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

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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

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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

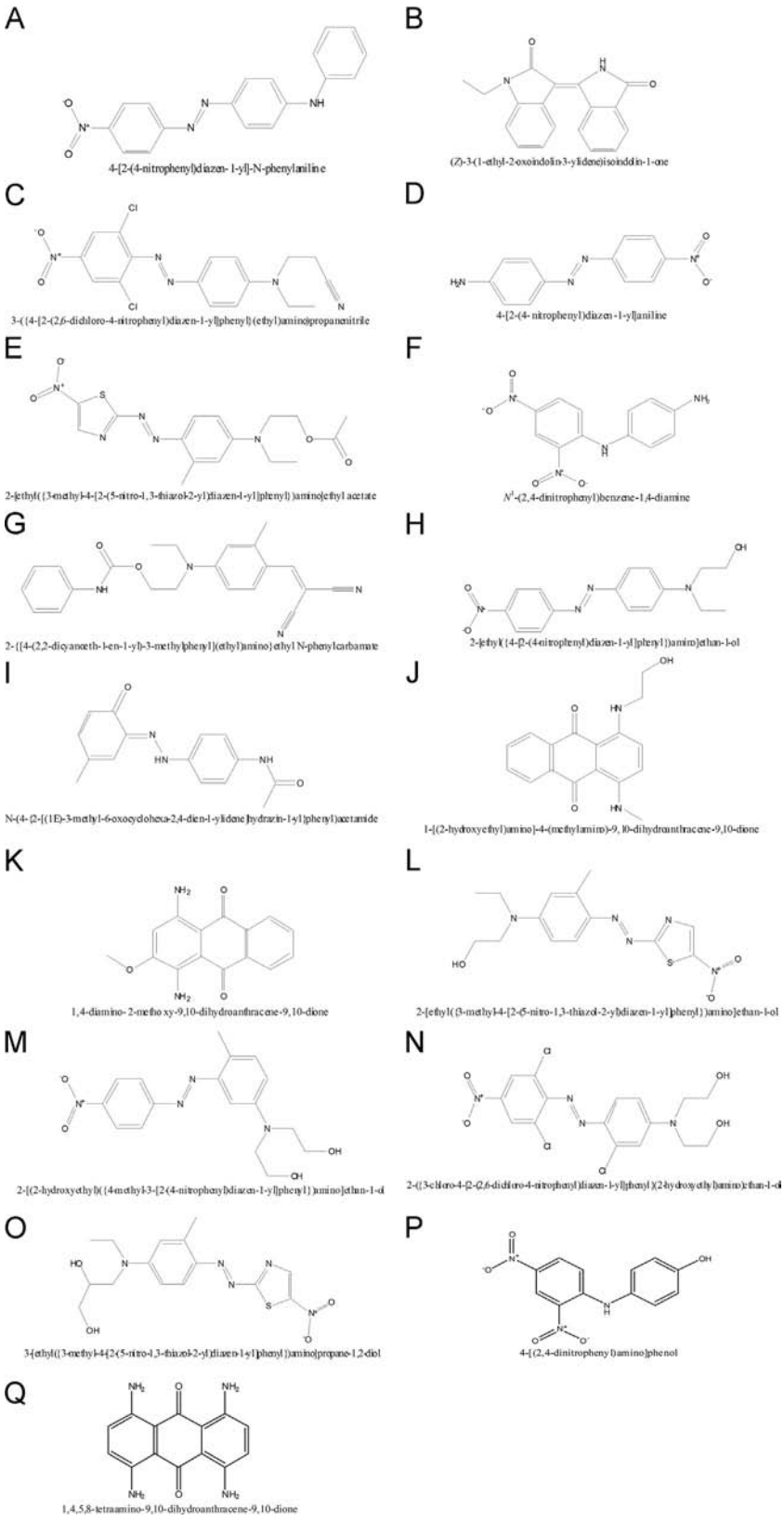

Fig. 1. Chemical structures of disperse dyes in the present study (the IUPAC name is below the structure): (A) orange 1; (B) yellow 39; (C) orange 37; (D) orange 3; (E) blue 124; (F) yellow 9; (G) yellow 49; (H) red 1; (I) yellow 3; (J) blue 3; (K) red 11; (L) blue 106; (M) red 17; (N) brown 1; (O) blue 102; (P) yellow 1; (Q) blue 1.

interactions [23]. This results in increased retention of anthraquinone solutes on this phase, in comparison to the other ones.

