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Technical Note

Quantum Yield of the Iodide–Iodate Chemical Actinometer: Dependence on Wavelength and Concentration¶

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ABSTRACT

The quantum yield (QY) of the iodide–iodate chemical actinometer (0.6 *M* KI–0.1 *M* KIO_3) was determined for irradiation between 214 and 330 nm. The photoproduct, triiodide, was determined from the increase in absorbance at 352 nm, which together with a concomitant measurement of the UV fluence enabled the QY to be calculated. The QY at 254 nm was determined to be 0.73 ± 0.02 when calibration was carried out against a National Institute of Standards and Technology traceable radiometer or photometric device. At wavelengths below 254 nm the QY increased slightly, leveling off at ~0.80 ± 0.05, whereas above 254 nm the QY decreases linearly with wavelength, reaching a value of 0.30 at 284 nm. In addition, the QY was measured at different iodide concentrations. There is a slight decrease in QY going from 0.6 to 0.15 *M* KI, whereas below 0.15 *M* KI the QY drops off sharply, decreasing to 0.23 by 0.006 *M* KI. Calibration of the QY was also done using potassium ferrioxalate actinometry to measure the irradiance. These results showed a 20% reduction in QY between 240 and 280 nm as compared with radiometry. This discrepancy suggests that the QY of the ferrioxalate actinometer in this region of the spectrum needs reexamination.

INTRODUCTION

The major purpose of this study was to determine values for the quantum yield (QY) of the iodide–iodate actinometer over a range of wavelengths, which include those that are within the 200–280 nm segment of the ultraviolet region (UV-C) of the spectrum or have germicidal effectiveness (or both). For irradiation at a given wavelength λ_n, the QY can be defined as the moles of photoproduct formed per mole of photons (einsteins) absorbed at that wavelength or

$$\mathrm{QY}\ (\lambda_n) = \text{moles of product formed/moles of photons } (\lambda_n) \text{ absorbed.} \quad (1)$$

Previously, a value of the QY for the iodide–iodate actinometer had been reported by Rahn (1) for 254 nm radiation and applied in subsequent studies (2) to measure the distribution of UV fluence in a room using low-pressure mercury lamps for disinfection of room air. To expand the use of the iodide–iodate actinometer to the measurement of UV radiation at wavelengths other than 254 nm, it is necessary to have the appropriate values of the QY at these wavelengths. In this study, QY values between 214 and 330 nm have been determined.

The use of the iodide–iodate actinometer for measuring UV-C is an alternative to the traditional potassium ferrioxalate actinometer developed by Parker and coworkers (3,4). As indicated by Parker (5), chemical actinometry has several advantages when compared with radiometry for measuring UV radiation. In the first place, chemical solutions can conform to the geometry of the sample vessel or object being irradiated. The use of spherical vessels, for example (2), allowed omnidirectional radiation to be measured and true fluence measurements to be made, where the fluence is the rate of photons incident on a small sphere in space. Second, actinometers are absolute standards in that the QY is invariant for a given set of conditions; hence, periodic calibration against a transfer standard is not necessary. A comprehensive review of chemical actinometry is available (6).

The iodide–iodate chemical actinometer on exposure to UV forms triiodide, the proposed reaction having the following

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‡Certain commercial equipment, instruments, or materials are identified in the article to foster understanding. Such identification does not imply recommendation or endorsement by NIST, and it does not imply that the materials or equipment identified are necessarily the best available for the purpose.

Abbreviations: BPI, Bolton Photosciences Inc.; NIST, National Institute of Standards and Technology; QY, quantum yield; UAB, University of Alabama at Birmingham; UV-C, 200–280 nm segment of the ultraviolet region.

stoichiometry according to Rahn (1):

$$8KI + KIO_3 + 3H_2O + h\nu \rightarrow 3I_3^- + 6OH^- + 9K^+. \quad (2)$$

Triiodide can be determined spectrophotometrically and used to calculate the UV fluence. The iodide–iodate actinometer has several advantages including the following: (1) it is easy to make and does not require special safety precautions; (2) it is optically opaque to all wavelengths below 290 nm for a 1 cm path of radiation; hence, it serves as a photon counter for germicidal effective wavelengths and all such photons incident on the solution are absorbed; and (3) it is optically blind to wavelengths above 330 nm; hence, fluence measurements can be made in the presence of room light.

Advantages of the iodide–iodate actinometer over the ferrioxalate actinometer include the following: (1) simplified preparation of starting solution using commercially available reagents; (2) direct detection of endpoint without subsequent addition of reagents and dilution; (3) elimination of acid solutions, thereby reducing health hazards; and (4) elimination of need to work in a darkened laboratory.

