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Application Note

Improving the Speed and Quantitative Performance for the Analysis of Allergenic and Carcinogenic Dyes in Industrial, Cosmetics, Personal Care and Consumer Products

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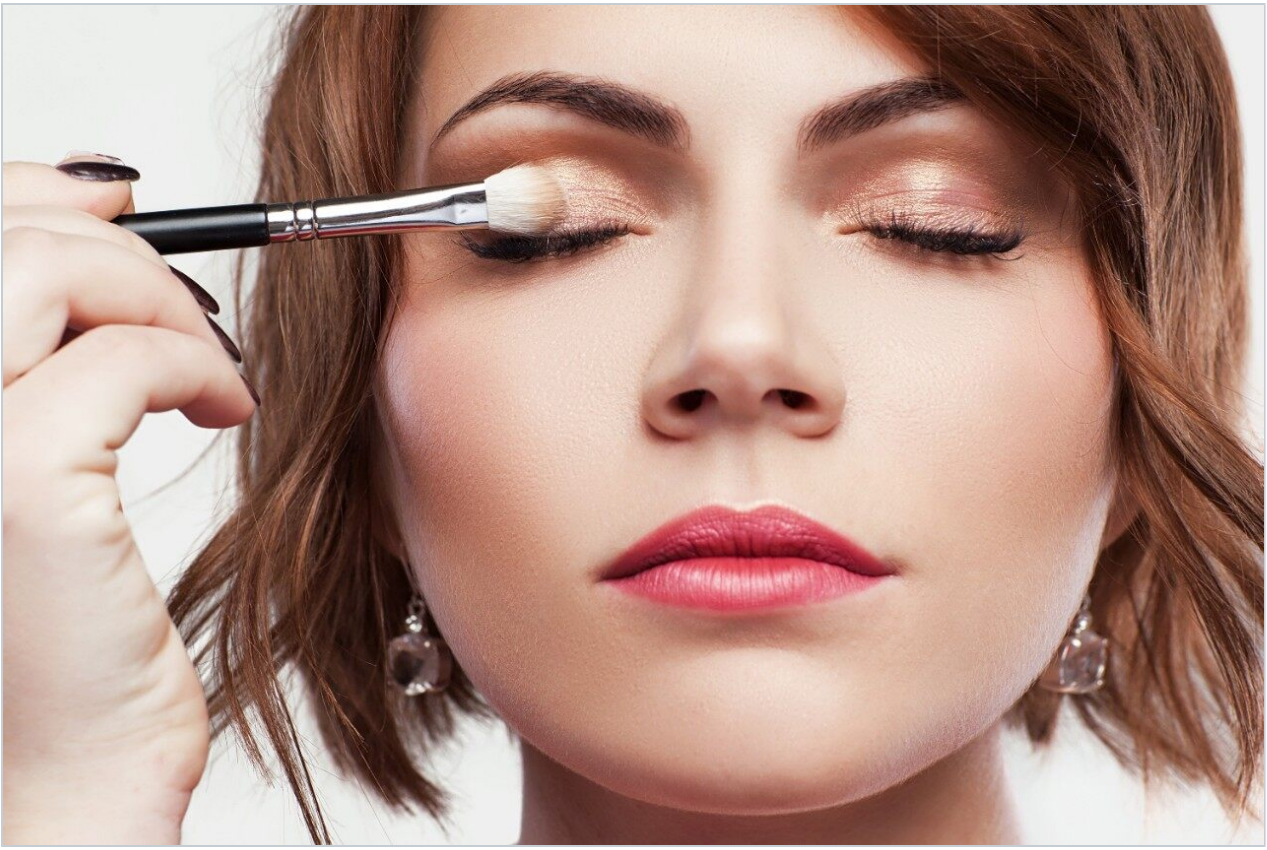


Abstract

In this application note, we describe the advantages of analyzing disperse, acid, direct, and basic dyes using the ACQUITY UPLC H-Class System coupled with the Xevo TQD. Our results show increased robustness, selectivity, and sensitivity, with reduced run times and associated savings in solvent usage compared to existing methodologies.

Benefits

This application note illustrates increased sample throughput for the identification and quantification of allergenic and carcinogenic disperse, acid, direct, and basic dyes in consumer products offering:

- Reduced solvent usage due to reduced run times.
- Improved sensitivity, selectivity, and robustness, compared with existing methodologies.

