Talanta 82 (2010) 261–269

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Fast throughput, highly sensitive determination of allergenic disperse dyes in textile products by use of sample composition

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ARTICLE INFO

Article history:
Received 4 January 2010
Received in revised form 12 April 2010
Accepted 16 April 2010
Available online 22 April 2010

Keywords:
Disperse dyes
LC–MS
Sample composition

ABSTRACT

A simple, highly sensitive and fast procedure for the control of allergenic disperse dyes in textile products was optimized. The method is based on ultrasound assisted extraction of textile samples with 20 mL of methanol under controlled conditions (15 min, 70 °C) followed by separation and analysis by LC–MS–MS. The sample preparation process was optimized by means of a surface response experimental design and provided quantitative recoveries of dyes, much better than the poor recoveries provided by current standard procedures. The chromatographic separation was optimized by means of computer-assisted method development by use of a special chemometric tool developed specifically for LC–MS systems, as previously reported by the authors. The result is a rapid chromatographic procedure that enables accurate quantification, at very low concentrations, of all 23 allergenic and/or carcinogenic disperse dyes considered. Matrix effects in the LC–MS procedure were studied. Under the experimental conditions, both conventional and strategic sample composition are proposed as efficient procedures that reduce the costs and work involved in the control of allergenic dyes in finished textile products. The benefits of strategic sample composition are demonstrated by means of an example case study, and the pros and cons of preparing the composite samples from sample extracts or directly from textile products are discussed.

1. Introduction

Disperse dyes are low molecular weight organic dyes that are derivatives of azo, anthraquinone and other compounds. Essentially planar and non-ionic with attached polar functional groups, these dyes have the capacity to slide between the tightly packed polymer chains in polyurethane and other synthetic fabrics, while the polar groups improve their solubility in water; the dipolar bonding between the dye and the polymer also affects the color of the dye [1]. Initially developed for dyeing cellulose acetate fibers, the main application of disperse dyes is now in dyeing polyester, although they may also used for nylon, polyacrylonitrile and many of the newer synthetic hydrophobic fibers, and can be found in a vast variety of consumer products including textiles, toys, paper, etc. Regrettably, a number of these dyes are contact dermatitis sensitizing agents [2–6]. Moreover, some of the dyes that contain azo groups in their structure can be reduced by azoreductases present in intestinal bacteria, liver enzymes and skin-surface micro-flora, thus forming potentially or known carcinogenic aromatic amines [7,8]. According to Hatch and Maibach [9], 49 dyes have been identified as contact allergens and two thirds of these are disperse dyes, although they represent a very small fraction of the total of about 8000 commercially used dyes.

Increased awareness of the potential risk to consumer health associated with exposure to such dyes led to German legislation coming into force in 1996; this legislation restricts the use of several allergenic disperse dyes for dyeing textile products that may come into direct and prolonged contact with human skin [10]. This awareness also led to the development and issue of the DIN 54231 standard procedure [11] for the analysis of 9 disperse dyes in textile products, which appears to be a routine procedure in many analytical laboratories.

A number of papers have been published as regards the determination of disperse dye residues in wastewaters [12–14], food and toys [15,16], and in the context of forensic studies [17–19]. Generally, solid phase or solvent extraction processes are applied for sample preparation. Capillary electrophoresis and liquid chromatography with UV or mass spectrometric detectors are used to separate and quantify extracted dyes. However, studies on textiles (other than for forensic studies) and related materials are scarce [20]. It should be stressed that only a few dyes are considered in the DIN 54231 standard procedure, in relation to the number of allergenic disperse dyes actually identified. Currently, at least 20 allergenic dyes are considered in commercial consumer care protocols issued by textile retailers worldwide. Furthermore, the detection limits are rather high with thin layer chromatogra-

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doi:10.1016/j.talanta.2010.04.031

Table 1
Allergenic disperse dyes considered in the study.

Number	Color index denomination [25]	CAS number	Chemical class	Notes
1	CI Disperse Blue 1	2475-45-8	Anthraquinone	a,b
2	CI Disperse Blue 102	69766-79-6	Monoazo (heterocyclic)	
3	CI Disperse Blue 106	12223-01-7	Monoazo (heterocyclic)	a
4	CI Disperse Blue 124	61951-51-7	Monoazo (heterocyclic)	a
5	CI Disperse Blue 26	3860-63-7	Anthraquinone	
6	CI Disperse Blue 3	2475-46-9	Anthraquinone	a
7	CI Disperse Blue 35	56524-77-7	Anthraquinone	a
8	CI Disperse Blue 7	3179-90-6	Anthraquinone	
9	CI Disperse Brown 1	23355-64-8	Monoazo	
10	CI Disperse Orange 1	2581-69-3	Monoazo	
11	CI Disperse Orange 3	730-40-5	Monoazo	a
12	CI Disperse Orange 37/76/59	13301-61-6	Monoazo	a
13	CI Disperse Red 1	2872-52-8	Monoazo	a
14	CI Disperse Red 11	2872-48-2	Anthraquinone	
15	CI Disperse Red 17	3179-89-3	Monoazo	
16	CI Disperse Yellow 1	119-15-3	Nitrodiphenylamine	
17	CI Disperse Yellow 3	2832-40-8	Monoazo	a,b
18	CI Disperse Yellow 39	12236-29-2	Indigoid	
19	CI Disperse Yellow 49	54824-37-2	Indigoid	
20	CI Disperse Yellow 9	6373-73-5	Nitrodiphenylamine	
21	CI Disperse Orange 11	82-28-0	Anthraquinone	c
22	CI Disperse Yellow 23	6250-23-3	Diazo	c
23	CI Disperse Yellow 7	6300-37-4	Diazo	

