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Leveraging Chemical Actinometry and Optical Radiometry to Reduce Uncertainty in Photochemical Research

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Preface

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Leveraging chemical actinometry and optical radiometry to reduce uncertainty in photochemical research

ABSTRACT

Subtle aspects of illumination sources and their characterization methods can introduce significant uncertainty into the data gathered from light-activated experiments, limiting their reproducibility and technology transition. Degradation kinetics of methyl orange (MO) and carbamazepine (CM) under illumination with TiO_2 were used as a case study for investigating the role of incident photon flux on photocatalytic degradation rates. Valerophenone and ferrioxalate actinometry were paired with optical radiometry in three different illumination systems: xenon arc (XE), tungsten halogen (W-H), and UV fluorescent (UV-F). Degradation rate constants for MO and CM varied similarly among the three light systems as $k_{W-H} < k_{UV-F} < k_{XE}$, implying the same relative photon flux emission by each light. However, the apparent relative photon flux emitted by the different lights varied depending on the light characterization method. This discrepancy is shown to be caused by the spectral distribution present in light emission profiles, as well as absorption behavior of chemical actinometers and optical sensors. Data and calculations for the determination of photon flux from chemical and calibrated optical light characterization is presented, allowing us to interpret photo-degradation rate constants as a function of incident photon flux. This approach enabled the derivation of a calibrated 'rate-flux' metric for evaluating and translating data from photocatalysis studies.

1. Introduction

Light-activated reactions are important to many fields of biology and chemistry, including organic [1] and environmental chemistry [2], materials science [3], and biomedicine [4]. In particular, photochemical reactions mediate the fate and transport of contaminants in the environment [5] and enable the removal of small-molecule toxins from wastewater streams [6–8]. Such processes provide a means to degrade biological and chemical contaminants from water with low energy requirements [9–12] even if only in very unique situations, such as water security in remote locations [13].

The attractive promise of degrading organic contaminants with sunlight has driven extensive research into a vast number of photocatalytic materials and systems in recent years [14]. In reality, commercialization of the technology has largely been limited to titanium dioxide (TiO_2) materials [15–18], which up to this point only show

promise in niche applications [13,19]. A drawback of TiO_2 is that it can only harvest a very small percentage of incident solar radiation in the UVA region [18,20]. There is great impetus to harness visible wavelengths by doping TiO_2 and identifying/developing new visible range active photocatalytic materials so that a broader range of solar radiation can be harnessed [21–25].

As much of photocatalysis research for water treatment has seen limited applications, literature reports commonly contain data that was collected without standard methods [26], in small, bench scale experiments, and with a diverse array of light sources. Often, the selection of these sources considers the wavelength dependence of the absorption processes, but other concerns, such as cost, availability, and ease of set-up frequently take precedence. As a result, many laboratories conducting photo-experiments have illumination set-ups that are unique in some way, making it nearly impossible to: i) repeat, reproduce, and otherwise compare photochemical results between laboratories; and

therefore ii) ascribe increased degradation kinetics to improvements in photocatalytic materials.

Herein, we present photochemistry experiments that were designed to emphasize the critical nature of light characterization when reporting light-activated research. We undertook photocatalysis as a case study, performing experiments in multiple light systems, which we characterized with chemical actinometry and optical (spectro)radio-metry. This approach enabled us to unravel conflicting aspects of illumination system characterization that can skew the measured reaction kinetics and confound the interpretation of photocatalysis research. In this report, we focus on improving chemical and optical methods of light characterization to support the development of a common language for reporting, translating, and ultimately transitioning light-activated research to useful applications.

2. Experimental

2.1. Materials

The purity of reagents was confirmed spectroscopically: methyl orange (MO, Reag. Ph. Eur.; Sigma Aldrich); carbamazepine, (CM, 98%, Alfa Aesar); valerophenone (VPh, Sigma Aldrich, 99%); titanium dioxide (TiO₂, P25, Degussa/Evonik); ammonium acetate (eluent additive for LC-MS, Sigma Aldrich); acetonitrile (HPLC grade, Fisher Chemical); methanol (HPLC grade, Fisher Chemical); FerroZine™ iron reagent (98%, Sigma Aldrich); ammonium iron(III) sulfate dodecahydrate (ACS Reagent grade, Sigma Aldrich); potassium oxalate monohydrate (ACS Reagent grade, Sigma Aldrich); HEPES buffer (≥99.5%, Sigma Aldrich); sulfuric acid (99.99%, Sigma Aldrich). Before UV-vis analysis, TiO₂ was filtered from the MO and CM solutions with a 0.22 μm filter (Millex, PTFE).

2.2. Illumination systems

Two different broad spectrum illumination systems were used: one based on two calibrated 50 W Tungsten-halogen bulbs and illuminator fixtures (W-H, ASD, Inc., Fig. S1a); another composed of a 150 W Xe-arc lamp operating at 100 W (XE, Newport Oriel, Fig. S1c) with a filter transmitting wavelengths 330–800 nm (Model 20-CLVS-1, Newport-Oriel). An illumination system based on six 4 W purple fluorescent bulbs in a reactor box [27,28] (UV-F; Fig. S1b) was used as (pseudo) single UV wavelength illumination source.

