SHIMADZU
Excellence in Science

Analytical and Testing Instruments for Artificial Photosynthesis

Index

What is Artificial Photosynthesis?

Artificial photosynthesis is a technique to harvest solar energy and stored it chemically. During the process, abundant materials such as CO_2 and H_2O are captured and converted into renewable energy sources.

The process of artificial photosynthesis requires the use of photocatalyst to enable the redox half-reactions to proceed efficiently. Specifically, it can take place in two forms: (1) water-splitting reaction (2) photochemical reduction of CO_2. In both cases, the reaction products such as H_2 and methanol can be directed into fuel-cell setup to generate clean energy.

With the increasing concentration of atmospheric CO_2 and worsening global warming, artificial photosynthesis is critical to establish the envisioned future of closed carbon cycle – where excess CO_2 generated from man-made activities would be captured and re-used as solar fuels.
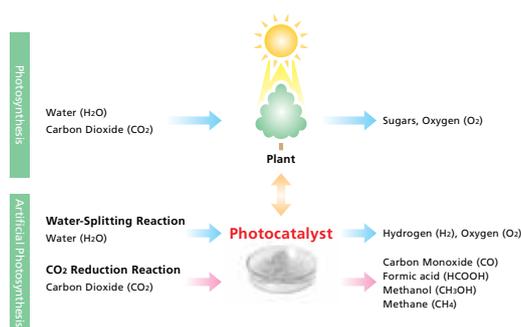
Types of Artificial Photosynthesis Research

The design of the artificial photosynthesis device can be inherently complex and challenging. Currently, there are 4 strategies to mimic the natural photochemical system:

1) Semiconductor Catalyst Systems
Inorganic and organic semiconductors can be used as light-harnessing materials in photovoltaic devices to convert solar energy into clean fuels. Recent research has probed into the use of semiconductor nanostructures to improve reaction efficiency.

2) Supramolecular Systems
Supramolecular chemistry is characterized by using non-covalent interactions to establish complex macromolecules. These systems typically utilize metal complexes such as ruthenium (Ru) and rhenium (Re) as photocatalysts.

3) Hybrid Systems
Hybrid systems combines semiconductor and supramolecular materials to capitalise on their advantages and hence create a synergistic effect in enhancing the overall efficiency of the photocatalytic reactions.

4) Biological Systems
Light-sensitive microorganisms such as microalgae and cyanobacteria can be cultured and used as biological converters to produce renewable biofuels from CO_2 and solar energy.

Role Of Analytical Instruments For Performance Evaluation

Analytical instruments such as GC, HPLC and absorption photometry are typically used for measuring the reaction products in artificial photosynthesis to evaluate its solar-to-chemical conversion efficiency or the catalytic activity performance of the photocatalysts. This can allow for further optimisation to drive artificial photosynthesis as the next-generation renewable energy.

Analysis of Hydrogen, Trace CH$_4$, & CO and Light Hydrocarbons

Permanent gases such as CO, CO$_2$, O$_2$, N$_2$, and methane are common analytes in refinery gases, natural gas, fuel cell gases, and many other industrial processes. It is important to understand the concentration of these gases for controlling manufacturing processes, and their negative impact on quality and commercial value of end products. This is a method for determining the gas composition described in the compound table below. It requires the use of a dedicated gas chromatographic system which is configured with an automatic sampling and back-flushing technique with multiple columns. Ranges can be varied by changing the size of the loop.

No.	Compound Name	Concentration Range		Typical Concentration
		Low Conc.	High Conc.	
1	C1 – C6	10 ppm	50 ppm	FID
2	H$_2$	10 ppm	50 ppm	TCD
3	CO	10 ppm	50 ppm	MTN-FID
4	CH$_4$	10 ppm	50 ppm	MTN-FID

System GC-2014C with TCD + MTN-FID + FID

User-friendly with high cost-performance, the GC-2014C gas chromatograph is an excellent option for routine analysis. It offers great flexibility with support for both packed and capillary columns and includes a self-diagnosis function to prevent downtime and maximize lab efficiency.

Configuration used in current experimentation includes GC-2014C with Thermal Conductivity Detector (TCD-2014) and Flame Ionization Detector (FID-2014) with methanizer.

Click here to know more.

Analytical Data

Analysis of H$_2$ using GC-TCD

With the increasing interest in using H$_2$ as the clean energy fuel, research have probed into investigating photocatalytic water splitting reactions to produce H$_2$. TCD is an universal detector that can identify and quantify fixed gases effectively. The results here demonstrate the analysis of H$_2$ generated during the water splitting reaction using GC-FID. H$_2$ is eluted within 1.5 min.
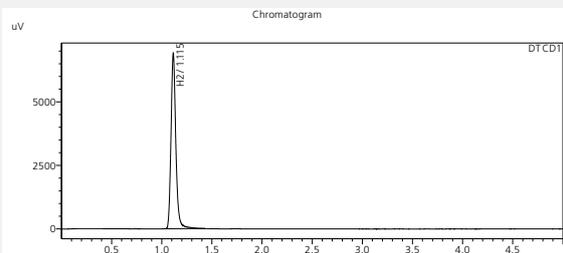
Quantitative Result						
DTCD1						
ID#	Name	Ret. Time	Area	Hei ght	Conc.	Unit
1	H$_2$	1.115	23157	6895	1.010	%
Total			23157	6895	1.010	

Analysis of CO, CO$_2$, and CH$_4$ using MTN FID

MTN-FID offers a complete solution to detect trace level of gases, such as CO$_2$ and CO alongside with the different hydrocarbon components. The results show the analysis of carbon reduction of CO$_2$ to CO, which is performed using different columns to achieve full separation. Since no traces of CO$_2$ are detected, it confirms the success of the carbon reduction reaction.
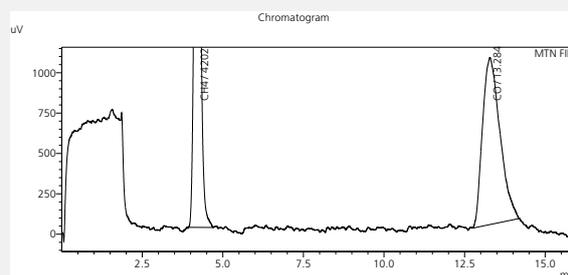
Quantitative Result						
MTN FID						
ID#	Name	Ret. Time	Area	Hei ght	Conc.	Unit
1	CH$_4$	4.202	48765	3998	5.262	ppm
2	CO	13.284	38889	1034	5.453	ppm
Total			87654	5032	10.715	

Analysis of any C2 or C3 hydrocarbons using GC-FID

In the analysis of hydrocarbons, permanent gases can be considered as impurities in the matrix. GC-FID is hence useful to focus the analysis on the target components. The results here illustrate the complete separation of 21 hydrocarbons (C2 and C3 components) formed during the carbon reduction process using GC-FID.

Chromatogram
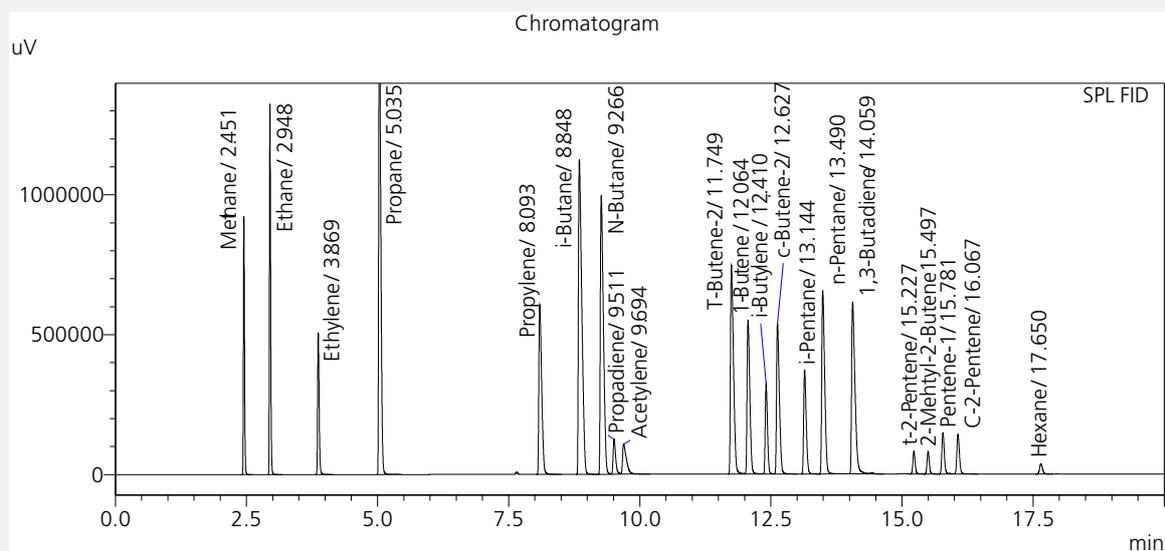
Quantitative Result

SPL FID

ID#	Name	Ret. Time	Area	Height	Conc.	Unit
1	Methane	2.451	1343879	891315	4.981	%
2	Ethane	2.948	2088780	1312564	3.967	%
3	Ethylene	3.869	1036963	499785	1.989	%
4	Propane	5.035	4654410	1623381	6.028	%
5	Propylene	8.093	2268188	604841	2.982	%
6	i-Butane	8.848	5025424	1119587	4.973	%
7	N-Butane	9.266	4084012	994866	3.999	%
8	Propadiene	9.511	419402	124262	0.990	%
9	Acetylene	9.694	551159	106716	1.004	%
10	T-Butene-2	11.749	3017277	746337	3.025	%
11	1-Butene	12.064	2012720	547008	1.990	%
12	i-Butylene	12.410	966270	320862	1.005	%
13	c-Butene-2	12.627	2010586	537177	2.010	%
14	i-Pentane	13.144	1258042	371842	1.000	%
15	n-Pentane	13.490	2532449	654287	2.011	%
16	1,3-Butadiene	14.059	2762716	612816	3.045	%
17	t-2-Pentene	15.227	235554	80977	0.202	%
18	2-Mehtyl-2-Butene	15.497	237500	80214	0.200	%
19	Pentene-1	15.781	483755	147230	0.402	%
20	C-2-Pentene	16.067	486355	142082	0.401	%
21	Hexane	17.650	145420	37185	0.102	%
Total			37620861	11555333	46.306	

Analysis of Alcohols, Organic acids, and Aldehydes by UHPLC

Photochemical reduction of CO$_2$ can generate high-energy fuels and value-added products such as alcohols, organic acids and aldehydes. It is critical to quantify these products to evaluate the reaction efficiency. To analyze multiple classes of compounds together with high throughput, the following method presents the simultaneous analysis of alcohol, organic acids, and aldehydes using Nexera Series UHPLC coupled to PDA and RID.

Analytical Conditions

Column	: BioRad HPX-87H (300 x 7.8 mm)
Mobile Phase	: 5 mM H$_2$SO$_4$
Elution Mode	: Isocratic
Flow Rate	: 0.6 ml/min
Oven Temperature	: 25 °C
Injection Volume	: 50 µL

Nexera with PDA & RID

Completely customizable and adaptable Nexera series is available in different configurations catering to variety of needs in experiments and column chemistries. Powered by Analytical Intelligence, Nexera series is capable of fully unattended operations from start-up to shutdown, complete with self-troubleshooting features for an ease of mind during data acquisition.

Click here to know more.

For this experiment, Nexera UHPLC was configured with Photodiode array (SPD-M40) and Refractive Index Detector (RID-20A).

Sample Preparation

Preparation of standards:

The single mixed standard solution (30-530 mM) was diluted in 0.1 M $KHCO_3$ to prepare a series of standards.

