

Rapid Screening of 36 Synthetic Dyes using the ACQUITY UPLC H-Class System with the ACQUITY QDa Detector

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GOAL

To selectively analyze 36 disperse, basic, acid, solvent and direct synthetic dyes to below EU legislative limits.

BACKGROUND

Synthetic dyes are classified according to how they are used in the dyeing process. For example, disperse dyes which are mostly azo- or anthraquinone compounds are generally used for dyeing synthetic textile materials such as polyester, nylon, and PVC. The type of bonds formed between the dyes and the fabric, determine the properties of the dyes. For example, disperse dyes are not chemically bonded to the fibers of the textile, thus they can easily migrate onto the skin of the person wearing the garment, especially if the textile fastness is poor.

A number of synthetic dyes are known to be allergenic when they come into contact with human skin or if they are classified as potentially sensitizing, carcinogenic, mutagenic, or toxic to reproduction. 20 known allergenic dyes are listed by the Oeko-tek Standard 100 and the permitted limit is <math>< 50 \text{ mg/kg}</math>. Other legislation such as European Union (EU) 2009/567/EC has banned the use of these sensitizing dyes.

The standard method for the analysis of disperse dyes in textile products and components is DIN 54231-2005 using HPLC-UV-MS with an analysis time of 17 minutes.

Reduce analysis times from 17 min to <math>< 5 \text{ min}</math>.

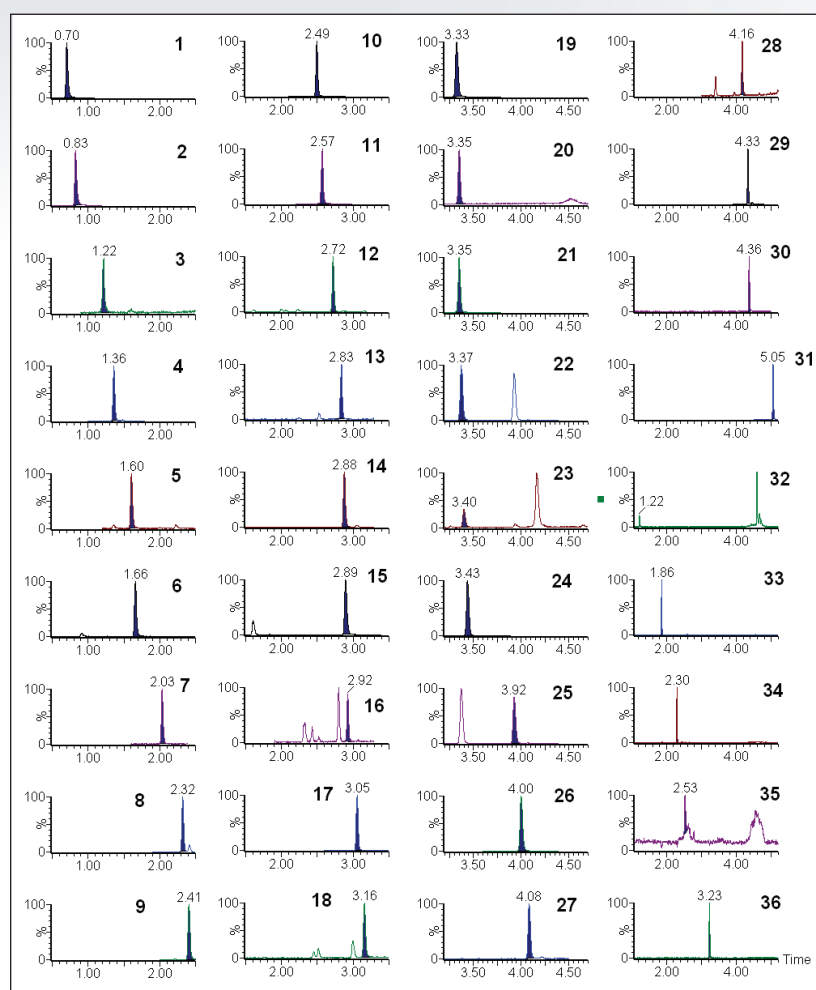


Figure 1. SIR chromatogram of 36 disperse, basic, acid, solvent and direct dye standards. SIR 1 to 31 were acquired in positive polarity, and 32 to 36 were acquired in negative polarity.

