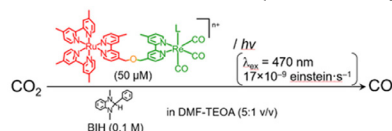
Materials and Methods

In this study, the photoreaction quantum yield in the carbon dioxide reduction reaction was measured using a Ru-Re supramolecular photocatalyst. The Lightway photoreaction evaluation system, which combines LED irradiation calibrated with an absolute power meter and a spectrophotometer capable of acquiring absorption spectra sequentially at intervals as short as 0.1 seconds, was used to automatically calculate the number of absorbed photons, a key parameter for photoreaction quantum-yield measurements. The carbon monoxide produced during the reaction was then quantified by gas chromatography (GC).



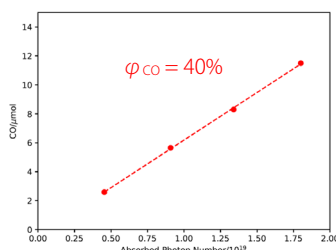
Optical Construction of Lightway

Ru-Re Supramolecular Complex Photocatalyst

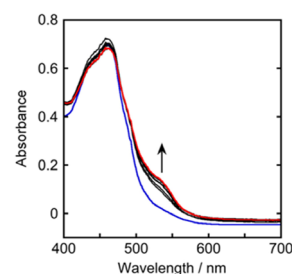


Measurement Results (Extract)

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 Oxidative Activity of a Photoredox Catalyst Using Methylene Blue

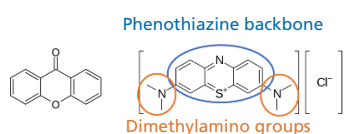
Application 

The reactivity of photocatalysts can be easily and quantitatively evaluated using a method based on the decomposition (color-fading) of an organic pigment.



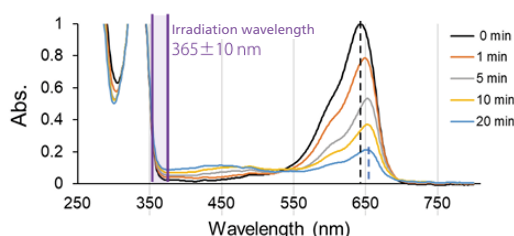
- The oxidation effect of photoredox catalysts can be quantitatively evaluated based on how methylene blue fades.
- Experiments that vary the amount of light exposure per unit time can be conducted using a neutral-density (ND) filter for dimming light.

Measurement Results (Extract)

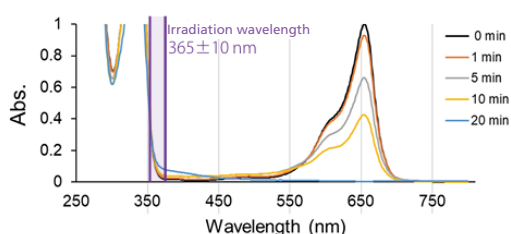


Structural Formulae of Xanthone and Methylene Blue

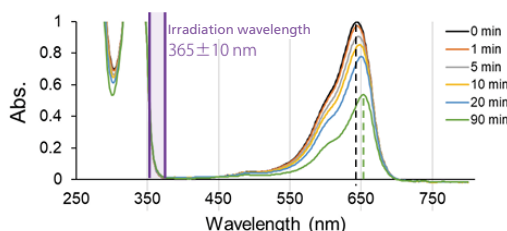
The results confirmed that absorption from methylene blue in the 550 to 650 nm range did not change when no light was shone, but changed when exposed to 365 nm light. This behavior was attributed to the photoexcitation of xanthone, which caused the dissociation of methylene blue. In addition, an evaluation of the photoreaction quantum yield, based on the decrease in the number of absorbed photons and the reduction in methylene blue quantity, confirmed a difference in the reaction efficiency that results from the solvent or light level.



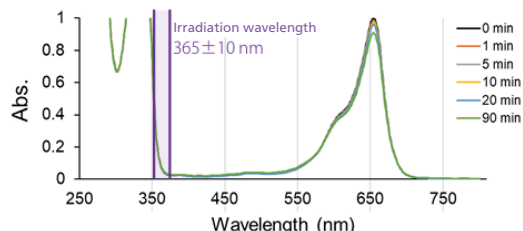
Change in Absorption Spectrum
(High irradiation and methanol solvent)



Change in Absorption Spectrum
(High irradiation and ethanol solvent)



Change in Absorption Spectrum
(Low irradiation and methanol solvent)



Change in Absorption Spectrum
(Low irradiation and ethanol solvent)

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 H_2O , where two H^+ ions are reduced to obtain one 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)

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

Comparison of Characteristics of Instruments Used to Analyze Gases Generated from Catalytic and Other Reactions

Application

Qualitative and quantitative analysis of gases generated from solvent-based reaction systems provides important indicators for evaluating the reaction systems. Gas analysis process flows can be optimized by selecting analytical instruments based on measurement objectives.



- CGT analyzers enable long-duration online measurements whereas FTIR systems support short-interval continuous measurements and qualitative analysis using spectral libraries.
- GC systems provide high-accuracy quantitative analysis.

Appearance and Characteristics Comparison of Respective Gas Measuring Systems

	GC	FTIR	CGT
			
	Nexis GC-2060	IRXross	CGT-7100
Quantitative Analysis Performance	Excellent	Good	Good
Qualitative Analysis	Good Requires standard gas	Excellent Enables qualitative analysis using a library	— Only specific components can be monitored
Standard Gas for Calibration Curve	Necessary	Necessary	Necessary ^{*1}
Zero Gas	Not necessary	Necessary ^{*2}	Necessary ^{*3}
Responsiveness Time from sample introduction to detection	Fair ^{*4}	Excellent From 1 s	Good Up to 3 min ^{*5}
Max Automatic Acquisition Period	— ^{*6}	Up to 48 h ^{*7}	Up to 8 h
Measurement Frequency	Fair From several minutes ^{*4}	Excellent From 1 s ^{*8}	Excellent From 1 s
Benefits	Enables accurate quantitation of many compounds	Good responsiveness Enables qualification of various gas components	Includes built-in pretreatment system (dust removal, moisture removal, and gas aspiration)

*1 Requires span gas for range calibration.

