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Disperse azo dyes, arylamines and halogenated dinitrobenzene compounds in synthetic garments on the Swedish market

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Keywords

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Conflicts of interest

None to declare

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Abstract

Background. Azobenzene disperse dyes (azo DDs) are well known as textile allergens, but the knowledge of their occurrence in garments is low. The numerous azo DDs and dye components found in textiles constitute a potential health risk, but only seven azo DDs are included in the European baseline patch test series (EBS).

Objectives. To investigate non-regulated azo DDs and dye components in synthetic garments on the Swedish market.

Methods. High-performance liquid chromatography/mass spectrometry, gas chromatography/mass spectrometry and computerized data mining.

Results. Sixty-two azo DDs were detected, with Disperse Red 167:1 occurring in 67%, and fourteen other DDs each found in >20% of the garments. Notably, the EBS dyes were less common, three even not detected, while arylamines were frequently detected and exceeded 1 mg/g in several garments. Also halogenated dinitrobenzenes were identified in 25% of the textiles.

Conclusions. Azo DDs and dye components, in complex compositions and with large variations, occurred frequently in the synthetic garments. The arylamines were shown to occur in much higher levels compared to the azo DDs, suggesting the former to constitute a potentially higher health risk. The role of arylamines and halogenated dinitrobenzenes in textile allergy have to be further investigated.

1. Introduction

Contact allergy towards textiles is commonly caused by chemical compounds in the fabric, such as dyes or formaldehyde resins, while more seldom by the fiber itself¹⁻³. Disperse dyes (DDs) are considered to be the most important textile allergens and DDs of both azo- and anthraquinone type are well-known strong skin sensitizers³. DDs are used to colour synthetic fibres as polyester, polyamide, acetate and in some cases nylon or blends of those. Due to the lipophilic characteristics of DDs, they diffuse into the hydrophobic fibres and typically heat and dispersive agents are applied to speed up the process⁴. Consequently, the DD molecules are not covalently bound to the textile fibres and in skin-close garments this may lead to migration to the skin, facilitated by sweat, heat and friction. The dye molecules can be either absorbed by the skin and then metabolized to protein-reactive skin-sensitizing substances, or activated by skin bacteria to allergenic arylamines prior to skin absorption⁵⁻⁷. Those azo DDs that may be reduced to any of the 22 known mutagenic and carcinogenic arylamines in concentrations above 30 µg/g are prohibited for use in textiles within the European Union according to REACH regulation Annex XVII⁸. There are also voluntary eco-labelling, such as the OEKO-TEX[®], which further restricts the use of some allergenic dyes⁹. However, there are few regulations today considering the large number of azo DDs used in the textile industry. Very little knowledge as well as information are available regarding the content of these compounds in garments. Data on reported prevalence of contact allergy to DDs between 1990 and 2012 have been evaluated in a review from 2012¹⁰. From these data, 26 DDs were identified as allergens. However, in the review it was pointed out that these compounds are only a tiny fraction of all possible allergenic DDs. Also, the relevant contact allergens among DDs in textile allergy can be very difficult to identify since the dyestuff used for textile colouring are often highly impure^{11,12}. It has been shown previously that the DDs used for patch testing may contain numerous pollutants¹³⁻¹⁵. A textile dye mix (TDM) with totally 6.6% (w/w) of eight DDs, the azo compounds Disperse Orange 1 and 3, Disperse Red 1 and 17, Disperse Yellow 3, Disperse Blue 106 and 124 and the anthraquinone dye Disperse Blue 35 (**Figure 1**), is now included in the European baseline series (EBS) for patch testing¹⁶⁻²¹. However, a study already in 2012 indicated that these TDM dyes are not frequent in textile garments¹¹. The majority of azo DDs used within the global textile industry are non-regulated, although they may contain or release arylamines of toxicological concern, with health effects such as skin sensitization²², genotoxicity²³, carcinogenicity^{22,23} and mutagenicity²⁴. It has also been shown that arylamines with

suspected toxic effects can be formed after reductive treatment of the dye content in clothes^{22,25,26}. Such arylamines have been detected at levels exceeding 0.2 mg/g in underwear garments from the US market²⁷. Further, an investigation of textiles from the Swedish market, detected arylamines at levels up to 0.5 mg/g²⁸.

The aim of this work was to investigate synthetic garments from the Swedish retail market and identify the most frequently occurring non-regulated azo DDs and dye components. Screening of a large number of suspect DDs based on published information and available reference standards were performed with high-performance liquid chromatograph/high-resolution mass spectrometry (HPLC/HRMS) and quantification with HPLC/triple-stage quadrupole (TSQ) MS. For semivolatile components, gas chromatography/mass spectrometry (GC/MS) was used.

2. Methods

2.1 Chemicals

Methanol, acetonitrile (both of HPLC-grade), dichloromethane (puriss.) and ammonium acetate (analytical reagent) were purchased from Riedel-de Haën (Seelze, Germany). Ultrapure water with resistivity of 18.2 MΩcm was obtained with a Synergy 185 system from Millipore (Molsheim, France). The purities and suppliers of the standard compounds are shown in Supplementary Information (**Table SI-1**).

2.2 Samples and sample preparation

Eighty-two low- to mid-price common textile garments were purchased from different suppliers. For eleven of the garments, the manufacturing country was unknown, while the rest were imported from different countries. The colours, materials and manufacturing countries are listed in **Table SI-2**. The selected textiles were all skin-close garments, such as T-shirts, socks etc., made of more than 70% polyester fibres. All analysed textiles were one-coloured, except one. The latter had two parts of different colours that were analysed separately. Thus, 83 samples were altogether subject for analysis. About one gram of textile was cut into pieces of approx. 4 x 4 mm and put into a 15-mL glass tube, and extracted with 2 x 6 mL of dichloromethane using ultrasonication (10 min, 100% amplitude at 50 °C, Sonorex Digital 10P, Bandeline Electronic, Berlin, Germany). This part of the sample preparation was the same for all analyses, while the following procedures differed slightly between the applied analytical methods, as described below.

Prior to analysis with HPLC/HRMS, a volume of 200 μL of water was added to the pooled dichloromethane extract and the resulting volume reduced to 200 μL under a gentle flow of nitrogen at 35 $^{\circ}\text{C}$. A volume of 800 μL of methanol was then added, followed by syringe filtration into a vial. A volume of 5 μL of this solution was injected into the HPLC/HRMS.

The sample preparation for HPLC/TSQ MS analysis was similar as for HPLC/HRMS, except that quinoline- d_7 , 3-nitroaniline- d_4 , 4-nitroaniline- $^{15}\text{N}_2$, and Sudan-I- d_5 were added as internal standards (IS) prior to the ultrasonic extraction. A volume of 10 μL of the final sample solution was injected into the HPLC/TSQ MS. The recoveries from the sample preparation for 22 DDs measured by HPLC/TSQ MS are given in **Table SI-3**.

For GC/MS analysis and quantification of arylamines and halogenated dinitrobenzene compounds, quinoline- d_7 , 3-nitroaniline- d_4 , 4-nitroaniline- $^{15}\text{N}_2$, and Sudan-I- d_5 were added as IS prior to the ultrasonic extraction. After filtration, the dichloromethane solvent was then evaporated to 1 mL, of which 1 μL was injected into the GC/MS. The recoveries from the sample preparation for arylamines and halogenated dinitrobenzenes are given in **Table SI-4**.

2.3 Instrumental analysis

A full description of the entire analytical methodology can be found in Supplementary Information. To summarize, HPLC/HRMS was used for screening of DDs, including detection and identification, but not quantification. For quantification, HPLC/TSQ MS and reference compounds were used. For the semivolatile classes of compounds, i.e. arylamines and halogenated dinitrobenzenes, GC/MS and reference compounds were used for both identification and quantification.

2.3.1 HPLC/HRMS

We have recently published a suspect screening workflow with HPLC/HRMS for identification purposes including data mining²⁹. In the present work, this was used for screening of more than 120 different DDs and some related dye components, suspected to be present in synthetic garments based on both published information regarding usage in industry²² and a number of available reference standards (**Table SI-5**). The instrument used for this suspect screening was a UHPLC/electrospray (ESI)-OrbitrapTM HRMS instrument (Q Exactive HF, Thermo Scientific, Rockford, IL, USA). A first stage identification of DDs was performed, utilizing accurate mass,

MS/MS spectra, isotopic pattern, and experimental HPLC retention times from those predicted, by a model shown in **SI-6**. No quantification was performed at this stage. **Figure 2** illustrates the HPLC/HRMS identification workflow.

2.3.2 HPLC/TSQ MS

HPLC/TSQ MS was used for quantification of the 14 DDs for which reference compounds were available. In this case, a Waters Acquity I-Class UPLC system (Waters, Manchester, UK), coupled to a Xevo TQ-S triple quadrupole MS instrument equipped with an ESI source was used. The instrumental settings are given in **Table SI-7**. No matrix effects on the ionisation could be observed and the instrumental response was linear ($R^2 > 0.99$) within the measured range of 0.02 to 1.6 ng amount injected. The relative standard deviation was within the range 1 – 13% ($n=3$) and the method limit of quantification ($S/N=10$) was determined to 0.7 – 20.5 ng/g of textile, depending on the dye.

2.3.3 GC/MS

For GC/MS of arylamines and halogenated dinitrobenzenes, an Agilent 5975C MSD was used, equipped with a 6890N GC, a 7693 autosampler, and a PTV-injector (Agilent Technologies, Palo Alto, CA, USA). The analysis was performed in full scan mode with electron ionisation (EI) at 70 eV. The instrumental settings and calibration data are given in **Table SI-8**. The method quantification limits ($S/N=10$) were in the range 9.9 - 319.2 ng/g of textile, depending on compound. **Figure 3** shows a GC/MS chromatogram representing an extract from a black t-shirt made of 100% polyester.

3. Results

3.1 Azo DDs in clothing garments

A selection of 20 garment samples with the highest detected levels of DDs are shown in **Figure 4**. A complete list of all the investigated textiles can be found in **Table SI-2**. Although the aim was to focus on the azo type of DDs, we included a number of anthraquinone DDs: Disperse Blue 35 since it is included in TDM, and Disperse Red 60 and Disperse Blue 14 since reference compounds were available. In total, 65 dyes (62 azo dyes) were identified in this screening, of which 11 azo dyes and 3 anthraquinone dyes were confirmed with reference compounds. For the majority of the dyes screened for, there were no reference compounds available. Identification was considered

sufficient without reference compound by using a combination of accurate mass, MS/MS spectra, isotopic pattern, and HPLC retention time predicted from logP values. The ten most frequently detected dyes in the investigated clothing are listed in **Table 1**. Only one TDM dye is included among the most frequent dyes, Disperse Orange 3 (**Figure 1** and **Table 1**). The TDM dyes Disperse Red 1 and 17, Disperse Yellow 3 and Disperse Blue 35 were all detected in less than 10%. Neither of the TDM dyes Disperse Orange 1, Disperse Blue 106 or Disperse Blue 124 could be detected in any of the textiles.

Disperse Orange 37, listed by OEKO-TEX® as a skin allergen, was detected in only 10% of the garments⁹. A complete list of all detected dyes is given in **Table SI-9**. Concentration ranges of quantified DDs are given in **SI-10**.

Table 1. The ten most frequently occurring DDs in 82 synthetic garments

Disperse dye (DD)	Frequency [%]	Type	Possible dye precursor/cleavage product
Disperse Red 167:1	67	Azo	2-chloro-4-nitroaniline ((3-acetamido-4-aminophenyl)azanediyl) bis(ethane-2,1-diyl) diacetate
Disperse Red 343	49	Azo	2-amino-5-methyl isophthalonitrile N-(2-amino-5-(diethylamino)phenyl) methanesulfonamide
Disperse Red 311	48	Azo	2,4-dinitroaniline dimethyl 3,3'-((3-acetamido-4-amino phenyl)azanediyl) dipropionate
Disperse Red 153	46	Azo	5,7-dichlorobenzo[d]thiazol-2-amine 3-((4-aminophenyl)(ethyl)amino) propanenitrile
Disperse Red 74	44	Azo	4-nitroaniline ((3-acetamido-4-aminophenyl)azanediyl) bis(ethane-2,1-diyl) diacetate
Disperse Orange 25	39	Azo	4-nitroaniline 3-((4-aminophenyl)(ethyl)amino) propanenitrile
Disperse Red 60	38	Anthra-quinone	- -
Disperse Blue 165	27	Azo	2-amino-3,5-dinitrobenzonitrile N-(2-amino-5-(dipropylamino)phenyl) acetamide
Disperse Orange 3	26	Azo	1,4-phenylenediamine 4-nitroaniline
Disperse Blue 291 (Cl)	26	Azo	6-chloro-2,4-dinitroaniline N-(2-amino-5-(diethylamino)-4-methoxy phenyl)acetamide

3.2 Arylamines and halogenated dinitrobenzene compounds in clothing garments

Apart from DDs, the present screening was able to identify other dye components in the garments, such as thirteen different arylamines (**Table 2**). Eight were found to occur at a frequency higher

than 10% and are shown in **Figure 5**. Except for 4-chloroaniline (4-Cl-A), neither of these substances are regulated by REACH. Arylamines may be formed by decomposition, i.e., reductive cleavage of the azo DDs. However, the azo DDs were found to be stable in the analytical procedure and not form arylamines as artifacts. Thus, it could be concluded that the identified arylamines were present in the garments as free compounds. For two of these compounds, 6-chloro-2,4-dinitroaniline (6-Cl-2,4-DNA) and 2-bromo-4,6-dinitroaniline (2-Br-4,6-DNA), the individual concentrations reached up to 3 mg/g. The garments with the highest total levels were all of black colour, as shown in **Figure 6**. Garments of recycled polyester were also investigated, and among these a pair of black training shorts (S-54) contained 2 mg/g of arylamines. It was also possible to identify halogenated dinitrobenzene compounds (**Table 2, Figure 5**), including the extreme skin sensitizer 1-chloro-2,4-dinitrobenzene (2,4-DNCB). As for the arylamines, the highest total levels were detected in black garments (**Figure 7**). Among these compounds was 2,4-DNCB, detected in 6% of the selected garments, while 2,5-DNCB and 1-bromo-3,5-dinitrobenzene (3,5-DNBB) was detected in 18 and 24%, respectively, of the garments.