For synthetic dyes that have very similar UV absorbance maxima, it can be challenging to correctly identify their presence. Whereas, for the dyes considered that have different molecular weights, utilizing mass spectrometry can provide more selectivity and confidence in their identification.

THE SOLUTION

The Waters® ACQUITY UPLC® H-Class System with the ACQUITY® QDa® Detector was used to monitor a total of 36 disperse, basic, acid, solvent, and direct dyes including 28 dyes listed in the Oeko-Tex Standard 100 and 2009/567/EC. The list of the synthetic dyes considered are provided in Table 1.

The time required for method development was greatly reduced using the pre-optimized source parameters in the ACQUITY QDa Detector, where the required sensitivity were achieved in both polarities for both positive and negative ionizing dyes. The low system dispersion in the ACQUITY UPLC H-Class System and the use of sub-2- μ m particle columns also greatly increased peak resolution and enhanced sensitivity. Here, two methods were developed for both positive and negative ionizing dyes with analysis time of 5 and 4 minutes respectively.

Dyes were monitored according to their respective retention time, ionizing polarity, and Single Ion Recording (SIR) mass-to-charge ratio (m/z), as described in Table 1. In the highly regulated inks and dyes industry, SIR provides more selectivity and sensitivity compared to HPLC-UV analysis. The SIR chromatograms, shown in Figure 1, indicate that synthetic dyes can be easily and confidently detected at low levels.

Current EU legislation prohibits the use of sensitizing dyes in textiles, while allowing 5 ppm limit on the other dyes. Quantitation was also carried out with concentrations ranging from 0.3 to 2.0 ppm, and linearity of >0.997 was achieved for all the dyes. The calibration curve of Disperse Blue 3 is shown in Figure 2.

Table 1. Retention times, SIR m/z , and polarity for 36 disperse, basic, acid, solvent, and direct dyes.