*2 Required if the positions of absorption peaks for target components overlap with those for atmospheric components.

*3 Requires N₂ gas for range calibration.

*4 Depends on separation measurement time.

*5 If standard flowrate, switchable between 15, 30, and 60 s.

*6 Possible if using a GC system with automated valves.

*7 Settable up to a maximum 48 hours, but background measurements are required partway through for some gas components.

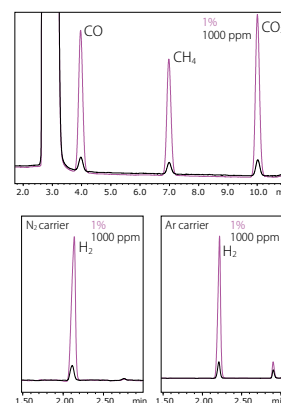
*8 Rapid scan mode can measure at speeds up to 1/20 of a second.

Gas Chromatograph

Gas chromatographs detect and quantify gas components separated by a column. They can measure a wide variety of compounds with high quantitative accuracy. By separating components individually, they can accurately quantify and check for both target components as well as impurities and trace components in generated gases. While they offer limited utility for continuous real-time monitoring of gases during reactions due to longer analysis times, they are well-suited for detailed determination of generated products after catalytic reactions or for identifying and quantifying abnormal or impurity components identified by FTIR or CGT analysis, making them essential instruments when high quantitative accuracy is required.



Product



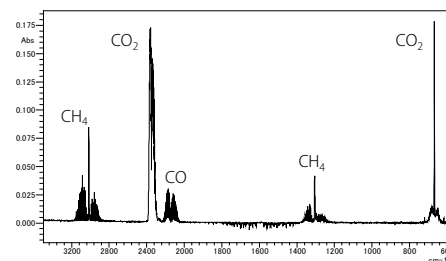
GC Chromatograms
Upper: CO, CO₂, and CH₄ each at 1000 ppm with 1 % N₂
Lower: H₂ at 1000 ppm with 1 % N₂
Note: N₂ (left) and Ar (right) used as carrier gases

Fourier Transform Infrared Spectrophotometer

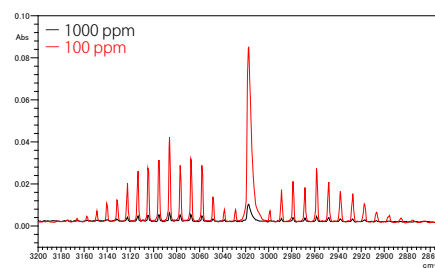
FTIR spectrophotometers can analyze gas components using molecule-specific infrared absorption spectra without having to separate them. Although FTIR systems offer lower quantitative accuracy than GC systems, they provide users with the ability to search spectral libraries for the qualitative analysis of a wide range of gas components. In addition, their extremely fast response times allow samples to be measure in about 1 second, allowing for quick determination of gas composition changes in response to changes in reaction parameter settings. With these short measurement times and their suitability for continuous data acquisition applications, FTIR systems are especially useful during the initial study phase, such as for determining the behavior of gases during catalytic reactions or for broadly identifying the components generated during reactions. Consequently, FTIR systems are widely valued for their excellent qualitative analysis capabilities and superior responsiveness.



Product



FTIR Spectrum of a 1000 ppm Gas



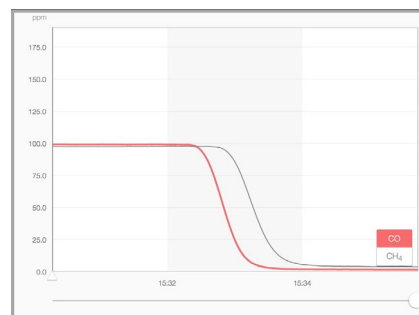
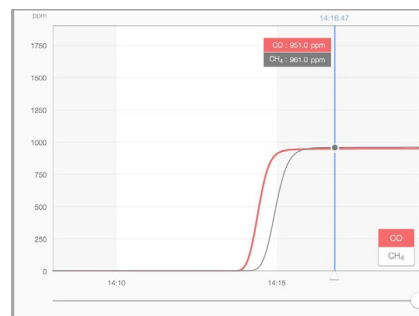
FTIR Spectra of 1000 ppm and 100 ppm CH₄

Transportable Gas Analyzer

Though it can only target a limited selection of components, such as CO, CO₂, CH₄, and O₂, it can continuously measure gas concentrations. The most significant feature is its ability to continuously monitor generated gas concentrations in real time for long periods, making it especially well-suited for applications where changes in gas concentrations during catalytic reactions need to be determined as a function of time. Furthermore, it features built-in pretreatment equipment, such as a pump, filter, and thermoelectric cooler (or chiller), allowing direct measurement of gases containing dust or moisture without separate pretreatment. Offering easy operation, it is also suitable for online measurements with the FTIR unit directly coupled to the reaction system, an ideal platform for determining reaction behavior or monitoring processes.