Table 2. Arylamines and halogenated dinitrobenzene compounds quantified in 82 synthetic garments

Compound	Abbrev.	Frequency [%]	Concentration [µg/g]			
			Min	Max	Mean	Median
Arylamines						
4-nitroaniline	4-NA	44	0.013	200	15	3.0
6-chloro-2,4-dinitroaniline	6-Cl-2,4-DNA	39	1.0	2900	440	39
2,6-dichloro-4-nitroaniline	2,6-DCI-4-NA	37	0.12	94	14	2.2
2-chloro-4-nitroaniline	2-Cl-4-NA	35	0.11	86	14	5.9
2-bromo-4,6-dinitroaniline	2-Br-4,6-DNA	34	0.38	3000	290	110
2,4-dinitroaniline	2,4-DNA	30	0.51	260	47	28
4-chloro-2-nitroaniline	4-Cl-2-NA	22	0.15	600	49	1.7
4-chloroaniline	4-Cl-A	11	0.073	6.9	1.4	0.48
1,4-phenylenediamine	PPD	9	0.26	27	7.5	1.6
2-nitroaniline	2-NA	7	0.18	48	12	5.5
2,6-dichloro-1,4-phenylenediamine	2,6-DCI-PPD	7	0.58	6.5	2.5	0.83
3-nitroaniline	3-NA	4	0.041	0.15	0.082	0.055
2,6-dimethylaniline	2,6-DMA	1	1.0	1.0	-	-
Halogenated dinitrobenzene compounds						
1-bromo-3,5-dinitrobenzene	3,5-DNBB	24	0.15	76	7.6	1.5
1-chloro-2,5-dinitrobenzene	2,5-DNCB	18	0.17	61	18	9.1
1-chloro-2,4-dinitrobenzene	2,4-DNCB	6	0.48	15	3.8	0.93
1-chloro-2,6-dinitrobenzene	2,6-DNCB	1	1.6	1.6	-	-

4. Discussion

A recent study was able to identify 12 different azo DDs in children's sports clothes purchased on the US market¹². The majority of these dyes were also identified in the present study together with more than 50 other azo DDs. Further, our results suggest that dyestuffs used in the manufacturing process contain not only a complex mixture of DDs, but also a variety of impurities and dye precursors. Nitroanilines, halogenated nitroanilines and halogenated dinitrobenzene compounds are most likely introduced already in the dyeing process and then remain in the finished garments. To the best of our knowledge, this is the first time halogenated dinitrobenzene compounds, such as 2,4-DNCB, have been identified in garments from the open market. Apart from the well-known skin sensitizer 2,4-DNCB, several of the other detected non-regulated chemicals might be skin sensitizing and play an important role in textile allergy.

Arylamines were detected as free compounds at high levels in the textiles, while azo DDs generally occurred at much lower levels. The total concentration of arylamines exceeded 1 mg/g in seven of the garments. For example, in the black T-shirt S-82 the total level of arylamines were approx. 3500 times higher than the concentration of the identified azo DDs (**Figure 4 and 6**). This suggests that arylamines in this apparel constitute a significantly higher health risk than the content of azo DDs. The highest concentrations for some arylamines, such as halogenated dinitroanilines, reached 3 mg/g, which is 100 times higher than the EU limits for regulated arylamines, i.e., 30 µg/g. Halogenated dinitroanilines were found to be frequently occurring, in total detected in about 50% of the garments. Interestingly, the black training shorts made of 100% recycled polyester, were also shown to contain high levels of arylamines. This emphasizes the need for a more extensive chemical control of the recycled textiles used as starting materials in the production of new textile fibres.

To summarize, exposure to other textile dyes and dye components seems to be more common than to the eight TDM dyes in the EBS, which is in agreement with previous findings¹¹. Two of these dyes could not be detected in any of the investigated textile samples, two had a detection frequency <5%, the rest <10% except for DO3 which was detected in 26% of the samples. Further, we have shown the occurrence of other potentially skin sensitizing dye components in the investigated garments at a high frequency, and occasionally very high concentrations. This implies two things. Firstly: The composition of dyes in the EBS is not representative for the dyes occurring in garments on the common market. Also, the content of dye components in the dyes used for patch testing has to be taken into consideration. Secondly: The frequent occurrence of arylamines, such as nitroanilines and halogenated dinitroanilines, in comparably much higher concentrations than the dyes in the garments, makes these arylamines possible candidates as culprits in skin sensitization and allergic reactions. Part of the skin reactions commonly reported from patch testing with TDM might be due to cross-reactions with one or several of these substances detected in the present study. According to the literature, it is not uncommon to observe cross-reactions among azo dyes and *p*-amino substituted compounds in already sensitized individuals³⁰.

This study has revealed that there are complex mixtures of chemicals present in garments from the open market. This is demonstrated in **Figure 2a** and **Figure 3**, where the latter shows the total ion chromatogram (TIC) from a GC/MS analysis in which several peaks have been assigned to

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arylamines and other aromatic compounds. As can be seen there are also a number of large peaks in the later part of the chromatogram representing compounds that so far not have been identified. Since this is a full scan MS using standard EI, the relative amount of each compound is roughly given by the peak areas. Thus, there is a number of unidentified compounds in this textile sample present in the same, or even higher, concentration range as the identified compounds. In **Figure 2a**, the chromatogram of the LC/MS analysis is shown where disperse dyes are determined, here with the example of Disperse Red 167:1. The TIC displayed in grey demonstrates the complex composition of the sample extract. It indicates the presence of more than eighty peaks, each representing one or more compounds. Since the ionization efficiency and thus response in HPLC/MS varies strongly between different compounds, it is not possible to estimate the amount in the unknown peaks.

5. Conclusions

The present study shows that synthetic skin-close garments from the Swedish open market contain a large variety of azo DDs, arylamines and halogenated dinitrobenzene compounds. Generally, arylamines were found to occur in the garments at much higher levels as compared to azo dyes, thus most likely constituting a higher health risk. As these are free compounds and non-covalently bound to the textile fibres, the arylamines are able to migrate to the skin. Many of the chemicals identified in this study are not regulated today, but could be possible health hazards and relevant for textile allergy. Thus, these substances should be further investigated in terms of migration from clothes to skin, skin uptake and sensitization potency. Furthermore, the efficiency of laundry should be investigated regarding removal of azo dyes, arylamines and halogenated dinitrobenzenes. The presence of these chemicals in textiles is also an important aspect when using recycled textiles in the manufacturing of new textile fibres with the goal to achieve a sustainable circular economy. This study has shown the importance of analytical chemical screening methods for textiles to enable identification and control of the content of possible skin sensitizers. Finally, the results demonstrate that complex mixtures of chemicals, not only azo DD:s and arylamines, are present in textiles sold on the open market. This clearly demonstrates that more research is needed to obtain a much better knowledge and understanding of the chemicals we are exposed to on a daily basis by wearing clothes.

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Figure Legends

Figure 1. Disperse dyes (DDs) in the textile dye mix (TDM). DO1 = Disperse Orange 1, DO3 = Disperse Orange 3, DR1 = Disperse Red 1, DR17 = Disperse Red 17, DY3 = Disperse Yellow 3, DB106 = Disperse Blue 106, DB124 = Disperse Blue 124, DB35 = Disperse Blue 35. DB35 is of anthraquinone type, all other DDs shown are azo DDs.

Figure 2. HPLC/HRMS analysis - Example of first stage identification of Disperse Red 167:1 in a sample extract from a black t-shirt made of 100% recycled polyester fibers (sample S-52). **a)** shows the total ion chromatogram (TIC) as a grey line. At retention time (RT) 13.4 min the extracted ion chromatogram (XIC, exact mass m/z 506.1437, black line) shows the peak identified as Disperse Red 167:1. The full MS isotopic pattern of this peak **b)** is matching with the theoretical spectrum of Disperse Red 167:1, the MS/MS fragmentation pattern is shown in **c)**. Disperse Red 167:1 is identified by HPLC retention time, full MS accurate mass isotopic pattern, as well as MS/MS accurate mass fragmentation pattern.

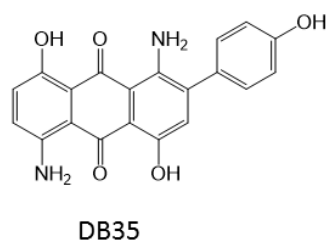
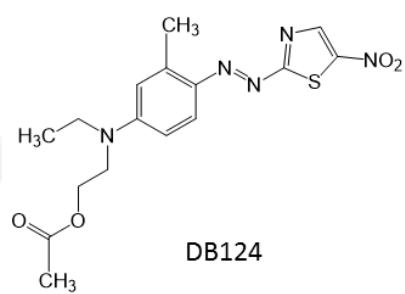
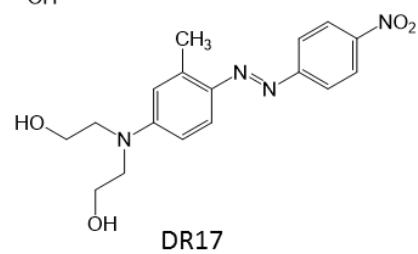
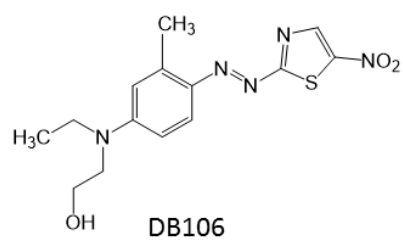
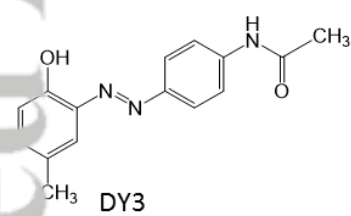
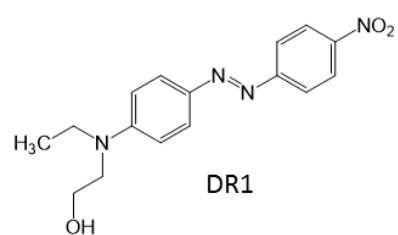
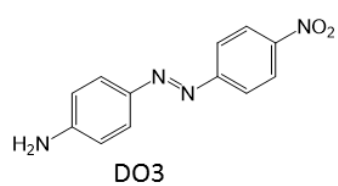
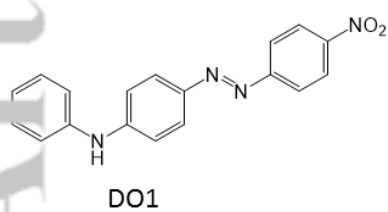
Figure 3. A GC/MS chromatogram, from retention time 10 to 40 min, of an extract from the same black t-shirt made of 100% recycled polyester fibers (sample S-52) as in Figure 2. The numbered peaks in the chromatogram corresponds to: 1. 1-chloro-4-nitrobenzene, 2. quinoline- d_7 (IS), 3. quinoline, 4. 4-chloro-2-nitrophenol, 5. indanone (IS), 6. 3-nitroaniline- d_4 (IS), 7. 1-chloro-2,5-dinitrobenzene, 8. 4-chloro-2-nitroaniline, 9. 4-nitroaniline, 10. 1-bromo-3,5-dinitrobenzene, 11. dichloro-dinitrobenzene[†], 12. chloro-nitroaniline[†], 13. 2-chloro-4-nitroaniline, 14. 2,6-dichloro-4-nitroaniline, 15. bromo-chloro-dinitrobenzene[†], 16. 6-chloro-2,4-dinitroaniline, 17. 2,4-dinitroaniline, 18. 2-bromo-4,6-dinitroaniline. For the compounds marked with [†], the exact positions of the substituents are not known since standard compounds were not available. IS = internal standard. The inset shows the identification of 1-chloro-2,5-dinitrobenzene by its mass spectrum and GC retention time compared to the reference compound.

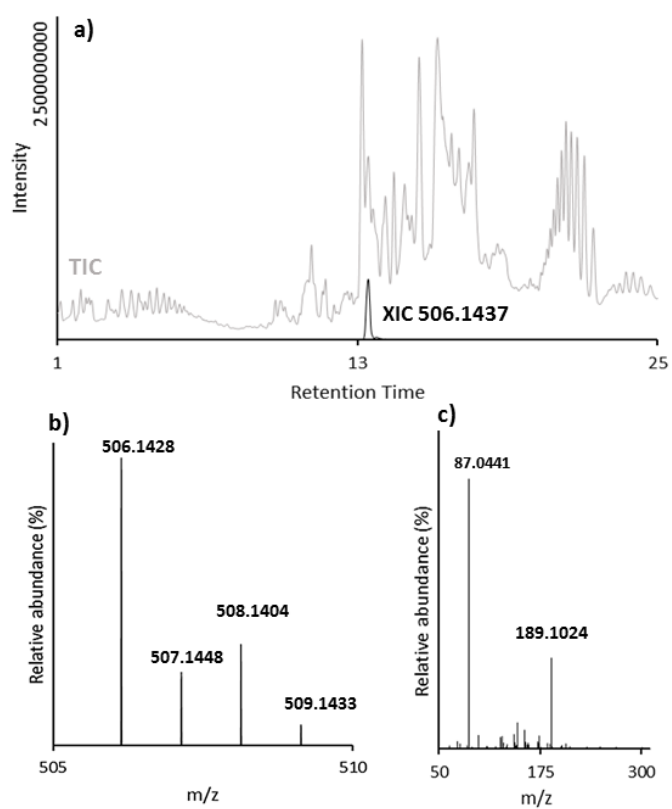
Figure 4. Quantified DDs in selected samples (n=20). Abbreviations within brackets. Disperse Red 1 (DR1), Disperse Red 13 (DR13), Disperse Red 17 (DR17), Disperse Red 19 (DR19), Disperse Black 2 (DB2), Disperse Brown 22 (DB22), Disperse Yellow 3 (DY3), Disperse Orange 3 (DO3), Disperse Orange 25 (DO25), Disperse Orange 37 (DO37), Disperse Blue 14 (DB14), Disperse Blue 35 (DB35), Disperse Blue 79 (DB79). [†] made of 100% recycled polyester. A complete list of the investigated garments with sample numbers (S-X) and textile materials are given in **Table SI-2**.