| | Compounds | CAS no. | Retention time | SIR | Polarity |
|----|-----------------------|------------|----------------|-----|----------|
| 1 | Basic Red 9 | 569-61-9 | 0.70 | 288 | + |
| 2 | Basic Violet 14 | 632-99-5 | 0.83 | 302 | + |
| 3 | Disperse Blue 7 | 3179-90-6 | 1.22 | 359 | + |
| 4 | Acid Violet 49* | 1694-09-3 | 1.36 | 712 | + |
| 5 | Disperse Red 11 | 2872-48-2 | 1.60 | 269 | + |
| 6 | Disperse Blue 3 | 2475-46-9 | 1.66 | 297 | + |
| 7 | Disperse Blue 102 | 69766-79-6 | 2.03 | 366 | + |
| 8 | Disperse Red 17 | 3179-89-3 | 2.32 | 345 | + |
| 9 | Solvent Yellow 1* | 60-09-3 | 2.41 | 198 | + |
| 10 | Disperse Blue 106 | 68516-81-4 | 2.49 | 336 | + |
| 11 | Disperse Orange 3 | 730-40-5 | 2.57 | 243 | + |
| 12 | Disperse Yellow 3 | 2832-40-8 | 2.72 | 270 | + |
| 13 | Disperse Yellow 39 | 12236-29-2 | 2.83 | 291 | + |
| 14 | Basic Violet 1* | 8004-87-3 | 2.88 | 358 | + |
| 15 | Disperse Blue 1 | 2475-45-8 | 2.89 | 268 | + |
| 16 | Disperse Brown 1 | 23355-64-8 | 2.92 | 433 | + |
| 17 | Disperse Red 1 | 2872-52-8 | 3.05 | 315 | + |
| 18 | Disperse Blue 35A | 56524-77-7 | 3.16 | 285 | + |
| 19 | Basic Violet 3* | 548-62-9 | 3.33 | 372 | + |
| 20 | Disperse Orange 11 | 82-28-0 | 3.35 | 238 | + |
| 21 | Disperse Yellow 49 | 54824-37-2 | 3.35 | 375 | + |
| 22 | Solvent Yellow 2* | 60-11-7 | 3.37 | 226 | + |
| 23 | Disperse Blue 26 | 3860-63-7 | 3.40 | 299 | + |
| 24 | Disperse Blue 124 | 61951-51-7 | 3.43 | 378 | + |
| 25 | Solvent Yellow 3* | 97-56-3 | 3.92 | 226 | + |
| 26 | Basic Blue 26* | 2580-56-5 | 4.00 | 470 | + |
| 27 | Disperse Orange 37/76 | 13301-61-6 | 4.08 | 392 | + |
| 28 | Disperse Blue 35B | 56524-76-6 | 4.16 | 299 | + |
| 29 | Disperse Orange 1 | 2581-69-3 | 4.33 | 319 | + |
| 30 | Disperse Yellow 23 | 6250-23-3 | 4.36 | 303 | + |
| 31 | Disperse Orange 149 | 85136-74-9 | 5.05 | 459 | + |
| 32 | Direct Blue 6 | 2602-46-2 | 1.22 | 421 | - |
| 33 | Acid Red 26 | 3761-53-3 | 1.86 | 435 | - |
| 34 | Direct Red 28 | 573-58-0 | 2.30 | 651 | - |
| 35 | Direct Brown 95* | 16071-86-6 | 2.53 | 357 | - |
| 36 | Direct Black 38 | 1937-37-7 | 3.23 | 736 | - |

* Compounds not listed in the Oeko-tek Standard 100 and EU 2009/567/EC

SUMMARY

The ACQUITY UPLC H-Class System with the ACQUITY QDa Detector provides a faster and more reliable analytical tool for the identification and quantification of synthetic dyes. Two methods of less than 5 minutes have been developed for both positive and negative ionizing dyes that provide increased throughput and reduced solvent usage.

The ACQUITY QDa Detector can also be easily integrated into current LC-UV analysis methods which allows unsurpassed sensitivity and selectivity, with limits of detection achieved well below the EU regulatory limit of 5 ppm.

Compound name: 2 Disperse Blue3
Correlation coefficient: $r = 0.999805$, $r^2 = 0.999610$
Calibration curve: $52363.3 * x + 3863.55$
Response type: External Std, Area
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None

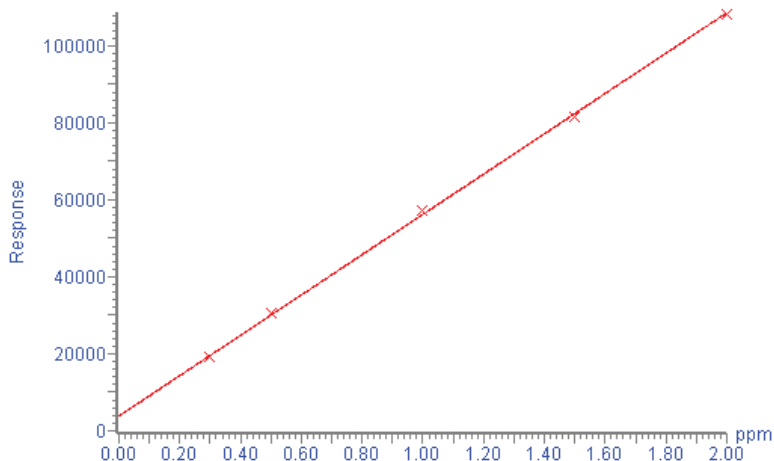


Figure 2. Calibration curve of Disperse Blue 3.

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