Samples were injected as they are.

Compound	Concentration (mmol/L)					
	S1	S2	S3	S4	S5	S6
Glycol Al dehyde	0.015	0.075	0.30	0.75	1.5	3.0
Formic Acid	0.27	1.33	5.30	13.25	26.5	53.0
Potassium Acetate	0.02	0.10	0.40	1.00	2.0	4.0
Ethylene Glycol	0.18	0.90	3.58	8.95	17.9	35.8
Acetaldehyde	-	0.89	3.58	8.94	17.9	35.8
Methanol	0.25	1.24	4.94	12.35	24.7	49.4
Ethanol	0.17	0.86	3.43	8.58	17.2	34.3
Allyl Alcohol	0.15	0.74	2.94	7.35	14.7	29.4
Acetone	0.136	0.68	2.72	6.80	13.6	27.2
1-Propanol	0.1335	0.6675	2.67	6.68	13.4	26.7

Results

The method was optimized for the analysis of 10 compounds in a single measurement using PDA and RID as modes of detection. From the overlay chromatogram, excellent separation was achieved within 30 minutes without compromise on the resolution.

Overlay chromatogram of 10 single standards, Inj Vol. 20 uL
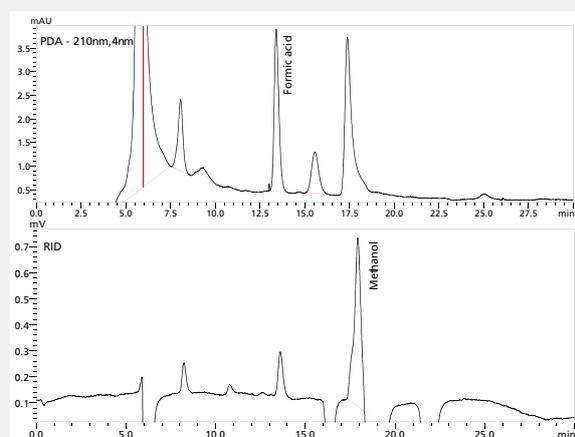
Based on developed method, real sample was analyzed. Formic acid and methanol were detected at concentrations 0.32 and 4.88 mM respectively.
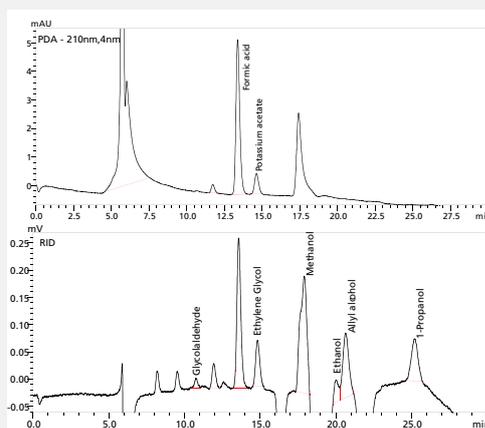
Chromatogram of 0.1mM mixed sample, Inj Vol. 50uL

Summary

UHPLC method was developed to achieve complete separation of 10 compounds in 30 minutes using PDA and RID as modes of detection. Calibration curves of 10 compounds were established with concentration range from 0.015 mM to 53.0 mM and their R^2 are 0.998 and above. In the unknown sample, formic acid and methanol were detected at concentrations 0.32 and 4.88 mM respectively. LOD and LOQ of the method are 0.01 – 0.3 mM and 0.02 – 0.9 mM respectively.

Analysis of CO Generated from CO_2 Reduction Reactions (GC-BID)

The photochemical CO_2 reduction reaction using a photocatalyst generates CO as a reaction product. The catalyst performance can be evaluated by determining the quantity of CO generated during a given unit period. This measurement is normally performed using GC. In the following example, a Tracera (GC-BID) system is used to measure CO as the reaction product.

Analytical Conditions

Gas Chromatograph	: Tracera (GC-2010 Plus A + BID-2010 Plus)
Column	: Micropacked ST (2 m × 1 mm I.D.)
Column Temperature	: 35 °C (2.5 min) – 20 °C/min – 180 °C (0.5 min), total 10.25 min
Carrier Gas Control	: Pressure
Pressure Program	: 250 kPa (2.5 min) – 15 kPa/min – 360 kPa (0.42 min) (He)
Injection Mode	: Split (1:10)
Injection Port Temperature	: 150 °C
Detector Temp.	: 280 °C
Plasma Gas Flowrate	: 70 mL/min
Injection Volume	: 50 µL

Tracera High Sensitivity Gas Chromatograph System

The barrier discharge ionization detector (BID) generates a Helium (He) plasma by applying high voltage to a quartz glass tube. The discharge created ionizes the compounds eluted from the column and the ions are detected as peaks. Due to the highly energetic 17.7eV helium plasma, BID is able to detect almost anything with excellent sensitivity except for Neon (Ne) and He. This makes BID truly the next-generation general-purpose plasma detector.

Tracera (GC-BID)
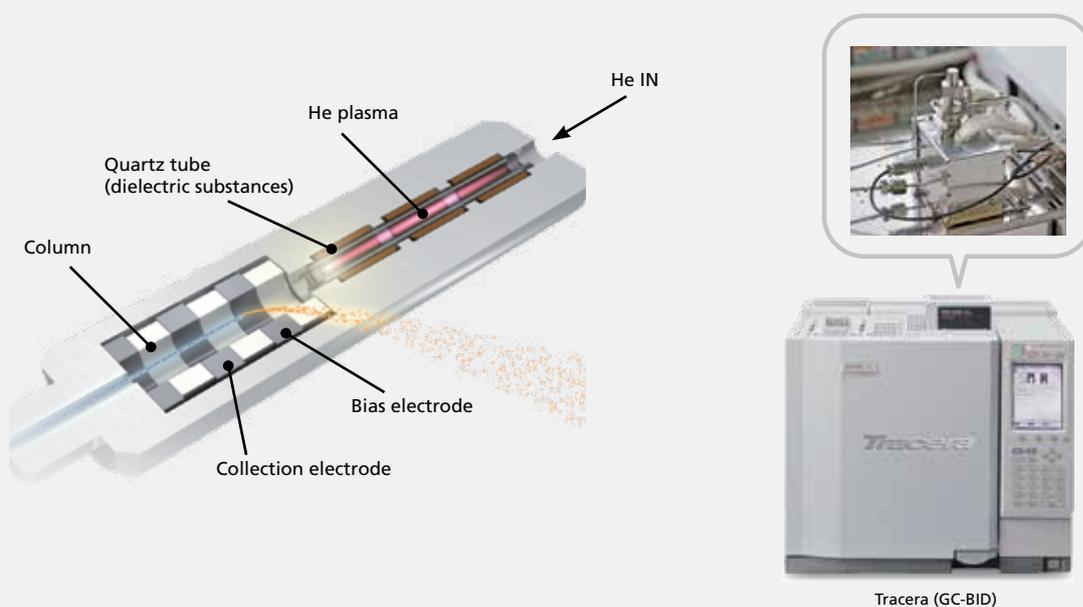
Analytical Data

CO and also H_2, O_2, and N_2 were all measured simultaneously with high sensitivity.
BID allows the measurement of almost all components except for Helium and Neon to obtain a wide variety of information in a single analysis.
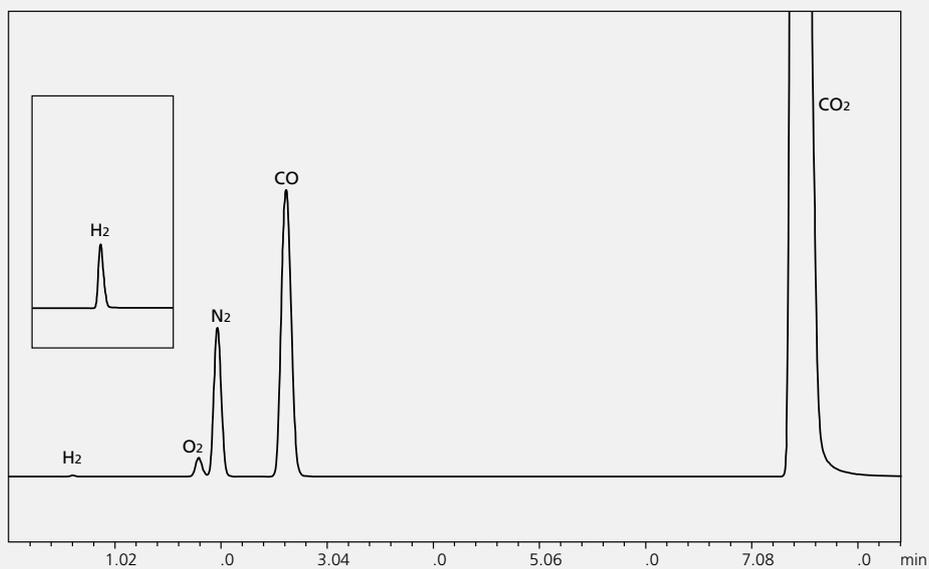
Chromatogram of Components in Gas Phase of Photochemical CO_2 Reduction Reaction
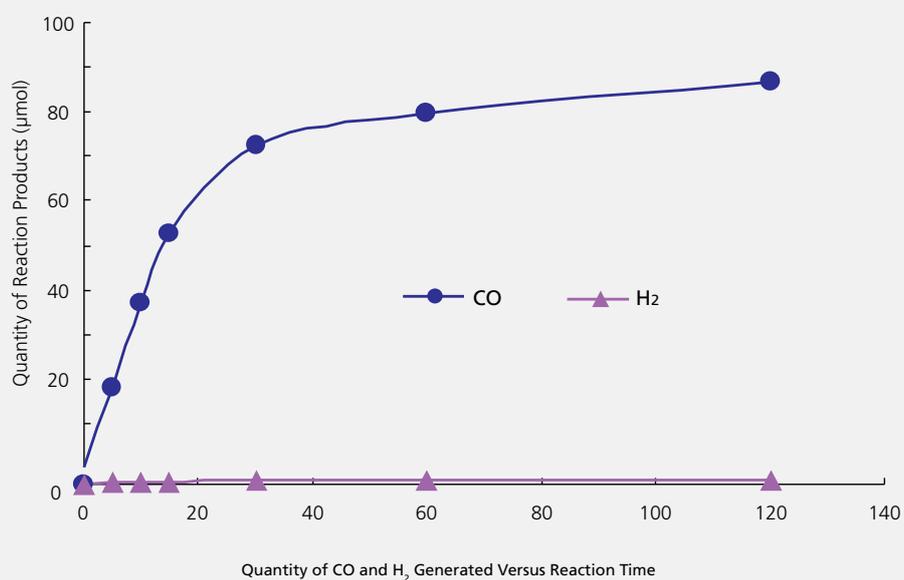
Quantity of CO and H_2 Generated Versus Reaction Time

Analysis of Formic Acid Generated from CO$_2$ Reduction Reactions (GC-BID)

The photochemical CO$_2$ reduction reaction using a photocatalyst generates formic acid as a reaction product.

Typically, instruments such as liquid chromatographs, ion chromatographs, or capillary electrophoresis systems are used to analyze formic acid. However, these instruments may not be able to analyze formic acid dissolved in organic solvents as it requires more than 10-fold dilution with water or mobile phase. This could cause its concentration to fall out of the instruments' detection range. With gas chromatography (GC), the dilution step is negated. Coupled with BID, a highly sensitive universal detector, concentration of formic acid down to ppm levels can be detected. This example describes using a GC-BID system to analyze formic acid in organic solvent.