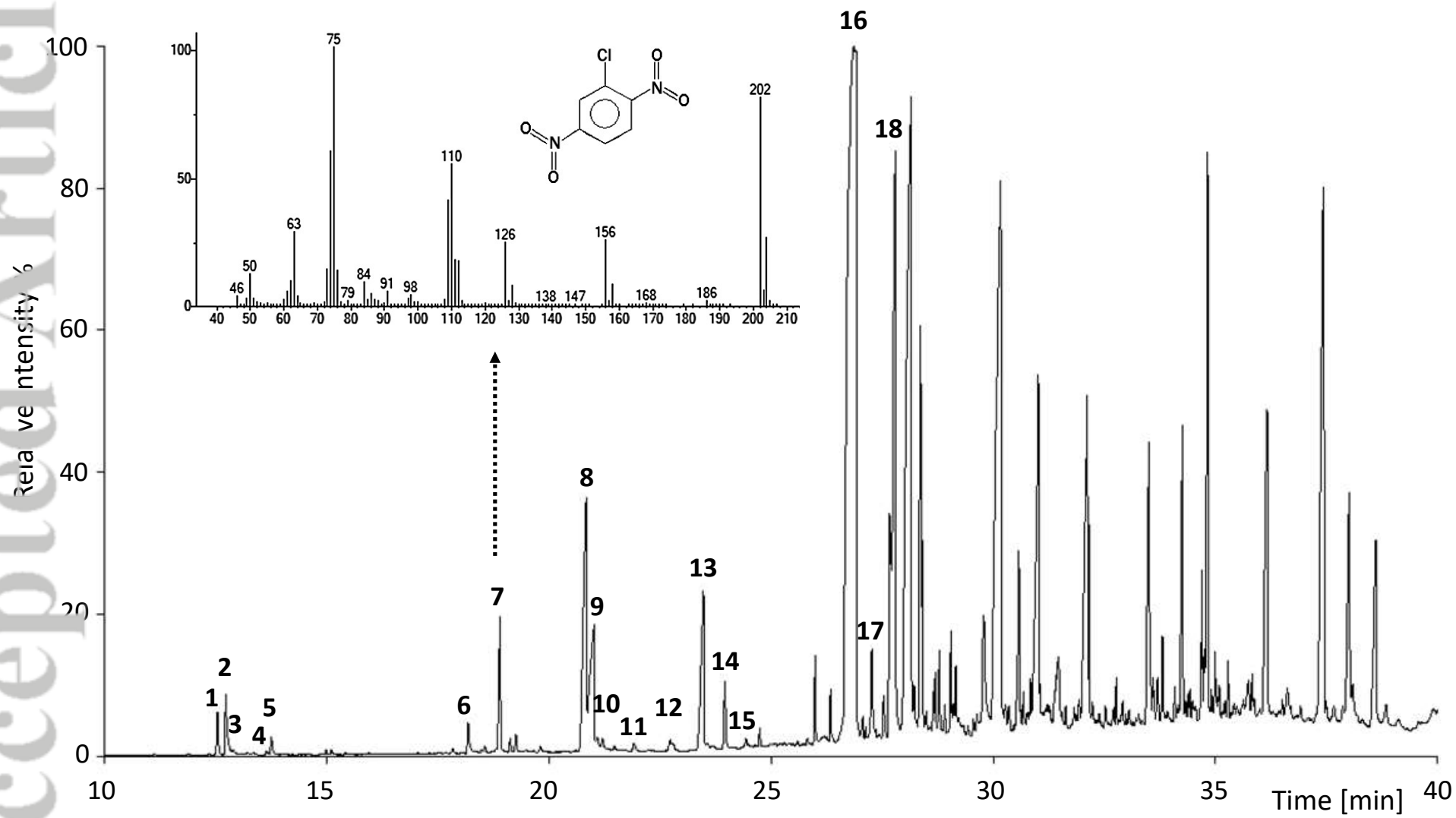
Figure 5. Arylamines detected in more than 10% of the investigated garments, and identified halogenated dinitrobenzenes. 4-NA = 4-nitroaniline, 4-ClA = 4-chloroaniline, 2,4-DNA = 2,4-dinitroaniline, 2-Cl-4-NA = 2-chloro-4-nitroaniline, 4-Cl-2-NA = 4-chloro-2-nitroaniline, 2,6-DCl-4-NA = 2,6-dichloro-4-nitroaniline, 6-Cl-2,4-DNA = 6-chloro-2,4-dinitroaniline, 2-Br-4,6-DNA = 2-bromo-4,6-dinitroaniline, 2,4-DNCB = 1-chloro-2,4-dinitrobenzene, 2,5-DNCB = 1-chloro-2,5-dinitrobenzene, 3,5-DNBB = 1-bromo-3,5-dinitrobenzene.

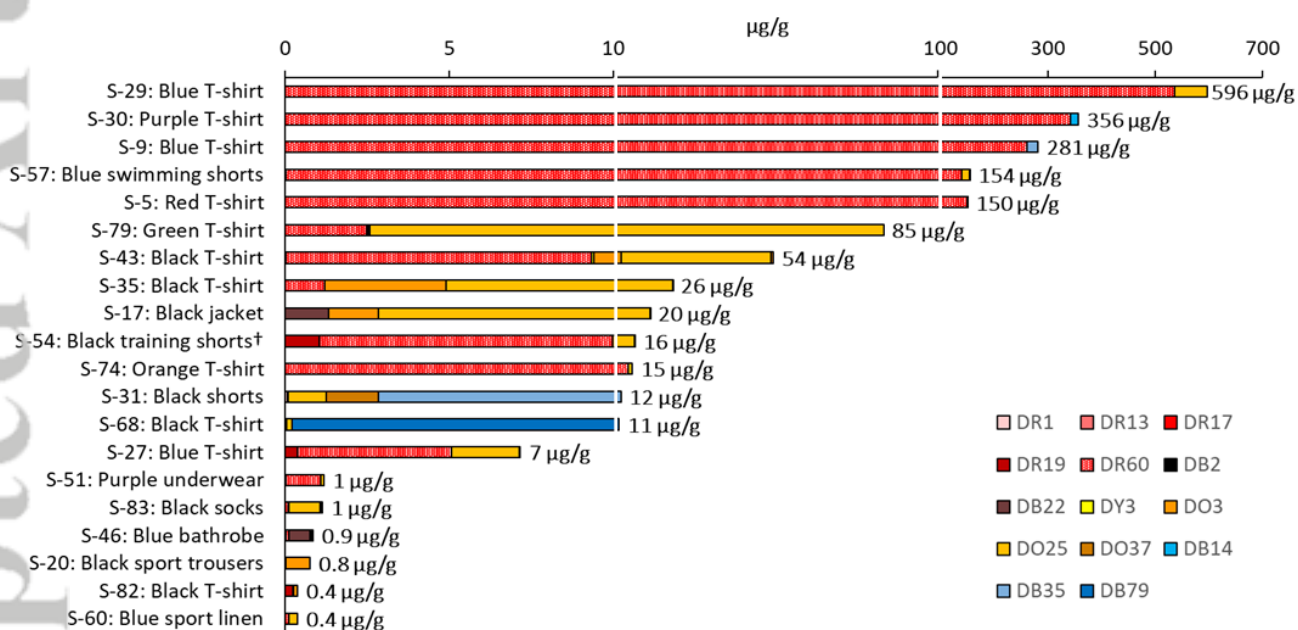
Figure 6. Quantified arylamines in selected samples (n=18). Abbreviations within brackets: 2,6-dimethylaniline (2,6-DMA), 4-chloroaniline (4-Cl-A), 2,6-dichloroaniline (2,6-DCIA), PPD, 2-nitroaniline (2-NA), 3-nitroaniline (3-NA), 4-nitroaniline (4-NA), 4-chloro-2-nitroaniline (4-Cl-2-NA), 2-chloro-4-nitroaniline (2-Cl-4-NA), 2,6-dichloro-4-nitroaniline (2,6-DCI-4-NA), 6-chloro-2,4-dinitroaniline (6-Cl-2,4-DNA), 2,4-dinitroaniline (2,4-DNA), 2-bromo-4,6-dinitroaniline (2-Br-4,6-DNA). † made of 100% recycled polyester. A complete list of the investigated garments with sample numbers (S-X) and textile materials are given in **Table SI-2**. The detection frequencies and levels of arylamines can be found in **Table 2**.

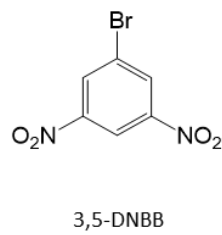
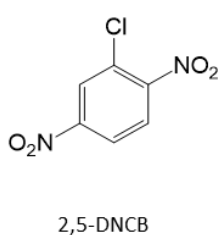
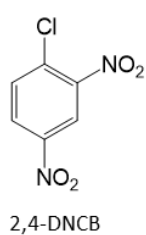
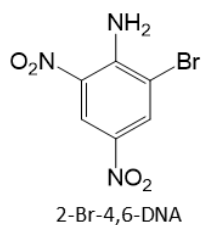
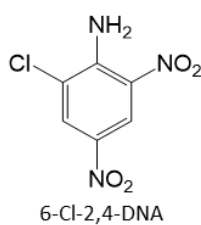
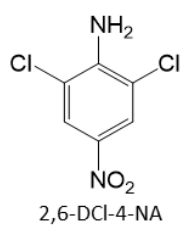
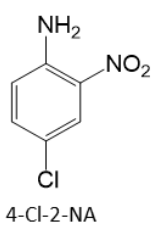
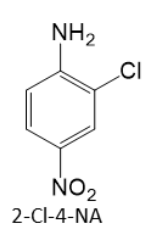
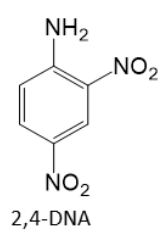
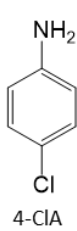
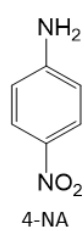
Figure 7. Quantified halogenated dinitrobenzenes in selected samples (n=14). Abbreviations within brackets: 1-chloro-2,5-dinitrobenzene (2,5-DNCB), 1-chloro-2,4-dinitrobenzene (2,4-DNCB), 1-bromo-3,5-dinitrobenzene (3,5-DNBB). † made of 100% recycled polyester. A complete list of the investigated garments with sample numbers (S-X) and textile materials are given in **Table SI-2**. The detection frequencies and levels can be found in **Table 2**.