In general, any well-defined photochemical reaction can be used as a chemical actinometer provided (1) the formation of the photoproduct is linear with the number of absorbed photons and (2) the QY is available. The QY of the iodide–iodate actinometer, together with the yield of photoproduct (triiodide) can be used, in accordance with Eq. 1, to determine the fluence (UV dose). However, the QY may be wavelength- and concentration-specific. Hence, these conditions must be specified in the determination of the QY. The basic question addressed in these studies is how the QY of the iodide–iodate actinometer depends on the wavelength of the absorbed photon and on the concentration of the actinometric solution.

MATERIALS AND METHODS

Experiments were conducted in three different laboratories as follows: (1) Bolton Photosciences Inc. (BPI) Laboratory; (2) University of Alabama at Birmingham (UAB) laboratory; and (3) National Institute of Standards and Technology (NIST) laboratory.

Solution preparation. The preparation and characterization of the iodide–iodate chemical actinometer has been described previously (1). The standard solution, consisting of 0.6 *M* KI, 0.1 *M* KIO_3 and 0.01 *M* $Na_2B_4O_7{\cdot}10\ H_2O$ (borax) at pH 9.25, is prepared from 9.96 g of KI, 2.14 g KIO_3 and 0.38 g of borax brought to 100 mL with distilled water. Over a period of hours this solution will undergo thermal oxidation, leading to an increase in the background level of triiodide. Hence, fresh solution should be prepared daily to avoid excessive background correction. Preparation of the appropriate solutions for carrying out ferrioxalate solution was done as described by Murov *et al*. (7). Absorbance measurements at BPI and UAB were carried out with a Hewlett–Packard model 8524 scanning diode array spectrophotometer.

QY determinations—general considerations. First, to obtain the absolute QY for the iodide–iodate actinometer at a given wavelength, one must have a means of irradiating the solution with monochromatic radiation. For 254 nm radiation a low-pressure mercury lamp will suffice. For other wavelengths the output of either a medium-pressure mercury lamp or a xenon lamp must be passed through either a monochromator or a narrowband interference filter to select a specific wavelength. Second, to measure the number of moles of photons or einsteins absorbed by the actinometer, a calibrated system must be used, which can be either another actinometric solution or a calibrated radiometer, photocell or photodiode. Third, one must have a measure of the number of moles of triiodide formed, which can be determined spectrophotometrically. A plot of the moles of product as a function of the fluence (UV dose) provides a fluence–response curve, which should be linear for each irradiation wavelength, the slope being proportional to the QY.

Absolute QY determinations made at the BPI laboratory. All irradiations were carried out on solutions in open beakers (5 mL) with the light source located above the solution. The irradiation area was 3.8 cm^2, and the solution depth was 1.3 cm. The lamp output was collimated by being passed through a 10 cm tube located between the lamp and the sample.

Fluence measurements at 254 nm using the low-pressure mercury lamp (12.5 W, Atlantic Ultraviolet Corporation, Hauppauge, NY) were carried out using either ferrioxalate actinometry in accordance with Murov *et al*. (7) assuming a QY of 1.25 or radiometry (International Light model 1400 with an SED240 detector, Newburyport, MA). The detector was calibrated at 254 nm by International Light (NIST traceable). For ferrioxalate actinometry the irradiance was corrected for contributions made by wavelengths longer than 254 nm. This contribution is estimated to be 11–12%. No such correction was found to be necessary for the radiometer measurement because the radiometer detector is solar blind and does not respond to radiation at wavelengths greater than 320 nm. Hence, the portion of light emitted at these longer wavelengths (11–12%) is not detected by the radiometer.

For irradiation with the medium-pressure lamp (1000 W, Calgon Carbon Corporation, Pittsburgh, PA) in combination with various narrowband (10 nm) interference filters (Acton Research Corp., Acton, NY) for wavelengths 214, 220, 228, 240, 255, 260, 270 and 280 nm, the incident fluence rate was measured using both radiometry and ferrioxalate actinometry. The radiometer was calibrated using the spectral response curve supplied by International Light, normalizing the response curve at 254 nm using iodide–iodate actinometry (QY = 0.74) to determine the 254 nm fluence. Ferrioxalate actinometry was done using a QY of 1.25 for all wavelengths between 214 and 280 nm.