It is interesting to note that on BEH, BEH 2-EP and CSH FP columns yellow 39 (marked as 2) was split into two peaks. This phenomenon can be explained by the presence of *cis*/*trans* isomers. Moreover, the distance between the two peaks gradually increased from BEH to CSH FP (Fig. 3) which may be due to the interaction of the fluoro phenyl group of CSH FP with aromatic

Table 1
MS/MS parameters on the parent and quantitative daughter ion (*m*/*z*) and collision energy of 17 dyes.

Dye name	Parent ion (*m*/*z*)	Quantitative daughter ion (*m*/*z*)	Collision energy (eV)	Assistantly qualitative daughter ion (*m*/*z*)	Collision energy (eV)
Disperse orange 3	243.2	121.9	20	91.9	20
Disperse red 11	269.3	254.0	25	226.2	25
Disperse yellow 3	270.3	107.0	20	150.0	25
Disperse yellow 9	275.3	228.2	25	258.2	20
Disperse yellow 39	291.3	129.9	30	245.1	25
Disperse blue 3	297.2	252.1	25	235.1	30
Disperse red 1	315.3	134.6	30	255.2	25
Disperse orange 1	319.2	169.1	30	121.9	25
Disperse blue 106	336.3	178.1	20	70.0	25
Disperse red 17	345.3	164.1	25	177.1	20
Disperse blue 102	366.3	208.1	25	147.1	25
Disperse yellow 49	375.3	238.2	20	164.0	20
Disperse blue 124	378.3	86.9	25	220.2	30
Disperse orange 37	392.2	351.2	25	323.1	30
Disperse brown 1	433.2	197.0	30	185.1	25
Disperse yellow 1	276.3	229.1	25	259.1	20
Disperse blue 1	269.2	106.8	35	253.2	30

structure in yellow 39. The result indicates that CSH FP has an excellent performance and high selectivity for *cis/trans* isomers with aromatic structure.

Compared to the retention times of dyes with similar structures like orange 1, orange 3, red 1 and red 17 (marked as 1, 4, 9 and 15, respectively), the polarity of the compounds is decreasing (anilino < amidogen < $-N(CH_2CH_3)CH_2CH_2OH$ < $-N(CH_2CH_3)CH_2CH(OH)CH_2OH$). The retention time gets shorter which indicates that on the BEH column the hydroxyl group has a stronger interaction with the stationary phase than the amino group. In addition, blue 124, blue 106 and blue 102 (marked as 5, 14 and 17, respectively) also have very similar structures. The only difference is the type of functional groups attached to nitrogen, for blue 124 it is $-CH_2CH_2COOCH_3$; for blue 106 it is $-CH_2CH_2OH$; for blue 102 it is $-CH_2CH(OH)CH_2OH$. The retention time was increased from blue 124 to blue 102 indicating that the hydroxyl group has stronger interaction with the stationary phase than the ester group. Furthermore, based on the elution characteristics of all disperse dyes, it was determined that substances which contain more hydroxyl groups have greater interaction with the BEH phase.

In conclusion, considering the better separation efficiency and higher sensitivity for the 17 disperse dyes on BEH than other three columns, Waters ACQUITY UPC$^{2™}$ BEH C18 was selected as the separation column.

3.1.2. Optimization of the gradient conditions

Modifiers are usually added to supercritical fluids to change eluent strength of the mobile phase and to improve peak shape and sensitivity by minimizing interactions with the silanol groups of the stationary phase. Janssen et al. [24] suggested that the interaction between polar solutes and residual silanol groups on the surface of stationary phase has a predominant influence on the peak shape and the column efficiency in practical supercritical fluid chromatography. Methanol as a modifier was added to liquid CO_2 mobile phase. The different amount of modifier (methanol) and gradients were evaluated to achieve the baseline separation in 5 min (Fig. 4). The final UHPSFC gradient conditions are described in Section 2.2.

3.1.3. Effects of column temperature

Column temperature can affect the density and viscosity of the mobile phase of carbon dioxide; chromatographic separation and sensitivity will also be influenced to a certain extent [18]. The temperature effect on retention is different from that of the reversed-phase LC. With the increase of column temperature, the density and viscosity of carbon dioxide are reduced, leading to the decrease in elution ability of the sample, resulting in greater retention. In contrast, the decrease of column temperature increases the density and viscosity of carbon dioxide which would enhance elution capacity to the sample. In this study, the column temperature was tested at 45, 50 and 55 °C (Fig. 5) under optimal gradient conditions; a compromise and reasonable choice was 45 °C.