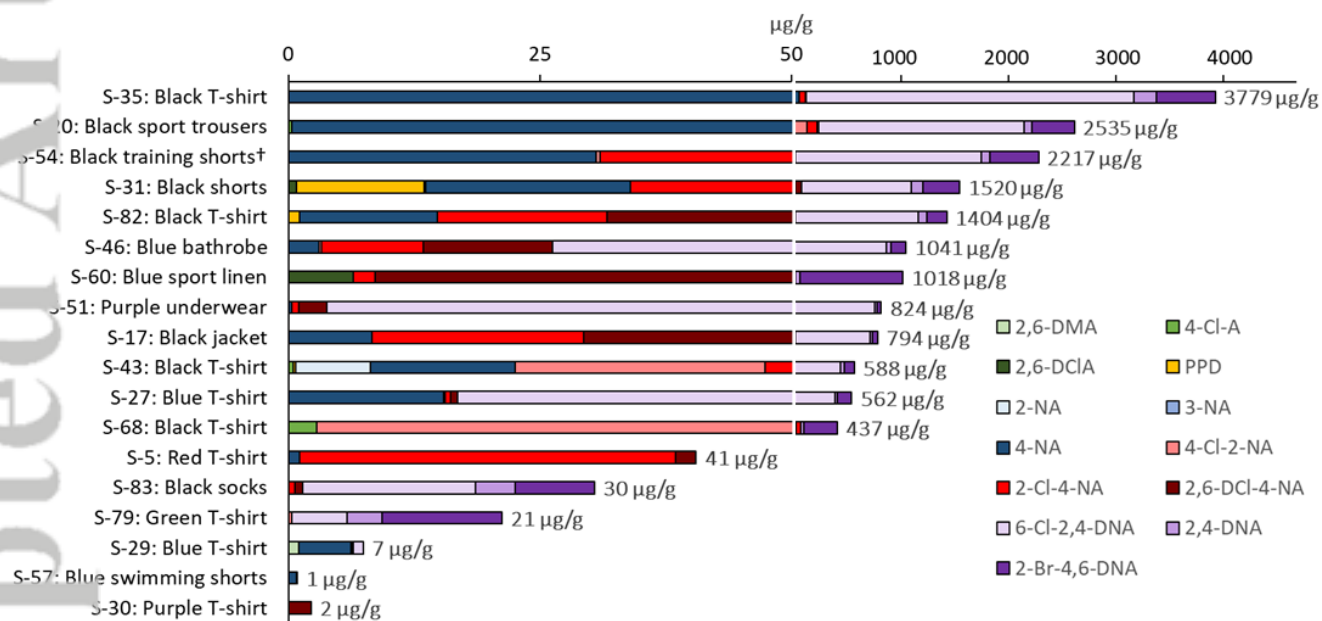


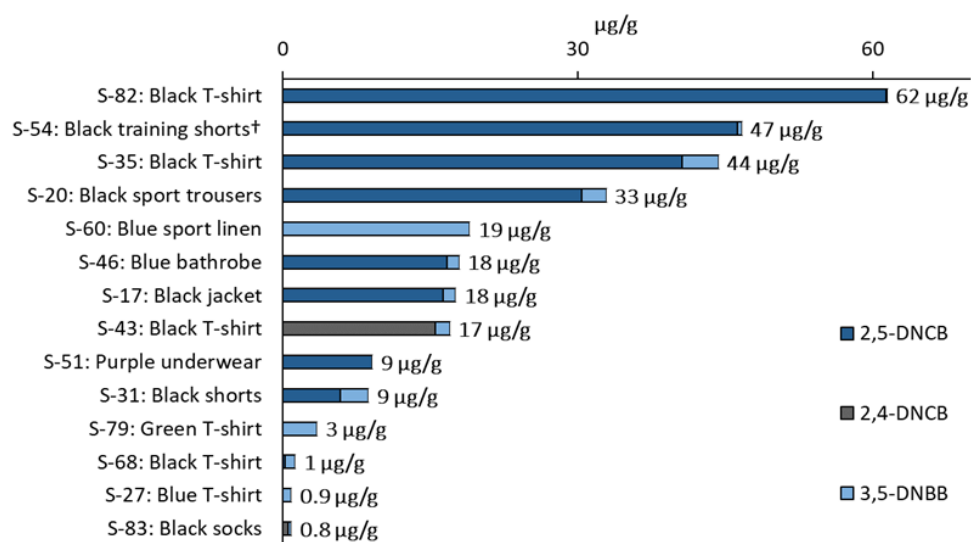




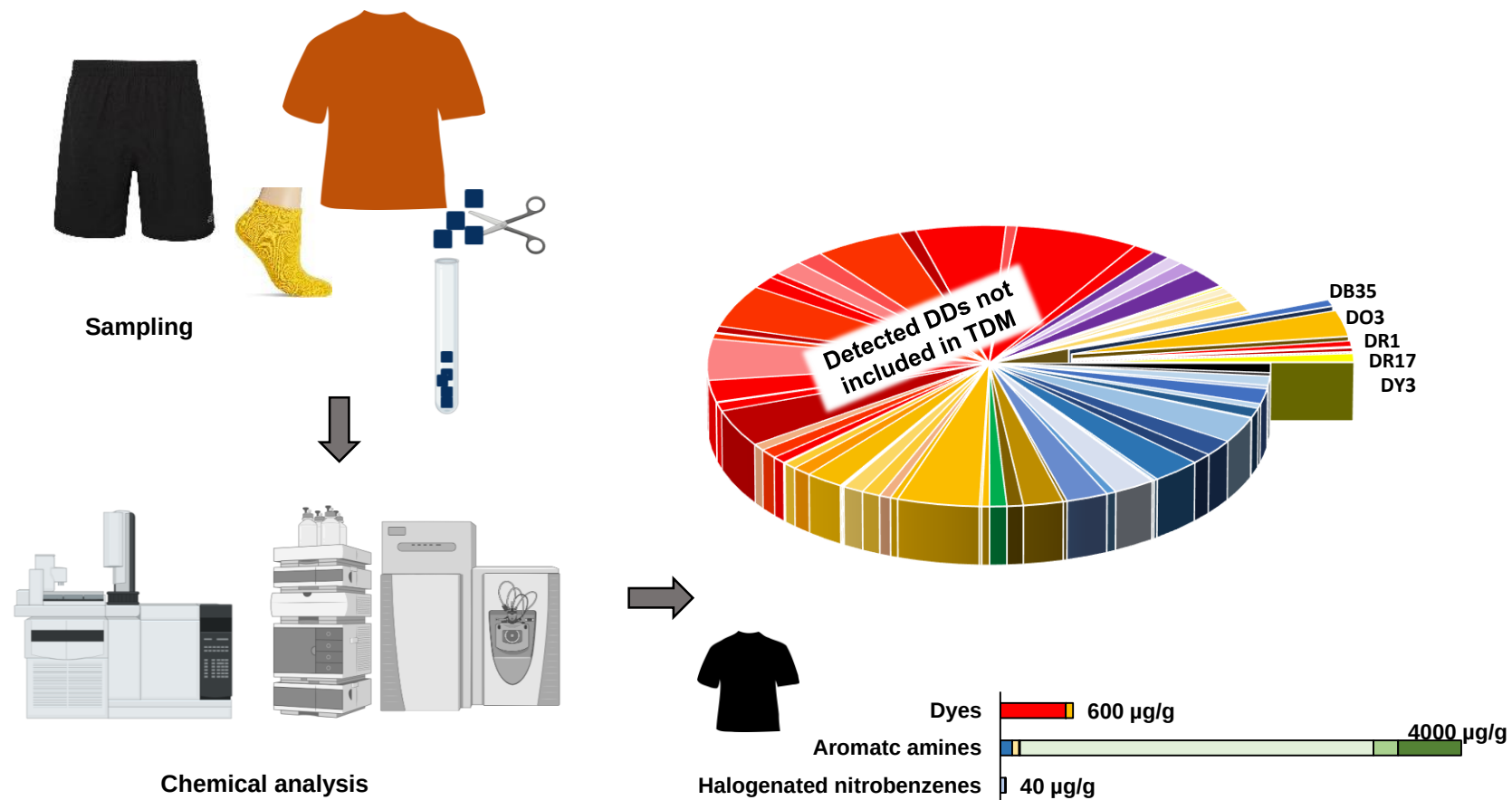








- Disperse Red 167:1 was the most frequent among 62 detected azo dyes in the investigated synthetic garments. The azo dyes in the European baseline patch test series were less common.
- Arylamines were detected at much higher levels than azo dyes
- Skin-sensitizing 1-chloro-2,4-dinitrobenzene (2,4-DNCB) was identified in 6% of the garments



**Disperse azo dyes, arylamines and halogenated dinitrobenzene compounds in
synthetic garments on the Swedish market**

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Detailed description of sample preparation and instrumental analysis

Sample preparation for HPLC/HRMS screening of disperse dyes (DDs)

After ultrasonic extraction, a volume of 200 μ L of ultrapure water was added to the pooled dichloromethane extract and the resulting volume reduced to 200 μ L under a gentle flow of nitrogen at 35°C. A volume of 800 μ L was then added, followed by syringe filtration (PTFE, 0.45 μ m, NTK Kemi, Uppsala, Sweden) into a vial. A volume of 5 μ L was injected into the HPLC/HRMS.

Sampling preparation for HPLC/TSQ MS of DDs

The sample processing was performed as for the HPLC/HRMS screening, except that 10 μ g each of surrogate internal standards (IS), quinoline-d₇, 3-nitroaniline-d₄ and 4-nitroaniline-¹⁵N₂, and 16.9 μ g of Sudan-I-d₅ were added prior to ultrasonic extraction. and the pooled extract volume was reduced to approx. 5 mL. Each sample was then subjected to filtration by using a syringe filter (RC, 0.2 μ m, Phenomenex, Torrance, CA, US) and the volume was further reduced to 1 mL, after which 5 μ g of 1-indanone was added as volumetric internal standard. A volume of 500 μ L of deionized water was added prior to and 500 μ L of acetonitrile after evaporation of the extraction solvent. An additional syringe filtration step was carried out if necessary. An injection volume of 10 μ L from each sample extract was subjected to HPLC/TSQ MS analysis for target screening and confirmation of disperse dyes. If necessary, to avoid matrix effects, the samples were diluted 5-10 times prior to injection on HPLC/TSQ MS.

Sampling preparation for GC/MS of arylamines and halogenated dinitrobenzenes

The sample processing was performed as for the HPLC/TSQ MS analysis, with addition of internal standards prior to ultrasonic extraction. The pooled dichloromethane extract was reduced to 1 mL, after which 5 μ g of 1-indanone was added as volumetric internal standard. One μ L of the reduced extract was injected on GC/MS.

HPLC/HRMS screening of disperse dyes (DDs)

A UHPLC/electrospray (ESI)-OrbitrapTM high-resolution mass spectrometry (HRMS) instrument (Q Exactive HF, Thermo Scientific, Rockford, IL, USA) was used for the analyses. HPLC was performed using an Acquity UPLC[®] BEH C₁₈ column (50x2.1 mm, 1.7- μ m particles), with a C₁₈ guard column (Waters, Aberdeen, Scotland) connected in front. Mobile phase A consisted of

ultrapure water with 10 mM of ammonium acetate, and mobile phase B was acetonitrile with 10% ultrapure water.

At a flow rate of 0.4 mL/min a linear gradient was applied starting with a composition of 5% B for one min and then ramped up during 20 min to the final composition of 95% B. The latter condition was kept for 5 min before returning to initial settings. Conditioning time prior to the next run was 2.5 min resulting in a total analysis time of 27.5 min.

The ESI settings in the positive mode were: sheath gas flow rate 25 (arbitrary units), auxiliary gas flow rate 7 (arbitrary units), spray voltage 4.1 kV, auxiliary gas temp 320°C, and auxiliary gas heater temp 240°C.

The MS acquisition was performed in full scan MS combined with data dependent MS² (dd-MS²) with an inclusion list activated (**Table SI-5**). The inclusion list of suspected non-regulated azo DDs was based on published information regarding usage in industry²² and available reference standards. The full scan range was set to 66.7 – 1000 m/z with a resolution (m/Δm, FWHM) 120,000 at m/z 400, automatic gain control (AGC) target at 3x10⁶, and maximum injection time 256 ms. For dd-MS², the resolution was set to 15,000 with AGC target at 10⁵ and maximum injection time 32 ms. The isolation window was set to 0.4 m/z and normalized collision energy (NCE) 50 eV.

We have recently published a data treatment workflow for suspect screening²⁹. This methodology was also used for the present suspect screening of disperse dyes. Briefly, detection of the adduct ions [M+H]⁺, [M+NH₄]⁺, [M+K]⁺, [M+Na]⁺ and [M+acetonitrile+H]⁺ was done by use of the Compound Discoverer 3.1 software (Thermo Scientific, Massachusetts). Obtained accurate mass and predicted molecular formulas were used for search in ChemSpider (Royal Society of Chemistry, London, England) within a 5-ppm mass accuracy. Compound Discoverer software matched the experimental obtained MS² data with mzCloud data (HighChem LLC, Slovakia). Further, the inclusion list (**Table SI-5**) was used for assigning molecular formulas and names with a 5-ppm tolerance. The obtained data were extracted to a datafile in csv-format for further processing with Excel. Further filtering of data was performed by comparison of experimental HPLC retention times to those predicted from logP (**SI-6**).

HPLC/TSQ MS of DDs

To confirm and quantify the dyes identified by the HPLC/HRMS screening, target analysis with HPLC/triple-stage quadrupole (TSQ) MS and standard compounds was performed with a Waters Acquity I-Class UPLC system (Waters, Manchester, UK) coupled with a Xevo TQ-S instrument

equipped with an ESI source (Waters, Manchester, UK). The LC column was a Kinetex EVO C18 column (150 mm x 2.1 mm, 2.6- μ m particles) from Phenomenex. A gradient system was used, with solvent A being 10% acetonitrile (aq) and B 90% acetonitrile (aq), both containing 10mM ammonium acetate. The column oven temperature was 40°C and the flow rate was set to 0.4 mL/min. The gradient program was as follows: 0-2 min 100% A; 2-8.5 min 100%-50% A; 8.5-15 min isocratic with 50% A; 15-16 min 50-25% A; 16-18.5 min 25% A; 19-21 min 0% A. The system was equilibrated at initial conditions for two min before next injection.

HPLC/TSQ MS in multiple-reaction mode (MRM) was performed in both positive ESI at a capillary voltage of 0.5 kV, and in negative ESI at -2.5 kV. The two most intense daughter ions were selected for each dye. For all compounds, the source temp was 150°C, desolvation temp 650°C, cone gas flow 80 mL/min and desolvation gas flow 850 mL/min. Details about the MRM settings and transitions are given in **Table SI-7**.

The method limit of quantification (S/N=10) was determined to 0.7 – 20.5 ng/g of textile, depending on the dye. No matrix effects could be observed and the instrumental response was linear ($R^2 > 0.99$) within the entire measured range of 0.02 to 1.6 ng amount injected. The relative standard deviation was within the range 1 – 13% (n=3).

The extraction recoveries were evaluated using a triplicate of a spiked dye-free sample, in this case a white sock made of 100% polyester. The recoveries normalised to IS were between 85% and 114%, except for Sudan IV which had a yield of approx. 50% from the textile, see **Table SI-3**.

GC/MS of arylamines

For detection of arylamines in the garments, an Agilent 5975C MSD equipped with a 6890N GC, a 7693 autosampler, and a PTV-injector (Agilent Technologies, Palo Alto, CA, USA) was used. The GC column was a CP-Sil 8 CB (30 m, $\varnothing$ = 0.25 mm, d_f = 0.25 μ m, Agilent Technologies). The GC injection temperature was held at 70°C for 0.05 min, and was then ramped at 700°C/min to 300°C, with the final setting held for 8 min. The GC oven program started at 50°C and was immediately ramped at 6°C/min to 165°C, which was held for 3.5 min, followed by a 15°C/min ramp to 250°C, held for 1.5 min. A third ramp of 15°C/min to a final temperature of 325°C was then applied, with the final setting held for 13.5 min. The total run time was 48.3 min. The MS analyses were performed in electron ionization mode at 70eV, with the ion source operating at

250°C. The temperature of the quadrupole mass analyzer was set to 200°C. The MS acquisition was performed in full scan mode monitoring m/z 45-570. For identification and quantification, three ions were used for each compound, one quantifier ion and two qualifier ions, to compare the ion ratios and retention times in samples with standards, see **Table SI-8**.

