

Application News

No. A478

Spectrophotometric Analysis

QYM-01 Photoreaction Quantum Yield Evaluation System

The QYM-01 photoreaction quantum yield evaluation system* permits accurate and easy quantitation measurements of absorbed photons when excitation light is irradiated onto a sample. This system also permits monitoring of the UV-visible absorption spectrum of the photoreaction. The QYM-01 has a built-in spectrometer which has been calibrated using a NIST (National Institute of Standards and Technology)-traceable actinometer of which absolute light intensity is managed. The built-in spectrometer eliminates the need for further calibration using a chemical actinometer. In typical photoreaction measurements, the quantity of irradiated light as well as the measured sample absorbance may not remain constant over the course of the reaction. As the quantity of absorbed photons is dependent on these two parameters, accurate measurement of the total photons absorbed may be difficult over the course of the reaction. The QYM-01 incorporates features which monitor and correct for changes in the light source luminous intensity and changes in the ultraviolet-visible absorption, allowing for accurate measurements. The QYM-01 is the ideal system for *in situ* measurement of photochemical reactions and internal quantum yield evaluation of homogeneous photocatalysts.

* The QYM-01 photoreaction quantum yield evaluation system is a special order product which was developed in conjunction with the Ishitani/Maeda Laboratory, Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology.

1. QYM-01 Photoreaction Quantum Yield Evaluation System 1.1 Instrument Construction

Fig. 1 and 2 show a photograph and component diagram of the QYM-01, respectively. The QYM-01 comprises a photoreaction excitation light source and a measurement unit, which are both controlled by the same software.

Excitation light is irradiated onto the sample through an optical fiber from the excitation light source. This light enters the spectrum detector through a second optical fiber, permitting wavelength-dependent light measurements using a calibrated PDA detector. The excitation light wavelength and irradiation intensity can be changed by the band-pass filter of the excitation light source and the continuously variable neutral density (ND) filter, respectively. In addition, an optional ND filter can be added inside the measurement unit, further reducing the irradiation intensity to 0.5 %.

The ultraviolet-visible absorption spectrum of the sample is measured in a direction perpendicular to the optical axis of the excitation photoreaction light source. The light source used to acquire the UV-Vis spectra (xenon flash lamp) illuminates the sample with white light repeatedly for 10 ms only at each set time interval.

The light that is transmitted by the sample is then collected and transmitted via optical fiber to the detector for spectral acquisition. UV-visible absorption spectra can be automatically acquired at a maximum speed of one measurement per second.

A cell stirring accessory is incorporated to allow stirring of the sample in both excitation light irradiation measurements and UV-Vis absorption measurements. Further, a water flow system is incorporated into the system allowing for adjustment of the sample temperature during sample measurements.



Fig. 1 Exterior View of QYM-01 Photoreaction Quantum Yield Evaluation System (system appearance with MAX-303 xenon light source)

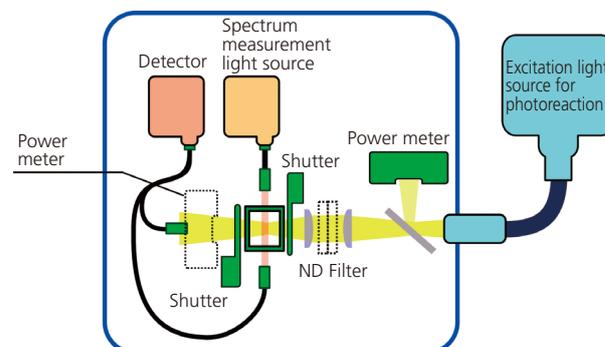


Fig. 2 Component Diagram of QYM-01

1-2. Absorbed Photon Counting Method
(Instrument Calibration, Measurement Value Calculation)

1-2-1. Instrument Calibration

Accurate determination of the number of photons absorbed requires precise wavelength information to obtain an accurate absolute light quantity value. The QYM-01 performs wavelength calibration using the emission lines of a mercury lamp. Light intensity calibration is conducted using the following method and assures that an accurate absolute light intensity is obtained.