2.3. TiO₂/MO photocatalysis

Aqueous methyl orange (MO) or carbamazepine (CM) solutions (25 μM, 40 mL) were placed in a jacketed beaker (W-H) or a quartz beaker (UV-F) maintained at 20 °C. Subsequently TiO₂ (P25, 4 mg) was added to the MO or CM solution and stirred in darkness for 15 min. Aliquots (~1 mL) were removed after 0, 10, 20, and 40 min. of illumination, then filtered and analyzed with a UV-vis spectrophotometer. Relative MO & CM concentrations were calculated based on the absorbance of the solution at 464 and 285 nm, respectively).

2.4. Ferrioxalate actinometry

Ferrioxalate (FeOx) actinometry was conducted following a modified procedure reported by Rao et al. [29]. The following solutions were prepared under normal laboratory light: 0.06 M potassium oxalate in 0.05 M sulfuric acid, 0.2 M ammonium ferric sulfate in 0.05 M sulfuric acid, 0.25 g FerroZine™ iron reagent (3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine-*p*'-disulfonic acid monosodium salt hydrate) dissolved in 5 mL of 0.05 M HEPES buffer. A Genesys-10S UV-vis spectrophotometer was blanked using a quartz cuvette filled with 1 mL 0.05 M sulfuric acid and 0.65 mL FerroZine™ solution. Under red illumination, 20 mL potassium oxalate solution was mixed with 20 mL ammonium

ferric sulfate solution in a quartz flask. The solution was stirred in the dark for 5 min. A 1 mL aliquot was removed from solution and placed in a foil-covered vial. Subsequent 1 mL aliquots were removed following 1, 2, 3, 4, and 5 min of illumination. Samples were analyzed by diluting 100 μL of each sample to 10 mL with 0.05 M sulfuric acid. 1 mL of the diluted sample was mixed in a quartz cuvette with 65 μL FerroZine™ solution and gently shaken. The absorbance of the solution at 563 nm was monitored until it reached equilibrium, about 2 min. The final absorbance was recorded and the rate of Fe(II) production was calculated (Eq. S1).

2.5. Valerophenone actinometry

Aqueous valerophenone (VPh) solution (40 mL, 50 μM, in < 1% acetonitrile) was placed in a jacketed beaker (W-H) or a quartz flask (UV-F). Then, 1 mL aliquots were taken after 0, 5, 10, 15, 20 and 25 min. of illumination and analyzed with high-performance liquid chromatography (HPLC), see also SI Eq. S3 & Fig. S3.

2.6. Chemical analysis instrumentation

The absorbances of FerroZine™, MO, and CM were measured in a quartz cuvette with a UV-vis spectrophotometer (Model Genesys-10s, Thermofisher, USA). VPh samples were analyzed using a HPLC system (Accela, ThermoFisher, USA) and a C18 column (Zorbax Eclipse Plus 4.5 x 150 mm, 5 μm). Samples were run isocratically with a 70/30 mixture of acetonitrile and 10 mM aqueous ammonium acetate.

2.7. Optical instrumentation

Single wavelength. Radiance from the various light systems was measured with a calibrated radiometer (Model UVX, UVP, LLC, Upland, CA, calibrated 06/2018), equipped with sensors for 254, 310, and 365 nm (Models UVX-25, -31, -36, calibrated 06/2018). Reported irradiance values are the average of 10 measurements.

Broad spectrum. A compact spectrometer (Model CCS200, range 200–1000 nm, with CCSA1 filter, ThorLabs, Newton, NJ) was used to obtain spectral intensity emitted by the various illumination systems. A 3 s. integration time was used for each of 5 measurements, which were average to arrive at the spectrum for each light source.

Spectral irradiance. Spectral irradiance was measured on the three light systems using a fully calibrated spectroradiometer (Model HR-1024i, range 340–2500 nm, Spectra Vista Corp., Poughkeepsie, NY) and a calibrated diffuse reflectance target (Spectralon, Labsphere, North Sutton, NH).

3. Results and discussion

3.1. photocatalysis case study with TiO₂

To investigate the implications of light source variability in photochemical research, we explored titanium dioxide (TiO₂) photocatalysis as a case study for the degradation of small molecule contaminants from water. By first surveying the literature, we designed experiments to probe the role of illumination characteristics (e.g., wavelength, intensity, spectral distribution) on photo-degradation kinetics with TiO₂. Identical photocatalysis experiments were conducted under several different illumination conditions and paired with light characterization by optical and chemical methods to explore the diverse effects of light source parameters on the degradation rates. Comparing the rates of identical processes under varying illumination conditions allowed us to identify and provide solutions to common pitfalls encountered in light-activated research.

3.1.1. Current status of TiO₂ photocatalysis

Research into water treatment technology is increasingly focused on

Table 1

A sampling of illumination sources and related light characterization reported in the literature for TiO₂ based materials in photocatalysis experiments.

