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Comparing different light-degradation approaches for the degradation of crystal violet and eosin Y

Mimi J. den Uijl [a,b,*], Anika Lokker [a,b], Bob van Dooren [a,b], Peter J. Schoenmakers [a,b], Bob W. J. Pirok [a,b], Maarten R. van Bommel [a,b,c]

[a] University of Amsterdam, van 't Hoff Institute for Molecular Sciences, Analytical-Chemistry Group, Science Park 904, 1098, XH, Amsterdam, the Netherlands
[b] Centre for Analytical Sciences Amsterdam (CASA), the Netherlands
[c] University of Amsterdam, Amsterdam School for Heritage, Memory and Material Culture, Conservation and Restoration of Cultural Heritage, P.O. Box 94552, 1090, GN, Amsterdam, the Netherlands

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ABSTRACT

Organic colourants have important applications in many fields. Their photostability is an important characteristic. Several methods to study photodegradation were compared in this work. Eosin Y (C.I. Generic name: Acid Red 87, EY) and crystal violet (C.I. Generic Name: Basic Violet 3, CV) were used as test compounds, both in solution and dyed on silk. Commonly applied methods were included, *viz*. Xenotest, Microfading-Tester, and light-box (Spectrolinker) experiments. A novel method was based on a liquid-core-waveguide (LCW) cell. After photodegradation on textile, extraction was performed using dimethyl sulfoxide (DMSO). The degraded solutions and extracts were analysed with liquid chromatography combined with diode-array detection and mass spectrometry. The degradation products were compared between techniques. Degradation in the LCW cell progressed much faster than in standard tests (Xenotest and Spectrolinker) and could be performed online, without a need for extraction or sample transfer. The degradation of CV in the LCW was comparable to its degradation in standard tests. For EY, there was a clear difference in degradation mechanisms between in-solution and on-textile samples. This could be due to the matrix or to incomplete extraction. Because the light sources used in the different experiments differed in energy and spectral emission, the results could not be quantitatively compared. However, the degradation products formed were shown to be independent of the light source. Therefore, the LCW is an attractive method for rapid and efficient studies into the chemistry of photodegradation.

1. Introduction

Organic colourants are important components in many products within fields such as food production, forensic science, cultural heritage, and the paint industry [1–5]. The stability of these colourants depends on many external stress factors, such as temperature and moisture and, most importantly, light [1,6]. The photostability of a colorant determines its applicability (*e.g.* in food or paint industry). Also, it may reveal information about the object it was applied to (*e.g.* in the field of forensics or conservation). Thus, there is significant interest in the photostability of colourants and a growing interest in degradation pathways and products [7–9]. In food science, a better understanding of the photodegradation pathway may lead to better products with longer shelf life [10]. Wastewater treatment may be improved if the influence of key parameters on the degradation of contaminants is known [11,12]. In cultural-heritage research, a better understanding of degradation processes of colourants can aid in dating the object, generating historical context, and developing mitigation strategies [8,13].

Techniques currently used in photodegradation research have serious limitations and tend to be very laborious. Many techniques investigate only the loss of colour and do not provide understanding of the chemical degradation process, or they focus solely on the degradation of the main compound [14,15]. Within the field of cultural heritage, photodegradation research is performed using many different

Abbreviations: BHBA, 2-(3,5-dibromo-2,4-dihydroxybenzoyl)benzoic acid; CV, crystal violet; DAD, diode-array detector; DMSO, dimethyl sulfoxide; EY, eosin Y; LC, liquid chromatography; LCW, liquid-core waveguide; MFT, microfading tester; MK, Michler's ketone; MS, mass spectrometry; SL, Spectrolinker; XT, Xenotest.

* Corresponding author. University of Amsterdam, van 't Hoff Institute for Molecular Sciences, Analytical-Chemistry Group, Science Park 904, 1098 XH, Amsterdam, the Netherlands.
E-mail address: M.J.denUijl@uva.nl (M.J. den Uijl).

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techniques. The most commonly used setup is the Xenotest (XT), which is a standardized method, widely used in the textile-manufacturing industry [16]. It has been developed to measure lightfastness of a wide range of materials, but not necessarily to study degradation pathways. When used in conservation science, model samples (mock-ups) are studied, which are freshly dyed samples that resemble an (often paper- or textile-based) original art object as closely as possible. The instrument consists of a casing with a xenon-arc lamp in the centre, surrounded by several sample holders, which rotate around their own axis and around the lamp to ensure a homogeneous light exposure of all the samples throughout. It is possible to selectively cover parts of a sample to conduct time-series experiments. Additionally, the humidity, temperature, emitted energy, and the illuminance can be controlled. After the desired exposure time, colour measurements can be performed. To study degradation pathways, the sample needs to be extracted and the degradation products must be analysed. The XT has several advantages in comparison with other photodegradation techniques, *viz. i)* the test is standardized, *ii)* it allows measurement of time series, *iii)* it works automatically, and *iv)* the effects of the substrate can be studied. The disadvantages of the technique are *i)* an extraction step is needed prior to analysis, *ii)* the duration of experiments (full degradation can take up to several weeks), *iii)* degradation can only be applied to mock-ups, and *iv)* relatively large surfaces are needed.

Another technique used for measuring the light stability is the MicroFading Tester (MFT) [15]. The MFT was developed to investigate colour fading directly on objects of cultural heritage that can be mounted under a microscope, such as paintings and fabrics. It measures the reflectance of radiation. Since the aim of the MFT is to study light ageing directly on objects, the sample spot is relatively small (0.3–0.4 mm) [17]. In MFTs, the light source is often a xenon-arc lamp equipped with UV-IR filters that eliminate light below 400 and above 700 nm, so as to mimic the light encountered in museums. The advantages of the MFT are the following: *i)* a small spot size, making it applicable to small sample areas of historical objects, *ii)* direct degradation of the colorant on the substrate, and *iii)* measurement of the colour change in real-time. To study degradation mechanisms and kinetics, the MFT has several disadvantages, *viz. i)* an extraction step is needed before analysis, *ii)* the small spot size yields small amount of degraded sample, and *iii)* time series are difficult to perform.

A third and simpler technique is a light box. In a light-box setup, a sample can be placed in a contained space, which is illuminated from the top with a selected light source. An example is a UV crosslinker (such as the Spectrolinker, SL), which is intended for polymerization and light-induced cross-linking of polymers [7]. In the SL a detector monitors the total light dosage. The benefits of this setup include *i)* the possibility to degrade colourants on a substrate or in solution for comparison studies, *ii)* the option to measure time series, *iii)* the possibility to perform many (different) degradations in parallel, and *iv)* the ease of use. The drawbacks of this approach include that it *i)* is time consuming, *ii)* needs relatively large samples to allow off-line analysis, and *iii)* employs a different light source than established methods. Care should be taken when comparing photodegradation in different matrices, since different sample pre-treatment, *i.e.* no sample pre-treatment for solutions but an extraction step for dyes applied on a solid matrix, can affect the composition of the components measured.