Relative QY determinations made at the UAB laboratory. To examine the wavelength dependence of the QY on a relative basis, the excitation monochromators of two different instruments were used, a photon-counting spectrofluorimeter model PC1 (ISS, Champaign, IL) referred to as UAB-1 and a FluoroMax-2 spectrofluorimeter (Instruments S.A., Inc. Jobin Yvon-Spex, Edison, NJ) referred to as UAB-2. Both instruments used 150 W xenon lamps and double-pass monochromators in the excitation mode. Both also allow for correction of the variation in the photon intensity of the exciting light as a function of wavelength, *i.e*. they are designed to provide corrected excitation spectra. For each instrument a beam splitter directs a small portion of the excitation output to a photon-counting device. In one case (UAB-1), this device is a rhodamine B–counting solution, which fluoresces in direct proportion to the number of incident photons per second, the fluorescence being monitored with a photomultiplier. In the other case (UAB-2), a photodiode samples a portion of the excitation energy and has a response signal that is proportional to the number of incident photons per second. This response has a small wavelength dependence, which was corrected for using the manufacturer's spectral correction factors.

In addition to the photon-counting properties of these devices, they also integrate the relative intensity over time. Hence, for each radiation period, a metric relative to the total number of photons incident on the sample is displayed and recorded.

Samples (0.5 mL volume in 1 cm rectangular, narrow-width quartz cuvettes) were placed in the sample compartment and irradiated for various times (up to 15 min depending on the excitation wavelength). The sample slits were set to give a bandwidth of 8 nm. Because the area of the sample beam incident on the sample cell is smaller than the area of the sample itself, only a fraction of the sample area is irradiated. However, it is assumed that this area remains constant throughout the experiment.

After irradiation, the cell was removed and the absorbance measured at 352 nm. The absorbance at each wavelength was normalized for a constant number of absorbed photons by dividing it by the photon intensity at that wavelength integrated over the irradiation period. The absorbance also required normalization for complete absorption of the incident radiation to correct for fractional light absorption that occurred at wavelengths equal to or greater than 290 nm. For normalization, the absorbance at 352 nm was divided by the fractional light absorption at each irradiation wavelength, values of which are given in Table 1. In this way, a plot of the formation of triiodide as a function of wavelength (*i.e*. the action spectrum) varies solely with respect to changes in the QY at each wavelength and not to variations in either the number of incident photons or in the fraction of light absorbed.

Absolute QY determinations made at NIST[‡]. The light source used for the calibration of the KI actinometer at NIST is a xenon lamp with its light made monochromatic by a 1/4 m grating monochromator. The resolution of the monochromator was set at approximately 3 nm. The wavelength accuracy of the system in the region of this work was calibrated by using a holmium oxide solution as a wavelength standard (NIST standard reference material [SRM] 2034) (8) to an uncertainty of ±0.2 nm. After the monochromator the light was reimaged onto the actinometer and a silicon

Table 1. Absorbance between 248 and 330 nm of the iodide–iodate mixture as compared with its separate components (measurements made in various cells varying from 0.01 to 10 cm and then normalized to 1 cm path length)

	Absorbance				
Wavelength (nm)	Iodide (0.6 *M*)	Iodate (0.1 *M*)	Sum of separated components*	Mixture†	Fraction absorbed‡
248	651	24	675	655	1.00
250	416	25	441	441	1.00
254	163	16	179	200	1.00
260	24.6	8.75	33.4	72	1.00
270	1.5	2.48	3.98	19.4	1.00
280	0.08	0.58	0.66	7.4	1.00
290	0.02	0.12	0.14	2	0.99
300	0.01	0.03	0.04	0.6	0.75
310	0.01	0	0.01	0.19	0.34
320	0	0	0.0	0.044	0.10
330	0	0	0.0	0.013	0.03

*Sum of iodide and iodate when separated.
†Iodide and iodate after mixing.
‡Fraction of light absorbed in a 1 cm path length cell for iodide–iodate mixture.

photodiode, located behind the cuvette, by a normal-incidence spherical mirror as indicated in Fig. 1. The solution for the actinometer was placed in a quartz cuvette that has an optical path length of 1 cm. A stir bar in the cuvette ensures uniform concentration of the solution during light exposure. For this calibration, 2 mL of solution was placed in the cuvette. The absolute spectral response (A/W) for the silicon photodiode was calibrated at the NIST UV facility (9) in the region from 200 to 400 nm with an uncertainty less than 1%. A CaF_2 beam splitter positioned in front of the cuvette-reflected part of the incident light to a second silicon photodiode to monitor any fluctuations of the light coming from the monochromator. The signals from both photodiodes were fed to a computer, which also controlled the monochromator and a light shutter.