3.1.4. Effects of ABPR backpressure

The ABPR backpressure also affects retention time of analytes by changing the density of the mobile phase [18]. With the increase of the ABPR, the density of mobile phase increases, which results in shorter retention time. The ABPR (1400, 1600, 1800 psi) was evaluated separately (Fig. 5). Considering the observed separation, the ultimate backpressure was 1600 psi.

3.2. Optimization of MS/MS conditions

3.2.1. Selection of parent ions and daughter ions

The stock solutions (1 mg mL^{-1}) of 17 dye standards were prepared with methanol. For the selection of parent ions, the ionization mode (ESI^+/ESI^-) first was decided according to chemical ionization characteristics of dyes. The parent ion *m*/*z* of each disperse dyes was subsequently confirmed by direct injection based on the optimization of MS/MS parameters. Results showed that much higher $[M+H]^+$ abundance of all the analytes was obtained under the ESI^+ mode compared to the ESI^- mode. Therefore, the ESI^+ ionization mode for all 17 dye standards was used in this study.

To further obtain high sensitivity of the dyes, the MS/MS parameters including capillary voltage, cone voltage, source temperature, desolvation temperature, cone gas flow and desolvation gas flow were tuned by an on-line scan (see details in Section 2.2). Based on the confirmation of parent ion, more than two daughter ions should be selected when using low resolution LC-MS analysis in accordance with relevant EU legislation [25]. Therefore, the optimization of daughter ions and their collision energy was performed under the daughter scan mode to establish the MRM quantification method. The final selection of daughter ions and the optimal collision energy is shown in Table 1. Because 17 dye standards required 34 ion monitoring channels, the whole run time was divided into 3 MRM acquisition time slices to obtain enough collection points of each chromatographic peak (15–25 points) and ensure the accuracy of quantitative analysis (Fig. 6).

