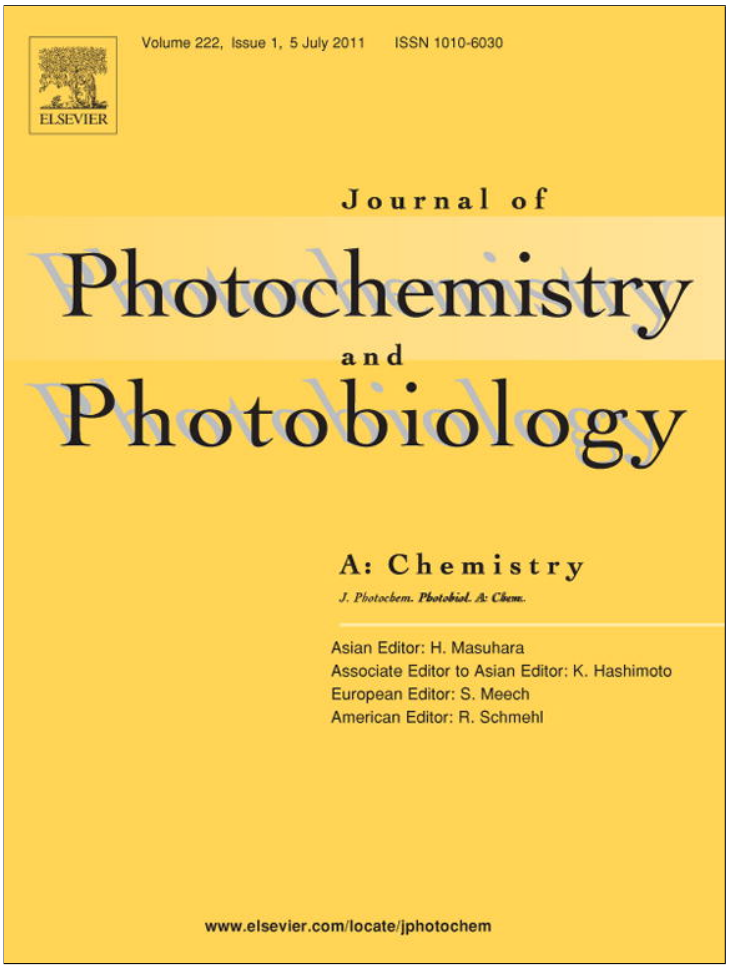

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Determination of the quantum yields of the potassium ferrioxalate and potassium iodide–iodate actinometers and a method for the calibration of radiometer detectors

James R. Bolton[a,*], Mihaela I. Stefan[b], Ping-Shine Shaw[c], Keith R. Lykke[c]

[a] Department of Civil and Environmental Engineering, University of Alberta, Edmonton, AB, Canada T6G 2W2
[b] Trojan Technologies, 3020 Gore Rd., London, ON, Canada N5V 4T7
[c] National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899, United States

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ABSTRACT

The quantum yields for two actinometers have been determined using a tunable laser light source at the National Institute of Standards and Technology (NIST) in Gaithersburg, MD. The power of this light source has been calibrated against an absolute cryogenic radiometer, considered accurate with an uncertainty better than 0.1% at a coverage factor $k = 2$. The quantum yield at 253.7 nm for the ferrioxalate actinometer was found to be 1.38 ± 0.03, which compares favorably with the value 1.40 ± 0.03 determined by Goldstein and Rabani. The quantum yield at 253.7 nm for the KI/KIO_3 actinometer was found to be 0.69 ± 0.02 at 23.5 °C. Again this compares favorably with 0.72 ± 0.03 determined by Goldstein and Rabani and 0.73 ± 0.02 determined by Rahn et al. Based on the determinations to date, including the present investigation, the recommended values for the quantum yields at 253.7 nm are 1.39 ± 0.02 (temperature independent) for the ferrioxalate actinometer and $[(0.71 \pm 0.02) + (0.0099 \pm 0.0004)(t - 24)]$ for the KI/KIO_3 actinometer, where t is the temperature (°C) of the actinometer solution. Finally, a protocol is recommended for the use of the KI/KIO_3 actinometer to calibrate radiometer detectors at 253.7 nm.