Light source			Light Characterization		
Type	Wave length (nm) ^b	Total Watts	Type ^a	Reported Value ^b	Ref. No.
Black light fluorescent lamp	300–420, peak at 350	125	N	n/s	[35]
Hg-Xe lamp	365	200	R	6 mW/cm ²	[41]
Medium pressure Hg lamp system, with filtering	> 366	n/s	A	2.38×10^{-6} , einstein/s	[42]
Custom T5 UV lamp system	365	16	N	n/s	[36]
Xe arc lamp, Suntest CPS+	300–800	1100	R	750 W/m ²	[38]
1000 W Xe arc lamp w/cut on 305 nm filter	> 305	1000	SR	6.13×10^{15} photons/cm ² s	[40]
Medium pressure Hg lamp	n/s	100	N	n/s	[20]
Custom UV system	n/s	24	R	18 W/m ²	[43]
Xe arc lamp system	> 320	300	R	1.7 W/cm ²	[39]
Med pressure Hg lamp	> 280	450	A	4.96×10^{-6} Einstein/Ls	[44]
Xe arc lamp system with filtering	400–500	1000	A	3.04×10^{-5} einstein/Ls	[25]
Custom UVA system	300–420, max ~350	640	R	6.3×10^{-5} einstein/m ² s	[45]
Custom LED Illumination System (UV)	390–410	10–12 mW	M	n/s	[46]
Custom Xe arc lamp apparatus	n/s	500	A	10.85×10^{-8} to 2.75×10^{-6} einstein/s	[47]

^a M, Manufacturer specifications; N, none reported; R, radiometer; SR, spectroradiometer; A, actinometry.

^b n/s: not specified.

the removal of small organic compounds, such as pharmaceuticals, dyes, and pesticides, with advanced oxidation processes (AOPs). One AOP method is the use of photocatalytic materials, such as TiO₂, which absorb light and generate reactive oxygen species that initiate the breakdown of contaminants. As a result of its commercial availability [30], TiO₂ is both frequently researched for materials improvements and commonly used as a reference material to benchmark the performance of new photocatalytic materials [31–33]. As a result, there is a wide range of results in the literature on TiO₂ photocatalysis; and very few common metrics by which to compare the results.

Much of the confusion in TiO₂ research stems from insufficient reporting on the light sources used during the experiments. For example, one group may report the manufacturer specifications of the light they used, while others might report actinometry or radiometry experiments. A survey of literature results from TiO₂ photocatalysis is compiled in Table 1. In particular, the entries illustrate the diversity of approaches used to characterize light sources and emphasize the need for a consistent approach to reporting such information.

The entries in Table 1 show that illumination systems vary widely and the characterization of and reporting on their bulbs, settings, filters, power, intensity, and photon flux is often missing or incomplete. There is even greater variation in the units used (see Ref. [34] for a thorough explanation of terms and units). Some accounts report manufacturer specifications [35–37], while others used single wavelength radiometers [38,39]. Only one report in the group used a fully calibrated spectroradiometer to determine the incident spectral irradiance [40]. With light as a key reagent, the measured degradation rates for contaminants in any light-activated experiment will depend on the intensity and the spectral distribution of incident light.³⁴ With incomplete characterization, photo-chemistry results are impossible to compare, reproduce or transition to applications.

3.1.2. TiO₂ photocatalysis with different illumination systems

To systematically study the role of incident light on TiO₂ photocatalysis, we performed degradation experiments with methyl orange (MO), a common probe dye, and carbamazepine (CM), a real-world contaminant of emerging concern, as case studies. We conducted the degradation experiments under illumination with some common laboratory systems and geometries: i) from the top with a broad band system (W-H); ii) from a single side with a quasi-collimated broad band system (XE); and iii) radially with a pseudo-single wavelength system (UV-F). See SI and Fig. S1 for detailed description of illumination setups.

Degradation of MO (Fig. 1a) in these three different light sources followed pseudo-first order kinetics, but the rates varied over an order

Fig. 1. First order rate plots for the photocatalytic degradation of a) methyl orange (MO) and b) carbamazepine (CM) with commercial TiO₂ under illumination three different light systems (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

of magnitude (W-H: $0.15 \pm 0.01E-02 \text{ min}^{-1}$; XE: $2.45 \pm 0.06E-02 \text{ min}^{-1}$; UV-F: $1.95 \pm 0.02E-02 \text{ min}^{-1}$), despite the absence of photobleaching in control experiments (Fig. S2). A similarly large variation was found in the CM degradation kinetics (Fig. 1b): W-H: $0.19 \pm 0.02E-02 \text{ min}^{-1}$; XE: $1.71 \pm 0.05E-02 \text{ min}^{-1}$; UV-F: $1.50 \pm 0.02E-02 \text{ min}^{-1}$. The contaminant degradation rates ranked as

W-H < UV-F < XE, for both MO and CM in identical experiments, implying differences in the emission of the three light sources.

For both contaminants, the degradation rate under the XE lamp is approximately 10x greater than the rate under W-H illumination, although both the XE and W-H setups have a reported power of 100 W. Furthermore, the degradation rates in the UV-F system, which have a combined power of 24 W, are not 1/4 of the rates of either 100 W system, but are in fact very similar to the degradation rates in the XE experiments. These inconsistencies emphasize that light emission is important, but wattage isn't the important parameter. Considering that the same commercial TiO₂ was used in all experiments, the variation in degradation rates is clearly not due variations in the photocatalyst material.