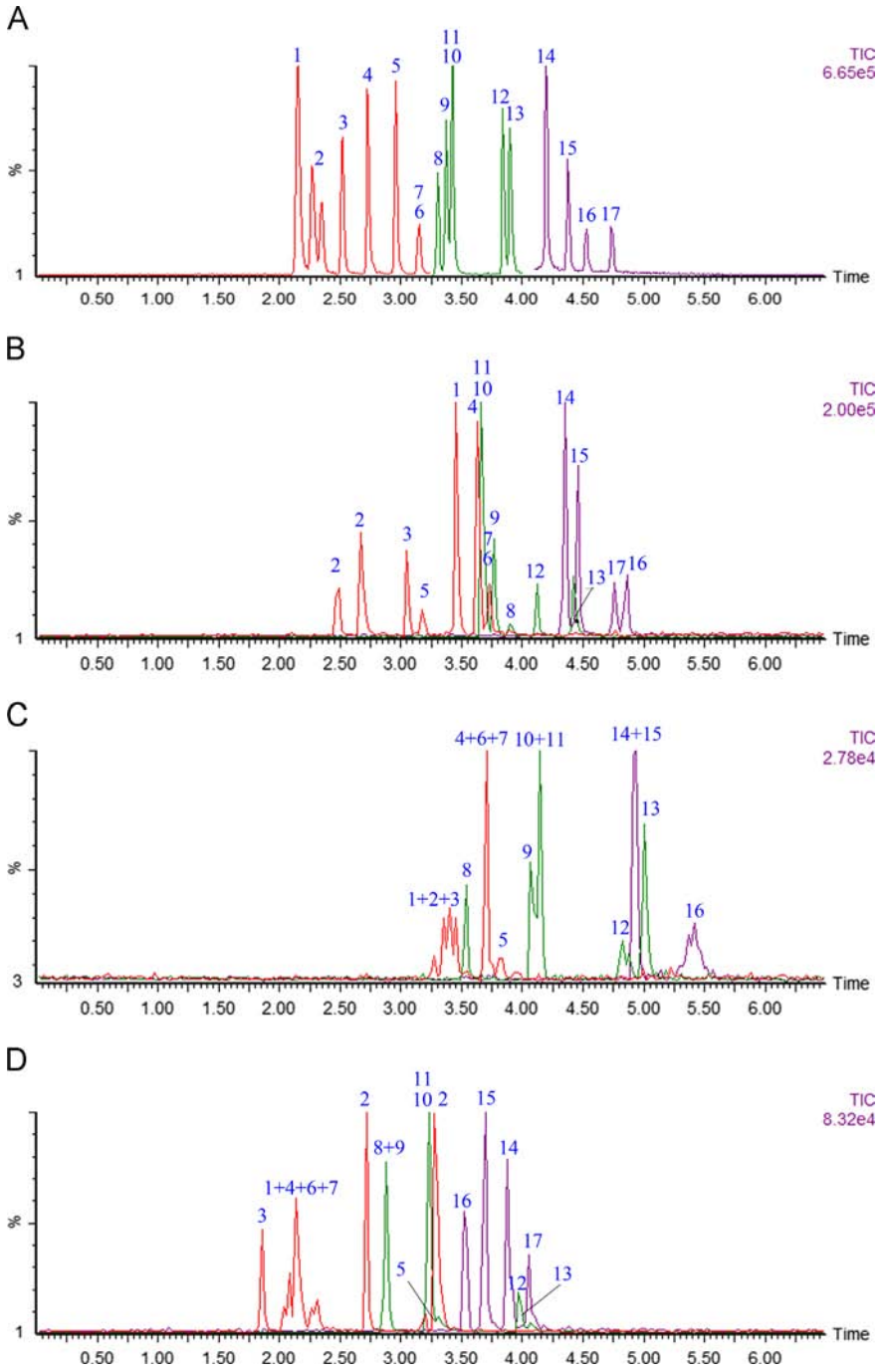

Fig. 2. Comparison of separation effects among three different candidate columns. (A) BEH (1.7 μm, 3 × 100 mm I.D.); (B) BEH 2-Ethyl-pyridine (1.7 μm, 3 × 100 mm I.D.); (C) HSS C18 SB (1.8 μm, 3 × 100 mm I.D.); (D) CSH Fluorophenyl (1.7 μm, 3 × 100 mm I.D.); (1) orange 1; (2) yellow 39; (3) orange 37; (4) orange 3; (5) blue 124; (6) yellow 9; (7) yellow 1; (8) yellow 49; (9) red 1; (10) yellow 3; (11) blue 1; (12) blue 3; (13) red 11; (14) blue 106; (15) red 17; (16) brown 1; (17) blue 102.

3.3. Calibration and method validation

The UHPSFC–MS/MS method for disperse dyes using standard solutions was validated. Each dye standard solution, with the concentrations of 2.5, 5.0, 10.0, 25.0, 50.0 mg L^{-1}, was prepared from 1 mg mL^{-1} stock solutions. The calibration curves of dyes were created after the injection (1 μL) of mixed standard solution (Table 2). Acceptable linear relationships and good coefficients of determination ($R \geq 0.99$) were achieved over the concentration range of 2.5–50 mg L^{-1}. Besides chemical structures of different dyes, the sensitivity of these analytes mainly depends on their ionization efficiency under MRM mode. In the confirmation test of LOQ and LOD, the blank textile sample was spiked with all of the above 17 disperse dye standards. After sample pretreatment and injection, the instrumental limits of detection (LOD) were calculated from signal-to-noise ratios (S/N) of standard solutions using the definition S/N > 3. The limits of quantification (LOQ) were determined as S/N > 10 by spiking samples prior to the extraction and analysis. The LOQ and LOD ranges of dyes were 0.1–2 μg mL^{-1} and 0.02–1 μg mL^{-1}, respectively (see the details in Table 2). No interference was detected in the textile sample by 34 selected channels monitoring of UHPSFC–MS/MS. Recovery of this validated method was performed also in the blank textile sample employing the method of standard addition. The samples were