Recently, a new photodegradation cell based on liquid-core-waveguide techniques (LCW) was introduced [18]. These LCW cells are made of amorphous-Teflon tubing, the refractive index of which is lower (RI = 1.29–1.31) than that of the liquid inside, resulting in total internal reflection, *i.e.* the light can be coupled in under a specific angle and remains within the liquid core until leaving the tubing at the other side [19]. Because of this, LCWs can be used as elements in photo-detection systems, especially in the ultraviolet and visible ranges (UV–vis) [20,21]. Both absorption and Raman spectroscopic detection [22,23] have been documented with the use of LCWs. When using a strong irradiation source, LCWs can be used to study photo-degradation processes, and when using gas-permeable Teflon tubing, it is possible to carry out such studies in an aerobic or anaerobic environment. The setup also allows studying the effects of solvents and of the addition of components which can affect the degradation mechanisms, such as catalysts or inhibitors [18,19]. Depending on the objectives of the study, the light spectrum can be changed by selecting different lamps and/or by incorporating filters. The recently developed cell allows studying light degradation online in a (multi-dimensional) liquid chromatography setup, as opposed to the offline techniques described above [7,18,24,25]. The LCW cell offers several potential benefits compared to other photodegradation techniques, *viz. i)* faster degradation, *ii)* analysis of the entire sample, *iii)* no need for sample preparation (eliminating sources of error), *iv)* degradation in solution, and *v)* small samples volumes (<60 μL) [18]. Potential disadvantages are the absence of a substrate, which can result in less-representative and less-realistic degradation pathways, and the fact that recording a time series requires a series of separate experiments.

Many of the current photodegradation approaches have not been developed with the intention to study degradation pathways. Currently, there is no consensus on the effects of the various techniques on the observed degradation pathways. The LCW technique is very attractive to study degradation pathways in solution, thanks to much greater versatility. However, for it to be accepted in the field of photodegradation research, the differences between this method and the other available techniques must be documented. This work aims to show how these photodegradation techniques can be compared and whether they can be used to analyse photodegradation mechanisms rather than just the main compound or the colour. Fig. 1 shows a classification of the different techniques used in this study. The techniques on the left illuminate the sample with a xenon lamp, while the right techniques consist of a mercury lamp. The techniques above degrade a sample on a substrate, while the techniques on the bottom degrade the sample in solution. Two techniques in diagonally opposed boxes cannot easily be compared. Observed (quantitative) differences between such techniques could be the result of different lamp spectra and intensities, different extraction efficiencies (*e.g.* in case of textile) or dyeing inconsistencies. Hence, the current study focusses on the practical aspects of different light degradation system and a qualitative comparison.

The current research focusses on the photodegradation of crystal violet (CV) and eosin Y (EY) as model components, both with a poor light fastness (ISO 2 and ISO 1, respectively) [26]. These two components are early synthetic organic dyes, both widely used towards the end of the 19th century, but with many recent applications [9,24,27–32]. Presently, EY is applied in cell staining, as pH indicator, as pigment in for example lipstick, and as a visible-light photocatalyst in organic synthesis [33,34]. CV is nowadays used as a pigment in inks (*e.g.* in inkjet printers) and as a histological staining agent [5,29]. Additionally, it has antibacterial properties and it is used as an alternative to penicillin

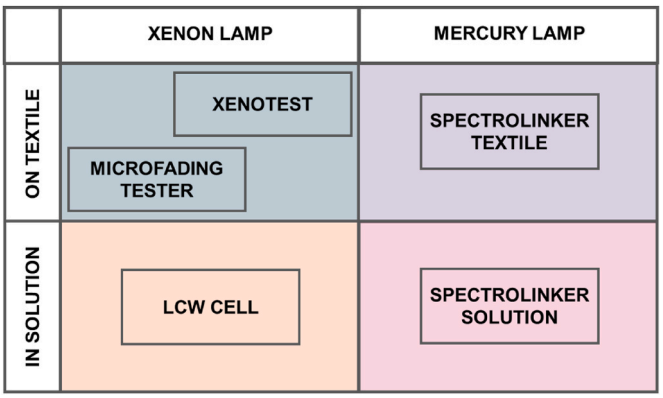

Fig. 1. Scheme of different photodegradation techniques, classified in terms of the type of lamp used and the degradation matrix.

[35]. Much is already known about the degradation pathways of EY and CV, but differences have been observed in degradation mechanisms, depending on many factors, such as the lamp spectrum and intensity, the availability of oxygen, and the matrix, *i.e.* whether the compound was in solution, on textile, or in oil [7,9,36,37].

The objective of the present work is to qualitatively compare degradation studies in the new LCW cell with those in other degradation systems, *i.e.* the Xenotest (XT), Microfading tester (MFT), and more-basic lightbox degradations in a Spectrolinker device (SL). The degradation of two popular colorants, crystal violet (CV) and eosin Y (EY), will be used for this comparison in two different matrices, *i.e.* in-solution and on textile. Finally, we aim to provide recommendations on how to implement the LCW in the field of light-degradation research.

2. Materials and methods

2.1. Chemicals

Milli-Q water (18.2 *M*Ω.cm) was obtained from a purification system (Arium 611UV, Sartorius, Germany). Methanol (MeOH, ULC/MS grade) was obtained from Biosolve (Valkenswaard, The Netherlands). Acetonitrile (ACN, LC-MS) was purchased from Biosolve (Dieuze, France). Eosin Y (C.I. Generic name: Acid Red 87, EY) (99%), crystal violet (C.I. Generic Name: Basic Violet 3, CV) (≥90%), ammonium formate (Fluka, BioUltra ≥99.0%) and dimethyl sulfoxide (DMSO, Chromasolv (≥99.0%) were purchased from Sigma Aldrich (Zwijndrecht, The Netherlands). Sulphuric acid (95–97%) and sodium sulphate (anhydrous for synthesis ≥99.0%) were obtained from Merck (Darmstadt, Germany). Formic acid (98%) was purchased from AnalaR (Poole, UK). All chemicals were used as purchased. The blue-wool standards used for the Xenotest and the Microfading tester that satisfied the BS EN ISO 105 B08 requirements were purchased from SDC Enterprises (Bradford, UK).

2.2. Instrumentation

2.2.1. Xenotest

Photodegradation of dyed silk was performed using a Xenotest 440 (Atlas, Ametek, Mount Proscpet, IL, USA) instrument, including two 2200-W xenon-arc lamps, room for 15 sample holders, and a black standard thermometer. After degradation, the colour change was measured with a Minolta MC-2600d spectrometer (Konica Minolta, Nieuwegein, The Netherlands). The degradation was performed at black standard temperature (BST, 47 °C). Further information about the Xenotest procedure can be found in the Supplementary Material section S-1.

2.2.2. Microfading tester

The microfading tester (MFT) was used to investigate photofading on silk. The instrument consisted of an HPX-2000 xenon-arc lamp (Ocean Optics, Duiven, The Netherlands), a microscope (Stemi SV 11, Zeiss, Breda, The Netherlands), a camera (DFK 41AU02, The Imaging Source, Bremen, Germany) and a detector which was connected using fibre guides to a spectrophotometer (Tidas S 300 MMS Vis/NIR 3011, J&M, Essingen, Germany). The sample was placed under the microscope and the detector was placed at a 45° angle. The light of the xenon lamp was directed through the objective of the microscope to the sample underneath. A removable UV-IR filter was placed between the xenon lamp and the objective of the microscope to filter out all the light below 400 nm. An external power meter (Thorlabs, PM100usb, Newton, NJ, USA) was used to estimate the energy of the lamp and to check its stability. The degradation was performed at room temperature. Further information about the Microfading Tester procedure can be found in the Supplementary Material section S-2.