3.1.3. Implications/considerations indicated by the case study

Light-activated processes require the wavelength of the incident radiation to match the energy transition(s) associated with the process of interest. For photocatalysis by TiO₂, the incident wavelength must match the bandgap (3.0–3.3 eV) [48], which requires excitation by UV–A (315–400 nm) light [20]. Since the rate of photochemical processes is proportional to the rate of photon absorption, all other factors constant [34], the photocatalysis results indicate that each of the lights are emitting different quantities of photons at key wavelengths. These results emphasize that, without rigorous characterization and reporting, variations in light intensity and spectral distribution can lead to erroneous conclusions about the efficacy of photocatalytic materials and photolytic processes across the fields of photochemistry and photobiology.

3.2. Chemical methods of light characterization

3.2.1. Background on chemical actinometry

One method for quantifying the output of an illumination system is chemical actinometry. A chemical actinometer is a well-characterized photo-activated reaction whose quantum yield is well-defined and relatively constant as a function of wavelength. With this criteria, the rate can be mathematically related to the number of photons incident on the reaction [49]. Importantly, each chemical actinometer has a specific absorption profile, based on the absorbance of the reactants (Fig. 2). For example, the potassium ferrioxalate actinometer (FeOx) responds to UV

and visible light [50,51] (250–500 nm), whereas the valerophenone actinometer (VlPh) is only sensitive to UV-B/A wavelengths (290–330 nm) [52]. Chemical actinometry is a low-cost approach to light characterization, but it is crucial and non-trivial to ensure that the absorption wavelengths of the actinometer match the absorption wavelength(s) of the photo-activated processes under study.

3.2.2. Ferrioxalate actinometer

The FeOx actinometer is based on the light-activated reduction of ferric ions to ferrous ions, and the subsequent complexation of ferrous ions with a developing agent [51]. Traditionally, 1,10-phenanthroline has been used as the developing agent but Ferrozine™ [53], which selectively complexes to Fe(II), can also be used as it avoids the errors and inconvenience caused by the long equilibration times needed for the phenanthroline complex to form [54,55]. We employed Ferrozine™ as a developing agent in our reactions. The moles of Fe(II) produced in this zeroth order reaction can be directly related to the photon flux incident on the solution through the quantum yield, which has been reported at a wide variety of wavelengths over the sensitivity range of the FeOx system, 250–500 nm [56].

Our FeOx actinometry experiments featured another important modification from the original procedure reported by Hatchard and Parker [57]. To avoid the difficulties of synthesizing and isolating the light-sensitive potassium FeOx complex, our experiment synthesizes this compound by thoroughly mixing potassium oxalate and ammonium iron(III) sulfate before illumination begins, using the method developed by Goldstein and Rabani [56]. The zeroth-order kinetics for Fe(II) production (Eq. S1) were found to be $3.41 \pm 0.02\text{E-}07$ mol/s in the W-H system, $5.0 \pm 0.1\text{E-}07$ mol/s in the XE system, and $2.67 \pm 0.03\text{E-}07$ mol/s in the UV-F system (Fig. 3a). Unlike the photocatalysis results, the rates only vary within a factor of two and indicate fluxes that vary between the three light systems as UV-F < W-H < XE.

The switch in relative rates between the W-H and UV-F may be a consequence of the wider absorption range of this actinometer. While FeOx technically spans the UVA range, it is also responsive to UVB and visible wavelengths. Even though the quantum yield of the FeOx reaction is lower in the visible region [51], any visible light under 500 nm will contribute to the reaction, thereby affecting the Fe(II) generation rates and thus the overall light flux measurement. As a result, FeOx may be less appropriate for understanding lamp irradiance in TiO₂ experiments depending on the emission from the source (Fig. 2).

3.2.3. Valerophenone actinometry

We also performed actinometry using VlPh. As described by Zepp et al., the photolysis rates of this first order reaction can be used to determine the incident photon flux available to a reaction [58]. Valerophenone has a large absorbance at 250 nm (Fig. 2), however the quantum yield is only defined over the range of 290–330 nm which limits the methods to these wavelengths. Use of this method with typical germicidal UVC bulbs, which have an emission peak at 254 nm, will result in misleading photon flux values due to the large absorption peak of VlPh at 250 nm.

Used much less commonly than FeOx actinometry, VlPh is more straightforward, as it is a direct photolysis reaction, which only requires the monitoring of VlPh absorbance at 250 nm [59]. As with the TiO₂ photocatalysis experiments, the rates of VlPh degradation were different under all three sources: $0.86 \pm 0.11\text{E-}04$ s⁻¹ in the W-H system, $3.58 \pm 0.04\text{E-}04$ s⁻¹ in the XE system, and $1.58 \pm 0.06\text{E-}04$ s⁻¹ in the UV-F system (Fig. 3b). These results imply a relative rank of bulb irradiance in the three systems as W-H < UV-F < XE.