Analytical Conditions

Gas Chromatograph   : Tracera (GC-2010 Plus A + BID-2010 Plus)
Column   : RESTEK Rtx-WAX (60 m × 0.53 mm I.D., df = 1.0 µm)
Column Temperature   : 80 °C – 5 °C/min – 130 °C – 15 °C/min – 230 °C (3 min)
Carrier Gas   : He at 50 cm/sec (constant linear velocity)
Injection Mode   : Split (1:2)
Injection Port Temperature : 240 °C
Detector Temperature   : 240 °C
Plasma Gas Flow Rate   : 50 mL/min
Injection Volume   : 1 µL

Sample Pretreatment Using Cation-Exchange Cartridge

If samples (or reaction solutions) contain salts or other contaminants, they must be removed by pretreatment. In this case, a cation-exchange cartridge was used to pretreat an actual sample with 0.1 M dissolved NEt$_4$-BF$_4$.

Cartridge conditioning → 5 mL DMA at 2 mL/min or less

Inject sample → 3 mL (dispose of 2 mL and recover 1 mL) at maximum 1 mL/min

GC analysis

Alltech Maxi-Clean 0.5 mL IC-H
50 pk P/N: 30264
Strong cation exchange

Retention volume 1.9 meq/mL, which allows processing about 9 mL, given a sample containing 0.1 M of a monovalent salt

Analytical Data

10 ppm of formic acid in the actual sample was detectable with high sensitivity.
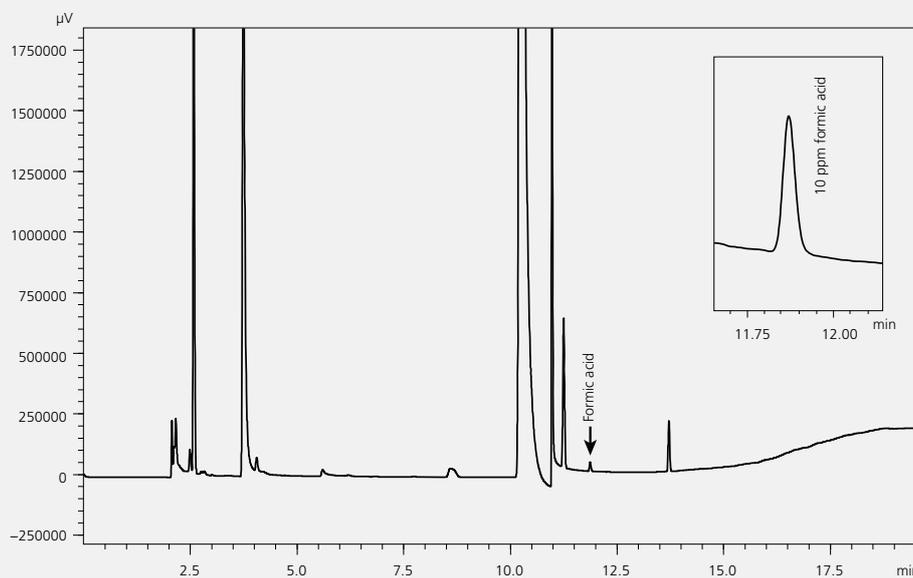
Chromatogram After Pretreating Actual Sample (DMA solvent and 0.1 M NEt$_4$-BF$_4$)

Sample source: Professor Osamu Ishitani, Graduate School of Science and Engineering, Tokyo Institute of Technology

When analyzing low concentration of formic acid using GC, loss of sensitivity and resolution can occur due to adsorption of formic acid to various component surfaces within the instrument. To prevent adsorption at the injection port and column, phosphoric acid treatment of the glass insert and column is conducted. Detailed information can be found in Shimadzu Application News G279.

In addition, sample pretreatment may be required prior to GC measurement to remove salts or other contaminants in the samples that may result in surface adsorption of formic acid in the GC injection unit. Detailed information can be found in Shimadzu Application News G280.

High-Sensitivity Simultaneous Analysis of Inorganic Gases and Light Hydrocarbons (Dual GC-BID)

Analyses for inorganic gases and light hydrocarbons are implemented in a variety of fields including petrochemistry, catalysts, batteries, resource and energy fields as well as environmental fields. The barrier discharge ionization detector (BID) installed in Nexis GC-2030 gas chromatograph is capable of detecting a wide variety of components with high sensitivity*. Thanks to Shimadzu's proprietary barrier discharge technology, this detector allows trace-level detection while maintaining the same level of stability as the previous general-purpose detectors. In this Application News, we introduce a high sensitivity simultaneous analysis of inorganic gases and light hydrocarbons using Nexis GC-2030 gas chromatograph, which is equipped with two columns and two BID detectors.

*Unable to detect helium and neon
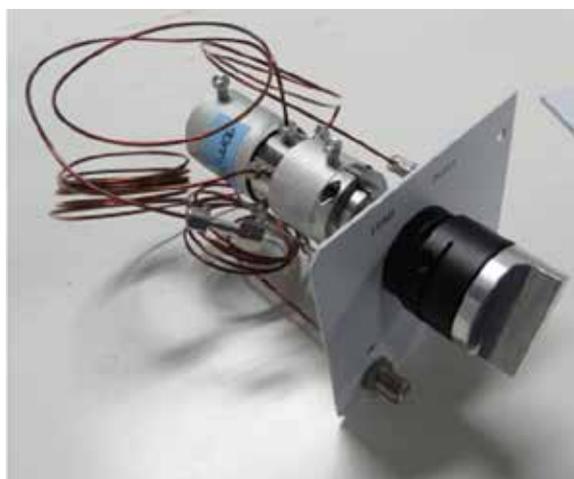
Valve Unit
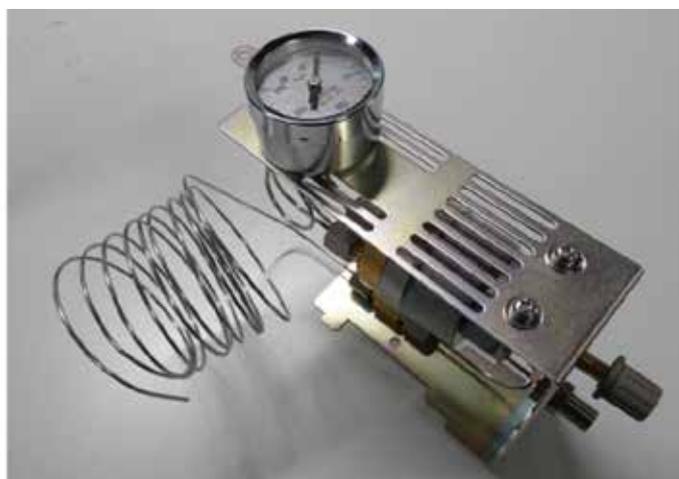
Manual Flow Controller for Purge

Fig. 1 MGS-2030 Gas Sampler

Analytical Conditions

Model	: Nexis GC-2030
Detector	: BID-2030
Gas Sampler	: MGS-2030
Column	: Line1: Rt-Msieve 5A (0.32 mm I.D. 15 m, d.f. = 30 μm)
	Line2: Rt-Q-BOND (0.32 mm I.D. 30 m, d.f. = 10 μm)
Column Temperature	: 40 °C (3 min) - 40 °C /min - 200 °C (2 min) Total 9 min
Injection Mode	: Split 1 : 10
Purge Gas	: 3 mL/min (He)
Carrier Gas Controller	: Pressure (He)
Pressure Program	: 114 kPa (5 min) - 100 kPa/min - 200 kPa (3.14 min) Total 9 min
Detector Temperature	: 280 C
Discharge Gas	: 50 mL/min
Injection Volume	: 1 mL

Nexis GC-2030

The Nexis GC-2030, Shimadzu's premier gas chromatograph, offers a modern approach to a classic chromatographic technique. Designed with the user in mind, new software and self-diagnosis features enable high-throughput analysis and maximize instrument uptime. The Nexis GC-2030 offers world-class sensitivity over a wide range of applications, with different system configurations available for flexible quantitative and qualitative analysis.

Click [here](#) to know more.

Analytical Data

Specific columns are required for full separation of inorganic gases and light hydrocarbons, and it is sometimes difficult to achieve using only one column. With Shimadzu's dual capillary column system, constructed using two detectors and two columns, faster separation with higher resolution can be achieved in the analysis compared to single-column methods.

Line 1   Rt-Msieve5A Column

1: Hydrogen
2: Oxygen
3: Nitrogen
4: Methane
5: Carbon monoxide
6: Air + Carbon monoxide
7: Methane
8: Carbon dioxide
9: Ethylene
10: Acetylene
11: Ethane
12: Water

Line 2   Rt-Q-BOND Column

Fig. 2 Chromatogram for 5 ppm Mixed Gas* * Helium balance
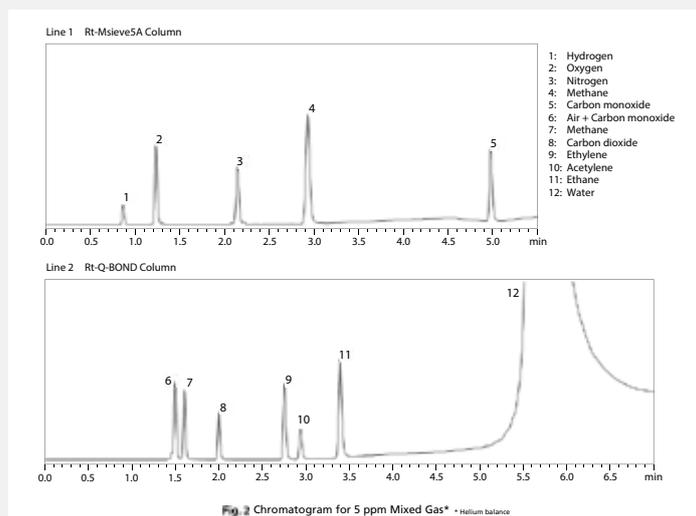
Table 2 Repeatability of Area Values (μV × sec) for Each Component

	1	2	3	4	5	6	Ave.	RSD%
Hydrogen	3996	4010	4040	4052	4096	4105	4050	1.10
Oxygen	15036	14983	15023	14973	15009	15067	15015	0.23
Nitrogen	17021	16490	16510	16472	16566	16589	16608	1.25
Methane	35142	35412	35561	35625	35784	35970	35582	0.81
Carbon monoxide	17143	17237	17330	17371	17441	17499	17337	0.76
Carbon dioxide	25817	25812	25829	25779	25925	26010	25862	0.34
Ethylene	49433	49439	49527	49481	49714	49833	49571	0.33
Acetylene	37416	37436	37446	37440	37604	37717	37510	0.33
Ethane	67092	67187	67263	67357	67579	67701	67363	0.35

Analysis of Gases Generated by the Splitting of Water Using a Photocatalyst (GC-PDD)

In splitting of water using a photocatalyst, high-sensitivity measurements of H$_2$ and O$_2$ generated must be performed to evaluate the catalyst efficiency. The gases generated inside the reaction chamber are sampled automatically to avoid contact with the atmospheric air, and then measured at high sensitivity using Pulsed Discharge Detector (PDD). Introduced here is an analysis system combining the GC-2014C gas chromatograph, which is equipped with a PDD, with an automatic sampling line.

GC-2014C

User-friendly with high cost-performance, the GC-2014C gas chromatograph is an excellent option for routine analysis. It offers great flexibility with support for both packed and capillary columns and includes a self-diagnosis function to prevent downtime and maximize lab efficiency.

Analytical Data

Flow Channel Configuration

The system's flow channels are shown in the figures below (a and b). The inside of the measurement tube is evacuated using a pump. The sample gas is then aspirated from inside the reaction chamber into the measurement tube through the operation of a solenoid valve (a). Next, 6-way valve 2 switches over, and the sample gas in the measurement tube is injected into the analysis column. After which, the gas is measured by PDD (b). All of the operations, from sampling to measurement, are performed automatically. In addition, measurements can be performed with only a few mL of sample gas.