Introduction

Dyes are added to change or add color to a product, with the aim to add appeal and improve sales by making the product more authentically pleasing.

Dyes are used in many products, for example industrial products such adhesive glues and industrial cleaning products; agricultural products such as seed colorants; cosmetics products (for example lipstick and eye shadow); personal care products (for example soaps, hair dye, and wigs); consumer products (for example inks, candles, fabric, paper, and leather); automotive products (for example car washes and polishes).

Originally, all dyes were natural compounds, but gradually a wide range of synthetic dyes were developed that could be produced faster at a lower cost. Synthetic dyes are classified according to how they are used in the dyeing process. Lipophilic disperse dyes are used for dyeing many synthetic fibers, such as polyester, nylon, cellulose acetate, synthetic velvets, and PVC. Whereas, water-soluble dyes, such as anionic acid dyes, cationic basic dyes, and direct dyes have a wide variety of uses on both natural and synthetic fibers. For example, acid dyes can be used on silk, wool, nylon, and modified acrylic fibers; basic dyes can be used on acrylic fibers, wool, silk, and paper; and direct dyes can be used on cotton, paper, leather, wool, silk, and nylon.

Many companies, in order to fulfill their commitment to protect the consumers of their products, their workers, and the community/environment, develop restricted substances lists (RSL). RSL detail both legislated and non-legislated requirements to be upheld in every part of their product supply production chains to reduce or eliminate hazardous substances and processes. In doing so, they also add environmental sustainability value to their products, and ensure that their products are safe and legally compliant. Many potentially hazardous disperse, acid, direct, and basic dyes are detailed in many consumer product suppliers' RSL.

Examples of both legislated and non-legislated regulations and standards developed by various countries and international organizations with regard to dyes include the following: European Committee for Standardization with regard to toy safety standards (BS EN 71 part 9),[1] Sustainable Textile Production (STeP),[2] European Union Commission Decision (2009/567/EC),[3] the German Food and Commodities law (LFGB 30), and Cosmetic Directive 1223/2009.[4] All detail many of the potentially sensitizing, carcinogenic, mutagenic, or toxic to reproduction dyes as prohibited.

The standard method for the analysis of disperse dyes in textile products and components is DIN54231,[5] using high performance liquid chromatography (HPLC) or thin layer chromatography (TLC) with either ultraviolet (UV), mass spectrometry (MS), or densitometry detection.

Other methodologies for the analysis of disperse dyes include: electrochromatography with electrospray ionization (ESI) and MS detection,[6] HPLC with: UV/VIS detection,[7] atmospheric pressure chemical ionization (APCI) and MS detection,[8] ESI and MS detection,[9,10] and ion-exchange high-performance liquid chromatography (HPIEC) with MS detection.[11]

This application note, using Waters ACQUITY UPLC H-Class System coupled with the Xevo TQD, describes the advantages of analyzing disperse, acid, direct, and basic dyes compared to previous methodologies. The results show increased robustness, selectivity, and sensitivity, with reduced run times and associated savings in solvent usage.

Experimental

Textile

- Textile (0.5 g) was cut up and extracted with 20 mL of methanol for 15 min using an ultrasonic bath (50 °C).

- 100 µL of the extract was transferred in an LC vial and diluted with 900 µL of water.

LC conditions

System:	ACQUITY UPLC H-Class
Run time:	7 min
Column:	ACQUITY UPLC BEH C_{18} 2.1 x 50 mm, 1.7 µm
Column temp.:	30 °C
Sample temp.:	10 °C
Mobile phase A:	Water (5 mmol/L ammonium acetate)
Mobile phase B:	Acetonitrile (5 mmol/L ammonium acetate)
Flow rate:	0.6 mL/min
Injection volume:	5 µL

The mobile phase gradient is detailed in Table 1.

Gradient

	Time (min)	Flow rate (mL/min)	%A	%B	Curve
1	Initial	0.60	90	10	–
2	0.50	0.60	90	10	6
3	3.00	0.60	5	95	6
4	5.00	0.60	5	95	6
5	5.01	0.60	90	10	6
6	7.00	0.60	90	10	6

Table 1. ACQUITY UPLC H-Class System mobile phase gradient.