The VlPh photolysis rate constant measured under the XE lamp is approximately 4x greater than the W-H rate constant, as opposed to more than 10x greater rate for TiO₂ photodegradation of CM and MO exposed to the XE source. Similarly, the rate constant for VlPh degradation under the UV-F lamps is only twice as fast as the W-H

Fig. 2. A conceptual graphic depicting the absorption profiles of ferrioxalate (FeOx) actinometry (250–500 nm) and valerophenone (VlPh) actinometry (290–330 nm). The absorption edge range for TiO₂, with published bandgap energies of 3.0–3.3 eV [48] is represented by the blue shaded rectangle. Note that the magnitudes of the FeOx and VlPh absorbances are arbitrary and are only meant to illustrate the wavelength dependence. Additionally, the listed range for VlPh actinometer is based on the wavelengths for which the quantum yield is defined (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Fig. 3. Chemical actinometry performed in a variety of illumination systems (a,b) to probe the relative radiance of each light system. The FeOx actinometer (a) results show UV-F < W-H < XE, but the VIPh actinometer (b) indicates a relative radiant flux from each system as W-H < UV-F < XE (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

reaction rate. This VIPh data may indicate that the XE and UV-F sources have less light intensity around 300 nm than they emit at 365 nm. Or, it might indicate that the W-H source may have more light intensity at 300 nm than at 365 nm. Without additional data on the spectral output of the light sources, these details cannot be clarified. Moreover, the sensitivity range of VIPh does not extend to the UV-A region, where TiO₂ is active (Fig. 2), so the photon flux values it yields are not sufficiently expansive to TiO₂ photocatalysis results.

3.2.4. Chemical actinometry interpretation of photocatalysis results

Regardless of the limitations on the actinometers, both can be used to calculate photon flux. The calculations for FeOx flux (E_{FeOx}) require the reaction rate ($Fe(II)$ generated), Surface area (SA), quantum yield (Φ), and illumination time (t) (Eq. (1)).

$$E_{FeOx} = \frac{Fe(II)_{generated}}{SA \cdot \Phi \cdot t} \quad (1)$$

Correct use of the FeOx actinometer requires the use of solution concentrations that ensure all incident photons are absorbed into the volume of solution [60,61]. This optically concentrated nature of the FeOx means it is a probe of the photon flux that is incident on the surface of the solution. As a result, surface area is important geometric quantity in the calculations. In contrast to FeOx, VIPh is an optically dilute solution, and the path length to volume ratio is needed to account for the fact that not every photon will be absorbed. Calculation of

Table 2

Calculated Photon Flux Values for Three Illumination Systems using Two Different Actinometers.

	Photon Flux (einsteins/s)	
	Valerophenone	Ferrioxalate
W-H	$4.6 \pm 0.5E-9$	$2.8 \pm 0.1E-07$
UV-F	$1.9 \pm 0.2E-8$	$2.2 \pm 0.1E-07$
XE ^a	$2.2 \pm 0.2E-8$	$4.4 \pm 0.4E-07$
Relative Rank	W-H < UV-F < XE	UV-F < W-H < XE

Set to 100 W.

^a Equipped with a filter transmitting 330–800 nm at > 95% Transmittance.

photon flux from VIPh (E_{VIPh}) requires the rate constant (k), quantum yield (Φ), and molar absorptivity (ϵ_λ), and path length to volume ratio (l/V) (Eq. (2)).

$$E_{VIPh} = \frac{k}{1000 \cdot 2.303 \cdot \Phi \cdot \sum_{\lambda=290}^{330} \epsilon_\lambda (l/V)} \quad (2)$$

For more details on the photon flux calculations, including the surface areas calculated for each light system, see SI, Figs. S3&S4, Eqs. S2–S9.

Photon flux values are compiled in Table 2. The values follow the same relative orders as the reaction rates for each actinometer. The fact that the XE lamp demonstrates the highest relative photon flux as measured by both actinometers indicates that it may have a relatively uniform output across a wide range of UV and visible wavelengths. Interestingly, the VIPh flux values are an order of magnitude smaller than the FeOx flux values. This could be because the FeOx actinometer samples a much larger range of wavelengths (250 nm as opposed to ~40 nm), so the total number of photons counted is much greater. It is important to note that the photon flux values derived from each actinometer are a sum of all photons incident on the reaction with wavelengths that correspond to the absorptivity of the actinometers. As a result, these values cannot be used to understand the spectral distribution emitted by each light system.

3.3. Optical methods of Light Characterization

3.3.1. Optical radiometry

Radiometry instruments use optical components to gather, separate, and detect wavelengths of light. Radiometers are designed to measure a single wavelength, while spectroradiometers can measure spectral emission across a wide range of wavelengths [51]. Radiometric instruments are available with a range of capabilities; those that yield qualitative measures of spectral intensity to those that quantitatively measure single and full spectral irradiances. In the context of photochemical experiments, radiometers offer a seemingly simple means to measure the power and/or spectral features of laboratory-based light systems.

3.3.2. Single wavelength characterization

If calibrated, ‘point radiometers’ can be used to quantitatively measure the radiant power emitted by a light source at a defined wavelength. Also known as the irradiance, these measurements require the use of an integrating sphere or a diffuse reflectance panel, as the quantity irradiance is defined as ‘wavelengths incident from all upward directions’ [34]. An example illustrating the correct use of a reflectance panel is include in SI (Fig. S5).