H$_2$: 0.13 ppm
O$_2$: 0.23 ppm
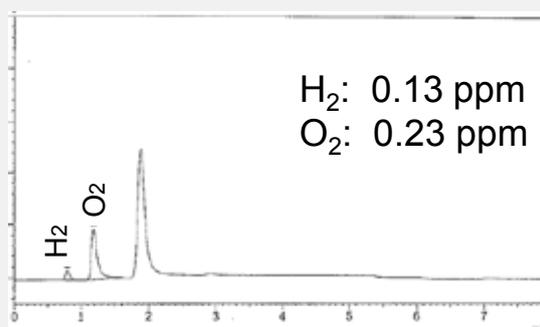
PDD Analysis Data from Automatic Sampling (Diluted Standard Gases)

(a) Sampling into the Measurement Tube

(b) Injection into the Analysis Column
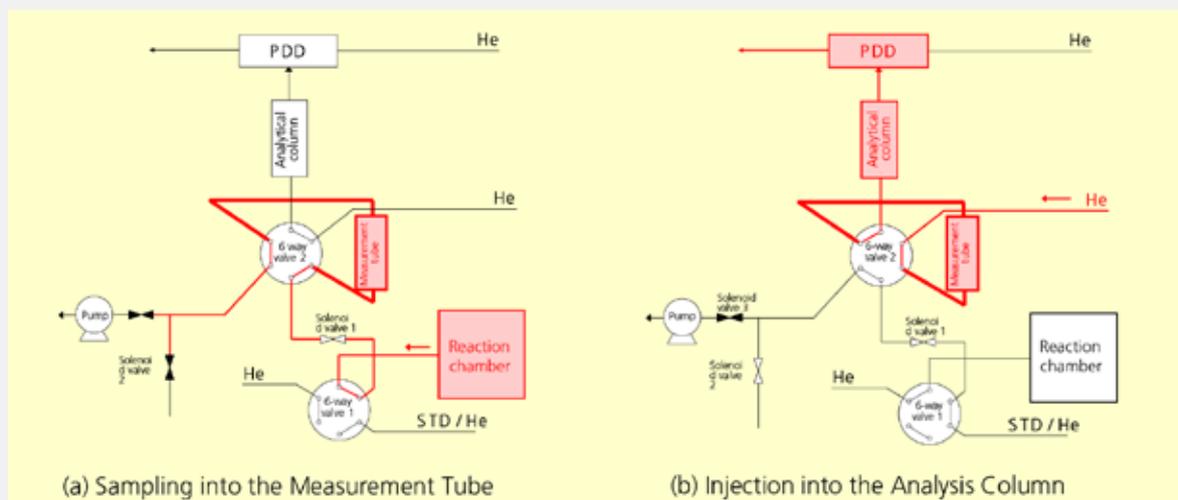
Other Analysis Systems

Shimadzu can provide the optimal system to suit a variety of requirements.

- Analysis of trace impurities in inorganic gases
- Analysis of trace components in automotive exhaust
- Analysis of trace quantities of ethylene oxide in air
- Structural analysis of liquefied natural gas (LNG)
- Analysis of trace quantities of ethylene generated by fruits and vegetables
- Analysis of trace quantities of N_2O in soil and air samples
- Analysis of trace impurities in ethylene and propylene

Analysis of Permanent Gases and Alcohols Generated from Water Splitting Reactions (GC-TCD & MTN-FID)

This method is for determining the gas composition described in the compound table below. It uses a dedicated gas chromatographic system which is configured with an automatic sampling and back-flushing technique with multiple columns. Ranges can be varied by changing the size of the loop.

No.	Name of Compound	Concentration Range	
		Low Conc.	High Conc.
1	H_2	0.01%	5%
2	N_2	0.01%	5%
3	CH_4	1 ppm	500 ppm
4	CO	1 ppm	500 ppm
5	CO_2	1 ppm	500 ppm
6	C_2H_6	0.01%	5%
7	Methanol	0.1 ppm	100 ppm
8	Ethanol	0.1 ppm	100 ppm
9	Isopropanol	0.1 ppm	100 ppm
10	1-Propanol	0.1 ppm	100 ppm

GC-2010 Pro

The GC-2010 Pro represents a new generation technology in routine GC analysis. Fast oven heating and cooling reduce the analysis time and allow high sample throughput. Based on **high-end GC** technology, it combines easy operation with efficient analysis while achieving excellence in sensitivity and precision.

Click here to know more.

Analytical Data

Method was initially optimized to achieve the desired separation of methanol, ethanol, isopropanol and 1-propanol.
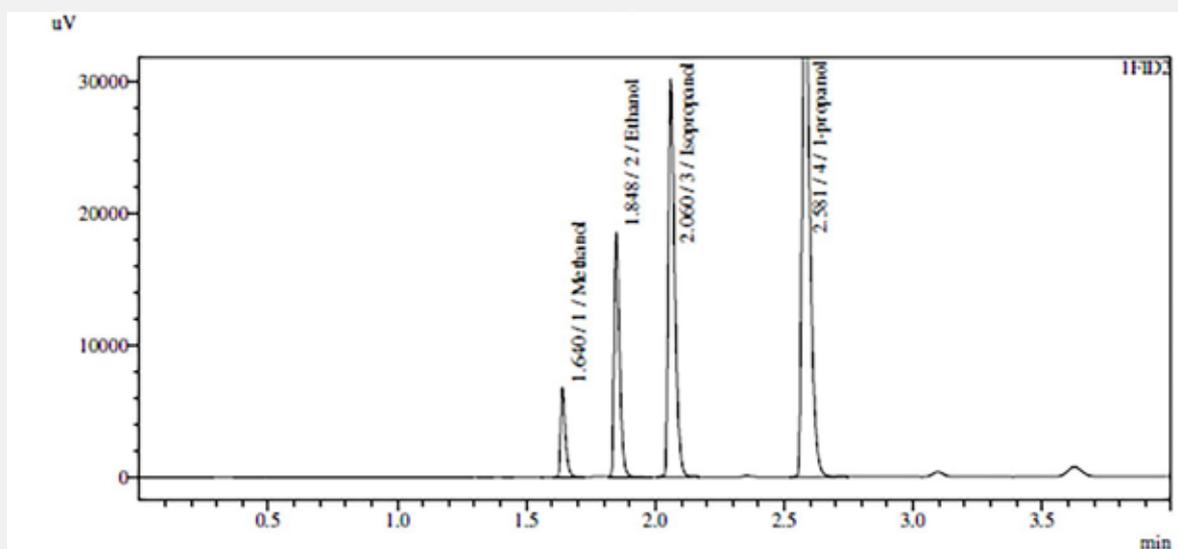
FID2

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	1.640	8870	6644	99.279	ppm		Methanol
2	1.848	27464	18041	100.197	ppm	V	Ethanol
3	2.060	52403	29879	99.890	ppm		Isopropanol
4	2.581	81110	37286	99.879	ppm		I-propanol
Total		169847	91850				

Sample analysis result (Photocatalytic reaction)
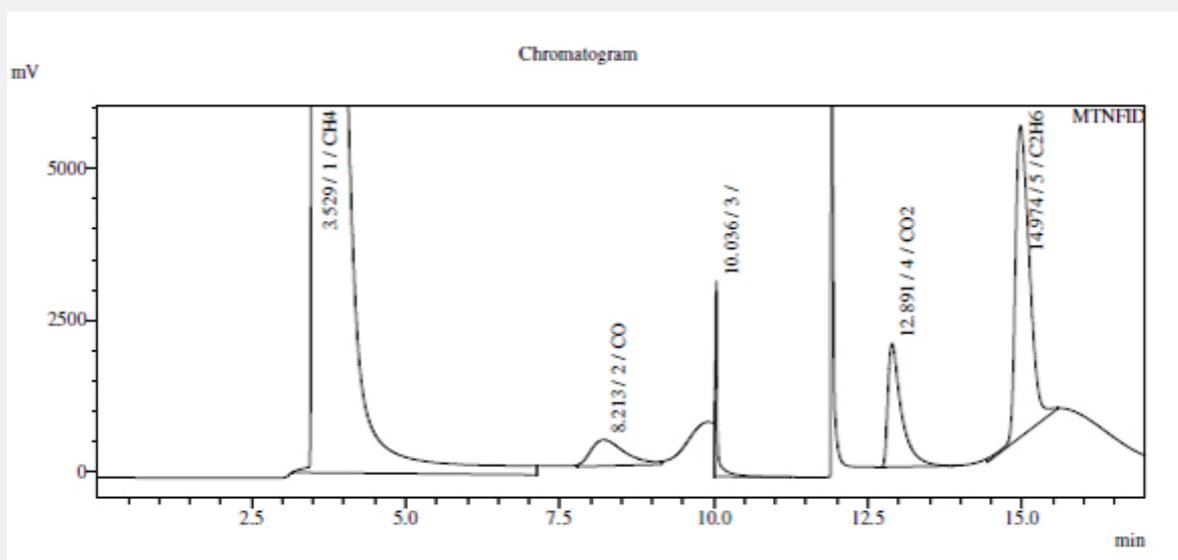
Analytical Data
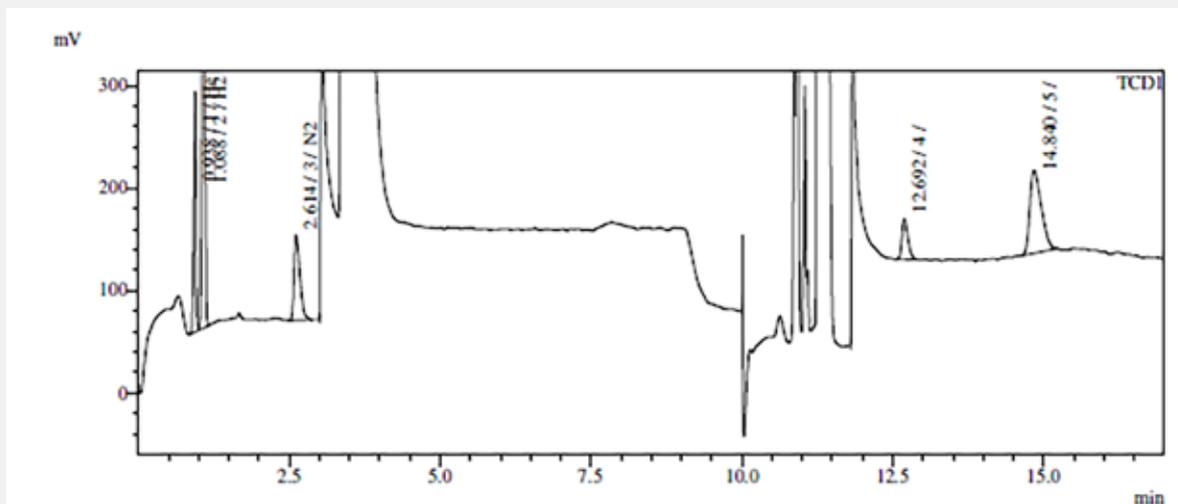
Peak Table

MTNFID

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.529	578626757	18351649	83.490	%		CH_4
2	8.213	16763794	432417	0.962	%	M	CO
3	10.036	8410848	3131909	0.000			
4	12.891	31194249	2039886	1.894	%	S	CO_2
5	14.974	81828397	5150999	3.002	%	M	C_2H_6
Total		716824044	29106859				

TCDI

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	0.938	606184	232606	0.888	%		He
2	1.088	2149742	773380	1.978	%	V	H_2
3	2.614	565793	82931	3.955	%		N_2
4	12.692	282285	39696	0.000			
5	14.840	1078450	80936	0.000			
Total		4682454	1209548				

Confirmation of Reaction Mechanism Using $^{13}CO_2$ (GC-MS)

The photochemical CO_2 reduction reaction using a photocatalyst generates CO as a reaction product. It is necessary to confirm whether the CO was produced from the reaction, as predicted, or originated from other sources. The occurrence of an expected reaction can be confirmed by using isotope-labeled $^{13}CO_2$ and then measure the resulting ^{13}CO using GC-MS. This example describe ^{13}CO measurements using a GC-MS system.