2.2.3. Spectrolinker

Both the in-solution and on-silk degradation studies were performed in a UV-light box Spectrolinker XL-1500 UV crosslinker (Spectronics, Westbury, NY; maximum wavelength 254 nm). The degradation was performed at room temperature. The degradation procedure is described in the Supplementary Material section S-3.1 for in-solution degradation and in the Supplementary Material section S-3.2 for the on-silk degradation.

2.2.4. Online liquid-core waveguide cell

Degradation in solution was performed with a prototype instrument, incorporating a Teflon AF liquid core waveguide exposure cell (Vrije Universiteit, Amsterdam, The Netherlands). An Argos 250b FL-Detector (Flux instruments, Basel Switzerland) xenon-arc lamp was used for irradiation. The light was directed into the exposure cell via a glass optical fibre. The degradation was performed at room temperature. Further details on the set-up can be found in Ref. [18] and the Supplementary Material section S-4.

2.2.5. Liquid chromatography coupled to diode array detector and mass spectrometry

All liquid-chromatographic (LC) analyses, besides the online LCW degradations, were performed on an Agilent Infinity 1290 2D-LC system (Agilent, Waldbronn, Germany) configured for one-dimensional operation. The system included an Infinity 1290 binary pump (G4220A), an Infinity 1290 diode-array detector (DAD; G4212A), an Infinity 1290 autosampler (G4226A) and an Infinity 1290 column compartment. An Agilent ZORBAX eclipse plus C18 column was used (150 mm length × 2.1 mm i.d., 3.5 μm particles, part nr. 959763-902). For the LC-DAD-MS measurements an LTQ Velos mass spectrometer (Thermo Scientific, Waltham, MA, USA) was coupled in series after the DAD with electrospray ionization. The precursor and product ions are enlisted in the Supplementary Material section S-5.

For online degradation studies, the LCW was coupled with a Shimadzu HPLC system (Shimadzu, Kyoto, Japan) was used, consisting of an LC-20AT vp binary pump (L20224708228), an SPD-M20A diode array detector (228-45005-38), an CBM-20A column module (L20234370270 US L) and a manual 6-port injection valve with a 50 μL injection loop. An Agilent ZORBAX eclipse plus C18 column was used (same as for the 1D-LC experiments), coupled to the LTQ Velos mass spectrometer with electrospray ionization.

2.3. Methods

2.3.1. Dyeing and extraction method

The dyeing and extraction process of the silk samples in this research is described in the Supplementary Material section S-6.

2.3.2. Analytical methods

For the LC analysis of both dyes, mobile phase A and B consisted of mixtures of aqueous buffer and MeOH in ratios of 95/5 (v/v) for mobile phase A and mobile phase B consisted of MeOH/buffer [v/v, 95/5]. The buffer was 10 mM ammonium formate at pH = 3 prepared by adding 0.390 g formic acid and 0.0952 g ammonium formate to 1 L of water. The flow rate is set at 0.2 ml/min. For the analysis of EY samples, the gradient program started isocratically at 100% A from 0 min to 1 min, followed by a linear gradient to 50% B in 1 min and then to 100% B in 4 min. For 3 min the composition was maintained at 100% B, and finally brought back to 100% A in 1 min. The mobile phase was kept at 100% A for 2 min before starting a new run. For the analysis of the CV samples, the gradient program started with an isocratic hold isocratic at 100% A from 0 min to 1 min, followed by a linear gradient to 80% B in 2 min. Until 7 min, the organic modifier concentration was kept at 80% B, followed by a linear gradient to 100% B in 1 min. Until 10 min the composition was maintained at 100% B, before it was brought back to 100% A in 1 min. The mobile phase was kept at 100% A for 2 min before starting a new run. The temperature of the injection chamber was 6 °C, the analyses were performed at room temperature, which was about

295 K. The injection volume for studying the degradation in solution was set at 10 μL for EY and 1 μL for CV (3 μL injection volume was used for trace degradation products). For the extracted XT samples, the injection volume was 20 μL and for the extracted samples irradiated using the MFT it was 10 μL. The solution subjected to online LCW degradation (60 μL) was transported to a 50 μL loop, which was coupled to the analytical system. Every sample was measured in duplicate.

For the online coupling of the LCW, it was coupled to a 6-port injection valve, which was positioned in-line in an LC-DAD-MS system between the pump and the column. Prior to irradiation, 60 μL of sample was injected into the LCW. After irradiation, the sample was transferred from the LCW to the injection loop by injecting 60 μL of elution solvent into the LCW cell. See the Supplementary Material section S-4 for a schematic setup. The gradient used for chromatographic analysis was similar as previously described, but the total analysis time was increased, because of the increased dwell volume of the system.

2.4. Data processing

The chromatograms and UV/vis spectra obtained on the Agilent LC system were processed with Agilent OpenLAB CDS software. The chromatograms and UV/vis spectra obtained on the Shimadzu system were processed with LabSolutions CS, version 5.42 (Shimadzu corporations, Kyoto, Japan). The mass-spectral data were processed with XCalibur, version 2.2 (Thermo Fisher Scientific, Waltham, MA, USA). Calculations performed using in-house routines written in MATLAB R2018b (Mathworks, Natick, MA, USA). Microsoft Excel was used for further data processing.

3. Results & discussion

Five different photodegradation techniques were tested with EY and CV as test analytes, varying the illumination source and the matrix of the dye, *i.e.* textile or solution. The extracted samples irradiated using the MFT turned out to be not very reliable, probably due to very small size of the actually degraded sample. This resulted in very low amounts of dye and degradation products extracted. Although the technique may be suitable to study the photostability, it cannot be used to study chemical degradation mechanisms. The photodegradation results obtained by the other four techniques are summarized in Fig. 2 and Fig. 3 for EY and CV, respectively.

3.1. Degradation in the Xenotest

The Xenotest (XT) is mostly used in the textile industry. It provides a standardized method for testing the light stability of colourants on a solid matrix. The large surface area of textile illuminated in the XT (*e.g.* 200 × 200 mm) allows performing time series and repeats on a single sample. A degradation series was created with a maximum duration of 35 h for EY (Fig. 2A) and 80 h for CV (Fig. 3A). This yielded a total light dose of 57 J/mm^2 and 129 J/mm^2, respectively. In the degradation of EY (Fig. 2A) the only debrominated product observed is the first debrominated species. The photo-oxidation product 2-(3,5-dibromo-2,4-dihydroxybenzoyl)benzoic acid (BHBA) was also observed. This product was recently identified by Chieli et al., who characterized it in both samples irradiated with visible light and with a combination of visible and UV light [38]. Since there is no further debromination of the first debromination product, its peak area can increase to more than 50% of that of EY. The degradation of EY in the XT test was stopped after 35 h (*vs.* 80 h for the degradation of CV), because the dyed textile was already completely faded at this time. This observation is not in line with the LC results, which show that the peak area of EY is still double that of the first debrominated product. The latter is also not colourless, while the other observed degradation product (BHBA) has a yellowish colour. One of the reasons for this discrepancy may be that the photodegradation of textile mainly affects the outside of the fibres, while the colorants present inside the fibre or fabric are less exposed. This is the main difference from in-solution degradation, where the sample is homogenized during fading. In addition, part of the EY may possibly be degraded to other (colourless) compounds that were not recorded during analysis.