To measure the number of photons incident on the sample, the light loss due to reflectance of the excitation light from the front surface of the cuvette must be determined. The signal from the photodiode at the position behind the cuvette was measured with and without the cuvette in place and with and without water in the cuvette. In this way it was determined that the reflectance from the front of the cuvette without water is around 10%, whereas for that with water the reflectance reduces to about 6%. Note that the cuvette was placed a few degrees off normal incidence during all measurements to ensure that back-reflected light did not interfere with the measurement.

The exposure to the excitation light, followed by a spectral transmittance measurement, was automated by the computer that used a program developed for this calibration. The computer first set the monochromator to the desired excitation wavelength, opened the shutter while keeping track of the exposure time, typically 5 min, and continuously recorded the signal from the monitor photodiode. The actual fluence was determined by integrating the photodiode signal over time and converting this quantity into the total energy incident on the cuvette using the calibration factors established for each excitation wavelength.

After each irradiation interval, the computer closed the shutter and set the monochromator to 352 nm for the spectral transmittance measurement. The computer then closed the shutter and set the wavelength back to the excitation wavelength for a second round of exposure. During one calibration, several rounds of exposure were performed with the transmittance of the solution recorded at the end of each exposure. The change of the absorbance was plotted against the absorbed photons, and the QY was derived from the best-fit slope.

RESULTS AND DISCUSSION

Absorbance properties of the standard actinometric solution: range 248–330 nm

The absorbance of the standard solution used for iodide–iodate actinometry (0.6 *M* iodide and 0.1 *M* iodate) was determined for the

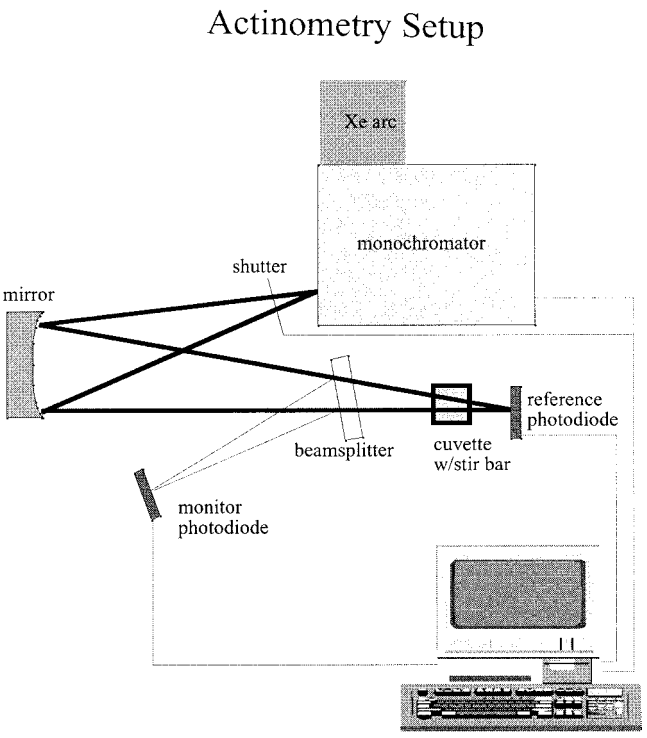

Figure 1. Experimental setup at the NIST laboratory.

separated components and for the mixed solution. The results are shown in Table 1 for measurements between 248 and 330 nm. Because the absorbance varied by more than four logs over this wavelength range, measurements were made using optical cells varying from 0.1 mm to 10 cm in path length. However, the values were all transformed to 1 cm path length values.

The following conclusions can be drawn for irradiation in a 1 cm path length optical cell: (1) When iodide and iodate are present together, the resulting absorption spectrum is considerably shifted to the red. Consequently, above 260 nm the absorption of the mixture is enhanced considerably relative to the sum of the absorbances measured separately. For example, at 300 nm, the mixture has an absorbance of 0.6, whereas the sum of the parts is only 0.04. The origin of this shift is unknown but may reflect a perturbation of the iodide charge-transfer absorption band in the presence of iodate. (2) Essentially, all of the radiation is absorbed at or below 290 nm. Hence, the system can be considered to be optically opaque or a ''photon counter'' over most of the spectral region considered to be germicidally effective. (3) Above 290 nm, fractional light absorption occurs, and by 330 nm the absorbance is essentially negligible. Therefore, above 330 nm the system can be considered to be optically transparent and operations can be carried out under