1. Introduction

If the quantum yield of a well-studied, reproducible photochemical reaction is known, the light absorber and the photoproduct are thermally stable under the experimental conditions, and the photoproduct does not absorb the light significantly and is photostable at the exposure wavelength, the yield of the photochemical product (or the depletion of the absorbing reactant) can be used to determine the photon flow entering a solution. Such a photochemical system is called an *actinometer*. The most popular actinometer in the ultraviolet wavelength range is the potassium ferrioxalate actinometer, involving the photochemical reaction

$$2Fe(C_2O_4)_3^{3-} + h\nu \rightarrow 2Fe^{2+} + 5C_2O_4^{2-} + 2CO_2$$

After exposure of a ferrioxalate solution to UV light (*e.g.*, at 253.7 nm), the Fe^{2+} generated can be assayed by a colorimetric method in which the Fe^{2+} is complexed with *o*-phenanthroline ($\varepsilon_{complex,\ 510\,nm} = 11{,}100\ M^{-1}\ cm^{-1}$). For many years, the quantum yield of the ferrioxalate actinometer at 253.7 nm has been assumed to be 1.25 [1–3].[1] Recently, Goldstein and Rabani [5] reported a quantum yield of 1.40 ± 0.03 at 253.7 nm. Nicodem and Aquilera [6] found that the quantum yield of the ferrioxalate actinometer is temperature independent over the range 5–80 °C.

Another popular actinometer for the 253.7 nm UV light is the potassium iodide–iodate (KI/KIO_3) actinometer introduced by Rahn [7], and is based on the following photochemical reaction:

$$8I^- + IO_3^- + 3H_2O + h\nu \rightarrow 3I_3^- + 6OH^-$$

The photoproduct (triiodide complex, I_3^-) can be easily assayed from its spectral absorption maximum at 352 nm. The advantage of this actinometer is that it can be used in room light, since it is not sensitive to UV light of $\lambda > 320$ nm. The quantum yield for the KI/KIO_3 actinometer has been determined by Rahn et al. [8] to be 0.73 ± 0.02 at 253.7 nm at 24 °C. Rahn [7] reported that the quantum yield increases linearly by 0.0156 per degree over the range 22–43 °C.

The use of a standard actinometer is a very convenient and reliable method to calibrate radiometer detectors. However, if such

* Corresponding author. Tel.: +1 780 439 4709; fax: +1 780 439 7792.
E-mail address: jb3@ualberta.ca (J.R. Bolton).

[1] According to the International Union of Pure and Applied Chemistry [4], the units of quantum yield should be '1', since it is a ratio of two amounts (moles of substance converted and moles of photons absorbed).

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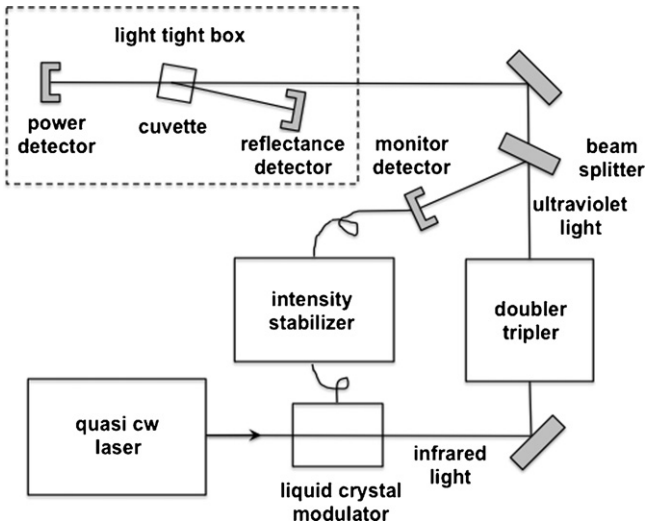

Fig. 1. Block diagram of the laser system at NIST.

calibrations are to be traceable to acceptable national standards, such as the National Institute of Standards and Technology (NIST) or other national metrology institutes (NMI), the quantum yields must be determined accurately, preferably with a standard light source or detector from an NMI.