In Fig. 3A, the degradation over time (up to 80 h) of CV in the XT experiment is shown. As can be seen in the figure, four demethylated products of CV are present in high concentrations relative to CV. A gradual increase in concentration of all these degradation products is

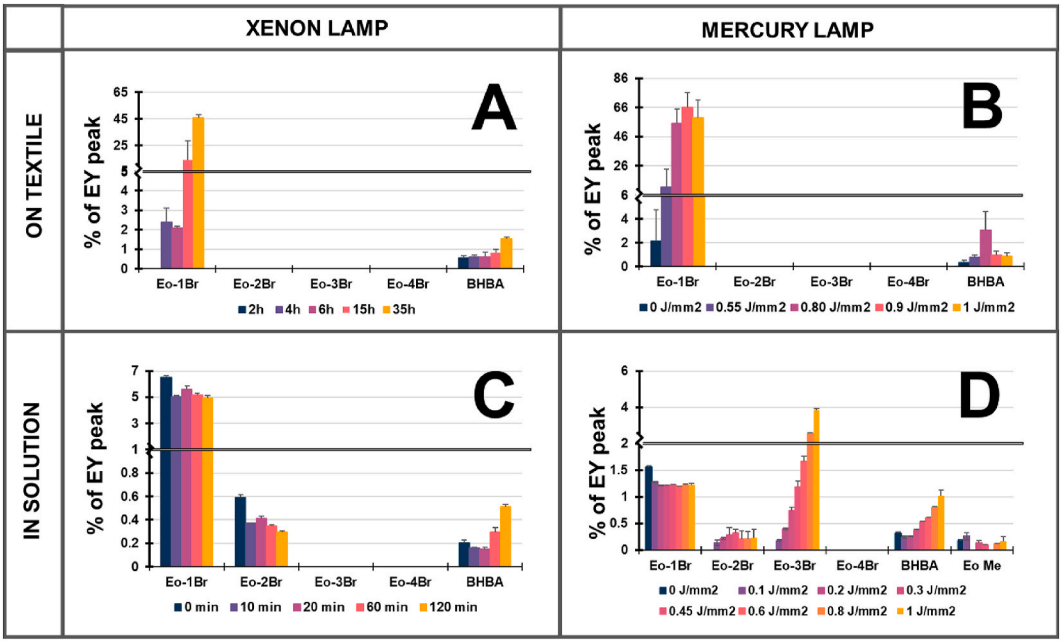

Fig. 2. Degradation of eosin Y (EY). The ratio of the areas of the degradation product peaks and the EY peak is shown for various light doses or illumination times, as indicated on the *y*-axis. The relative areas of the four debrominated products and the oxidation product BHBA are shown. Experiments with the Xenon lamp were performed using the Xenotest instrument on textile (Fig. 2A) or the LCW cell for solutions (Fig. 2C). Experiments with the mercury lamp were performed using the Spectrolinker instrument (Fig. 2B and D for textile and solutions, respectively). The thick horizontal line indicates a change in the vertical axis.

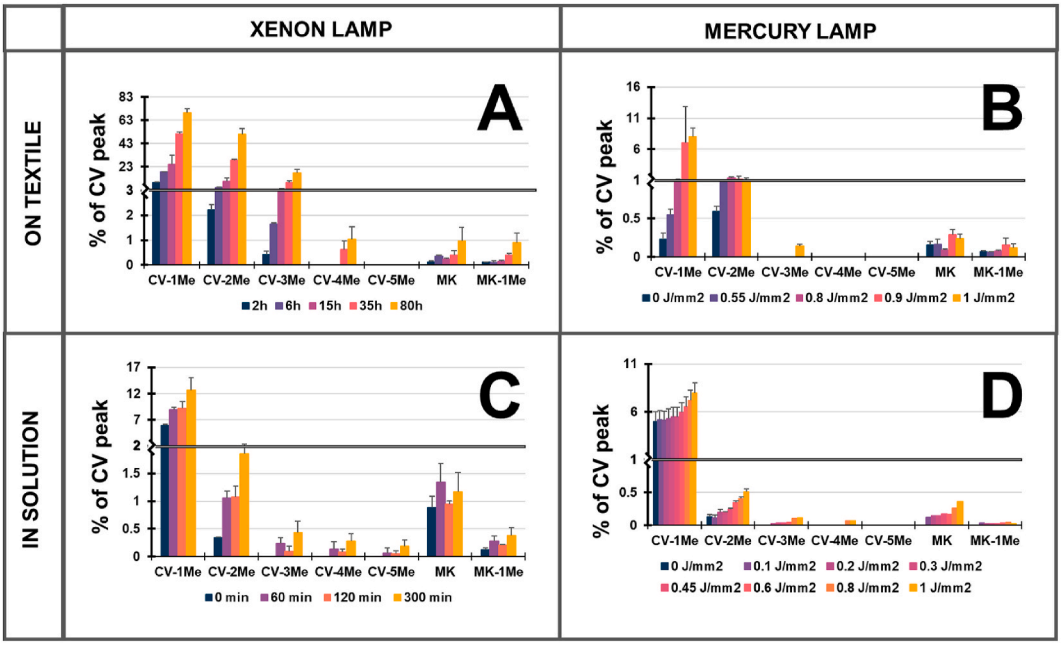

Fig. 3. Degradation of crystal violet (CV). The ratio of the areas of the degradation product peaks and the CV peak is shown for various light doses or illumination times, as indicated on the *y*-axis. Peak areas relative to that of CV are shown for the five demethylation products (CV–1Me through CV-5Me), the oxidation product MK, and its demethylated form (MK-1Me). The thick horizontal line indicates a change in the vertical axis.

visible and, since all these degradation products are formed sequentially (*i.e.* the second demethylated product can only be formed from the first demethylated crystal violet, the third from the second, and so on), greater amounts of the daughter compounds are formed than are being consumed. Next to the coloured demethylated products, Michler's ketone (MK), which is the product of oxidation of the central carbon atom [31], and the demethylated MK, which is the oxidation product after the first demethylation reaction, are both formed.

While degradation of EY and CV in the XT instrument is time-consuming, it is an easy-to-use technique and time series can be generated relatively easily. The downside is that the sample needs to be extracted prior to analysis, which is quite time-consuming, easily doubling the total experiment time. Furthermore, it is clear the EY sample is not degraded homogeneously and likely the same is true for CV. Besides the possible introduction of error, the extraction method can be analyte dependent and exhibit different specificity for the different degradation products, leading to possible invalid conclusions about the degradation mechanism.