Product



CGT-7100 Real-Time Measurement of 1000 ppm (Upper) and 100 ppm (Lower) Samples

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

Application 

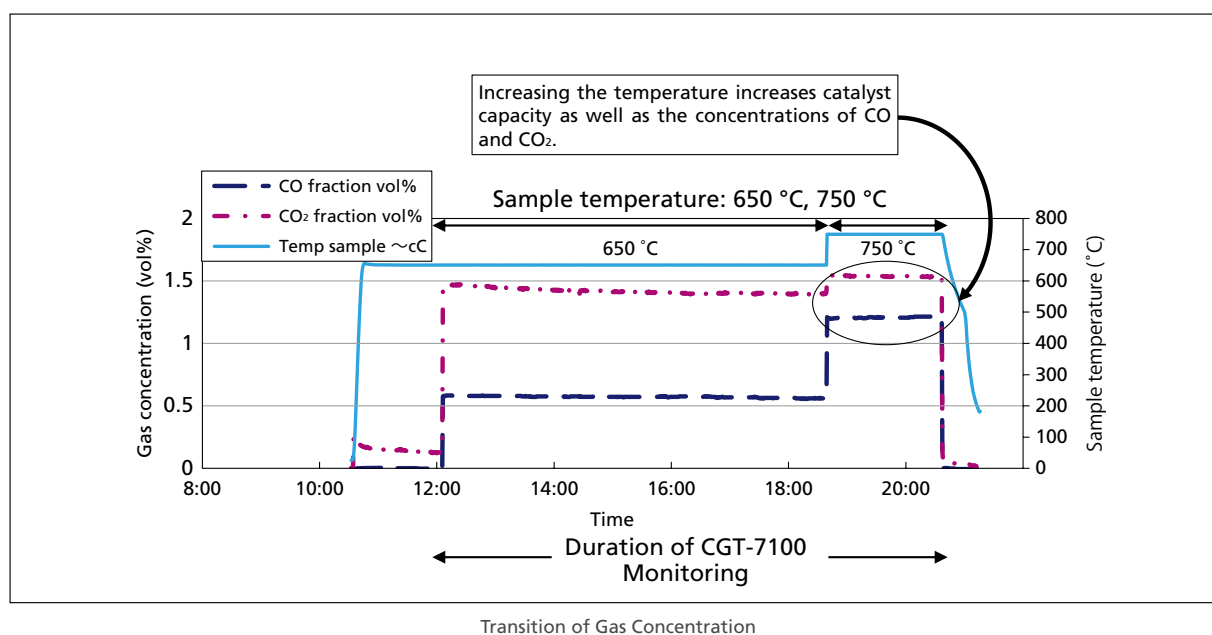
It is important to monitor gas generation over time to assess changes in catalytic capacity and the degree of degradation.



- 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 increases its reforming capacity.



Portable 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 

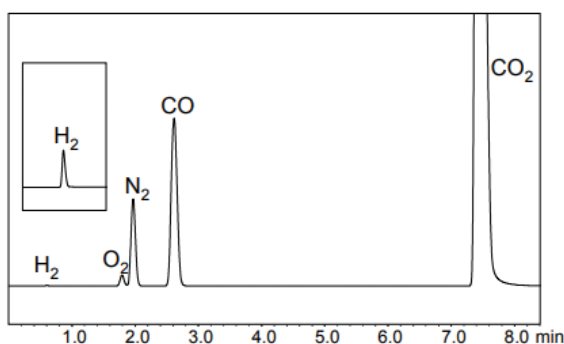
In a photochemical carbon dioxide reduction utilizing a photocatalyst, efficiency can be evaluated by quantifying carbon monoxide and hydrogen.



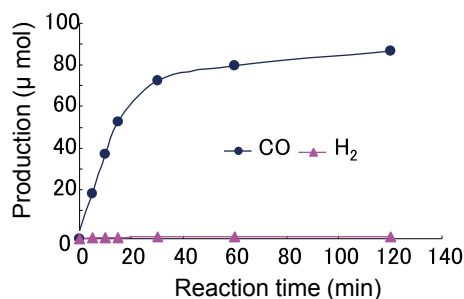
- The Barrier discharge Ionization Detector (BID) can provide simultaneous high-sensitivity measurements of carbon monoxide and hydrogen.
- Almost all components can be detected in addition to the target component in a single measurement.

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



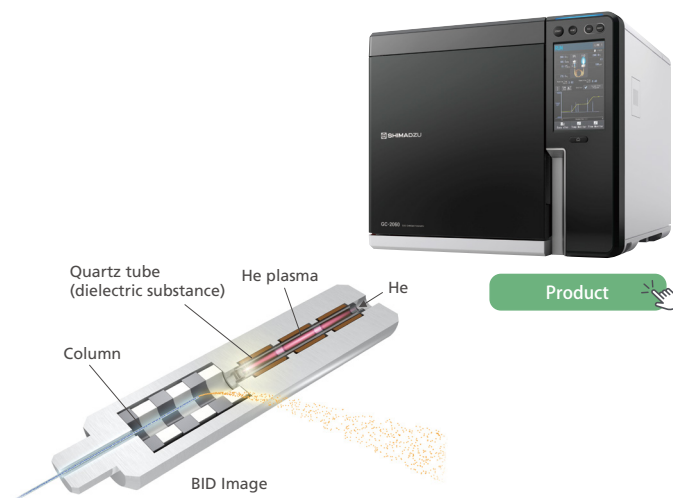
CO and H₂ Production Versus Reaction Time

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.



GC Analysis of Inorganic Gases and Hydrocarbons Using an Automatic Gas Injector

Application 

Analytical targets for artificial photosynthesis reactions can include carbon monoxide, hydrogen, and a variety of other inorganic gases and hydrocarbons.

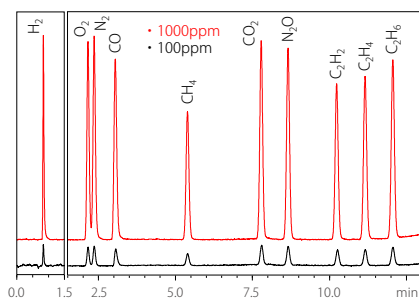


- Achieves high reproducibility using an automatic gas injector.
- Reduces air ingress by using valve purging functionality and an optional dedicated injection port.
- A new thermal conductivity detector (TCD) stabilizes faster and supports a wider dynamic range, including high concentrations.
- Inorganic gases and light hydrocarbons can be analyzed with high sensitivity using a barrier discharge ionization detector (BID).