Table 2. Molar absorption coefficients for triiodide at different wavelengths

Wavelength (nm)	Molar absorption coefficient (M^{-1} s^{-1})
352	27 600
376	18 100
400	7100
426	3100
450	1600
476	610

Table 3. QY at 254 nm

Run no.	Rate of formation of triiodide (10^{-10} mol s^{-1})	Rate of UV absorption (10^{-10} einstein s^{-1})		QY	
		Actinometry	Radiometry	Actinometry	Radiometry
1	6.39	11.3	8.88	0.57	0.72
2	6.13	10.1	8.17	0.61	0.75
3	7.70	12.1	9.43	0.63	0.82
4	6.23	10.8	—	0.58	—
5*	1.19	2.14	—	0.61	—
			Average	0.60 ± 0.02†	0.76 ± 0.03†

*Irradiation done with low-pressure lamp and a 255 nm interference filter.
†The errors are standard deviations of the mean.

most laboratory conditions in the presence of room light. Note, however, that for the case of fluorescent lamps without a plastic cover or screen over the lamp, it has been reported (Melvin First, personal communication) that some short-wavelength light appears to be present that can be absorbed by the iodide–iodate system, resulting in unwanted triiodide formation. Hence, exposure to naked fluorescent lamps should be avoided.

Absorbance properties of triiodide (352–476 nm)

The molar absorption coefficient of triiodide varies according to the solvent conditions (10). In the presence of 0.15 *M* iodide, values have been reported to vary between 25 800 (11) and 26 400 M^{-1} cm^{-1} (12), averaging 26 100 M^{-1} cm^{-1}. It was necessary to determine the value of the molar absorption coefficient under the conditions used in this actinometer, *i.e.* in the presence of 0.6 *M* iodide and 0.1 *M* iodate. This was carried out by adding the same amount of iodine (10 μL of a concentrated solution) to 1 mL of either 0.15 *M* iodide or 0.6 *M* iodide–0.1 *M* iodate. After repeating this process nine times, it was determined that the absorbance of triiodide was on average 1.055 times greater in the iodide–iodate solution. Hence, one calculates that the molar absorption coefficient in this mixture was equal to $26\,100 \times 1.055 = 27\,540$ M^{-1} cm^{-1}.

A measurement of the molar absorption coefficient (M^{-1} cm^{-1}) was also made by weighing out a known amount of iodine and adding it to a known volume of the standard iodide–iodate actinometric solution. The resulting molar absorption coefficient at 352 nm, ε_{352}, was 27 600 M^{-1} cm^{-1}, in good agreement with the value obtained above. This value will be the one used to calculate triiodide concentrations.

Table 2 contains values of the molar absorption coefficient at 376, 400, 425, 450 and 476 nm determined relative to the value at 352 nm of 27 600 M^{-1} cm^{-1}. These values were obtained by measuring the absorbance of triiodide over a range of concentrations and taking the ratio at one wavelength relative to another in an iterative process. At 476 nm, the absorbance is nearly 50 times less than at 352 nm. Shifting the monitoring wavelength increases the dynamic range of measurement and allows the absorbance reading to remain on scale over a wide range of UV fluence (UV dose) without the necessity of changing cell path length or diluting the solution.

Absolute QY measurements at 254 nm (BPI laboratory)

To determine the QY as defined in Eq. 1, one must measure for a given wavelength of irradiation the number of moles of triiodide formed per einstein of absorbed photons. Standard iodide–iodate actinometric solutions were irradiated with a low-pressure mercury lamp and the number of moles of triiodide calculated using Beer's Law:

$$\text{moles of triiodide} = 0.005\ A_{352\,nm} \times 27\,600^{-1}, \quad (3)$$

where the factor 0.005 is the ratio of the volume of the sample (5 mL) divided by the volume of 1 liter (1000 mL), and 27 600 is the molar absorption coefficient. The number of moles of triiodide formed after 10 different exposure times was plotted as a function of the exposure time, and from the slope, the rate of generation of triiodide (in moles per second) shown in Table 3 was obtained. It is assumed that triiodide formation is due solely to 254 nm radiation because a test carried out with a Pyrex window indicated that less than 1% of the generated triiodide is due to wavelengths greater than 300 nm.