Analytical Conditions

GC-MS : GCMS-QP Series
Column : RT®-Msieve 5A (30 mL, 0.32 mm I.D., df = 30 µm, RESTEK P/N 19722) +
Rtx®-1 (5 m × 0.25 mm I.D., df = 0.5 µm, particle trap)

[GC]
Injection Unit Temperature : 200 °C
Column Oven Temperature : 35 °C (2 min) $\longrightarrow$ 10 °C /min) $\longrightarrow$ 150 °C (5 min)
Injection Mode : Split (50:1)
Control Mode : Pressure (100 kPa)
Carrier Gas : Helium
Injection Volume : 100 µL (injected using a gas-tight syringe)

[MS]
Interface Temperature : 200 °C
Ion source Temperature : 200 °C
Measurement Mode : Scan
Measurement Range : m/z 10 to 100
Event Time : 0.3 sec
Ionization Method : EI
Ionization Voltage : 70 eV
Emission Current : 150 µA

GCMS-QP2020 NX Ultra Gas Chromatograph Mass Spectrometer

The Shimadzu single quadrupole GCMS-QP2020 NX gas chromatograph-mass spectrometer (GC-MS) not only boasts the best performance in its class, but also the highest efficiency. This new high-end single-quad GCMS excels in both ease-of-use and robustness. The role of high-performance analytical instruments is expanding in areas as diverse as environmental pollution monitoring, forensics and material science. Whatever your field, the efficient and reliable GCMS-QP2020 NX is tailored to meet the needs of your laboratory.

Analytical Data

A	B
Using regular CO_2	Using $^{13}CO_2$ (^{13}C 99%)
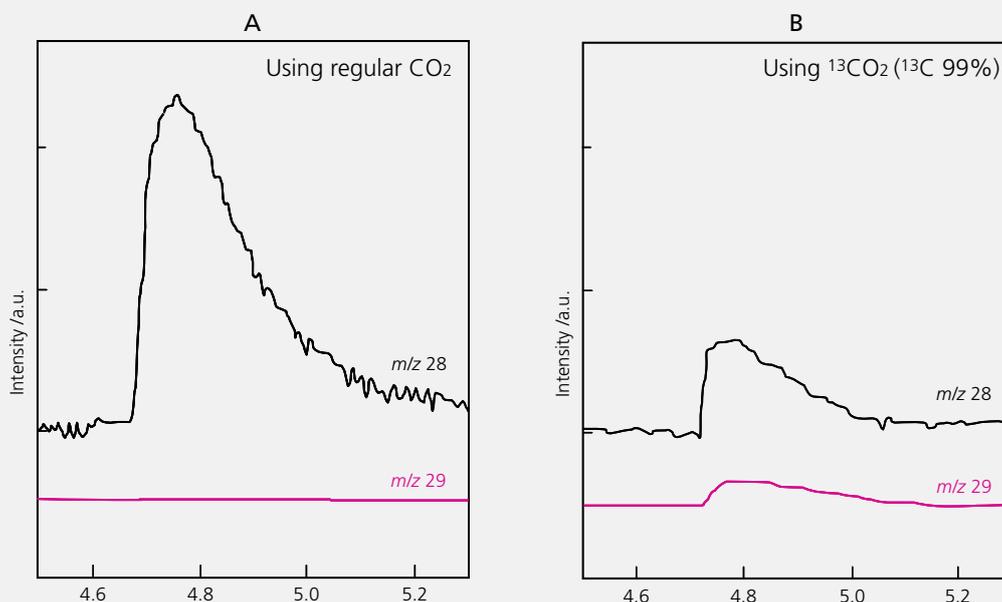
Fig. 1 Extracted Ion Chromatogram from Measuring Photocatalyst Reaction Products in Gas Phase Sample
(A) Experiment using regular CO_2 (B) Experiment using $^{13}CO_2$

A is an extracted ion chromatogram of CO obtained with an experimental system using unlabeled CO_2 (methanol solvent), whereas B was obtained using $^{13}CO_2$ (methanol solvent). B shows a peak at m/z 29 (^{13}CO), but it also shows a peak at m/z 28 (CO). Therefore, it indicates that the CO generated from CO_2 in this reaction is only a portion of the total CO.

Source: Professor Osamu Ishitani, Graduate School of Science and Engineering, Tokyo Institute of Technology

Sekizawa, K; Maeda, K; Domen, K; Koike, K; Ishitani, O. J. Am. Chem. Soc., 2013, 135, 4596. Artificial Z-Scheme Constructed with a Supramolecular Metal Complex and Semiconductor for the Photocatalytic Reduction of CO2

Simultaneous Analysis of Formic Acid and Formaldehyde (HPLC-ECD & RID)

Some reaction systems using photocatalysts produce both formic acid and formaldehyde in the reaction solution. This example describes the use of Shimadzu's organic acid analysis system to analyze both formic acid and other organic acids based on the pH buffering method. Formaldehyde is also simultaneously analyzed with a differential refractive index detector.

Analytical Conditions

Column	: YMC Hydrosphere C18 (150 mm L. × 4.6 mm I.D.)
	Shim-pack SCR-102H (300 mm L. × 8.0 mm I.D.) × 2
Mobile Phase	: 5 mmol/L Perchloric acid
Flow Rate	: 0.6 mL/min
Column Temperature	: 40 °C
Reaction Reagent	: 5 mmol/L Perchloric acid
	20 mmol/L Bis-Tris
	0.1 mmol/L EDTA-4H
Flow Rate	: 0.6 mL/min
Reaction Temperature	: 40 °C
Detectors	: Electrical conductivity and reflective index
Injection Volume	: 100 μL

Nexera Series Ultra High Performance Liquid Chromatograph

Maximizing the Potential of UHPLC/HPLC Analysis

The Nexera Series is a UHPLC system that is even more advanced than the Nexera. The flexible system design achieves a true fusion between UHPLC and HPLC, which allows Nexera Series to be used for a much broader range of applications. The Nexera Series is a completely new UHPLC system that offers the highest levels of speed, sensitivity, separation, stability, and reliability.

Analytical Data

Analysis of Organic Acids Using an Electrical Conductivity Detector

Analysis of Formaldehyde and Organic Acids Using a Differential Refractive Index Detector

Peaks:
1. Formic Acid
2. Acetic Acid
3. Propionic Acid
4. Formaldehyde
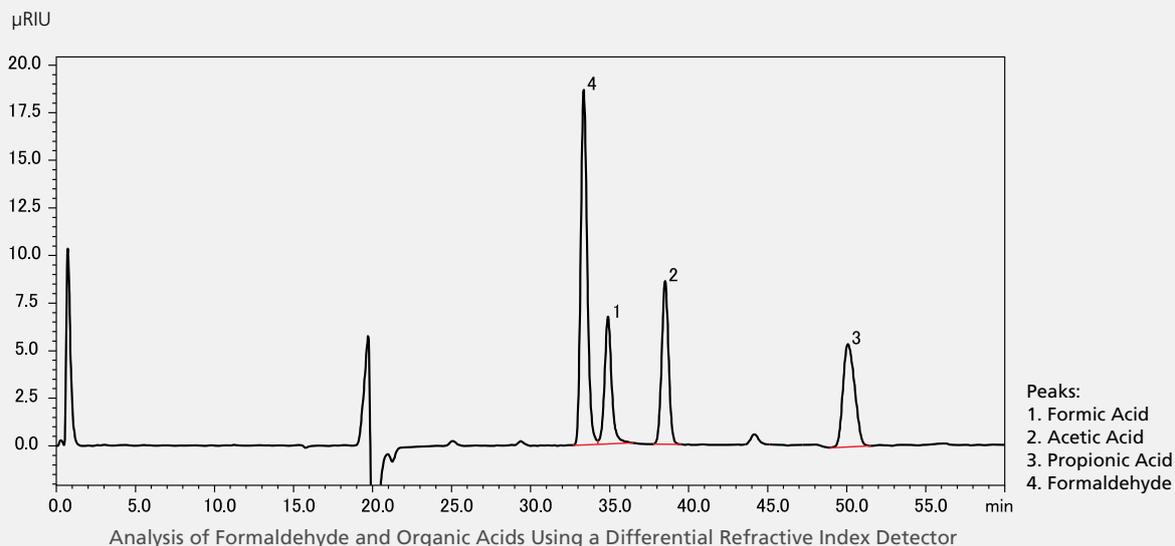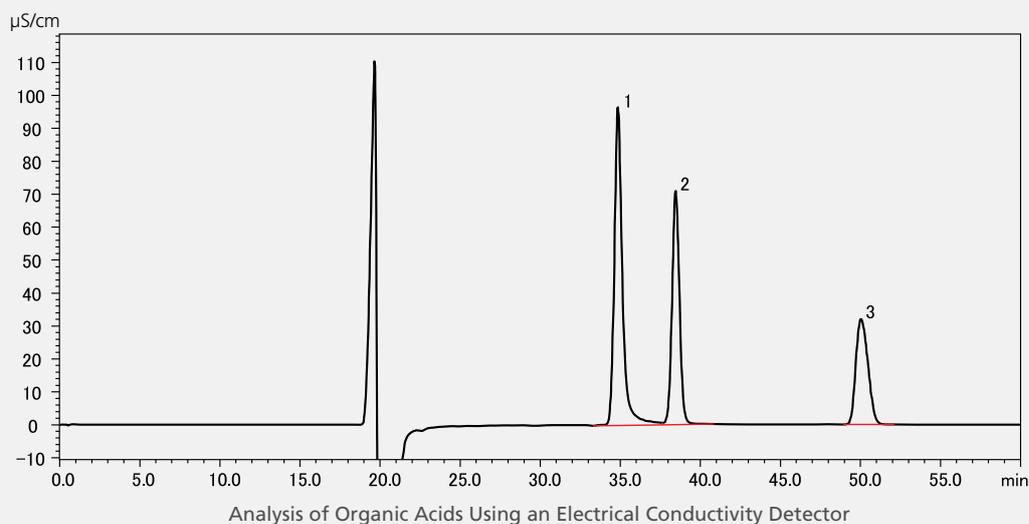
Shimadzu's organic acid analysis system is often used to analyze organic acids based on the pH buffering method, which offers superior separation and selectivity. However, the Shim-pack SCR-102H ion-exclusion column used with that system results in overlapping between formic acid and formaldehyde peaks. Therefore, a reversed-phase YMC Hydrosphere C18 column was added to improve separation.

In addition, because formaldehyde cannot be detected with an electrical conductivity detector, a differential refractive index detector was also connected in series.

The figures show an example of analyzing a standard sample containing a few hundred ppm of each component. Note that differential refractive index detectors are inferior to other detectors both in terms of sensitivity and selectivity.

Analysis of Hydrogen Peroxide (HPLC-ECD)

In some cases hydrogen peroxide is produced in reaction systems using photocatalysts. To analyze hydrogen peroxide it is useful to use a HPLC system equipped with an electrochemical detector (ECD). In this example, hydrogen peroxide is detected with high sensitivity in water.