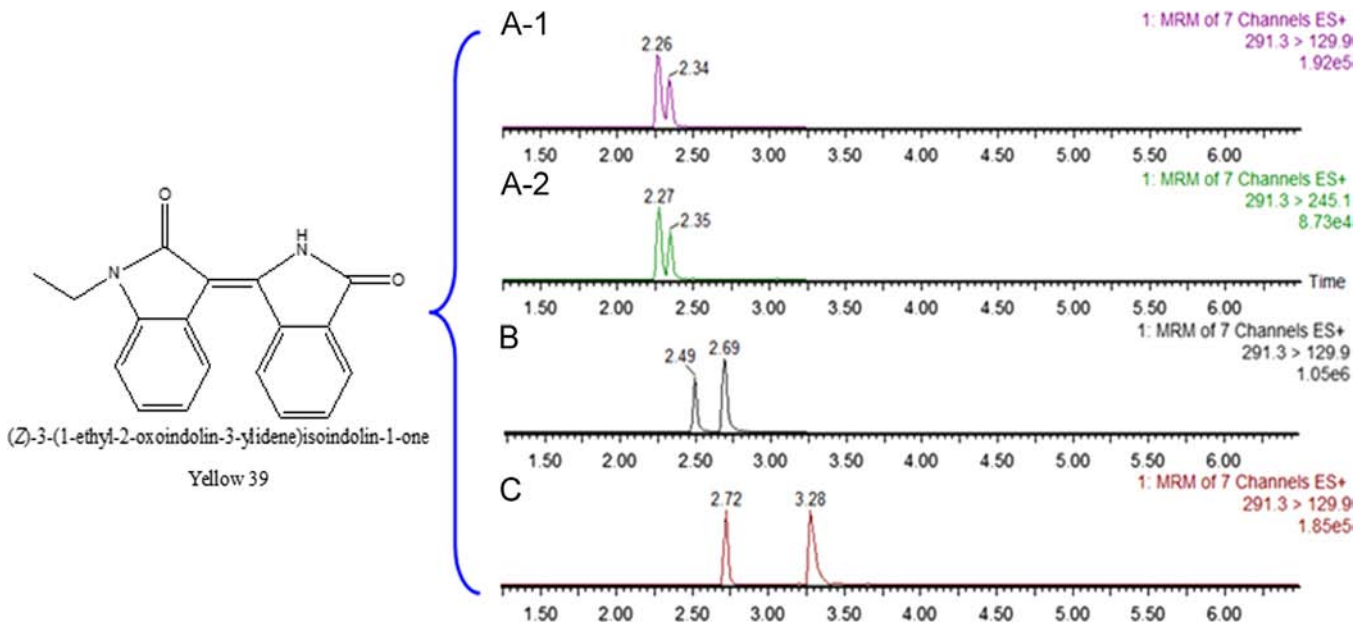

Fig. 3. The quantitative and qualitative daughter ion chromatograms of yellow 39 (structure shows on the left) on different columns: (A-1) quantitative daughter ion chromatogram on BEH, (A-2) qualitative daughter ion chromatogram on BEH (which fully proved split peak was yellow 39); (B) BEH 2-Ethyl-pyridine; (C) CSH Fluorophenyl.

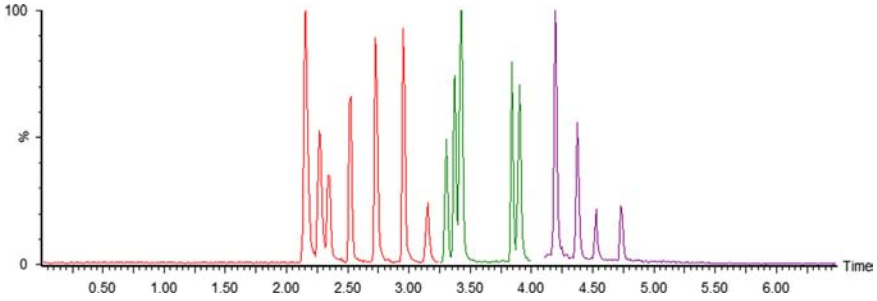

Fig. 4. Chromatogram of the 17 standards in Fig. 1 on BEH, CO_2–methanol 99:1 (v/v), P_{out}=1600 psi, T=45 °C, flow rate=2 mL min^{-1}.

