Forensic Science International 278 (2017) 338–350

Contents lists available at ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

Application of dye analysis in forensic fibre and textile examination: Case examples

Tom G. Schotman, Xiaoma Xu, Nicole Rodewijk, Jaap van der Weerd*

Netherlands Forensic Institute, Division of Chemical and Physical Traces, P.O. Box 24044, 2490AA The Hague, The Netherlands

ARTICLE INFO

Article history:
Received 23 March 2017
Received in revised form 21 July 2017
Accepted 24 July 2017
Available online 31 July 2017

Keywords:
Dye
HPLC
Chromatography
Mass spectrometry
Fibres and Textiles

ABSTRACT

Seven cases and a quality assurance test are presented. In these cases, fibres or textiles submitted for investigation were analysed by HPLC–DAD–MS to identify the dyes present. The cases presented illustrate that it is possible to identify textile dyes in fibre traces recovered for forensic analysis. The results show that a mixture of dyes is present in all textiles investigated, except one sample that was taken from a manufacturer dye shade card. It is concluded that dye analyses improves the evidential value of forensic fibre examinations, as it becomes possible to distinguish textiles that are different in dye chemistry, but have a similar colour. In addition dye analysis makes the examination more robust, as it becomes possible to attribute colour differences between samples to identical dyes (mixed in different ratios) or to chemically different dyes.

1. Introduction

Forensic investigation of trace evidence provides invaluable information on the circumstances of and items involved in many criminal activities. Trace examiners routinely deal with traces that cannot or barely be seen by bare eye. Analytical instrumentation used in the analysis of trace evidence must be very sensitive to facilitate analyses of these minute traces. In addition such instrumentation should be highly accurate: the more information can be retrieved from a trace, the better it can be described, provenanced and related to a known source.

Fibres are a commonly known instance of trace evidence. They are very informative from a criminalistic point of view, as they can be transferred from many textiles by only a slight contact. The main instrument used in the examination of fibres is the microscope. Experienced microscopists provide accurate descriptions of fibres, while several colour block studies, such as those summarised by Vooijs et al. [1], have shown that fibres from many sources can effectively be discriminated. Other techniques used routinely in most laboratories are UV/vis microspectrometry (MSP) and Fourier-transform infrared spectrometry (FT-IR). Many laboratory use additional techniques, such as Raman spectrometry, thin layer chromatography, chemical and melting tests.

Several groups have proposed chromatographic analyses to chemically identify dyes used to colour textiles. Information on the chemical nature of a dye or dye mixture may have pronounced advantages, as it is complementary to colour information observed by microscopists or analysed by MSP. It may e.g. (a) discriminate between dyes with a similar colour, but different chemical compositions; (b) reveal the presence of additional dyes (next to the main dyes present) in quantities that are too small to induce a noticeable colour difference in fibres; (c) relate fibres to a source that contains very heterogeneous fibres; (d) provide information on the original application of the investigated fibres. This is possible as textile dyers use several criteria (stability/fastness, price, application method) to select a dye for a specific application.

In a previous paper, the authors presented a method that combines spectrometric separation by high pressure liquid chromatography with analysis by diode array detection (DAD) and mass spectrometry [2]. That contribution contains an overview of earlier dye analyses, which is not be repeated here. Later studies include the chromatographic studies on disperse dyes by Kato et al. [3,4], studies on broader sets of fibres by Hoy [5] and Morgan [6], the direct mass spectrometric study by Cochran et al. [7], the microspectrometric [8–10] and Raman spectrometric studies [9,11]. The main innovation of the method presented earlier is the possibility to analyse a broad variety of dyes (disperse, direct, reactive, basic and acid dyes) with a single chromatographic

* Corresponding author.
E-mail addresses: tosch@nfi.minvenj.nl (T.G. Schotman), x.xu@nfi.minvenj.nl (X. Xu), nirod@nfi.minvenj.nl (N. Rodewijk), jawee@nfi.minvenj.nl (J. van der Weerd).

http://dx.doi.org/10.1016/j.forsciint.2017.07.026
0379-0738/

method. Also, the inclusion of both DAD and MS analyses allows an accurate and sensitive analysis of the dyes present in a single fibre.

In recent years, the authors have applied the developed method in several cases. The present contribution presents a selection of cases in order to provide insights into the data that can be obtained and their evaluation in the framework of a case.

In three of the presented cases, analytical data is presented in order to provide a general overview of the data that can be acquired. The presented data is not complete, but comprises only a small fraction of the acquired data sets. Inclusion of all relevant data would make the article very long and would probably distract from its main topic, i.e. the evaluation of the obtained results rather than the results themselves.

Evaluation may vary from a simple confirmation of the microscopic examination, to more relevant information on the application of the investigated dye or textile or the heterogeneity of a sample.

The case-descriptions presented here are based on the information provided to us by the police or the prosecutor at the time of the investigation. No additional information on the backgrounds of the case or lawsuits were gathered, as the focus of the current contribution is on laboratory procedures rather than on case reconstruction.

2. Experimental

2.1. Experimental procedures

Presented MSP spectra were acquired using an J&M MSP800 (J&M Analytik AG, Essingen, Germany).