Analytical Conditions

Mobile Phase	: 50 mmol/L sodium sulfate + 100 µmol/L aqueous EDTA 2Na solution
Column	: Inertsil CX (250 mm L. × 4.6 mm I.D., 5 µm)
Flow Rate	: 0.8 mL/min
Injection Volume	: 10 µL
Column Temperature	: 40 °C
Detector	: Eicom-ECD + 500 mV vs. Ag/AgCl 1.0 sec time constant, 25 °C
Standard Sample	: Hydrogen peroxide (30 % aqueous hydrogen peroxide),
	Wako Pure Chemical Industries super special grade
Concentration of Standard	
Samples for Calibration Curve	: 0.001, 0.004, 0.04, 0.4, 4 mg/L (prepared with mobile phase)

HPLC Equipped With Electrochemical Detector (ECD)

Electrochemical detectors operate based on redox reaction principles. Due to its high selectivity, it is able to detect target components with high sensitivity even in complex samples with strong matrix interferences.

Nexera Series

Analytical Data

Chromatograms

mV (x1,000)

ECD

Rt : 3.947/Area : 6588953

STD 4 mg/L

mV (x100)

ECD

Rt : 3.945/Area : 858370

STD 0.4 mg/L

mV (x10)

ECD

Rt : 3.947/Area : 92400

STD 0.04 mg/L

mV

ECD

Rt : 3.945/Area : 13679

STD 0.004 mg/L

mV

ECD

Rt : 3.944/Area : 7858

STD 0.001 mg/L

Chromatograms for Different Concentrations
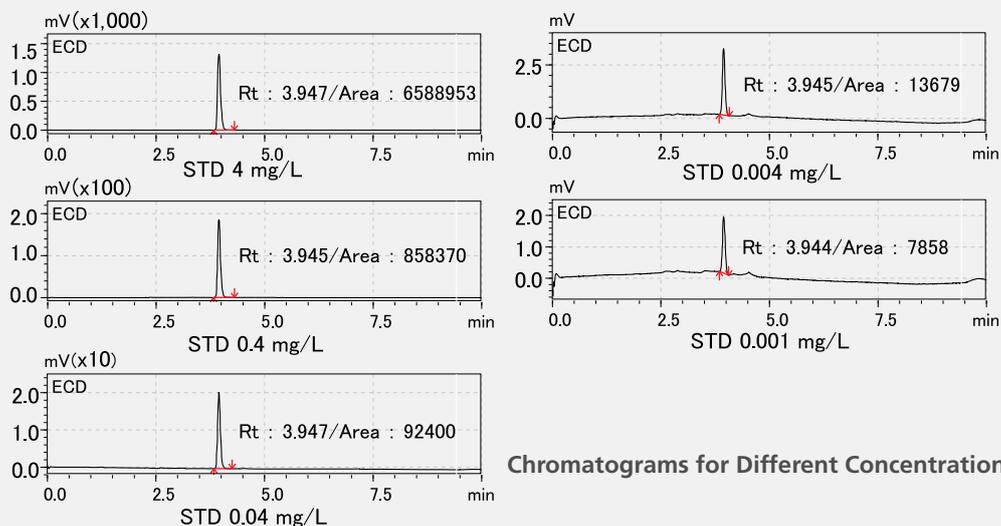
Summary of Results

Level	Conc.	Avg. Area	Area %RSD	Area 1	Area 2	Area 3
1	4	6584697	0.076	6579170	6585967	6588953
2	0.4	856046	0.399	852120	857648	858370
3	0.04	92544	0.177	92722	92509	92400
4	0.004	13715	0.265	13713	13752	13679
5	0.001	7873	0.324	7858	7902	7859

Calibration Curve

Area
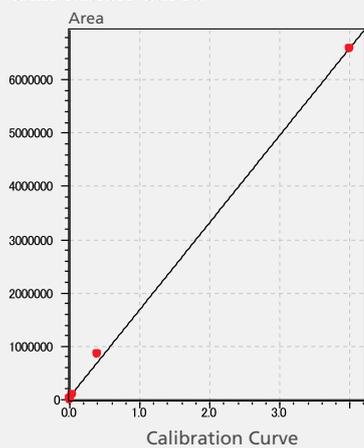
Calibration Curve Information
Y = aX + b
a = 2.18074e+006
b = 52520.7
R^2 = 0.9991648
R = 0.9995823

External standard method
Calibration curve: Straight line
Intercept at origin: No
Weighted: No

Calibration Curve

mV
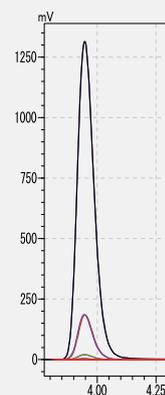
Chromatograms for Different Concentrations
(Overlaid)

Hydrogen peroxide was measured with high sensitivity in water at µg/L level concentrations. The results showed good linearity and reproducibility.

Light Irradiation In-Situ Measurement of Semiconductor Photocatalyst (SPM)

In addition to observing the morphology of the surface at nanoscale level, scanning probe microscopes (SPM) can also be used to acquire various information about the properties of the surface, such as phase, magnetic force, and viscoelasticity. In this example, the electrical potential on a surface irradiated with light was measured to determine the excitation level of a photocatalyst.

Measurement Conditions

Instruments   : SPM-9700 and light irradiation unit (top surface irradiation)
Atmosphere   : Atmospheric air
Scan speed   : 0.3 Hz
Pixels   : 256 × 256
Mode   : KFM
UV exposure   : Ozone-free Mercury-Xenon lamp, 300 to 450 nm

SPM-9700 Light Irradiation-Scanning Probe Microscope System

SPM-9700

Light Irradiation-Scanning Probe Microscope System allows the observation of surface shapes and the measurement of the surface properties by illuminating the surface with light. Because it allows performing in-situ measurements during illumination of surface, it can be used to analyze sample that is absorbing light, such as measuring the photocatalyst excitation status or electrical generation status of solar cells. Therefore, it is ideal for monitoring and evaluating changes in sample status in response to photoirradiation.

Optical Fiber

Light Irradiation Unit (Top Surface)

Optical fiber is routed to the sample surface to illuminate it with light from above.

Light Source

Sample Bottom Surface Laser Illumination Kit (Bottom Surface)

Optical fiber is routed to the sample surface to illuminate it with light from above.

Measurement Data

Surface Potential Image

UV irradiation

Surface potential changed significantly by UV irradiation.
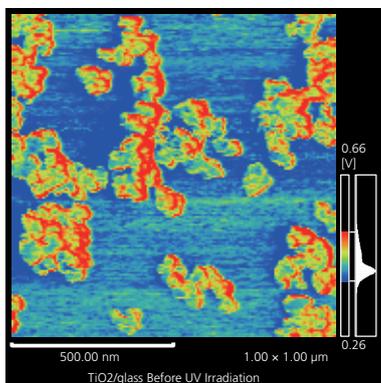
Surface Potential Image Before UV Irradiation
200 mV Average Difference in Potential Between
Glass Substrate and Catalyst Particles
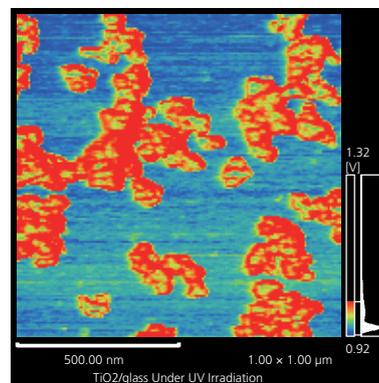
Surface Potential Image Under UV Irradiation
330 mV Average Difference in Potential Between
Glass Substrate and Catalyst Particles

AFM Profile Image

UV irradiation

The profile was not changed by UV Irratiation.
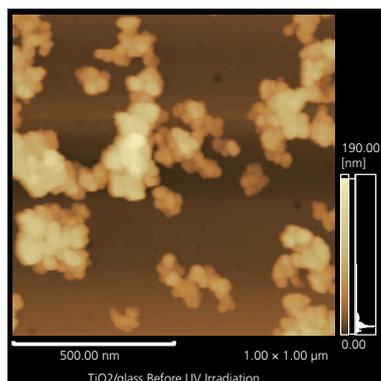
AFM Profile Image Before UV Irradiation
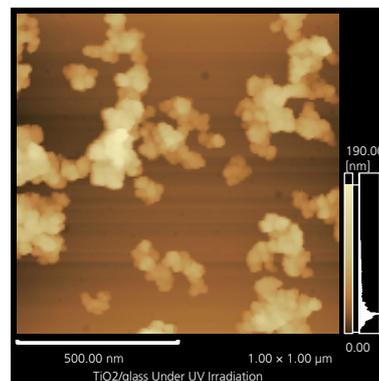
AFM Profile Image Under UV Irradiation

Platinum-supported titanium (TiO_2) microparticles used as semiconductor catalysts were secured to a glass substrate and then the surface potential and shape were observed using a scanning probe microscope (SPM).

The left image was obtained in atmospheric air, whereas the right image was obtained from the identical location illuminated with UV light from above.

In the atomic force microscope (AFM) 3D contour images (lower left and right), the shape of the catalyst particles was not change by UV irradiation.

However, the surface potential images (upper left and right) indicate that the surface potential of the catalyst particles increases by an average of 130 mV after exposure to UV light, which was a reversible change. This indicates that charge separation occurs at the catalyst surface by photoirradiation.

Sample source: Associate Professor Kazuhiko Maeda, Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology

Band Gap Measurement of Titanium Oxide (UV)

Photocatalysts provide catalytic effects when they absorb light and become excited. Because each photocatalyst has a characteristic band gap, they are excited in different wavelength regions. Since UV-visible absorption spectra are used to confirm the excitation wavelengths, they serve as the most fundamental of tools for evaluating photocatalysts. In this example, the band gap of titanium oxide was measured using a UV spectrophotometer.

Analytical Conditions

Instruments Used   : UV-2600i UV-VIS Spectrophotometer
                                               ISR-2600 Plus Integrating Sphere Attachment
Measurement Wavelength Range   : 200 to 1400 nm
Scan Speed   : Medium
Sampling Pitch   : 1.0 nm
Photometric Value   : Reflectance
Slit Width   : 5 nm
Detector Switchover Wavelength   : 830 nm

Titanium oxide, which is a material typically used in photocatalysts, has three types of crystal structures— anatase, rutile, and brookite forms. Each type has different density, refractive index, and other properties.

The band gap was determined via measuring the diffuse reflectance for titanium oxide powder in both anatase and rutile phase, which are the most commonly used types for industrial applications.

UV-2600i UV-VIS Spectrophotometer

• Featuring a compact size and a proprietary Lo-Ray-Ligh grade diffraction grating, the UV-2600i achieves especially high efficiency and low stray light levels.
• The ISR-2600 Plus integrating sphere unit includes two detectors, a photomultiplier tube and InGaAs detector, for high sensitivity measurement capability over a wavelength range from 220 to 1400 nm.
• Combination of the UV-2600i and ISR-2600 Plus, which allows the measurement of wavelengths ranging from UV to near infrared, is ideal for evaluating the wavelengths absorbed by photocatalysts.