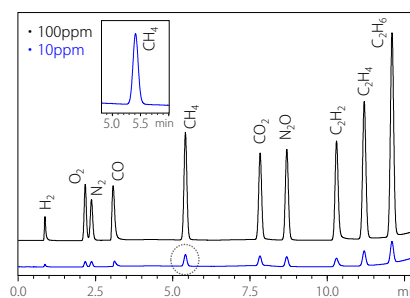
Measurement Results (Extract)

A standard gas cylinder was analyzed by connecting it to gas chromatographs equipped with either a BID or TCD.

Using the GI-30 automatic gas injector for sample introduction resulted in high peak-area reproducibility, which is difficult to obtain with manual injection. In addition, valve purging and the dedicated injection port option reduced air ingress, enabling accurate analysis of N_2 , O_2 , and other trace components.



Chromatogram from TCD Analysis
(Left: N_2 carrier; Right: He carrier)

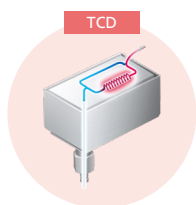


Chromatogram from BID Analysis
(Upper left: Enlargement of Chromatogram for 10 ppm CH_4)

Gas Chromatograph

Gas chromatographs can qualitatively and quantitatively analyze vaporized components in air and liquid samples. BID detectors are suitable for analyzing low-concentration gases whereas TCDs are suitable for analyzing high-concentration gases. The new TCD stabilizes within 10 minutes after startup, enabling prompt analysis. The BID allows high-sensitivity measurement for all components except helium and neon, enabling simultaneous analysis including H_2 .

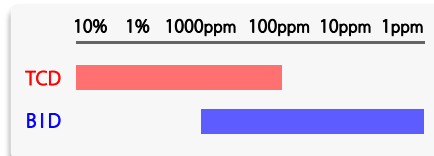
An automatic gas injector simplifies analysis while also achieving high reproducibility. Furthermore, the valve purging functionality and dedicated injection port option minimize air ingress before the gas is injected while the sample loop maintains the temperature to help reduce carryover.



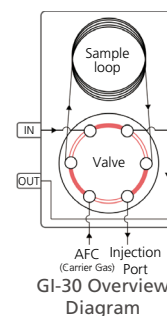
- ✓ Enables analysis of components other than the carrier gas
- ✓ Short stabilization time
- ✓ Suitable for high-concentration ranges



- ✓ Enables analysis of all components except He and Ne
- ✓ No carrier change required when analyzing H_2
- ✓ Suitable for low-concentration ranges



Approximate Concentration Ranges Suitable for TCD and BID Detectors
(Varies depending on the compound, analytical conditions, and GC unit)

Product 

GC-MS Analysis of Inorganic Gases and Hydrocarbons Using an Automatic Gas Injector

Application 

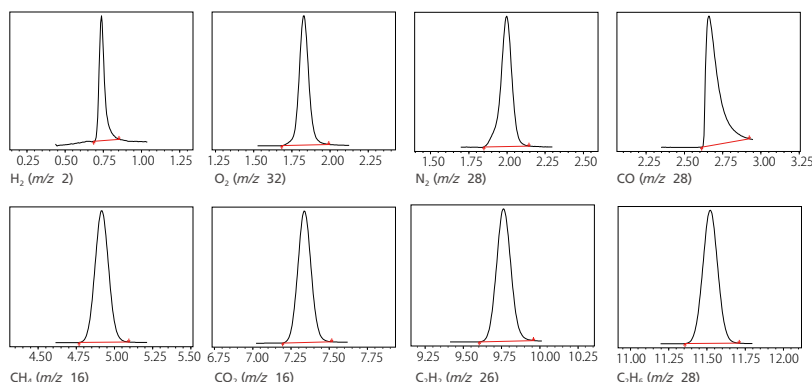
In addition to expected gas components, unexpected and unknown reaction products formed during catalytic reactions can provide important information.



- Enables qualitative analysis without using a standard sample.
- By using GC-MS to select target ions, the gas chromatograph can be used to analyze even unseparated components.
- Achieves high reproducibility using an automatic gas injector.
- Reduces air ingress by using valve purging functionality and an optional dedicated injection port.

Measurement Results (Extract)

During gas analysis, air components and water can cause baseline fluctuations, but consistent, high-sensitivity analysis can be achieved by selecting ions (m/z) appropriate for respective compounds. As indicated above, using an automatic gas injector can simplify analysis, reduce air ingress, and achieve good reproducibility.

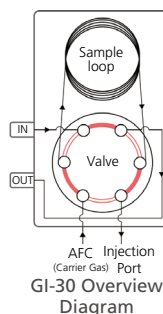


SIM Chromatogram of Standard 10 ppm Mixture Sample

GC systems require standard substances for qualitative analysis, which makes it difficult to qualitatively analyze impurities and other unknown components contained in gas samples. Furthermore, qualitative and quantitative analysis is difficult if peaks cannot be completely separated. In contrast, with GC-MS, mass spectra can be used to enable qualitative analysis of unknown components without using standard substances. Plus, mass chromatograms allow substances to be quantified even if the peaks overlap. In addition, H_2 , which is normally difficult to detect, can be measured with high sensitivity by employing specialized ionization techniques.

Gas Chromatograph Mass Spectrometer

Gas chromatograph mass spectrometer (GC-MS) systems combine a gas chromatograph and a mass spectrometer in a single system. They peak identification by mass spectra, eliminating the need to prepare standard gases. Furthermore, even peaks obscured by atmospheric components or moisture can be detected. The GCMS-QP2050 is especially compact and can even be retrofitted to a GC unit. An automatic gas injector simplifies analysis while also achieving high reproducibility. Furthermore, the valve purging functionality and dedicated injection port option minimize air ingress before the gas is injected while the sample loop maintains the temperature to help reduce carryover.