3.2. Degradation in the microfading tester

Another technique that is used to test the photostability of colourants in the field of cultural heritage is the Microfading Tester (MFT) [15]. This technique performs the degradation on a solid sample, for example a textile or a painting, similar to the XT experiment, but on a smaller area. In the MFT, the goal is to test the light stability of an art object with minimal damage. For the current research, the spot size of the MFT experiment was increased to enlarge the area of the illuminated sample, which was later extracted. Because the spot size exceeded the range of the microscope, the total dose of this degradation could only be estimated (130 J/mm2), a dose comparable with 80 h exposure in the XT. For the degradation of EY-dyed textile no degradation products were found, probably due to the small sample area. In addition, we noticed variations in the concentrations of EY in different samples, indicating that the dyeing process was not very homogeneous. Since the same sample spot of the textile cannot both serve as starting point (t = 0) and as degraded sample, and since the EY peak area found in the analysis is susceptible to variations, the MFT instrument cannot be used reliably to perform quantitative degradation-mechanism studies for EY. For the CV degradation using the MFT slightly better results were obtained. The degradation was performed during 20 min in threefold, after which the samples were extracted, and analysed. The results are presented in Fig. 4.

The first demethylated product yielded an average percentage peak area of 5.3% relative to CV. The average relative peak area of the second degradation product (CV–2Me) was 0.24%. The average percentage peak area of Michler's ketone (MK) relative to CV was 0.25%. However, a large variation in response was observed, which could be due to inhomogeneous dyeing, incomplete fading (*i.e.* only the top surface), or the low amount of sample extracted.

When comparing these results to those in Fig. 3, the total degradation of CV is seen to be very limited, despite the high total dose (estimated at 130 J/mm^2). Similar to the XT experiment, fading occurs superficially and the core of the fabric may be degraded less. The small spot size results in a low amount of sample extracted. The present results suggest that the contemporary MFT set-ups, such as the one used in this study, cannot be used as a tool for studying chemical photodegradation

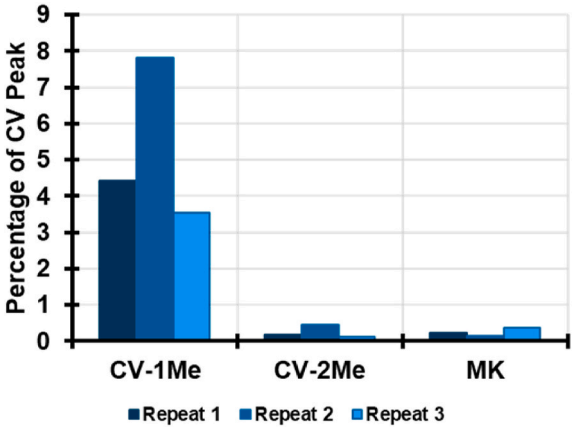

Fig. 4. Degradation of CV on textile using the MFT instrument (triplicate results).

mechanisms. However, reflectance measurements of the extent of discolouration (Supplementary Material section S-7) can accurately be used to confirm the photodegradation of the dye on the surface of the object.

3.3. Degradation in the spectrolinker

In this research, degradation of EY and CV was performed in the Spectrolinker, which is a controlled light box, designed for photopolymerization. The main reason to include this light box in this research is that it allows both in-solution and in on-textile degradation. Therefore, recommendations can possibly be made by comparing degradation of dyes in different matrices. The instrument was previously used to study the effect of the solvent on the degradation of EY [7]. The degradation of EY in DMSO was found to yield one additional degradation product than in water. In the present work a broad-spectrum mercury lamp was used as irradiation source, with the lower UV range (<300 nm) being blocked with a glass sheet. The degradation of EY is compared in Fig. 2B (on textile) and in Fig. 2D (in solution). The first clear difference is that on textile the debromination reaction only results in the mono-debromination product, while EY debrominates further in solution. The absence of further degradation products of EY is analogous to the results of XT degradation seen in Fig. 2A, confirming the hypothesis that further debromination is not favoured on a textile matrix. The difference in relative peak areas between Fig. 2A and B may be due to different illumination spectra or to the total dose, which differs by a factor of 50. Comparing the degradation of EY in the SL (Fig. 2B) and in the XT (Fig. 2A), the debromination of EY seems to progress much faster in the former. These two techniques cannot directly be compared, because the SL has a lower dose and employs a lower-wavelength spectrum, while the XT produces a higher dose at higher wavelengths during a longer period of time. The faster formation of the debromination products in the SL, despite the lower overall dose, indicates that the photodegradation proceeds much faster at lower wavelengths. The ratio of the first debrominated product of EY to EY on exposed textile is higher than in solution, which can be explained by the observation that debromination continues in the latter case. The amount of BHBA (the oxidation product of EY) formed is similar in both matrices. When examining the degradation in solution (Fig. 2D) a plateau can be observed in the relative concentration of the first debromination product. This indicates that the singly debrominated product is formed about as fast as it degrades, since there is a clear increase in the thrice debrominated product.

The degradation of CV in the Spectrolinker for two different matrices is compared in Fig. 3B (on textile) and in Fig. 3D (in solution). There are no large differences between the degradation mechanisms when comparing on-textile to in-solution degradation. The degradation seems to progress slightly faster in solution, but the differences are small. However, when the degradation in the SL on textile (Fig. 3B) is compared to that in the XT experiment (Fig. 3A), the degradation in the latter is more severe. The demethylation products are formed until four methyl groups have been lost, while the SL degradation only progresses through three demethylation steps after a total dose of 1 J/mm^2. The two degradation systems (SL and XT) contain different light sources. The emission spectrum of the XT lamp resembles the absorption spectrum of CV, while this is not the case of the emission spectrum of the SL lamp. Moreover, the difference in dose, which is 1 J/mm^2 in the SL and 129 J/mm^2 in the XT, differs by more than a factor 100, which could explain why the degradation in the SL does not progress quite as far as that in the XT. Smaller differences in degradation rates are observed when observing the formation of MK and demethylated MK (Fig. 3A and B). This may be due to the differences in initiation wavelength for the photo-oxidation and demethylation reactions. The ratio of MK-1Me relatively to MK is higher in the degradation of CV in XT (Fig. 3A) since there is more demethylated product. In future research this hypothesis could be tested with similar setups with a Xenon lamp, such as the Solarbox device [39]. The sample throughput of the SL is lower than that of the XT, because for every 0.01 J/mm^2 in the SL the instrument needs to be started manually. It must be noted that the SL was designed for other purposes than photodegradation. The XT is computer controlled and can be programmed according to the requirements. The main advantages of the SL are that it can accommodate both solutions and solid matrices and that the total dose can be closely monitored.

3.4. Degradation in the liquid-core waveguide

3.4.1. Online coupling of the liquid-core waveguide to LC-DAD-MS

In this research, the LCW cell has been applied for the first time as a device for online degradation coupled to LC-DAD-MS. By coupling the LCW cell to a six-port valve equipped with a 50-μL loop, the degraded solution can be transferred to the LC column. This analysis was performed on a different LC-DAD-MS system than the off-line measurements of the XT, MFT, and SL. Since the degraded sample is transferred completely to the LC system, time series can only be obtained by repeating the experiment with different irradiation times. Prior to performing degradation studies on EY and CV, the coupling of the LCW cell to LC had to be validated. To confirm that the sample is transferred from the LCW cell to the LC system completely, a manual injection in the loop of the six-port injection valve was compared to a manual injection from the LCW cell. These experiments were performed for both EY and CV. To investigate the adsorption of CV on the Teflon wall, CV was dissolved in either 100% H_2O or 50%/50% H_2O/MeOH (by volume).