UV-2600i + ISR-2600Plus

Analytical Data

Diffuse Reflectance Spectra of Titanium Oxide
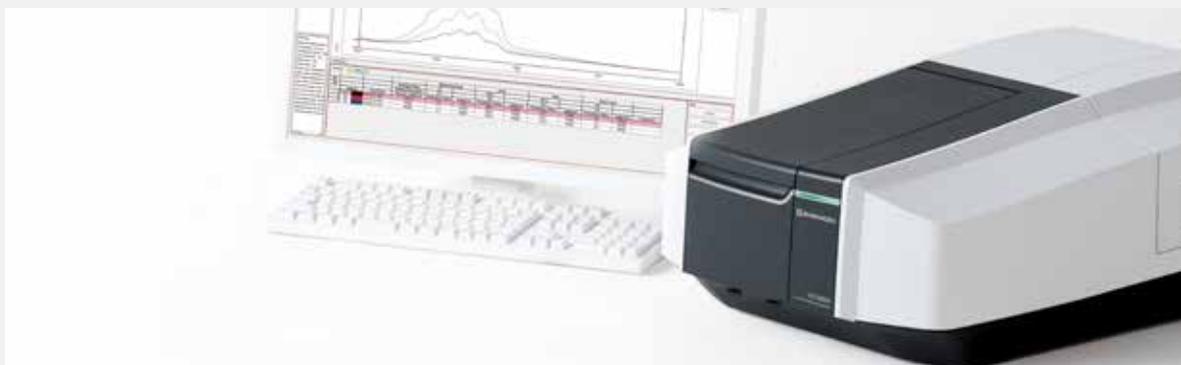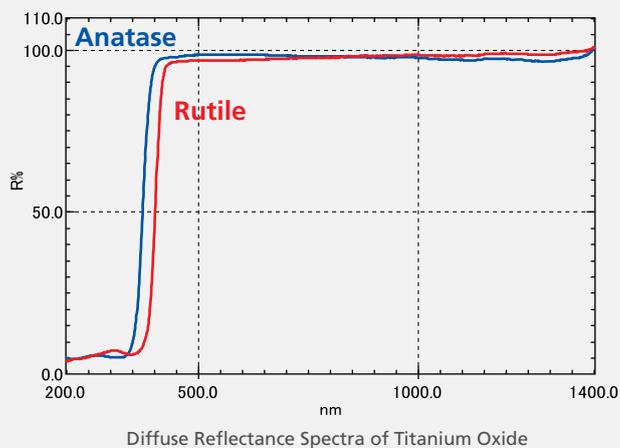
Excel Macro Program for Calculating Band Gap
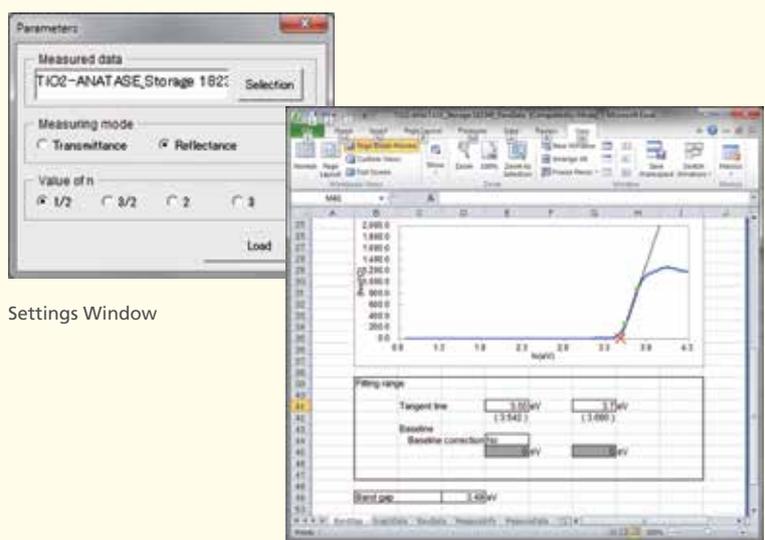
Settings Window

Calculation Results Window

Band Gap Calculation Results
Rutile: 3.20 eV
Anatase: 3.49 eV

The band gap was determined from the diffuse reflectance spectra. The Band Gap Calculation Excel Macro allows straightforward calculation by loading spectral data, selecting [Measuring mode (Transmittance/Reflectance)] and [Value of n] (type of transition process), and then specifying the range that can be approximated as a straight line near the inflection point as the tangent line. This makes it easy to determine the band gap value using a Tauc plot.

Measurement of Trace Semiconductor Photocatalyst Powder (XRD)

Semiconductor photocatalysts such as metal oxides and nitrides are identified, qualified, or have their crystallinity evaluated using X-ray diffractometers (XRD). XRD results show diffraction patterns that are plotted with diffraction angle on the horizontal axis and diffraction intensity on the vertical axis. These patterns can then be compared to the database for identification and qualification. However, sufficiently large quantity of sample is generally required for flat surface measurement to obtain accurate diffraction pattern results. Shimadzu's polycapillary parallel-beam optical system in XRD helps to overcome this obstacle by enabling high measurement sensitivity and precision even with small sample quantity. In this example, multiple semiconductor photocatalysts were measured and compared.

Measurement Conditions

XRD was used to measure $KCa_2Nb_3O_{10}$, which is a layered ion-exchange material comprising of calcium niobate perovskite layers and potassium ion layers, used as a semiconductor photocatalyst. 5.6 mg of the powder sample was placed on the non-reflective sample plate for measurement.

Item	Polycapillary Optical System	Focused Beam Optical System
Instruments	XRD-7000	XRD-7000
Goniometer Radius	200 mm	200 mm
X-Ray Source	LFF Cu tube + polycapillary	LFF Cu tube
Tube Voltage/Current	40 kV / 40 mA	40 kV / 40 mA
Anti-Scattering Plate Height	4 mm	None
Slit	None	DS 1 deg., SS 1 deg., RS 0.3 mm
Monochromator	Yes	Yes
Stage	Standard sample stand	Standard sample stand
Scan Range	5 to 35 deg	5 to 35 deg
Scan Step Size	0.02 deg	0.02 deg
Scan Speed	2 deg/min	2 deg/min
Integration Time	0.6 sec/step	0.6 sec/step

Anti-scattering plate (polycapillary optics system only)

Sample (5.6 mg)

Non-reflective sample plate

Powder Sample on
Non-Reflective Sample Plate
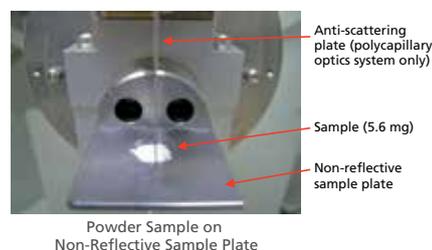
XRD Polycapillary Optics System

XRD-7000

0.22 degree angle of divergence

30 % take-out efficiency

Output beam 10 × 10 mm

X-ray tube

Unit comprising hundreds of thousands of fibers
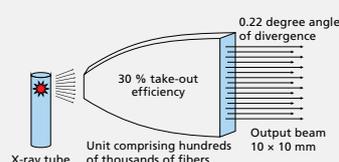
Polycapillary Parallel Beam Optics System
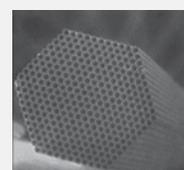
SEM Image

Polycapillaries are multiple narrow glass tubes used to guide X-rays. These capillary tubes guide the X-rays emitted from a point-source at a very high solid angle into parallel beams at the output port on the opposite end. Compared to a standard optics system (Bragg–Brentano method), this system utilizes the X-rays emitted from the X-ray tube more efficiently, which allows achieving higher diffracted X-ray intensities. Furthermore, because the optical system uses parallel beams, the diffraction angle remains unchanged even if the sample measurement surface shift positions. Consequently, it resolves problems that standard optics systems can have with separation of diffracted rays or angle shifting. It also allows measuring small quantities of powder samples without a flat surface or curved samples with high sensitivity and precision.

Analytical Data
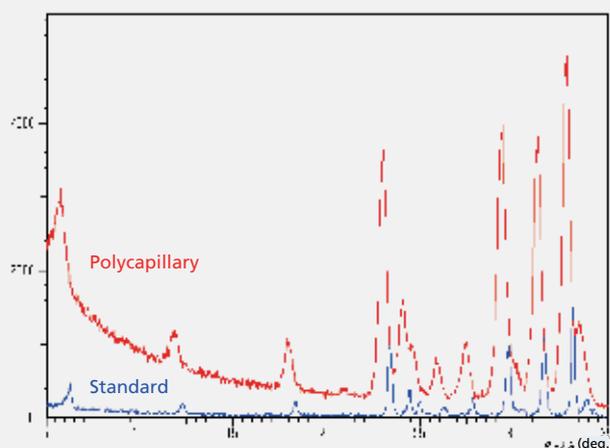
Diffraction Pattern from Polycapillary and Focused Beam Optical Systems

The figure shows results from using polycapillary and standard optics systems to measure KCa$_2$Nb$_3$O$_{10}$ powder synthesized by baking at 1423 K for 10 hours using the SSR (solid state reaction) method. The polycapillary optics system resulted in about three times higher intensity levels than the standard optics system, where the error in 2θ due to sample status (height) is assumed to be small.
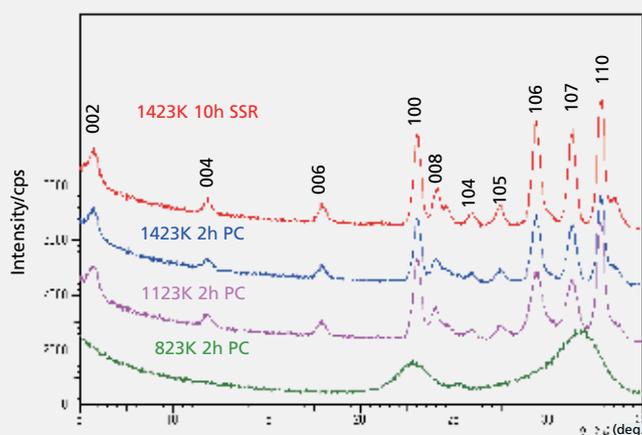
Diffraction Patterns for KCa₂Nb₃O₁₀ Powder Samples Prepared Using Different Synthesis Parameters

The figure shows results from using the polycapillary optics system to measure KCa$_2$Nb$_3$O$_{10}$ powder samples prepared using four different synthesis conditions. At 823 K, the peaks are much broader than the other three samples, which indicates low crystallinity. Based on the measurement results for the samples synthesized using the PC (polymerized complex) method at 1123 K and 1423 K for 2 hours respectively, it is found that higher temperature resulted in a smaller FWHM value, which is presumably due to higher crystallinity. The results also showed a difference in FWHM between 1423 K 2-hour PC and 1423 K 10-hour SSR methods, which confirms that the differences in synthesis parameters affected the crystallinity of the structure.

Evaluation of Photoreaction Quantum Yield of Supermolecular Complex (QYM)

The photoreaction quantum yield is one performance indicator for photochemical reactions or photocatalysts. It is the ratio between the number of reaction product molecules from a photochemical reaction (or alternatively the reduction in number of molecules in the substrate) and the number of photons absorbed. Conventionally, chemical actinometers based on substances with known quantum yield, such as iron oxalate, were used. However, this method requires performing experiments for long periods in a dark room by skilled personnel and also requires repeating the experiments if irradiation parameters are changed. It also has other problems, such as not being able to compensate for changes in light absorption by samples due to reactions. Therefore, we developed the QYM-01 photoreaction quantum yield evaluation system which permits accurate and easy quantitation measurements of absorbed photons in conjunction with Professor Osamu Ishitani, Graduate School of Science and Engineering, Tokyo Institute of Technology. In this example, we confirmed how results from the new system correlate with the conventional method.

UV-2600i UV-VIS Spectrophotometer

QYM-01
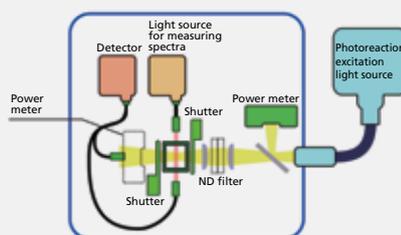
QYM-01 Overview

Allows continuous measurement of UV-VIS absorption spectra during photoreactions
Capable of sample cell temperature control, sample solution stirring, and automatic excitation light shuttering

Accurately and easily measure of the number of photons absorbed by sample solutions.