Product 

Automatic High-Speed Analysis Using FluxEdge

Application 

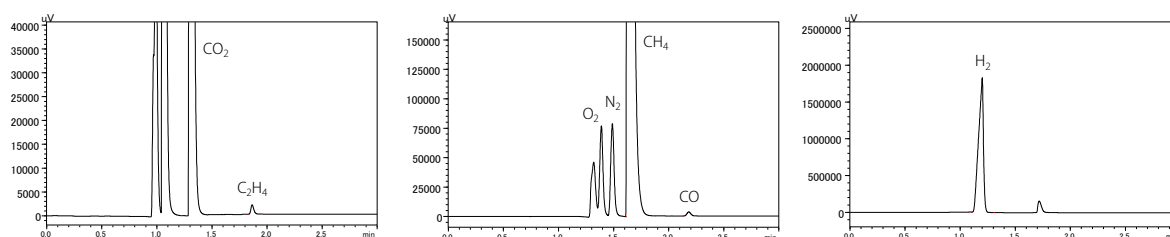
Catalytic reaction research and development require monitoring changes in component composition before and after reactions. This requires shorter measurement times. High-accurate measurements are also essential, even if only a small amount of gas is generated after reactions.



- Organic and inorganic gas components can be analyzed simultaneously in 4 minutes or less.
- Low carryover and excellent analysis reproducibility can be achieved with small sample quantities.
- A durable valve system with backflush functionality ensures rugged, consistent operation over long periods.

Measurement Results (Extract)

H₂, O₂, N₂, CO, CO₂, CH₄, and C₂H₄ peaks were detected within 3 minutes. The total sample quantity used per cycle was 8.5 mL, which is less than one-tenth of the previous quantity. These results confirm that sufficient sample cleaning and excellent analysis reproducibility can be achieved with small sample quantities.



Chromatograms of Standard Gas Mixture Samples
(Shown from left to right: TCD1, TCD2, TCD3)

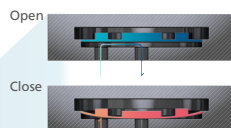
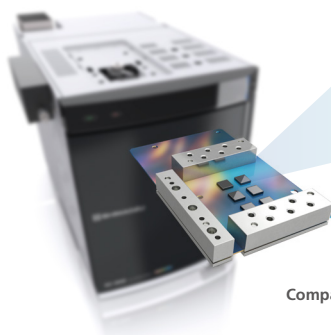
Results also show that the backflush function protects the column by preventing ingress of components that would impair column retention. In addition, the microvalves in the system are several hundred times more durable than previous rotary valves, which enables consistent, long-term system operation.

FluxEdge: A Cutting-Edge GC System

Product 

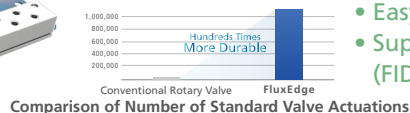
FluxEdge = Flux (Flow) + (Cutting-) Edge

The FluxEdge GC system redefines expectations about analyzing gases with a GC system



Cross Section of FluxEdge Microvalve

- High-speed gas analysis
- Enables sampling small quantities
- Low carryover
- High reproducibility
- No valve replacement required
- Easy maintenance using standard GC columns
- Supports a wide range of detectors (FID, TCD, and BID)



The microvalves used in FluxEdge GC systems have a diaphragm structure developed with microfabrication technology used by semiconductor manufacturers in combination with Shimadzu's advanced deactivation technology. Consequently, they offer several hundred times greater durability than rotary valves typically used for gas analysis. They also achieve faster analysis speeds due to the minimized size and deactivated surfaces of analysis flow channels between the sample injection unit and the column.

High-Speed Analyzer for Inorganic Gases and Hydrocarbons

Application 

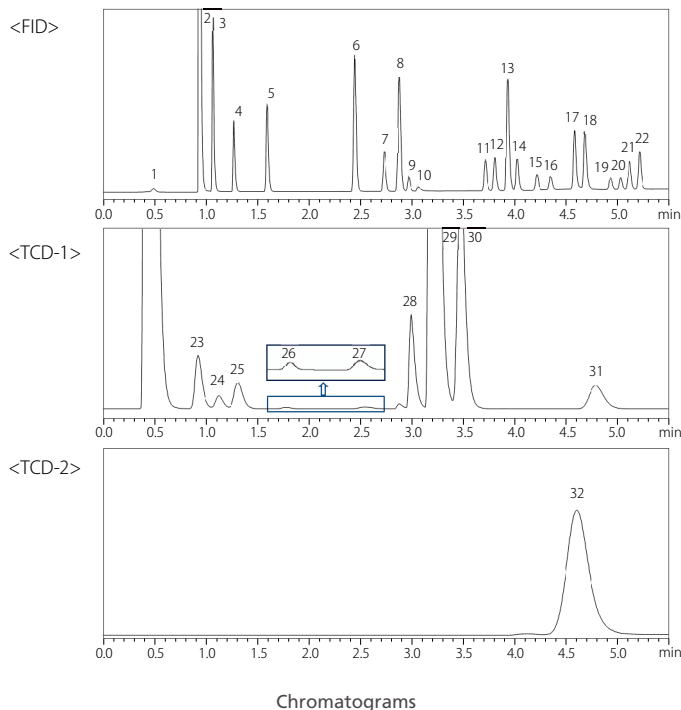
A shorter analysis time enables comparison of various catalysts and reaction conditions.



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.



<FID>

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

<TCD1>

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

<TCD2>

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 

Analysis of Gases from CO₂ Reduction

Application

Selecting an appropriate combination of columns and detectors for the target compounds enables simultaneous analysis and improves research efficiency.