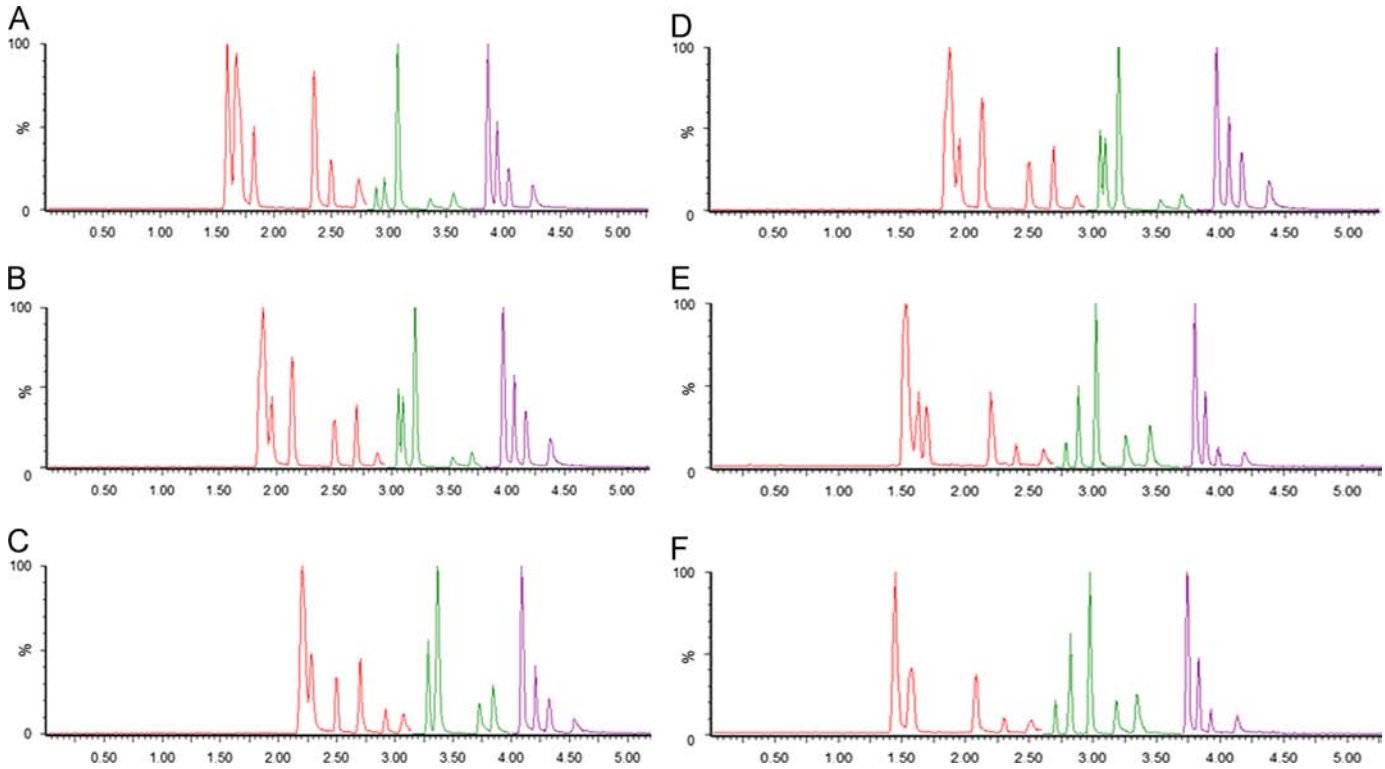

Fig. 5. Effects of temperature and pressure changes on retention and separation of the 17 standards in Fig. 1 on BEH. Mobile phase CO_2–methanol 99:1 (v/v), flow rate=2 mL min^{-1}. (A) T=45 °C; (B) T=50 °C; (C) T=55 °C all with P_{out}=1400 psi; (D) P_{out}=1400 psi; (E) P_{out}=1600 psi; (F) P_{out}=1800 psi all with T=50 °C.