<Relative Sensitivity Correction at Each Wavelength>

Light from 250 nm to 800 nm can be measured simultaneously using a Photodiode Array (PDA) detector. However, in PDA detectors, the detection sensitivity can vary depending on the wavelength. To compensate for this, calibration is performed using a standard light source to conduct sensitivity correction measurements between wavelengths. Light quantity evaluation is conducted at each wavelength with a standard light source, and the correlation obtained between that value and that of the spectrum measured using the light source of the instrument is used for relative sensitivity correction at each wavelength.

<Absolute Energy Calibration at the Excitation Wavelength>

The excitation light emitted from the excitation light source is measured with a power meter where the absolute light intensity is managed. The same excitation light is then introduced into the PDA spectral detector by means of an optical fiber, where measurement is conducted. Then the correlation coefficient between these two measurements (measurement by the power meter and that by the PDA detector) is determined, and used to calibrate the value measured by the PDA detector. Actually, the wavelengths of the light emitted from the excitation light source represent only a portion of the wavelengths transmitted due to the band-pass filter, which has a width of about 20 nm. Therefore, the light intensity distribution with respect to the wavelengths is recorded via the PDA detector and the number of photons at each wavelength is calculated to achieve highly accurate measurements.

1-2-2. Calculation of Number of Photons Absorbed

The amount of absorbed light intensity is determined from measurements of the irradiated excitation light intensity and the measured ultraviolet-visible absorption, and this is used to then calculate the number of absorbed photons.

Since a portion of the irradiated excitation light is transmitted rather than absorbed by the sample, the light quantity per unit time absorbed by the sample can be expressed by Equation 1. In addition, because a relationship in Equation 2 exists between the quantity of light (energy) and number of photons, the number of photons absorbed per unit time can be determined from both equations. In the actual calculation, the total number of absorbed photons is obtained by conducting integration of the number of absorbed photons at each wavelength over the irradiation time.

$$E_a = E_i \times (1 - T) \quad - 1$$

E_a : Absorption light quantity per unit time
 E_i : Irradiation light quantity per unit time
 T : Transmittance of sample

Number of photons absorbed per unit time = $E_a \times \lambda / hc - 2$
 λ : Wavelength, h : Planck's constant, c : Speed of light

$$\text{Total number of absorbed photons} = \int \int E_i(\lambda, t) \times [1 - T(\lambda, t)] \frac{\lambda}{hc} d\lambda dt \quad - 3$$

t : Time

2. Comparison with Conventional Method

One method of measuring the quantum yield of a photochemical reaction is to use a chemical actinometer. A substance of known quantum yield is irradiated with excitation light for generating the photoreaction, and the intensity of the irradiated light is determined from the reaction product. Iron oxalate is a substance that is typically used as a chemical actinometer, and by utilizing the reaction in which trivalent iron is reduced to bivalent iron through absorption of ultraviolet or visible light, the intensity of irradiated light can be determined from the quantitative value of the bivalent iron that is formed and the quantum yield of iron oxalate.

With this method, an iron oxalate chemical actinometer is used first to determine the quantity of irradiation light from the excitation light source for photoreaction, and then, a photoreaction is generated using an actual sample solution with the same irradiation conditions, making it possible to conduct photoreaction experiments under conditions in which the quantity of irradiated light is known. While this iron oxalate chemical actinometer is widely used as a standard method, it does have the following drawbacks.

- (1) As iron oxalate reacts to sunlight as well as fluorescent and other indoor light, almost all experimental operations, from sample preparation to conducting the experiment, must be conducted in a dark room, which requires a degree of proficiency to conduct accurate measurements.
- (2) Whenever the irradiation conditions, such as wavelength or light intensity, are changed, the irradiation light intensity determination must be repeated using the chemical actinometer.
- (3) When a chemical actinometer is used to determine the radiation light intensity, separate absorbance measurements with a UV-visible spectrophotometer is required to obtain the amount of light absorbed using an actual sample solution.
- (4) Changes in the absorbance of the sample solution during the photoreaction due to reaction intermediates, etc. cannot be corrected for.
- (5) Correction for the decreased light intensity resulting from extended periods of testing is not possible.
- (6) A bandpass filter is used in the excitation light source which yields a distribution of emitted wavelengths to the sample. It is not possible to correct for the wavelength distribution.