Three procedures have been developed to isolate dye molecules from different types of fibres. The method is made for single fibre analysis. The first procedure, developed to isolate basic dyes from acrylic fibres, has not been used in the current study. The second procedure has been developed to isolate reactive dyes from cotton or viscose fibres. In this procedure, 10 mm of fibre is submerged in 10 μL NaOH (3 M, 4 °C, 4 h). Afterwards, the fibre is rinsed twice in acetic acid solution (0.5 M) and in cellulase solution (Trichoderma Viride, 1.1 U/mg, Brunschwig Chemie, 0.01 g in 10 mL acetic acid solution at pH 5), submerged in 10 μL cellulase solution, and mixed in a thermo mixer (Eppendorf Comfort, 50 °C, 550 rpm, 20 h). Finally, the samples are centrifuged (5000 rpm, 5 min) and 10 μL methanol (HPLC grade) is added. The third procedure is used to extract direct, disperse and acid dyes. 10 mm of fibre is submerged in 20 μL DMSO (z.a.) and heated to 100 °C until the fibre is discoloured or to a maximum of 2 h.

HPLC Analyses are carried out on a system consisting of an auto sampler (Thermo Scientific Finnigan Surveyor Auto sampler Plus), a pump (Thermo Scientific Finnigan Surveyor MS Pump Plus), a pre-column (AJO-4286 and Guard cartridge holder KJ10-4282), a column (Grom-sil 120 ODS-5 ST 150 × 2.0 mm i.d., 3 μm, Grace Davison Discovery Sciences, Deerfield, USA). The column is kept at 22 °C by a column oven Spark Holland Mistral. The column oven is equipped with both a heating and a cooling system to accurately maintain the set temperature. The injection volume amounted to 10 μL for DMSO extracts and 20 μL for cellulose extracts. A linear gradient ammonium acetate 10 mM in water/methanol (95:5) and ammonium acetate 25 mM in acetonitrile/methanol (50:50) was used as mobile phase. The analysis time was 78 min. Eluents were analysed by diode array detection (DAD, Thermo Scientific Finnigan Surveyor PDA Plus Detector, spectral range 200–800 nm) and mass spectrometry (Thermo Scientific LTQ Orbitrap, scan range 150–2000 m/z). The obtained mass accuracy of the Orbitrap system is better than 2 ppm with the use of a lock mass. Entrance of the eluents into the mass spectrometer was enabled by an ESI source at 4 kV, a discharge current of 20 μA, and a capillary temperature of 300 °C. A nitrogen flow was used as sheath gas. A more elaborate description is provided elsewhere [2]. The only alteration concerns the length of the HPLC run, which is now 78 min and a higher amount of injection volume for cellulose extracts. Incompatibility of extraction solvents and eluents has been reported [12]. Such issues were not encountered using the procedures described above since the liquids are compatible with MS systems.

All plots were prepared using Matlab (release 2015B, The Mathworks).

2.2. Data interpretation

An analysis by HPLC–DAD–MS results in time series of DAD and mass spectra. In these series, signals due to dyes can be recognised by their absorbency of visible light (DAD spectrum). Corresponding mass spectra can be selected on the basis of the derived retention time. Often, mass spectra contain signals of other compounds, such as adulterants and background ions as present in the eluent. Mass peaks caused by the dye of interest can generally be recognised, as they elute only at the retention time observed in DAD analysis. The three relevant analysis parameters (retention time, DAD spectrum, mass spectrum) can be related to a specific dye. An effective and efficient way to achieve identification is by compilation of a database with known dyes. In recent years, over 250 samples with known dyes have been analysed. These were obtained from shade cards or quality tests by dye suppliers. Known dyes present in the database can easily be recognised by comparison of the relevant parameters. Dyes that are not in the database require a more elaborate search. This search is based on the molecular composition of the dye (as derived from the accurate mass) and comparison of DAD spectra to those in the database. This last step is useful as similar dye structures normally lead to similar DAD spectra. The derived information on the molecular composition can then be combined with information provided by the colour index or information provided by dye suppliers. Sometimes, identification is not possible, as the different sources of information do not yield a consistent pattern, or no structure is registered to a dye name. The dyes mentioned in the current paper are provided in Table 1. No molecular structures are provided in this manuscript (except those in Fig. 10), as these can easily be obtained by an internet search.

The amount of data acquired for each sample is large and stored in different software programs. As a result, the data collected from reference samples cannot currently be shared in an easy format. The interested reader is however invited to contact the corresponding author for collaboration or data exchange.

2.3. Data extraction and images

An HPLC–DAD–MS run yields a large amount of information, and only a small fraction of the acquired data can be shown. In the current manuscript, analytical data are presented in Figs. 2, 5, 8 and 9. The structure of these figures is kept constant for clarity. The current section explains this structure. All figures contain data on both the known source (black lines) and the compared trace material (grey lines). Sub plots (a) present the chromatograms derived from DAD spectra (dotted line) and mass spectra (solid lines). The mass chromatograms are prepared by extracting the intensity at a specific mass or masses from the acquired data set. The used mass and the corresponding retention time (along with their elemental composition and identification) are printed as bold lines in Table 1. The DAD chromatogram is prepared by extracting the maximum absorbency in the visible range of the DAD spectrum shown in sub-plot (b). Sub plots (b) present DAD spectra extracted at the retention times shown in bold font in Table 1 (unless stated