We used a calibrated point radiometer, equipped with three different UV (254, 310, 365 nm) sensors to measure the light emitted by each of the three light systems. The data (Fig. 4a) indicate that the UV-F system has the greatest irradiance at 365 nm, but the XE light system emits the greatest irradiance at 310 nm, despite the fact that the XE

Fig. 4. Optical characterization of the three different illumination systems used for experiments: (a) Line radiance as measured on the three different systems with a point radiometer equipped with single wavelength sensors. The absence of data in the XE and W-H series at 254 nm is consistent with the filtering and specifications of the lights at these low wavelengths; (b) Broad spectrum intensity measured with an uncalibrated compact spectrometer; (c) Full spectral irradiance characterization performed with a calibrated spectroradiometer. The insets highlight the dominant spectral features in the vicinity of the TiO₂ bandgap (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

light system was equipped with a filter transmitting only 330–800 nm. At 254 and 310 nm, the irradiance from the W-H light system is negligible and only approaches a measurable value (0.03 W/m²) at 365 nm.

The results from the 310 nm sensor match the relative intensity measured with the VIPh actinometer (290–330 nm) where the relative rank was W-H < UV-F < XE. However, the relative rank of the irradiance from the different light sources measured at 365 nm doesn't

match the FeOx results, which placed UV-F < W-H < XE. Likely it is the longer wavelength emissions from the light systems that affected the precision of the FeOx actinometry results. Looking again to the TiO₂ case study, we find that the relative rank of the irradiances from the three lights at 365 nm doesn't match the relative degradation rates for MO and CM, which both went as W-H < UV-F < XE.

One possible explanation for these contradictions is revealed with a close examination of the point radiometer sensor absorption profiles. In practice, point radiometer sensors are designed to be used on single wavelength light sources (i.e., lasers, LEDs) because they actually absorb a distribution of wavelengths [62]. For example, the response range of the 310 nm sensor we used shows a Gaussian distribution which is centered on 310 nm but stretches from 260 to 360 nm. Thus the XE system transmitting 330 < λ < 800 exhibits measureable output with the 310 nm sensor. Moreover, the 365 nm sensor absorption profile is represented by a dual peak, where in the maximum is just below 360 nm.

When point radiometers are used to measure broad spectrum sources like the ones used in this study (XE, W-H), the sensors may incorrectly represent the full integrated output of a light from 260 to 360 nm as the irradiance at a single wavelength, 310 nm in this example. Even single wavelength sources, such as LEDs, have emission spectra which span ≥ 50 nm and will contribute to the single wavelength measurements with varying weighting. It is critical to keep calibrations current, since the sensor absorption is normalized to unity at its listed wavelength. Regardless, a full understanding of light output, and its consequences on chemical reactions (e.g., kinetic) data can only be accomplished with broad spectrum characterization.

3.3.3. Broad Spectrum characterization

Fundamentally, a spectrometer is an optical instrument for measuring light properties as a function of wavelength; the light emission from an external source is spectrally separated by means of a monochromator. The wavelength sensitivity ranges vary between spectrometer models, allowing researchers to probe the relevant spectral range for their experiments. To fully illustrate the capabilities and limitations of these optical instruments, we used two types of spectrometers; a qualitative compact spectrometer and a calibrated spectro-radiometer.

3.3.3.1. Qualitative measures of spectral intensity. We measured the light emitted from our three different light sources with a compact spectrometer, which returned qualitative values of intensity in arbitrary units (Fig. 4b) over the range of 190–1000 nm. As with the point radiometer, measurements were performed using a diffuse reflectance panel. Each light source had a unique fingerprint and spectral range. The UV-F illumination system is characterized by a single peak in the UV-A range. The XE source revealed a broad peak centered on 600 nm, spanning from 375 nm to 850 nm. The W-H source also exhibited a broad peak, which spanned from 400 to over 1000 nm. These findings illustrate that the illumination intensity from the three lights varies as a function of wavelength, even for the pseudo-single wavelength source (UV-F).

The relative intensities of the lights measured by the compact spectrometer show very good correspondence to the irradiances measure with the calibrated point radiometer at 365 nm: UV-F > XE > W-H. These consistencies contrast with the relative MO and CM degradation rate constants (XE > UV-F > W-H) and the FeOx and VIPh kinetics (XE > W-H > UV-F and XE > UV-F > W-H, respectively), which all implicate XE as emitting the greatest light flux. The spectral distribution 'seen' by the compact spectrometer does provide some insight into these discrepancies. The XE and W-H lights are broad spectrum sources, but the W-H system has negligible emission below 400 nm and the XE source emission begins to increase near 375 nm. As a result of the greater emission of XE and W-H in the visible range, their FeOx values are greatest; due to the negligible emission of the UV-F and W-H lights in the UV-C range, the VIPh rate constants are (relatively)

the lowest.

While the qualitative spectral data gathered with the compact spectrometer provides valuable insight, it must be stressed that these values are qualitative. To comprehensively interpret data from light-activated reactions, a quantitative spectral distribution of light emitted by a particular illumination source is needed. To achieve this, measurements with a calibrated spectro-radiometer are needed.