This investigation utilized a tunable laser system at NIST coupled with standard detectors to determine the quantum yields of potassium ferrioxalate and KI/KIO_3 actinometers at selected wavelengths. The laser system is tunable in the range $\lambda = 210–3000$ nm with a bandwidth of <0.1 nm and a power in the 100 mW range. The quantum yields for the ferrioxalate and KI/KIO_3 actinometers were determined at NIST near $\lambda = 253.7$ nm and at a few other selected wavelengths in the ultraviolet spectral region.

2. Experimental

2.1. Actinometer solutions and laser exposure procedures

A detailed description of the preparation of the actinometer solutions and the procedures for the laser exposures is given in Appendix A (ferrioxalate actinometer) and Appendix B (KI/KIO_3 actinometer) in the Supplementary Material [15,16].

2.2. Description of the NIST tunable laser

The quantum yield experiments at NIST were performed using the Spectral Irradiance and Radiance Responsivity Calibrations using Uniform Sources (SIRCUS) tunable laser facility. This laser system (see Fig. 1) consists of an intensity-stabilized, frequency-tripled *quasi*-continuous wave Ti:Sapphire laser. The fundamental radiation is generated in a commercial mode-locked Ti:Sapphire laser (Coherent Mira-P laser, 76 MHz, 2 ps, about 3 W)[2] pumped by a Nd:Vanadate laser (Coherent Verdi 18, 532 nm, 18 W). The laser beam is then directed through a liquid crystal variable retarder (BEOC laser stabilizer) and into a frequency tripler (Inrad doubler, tripler, quadrupler). The UV beam (up to 300 mW) is then directed through a beam splitter and a timed shutter for known exposure times and mildly focused into the 1 cm spectrophotometer quartz cuvette containing the solution under test. The beam splitter directs a portion of the UV light onto a photodiode and the signal from the photodiode is fed back to the intensity stabilizer to produce highly stable UV radiation. The laser system is tunable from 210 to 3000 nm. The absolute power (with an uncertainty of 0.1% at a coverage factor of $k = 2$) can be determined using silicon photodiodes that have been calibrated against an absolute cryogenic radiometer [9,10]. It is possible to measure the absolute reflected UV power from the front of the quartz cuvette, so that the absolute power entering the solution can be determined. See Brown et al. [11] and Ahtee et al. [12] for further details concerning the tunable laser facility.

[2] Certain commercial equipment, instruments, or materials are identified in this article to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Table 1a
Quantum yields for the ferrioxalate actinometer.

Wavelength (nm)	Quantum yield		
	This work (NIST 2)[a]	GR[b]	HP[c]
240	1.42 ± 0.01	1.45 ± 0.03	
253.0	1.38 ± 0.03		
253.7	1.38 ± 0.03[d]	1.40 ± 0.03	1.25
255.3	1.40 ± 0.02		

[a] Uncertainties with a coverage factor of $k = 2$.
[b] Goldstein and Rabani [5].
[c] Hatchard and Parker [1].
[d] Linear interpolation of the quantum yields determined at 253.0 and 255.3 nm.

3. Results

3.1. Quantum yields

The quantum yields from this study are compared with data from earlier studies in Tables 1a and 1b. The quantum yields determined in this study were the average of at least three determinations at each wavelength. Because of interference with oxygen absorption lines around 760 nm, which makes it difficult to mode-lock the lasers, it was not possible to select a laser wavelength of 253.7 nm. Thus two wavelengths on either side (253.0 and 255.3 nm) were selected. The quantum yields at 253.7 nm were estimated as a linear interpolation between the quantum yields at 253.0 nm and 255.3 nm All measurements were made at a temperature of (23.5 ± 1) °C. All errors reported are at a coverage of $k = 2$ at the 95% confidence level.

Table 1b
Quantum yields for the KI/KIO_3 actinometer.