There are alternative commercial measurement devices such as power meters and silicon light meters, etc. that offer easier methods for measuring light intensity than that possible with a chemical actinometer. However, these also have the same drawbacks as those described for the chemical actinometer in items (2) – (6) listed above. Furthermore, measurement results can easily be affected by the measurement position and angle of the device.

The QYM-01, has a built-in spectrometer calibrated with an actinometer having a traceable absolute light intensity. In addition, the QYM-01 permits ultraviolet-visible absorption spectrum monitoring and light source intensity change correction, overcoming the drawbacks of the conventional method. Further, excitation light irradiation conditions, such as wavelength and light intensity, etc., are set and verified using dedicated software. For this reason, the QYM-01 allows the number of photons absorbed to be easily and accurately measured.

3. Measurement Examples

3-1. Comparative Verification of QYM-01 and Chemical Actinometer (Iron Oxalate) in Irradiation Light Intensity Measurements

In addition to comparing the results obtained using the QYM-01 and an aqueous solution of potassium iron (III) oxalate, we also determined the number of photons absorbed from the amount of iron (II) formed using a "potassium iron (III) oxalate chemical actinometer". This was accomplished by using solutions which were exposed to irradiated light over different time periods

as specified in the "Fifth Series of Experimental Chemistry."

The test results, consisting of plots of the irradiation time versus the number of absorbed photons, are shown in Fig. 3 and 4, and the experimental conditions with the corresponding number of absorbed photons per second are shown in Table 1.

These results confirm the similarity of results obtained using the QYM-01 and the iron oxalate chemical actinometer, in which the degree of difference is only 5 to 6 %.