MS conditions

Mass spectrometer:	Xevo TQD
Ionization mode:	ESI positive and negative
Capillary voltage:	0.7 kV
Source temp.:	150 °C
Desolvation temp.:	500 °C
Desolvation gas:	1000 L/h
Cone gas:	20 L/h
Acquisition:	Multiple Reaction Monitoring (MRM)

MS conditions were optimized, as shown in Table 3, for the analysis of disperse, acid, direct, and basic dyes. CAS numbers, empirical formulas, and structures are displayed in Table 2. The established dyes MRM method, which utilizes fast polarity switching available on the Xevo TQD, is illustrated in Figure 1. This enables the analysis of positive and negative dyes within the same analytical analysis.

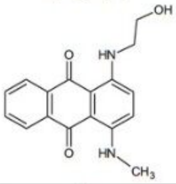
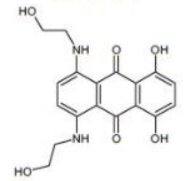
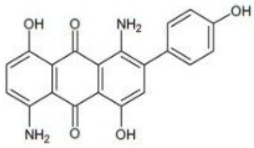
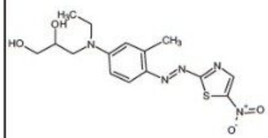
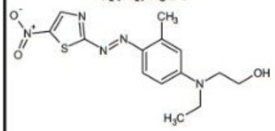
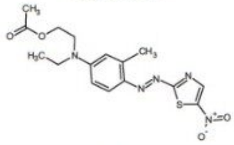
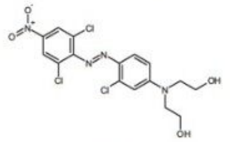
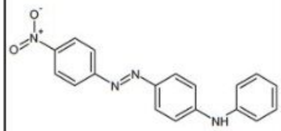
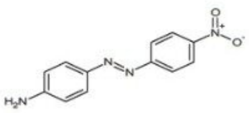
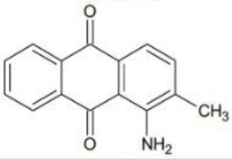
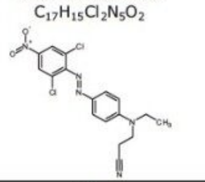
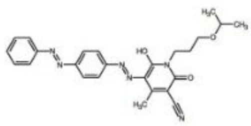
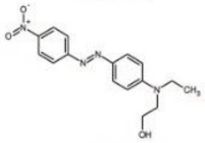
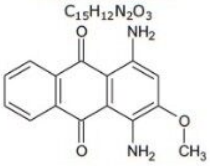
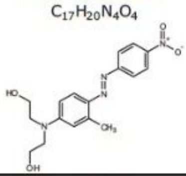
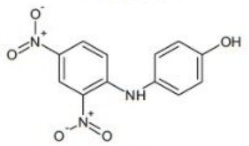
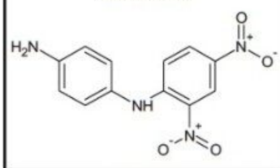
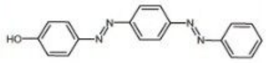
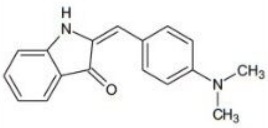
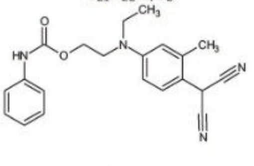
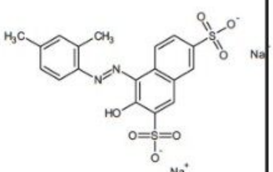
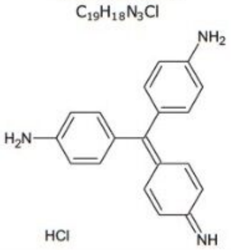
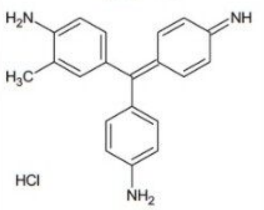
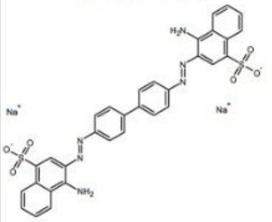
Disperse, acid, direct, and basic dyes			
1. **Disperse Blue 3** CAS: 2475-46-9 $C_{17}H_{16}N_2O_3$ 	2. **Disperse Blue 7** CAS: 3179-90-6 $C_{18}H_{18}N_2O_6$ 	3. **Disperse Blue 35** CAS: 12222-75-2 $C_{20}H_{14}N_2O_5$ 	4. **Disperse Blue 102** CAS: 69766-79-6 $C_{15}H_{19}N_5O_4S$ 
5. **Disperse Blue 106** CAS: 68516-81-4 $C_{14}H_{17}N_5OS$ 	6. **Disperse Blue 124** CAS: 61951-51-7 $C_{16}H_{19}N_5O_4S$ 	7. **Disperse Brown 1** CAS: 23355-64-8 $C_{16}H_{15}Cl_3N_4O_4$ 	8. **Disperse Orange 1** CAS: 2581-69-3 $C_{18}H_{14}N_4O_2$ 
9. **Disperse Orange 3** CAS: 730-40-5 $C_{12}H_{10}N_4O_2$ 	10. **Disperse Orange 11** CAS: 82-28-0 $C_{15}H_{11}NO_2$ 	11. **Disperse Orange 37** CAS: 13301-61-6 $C_{17}H_{15}Cl_2N_5O_2$ 	12. **Disperse Orange 149** CAS: 85136-74-9 $C_{25}H_{26}N_6O_3$ 
13. **Disperse Red 1** CAS: 2872-52-8 $C_{16}H_{18}N_4O_3$ 	14. **Disperse Red 11** CAS: 2872-48-2 $C_{15}H_{12}N_2O_3$ 	15. **Disperse Red 17** CAS: 3179-89-3 $C_{17}H_{20}N_4O_4$ 	16. **Disperse Yellow 1** CAS: 119-15-3 $C_{12}H_9N_3O_5$ 
17. **Disperse Yellow 3** CAS: 2832-40-8 $C_{15}H_{15}N_3O_2$ 	18. **Disperse Yellow 23** CAS: 6250-23-3 $C_{18}H_{14}N_4O$ 	19. **Disperse Yellow 39** CAS: 12236-29-2 $C_{17}H_{16}N_2O$ 	20. **Disperse Yellow 49** CAS: 54824-37-2 $C_{21}H_{22}N_4O_2$ 
21. **Acid Red 26** CAS: 3761-53-3 $C_{18}H_{14}N_2Na_2O_7S_2$ 	22. **Basic Red 9** CAS: 569-61-9 $C_{19}H_{18}N_3Cl$ 	23. **Basic Violet 14** CAS: 632-99-5 $C_{20}H_{20}ClN_3$ 	24. **Direct Red 28** CAS: 573-58-0 $C_{32}H_{22}N_6Na_2O_6S_2$ 