The irradiance or rate of UV absorption as measured using ferrioxalate actinometry provided values in einsteins per second directly, and these are presented in Table 3. For radiometry, carried out simultaneously, the following relation was used to convert the irradiance (mW cm^{-2}) at the surface of the beaker (area = 3.8 cm^2) into einsteins absorbed per second by the total solution:

$$\text{einstein } s^{-1} = 0.975 \times \text{irradiance} \times (4.716 \times 10^8)^{-1} \times 3.8, \quad (4)$$

where the factor 0.975 accounts for the fact that 2.5% of the incident UV is reflected from the surface of the solution, and the factor (4.716×10^8) represents the number of millijoules per einstein of 253.7 nm photons. The rates of UV absorption obtained using radiometry in units of einsteins per second are also presented in Table 3. Note that the values obtained using actinometry are approximately 20% higher than those obtained using radiometry.

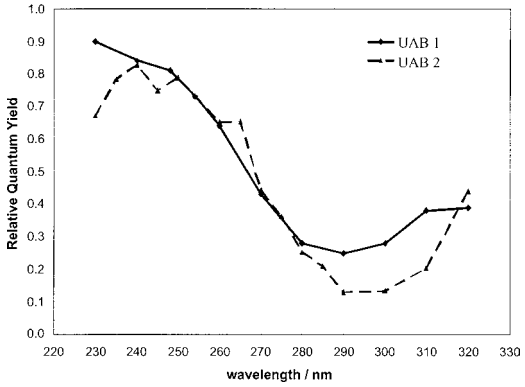

Figure 2. Wavelength dependence of the relative QY determined using spectrofluorimeters; measurements carried out at the UAB laboratory.

Table 4. QY (214–280 nm): BPI laboratory

Wavelength (nm)	Rate of formation of triiodide (10^{-10} mol s^{-1})	Rate of UV absorption (10^{-10} einstein s^{-1})		QY		
		Actinometry*	Radiometry	Actinometry*	Radiometry	Ratio†
214	4.63	5.97	5.50	0.78	0.84	0.93
220	5.57	6.75	6.77	0.83	0.82	1.01
228	11.4	15.5	14.3	0.74	0.80	0.93
240	9.53	12.5	10.0	0.76	0.95	0.80
255	13.8	23.0	18.7	0.60	0.74	0.81
260	5.73	11.1	8.82	0.52	0.65	0.80
270	5.20	11.7	10.2	0.44	0.51	0.86
280	5.59	18.8	15.0	0.30	0.37	0.81

*Actinometry using ferrioxalate.
†Ratio of actinometry to radiometry.

The QY shown in Table 3 were obtained, in accordance with Eq. 1, by dividing the moles of triiodide formed per second by the number of einsteins absorbed per second. An average QY of 0.60 was obtained for the ferrioxalate calibration and 0.76 for the radiometer calibration. The 20% difference is a reflection of the difference in the measured values of the rate of UV absorption.

Relative QY measurements: range 230–320 nm (UAB laboratory)

Samples positioned in the sample cell of the spectrofluorimeter were irradiated at various wavelengths between 230 and 320 nm for time periods ranging from 5 to 15 min. The absorbance was measured at 352 nm, normalized for constant photon incidence and corrected for fractional absorbance as described in Materials and Methods. In addition, the results were further normalized at 254 nm using 0.76 as the value of the QY at this wavelength (Table 3). The results, shown in Fig. 2, are comparable for both instruments (UAB-1 and UAB-2). The relative QY is a maximum at the shortest wavelengths and decreases with increasing wavelength up to 290 nm. Above 290 nm the yield increases with wavelength instead of decreasing. This inexplicable reversal of behavior requires verification and warrants additional investigation into this spectral region.

Absolute QY measurements using a medium-pressure mercury lamp and interference filters: range 214–280 nm (BPI laboratory)

Standard iodide–iodate actinometric solutions were irradiated in an open 5 mL dish with the output of a 1000 W medium-pressure mercury lamp passed through narrowband interference filters ranging from 214 to 280 nm. The absorbance at 352 nm was plotted as a function of the time of irradiation and the resulting slope used to determine the rate of triiodide formation per second given in Table 4.

The rate of UV absorption was determined using either ferrioxalate actinometry or radiometry, the latter requiring conversion of the irradiance in units of mW cm^{-2} into einstein s^{-1}. This conversion was done using an expression similar to Eq. 4, inserting the appropriate factor at each wavelength for converting millijoules into einsteins. The resulting fluence rates are presented in Table 4 for each wavelength of irradiation and for each calibration method.

