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Simultaneous determination of 17 disperse dyes in textile by ultra-high performance supercritical fluid chromatography combined with tandem mass spectrometry

Ying Zhou, Zhenxia Du*, Yun Zhang

College of Science, Beijing University of Chemical Technology, No. 15 BeiSanhuan East Road, Box 89, 100029 ChaoYang, Beijing, China

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ABSTRACT

A simple, highly sensitive and fast procedure for the control of 17 allergenic and prohibited disperse dyes in textile products was optimized. The method was based on ultrasound assisted extraction of textile samples with 10 mL of methanol under controlled conditions (30 min, 70 °C). The extracts were analyzed by the ultra-high performance supercritical fluid chromatography (UHPSFC) system coupled with triple quadrupole tandem mass spectrometry (MS/MS). Four stationary phases (BEH, BEH 2-ethyl-pyridine, HSS C18 SB and CSH fluorophenyl) were screened as well as analytical conditions (modifier percentage, backpressure and column temperature) were investigated to improve the separation. All 17 disperse dyes were simultaneously separated and determined by UHPSFC–MS/MS in 5 min. The dyes were monitored via the ESI^+ ionization method and quantified by 3-channel multiple reaction monitoring (MRM). The calibrations were performed and good linear relationship ($R \geq 0.99$) was observed within the concentration range of 2–50 μg mL^{-1}. Satisfactory recoveries (70.55–103.03%) of all the disperse dyes spiked with standards at different levels were demonstrated. This is the first report on the simultaneous analysis of disperse dyes using UHPSFC–MS/MS.

1. Introduction

Disperse dyes are low molecular weight organic dyes that are derivatives of azo, anthraquinone and other compounds. Most of the disperse dyes are planar and non-ionic. In order to improve the adherent to the fibers, polar groups are usually attached to the molecules [1]. The main application of disperse dyes is now used in a vast variety of consumer products including textiles, toys, paper, etc. Regrettably, a number of these dyes are allergic substances and easily cause contact dermatitis [2–4]. Moreover, some of the dyes that contain azo groups in their structure can be reduced by azo reductases present in intestinal bacteria, liver enzymes and skin-surface micro-flora, thus forming potential or known carcinogenic aromatic amines [5]. According to Hatch and Maibach [6], 49 dyes have been identified to be contact allergens and two thirds of these are disperse dyes. Increased awareness of the potential risk to consumer health associated with the exposure to such dyes have led to the introduction of some legislations, such as EU Eco-label (EU 2002/371/EC) and Oekotex Standard 100 (2009 edition) [7]. Therefore, an analysis method that simultaneously detects multiple dyes in textiles is highly sought.

Although the TLC approach described in the DIN 54231 standard procedure [8]can be used as a screening process to enable detection of controlled disperse dyes so that only the positive samples are analyzed further by HPLC-DAD or LC-MS, the time and handling involved are considerable [9]. As we all known, HPLC is a good method for qualitative and quantitative analysis [10–15]. However, the analyses of the complex samples by HPLC require high resolution and long analysis time, the latter being an important limitation when high throughput samples need to be analyzed for research or quality control purposes.

Supercritical fluid chromatography (SFC) is a promising analytical technique for its advantages in comparison to traditional liquid chromatography (LC) such as green, low cost, faster separations and better resolution, which make its application in a routine or high-throughput analysis more attractive [16–18]. Recently, there were several reports of UHPSFC analysis on basic compounds [19], pesticides [20], isomers [21] and pharmacokinetics [22]. These previous studies indicated that UHPSFC is suitable for analyzing a wide range of analytes, and could serve as an alternative or a complementary method for HPLC. To date, UHPSFC has not been tested for its application in separating disperse dyes in textiles.

The goal of this study was to develop a rapid method to analyze 17 disperse dyes by SFC coupled to electrospray ionization tandem mass spectrometry (ESI-MS/MS) using standard samples. Their

* Corresponding author. Tel./fax: +86 10 64433909.
E-mail address: duzx@mail.buct.edu.cn (Z. Du).

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residue contents should not be more than 50 mg kg^{-1} in textile [7]. These 17 disperse dyes contain derivatives of azo, anthraquinone and other compounds (Fig. 1). The separation conditions such as column stationary phase, mobile phase, backpressure, and column temperature were examined. All 17 disperse dyes were simultaneously separated and determined by UHPSFC–MS/MS in 5 min. Subsequently, this method was applied to the quantification of 17 disperse dyes in real samples of textile. This is the first report on the simultaneous analysis of 17 disperse dyes using UHPSFC–MS/MS.

2. Experimental

2.1. Chemicals and reagents

The standards of 17 disperse dyes – disperse yellow 1, disperse blue 1, disperse orange 3, disperse red 11, disperse yellow 3, disperse yellow 9, disperse yellow 39, disperse blue 3, disperse red 1, disperse orange 1, disperse blue 106, disperse red 17, disperse blue 102, disperse yellow 49, disperse blue 124, disperse orange 37 and disperse brown 1 were all purchased from Dr. Ehrenstorfer (Ausberg, Germany).

Methanol was purchased from Fisher Scientific (Pittsburgh, PA, USA).