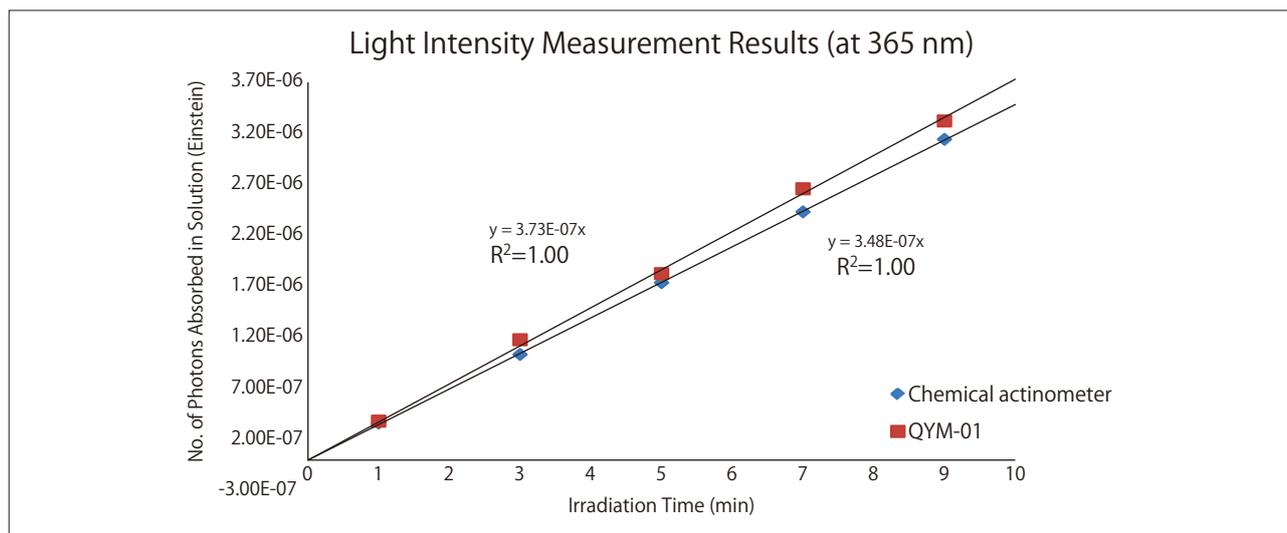


Fig. 3 Measurement Results for the Number of Absorbed Photons at 365 nm

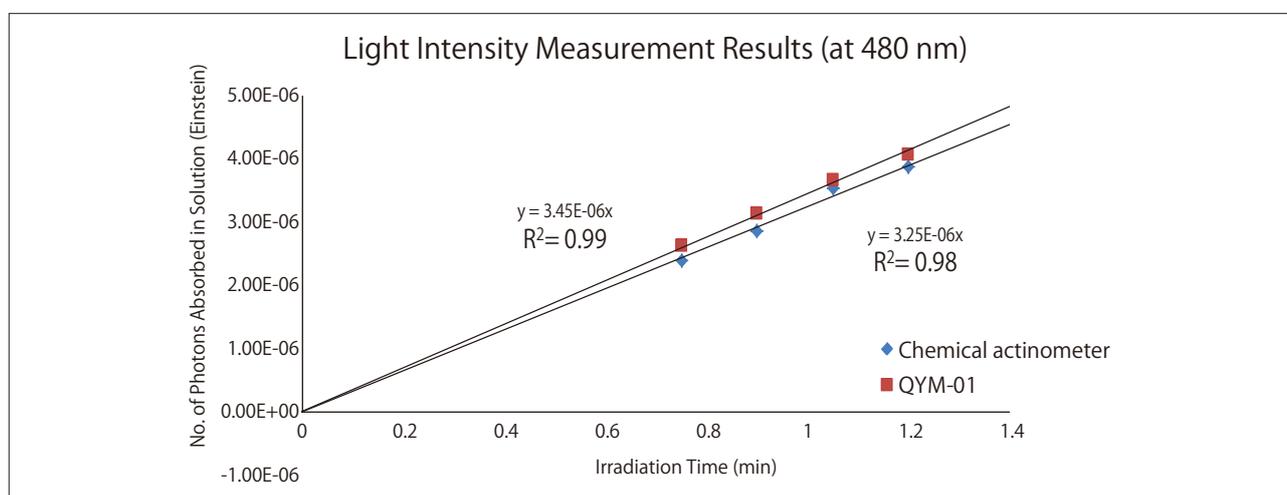


Fig. 4 Measurement Results for the Number of Absorbed Photons at 480 nm

Table 1 Experimental Conditions and Numbers of Absorbed Photons

	Experiment 1	Experiment 2
Excitation light wavelength	365 nm (Xenon lamp)	480 nm (Xenon lamp)
Sample concentration	6 mM	150 mM
Quantum yield (value listed in "Fifth Series of Experimental Chemistry")	1.22	0.94
	Absorbed Photons (Einstein/s)	
Chemical actinometer	5.84×10^{-9}	5.40×10^{-8}
QYM-01	6.19×10^{-9}	5.78×10^{-8}

3-2 Quantum Yield Measurement of CO₂ Reduction Reaction Using Ru-Re Supramolecular Complex Photocatalyst

We conducted a quantum yield measurement of a carbon dioxide reduction reaction with a Ru-Re supramolecular complex photocatalyst. After measuring the absorbed photons using the QYM-01, the quantity of carbon monoxide produced in the reduction reaction was measured using a gas chromatograph. The experimental conditions are shown in Table 2, and the absorbed number of photons and plot of carbon monoxide yield are shown in Fig. 5. The slope of the plot in Fig. 5 represents the quantum yield. Using these experimental conditions, a quantum yield of 0.16 was obtained in this experiment, which corresponded well to a previously reported quantum yield value of 0.15 for the carbon monoxide formation reaction.¹⁾

4. Conclusions

The QYM-01 photoreaction quantum yield evaluation system permits a more exact and convenient measurement method for absorbed photons than is possible with a chemical actinometer. Furthermore, with the QYM-01, it is possible to monitor the ultraviolet-visible absorption spectrum during an irradiation experiment. The QYM-01 is an ideal system for *in situ* measurements of photochemical reactions and internal quantum yield evaluations of homogeneous photocatalysts.