The QY values obtained in accordance with Eq. 1, as well as the ratios of the QY values determined by ferrioxalate actinometry relative to radiometry, are presented in Table 4. The following observations are noted: (1) Overall, the variation in absolute QY with wavelength up to 280 nm follows the trend obtained previously (Fig. 2) using relative QY values. (2) The QY values at 255 nm for both calibration methods are essentially the same as those obtained using the low-pressure lamp (Table 3). (3) The QY between 240 and 280 nm obtained using radiometry are approximately 20% greater than those obtained using ferrioxalate actinometry. Below 240 nm, this difference decreases to 7% or less. These differences are purely a reflection of the difference in the rate of UV absorption as measured using these two methods of calibration.

Absolute QY measurements using a xenon lamp and a monochromator: range 234–284 nm (NIST)

To resolve the calibration differences observed between radiometry and ferrioxalate actinometry, QY determinations were carried out at NIST. Using the experimental setup described in Materials and Methods, irradiation was carried out using wavelengths selected every 10 nm between 234 and 284 nm. At each wavelength the UV flux was measured after correcting for scattering. The sample is assumed to be optically opaque. The spectral transmittance at 352 nm was monitored after each exposure period. The corresponding absorbance was determined and plotted as a function of absorbed photons. The response for each irradiation wavelength was linear over the range of absorbed photons used (Fig. 3). The slopes provided the QY shown in Table 5.

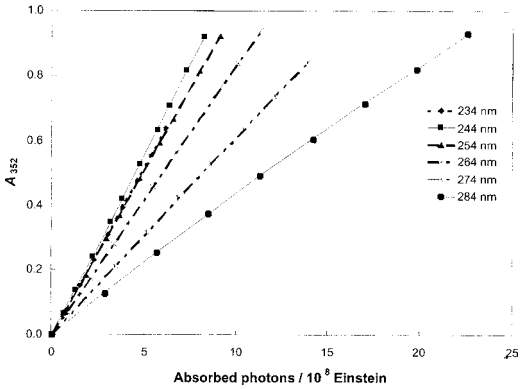

Figure 3. Absorbance (352 nm) *versus* absorbed photons for various wavelengths of incident UV light; measurements carried out at the NIST laboratories.

Table 5. QY (234–284 nm): NIST

Irradiation wavelength (nm)	QY*
234	0.75
244	0.82
254	0.73
264	0.60
274	0.44
284	0.30

*Uncertainty = 3% (see Table 6).

The overall uncertainty for the NIST data was estimated to be approximately 3% based on the uncertainties shown in Table 6. A major source of uncertainty comes from the transmission of the front surface of the cuvette. This uncertainty can be reduced in future work by using a laser beam and directly measuring the reflected light from the cuvette as shown previously (13). Another major uncertainty component is the temperature, which can again be improved in future work by using active temperature control. Taken together, a reduction of these specific uncertainties would result in an overall uncertainty of 2% or less.

The QY in Tables 4 and 5 were plotted as a function of wavelength and are shown in Fig. 4. The NIST data and the radiometry results from the BPI laboratory show excellent agreement between 254 and 284 nm, whereas the QY obtained using ferrioxalate actinometry are consistently lower in this region by approximately 20%. Below 240 nm the three methods examined in this study give approximately the same result for the QY or approximately 0.80.

Influence of the iodide–iodate concentration on the QY (254 nm)

The concentration dependence of the iodide–iodate actinometer was examined previously (1) to arrive at the best conditions for obtaining reproducible results. These conditions (0.6 *M* KI–0.1 *M* KIO_3 in 0.01 *M* $Na_2B_4O_7 \cdot 10\ H_2O$) are the so-called standard conditions for which the QY shows minimal dependence on variations in the concentration. Hence, the margin of error in preparing solutions is minimized. As a check on the proper concentration of the standard solution, the absorbance at 300 nm should read ~0.60.

The concentration dependence of the QY was examined to verify the previous results and to determine the feasibility of using lower concentrations of the reactants for cases where economic factors might prohibit the use of high concentration of materials.

Table 6. Components of the combined relative standard uncertainty for the calibration of the potassium iodide actinometer: NIST data

Source of uncertainty	% uncertainty
Reference photodiode calibration	1.0
Photodiode uniformity	0.2
Cell transmittance	2.0
Volume of KI solution	0.85
Chemical weight measurement for KI solution	0.2
Temperature	1.5
Dose measurement	0.5
Molar absorption coefficient (27 600 M^{-1} cm^{-1})	1.0–2.0
Relative combined standard uncertainty*	3.1

*Quadratic sum of all uncertainties.