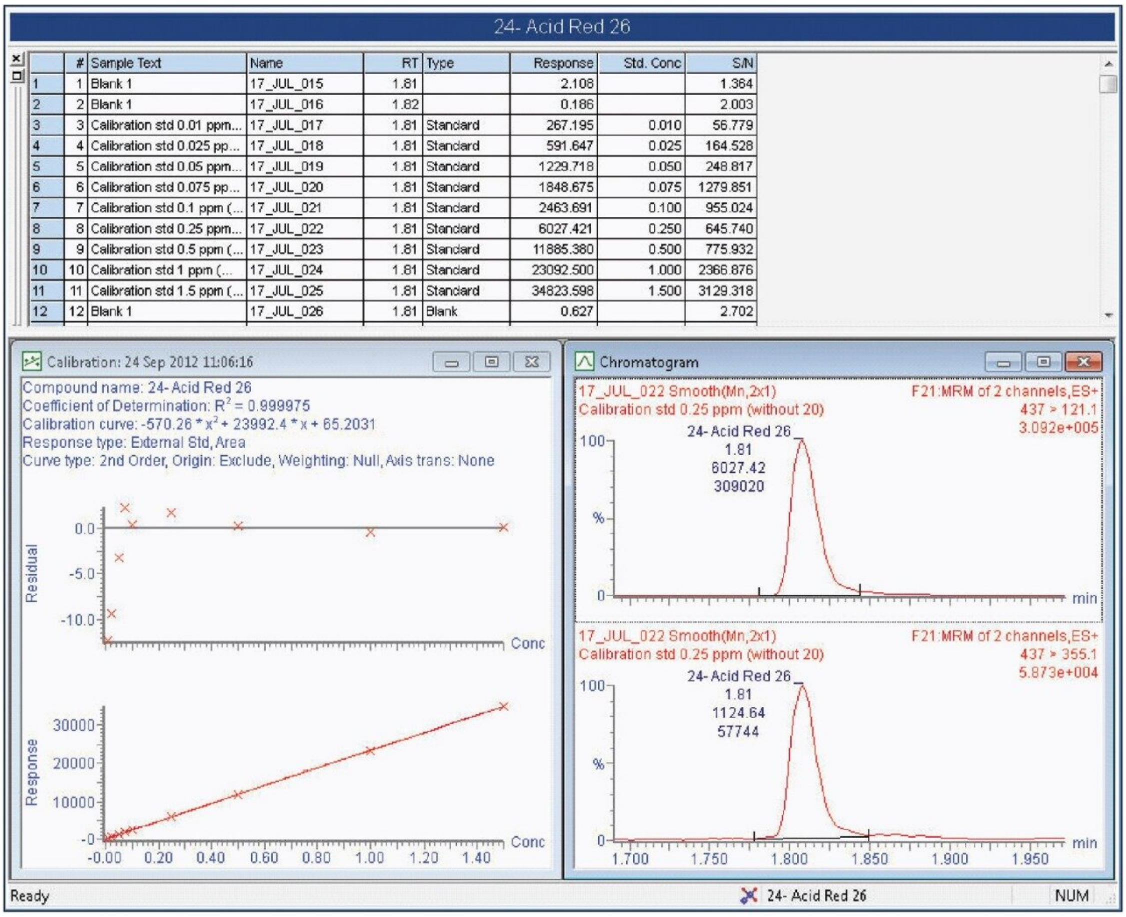
Table 2. Disperse, acid, direct, and basic dyes, associated CAS numbers, empirical formulas, and structures.

