Journal of Cultural Heritage 38 (2019) 29–36

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Original article

Mapping degradation pathways of natural and synthetic dyes with LC-MS: Influence of solvent on degradation mechanisms

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ARTICLE INFO

Article history:
Received 11 September 2018
Accepted 8 January 2019
Available online 24 January 2019

Keywords:
Art conservation
Mass spectrometry
Dye degradation
Eosin
Carminic acid

ABSTRACT

To help conserve the vast array of (combinations of) dyestuffs and pigments encountered in cultural-heritage objects and application materials, a rapid and convenient method for dye-degradation research is required. In-solution degradation studies of dyes in a strong solvent, such as the commonly used dimethyl sulfoxide (DMSO), are potentially of interest, in addition to studies involving other solvents, such as water. The degradation of eosin and carminic acid under the influence of light was investigated in two solvents, i.e. in a mixture of DMSO and acetonitrile and in pure water. A liquid chromatography – mass spectrometry (LC-MS) method was developed for analysis of the degraded samples and identification of the individual components. The presence of DMSO generally facilitated faster degradation, which, in combination with its universal solvating properties are advantageous. However, different products were formed in the presence of DMSO. Degradation pathways for eosin and carminic acid in these solvents are proposed.

1. Introduction

Whether applied as pigments or dyes, organic colorants in cultural-heritage objects are subjected to various external conditions throughout their lifetime. This often results in degradation. As a result, cultural-heritage objects can change appearance and the original intention of the artist or craftsman can be lost. Conservation of the object for future generations requires extensive research into the identity of the colorants and their degradation. The latter is particularly important, because the current state of a cultural-heritage object may no longer feature the originally applied colorants. Instead a mixture of degradation products may be present. Chemical analysis is conducted with the aims of:

- determining the original composition to understand the creation of the artwork;
- assessing the progress of degradation, which may result in a better understanding of the original appearance, and;
- elucidating the mechanism and state of degradation to allow protective measures to be taken.

The chemical analysis of thousands of – often impure – dyestuffs, used across millions of old and new cultural-heritage objects, poses an immense challenge. Moreover, the mechanism of degradation is intrinsically dependent on the external conditions to which the object is exposed (e.g. temperature, humidity, air composition, light) [1]. Degradation may also be greatly affected by the material to which the dye was applied [2,3]. Therefore, the number of potential cases that must be studied is colossal and rapid convenient methods for chemical analysis are required.

While a large number of non-invasive analytical methods exist to obtain useful information on the dyes applied in the object, crucial information is often missing. Indeed, non-invasive tools, such as Raman, UV-vis, FORS, and fluorescence spectroscopy [4–7], are useful to identify the overall composition of the applied dyes. However, the information is often distorted by signals arising from other materials present in the object, such as varnishes, fillers, additives and, most importantly, bulk materials, such as textile yarns, and binding media necessary to apply organic pigments as paint. In-situ

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https://doi.org/10.1016/j.culher.2019.01.003
1296-2074/

methods typically provide an averaged perspective with signals of all compounds present within the scanning domain confounded.

Alternative methods focus on the extraction of the dyes from the original material and subsequent analysis by separation techniques, such as liquid chromatography (LC) coupled with mass spectrometry (MS) [8–11]. While these methods allow detailed quantitative information to be obtained, there are a number of disadvantages. For example, the extraction procedure can show bias to interaction with specific groups of analytes, which may then be overrepresented in the results. Also, the state of the colorants and their degradation products may be altered by the extraction process

To understand the degradation of dyes, accelerated ageing on textiles or paintings needs to be carried out. This is normally conducted using so-called mock-ups. While the ageing can be accelerated using highly focussed light sources, it may still easily take several weeks before a significant fading is observed. Although this largely depends on the dye and wavelengths used, realistic case studies tend to be time consuming.

As an alternative, we previously investigated the possibility of dissolving dyes and age the solution instead of solid coloured materials [2]. This has the advantages that samples can be taken at regular time intervals and that no sample preparation is required. We observed that the degradation products found in solution match those found when the dye is applied on textile or as ink on paper. Unfortunately, many colorants, in particular organic pigments, are not soluble in water. Moreover, there is a possibility that hydrophobic degradation products are formed during degradation, and that these are excluded from the matrix. One relatively universal and popular extraction solvent is dimethyl sulfoxide (DMSO), which was found to be a fairly good solvent for a vast array of distinct dyes [10].

2. Research aim

In this work, the degradation is investigated of one natural dye, carminic acid, and one synthetic dye, eosin, aged in-solution in water, and acetonitrile with DMSO, under the influence of UV-light. In particular, the applicability and influence of the more-universal solvent DMSO is studied. Ultimately, we hope to establish a universal system for degradation studies using (multi-dimensional) LC-MS analysis.