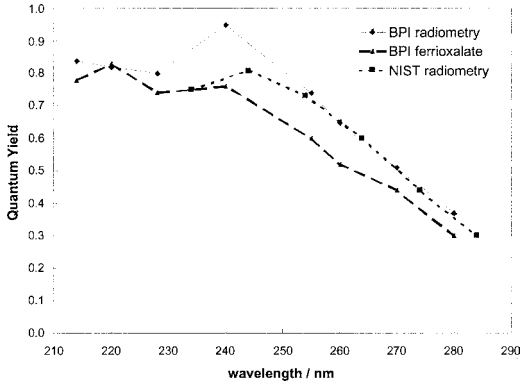

Figure 4. Wavelength dependence of the QY determined at the BPI and NIST laboratories. (a) BPI laboratory—radiometry; (b) BPI laboratory—ferrioxalate actinometry; (c) NIST laboratory—photodiode.

One complication associated with carrying out a concentration dependence study is the existence of an equilibrium between triiodide and free iodine:

$$I_3^- \rightleftharpoons I^- + I_2. \quad (5)$$

The dissociation constant for this equilibrium is on the order of 0.00143 (14). Hence, concentrations of iodide on the order of 0.15 *M* are necessary to maintain essentially all the iodine in the form of triiodide. Therefore, depending on the concentration of KI present in the system, the triiodide complex, as determined by means of the increase in absorbance at 352 nm, may or may not reflect correctly the photochemical yield of iodine released under irradiation of the iodide–iodate actinometric solution. Hence, the absorbance of iodine in the form of triiodide was investigated as a function of the concentration of iodide–iodate. For this investigation, ''pseudo–molar absorption coefficients'' were obtained and used in the determination of the QY of the iodide–iodate actinometer as a function of concentration.

The pseudo–molar absorption coefficient of triiodide at different concentrations was determined by dissolving known amounts of iodine in various concentrations of actinometric solution down to a 100-fold dilution of the standard solution. The absorbance was measured at 352 nm in a 1 cm cell. This value was then divided by the molar concentration of added iodine to obtain the pseudo–molar absorption coefficient. Because iodine (used in the molar absorption coefficient measurements) is a very weak absorber at

Table 7. Pseudo–molar absorption coefficients of triiodide complex in actinometric solutions of various concentrations ([KI]–[KIO_3] = 6; 0.01 *M* $Na_2B_4O_7$)

[KI] (*M*)	Pseudo–molar absorption coefficient (M^{-1} cm^{-1})
0.600	27 600
0.306	26 700
0.155	26 200
0.105	26 000
0.075	25 600
0.043	24 900
0.016	23 200
0.012	22 700
0.006	19 300
0.0006	3100

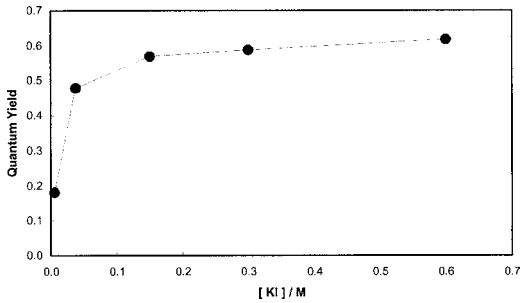

Figure 5. Concentration dependence of QY. The molar ratio of iodide to iodate was fixed at 6. Buffer was 0.01 borax, pH 9.25. QY were determined using ferrioxalate actinometry and then normalized to a value of 0.75 for 0.6 *M* iodide.

352 nm ($\varepsilon = 189\ M^{-1}\ cm^{-1}$), its contribution to the absorbance can be neglected.

The pseudo–molar absorption coefficients (Table 7) of triiodide decrease by about 6% as the actinometer concentration decreases from 0.6 to 0.1 *M* KI. A much sharper change occurs at lower concentrations of KI, which is associated with the dissociation of the complex according to the equilibrium shown in Eq. 5.

Irradiation of the actinometric solutions in the range of concentrations 0.006 *M*–0.6 *M* KI ([KI]–[KIO_3] = 6 in 0.01 *M* $Na_2B_4O_7$) were conducted with a 1 kW medium-pressure Hg lamp and a 255 nm interference filter. The QY for triiodide generation was calculated for each concentration using the pseudo–molar absorption coefficients.

As indicated in Fig. 5, the QY does not change significantly as the concentration changes from 0.6 to 0.15 *M* KI. At lower concentrations, however, the QY decreases markedly. This decrease is not due to a decrease in fractional light absorption because, even at the lowest concentration used in this study, more than 98% of the 254 nm radiation is absorbed by the sample.

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