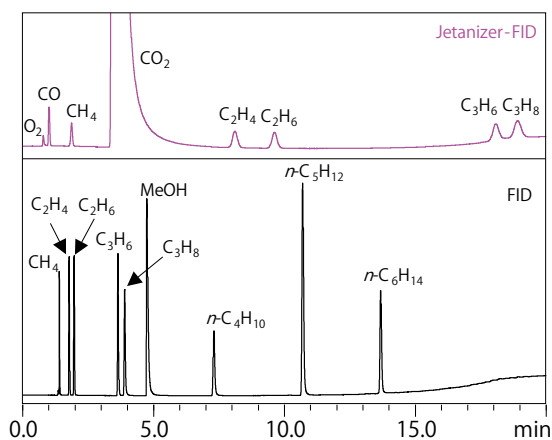
benefits

- With branched injection ports and a methanizer (Jetanizer), carbon monoxide, methanol, and light hydrocarbons can be quantified in a single analysis.
- The Jetanizer enables simultaneous measurement of hydrocarbons, CO, and CO₂.
- The general-purpose TCD detector can measure a wide variety of compounds, including permanent gases.

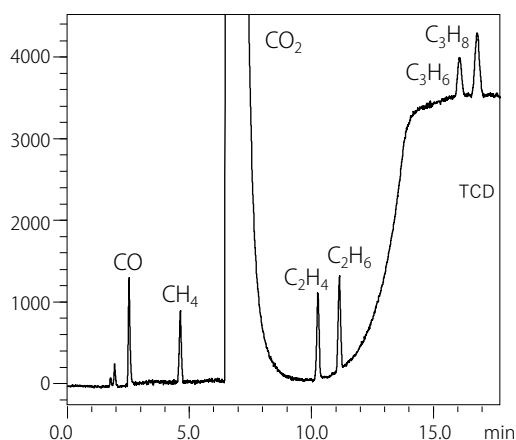
Measurement Results (Extract)

Using 2 different columns and detectors at the same time, methanol, CO, and hydrocarbons contained in CO₂ can be measured with a single injection. If CO and hydrocarbons are the only compounds being measured, a TCD and one column can be used.

Note: Patent pending



Chromatogram of Methanol, CO, and Hydrocarbon Mixture in CO₂
Measured Using a System with a Branched Injection Port
(MeOH: 300 ppm; Others: 50 ppm each)



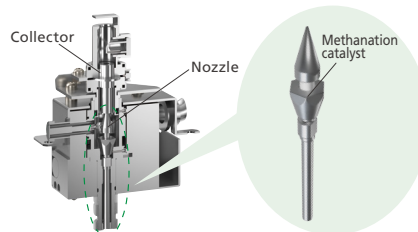
Chromatogram and S/N Ratios of CO and Hydrocarbon Mixture
(100 ppm Each) in CO₂ Measured with a TCD

Gas Chromatograph

Gas chromatographs can qualitatively and quantitatively analyze vaporized components in air and liquid samples. While CO and CO₂ cannot be detected with a general-purpose FID, the Jetanizer can detect them. Benefits include higher sensitivity than a TCD and the ability to use N₂ as the carrier gas. Also, the Jetanizer can be easily installed by simply replacing the FID nozzle.

Because a TCD detects compounds non-destructively, gases can be simultaneously measured with an FID or other detector connected to the outlet.

Furthermore, despite the compact size of the Brevis GC-2050, 2 columns can be installed to enable simultaneous dual-line measurements with different columns or detectors.



Product

Simultaneous High-Sensitivity Analysis of CO, CO₂, and CH₄ Using a Jetanizer

Application 

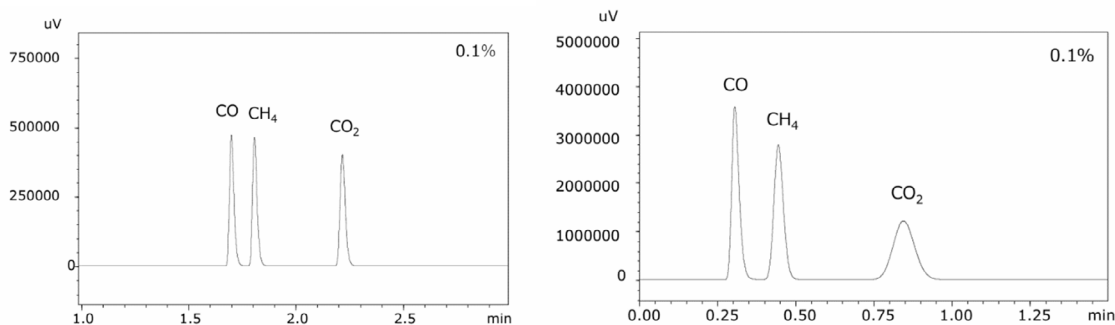
Simultaneous analysis of CO₂, CO, other hydrocarbons, and alcohols is useful when evaluating CO₂ reduction reactions.



- Enabling CO and CO₂ detection by FID simplifies the system configuration.
- The system can be implemented inexpensively by replacing parts in existing FID units.
- Trace analysis of CO and CO₂ can be performed with excellent reproducibility using N₂ as the carrier gas.

Measurement Results (Extract)

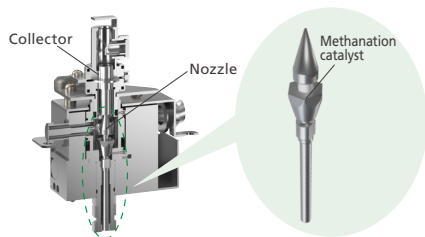
A standard gas (with a base of N₂ gas) containing 0.1 % each of CO, CH₄, and CO₂ was analyzed using a capillary column and packed column.