In Fig. 5 the results are shown for an injection of 5 ppm CV solution in either 100% H_2O or 50/50H_2O/MeOH in the LCW cell and for an injection of 50 ppm EY in H_2O. Each sample was either directly injected in the loop or transferred from the LCW to the LC system with a flush of H_2O or transferred with a flush of MeOH. From the latter two experiments, the first bar indicates the total area of CV or EY in the transferred sample (in the sample solvent), while the second bar indicates the total area of CV or EY in the flush solvent, *i.e.* H_2O or MeOH. For all three samples, a direct injection of sample yields a higher response compared than an LCW transfer. For EY, the signal from direct injection (C1) is 37% higher (average of C2 and C4). For CV, this is 50% (A1 compared to A2 and A4) for the 50/50 MeOH/H_2O sample and 130% (B1 compared to B2 and B4) for the H_2O sample. The difference between the latter two numbers indicates the higher adsorption of CV to the Teflon wall from a fully aqueous solution. A similar trend is visible in the flush with water compared to the flush with MeOH, *i.e.* a flush with water yields smaller areas than a MeOH flush. From the results for CV, 50/50H_2O/MeOH was chosen as the degradation solvent in further experiments. For EY, the differences between the H_2O flush and the MeOH flush were smaller, indicating that EY is less prone to adsorb to the cell wall. No second flush was performed in further experiments for either dye, since the yield of the first flush (70%) and the repeatability (RSD <5%) were found to be acceptable.

3.4.2. Degradation in the liquid-core waveguide coupled to LC-DAD-MS

The experiments with the online LCW coupling were performed on a different system than the offline analyses. The online system featured a different UV detector, which showed higher limits of detection, so that not all degradation products could be observed. Therefore, MS detection was used. In Figs. 2C and 3C, the results of the degradation of both dyes in the LCW cell are shown, based on the mass spectra instead of the DAD results. The ionization efficiencies of the debromination products of EY are expected to be similar to that of EY, as well as the demethylation products of CV to CV, because the ionized groups are the same. Recording a time series using the LCW required a series of independent experiments, resulting in somewhat higher standard deviations. When comparing online degradation in the LCW cell to in-solution degradation using the SL, there were some specific differences that could affect the degradation. First, the dye solution was illuminated with a different light source. In the LCW cell a xenon lamp was used with a glass optic fibre, blocking the lower UV (<300 nm) from the spectrum. The SL

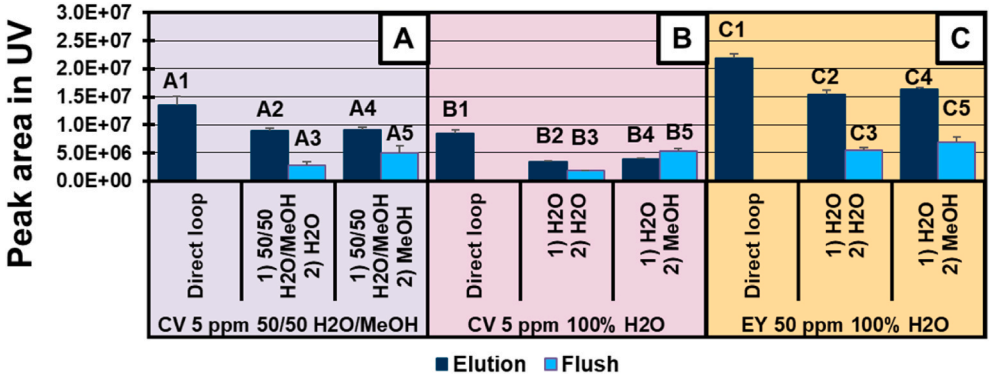

Fig. 5. Sample transfer directly from the six-port injection valve ("Direct loop") or from the LCW. The experiments in box A show the injection of a 5 ppm CV solution in 50/50H_2O/MeOH, the experiments in box B show the injection of a 5 ppm CV solution in 100% H_2O and the experiments in box C show the injection of a 50 ppm EY solution in 100% H_2O. Within each box the first bar (A1, B1, and C1) shows the peak area obtained from the direct loop injection of the sample. The second experiment in each box shows the elution of the sample (A2, B2 and C2) and a flush with water (A3, B3, and C3). The last experiment shows the elution of the sample (A4, B4, C4) and a flush with MeOH (A5, B5 and C5). Standard deviations are indicated with an error bar ($n = 3$).

contained a mercury lamp in combination with a glass sheet, also blocking the lower UV range. This resulted in different irradiation spectra, which might affect the degradation of the two target compounds absorbing at higher wavelengths. This could potentially lead to different reaction mechanisms or reaction kinetics. Another difference was the introduction of the sample. The LCW cell was coupled online to an LC-DAD-MS system. Since the degradation in the SL was performed off-line, there is a greater chance of introducing errors in the handling of the sample or because of evaporation of the solution during degradation. For the degradation of EY, a similar plateau is seen for the first debrominated product degraded in the LCW (Fig. 2C) and the SL (Fig. 2D). Thrice and fully debrominated products were not found within 120 min of degradation. The formation of BHBA followed similar pattern in the two systems, but the %-area was lower in the SL. This difference could be due to the detection method (MS in the LCW degradation and UV in the SL degradation). Since BHBA was an oxidation product, photo-oxidation could be observed in the LCW, presumably due to its gas permeability.

The degradation of CV during 5 h in the LCW (Fig. 3C) is seen to progress to the fifth demethylation product, which is not observed during the 80-h degradation in the XT system (Fig. 3A) and the SL experiments (Fig. 3B and D). Michler's ketone was detected in the LCW system, again confirming that photo-oxidation occurred. Longer degradation times could lead to more adsorption of CV to the Teflon tubing or to a loss of light due to the formation of air bubbles. This is reflected in Fig. 3C by an increase in the standard deviations at longer irradiation times. Since the volume of the LCW is fixed, the absolute peak areas of EY and CV can be compared over time. This is shown in Fig. 6.

From the error bars in Fig. 6A, the decrease in EY is seen to be precise. For the degradation of CV (Fig. 6B) the standard deviation seems to increase with increasing degradation time. Possible explanations include an increase of adsorption to the fibre or a memory effect. When implementing this system in further degradation studies, care should be taken to minimize the effects of adsorption of apolar compounds on the interpretation of the data, by following cleaning procedures between degradations.

The LCW cell has proven to be a good alternative to off-line degradations in the SL instrument. The difference between in-solution and on-textile degradation has been shown to depend on the dye examined. The LCW cell promises to provide fast and accurate degradation experiments.