The method quantification limit for amines (S/N=10) was determined to 9.9 - 319.2 ng/g of textile, depending on compound. The corrected recoveries for spiked matrix were in the range 83 - 106 %, except for 1,4-phenylenediamine (28%) and 2,6-dichlorobenzene-1,4-diamine (66%), **Table SI-4**. No matrix effects could be observed and the instrumental response was linear, with coefficients of determination (R^2) in the range 0.957 - 0.996 for the entire measured range 0.4 - 9.6 ng amount injected, except for PPD. This compound suffered from chromatographic peak distortion with poor linearity as a result. The relative standard deviation for triplicate samples was in the range 1 - 7%, except for PPD (22%).

SI-1 – Analytical standards

A.S. = Analytical standard, NS = Not specified

Name	CAS #	Abbreviation	Molecular formula	Purity	Supplier
Dyes					
Disperse Orange 3	730-40-5	DO3	C ₁₂ H ₁₀ N ₄ O ₂	90%	Sigma Aldrich, St Louis, USA
Disperse Yellow 3	2832-40-8	DY3	C ₁₅ H ₁₅ N ₃ O ₂	30%	Sigma Aldrich, St Louis, USA
Disperse Orange 1	2581-69-3	DO1	C ₁₈ H ₁₄ N ₄ O ₂	A.S.	Sigma Aldrich, St Louis, USA
Disperse Orange 37	13301-61-6	DO37	C ₁₇ H ₁₅ Cl ₂ N ₅ O ₂	A.S.	Sigma Aldrich, St Louis, USA
Disperse Orange 13	6253-10-07	DO13	C ₂₂ H ₁₆ N ₄ O	90%	Sigma Aldrich, St Louis, USA
Disperse Orange 25	31482-56-1	DO25	C ₁₇ H ₁₇ N ₃ O ₂	90%	Sigma Aldrich, St Louis, USA
Disperse Blue 14	2475-44-7	DB14	C ₁₆ H ₁₄ N ₂ O ₂	97%	Sigma Aldrich, St Louis, USA
Disperse Red 1	2872-52-8	DR1	C ₁₆ H ₁₈ N ₄ O ₃	95%	Sigma Aldrich, St Louis, USA
Disperse Red 13	3180-81-2	DR13	C ₁₆ H ₁₇ ClN ₄ O ₃	95%	Sigma Aldrich, St Louis, USA
Disperse Blue 124	61951-51-7	DB124	C ₁₆ H ₁₉ N ₅ O ₄ S	Microscopy	Sigma Aldrich, St Louis, USA
Disperse Blue 35	12222-75-2	DB35	C ₁₅ H ₁₂ N ₂ O ₄	Microscopy	Sigma Aldrich, St Louis, USA
Disperse Blue 106	12223-01-7	DB106	C ₁₄ H ₁₇ N ₅ O ₃ S	NS	Chemotechnique, Vellinge, Sweden
Disperse Red 17	3179-89-3	DR17	C ₁₇ H ₂₀ N ₄ O ₄	A.S.	Sigma Aldrich, St Louis, USA
Sudan IV	85-83-6	SRIV	C ₂₄ H ₂₀ N ₄ O	≥80%	Sigma Aldrich, St Louis, USA
Sudan I	842-07-9	SRI	C ₁₆ H ₁₂ N ₂ O	>95%	Sigma Aldrich, St Louis, USA
Disperse Black 2	6232-57-1	DB2	C ₁₄ H ₁₆ N ₄ O	NS	Sigma Aldrich, St Louis, USA
Disperse Blue 337	65916-12-3	DB337	C ₂₄ H ₂₇ N ₇ O ₅	NS	Sigma Aldrich, St Louis, USA
Disperse Blue 79	12239-34-8	DB79	C ₂₄ H ₂₇ BrN ₆ O ₁₀	NS	Sigma Aldrich, St Louis, USA

Disperse Brown 22	63467-07-2	DB22	C ₁₆ H ₁₆ Cl ₂ N ₄ O ₄	NS	Sigma Aldrich, St Louis, USA
Disperse Red 5	3769-57-1	DR5	C ₁₇ H ₁₉ ClN ₄ O ₄	NS	Sigma Aldrich, St Louis, USA
Disperse Red 60	17418-58-5	DR60	C ₂₀ H ₁₃ NO ₄	NS	Sigma Aldrich, St Louis, USA
Methyl Orange	547-58-0	MO	C ₁₄ H ₁₄ N ₃ NaO ₃ S	NS	BDH Chemicals Ltd, Poole, England
Disperse Red 19	2734-52-3	DR19	C ₁₆ H ₁₈ N ₄ O ₄	97%	Sigma Aldrich, St Louis, USA
Sudan I-d ₅ (IS)	752211-63-5	SRI-d5	C ₁₆ D ₅ H ₇ N ₂ O	A.S.	Sigma Aldrich, St Louis, USA
Arylamines					
4-chloroaniline	106-47-8	4-Cl-A	C ₆ H ₆ ClN	98%	Sigma Aldrich, St Louis, USA
2-bromoaniline	615-36-1	2-Br-A	C ₆ H ₆ BrN	98%	Sigma Aldrich, St Louis, USA
3-bromoaniline	591-19-5	3-Br-A	C ₆ H ₆ BrN	98%	Sigma Aldrich, St Louis, USA
4-bromoaniline	106-40-1	4-Br-A	C ₆ H ₆ BrN	97%	Sigma Aldrich, St Louis, USA
2,6-dimethylaniline	87-62-7	2,6-DMA	C ₈ H ₁₁ N	98%	Fluka Chemicals, Germany
<i>p</i> -anisidine	104-94-9	<i>p</i> -Ani	C ₇ H ₉ NO	99%	Sigma Aldrich, St Louis, USA
1,4-phenylenediamine	106-50-3	PPD	C ₆ H ₈ N ₂	NS	Sigma Aldrich, St Louis, USA
2-amino- <i>p</i> -cresol	95-84-1	Cresol	C ₇ H ₉ NO	97%	Sigma Aldrich, St Louis, USA
2,6-dichloro-1,4-phenylenediamine	609-20-1	2,6-DCI-PPD	C ₆ H ₆ Cl ₂ N ₂	96%	Sigma Aldrich, St Louis, USA
2,6-dichloroaniline	608-31-1	2,6-DCIA	C ₆ H ₅ Cl ₂ N	96%	Sigma Aldrich, St Louis, USA
Diphenylamine	122-39-4	Di-ph-A	C ₁₂ H ₁₁ N	A.S.	Sigma Aldrich, St Louis, USA
2-nitroaniline	88-74-4	2-NA	C ₆ H ₆ N ₂ O ₂	98%	Sigma Aldrich, St Louis, USA
3-nitroaniline	99-09-2	3-NA	C ₆ H ₆ N ₂ O ₂	98%	Sigma Aldrich, St Louis, USA
4-nitroaniline	100-01-6	4-NA	C ₆ H ₆ N ₂ O ₂	≥99%	Sigma Aldrich, St Louis, USA
5-chloro-2-nitroaniline	1635-61-6	5-Cl-2-NA	C ₆ H ₅ ClN ₂ O ₂	97%	Sigma Aldrich, St Louis, USA
4-chloro-2-nitroaniline	89-63-4	4-Cl-2-NA	C ₆ H ₅ ClN ₂ O ₂	99%	Sigma Aldrich, St Louis, USA
2-chloro-4-nitroaniline	121-87-9	2-Cl-4-NA	C ₆ H ₅ ClN ₂ O ₂	99%	Sigma Aldrich, St Louis, USA
2,4-dinitroaniline	97-02-9	2,4-DNA	C ₆ H ₅ N ₃ O ₄	98%	Sigma Aldrich, St Louis, USA
2,6-dichloro-4-nitroaniline	99-30-9	2,6-DCI-4-NA	C ₆ H ₄ Cl ₂ N ₂ O ₂	96%	Sigma Aldrich, St Louis, USA
6-chloro-2,4-dinitroaniline	3531-19-9	6-Cl-2,4-DNA	C ₆ H ₄ ClN ₃ O ₄	97%	Sigma Aldrich, St Louis, USA
2-bromo-4,6-dinitroaniline	1817-73-8	2-Br-4,6-DNA	C ₆ H ₄ BrN ₃ O ₄	94%	Sigma Aldrich, St Louis, USA
Halogenated dinitrobenzene compounds					
1-chloro-2,4-dinitrobenzene	97-00-7	2,4-DNCB	C ₆ H ₃ ClN ₂ O ₄	97%	Sigma Aldrich, St Louis, USA
1-chloro-2,5-dinitrobenzene	619-16-9	2,5-DNCB	C ₆ H ₃ ClN ₂ O ₄	NS	Toronto Research Chemicals, Toronto, CA
1-chloro-2,6-dinitrobenzene	606-21-3	2,6-DNCB	C ₆ H ₃ ClN ₂ O ₄	NS	Toronto Research Chemicals, Toronto, CA
1-chloro-3,4-dinitrobenzene	610-40-2	3,4-DNCB	C ₆ H ₃ ClN ₂ O ₄	90%	Alfa Aesar, Kandel Germany
1-bromo-3,5-dinitrobenzene	18242-39-2	3,5-DNBB	C ₆ H ₃ BrN ₂ O ₄	NS	Apollo Scientific, Stockport, UK

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118

119 **SI-2 – Investigated garments**

120 Sample # refers to sample number (S-X in Figure 4, 6, 7).

Sample #	Color	Sort	Fiber composition		Country
			Polyester [%]	Other [%]	
1	Pink	Top	88	12% elastane	Unknown
2	Blue	Trousers	100		China
3	Pink	Top	88	12% elastane	Sri Lanka
4	Pink	T-shirt	100		Vietnam
5	Red	T-shirt	100		Unknown
6	Yellow	T-shirt	100		Cambodia
7	Blue	T-shirt	100		Philippines
8	Red	T-shirt	100		Georgia
9	Blue	T-shirt	100		Indonesia
10	Yellow	T-shirt	100		Bangladesh
11	Yellow	T-shirt	100		China
12	Green	T-shirt	87% recycled	13% elastane	China
13	Blue	T-shirt	90	10% elastane	China
14	Blue	Trousers	100		China
15	Orange	Skirt	87	13% elastane	Indonesia
16	Black	Shorts	88	12% elastane	Vietnam
17	Black	Jacket	100		China
18	Purple	T-shirt	100% recycled		Thailand
19	Blue	T-shirt	100		Cambodia
20	Black	Sport trousers	100		China
21	Orange	T-shirt	100		Thailand
22	White	Socks	70	25% cotton 5% elastane	Unknown
23	Pink	T-shirt	100		China
24	Pink	T-shirt	100		Bangladesh
25	Blue	Dress	85	15% elastane	Cambodia
26	Pink	T-shirt	100		China
27	Blue	T-shirt	90	10% elastane	Unknown
28	Blue	T-shirt	100		Unknown
29	Blue	T-shirt	91	9% elastane	Indonesia
30	Purple	T-shirt	88	12% elastane	Unknown
31	Black	Shorts	100		China
32	Pink	T-shirt	95	5% elastane	Unknown
33	Blue	T-shirt	100		Indonesia
34	Black	T-shirt	100		Vietnam
35	Black	T-shirt	100		India
36	Black	Socks	70	25% cotton 5% elastane	Unknown
37	Blue	T-shirt	100		Unknown
38	Pink	Swimsuit	100		Indonesia
39	Yellow	T-shirt	100		Indonesia
40	Blue	T-shirt	85	15% elastane	China

41	Black	T-shirt	100		Vietnam
42	Red	T-shirt	85	15% cotton	China
43	Black	T-shirt	100		China
44	Red	T-shirt	87	13% elastane	China
45	Pink	Bra	100		China
46	Blue	Bathrobe	100		Unknown
47	Blue	Bathrobe	100		China
48	White	Shorts	100		China
49	Yellow	Underwear	90	10%elastane	Bangladesh
50	Red	Underwear	90	10% elastane	Bangladesh
51	Purple	Underwear	90	10% elastane	Bangladesh
52	Black	T-shirt	100% recycled		Bangladesh
53	Yellow	T-shirt	100% recycled		Bangladesh
54	Black	Training shorts	100% recycled		Bangladesh
55	Red	Jumpsuit	100		Unknown
56	Red	Dress	99	1% elastane	China
57	Blue	Swimming shorts	93	7% elastane	China
58	Blue	Top	86	14% elastane	China
59	Blue	UV-overall	82	18% elastane	China
60	Blue	Sport linen	100		China
61	Orange	T-shirt	92	8% elastane	Bangladesh
62	Pink	Swimsuit	90	10% elastane	China
63	Black	Underskirt	100		Bangladesh
64	Yellow	T-shirt	100		Bangladesh
65	Blue	T-shirt	100		Bangladesh
66	Blue	T-shirt	100		Bangladesh
67	Green	T-shirt	100		Bangladesh
68	Black	T-shirt	72	24% viscose, 4% elastane	Bangladesh
69	Green	T-shirt	100		Bangladesh
70	Red	Sweater	97	3% metal fiber	China
71	Dark Red	T-shirt	88	12% elastane	Bangladesh
72	Orange	T-shirt	100% recycled		Cambodia
73	Green	T-shirt	92	8% elastane	Cambodia
74	Orange	T-shirt	100		Cambodia
75	Blue	T-shirt	90	10% elastane	Bangladesh
76	Yellow	T-shirt	96	4% elastane	China
77	Yellow/Green	T-shirt	92	8% elastane	Cambodia
78	Green	T-shirt	88	12% elastane	Bangladesh
79	Green	T-shirt	100		Cambodia
80	Green	T-shirt	95	5% cotton	Bangladesh
81	Blue	Shorts	100		China
82	Black	T-shirt	100		Cambodia
83	Black	Socks	100		China