0.1 % Standard Gas Analytical Results
(Left: Capillary column; Right: Packed column)

Analyzing standard CO and CO₂ with concentrations ranging from 1 ppm to 25 % resulted in good area reproducibility and linearity. These results confirm adequate sensitivity. The limit of detection was approximately 0.3 ppm for the capillary column and 0.1 ppm for the packed column.

Option for High-Sensitivity Analysis of CO and CO₂ – Jetanizer –



- Enables simultaneous measurement of CO, CO₂, and organic compounds
- Can be deployed inexpensively by replacing only existing parts
- High oxygen tolerance

	Jetanizer	Conventional Methanizer
Installation Location	FID nozzle	Next to GC unit
AUX Power Supply	Not necessary	Required
Catalyst	Nickel-free (proprietary catalyst)	Nickel (Ni)
O ₂ Durability	Good	Poor
Additional H ₂ Supply	Not necessary	Required

The Jetanizer is a methanizer that offers outstanding durability and can be installed and used easily by customers. By converting CO and CO₂ to methane, concentrations from below 1 ppm up to 100 % can be detected with high sensitivity.

Models are available for Shimadzu Nexis GC-2060, Nexis GC-2030, and Brevis GC-2050 systems, and for select non-Shimadzu GC systems.

Product 

Simultaneous Multi-Component Quantitative Analysis Using a Polyarc System

Application

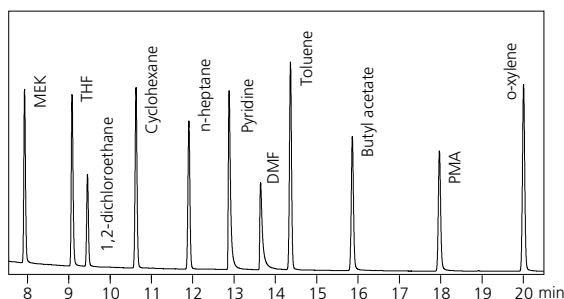
The CO₂ reduction reaction generates hydrocarbons and oxygenated compounds, which must be efficiently quantified to accelerate research.



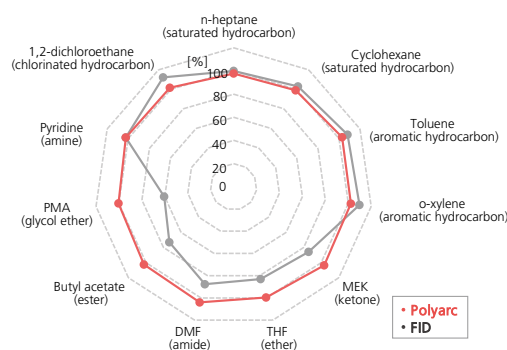
- Carbon-based detection eliminates the need for individual calibration curves, saving time and effort.
- The Polyarc system can be added to existing GC-FID systems.
- The Polyarc system reduces sensitivity differences for oxygenated and unsaturated compounds, which typically show low FID sensitivity.
- Even compounds lacking available standards can be quantified.

Measurement Results (Extract)

Eleven organic compounds with different functional groups were dissolved in methanol to prepare 500 ppm (v/v) concentrations of compound. The solution was then analyzed. Using the Polyarc system, compounds containing heteroatoms or unsaturated bonds were analyzed, with results showing sensitivity comparable to hydrocarbons.

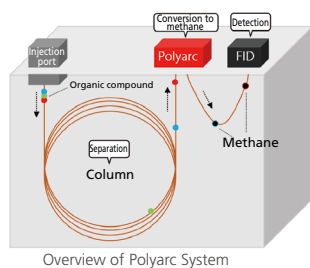


Chromatogram Obtained Using the Polyarc System

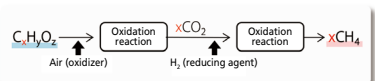


Relative Sensitivity (%) Using a FID Detector or Polyarc System

Polyarc Enables Carbon-Based Detection – Polyarc –



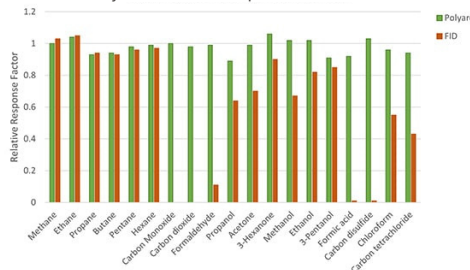
Overview of Polyarc System



Methane Conversion Reaction in Polyarc System

- Carbon-based detection eliminates the need for individual calibration curves
- No additional space required
- High oxygen tolerance

Polyarc-FID vs FID Response Factors



The Polyarc system converts a hydrogen flame ionization detector (FID) into a quantitative carbon detector (QCD). It can normalize response sensitivity by converting all organic compounds to methane molecules before FID detection, which also reduces the time and trouble involved in creating calibration curves. The system can be added to new or existing Shimadzu Nexis GC-2060, Nexis GC-2030, or Brevis GC-2050 systems.

Product

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

[Application](#)

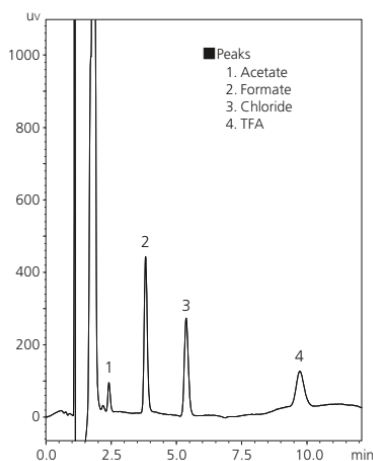
The measurement of formic and acetic acid is important to evaluate the efficiency of carbon dioxide reduction reactions.