3.3.3.2. Quantitative spectral distribution. We used a calibrated spectro-radiometer to measure the spectral irradiance (in $\text{W}/\text{m}^2 \text{ nm}$) from our three light sources from 340 to 2500 nm. Again, a diffuse reflectance panel was used for the measurements. The data illustrate the blackbody characteristics of the W-H source and the single wavelength nature of the UV-F source and the fairly constant emission from the XE source over 330 to 800 nm (excepting the Xe emission lines) (Fig. 4c). Upon looking closer at the UV-A range (Fig. 4c, inset), we observe that the single peak in the UV-F system is ~ 40 nm at its base, the XE emission is mostly constant across this range, and the W-H system has very little irradiance below 375 nm.

The quantitative spectral distribution obtained for the three light sources shows similarities to that measured with the compact spectrometer, but also there are crucial differences. The qualitative compact spectrometer shows the primarily visible and near IR emission of the XE and W-H illumination systems, but it does not correctly represent their peak shapes or positions. Because they are both calibrated instruments, the spectro-radiometer data can be compared to the point radiometer data taken with the 365 nm sensor (Fig. 4a). The relative irradiances of the three lights matches well with these two calibrated instruments, but the magnitude of the irradiance values is inflated in the point radiometer data, likely due to the sensitivity profile of the 365 nm sensor, discussed above (Sec. 3.3.2).

The spectro-radiometer data helps to interpret the results from photocatalysis and actinometry experiments. While the W-H does have high wattage (100 W) as compared to the UV-F system (24 W) it has the smaller photocatalysis rate constant (Fig. 1a and b), and the highest FeOx flux (Table 2) because it emits primarily visible and IR light. The UV-F bulbs have a single peak centered at 365 nm but have virtually no output either above or below this peak. By contrast, the XE lamp has a relatively constant output across the UV-A and visible regions, resulting in the highest photon flux and greatest MO and CM degradation rate constants overall.

These results, which indicate that the XE source emits the greatest photon flux at key absorption wavelengths for TiO_2 , imply that the TiO_2 photocatalysis is responding to wavelengths that are not on the center of the UV-F peak. By illustration of the spectro-radiometer data, the TiO_2 bandgap of the P25 we used must be closer to 380 nm, the position where the flux from XE exceeds UV-F and W-H (see Fig. 4c, inset). This data highlights the importance of matching light source emission to the absorption profile associated with the experiments being conducted. Clearly, the W-H source is suitable for a wide variety of experiments with visible and IR activated processes, but not for UV-active materials like TiO_2 . On the other hand, the XE source is well-suited for TiO_2 experiments and the UV-F system may be a suitable alternative. A critical corollary is that for materials which may have variable or poorly-defined bandgaps, a single wavelength illumination system is inadequate, because a simple modulation to the bandgap of the material can shift its absorbance off the peak maxima, introducing uncertainty into the amount of light absorbed by the material. Lastly, routine calibration of optical instruments and regular light characterization is needed due to loss of intensity over time (Fig. S6).

3.4. Rectifying optical and chemical approaches to light characterization

An additional benefit of the calibrated spectroradiometer is that the spectral irradiance data can be used to calculate photon flux as a function of wavelength, allowing for comparison of optically- and

chemically-derived light characterization. Using Eq. (3), we calculated the photon flux for each of the three illumination systems,

$$E_{SR} = \int R^*SA^* \frac{\lambda}{hc} \frac{1}{N_a} \quad (3)$$

where E_{SR} is the photon flux in einsteins $\text{s}^{-1} \text{ nm}^{-1}$, R is the irradiance in $\text{W m}^{-2} \text{ nm}^{-1}$, SA is the surface area sampled by the field of view of the spectrometer ($6.355\text{E-}04 \text{ m}^2$), λ is the wavelength in m, h is Planck's constant, c is the speed of light, and N_a is Avogadro's number. While the entire spectrum of photon flux can be obtained this way (Figs. S7), we focused on those wavelengths with relevance to TiO_2 photocatalysis. We chose a 50 nm integration range centered on 365 nm, (340–390 nm) and integrated the spectral photon flux values at each wavelength to arrive at an estimate for photon flux.

The quantitative photon flux values for the three light sources over 340–390 nm were $2.45\text{E-}09$, $3.70\text{E-}09$, and $4.37\text{E-}09$ einsteins/s for the W-H, UV-F and XE illumination sources respectively. This positions the relative rank of their light emission as $\text{W-H} < \text{UV-F} < \text{XE}$ and is consistent with the photocatalysis degradation rate constants. Having finally arrived at a complete and quantitative description of our illumination systems, we are able to more deeply study the relationship between photo-degradation and incident illumination.

The actinometry and radiometry results presented above illustrate the dependence of photo-degradation kinetics on the spectral features of the incident illumination. To further study this relationship, we performed a series of MO and CM photo-degradations with TiO_2 under variable output power (64–136 W) in the XE illumination system, thereby allowing us to access variable incident irradiance without significant changes in the spectral distribution. Then we measured the spectral irradiance for each of the XE power settings (Fig. S8b) and photon flux (Fig. 5). The rate constants for the photocatalytic degradation of both MO and CM show a linear dependence on incident photon flux over the range of $1.5\text{--}4.5\text{E-}9$ einsteins/s.