4. Concluding remarks

In this study, a newly developed on-line photo-degradation system using a liquid-core-waveguide (LCW) cell implemented. Its performance was compared with that of other photodegradation techniques used in the field of cultural heritage (Spectrolinker, SL; Xenotest, XT; Microfading Tester, MFT). The degradation of two dyes was studied, *i.e.* eosin Y and crystal violet, on two different matrices (in-solution and on-textile) and the advantages and disadvantages of each technique were established. Degradation in the LCW cell progressed much faster than in standard tests (XT and SL) and was performed online, *i.e.* without a need for extraction or sample transfer.

While the degradation in the XT system was slower, it was an easy-to-use technique, although it needed relatively large samples. The required extraction step made the process more difficult and potentially more error prone. The SL method was more labour intensive, since the system had to be started many times. The main advantage of this technique was that it could be applied to both solid and liquid matrices. For the MFT experiment the extraction results showed that the current setup could not be used for the analysis of the chemical photodegradation mechanisms. The XT, MFT, and the SL setups were used to degrade solid

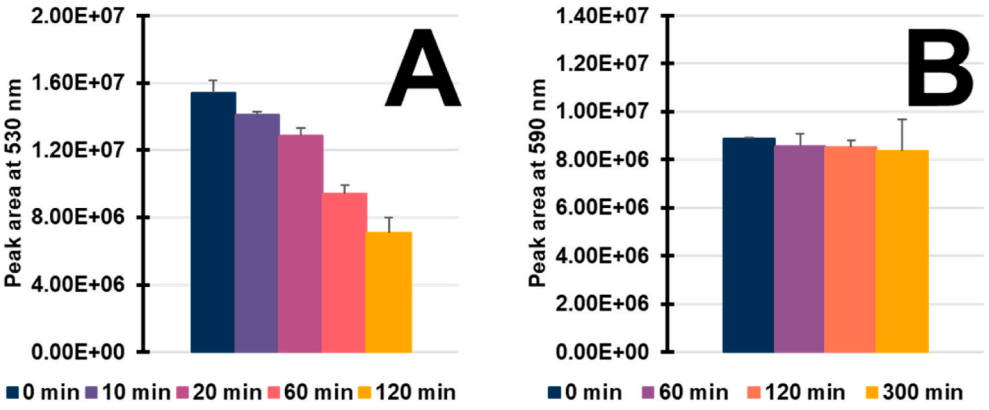

Fig. 6. Total area of EY (left, 530 nm) and CV (right, 590 nm) in the DAD signal over time in the LCW cell degradation.

matrices, while the SL system could also degrade other matrices, such as solutions. The LCW could only be used to degrade liquid samples. The light source of the SL was a mercury lamp, while the other techniques all employed a Xenon lamp. While the degradation of CV in the LCW was comparable to its degradation in standard tests, this was not true for the degradation of EY. In the latter case, there was a clear difference in degradation mechanisms between in-solution and on-textile samples. Indeed, photodegradation can depend on the matrix and some degradation routes may be more-or-less favourable in paper, textile, oil, aqueous solution, etc. Difference in the apparent degradation on textile vs. that in solution may also result from incomplete extraction, since only the compounds that are extracted from the textile are analysed.

The light sources used differ in energy and spectral emission. Therefore, the results of degradation studied cannot be directly compared. Obviously, a higher light intensity leads to increased degradation. In addition, for EY clear effects were observed of the wavelength on the degradation kinetics. However, in the present study the degradation products formed did not depend on the light source. The LCW is good candidate technique for studying the chemistry of photodegradation, especially for small samples. In future experiments the effect of oxygen, the illumination wavelength, and the solution composition (solvent, pH, presence of additives, such as inhibitors or catalysts) on the photodegradation will be studied.

Credit author statement

Mimi J. den Uijl: Conceptualization, Methodology, Validation, Investigation, Formal Analysis, Writing - Original Draft, Visualization. **Anika Lokker:** Validation, Investigation. **Bob van Dooren:** Validation, Investigation. **Peter J. Schoenmakers:** Supervision, Writing - Review & Editing. **Bob W.J. Pirok:** Supervision, Writing - Review & Editing. **Maarten R. van Bommel:** Conceptualization, Resources, Supervision, Writing - Review & Editing, Project Administration, Funding Acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2021.109882.