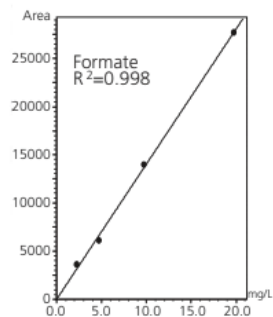
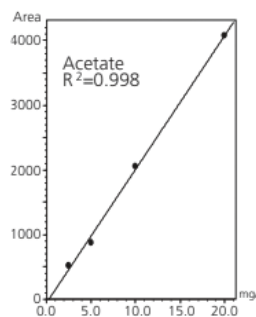
- Formic acid and acetic acid in aqueous solutions can be detected.
- Shimadzu's unique post-column buffering method enables highly sensitive analysis, even of samples with many contaminants.

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 System

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

[Application](#)

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](#)

High-Sensitivity GC-FID (Jetanizer) Analysis of Formic Acid in Methanol Solution

[Application](#)

This gas chromatograph is especially useful for cases where carbon dioxide reduction reaction products can be dissolved in an organic solvent.

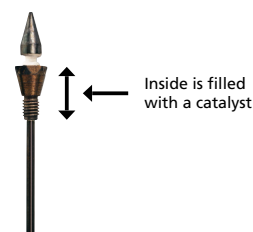
**benefits**

- The Jetanizer enables accurate measurement of formic acid in solution by GC-FID.
- The Jetanizer is both easy to install and less expensive to operate.
- A nitrogen carrier gas can be used for analysis.

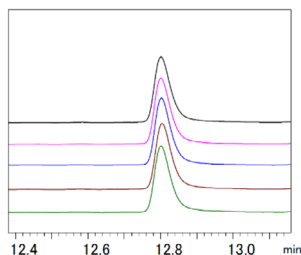
Measurement Results (Extract)

FIDs, general-purpose detectors for gas chromatography, can only detect formic acid with low sensitivity; however, by replacing the catalyst in the FID nozzle with a Jetanizer and making minor adjustments to the analytical conditions, an FID can achieve ppm-level detection.

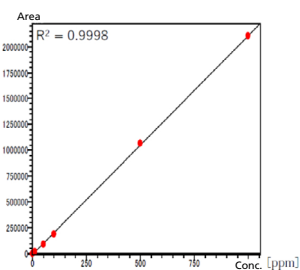
Obtaining good peaks for formic acid is difficult because it tends to adsorb to the injection port and column. For this reason, treating the glass insert and column with phosphoric acid before starting measurement is recommended. When this is done, good sensitivity, reproducibility, and linearity can be achieved.



Treating the Glass Insert
with Phosphoric Acid



Chromatogram Obtained from 5 Successive
Measurements of 10 ppm Formic Acid Solution



Formic Acid Calibration Curve (1 to 1000 ppm)

Related Applications

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

Formic acid can be detected using a high-sensitivity barrier discharge ionization detector (BID).

[Application](#)

■ Analysis of Formic Acid and Formaldehyde Using GC-MS

This application provides an example of analyzing formic acid and formaldehyde using a gas chromatograph mass spectrometer system.

[Application](#)

Gas Chromatograph

Gas chromatographs can qualitatively and quantitatively analyze vaporized components in gas and liquid samples. The Jetanizer-FID configuration enables detection of CO, CO₂, and formic acid components that cannot be detected with a standard FID. Because it detects them with higher sensitivity than a TCD, the Jetanizer-FID can analyze samples using less helium than a BID-based system.

[Product](#)

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.

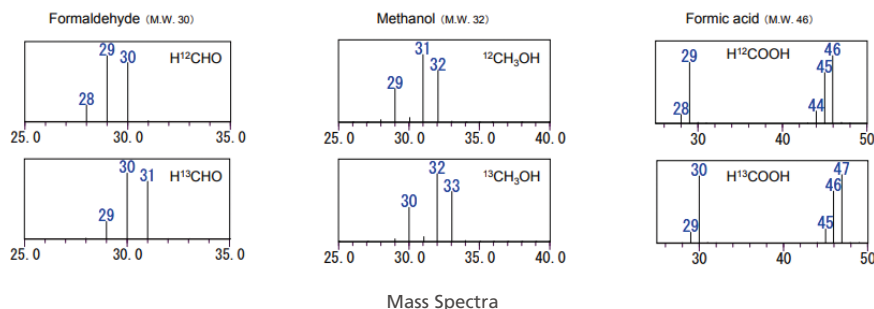


- By utilizing a mass spectrometer (MS), isotope-based labeling experiments can be performed.
- It is easy to determine whether a compound is generated from an experimental system or from contamination from the environment.

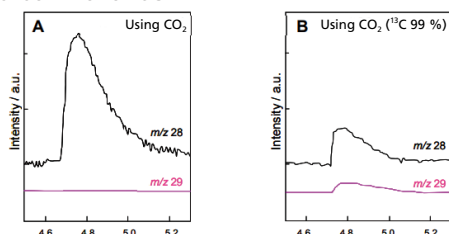
Measurement Results (Extract)

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

The ^{13}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}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. The GCMS-QP2050 is particularly compact and can be retrofitted to existing GC systems.

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.

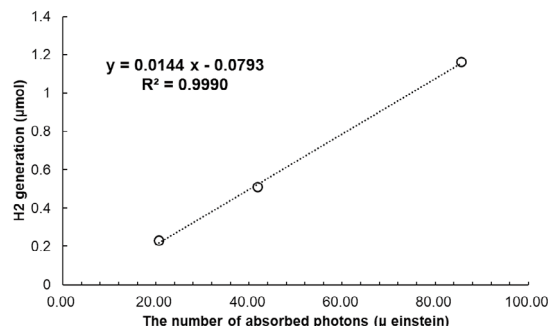


Measurement of the Number of Absorbed Photons by Photoreaction Evaluation System

×



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. The compact Brevis GC-2050 saves space, even when installed alongside a Lightway or other pretreatment unit.

Product 



Shimadzu Corporation

www.shimadzu.com/an/

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