These results support the views presented in this report; that thorough reporting on the illumination conditions used during light-activation experiments is crucial to the development of these processes for environmental technologies. Going further, the slopes of these plots may also form the basis of a metric for evaluating heterogeneous photocatalytic processes. With units of inverse einsteins, which is moles of photons, the slope of a rate constant vs. photon flux plot is very

Fig. 5. Kinetic rate constants for MO and CM degradation plotted as a function of variable optically-derived photon flux achieved by varying output wattage of the XE power source. The linear relationship between rate and photon flux i) emphasizes the importance of illumination system characteristics in light-activated reactions and ii) indicates the slope as a promising universal metric for evaluating the efficacy of photocatalytic materials to degrade various contaminants. Note: The spectrally-derived photon flux values were found by integrating the calibrated spectral irradiance from 340 to 390 nm.

similar to a quantum yield, as it represents the ‘number of degradation events’ per mole of incident photons [34]. Important details to this plot (Fig. 5) are that the slope as a metric, hereafter referred to as the Rate-Flux Metric (RFM), only applies to a single contaminant and photocatalyst concentration, 25 μ M and 0.1 g/L in this work respectively, under well-defined conditions including impurities and temperature.

Great difficulties have been encountered in calculating quantum yields for heterogeneous photocatalysis because of scattering by the photocatalyst [63] and the requirement of a monochromatic illumination source [64]. Other metrics have been developed in an effort to facilitate comparisons of heterogeneous photocatalysis data, since reaction rates alone are insufficient. Apparent quantum yields and relative photonic efficiencies require a laborious set of experiments, but ultimately can be used to determine the quantum yield [65–68]. Turnover numbers offer a simple efficiency parameter, but do not take into account the role of incident light flux [69]. Other reports have included concentration vs. photon fluence plots [12,70] and rate vs light intensity [71]. Still others have reported degradation rates as a function of photon flow [72]. In all cases, the plots do not show consistent trends, leaving very little commonality between the experiments for identification of a metric. In contrast, by correctly pairing light source spectral emission with the absorption energies of the relevant process, consistent values can be compared and translated. Essentially, determination of the RFM is achieved by simply performing replicates of identical experiments in an illumination system with variable output. Moreover, this approach is applicable to reactions performed under broad spectrum illumination, provided that the photon flux was derived from the full spectral emission of the illumination source.

4. Conclusion

Our photocatalysis and photolysis (actinometry) data demonstrate the effects light emission can have on the observed reaction rates. In addition, the actinometry and optical characterization presented shows the difficulty in fully understanding and characterizing the output of a light source, as well as the ability of some characterization methods to present misleading and/or contradictory results. When these factors are not considered, or properly reported in publications, literature results can be extremely difficult to interpret and compare. Because of this, reported photocatalysis rates should be examined carefully: are stellar degradation rates a result of a lucrative photocatalyst, a very powerful light source, or an optimal emission/absorption overlap? In addition, such results are extremely difficult to replicate. Perhaps an unsuccessful experiment is a result of a poor material, or simply different light source characteristics. To open communication about this and provide clarifications, we performed a case study of TiO_2 photocatalysis of MO and CM in three different illumination systems, which were thoroughly characterized with multiple chemical actinometers and optical radiometers.

Rate constants for MO and CM photocatalytic degradation were shown to be highly dependent on the incident light intensity and spectral distribution. We performed experiments that illustrate the limitations of chemical actinometry due to its wavelength sensitivity. We demonstrated that in concert, point radiometers and compact spectrometers offer a low cost means to sample the characteristic emission spectrum of a light. We also showed that by characterizing the illumination systems with a calibrated spectroradiometer, rigorous quantitative data could be obtained that revealed the linear dependence of MO and CM rate constants on incident photon flux, allowing us to propose the slope as a ‘rate-flux’ metric for comparing and translating results between laboratories. In the absence of any single metric that can fully encompass the many aspects of a photocatalyst, including light scattering, surface area effects, and contaminant concentrations, only thorough reporting can ensure effective technology transition of photocatalysis and other light-activated AOPs from the laboratory to the real world.

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Appendix A. Supplementary data

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14. ABSTRACT Subtle aspects of illumination sources and their characterization methods can introduce significant uncertainty into the data gathered from light-activated experiments, limiting their reproducibility and technology transition. Degradation kinetics of methyl orange (MO) and carbamazepine (CM) under illumination with TiO ₂ were used as a case study for investigating the role of incident photon flux on photocatalytic degradation rates. Valerophenone and ferrioxalate actinometry were paired with optical radiometry in three different illumination systems: xenon arc (XE), tungsten halogen (W-H), and UV fluorescent (UV-F). Degradation rate constants for MO and CM varied similarly among the three light systems as $k_{W-H} < k_{UV-F} < k_{XE}$, implying the same relative photon flux emission by each light. However, the apparent relative photon flux emitted by the different lights varied depending on the light characterization method. This discrepancy is shown to be caused by the spectral distribution present in light emission profiles, as well as absorption behavior of chemical actinometers and optical sensors. Data and calculations for the determination of photon flux from chemical and calibrated optical light characterization is presented, allowing us to interpret photo-degradation rate constants as a function of incident photon flux. This approach enabled the derivation of a calibrated 'rate-flux' metric for evaluating and translating data from photocatalysis studies.					
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