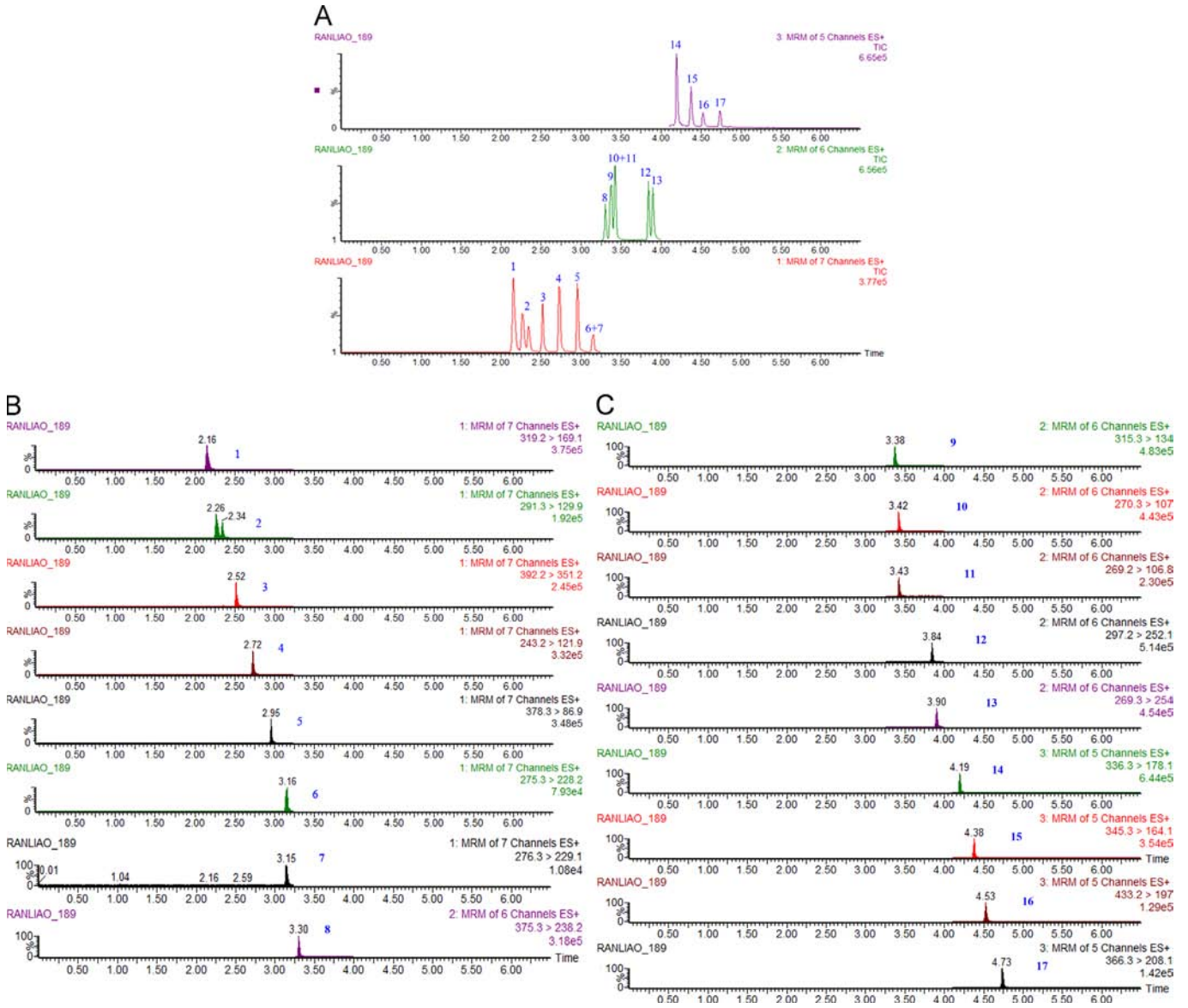

Fig. 6. (A) The total ion chromatograms (TICs) and (B and C) quantitative daughter ion chromatograms of 17 disperse dyes. (1) orange 1; (2) yellow 39; (3) orange 37; (4) orange 3; (5) blue 124; (6) yellow 9; (7) yellow 1; (8) yellow 49; (9) red 1; (10) yellow 3; (11) blue 1; (12) blue 3; (13) red 11; (14) blue 106; (15) red 17; (16) brown 1; (17) blue 102. The UHPSFC and MS/MS conditions were described in Section 2.2.

Table 2
Linear relationships and sensitivity of disperse dyes.[a]

Dye name	LOQ (μg mL^{-1})	LOD (μg mL^{-1})	Coefficient
Disperse orange 3	0.1	0.02	0.9954
Disperse red 11	0.5	0.1	0.9981
Disperse yellow 3	0.1	0.02	0.9994
Disperse yellow 9	1	0.2	0.9960
Disperse yellow 39	1.5	0.3	0.9963
Disperse blue 3	1	0.2	0.9944
Disperse red 1	1	0.2	0.9958
Disperse orange 1	1	0.2	0.9960
Disperse blue 106	0.3	0.06	0.9979
Disperse red 17	0.25	0.05	0.9988
Disperse blue 102	2	1	0.9958
Disperse yellow 49	0.35	0.07	0.9919
Disperse blue 124	0.625	0.125	0.9942
Disperse orange 37	0.75	0.15	0.9961
Disperse brown 1	1	0.2	0.9950
Disperse yellow 1	2	1	0.9972
Disperse blue 1	2	1	0.9989