122 **SI-3 - Matrix-spiked normalized recoveries of disperse dyes**

123 Mean $\pm$ standard deviation, and relative standard deviation (CV) for
 124 recovery experiments of 22 selected dyes. The recoveries are
 125 normalized against IS Sudan I-d₅

126

Compound	Mean $\pm$ std [%]	CV [%]
Disperse Red 19	107.2 $\pm$ 3.9	4
Disperse Black 2	94.8 $\pm$ 3.1	3
Disperse Red 17	107.4 $\pm$ 5.6	5
Disperse Yellow 3	105.6 $\pm$ 3.6	3
Disperse Brown 22	105.6 $\pm$ 5.9	6
Disperse Blue 106	101.2 $\pm$ 3.1	3
Disperse Orange 3	114.4 $\pm$ 4.2	4
Disperse Red 5	108.5 $\pm$ 3.6	3
Disperse Blue 14	97.7 $\pm$ 0.6	1
Disperse Blue 35	96 $\pm$ 1.6	2
Disperse Red 1	112.2 $\pm$ 4.6	4
Disperse Blue 124	109.9 $\pm$ 4.6	4
Disperse Orange 25	103.3 $\pm$ 4.4	4
Sudan I	94.4 $\pm$ 3.2	3
Disperse Red 60	93 $\pm$ 5.6	6
Disperse Blue 337	96.4 $\pm$ 3.3	3
Disperse Orange 37	101.2 $\pm$ 4.2	4
Disperse Orange 1	111.7 $\pm$ 3.9	3
Disperse Blue 79	108.1 $\pm$ 5.7	5
Disperse Orange 13	85 $\pm$ 2.3	3
Sudan IV	47.7 $\pm$ 6.2	13
Disperse Red 13	110.9 $\pm$ 4.2	4

SI-4 –Matrix-spiked recoveries of arylamines and halogenated dinitrobenzenes from the analytical procedure

Mean $\pm$ standard deviation, and relative standard deviation (CV) for recovery experiments. Both absolute recoveries and recoveries normalized against IS (quinoline-d₇, 3-nitroaniline-d₄, 4-nitroaniline-¹⁵N₂)

Compound	Absolute recovery [%]		Normalized recovery [%]	
	Mean $\pm$ std	CV	Mean $\pm$ std	CV
4-chloroaniline	73.5 $\pm$ 1.7	2	96 $\pm$ 2.4	2
1,4-phenylenediamine	21.4 $\pm$ 4.3	20	28 $\pm$ 6.2	22
2-nitroaniline	81.3 $\pm$ 2.2	3	106.1 $\pm$ 1.6	2
3-nitroaniline	71.8 $\pm$ 2.3	3	84.3 $\pm$ 0.9	1
1-chloro-3,4-dinitrobenzene	75.1 $\pm$ 2.1	3	88.1 $\pm$ 0.9	1
1-chloro-2,4-dinitrobenzene	75.8 $\pm$ 3.5	5	88.8 $\pm$ 1.8	2
2,6-dichloro-1,4-phenylenediamine	56 $\pm$ 3	5	65.7 $\pm$ 3.5	5
5-chloro-2-nitroaniline	77 $\pm$ 1.7	2	90.3 $\pm$ 1.4	2
1-bromo-3,5-dinitrobenzene	74.5 $\pm$ 2.5	3	87.3 $\pm$ 0.6	1
4-nitroaniline	72.6 $\pm$ 1.7	2	85.2 $\pm$ 1	1
4-chloro-2-nitroaniline	71 $\pm$ 1.3	2	83.3 $\pm$ 1.4	2
2-chloro-4-nitroaniline	83.2 $\pm$ 3.3	4	97.5 $\pm$ 1.8	2
2,6-dichloro-4-nitroaniline	78.7 $\pm$ 3.7	5	92.3 $\pm$ 2.4	3
6-chloro-2,4-dinitroaniline	90.9 $\pm$ 3	3	106.6 $\pm$ 1.8	2
2,4-dinitroaniline	86.4 $\pm$ 2.1	2	101.4 $\pm$ 2.1	2
2-bromo-4,6-dinitroaniline	83.4 $\pm$ 3.2	4	97.8 $\pm$ 3.4	4

133 **SI-5 – Inclusion list for suspect screening with HPLC/HRMS**

134 Exact m/z for [M+H]⁺ of selected analytes. The charge state is +1 for all analytes. Colorants
135 marked with † contains more than one component.

Ion [m/z]	Molecular formula	Compound name
120.05562	C ₆ H ₅ N ₃	1-H-benzotriazole
128.02615	C ₆ H ₆ ClN	4-chloroaniline
130.06513	C ₉ H ₇ N	quinoline
134.07127	C ₇ H ₇ N ₃	methyl-1H-benzotriazole
136.02155	C ₇ H ₅ NS	benzothiazole
138.11689	C ₉ HD ₇ N	quinoline-d ₇
139.0502	C ₆ H ₆ N ₂ O ₂	4-nitroaniline
144.08078	C ₁₀ H ₉ N	2-methylquinoline
148.08692	C ₈ H ₉ N ₃	5,6-dimethyl-2H-benzotriazole
158.09643	C ₁₁ H ₁₁ N	2,6-dimethylquinoline
173.01123	C ₆ H ₅ ClN ₂ O ₂	4-chloro-2-nitroaniline
182.00927	C ₈ H ₇ NS ₂	2-methylthiobenzothiazole
184.03528	C ₆ H ₅ N ₃ O ₄	2,4-dinitroaniline
195.12557	C ₁₂ H ₂ D ₈ O ₂	4,4-dihydroxybiphenyl-d ₈
206.97226	C ₆ H ₄ Cl ₂ N ₂ O ₂	dichloran
217.99631	C ₆ H ₄ ClN ₃ O ₄	2-chloro-4,6-dinitroaniline
226.09749	C ₁₃ H ₁₁ N ₃ O	2-(benzotriazol-2-yl)-4-methylphenol
243.08765	C ₁₂ H ₁₀ N ₄ O ₂	Disperse Orange 3
249.10224	C ₁₆ H ₁₂ N ₂ O	Sudan 1
254.13362	C ₁₆ D ₅ H ₇ N ₂ O	Sudan 1-d ₅
257.13969	C ₁₄ H ₁₆ N ₄ O	Disperse Black 2
261.94579	C ₆ H ₄ BrN ₃ O ₄	2-bromo-4,6-dinitroaniline
263.12912	C ₁₆ H ₁₄ N ₄	Disperse Black 1
265.08277	C ₁₃ H ₁₆ N ₂ S ₂	N-cyclohexyl-2-benzothiazolesulphenamide
266.0924	C ₁₅ H ₁₁ N ₃ O ₂	Disperse Yellow 4
267.1128	C ₁₆ H ₁₄ N ₂ O ₂	Disperse Blue 14
270.1237	C ₁₅ H ₁₅ N ₃ O ₂	Disperse Yellow 3
285.08698	C ₁₅ H ₁₂ N ₂ O ₄	Disperse Blue 35
300.10912	C ₁₄ H ₁₃ N ₅ O ₃	Disperse Orange 1.1
301.12952	C ₁₅ H ₁₆ N ₄ O ₃	Disperse Red 41
315.14517	C ₁₆ H ₁₈ N ₄ O ₃	Disperse Red 1
319.11895	C ₁₈ H ₁₄ N ₄ O ₂	Disperse Orange 1
324.1455	C ₁₇ H ₁₇ N ₅ O ₂	Disperse Orange 25
325.09313	C ₁₆ H ₁₂ N ₄ O ₄	Disperse Yellow 5
328.10403	C ₁₅ H ₁₃ N ₅ O ₄	Disperse Yellow 119
331.14008	C ₁₆ H ₁₈ N ₄ O ₄	Disperse Red 19
332.13935	C ₂₀ H ₁₇ N ₃ O ₂	Disperse Yellow 27

332.18697	$C_{20}H_{21}N_5$	Disperse Red Dye
332.96431	$C_{14}H_8N_2S_4$	2,2'-dithiobisbenzothiazole
336.11249	$C_{14}H_{17}N_5O_3S$	Disperse Blue 106
337.02536	$C_{14}H_{10}Cl_2N_4O_2$	Disperse Yellow 241
340.14042	$C_{17}H_{17}N_5O_3$	Disperse Orange 31
345.15573	$C_{17}H_{20}N_4O_4$	Disperse Red 17
349.10619	$C_{16}H_{17}ClN_4O_3$	Disperse Red 13
349.14075	$C_{18}H_{16}N_6O_2$	Disperse Red 73
352.1768	$C_{19}H_{21}N_5O_2$	Disperse Orange 33
352.23834	$C_{22}H_{29}N_3O$	2-(2H-benzotriazol-2-yl)-4,6-di-tert-pentylphenol
353.13969	$C_{22}H_{16}N_4O$	Disperse Orange 13
357.13797	$C_{18}H_{20}N_4O_2S$	Disperse Red 379
358.10653	$C_{17}H_{16}ClN_5O_2$	Disperse Red 50
358.16807	$C_{20}H_{24}ClN_3O$	2,4-di-tert-butyl-6-(5-chlorobenzotriazol-2-yl)phenol
361.15065	$C_{17}H_{20}N_4O_5$	Disperse Red 2
362.06506	$C_{15}H_{12}ClN_5O_4$	Disperse Yellow 211
363.09755	$C_{20}H_{14}N_2O_5$	Disperse Blue 35 (2)
363.1564	$C_{19}H_{18}N_6O_2$	Disperse Blue 366
366.12305	$C_{15}H_{19}N_5O_4S$	Disperse Blue 102
368.11018	$C_{16}H_{13}N_7O_4$	Disperse Orange 56
368.1387	$C_{15}H_{21}N_5O_4S$	Disperse Blue 102
369.05157	$C_{15}H_{14}Cl_2N_4O_3$	Disperse Orange 5
370.08877	$C_{18}H_{16}ClN_5S$	Disperse Red 153
370.15098	$C_{18}H_{19}N_5O_4$	Disperse Violet 33
372.12218	$C_{18}H_{18}ClN_5O_2$	Disperse Red 65
374.10144	$C_{17}H_{16}ClN_5O_3$	Disperse Red 54:1
376.14379	$C_{17}H_{21}N_5O_3S$	Disperse Blue 124
378.11968	$C_{19}H_{15}N_5O_4$	Disperse Orange 29
378.12305	$C_{16}H_{19}N_5O_4S$	Disperse Blue 124
379.11676	$C_{17}H_{19}ClN_4O_4$	Disperse Red 5
381.16697	$C_{19}H_{20}N_6O_3$	Disperse Violet 63
381.17099	$C_{24}H_{20}N_4O$	Sudan IV
382.15098	$C_{19}H_{19}N_5O_4$	Disperse Orange 31
383.10178	$C_{18}H_{15}ClN_6O_2$	Disperse Orange 44
384.14887	$C_{19}H_{21}N_5O_2S$	Disperse Red 107
392.06756	$C_{17}H_{15}Cl_2N_5O_2$	Disperse Orange 37
393.16697	$C_{20}H_{20}N_6O_3$	Disperse Orange 80
395.12847	$C_{19}H_{18}N_6O_2S$	Disperse Red 179
397.11743	$C_{19}H_{17}ClN_6O_2$	Disperse Orange 45 (component) [†]
397.99728	$C_{15}H_{10}Cl_3N_5O_2$	Disperse Orange 41
399.06214	$C_{16}H_{16}Cl_2N_4O_4$	Disperse Brown 22
402.1772	$C_{19}H_{23}N_5O_5$	Disperse Violet 13
404.0498	$C_{18}H_{15}Cl_2N_5S$	Disperse Red 153