No	Chemical substance	Retention time (min)	ESI (+/-)	Cone voltage (V)	Transition	Collision energy
1	Disperse Blue 3	2.41	+	45	297.0 > 235.1	33
					297.0 > 252.0 *	21
2	Disperse Blue 7	2.26	+	50	359.0 > 283.0 *	32
					359.0 > 314.0	20
3	Disperse Blue 35	2.97	+	36	285.0 > 185.0	12
					285.0 > 270.0*	28
4	Disperse Blue 102	2.53	+	42	366.0 > 147.0	31
					366.0 > 208.1*	18
5	Disperse Blue 106	2.71	+	42	336.0 > 147.0	35
					336.0 > 178.0*	17
6	Disperse Blue 124	3.04	+	39	378.1 > 160.1	23
					278.0 > 220.1*	16
7	Disperse Brown 1	2.84	+	53	433.0 > 197.1*	31
					433.0 > 357.0	37
8	Disperse Orange 1	3.36	+	49	319.0 > 122.0*	22
					319.0 > 169.0	26
9	Disperse Orange 3	2.77	+	45	243.0 > 92.0	22
					243.0 > 122.0*	18
10	Disperse Orange 11	2.80	+	53	238.0 > 165.0*	30
					238.0 > 223.0	25
11	Disperse Orange 37	3.27	+	50	392.0 > 133.0*	38
					392.0 > 350.9	22
12	Disperse Orange 149	3.60	-	69	457.1 > 121.0*	52
					457.1 > 266.0	33
13	Disperse Red 1	2.91	+	51	315.1 > 134.0*	25
					315.1 > 284.1	23
14	Disperse Red 11	2.40	+	51	268.0 > 225.0*	28
					268.0 > 253.0	21
15	Disperse Red 17	2.64	+	53	345.1 > 164.1*	26
					345.1 > 269.1	28
16	Disperse Yellow 1	2.57	-	32	274.0 > 166.0*	12
					274.0 > 226.0	15
17	Disperse Yellow 3	2.80	-	37	268.0 > 134.0*	18
					368.0 > 253.0	18
18	Disperse Yellow 23	3.37	+	46	303.1 > 105.0*	21
					303.1 > 181.0	17
19	Disperse Yellow 39	2.83	+	55	291.0 > 130.0*	29
					291.0 > 245.1	28
20	Disperse Yellow 49	3.02	-	22	373.1 > 168.0*	27
					373.1 > 209.1	21
21	Acid Red 26	1.80	+	47	437.0 > 121.1*	25
					437.0 > 355.1	19
22	Basic Red 9	2.01	+	60	288.2 > 195.1*	33
					288.2 > 271.1	35
23	Basic Violet 14	2.12	+	68	302.1 > 195.1	35
					302.1 > 209.1*	32
24	Direct Red 28	2.02	-	81	325.0 > 81.0	27
					325.0 > 152.0*	23