Acknowledgment

We offer our deep appreciation for the two types of experimental data obtained courtesy of Ishitani/Maeda Laboratory, Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology.

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

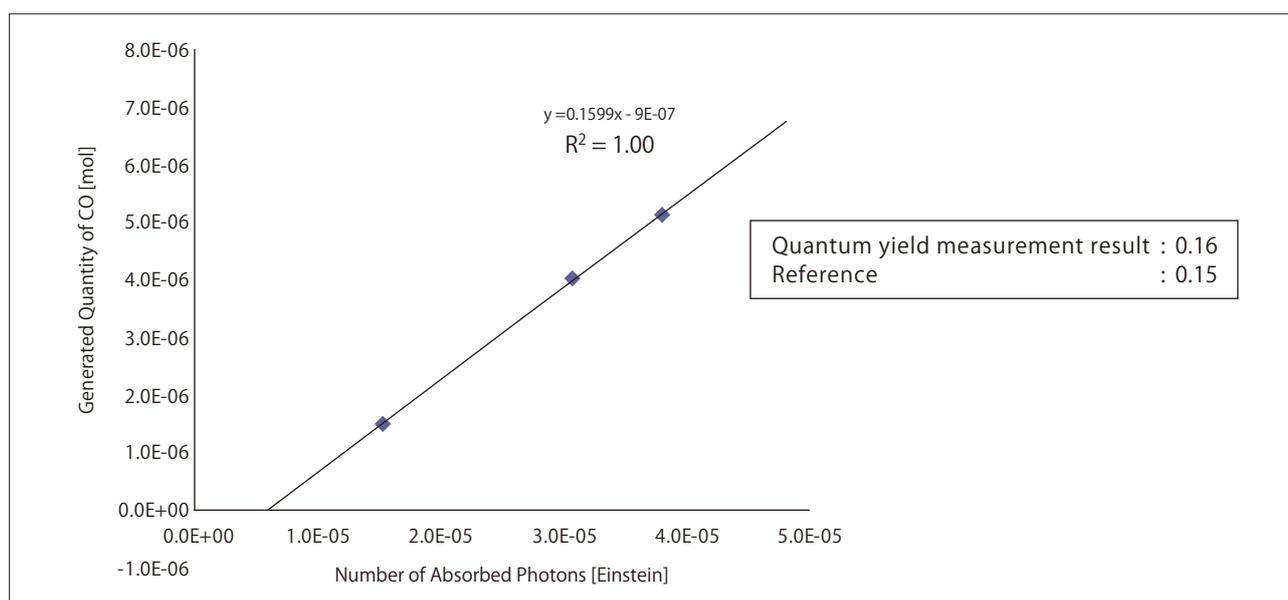


Fig. 5 Quantum Yield of CO Formation by Ru-Re Supramolecular Complex Photocatalyst

Table 2 Experimental Conditions of CO₂ Photoreduction Reaction by Ru-Re Supramolecular Complex Photocatalyst

Photocatalyst	Ru-Re (FPh) (Tokyo Chemical Industry Co., Ltd., Product No. R0100, used without further purification)	
Reaction Conditions	Catalyst	Ru-Re (FPh) (0.3 mM)
	Expendable reducing agent	BNAH (0.1 M)
	Solvent	DMF-Triethanolamine (5:1 v/v mixed solvent)
	Solution volume	4 mL
	Irradiated light	480 nm Xenon lamp
	Reaction vessel	Tetrahedral quartz cell with branch (Volume 11 mL, gas layer 7 mL, liquid layer 4 mL)
Operation Procedure	4 mL of the prepared solution was transferred to a branch-equipped tetrahedral cell, and after bubbling with CO ₂ for 30 min, it was sealed with a septum (3 were prepared). Irradiation was conducted for 1 hour, 2 hours, and 2.5 hours, and 100 μL was harvested from each of the respective gas layers with a gas-tight syringe and injected into a GC for CO quantitation.	
Reference	Y. Tamaki, K. Watanabe, K. Koike, H. Inoue, T. Morimoto, O. Ishitani, Faraday Discuss. 2012, 155, 115.	