406.16221	$C_{20}H_{19}N_7O_3$	Disperse Blue 165
407.11321	$C_{16}H_{18}N_6O_5S$	Disperse Green 9
407.14623	$C_{20}H_{18}N_6O_4$	Disperse Red 72
409.0965	$C_{20}H_{16}N_4O_4S$	Disperse Yellow 114
409.18388	$C_{18}H_{28}N_6OS_2$	Disperse Red 338
411.15977	$C_{20}H_{22}N_6O_2S$	Disperse Red 343
414.12305	$C_{19}H_{19}N_5O_4S$	Disperse Blue 148
416.07562	$C_{18}H_{14}ClN_5O_5$	Disperse Blue 85
416.11201	$C_{19}H_{18}ClN_5O_4$	Disperse Red 54, Disperse Red 54:1
417.06281	$C_{18}H_{14}Cl_2N_6O_2$	Disperse Yellow 163
418.06545	$C_{19}H_{17}Cl_2N_5S$	Disperse Red 152
424.23432	$C_{23}H_{29}N_5O_3$	Disperse Yellow 198
425.17205	$C_{24}H_{20}N_6O_2$	Disperse Red 184
426.07304	$C_{17}H_{17}Cl_2N_5O_4$	Disperse Red 324
426.15204	$C_{19}H_{19}N_7O_5$	Disperse Blue 165:1
429.01856	$C_{16}H_{14}Cl_2N_4O_4S$	Disperse Yellow 108
429.14364	$C_{20}H_{21}ClN_6O_3$	Disperse Violet 63
429.17686	$C_{21}H_{24}N_4O_6$	Disperse Yellow 126
430.10021	$C_{19}H_{19}N_5O_3S_2$	Disperse Red 137
433.02316	$C_{16}H_{15}Cl_3N_4O_4$	Disperse Brown 1
433.13856	$C_{19}H_{21}ClN_6O_4$	Disperse Violet 93, Disperse Violet 93:1
434.19351	$C_{22}H_{23}N_7O_3$	Disperse Blue 165
439.1183	$C_{20}H_{18}N_6O_4S$	Disperse Red 177
439.19107	$C_{22}H_{26}N_6O_2S$	Disperse Red 343 (Dipropylamino)
440.15646	$C_{21}H_{21}N_5O_6$	Disperse Red 82
441.18809	$C_{21}H_{24}N_6O_5$	Disperse Violet 77
444.16663	$C_{24}H_{21}N_5O_4$	Disperse Orange 73
445.18703	$C_{25}H_{24}N_4O_4$	Disperse Yellow 231
447.14451	$C_{19}H_{22}N_6O_5S$	Disperse Blue 149
448.23834	$C_{30}H_{29}N_3O$	2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol
450.07304	$C_{19}H_{17}Cl_2N_5O_4$	Disperse Orange 30, Disperse Orange 61
454.17211	$C_{22}H_{23}N_5O_6$	Disperse Violet 33
459.07748	$C_{19}H_{19}BrN_6O_3$	Disperse Blue 183:1
459.17753	$C_{24}H_{22}N_6O_4$	Disperse Orange 49
465.12839	$C_{19}H_{21}ClN_6O_6$	Disperse Blue 291 (Cl)
472.11077	$C_{21}H_{21}N_5O_4S_2$	Disperse Red 136
472.18267	$C_{22}H_{25}N_5O_7$	Disperse Red 74
473.09313	$C_{20}H_{21}BrN_6O_3$	Disperse Blue 183
473.13347	$C_{21}H_{21}ClN_6O_5$	Disperse Red 202
474.11749	$C_{21}H_{20}ClN_5O_6$	Disperse Red 167
476.97265	$C_{16}H_{15}BrCl_2N_4O_4$	Disperse Brown 4
479.06731	$C_{18}H_{19}BrN_6O_5$	Disperse Violet 93:1
479.96653	$C_{17}H_{15}Br_2N_5O_2$	Disperse Orange 61

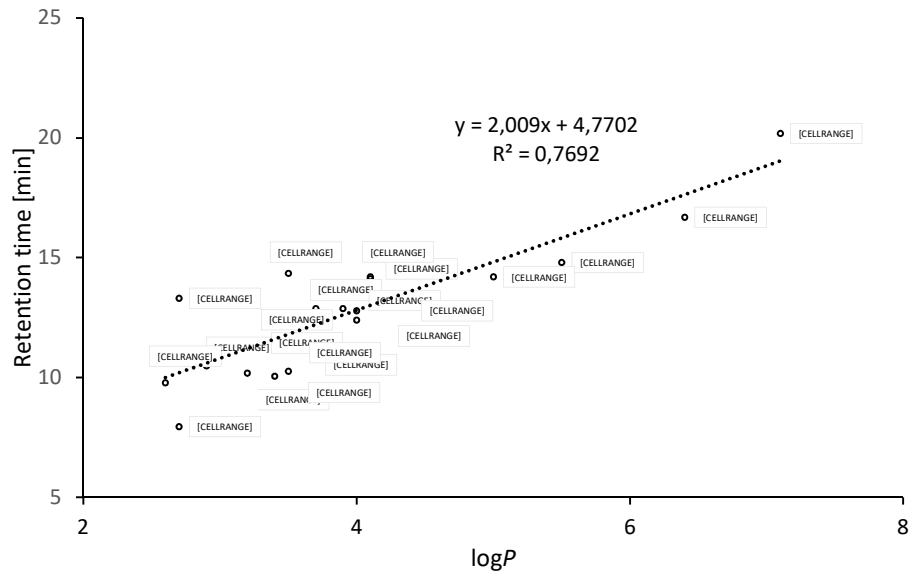
486.19832	$C_{23}H_{27}N_5O_7$	Disperse Red 74
488.05641	$C_{20}H_{18}BrN_5O_5$	Disperse Blue 321
489.12839	$C_{21}H_{21}ClN_6O_6$	Disperse Blue 291:1 (Cl)
491.06731	$C_{19}H_{19}BrN_6O_5$	Disperse Blue 128
494.21464	$C_{24}H_{27}N_7O_5$	Disperse Blue 337
506.1437	$C_{22}H_{24}ClN_5O_7$	Disperse Red 167:1
509.07787	$C_{19}H_{21}BrN_6O_6$	Disperse Blue 291
517.16775	$C_{22}H_{24}N_6O_9$	Disperse Red 311
520.15935	$C_{23}H_{26}ClN_5O_7$	Disperse Red 167
527.03275	$C_{20}H_{20}BrClN_4O_6$	Disperse Brown 19
533.07787	$C_{21}H_{21}BrN_6O_6$	Disperse Blue 291:1, Disperse Blue 373
534.07312	$C_{20}H_{20}BrN_7O_6$	Disperse Blue 281
534.19832	$C_{27}H_{27}N_5O_7$	Disperse Red 135
545.22554	$C_{27}H_{28}N_8O_5$	Disperse Red 279
551.18849	$C_{26}H_{26}N_6O_8$	Disperse Blue 130 (component) [†]
570.98224	$C_{20}H_{20}Br_2N_4O_6$	Disperse Brown 19
581.13935	$C_{23}H_{25}ClN_6O_{10}$	Disperse Blue 79:1 (Cl)
585.14952	$C_{26}H_{25}ClN_6O_8$	Disperse Blue 130 (component) [†]
595.155	$C_{24}H_{27}ClN_6O_{10}$	Disperse Blue 79:1
625.08883	$C_{23}H_{25}BrN_6O_{10}$	Disperse Blue 79:1
639.10448	$C_{24}H_{27}BrN_6O_{10}$	Disperse Blue 79
693.10681	$C_{30}H_{24}N_6O_{10}S_2$	Disperse Blue 29

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SI-6 – Retention time prediction model for disperse dyes

The retention time prediction model used as one of the data filtering steps in the suspect screening of dye compounds. Experimental retention times of standards run on the HPLC system is plotted against log P for 21 standard dyes. Retention times, log P and number of azo bonds are listed in the table below.



Dye	Molecular formula	# of azo bonds	RT [min]	Log P
Disperse Black 2	C ₁₄ H ₁₆ N ₄ O	1	7.95	2.7
Disperse Red 17	C ₁₇ H ₂₀ N ₄ O ₄	1	9.78	2.6
Disperse Blue 106	C ₁₄ H ₁₇ N ₅ O ₃ S	1	10.1	3.4
Disperse Orange 3	C ₁₂ H ₁₀ N ₄ O ₂	1	10.2	3.2
Disperse Brown 22	C ₁₆ H ₁₆ Cl ₂ N ₄ O ₄	1	10.3	3.5
Disperse Yellow 3	C ₁₅ H ₁₅ N ₃ O ₂	1	10.5	2.9
Disperse Blue 35	C ₁₅ H ₁₂ N ₂ O ₄	0	11.1	3.2
Disperse Red 5	C ₁₇ H ₁₉ ClN ₄ O ₄	1	11.1	3.3
Disperse Red 1	C ₁₆ H ₁₈ N ₄ O ₃	1	11.4	3.3
Disperse Blue 124	C ₁₆ H ₁₉ N ₅ O ₄ S	1	12.4	4.0
Disperse Red 13	C ₁₆ H ₁₇ ClN ₄ O ₃	1	12.8	4.0
Disperse Orange 25	C ₁₇ H ₁₇ N ₅ O ₂	1	12.9	3.7
Disperse Blue 14	C ₁₆ H ₁₄ N ₂ O ₂	1	12.9	3.9
Disperse Blue 337	C ₂₄ H ₂₇ N ₇ O ₅	1	13.3	2.7
Sudan I-d ₅ (IS)	C ₁₆ D ₅ H ₇ N ₂ O	1	14.1	4.1
Disperse Orange 37	C ₁₇ H ₁₅ Cl ₂ N ₅ O ₂	1	14.2	5.0
Sudan I	C ₁₆ H ₁₂ N ₂ O	1	14.2	4.1
Disperse Blue 79	C ₂₄ H ₂₇ BrN ₆ O ₁₀	1	14.3	3.5
Disperse Orange 1	C ₁₈ H ₁₄ N ₄ O ₂	1	14.8	5.5
Disperse Orange 13	C ₂₂ H ₁₆ N ₄ O	2	16.7	6.4
Sudan IV	C ₂₄ H ₂₀ N ₄ O	2	20.2	7.1

143 **SI-7 – Instrumental HPLC/TSQ MS-MRM settings for disperse dyes**

144 Selected settings for the MRM-MS analysis are listed below: polarity mode, cone voltage, quantifier and
 145 qualifier ions, collision energy (CE), and dwell time.

Compound	Mw [Da]	Polarity mode	Cone voltage [V]	Quantifier ion		Qualifier ion		Dwell time [ms]
				m/z	CE [eV]	m/z	CE [eV]	
Disperse Orange 3	242.1	Positive	2	75.3	28	122	18	20
Disperse Yellow 3	269.1	Positive	2	150	16	122	14	20
Disperse Orange 1	318.1	Positive	8	122	20	169.1	22	125
Disperse Orange 37	391.1	Positive	2	133.1	34	351.1	20	20
Disperse Orange 13	352.1	Positive	6	93	26	260.3	16	125
Disperse Orange 25	323.1	Positive	2	122	36	283.1	18	126
Disperse Blue 14	266.1	Positive	52	252	18	235	28	94
Disperse Red 1	314.1	Positive	2	134.1	24	255.1	26	94
Disperse Red 13	348.1	Positive	78	134.1	24	289	28	126
Disperse Blue 124	377.1	Positive	2	87	26	220.1	16	126
Disperse Blue 35	362.1	Positive	42	270.1	55	141.9	24	94
Disperse Blue 106	335.1	Positive	5	147.2	30	178.1	16	20
Disperse Red 17	344.1	Positive	2	164.1	26	269.1	28	20
Sudan IV	380.2	Positive	2	91	28	224.5	20	125
Sudan I	248.1	Positive	2	93	24	156	14	20
Disperse Red 19	493.2	Positive	18	150.1	24	255.1	28	20
Disperse Black 2	638.1	Positive	52	92	20	120	14	20
Disperse Blue 337	398.1	Positive	10	191.1	24	120.9	64	126
Disperse Blue 79	378.1	Positive	2	87	25	233.1	30	20
Disperse Brown 22	253.1	Positive	3	118.9	40	163.1	28	20
Disperse Red 5	378.8	Positive	2	177.1	28	164.2	26	20
Methyl Orange	327.3	Negative	22	156	26	225	26	250
Sudan I-d ₅ (IS)	253.3	Positive	4	98.8	20	156.1	18	20
Disperse Red 60	331.3	Positive	24	127.1	58	238.9	30	20

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148 **SI-8 - Instrumental settings and calibration data for GC/MS analysis**

149 Quantifier and qualifier ions in full scan, slope, intercept and coefficient of determination (R^2) for the
 150 linear calibration curves, as well as the RMSE and limit of detection (LOD), the latter given as the
 151 injected amount.

Compound	Quantifier ion	Qualifier ions	Slope	Intercept	R^2	RMSE	LOD [pg]
4-chloroaniline	127	92/65	0.21	-0.08	0.9948	5.50%	10.5
1,4-phenylenediamine	108	80/53	0.1	-0.02	0.8413	16.10%	4.8
2-nitroaniline	138	92/65	0.1	-0.06	0.9923	3.20%	25.3
3-nitroaniline	92	92/138	0.34	0.03	0.9957	8.30%	26.2
1-chloro-3,4-dinitrobenzene	75	202/110	0.27	-0.1	0.9953	6.80%	23.5
1-chloro-2,4-dinitrobenzene	75	202/110	0.19	-0.1	0.9958	7.20%	65.2
2,6-dichlorobenzene-1,4-diamine	176	78/52	0.44	-0.08	0.9951	11.30%	8.9
5-chloro-2-nitroaniline	172	142/99	0.23	-0.04	0.9956	5.70%	13.7
4-chloro-2-nitroaniline	172	126/99	0.28	-0.01	0.9953	7.00%	10.4
4-nitroaniline	138	65/108	0.28	-0.09	0.9959	6.60%	279.4
1-bromo-3,5-dinitrobenzene	75	246/155	0.41	-0.14	0.9957	10.20%	24.3
2-chloro-4-nitroaniline	172	90/142	0.22	-0.1	0.9948	5.80%	21.1
2,6-dichloro-4-nitroaniline	124	206/176	0.2	-0.03	0.9955	5.00%	1.3
6-chloro-2,4-dinitroaniline	217	125/90	0.14	-0.15	0.9737	8.50%	10
2,4-dinitroaniline	183	153/107	0.14	-0.2	0.9575	11.30%	237
2-bromo-4,6-dinitroaniline	261	231/169	0.04	-0.04	0.9774	2.20%	240.4

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SI-9 – Disperse dyes detected in textile garments

Detection frequencies of disperse dyes in clothing and theoretical precursors/cleavage products from reduction. Confirmation by reference compounds are marked with †. The “MS²” refers to when [M+H]⁺ has been extracted with 5 ppm mass accuracy, the LC retention time is within ±3 min from predicted, the isotopic pattern is within ±5 % from the theoretical relative abundance, and MS² data are acquired. “No MS²” refers to the number of samples for which the ion intensities were too low to yield MS²-data. The frequency is based on the total detected, i.e. the sum of “MS²” and “No MS²”. Azo = the dye contains one azo-bond, 2 x azo = the dye contains 2 azo-bonds, anthraq. = anthraquinone-based dye.