Table 3. Disperse, acid, direct, and basic dyes, expected retention times, ionization mode, cone voltages, M

Instrument control, data acquisition, and results processing

g/mL, were prepared and analyzed for all of the compounds considered (equivalent range of 4 to 600 µg/g in textile samples). The TargetLynx Quantify results for acid red 26 are shown in Figure 3, and the MRM chromatograms for each compound are shown in Figure 4.



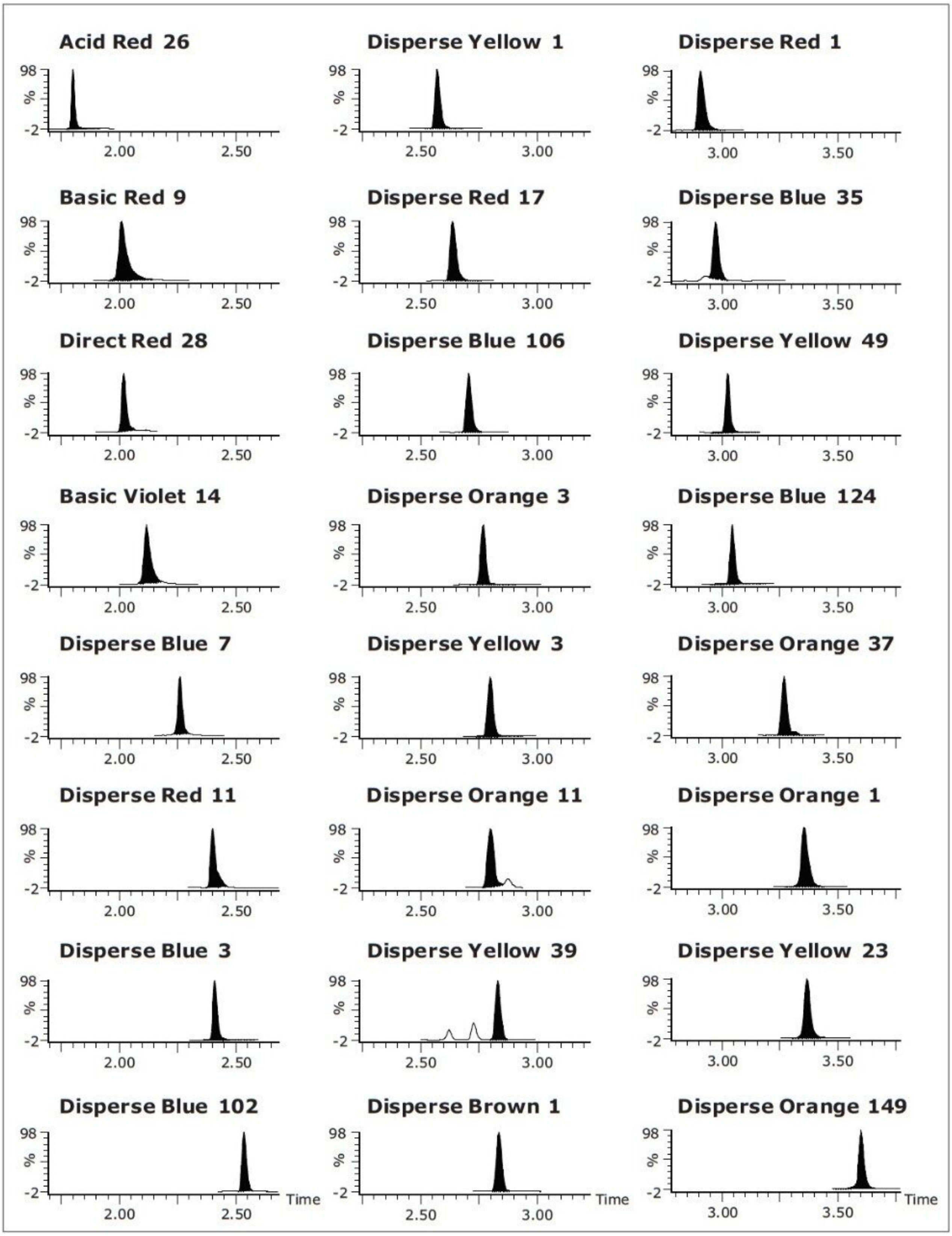


Figure 4. MRM chromatograms for disperse, acid, direct, and basic dyes in a mixed 0.5 µg/mL calibration

standard (equivalent to 200 μg/g in textile samples).

Textile analysis

The MRM mass detection method, shown in Figure 1, was used after appropriate sample preparation to quantify for dyes.

Using the extraction protocol (based on DIN 54231)[5] and the instrument parameters as detailed, the results obtained for the analysis of synthetic textile samples spiked at 75 and 30 μg/g are shown in Table 4. Many laboratories that base their extraction protocol for disperse dyes on DIN 54231,[5] accept 75 μg/g as the practical detection limit. Recoveries were obtained by comparing extracted spiked textile samples with calibration standards.

Dye	Sample	Replicate injection results (μg/g)			Average recovery (blank corrected) %	RSD (%)
		1	2	3		
Disperse Brown 1	Blank	ND	ND	ND	-	-
	75 μg/g	67.7	71.6	74.8	95.1	5.0
	30 μg/g	27.7	27.2	27.2	91.2	1.1
Disperse Red 1	Blank	ND	ND	ND	-	-
	75 μg/g	75.3	75.0	78.8	102	2.8
	30 μg/g	33.2	31.8	33.7	110	3.3
Disperse Yellow 1	Blank	ND	ND	ND	-	-
	75 μg/g	77.1	80.9	82.2	107	3.3
	30 μg/g	28.0	30.4	29.5	97.7	4.1
Disperse Yellow 39	Blank	0.28	0.36	0.40	-	-
	75 μg/g	74.0	80.8	81.6	105	5.4
	30 μg/g	30.3	30.4	31.2	101	1.6
Disperse Yellow 49	Blank	ND	ND	ND	-	-
	75 μg/g	71.2	72.6	73.8	96.7	1.8