Simultaneously measure changes in UV-VIS absorption spectra in photoreaction solutions.

Features

Accommodates a wide range of photoreaction excitation light conditions (wavelength and light level)

• Allows changing the excitation wavelength and measuring the number of absorbed photons anywhere between 250 nm to 800 nm.
• The excitation light level can be set by adjusting the number of photons irradiated.

Easy Measurements

• Includes a built-in spectrometer which has been calibrated using a NIST (National Institute of Standards and Technology)-traceable actinometer of which absolute light quantity is managed.
• Eliminates the need for calibration using a chemical actinometer.
• The excitation light level and wavelength switching are controlled via computer software.
• Includes simple computer software. Measures the number of photons using optimal measurement parameters.

Supports accurate measurements

• Simultaneous UV-VIS absorption spectra measurement capability, a correction function for changes in the light level of the excitation light source, and other features that ensure the accurate measurement of the number of absorbed photons.
• Displays the photo count in real time. Allows the confirming of the current measurement status.

The QYM-01 was developed jointly with Ishitani–Maeda Laboratory, Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology.

Analytical Data

Comparison of QYM-01 and Chemical Actinometer (Iron Oxalate) by Measuring Light Intensities

The QYM-01 was verified by comparing measurements of the absorbed light intensity by the QYM-01 and a chemical actinometer. The QYM-01 was used to irradiate an aqueous potassium trioxalatoferrate (III) sample with photoreaction excitation light. Then the number of photons absorbed was determined from the amount of iron (II) produced in solutions with different irradiation periods in accordance to the relevant section in the fifth edition of "Jikken Kagaku Koza" (Series of Experimental Chemistry), published by the Chemical Society of Japan.

Experiment Conditions

	Experiment 1	Experiment 2
Excitation Light Wavelength	365 nm (Xenon lamp)	480 nm (Xenon lamp)
Sample Concentration	6 mM	150 mM
Photon Yield (value indicated in the fifth edition of "Jikken Kagaku Koza")	1.22	0.94

Experiment 1   Light Intensity Measurement Result (at 365 nm)

$y = 3.73E\text{-}07x$
$R^2 = 1.00$

$y = 3.48E\text{-}07x$
$R^2 = 1.00$

Experiment 2   Light Intensity Measurement Result (at 480 nm)

$y = 3.45E\text{-}06x$
$R^2 = 0.99$

$y = 3.25E\text{-}06x$
$R^2 = 0.98$
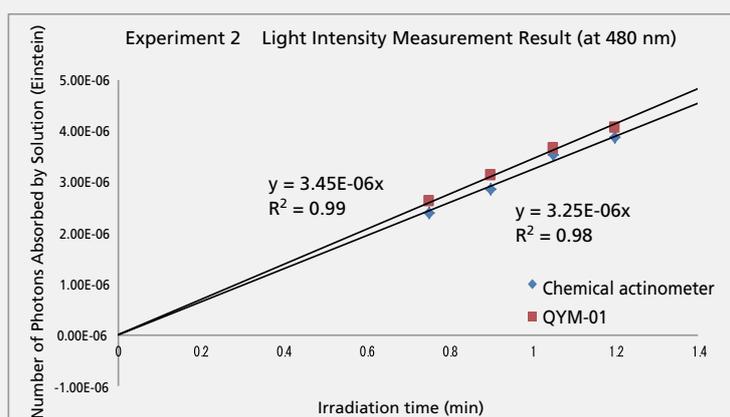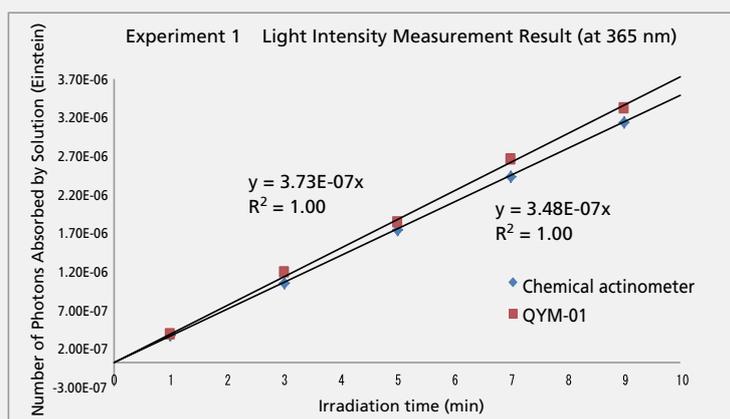
Number of Absorbed Photons

	Number of Absorbed Photons (Einstein/s)	
	Experiment 1	Experiment 2
Chemical Actinometer	5.84×10^{-9}	5.40×10^{-8}
QYM-01	6.19×10^{-9}	5.78×10^{-8}

Source: Ishitani–Maeda Laboratory, Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology.

Measurement of Quantum Yield of CO2 Reduction Reaction by Ru-Re Supramolecular Complex Photocatalyst

We measured the quantum yield of a carbon dioxide reduction reaction by a Ru-Re supramolecular complex photocatalyst. Absorbed photons were measured using the QYM-01 and the amount of carbon monoxide generated from the reduction reaction was quantitated using a gas chromatograph. The reference quantum yield reported for carbon monoxide assuming the experimental conditions used was 0.151. The current experiment resulted in a higher quantum yield of 0.16.

Experiment Conditions

Photocatalyst	Ru-Re (FPh) (From Tokyo Chemical Industry, Product No. R0100, used without purification)	
Reaction Conditions	Photocatalyst	Ru-Re (FPh) (0.3 mM)
	Donor reducing agent	BNAH (0.1 M)
	Solvent	DMF-triethanolamine (5:1 v/v solvent mixture)
	Solution volume	4 mL
	Irradiation light	480 nm xenon lamp
	Reaction vessel	Quartz cell with branch (4 polished windows) (11 mL volume, 7 mL gas phase, 4 mL liquid phase)
Operating Procedure	Transfer the prepared solution to the 4-sided quartz cell with branch using a 4-mL transfer pipette. Bubble with CO_2 for 30 minutes and then seal the cell with a septum (prepare 3). Then after irradiating with light for 1, 2, or 2.5 hours, use a gas-tight syringe to acquire 100 μL of gas from the gas phase and quantitate the CO by GC.	

CO Product Quantum Yield Using TCI Brand Ru-Re

$y = 0.1599x - 9E-07$
$R^2 = 1.00$

X-axis: Number of Photons Absorbed (Einstein)
Y-axis: Quantity of CO Produced (mol)
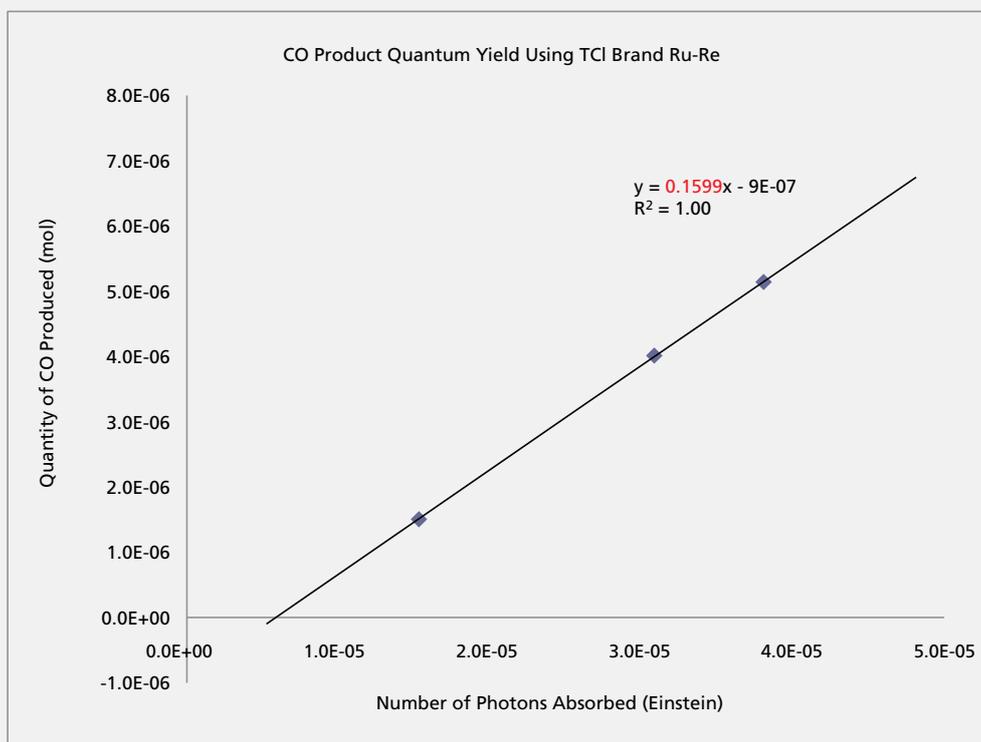
Quantum Yield Measurement Result	0.16
Reference Document	0.15

References 1) Y. Tamaki, K. Watanabe, K. Koike, H. Inoue, T. Morimoto, O. Ishitani, Faraday Discuss. 2012, 155, 115.

Source: Ishitani–Maeda Laboratory, Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology.

Particle Size Measurement of Titanium Oxide (Particle Size Analyzer)

Reactions that generate hydrogen, formic acid, or other products, in artificial photosynthesis with photocatalysts occur at the surface of the photocatalyst. Therefore, an understanding of the particle size distribution is needed for evaluating reaction efficiency and other purposes. In addition, it is also necessary to control the particle size distribution of semiconductor catalysts, which is used in self-cleaning glass, antimicrobial coatings, and other products related to preventing contamination or cleaning the environment. In this example, the photocatalyst titanium dioxide was measured using a particle size analyzer.

Analytical Data

SALD-2300

SALD-2300 Laser Diffraction Particle Size Analyzer

The SALD-2300 laser diffraction particle size analyzer is capable of measuring a very wide range of particle diameters, from 17 nm to 2500 µm. Furthermore, it can be used not only for wet-mode measurements, with powder samples dispersed in liquid, but also for dry-mode measurements of powders as they are.
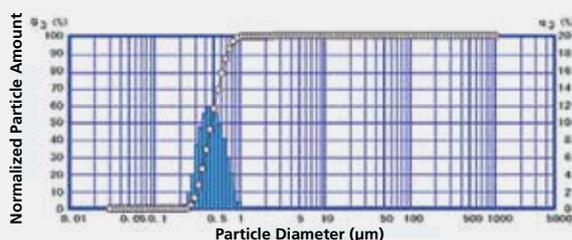
Titanium Dioxide Particle Size Measurement Results (up to 1 µm diameter particles)

IG-1000 Plus

IG-1000 Plus Single Nano Particle Size Analyzer

The IG-1000 Plus uses a new induced grating (IG) measurement principle to analyze particle diameters ranging from 0.5 nm to 200 nm.
In particular, it achieves high reproducibility when measuring particles smaller than 10 nm, which were difficult to measure using conventional dynamic light scattering method.
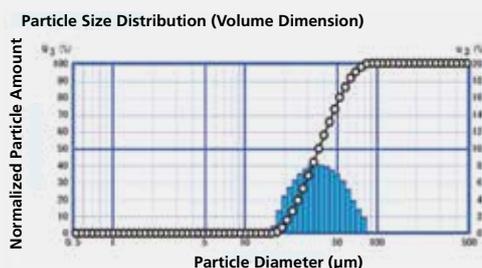
Titanium Dioxide Particle Size Measurement Results (particles with diameters in the tens of nm)

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