Dye	CAS #	Dye type	Precursor/cleavage product	CAS #	MS ² (#)	No MS ² (#)	Frequency [%]
Disperse Black 1	6054-48-4	azo	1,4-phenylenediamine	106-50-3	3	5	10
			naphthalene-1,4-diamine	2243-61-0			
†Disperse Black 2	6232-57-1	azo	1,4-phenylenediamine	106-50-3	2	0	2
			2-methoxy-5-methylbenzene-1,4-diamine	5307-00-6			
†Disperse Blue 14	2475-44-7	anthraq.	-	-	6	0	7
†Disperse Blue 35	12222-75-2	anthraq.	-	-	6	0	7
†Disperse Blue 79 (Br)	12239-34-8	azo	2-bromo-4,6-dinitroaniline	1817-73-8	4	0	5
			((5-acetamido-4-amino-2-ethoxyphenyl)azanediyl)bis(ethane-2,1-diyl) diacetate	-			
Disperse Blue 79 (Cl)	3618-73-3	azo	2-chloro-4,6-dinitroaniline	3531-19-9	7	6	16
			((5-acetamido-4-amino-2-methoxyphenyl)azanediyl)bis(ethane-2,1-diyl) diacetate	-			
Disperse Blue 149	32569-24-7	azo	5-nitro-3H-2l4-benzo[c]isothiazol-3-amine	-	1	0	1
			N-(2-amino-5-(bis(2-hydroxyethyl)amino)phenyl)acetamide	-			
Disperse Blue 165	56532-53-7	azo	2-amino-5-nitrosophthalonitrile	-	6	16	27
			N-(2-amino-5-(dipropylamino)phenyl)acetamide	-			
Disperse Blue 165:1	24170-60-3	azo	2-amino-3,5-dinitrobenzonitrile	22603-53-8	2	2	5
			N-(2-amino-5-(diethylamino)phenyl)acetamide	2359-47-9			
Disperse Blue 183	2309-94-6	azo	2-amino-3-bromo-5-nitrobenzonitrile	17601-94-4	1	13	17
			N-(2-amino-5-(diethylamino)phenyl)propionamide	-			
Disperse Blue 183:1	2537-62-4	azo	2-amino-3-bromo-5-nitrobenzonitrile	17601-94-4	12	6	22
			N-(2-amino-5-(diethylamino)phenyl)acetamide	2359-47-9			
Disperse Blue 291 (Br)	56548-64-2	azo	2-bromo-4,6-dinitroaniline	1817-73-8	2	7	11
			N-(2-amino-5-(diethylamino)-4-methoxyphenyl)acetamide	-			
Disperse Blue 291 (Cl)	79295-99-1	azo	6-chloro-2,4-dinitroaniline	3531-19-9	11	10	26
			N-(2-amino-5-(diethylamino)-4-methoxyphenyl)acetamide	-			
†Disperse Blue 337	65916-12-3	azo	2-amino-5-nitrosophthalonitrile	20033-48-1	1	0	1
			N-(2-amino-5-((2-(2-ethoxyethoxy)ethyl)ethyl)amino)phenyl)acetamide	-			
Disperse Blue 366	84870-65-5	azo	4-diethylamino-o-toluidine	148-71-0	10	8	22
			2-amino-5-nitrosophthalonitrile	20033-48-1			

Disperse Brown 19	55619-18-6	azo	2,6-dibromo-4-nitroaniline	827-94-1		1	16	21
			((4-aminophenyl)azanediyl)bis(ethane-2,1-diyl) diacetate	-				
†Disperse Brown 22	63467-07-2	azo	2,6-dichloro-4-nitroaniline	99-30-9		6	0	7
			2,2'-((4-aminophenyl)azanediyl)bis(ethan-1-ol)	-				
Disperse Green 9	58979-46-7	azo	2-amino-3,5-dinitrothiophene	2045-70-7		6	1	9
			N-(2-amino-5-(diethylamino)phenyl)acetamide	2359-47-9				
Disperse Orange 1.1	26311-09-1	azo	4-nitroaniline	100-01-6		1	2	4
			N-(2,5-diaminophenyl)acetamide	-				
†Disperse Orange 3	730-40-5	azo	1,4-phenylenediamine	106-50-3		21	0	26
			4-nitroaniline	100-01-6				
†Disperse Orange 25	31482-56-1	azo	4-nitroaniline	100-01-6		32	0	39
			3-((4-aminophenyl)(ethyl)amino)propanenitrile	-				
Disperse Orange 29	19800-42-1	2 x azo	4-amino-phenol	123-30-8		2	1	4
			1,4-diamino-2-methoxybenzene	5307-02-08				
			4-nitroaniline	100-01-6				
Disperse Orange 33	69472-19-1	azo	4-nitroaniline	100-01-6		3	2	6
			3-((4-(4-aminophenyl)butyl)amino)propanenitrile	-				
†Disperse Orange 37	13301-61-6	azo	2,6-dichloro-4-nitroaniline	99-30-9		8	0	10
			2,2'-((4-aminophenyl)azanediyl)bis(ethan-1-ol)	-				
Disperse Orange 44	4058-30-4	azo	2-chloro-4-nitroaniline	121-87-9		4	5	11
			3,3'-((4-aminophenyl)azanediyl)dipropanenitrile	-				
Disperse Orange 61	55281-26-0	azo	2,6-dibromo-4-nitroaniline	827-94-1		2	14	20
			3-((4-aminophenyl)(ethyl)amino)propanenitrile	-				
Disperse Orange 73	40690-89-9	azo	4-nitroaniline	100-01-6		5	3	10
			2-((4-aminophenyl)(2-cyanoethyl)amino)ethyl benzoate	-				
Disperse Orange 80	70210-10-5	azo	4-nitroaniline	100-01-6		1	5	7
			3-((4-aminophenyl)(2-(2-cyanoethoxy)ethyl)amino)propanenitrile	-				
†Disperse Red 1	2872-52-8	azo	4-nitroaniline	100-01-6		5	0	6
			2-((4-aminophenyl)(ethyl)amino)ethan-1-ol	1225351-20-1				
Disperse Red 2	3769-58-2	azo	4-nitroaniline	100-01-6		1	0	1
			3-((4-aminophenyl)(2hydroxyethyl)amino)propane-1,2-diol	-				
†Disperse Red 13	3180-81-2	azo	2-chloro-4-nitroaniline	121-87-9		4	0	5
			2-((4-aminophenyl)(ethyl)amino)ethan-1-ol	1225351-20-1				
†Disperse Red 17	3179-89-3	azo	4-nitroaniline	100-01-6		3	0	4
			2,2'-((4-amino-3-methylphenyl)azanediyl)bis(ethan-1-ol)	-				
†Disperse Red 19	2734-52-3	azo	4-nitroaniline	100-01-6		7	0	9
			2,2'-((4-aminophenyl)azanediyl)bis(ethan-1-ol)	-				
Disperse Red 50	40880-51-1	azo	2-chloro-4-nitroaniline	121-87-9		4	2	7

			3-((4-aminophenyl)(ethyl)amino)propanenitrile	-			
Disperse Red 54:1	6657-33-6	azo	2-chloro-4-nitroaniline	121-87-9	2	8	12
			3-((4-aminophenyl)(2-hydroxyethyl)amino)propanenitrile	-			
[†] Disperse Red 60	17418-58-5	anthraq	-		31		38
Disperse Red 65	16586-43-9	azo	2-chloro-4-nitroaniline	121-87-9	5	2	9
			3-((4-amino-3-methylphenyl)(ethyl)amino)propanenitrile	-			
Disperse Red 72	12223-39-1	azo	2-amino-5-nitrobenzonitrile	17420-30-3	1	0	1
			2-((4-aminophenyl)(2-cyanoethyl)amino)ethyl acetate	-			
Disperse Red 73	16889-10-4	azo	2-amino-5-nitrobenzonitrile	17420-30-3	7	12	23
			3-((4-aminophenyl)(ethyl)amino)propanenitrile	-			
Disperse Red 74	1533-74-0	azo	4-nitroaniline	100-01-6	20	16	44
			((3-acetamido-4-aminophenyl)azanediyl)bis(ethane-2,1-diyl) diacetate	-			
Disperse Red 82	30124-94-8	azo	2-amino-5-nitrobenzonitrile	17420-30-3	4	1	6
			((4-aminophenyl)azanediyl)bis(ethane-2,1-diyl) diacetate	-			
Disperse Red 152	78520-83-9	azo	2-amino-5,6-dichlorobenzothiazole	25150-27-0	6	0	7
			3-((4-amino-3-methylphenyl)(ethyl)amino)propanenitrile	-			
Disperse Red 153	25150-28-1	azo	5,7-dichlorobenzo[d]thiazol-2-amine	-	21	17	46
			3-((4-aminophenyl)(ethyl)amino)propanenitrile	-			
Disperse Red 167	26850-12-4	azo	2-chloro-4-nitroaniline	121-87-9	7	4	13
			((4-amino-3-propionamidophenyl)azanediyl)bis(ethane-2,1-diyl) diacetate	-			
Disperse Red 167:1	79300-13-3	azo	2-chloro-4-nitroaniline	121-87-9	26	29	67
			((3-acetamido-4-aminophenyl)azanediyl)bis(ethane-2,1-diyl) diacetate	-			
Disperse Red 177	58051-98-2	azo	2-amino-6-nitrobenzothiazole	6285-57-0	1	4	6
			2-((4-aminophenyl)(2-cyanoethyl)amino)ethyl acetate	-			
Disperse Red 179	16586-42-8	azo	2-amino-6-nitrobenzothiazole	6285-57-0	5	8	16
			3-((4-amino-3-methylphenyl)(ethyl)amino)propanenitrile	-			
Disperse Red 202	28462-17-1	azo	2-chloro-4-nitroaniline	121-87-9	8	4	15
			2-((3-acetamido-4-aminophenyl)(2-cyanoethyl)amino)ethyl acetate	-			
Disperse Red 311	70729-65-6	azo	2,4-dinitroaniline	97-02-09	16	23	48
			dimethyl 3,3'-((3-acetamido-4-amino phenyl)azanediyl)dipropionate	-			
Disperse Red 324	71617-28-2	azo	2-chloro-4-nitroaniline	121-87-9	2	5	9
			N-(2-amino-4-chloro-5-((2-hydroxy propyl)amino)phenyl)acetamide	-			
Disperse Red 343	68385-96-6	azo	2-amino-5-methylisophthalonitrile	-	17	23	49
			N-(2-amino-5-(diethylamino)phenyl)methanesulfon amide	-			
Disperse Violet 63	52583-54-7	azo	2-amino-5-nitrobenzonitrile	17420-30-3	10	7	21
			N-(2-amino-6-(diethylamino)phenyl)acetamide	-			

Disperse Violet 77	52549-57-2	azo	2-amino-5-nitrobenzonitrile	17420-30-3		2	5	9
			N-(2-amino-5-(bis(2-methoxyethyl)amino)phenyl)acetamide	-				
Disperse Violet 93:1	52697-38-8	azo	2-bromo-4,6-dinitroanilin	1817-73-8		6	3	11
			N-(2-amino-5-(diethylamino)phenyl)acetamide	2359-47-9				
†Disperse Yellow 3	2832-40-8	azo	2-amino-4-methylphenol	95-84-1		7	0	9
			N-(4-aminophenyl)acetamide	122-80-5				
Disperse Yellow 119	49744-25-4	azo	2-nitroaniline	88-74-4		4	0	5
			5-amino-1-ethyl-6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile	-				
Disperse Yellow 126	49744-26-5	azo	2-(2-methoxyethoxy)ethyl-anthranilate	49744-35-6		1	1	2
			5-amino-1-ethyl-6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile	-				
Disperse Yellow 163	67923-43-7	azo	2,6-dichloro-4-nitroaniline	99-30-9		2	0	2
			3,3'-((4-aminophenyl)azanediyl)dipropene nitrile	-				
Disperse Yellow 211	70528-90-4	azo	4-chloro-2-nitroaniline	89-63-4		4	6	12
			5-amino-1-ethyl-6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile	-				
Disperse Yellow 231	75199-13-2	azo	benzyl p-aminobenzoate	19008-43-6		1	0	1
			5-amino-1-butyl-6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile	-				
Disperse Yellow 241	83249-52-9	azo	3,4-dichloroaniline	95-76-1		1	1	2
			5-amino-6-hydroxy-1,4-dimethyl-2-oxo-1,2-dihydropyridine-3-carbonitrile	-				

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164 **SI-10 – Disperse dyes quantified in textile garments**

165 Quantified disperse dyes for which reference compounds were available.

Compound	Frequency [%]	Concentration [µg/g]			
		Min	Max	Mean	Median
Azo type dyes					
Disperse Orange 25	39	0.0073	82	8.0	0.16
Disperse Orange 3	26	0.0054	3.7	0.46	0.049
Disperse Orange 37	10	0.0049	1.6	0.32	0.036
Disperse Red 19	9	0.012	1.0	0.25	0.040
Disperse Yellow 3	9	0.011	0.075	0.037	0.024
Disperse Brown 22	7	0.015	1.3	0.37	0.095
Disperse Red 1	6	0.00067	0.079	0.043	0.033
Disperse Blue 79	5	0.016	11	4.9	4.3
Disperse Red 13	5	0.0056	0.12	0.04	0.019
Disperse Red 17	4	0.027	0.058	0.038	0.029
Disperse Black 2	2	0.011	0.014	0.013	0.013
Anthraquinone type dyes					
Disperse Red 60	38	0.019	540	50	1.2
Disperse Blue 14	7	0.0016	14	2.3	0.033
Disperse Blue 35	7	0.025	23	8.6	4.6

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