	30 μg/g	27.3	27.0	27.7	91.1	1.3

Table 4. Textile samples spiked with selected disperse dyes recovery data. Results obtained using mass spectrometric detection and quantified against mixed calibration standards. ND = not detected.

Efficient recoveries were obtained, ranging between 91% and 110% for the three replicates.

Additional benefits over previous methodology include improved selectivity and sensitivity for the analysis of dyes using the ACQUITY UPLC H-Class System coupled with the Xevo TQD with reduced run times, and associated savings in solvents.

Conclusion

By utilizing the ACQUITY UPLC H-Class System coupled with the Xevo TQD, a fast, selective, and sensitive method was developed for the analysis of disperse, acid, direct, and basic dyes.

Rapid polarity switching technologies, available on the Xevo TQD, enabled UPLC analysis of positive and negative dyes from a single injection.

The described approach offers the following benefits when compared with standard methodology:

- Business benefits of using UPLC analysis, when comparing HPLC/UV to UPLC/MS analysis, include a greater than five times increase in sample throughput and more than an 86% reduction in solvent usage.
- Enhanced sensitivity and selectivity resulting in improved confidence in the identification and quantification offered by the ACQUITY UPLC H-Class System coupled with the Xevo TQD.
- Fast method migration from HPLC to UPLC aided by the use of tools developed by Waters including the following: the Column Selectivity Chart used to aid the selection of a suitable UPLC column, and the ACQUITY UPLC Column Calculator used to aid the development of UPLC conditions.

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TargetLynx <https://www.waters.com/513791>

720004492, November 2015