[a] Dyes included in German l Law LMGB (1/1/96) and in the DIN 54231 standard.
[b] Potentially carcinogenic.
[c] Releasing carcinogenic aromatic amines by reductive decomposition.

phy (TLC) or diode array-high performance liquid chromatography (HPLC-DAD), both of which are accepted in the DIN 54231 standard procedure, as well as the LC–MS procedure. In general, laboratories using the DIN procedure accept 5 mg L^{-1} as the detection limit in extracts, which for 0.5 g samples (as recommended) means a practical detection limit of 75 μg g^{-1} in consumer products. Moreover, the available results on international proficiency tests for laboratories, many of which use the DIN 54231 standard procedure, have indicated poor recoveries and reproducibility [21].

The globalized economy has dramatically changed many quality control practices because retailers are now selling goods produced outside their area of control. This means that in many cases quality and safety control tests must be carried out on finished goods, involving huge additional costs. Although the TLC approach described in the DIN 54231 standard procedure can be used as a screening process to enable detection of controlled disperse dyes so that only the positive samples are analyzed further (densitometry in the case of TLC or the complete analysis by HPLC-DAD or LC–MS), the time and handling involved are considerable.

A highly sensitive procedure for the analysis of 23 disperse dyes is presented here. The procedure uses LC–MS–MS to separate and quantify the dyes extracted from textile samples. The extraction process was optimized by means of factorial designs and the chromatographic separation was developed by means of computer assisted method development, which uses a specific tool for LC–MS separations [22]. Because the final objective is to reduce the cost and to speed up the routine analytical processes for finished consumer products, sample composition by application of the principles of strategic sample composition [23,24] is proposed.

2. Experimental

2.1. Reagents, standards and special samples

The mixture of dyes considered included the 23 disperse dyes listed in Table 1. Dyes number 2, 3, 4, 9, 11, 12 and 18 were supplied by Dr. Ehrenstorfer GMbH (Augsburg, Germany). Dyes number 5, 7, 8, 14, 15, 16, 19 and 21 were supplied by the Institute for Engineering of Polymer Materials and Dyes (Zgierz, Poland). The remaining dyes in Table 1 were supplied by Sigma–Aldrich (Steimheim, Germany). Individual stock and diluted solutions and mixtures of dyes were prepared in acetonitrile:water (60:40), filtered through 0.22 μm Durapore syringe filters (Millipore) and stored at −18 °C when not in use.

HPLC gradient grade methanol and acetonitrile were purchased from Merck (Darmstadt, Germany). Formic acid was supplied by Sigma–Aldrich (Madrid, Spain). Ultrapure water was produced in the laboratory with a Milli-Q gradient system from Millipore (Bedford, MA, USA).

A few dyed polyester textiles were prepared in-house to have available fully controlled real samples containing disperse dyes of known nature and origin (CI Disperse Blue 106 and CI Disperse Yellow 23). The material containing the CI Disperse Yellow 23 was used to optimize the sample extraction process whereas the one containing the CI Disperse Blue 106 was used to control the sample composition process. The remaining samples considered in this study were commercial products obtained from local stores.

2.2. Apparatus

Samples were ground and homogenized in a Retsch SM100 cutting mill (Haan, Germany), sieved (2 mm) and stored in polypropylene bags at room temperature until analysis. Grinding samples is only necessary for developing sample composition schemes based on raw textile products, but is not necessary for application of the described procedure to individual samples.

Extraction of dyes from samples was carried out with a Branson Sonifier S-450D (400 W output power), with a temperature control system (Danbury, CT, USA).

Two chromatographic systems were used in the study. A Waters Alliance 2695 quaternary solvent module (Milford, MA, USA) equipped with a photodiode array detector (Waters 2996) was used to develop the retention model for the set of dyes under study. This equipment has a dwell volume of 0.85 mL, and an extra column volume of 0.12 mL. It was controlled by Empower 2 software (Waters). In general, standard HPLC equipment can be used to develop retention models without blocking LC–MS instrumentation, with the only condition that the same column is used in both