Wavelength (nm)	This work (NIST 2)[b]	Quantum yield[a]	
		GR[c]	NIST 1[d]
240		0.88 ± 0.03	
240.7	0.82 ± 0.01		
244			0.82
253.0	0.68 ± 0.02		
253.7	0.69 ± 0.02[e]	0.72 ± 0.03	0.73 ± 0.02
255.3	0.73 ± 0.01		
264			0.60
274		0.37 ± 0.01	0.44
284			0.30
289.0	0.26 ± 0.01		
290		0.32 ± 0.01	
300		0.28 ± 0.01	
302.0	0.15 ± 0.01		

[a] Uncertainties with a coverage factor of $k = 2$.
[b] At 23.5 ± 1 °C.
[c] Goldstein and Rabani [5] at 24 ± 1 °C.
[d] Rahn et al. [8]; NIST 1 stands for experiments conducted at the National Institute of Standards and Technology in 2003.
[e] Linear interpolation of the quantum yields determined at 253.0 and 255.3 nm.

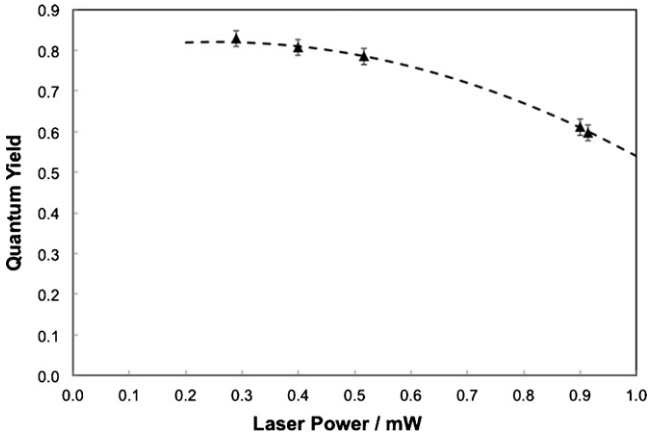

Fig. 2. Apparent quantum yield of the KI/KIO_3 actinometer at 240.7 nm as a function of the laser power.

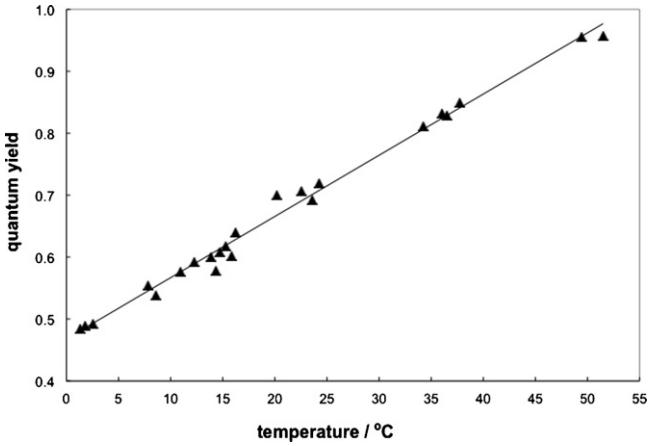

Fig. 3. Temperature dependence of the quantum yield for the Ki/KIO_3 actinometer: each data point represents 1–5 replicates; the average error in the quantum yield for each temperature is ±0.006.

At each wavelength, the reflectance from the front surface of the quartz cuvette was measured by placing a silicon diode detector in front of the cell. The ratio of the reflected power to the incident power is the reflection coefficient. In all cases the reflection coefficient was very close to the value expected (0.0445) from the Fresnel equation [13] based on reflection from the front air/quartz interface and the inner quartz/water interface using the refractive indices of quartz (1.516), water (1.372) and air (1.000).