3. Material and methods

3.1. Chemicals

Acetonitrile (LC-MS grade) was obtained from Biosolve (Valkenswaard, NL), deionized water (MS-grade) was procured from Merck (Darmstadt, Germany). Triethylamine (≥ 99.5%), dimethyl sulfoxide (DMSO, ≥ 99%, SAFC) and formic acid (≥ 96%) were obtained from Sigma-Aldrich (Darmstadt, Germany). The dyestuffs were obtained from the reference collection of the Cultural Heritage Agency of the Netherlands (RCE, Amsterdam, The Netherlands). For comparison, carminic acid was also obtained from Sigma-Aldrich.

3.2. Instrumentation

A Spectrolinker XL-1500 UV Crosslinker (Spectronics Corporation, 254 nm, ca. 1–3 μW/cm^2) was used for degradation of the dyestuffs in-solution. The LC system used for LC-MS analysis comprised an Agilent 1100 series quaternary pump (G1311 A), an Agilent 1260 Infinity degasser (G1322 A), an Agilent Infinity 1290 diode-array detector (DAD, G4212 A) equipped with an Agilent Max-Light Cartridge Cell (G4212-6008, V_{det} = 1.0 μL) and an Agilent 1100 series autosampler (G1313 A). The injection volume was set to 20 μL and DAD data were recorded at several wavelengths at 160 Hz. The system was controlled by OpenLAB CDS ChemStation software (Edition Rev. C.01.04) [Build 35]. An Agilent ZORBAX Eclipse Plus C18 Rapid Resolution HT column (959941-902, 50 × 4.6 mm i.d., 1.8-μm particles) was used. The flow was split using a stainless-steel tee-connection (P/N: U- 428, IDEX, Lake Forest, IL, USA), with a 500 mm × 0.25 mm i.d. tubing to the DAD and 500 mm × 0.12 mm i.d. to the MicroTOF-Q mass spectrometer (S/N 228888.00132, Bruker Daltonik, Bremen, Germany). The MS was equipped with an electrospray-ionization source and configured to run in negative mode at an acquisition rate of 4 Hz. The system was controlled with Compass 1.3 for MicroTOF-SR1 (MicroTOF control Version 3.0, Build 53) from Bruker.

3.3. Procedures

3.3.1. Sample preparation

The dye samples were dissolved in:

- 0.5 mL acetonitrile/dimethyl sulfoxide 1:1 (v/v), and;
- water, in concentrations of about 200 mg/L and were put in 1.8-mL Clear-Glass grade vials obtained from Waters (Milford, MA, USA).

Acetonitrile was used as a part of the sample solution to enhance dye solubility and to improve compatibility of the sample solvent with the LC mobile phase. As a consequence, we cannot rule out that the presence of acetonitrile also affects the degradation (see also section 4). These vials were placed horizontally (with identification on the bottom) on a slat with notches in the UV cabinet. The samples were irradiated with 254-nm UV light for different durations (specified in section 3 below). Samples were taken at regular time intervals (at every 20 min from 0 to 160 min and after 330 min of degradation) and stored in darkness at –24 °C prior to analysis. The dye samples were also dissolved in water for reference, following the same procedure as described above.

3.3.2. Analytical methods

The LC separation was adapted from our earlier described fast ion-pair reversed-phase chromatography method [9]. A buffer containing triethylamine (5 mM) in water and formic acid (to obtain a pH of 3) was prepared. Mobile phase A consisted of buffer/acetonitrile 95:5 [v/v] and B of buffer/acetonitrile 5:95 [v/v]. The flow rate was 1.85 mL/min. The gradient used was as follows. 0 – 0.25 min, isocratic at 100% A; 0.25 – 8.25 min, linear gradient to 100% B, maintained at B for 0.5 min; 8.75 – 9.5 min linear gradient to 100% A. For MS and MS/MS the following operating conditions were used. End-plate offset −500 V; capillary voltage 3800 V (positive mode −4400V); nebulizer-gas pressure 2.0 bar; drying-gas flow 10 L·min^{-1}, source temperature 250 °C. RF1 and RF2 funnels operated at 250V, and the hexapole at 400V. The quadrupole ion energy was 4.0eV and the collision energy used for the different samples ranged from 1.5 to 35eV. The collision RF was at 1500V, the transfer time was 80 μs and the pre-pulse storage time 4 μs. For MS/MS analyses the mass of interest was set to pass the filter with a margin of 0.5 m/z. The isolation width was 8 up until a m/z of 500, then a linear gradient from 8 to 10 from 500 to 1000 m/z.

3.4. Data analysis

For exploratory purposes, the data were analyzed with the DataAnalysis Version 4.0 Sp 4 software (Build 281; Bruker Daltonik). Processing of the chromatograms and comparison of the LC-MS data was carried out using the in-house-written PIOTR program [12].