2.2. UHPSFC–MS/MS system

UHPSFC–MS/MS analysis was performed using an ACQUITY UPC^2 system which stands for Ultra-Performance Convergence Chromatography™ (Waters, Milford, MA) with a quattro premier XE tandem mass spectrometer (Waters). The SFC system is equipped with a convergence manager, which controls backpressure, binary solvent manager, temperature-controlled column manager and fixed loop sample manager. The MS is equipped with an ESI source. The flow is split into MS and convergence manager after the column so that supercritical fluid conditions of CO_2 can be maintained. The final SFC conditions were as follows: a gradient program was used with a standard elution gradient of methanol (B) in CO_2 (A) ($\geq$ 99.99% of purity), 1% B (initial), 1–3% B (0–1.5 min), 3–7% B (1.5–2 min), 7–10% B (2–3 min), 10–15% B (3–3.3 min), 15–16% B (3.3–4.0 min), 16–20% B (4.0–4.5 min). A subsequent re-equilibration time before the next injection was 1.5 min. The back pressure was set at 1600 psi. The flow rate was 2 mL min^{-1} while the injection volume was 1 μL. The column and sample temperature were maintained at 45 and 22 °C, respectively. Columns – (1) Waters ACQUITY UPC$^{2™}$ BEH (1.7 μm, 3 × 100 mm I.D.), (2) Waters ACQUITY UPC$^{2™}$ BEH 2-Ethyl-pyridine (1.7 μm, 3 × 100 mm I.D.), (3) Waters ACQUITY UPC$^{2™}$ HSS C18 SB (1.8 μm, 3 × 100 mm I.D.) and (4) Waters ACQUITY UPC$^{2™}$ CSH Fluorophenyl (1.7 μm, 3 × 100 mm I.D.).

The parameters used for the mass spectrometer with the ESI^+ mode were as follows: the capillary voltage at 2.7 kV, the desolvation gas flow rate set to 650 L h^{-1} at a temperature of 350 °C, the cone gas flow rate set at 50 L h^{-1} and the source temperature at 120 °C. The parameters for the *m*/*z* and collision energy of parent ions and quantitative daughter ions from dyes are shown in Table 1. The UHPSFC/ESI–MS/MS system was controlled by MassLynx version 4.1 (Waters). MassLynx version 4.1 equipped with application manager TargetLynx was used for acquisition, processing and calibration of the UHPSFC/ESI–MS/MS data.

2.3. Preparation of standard solutions

Accurately weighed solid portions of 17 disperse dye standards were dissolved in methanol to prepare 1 mg mL^{-1} of stock solutions. These stock solutions were further diluted with methanol to 2.5, 5.0, 10.0, 25.0, 50.0 mg L^{-1} in order to obtain calibration curves. Both sets of mixed standard solutions were stored at 4 °C until use and filtered through a 0.22 μm membrane prior to injection.

2.4. Sample pretreatment

Prior to extraction, the textile was cut into 5 mm × 5 mm pieces to increase the contact area with the organic solvent. Extraction solvent (5 mL) was added in glass tubes which contained 0.5 g cut textiles and the glass tubes were placed in an ultra-sonication bath for 15 min at 70 °C. The extraction procedure was repeated twice and the extraction solvents were combined afterwards. The extract was evaporated to near dryness under a gentle stream of nitrogen at 40 °C, and the residues were re-dissolved in 1 mL methanol, filtered with 0.22 μm organic membrane. Finally, the extract was injected into the UHPSFC–MS/MS system for analysis.

3. Results and discussion

3.1. Optimization of UHPSFC conditions

3.1.1. Selection of stationary phases

A proper election of a suitable chromatographic column is very important for a good separation of the analyzed components. A major difficulty faced in column screening was to obtain a good peak shape, resolution and sensitivity for each compound. The four columns – (1) Waters ACQUITY UPC$^{2™}$ BEH (hybrid silica without bonding, non-endcapped), (2) Waters ACQUITY UPC$^{2™}$ BEH 2-Ethyl-pyridine (hybrid silica with a 2-ethylpyridine bonding, non-endcapped), (3) Waters ACQUITY UPC$^{2™}$ HSS C18 SB (classical silica bonded with C18, non-endcapped) and (4) Waters ACQUITY UPC$^{2™}$ CSH Fluorophenyl (charged surface hybrid silica bonded with a fluoro phenyl group, non-endcapped) were evaluated based on the signal intensity and separation efficiency of 17 disperse dyes. Justifying their selection for this study with the same CO_2/methanol (99/1, v/v) mobile phase.

Fig. 2 shows the UHPSFC–MS/MS chromatograms of disperse dye standards on these four columns (BEH, BEH 2-EP, HSS C18 SB and CSH FP), all under identical conditions. The retention order is almost identical on these phases, despite the presence of C18 bonded chains on the HSS C18 phase, meaning that this HSS C18 SB phase presents a significantly polar characteristic [23]. With the exception of HSS C18 SB, for which longer analysis time was needed, the separation of 17 disperse dyes could be successfully achieved in 5 min when using the other three columns. From these 3 columns, BEH column showed the best separation efficiency and highest sensitivity.

According to E. Lesellier's LSER (a linear solvation energy relationship) studies [23], the coefficients (*e*, *s*, *a*, *b*, *v*) which reflect the magnitude of difference for that particular property between the mobile and stationary phases were evaluated. The *v* coefficient related to the hydrophobic volume is negative (solutes interact strongly with the mobile phase) while HSS C18 SB which is positive (solutes interact strongly with the stationary phase), meaning that the compounds containing hydrophobic moieties favor fast elution on BEH, BEH 2-EP and CSH FH, but for HSS C18 SB column, which elution rate is not so fast.

Blue 3 and red 11 (marked as 12 and 13, respectively) belong to the anthraquinones. In terms of selectivity, a significant difference was observed between CSH FP and other three stationary phases. What is interesting is that on CSH FP column, blue 3 and red 11 were almost finally eluted. The reason may be due to the presence of an aromatic ring in the bonded ligand enhances the *e* value which refers to π–π interactions and dipole–induced dipole