3.2. Saturation effect

In the case of the KI/KIO_3 actinometer, a 'saturation' effect was observed. Fig. 2 shows the 'apparent' quantum yield calculated at $\lambda = 240.7$ nm as a function of the laser power level. The saturation effect results in erroneous, significantly lower quantum yields than the actual ones. For this reason, laser power levels were kept below 0.4 mW. The saturation effect probably arises because the triiodide photo-product, generated at high levels near the cuvette surface when high incident irradiance is used, absorbs the UV light at the exposure wavelength and thus exerts an inner filter effect on the absorbing actinometer. This is an important aspect that should be considered in actinometry practice. Although the saturation effect was investigated only at 240.7 nm, it is expected that the behavior will be similar at other wavelengths, since over the narrow wavelength range investigated, the laser power is directly related to the photon flux.

3.3. Temperature dependence of the quantum yields

Nicodem and Aquilera [6] have established that the quantum yield of the potassium ferrioxalate actinometer is temperature independent over the range of 5–80 °C. Rahn [7] found that the quantum yield of the KI/KIO_3 actinometer is strongly temperature dependent and reported data within the temperature range of 22–42 °C. In this study, the range of quantum yield measurements was extended to temperatures as low as 2 °C and as high as 50 °C. The results are shown in Fig. 3.

From the linear regression of all data presented in Fig. 3, one can deduce that the equation for the temperature dependence of the KI/KIO_3 actinometer quantum yield (Φ) at 253.7 nm is:

$$\Phi = (0.471 \pm 0.020) + (0.0099 \pm 0.0004)t$$

where t is the temperature (°C).

4. Discussion

In general, the quantum yields in this study for both the potassium ferrioxalate and KI/KIO_3 actinometers as determined against the primary light source at NIST agree very well with earlier studies [5,8]. The one exception is around 300 nm for the KI/KIO_3 actinometer. At this wavelength, not all the incident laser beam entering the actinometer is absorbed when the standard actinometer solution (0.6 M KI/0.1 M KIO_3 in 0.01 M $Na_2B_4O_7{\cdot}10H_2O$) is used, due to the very small molar absorption coefficients of actinometer at wavelengths around 300 nm. In our study, the laser power transmitted through the actinometer solution cell was determined, and thus an accurate determination of the laser power absorbed was obtained for use in the quantum yield calculations.

In our opinion, there is sufficient data to date on the quantum yields of the ferrioxalate and KI/KIO_3 actinometers, such that recommendations can be made. Thus, based on the data obtained with NIST traceable light source in the past [8] and in this study, and on the results reported by Goldstein and Rabani [5], we recommend the following 'standard' quantum yields at $\lambda = 253.7$ nm:

$$\Phi = 1.39 \pm 0.02 (\text{temprature independent in the range } 5 - 80^{\circ}C)$$

for the ferrioxalate actinometer (6 mM $K_3[Fe(C_2O_4)_6]$), and

$$\Phi = (0.71 \pm 0.02) + (0.0099 \pm 0.0004)(t - 24)$$

for the KI/KIO_3 actinometer (0.6 M KI; 0.1 M KIO_3 in 0.01 M sodium tetraborate), where t is the temperature (°C) of the solution.

4.1. Protocol for the determination of irradiance at 253.7 nm in a quasi-collimated beam apparatus using the KI/KIO_3 actinometer

A *quasi*-collimated beam apparatus is a very important tool in experiments assessing UV disinfection, direct UV photolysis and UV light-driven advanced oxidation processes (see Bolton and Linden [14] for a detailed description of a *quasi*-collimated beam apparatus and protocols associated with its use). For such studies, it is important to have available a radiometer with a detector accurately calibrated at 253.7 nm. Usually, the manufacturer requires that the radiometer and the detector be returned to their laboratory for recalibration after a 12-month period.

Now that a reliable quantum yield is available for the KI/KIO_3 actinometer at 253.7 nm, we propose that this actinometer can be used to calibrate a radiometer detector at any time. The procedure takes less than 2 h to complete.

The proposed detailed protocol is given in Appendix C in the Supplementary Material.

5. Conclusions

This work provides quantum yields directly determined against an absolute laser light standard based on standard detectors at NIST. If these quantum yields are accepted as standard reference values, the potassium ferrioxalate and KI/KIO_3 actinometers provide a convenient method for calibrating optic instruments, at least at 253.7 nm.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2011.05.017.

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