References

[1] Verduin J, Den Uijl MJ, Peters RJ, Van Bommel MR. Photodegradation products and their analysis in food. J Food Sci Nutr 2020;6. https://doi.org/10.24966/FSN-1076/100067.
[2] Nigel Corns S, Partington SM, Towns AD. Industrial organic photochromic dyes. Color Technol 2009;125:249–61. https://doi.org/10.1111/j.1478-4408.2009.00204.x.
[3] Goodpaster JV, Liszewski EA. Forensic analysis of dyed textile fibers. Anal Bioanal Chem 2009;394. https://doi.org/10.1007/s00216-009-2885-7. 2009–18.
[4] Terán JE, Millbern Z, Shao D, Sui X, Liu Y, Demmler M, et al. Characterization of synthetic dyes for environmental and forensic assessments: a chromatography and mass spectrometry approach. J Separ Sci 2021;44:387–402. https://doi.org/10.1002/jssc.202000836.
[5] Weyermann C, Kirsch D, Costa Vera C, Spengler B. Evaluation of the photodegradation of crystal violet upon light exposure by mass spectrometric and spectroscopic methods. J Forensic Sci 2009;54:339–45. https://doi.org/10.1111/j.1556-4029.2008.00975.x.
[6] Hao Z, Iqbal A. Some aspects of organic pigments. Chem Soc Rev 1997;26:203. https://doi.org/10.1039/cs9972600203.
[7] Pirok BWJ, Moro G, Meekel N, Berbers SVJ, Schoenmakers PJ, van Bommel MR. Mapping degradation pathways of natural and synthetic dyes with LC-MS: influence of solvent on degradation mechanisms. J Cult Herit 2019;38:29–36. https://doi.org/10.1016/j.culher.2019.01.003.
[8] Pérez-Alonso M, Castro K, Madariaga JM. Investigation of degradation mechanisms by portable Raman spectroscopy and thermodynamic speciation: the wall painting of Santa María de Lemoniz (Basque Country, North of Spain). Anal Chim Acta 2006;571:121–8. https://doi.org/10.1016/j.aca.2006.04.049.
[9] Alvarez-Martin A, Trashin S, Cuykx M, Covaci A, De Wael K, Janssens K. Photodegradation mechanisms and kinetics of Eosin-Y in oxic and anoxic conditions. Dyes Pigments 2017;145:376–84. https://doi.org/10.1016/j.dyepig.2017.06.031.
[10] Duncan SE, Chang HH. Implications of light energy on food quality and packaging selection. Adv Food Nutr Res 2012;67:25–73. https://doi.org/10.1016/B978-0-12-394598-3.00002-2. Academic Press Inc.
[11] Hisaindee S, Meetani MA, Rauf MA. Application of LC-MS to the analysis of advanced oxidation process (AOP) degradation of dye products and reaction mechanisms. TrAC Trends Anal Chem (Reference Ed) 2013;49:31–44. https://doi.org/10.1016/j.trac.2013.03.011.
[12] Kolkman A, Martijn BJ, Vughs D, Baken KA, van Wezel AP. Tracing nitrogenous disinfection byproducts after medium pressure UV water treatment by stable isotope labeling and high resolution mass spectrometry. Environ Sci Technol 2015;49:4458–65. https://doi.org/10.1021/es506063h.
[13] Degano I, Ribechini E, Modugno F, Colombini MP. Analytical methods for the characterization of organic dyes in artworks and in historical textiles. Appl Spectrosc Rev 2009;44:363–410. https://doi.org/10.1080/05704920902937876.
[14] Kansal SK, Singh M, Sud D. Studies on photodegradation of two commercial dyes in aqueous phase using different photocatalysts. J Hazard Mater 2007;141:581–90. https://doi.org/10.1016/j.jhazmat.2006.07.035.
[15] Whitmore PM, Pan X, Bailie C. Predicting the fading of objects: identification of fugitive colorants through direct nondestructive lightfastness measurements. J Am Inst Conserv 1999;38:395–409. https://doi.org/10.1179/019713699806113420.
[16] Friele LFC. A comparative study of natural and xenotest exposure condition: for measuring fading and degradation. J Soc Dye Colour 2008;79:623–31. https://doi.org/10.1111/j.1478-4408.1963.tb02522.x.
[17] Whitmore PM, Bailie C, Connors SA. Micro-fading tests to predict the result of exhibition: progress and prospects. Stud Conserv 2000;45:200–5. https://doi.org/10.1179/sic.2000.45.supplement-1.200.
[18] Groeneveld I, Schoemaker SE, Somsen GW, Ariese F, van Bommel MR. Characterization of a liquid-core waveguide cell for studying the chemistry of light-induced degradation. Analyst 2021. https://doi.org/10.1039/D1AN00272D.
[19] Altkorn R, Koev I, Van Duyne RP, Litorja M. Low-loss liquid-core optical fiber for low-refractive-index liquids: fabrication, characterization, and application in Raman spectroscopy. Appl Opt 1997;36:8992. https://doi.org/10.1364/ao.36.008992.
[20] Bescherer K, Barnes JA, Loock HP. Absorption measurements in liquid core waveguides using cavity ring-down spectroscopy. Anal Chem 2013;85:4328–34. https://doi.org/10.1021/ac4007073.
[21] Rubles T, Paige D, Anastasio C. Lens-coupled liquid core waveguide for ultraviolet-visible absorption spectroscopy. Rev Sci Instrum 2006;77:073103. https://doi.org/10.1063/1.2219973.
[22] Marquardt BJ, Vahey PG, Synovec RE, Burgess LW. A Raman waveguide detector for liquid chromatography. Anal Chem 1999;71:4808–14. https://doi.org/10.1021/ac9907336.
[23] Dijkstra RJ, Bader AN, Hoornweg GP, Brinkman UAT, Gooijer C. On-line coupling of column liquid chromatography and Raman spectroscopy using a liquid core waveguide. Anal Chem 1999;71:4575–9. https://doi.org/10.1021/ac9902648.
[24] Confortin D, Neevel H, van Bommel MR, Reissland B. Study of the degradation of an early synthetic dye (crystal violet) on cotton linters, lignin and printing paper by the action of UV-Vis and Vis light and evaluation of the effect of gum Arabic on degradation products and on colour change. In: Creat 2010 conf proc - 'colour coded'; 2010. 81–5.
[25] Sabatini F, Degano I, Bommel M van. Investigating the in-solution photodegradation pathway of Diamond Green G by chromatography and mass spectrometry. Color Technol 2021. https://doi.org/10.1111/COTE.12538.

[26] Society of Dyers and Colourists (Great Britain). American association of textile chemists and colorists. Colour index. third ed. Bradford: Yorkshire; 1974.
[27] Sabatini F, Giugliano R, Degano I, Lluveras-Tenorio A, Sokolová R, Thoury M, et al. Development of a multi-analytical approach to investigate the fading of eosin in painting matrices. IOP Conf Ser Mater Sci Eng 2018;364:012066. https://doi.org/10.1088/1757-899X/364/1/012066. Institute of Physics Publishing.
[28] Alvarez-Martin A, Cleland TP, Kavich GM, Janssens K, Newsome GA. Rapid evaluation of the debromination mechanism of eosin in oil paint by direct analysis in real time and direct infusion-electrospray ionization mass spectrometry. Anal Chem 2019;91:10856–63. https://doi.org/10.1021/acs.analchem.9b02568.
[29] Cooksey C. Quirks of dye nomenclature. 10. Eosin Y and its close relatives. Biotech Histochem 2018;93:211–9. https://doi.org/10.1080/10520295.2017.1413207.
[30] Anselmi C, Capitani D, Tintaru A, Doherty B, Sgamellotti A, Miliani C. Beyond the color: a structural insight to eosin-based lakes. Dyes Pigments 2017;140:297–311. https://doi.org/10.1016/j.dyepig.2017.01.046.
[31] Favaro G, Confortin D, Pastore P, Brustolon M. Application of LC-MS and LC-MS-MS to the analysis of photo-decomposed crystal violet in the investigation of cultural heritage materials aging. J Mass Spectrom 2012;47:1660–70. https://doi.org/10.1002/jms.3110.
[32] Cesaratto A, Lombardi JR, Leona M. Tracking photo-degradation of triarylmethane dyes with surface-enhanced Raman spectroscopy. J Raman Spectrosc 2017;48:418–24. https://doi.org/10.1002/jrs.5056.
[33] Haria DP, König B. Synthetic applications of eosin Y in photoredox catalysis. Chem Commun 2014;50:6688–99. https://doi.org/10.1039/c4cc00751d.
[34] Derayea SM, Nagy DM. Application of a xanthene dye, eosin y, as spectroscopic probe in chemical and pharmaceutical analysis; A review. Rev Anal Chem 2018;37. https://doi.org/10.1515/revac-2017-0020.
[35] Ozkan E, Allan E, Parkin IP. The antibacterial properties of light-activated polydimethylsiloxane containing crystal violet. RSC Adv 2014;4:51711–5. https://doi.org/10.1039/c4ra08503e.
[36] Confortin D, Neevel H, Brustolon M, Franco L, Kettelarij AJ, Williams RM, et al. Crystal violet: study of the photo-fading of an early synthetic dye in aqueous solution and on paper with HPLC-PDA, LC-MS and FORS. J Phys Conf Ser 2010;231:012011. https://doi.org/10.1088/1742-6596/231/1/012011. Institute of Physics Publishing.
[37] Huang YR, Kong Y, Li HZ, Wei XM. Removal of crystal violet by ultraviolet/persulfate: effects, kinetics and degradation pathways. Environ Technol Innov 2020;18:100780. https://doi.org/10.1016/j.eti.2020.100780.
[38] Chieli A, Miliani C, Degano I, Sabatini F, Tognotti P, Romani A. New insights into the fading mechanism of Geranium lake in painting matrix". Dyes Pigments 2020;181:108600. https://doi.org/10.1016/j.dyepig.2020.108600.
[39] Aguirre M, Goikoetxea M, Otero LA, Paulis M, Leiza JR. Accelerated ageing of hybrid acrylic waterborne coatings containing metal oxide nanoparticles: effect on the microstructure. Surf Coating Technol 2017;321:484–90. https://doi.org/10.1016/J.SURFCOAT.2017.05.013.