[a] Linear ranges were designed as 2.5–50 μg mL^{-1}.

spiked with the low (10 μg mL^{-1}), intermediate (20 μg mL^{-1}) and high levels (50 μg mL^{-1}) of mixed disperse dye standards. Samples were routinely pretreated and results are summarized in Table 3. The recovery ranges at low, intermediate and high spiked levels were 76.32–96.65, 72.0–103.03 and 70.55–94.32%, respectively. The recovery levels were acceptable for all dyes. In addition, good repeatability of the recovery test (RSD < 9.0%) in all spiked levels was achieved (n=5). Considering all of the above data for method validation, the current UHPSFC–MS/MS method and sample pretreatment procedures employed in the present work can be regarded as a robust quantification method with a successful application in quantification of disperse dyes.

3.4. Determination of disperse dyes in the samples

The developed method was applied to some textile samples which were bought randomly from a local market and analyzed by the validated method in the present study. Samples were prepared and analyzed in triplicate. Among these tested samples, yellow 3, orange 1, red 1, blue 3, blue 106 and blue 102 are detected, the

Table 3
Recovery tests of the current UHPSFC–MS/MS method ($n=5$).

Dye names	Spiked recovery of dyes (%)			Precision (RSD, %), $n=5$		
	10 μg g^{-1}	20 μg g^{-1}	50 μg g^{-1}	10 μg g^{-1}	20 μg g^{-1}	50 μg g^{-1}
Disperse orange 3	83.12	88.13	75.78	4.9	4.7	5.7
Disperse red 11	86.41	88.71	92.78	1.9	3.40	2.7
Disperse yellow 3	85.45	90.91	83.61	2.4	4.0	4.3
Disperse yellow 9	82.16	89.95	81.24	3.7	8.9	4
Disperse yellow 39	85.62	90.15	94.32	2.0	4.5	4.0
Disperse blue 3	89.15	99.99	87.00	5.1	3.0	6
Disperse red 1	82.13	90.05	86.20	3.0	5.0	5.7
Disperse orange 1	90.38	86.74	93.46	4.0	2.5	3.0
Disperse blue 106	95.83	90.62	95.70	5.5	3.7	6.7
Disperse red 17	91.52	95.45	89.42	6.2	3.1	7.0
Disperse blue 102	96.65	91.34	88.75	7.2	4.5	3.4
Disperse yellow 49	85.31	80.65	87.72	2.6	5.6	3.0
Disperse blue 124	86.86	103.03	90.78	2.5	3.4	5.5
Disperse orange 37	87.38	82.68	79.35	5.8	6.6	7.2
Disperse brown 1	84.81	93.63	92.59	2.4	6.1	2.2
Disperse yellow 1	77.82	72.54	79.22	5.0	3.0	6.5
Disperse blue 1	76.32	72.00	70.55	6.0	3.9	5

concentrations are 19.2 mg kg^{-1}, 15.0 mg kg^{-1}, 15.7 mg kg^{-1}, 150.0 mg kg^{-1}, 2.6 mg kg^{-1} and 48.7 mg kg^{-1}, respectively.

4. Conclusion

In this study, a simple, highly sensitive and fast procedure was developed utilizing UHPSFC coupled with triple quadrupole tandem mass spectrometry for the control of 17 different allergenic disperse dyes in textile products. For the optimization of UHPSFC, these dyes were separated by ACQUITY UPC^2 BEH column (1.7 μm, 3 × 100 mm I.D., Waters) with an elution gradient of methanol and CO_2. The optimized separation method enabled accurate detection and measurement of all 17 allergenic dyes within 5 min. The method uses ultrasound assisted-extraction of 0.5 g of textile samples with 10 mL of methanol during 30 min at 70 °C. Under optimal conditions, disperse dyes were quantitatively recovered from samples. For the optimization of MS/MS, the disperse dyes were detected in samples in MRM mode. In addition, the considerably reduced consumption of the organic solvent in analysis demonstrated that UHPSFC is a much more environmentally friendly method. The UHPSFC–MS/MS method provided an efficient procedure for reducing the costs and work involved in the control of allergenic dyes in finished textile products and might have a prospective future in other areas.

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