

DIFFERENT METHODS OF EXTRACTION, REDUCTION AND PURIFICATION OF AROMATIC AMINES FROM TEXTILE MATERIALS

Elena PERDUM, Emilia VISILEANU, Iuliana DUMITRESCU,
Elena-Cornelia MITRAN, Ovidiu-George IORDACHE

National R&D Institute for Textiles and Leather Bucharest (INCDTP)
16 Lucretiu Patrascanu, Bucharest, Romania

Corresponding author email: elena.varzaru@certex.ro

Abstract

Chemicals safety control and eco-properties have become a priority for the textile industry to avoid the negative effects on humans and environment. The European regulations limit the presence of 24 listed carcinogenic aromatic amines by 30 mg/kg of textile material.

The paper aims to present a comparison between different parameters of procedures for the extraction, reduction and purification of the amines obtained by the reductive cleavage of azo dyes in order to choose the optimal method. In order to test the amine extracts obtained, the 8-point calibration curve was performed for the mixture of the 24 standard amines and the solutions obtained from the extraction of the dyestuffs from the textile samples were analysed. Their testing was performed by liquid chromatography and the results were confirmed by the gas chromatography method.

Key words: aromatic amines, textile ecology, azo dye, carcinogenic effect.

INTRODUCTION

The key factor in textile ecology is the use of chemical substances and their effect on human health and environment. Beginning with fiber cultivation but extending to the production of yarns and fabrics, the tanning of leather, and including operations as dyeing, printing, finishing and surfacing, in every step the choice to be made is between hazardous and harmless chemicals. There is a logical connection between the use of chemicals in production and the health threatening substances found in textile products. Many toxins can be removed during the production processes but, unfortunately, not all. Detergents or sweat can leach these toxins out of fibers or leather. They can then enter the body through the skin. Or they can leak into the environment through washing and do their damage there. (International Association of Natural Textile Industry).

Chemicals as azo colourants are used to colour textile fibres, leather, plastics, papers, hair, mineral oils, waxes, foodstuffs and cosmetics (Lavandeira et al., 2010; Hunger, 2003). The word 'Azo' signifies the presence of a chemical azo group (-N=N-) in the dye. A unique feature

of azo dyes is that the nature does not produce analogous coloured substances (Nadiger, 2001).

The biggest concern regarding azo dyes is their toxic effect; it was stated that azo dyes, after cleavage, present the capacity to release aromatic amines considered as carcinogenic. Three different mechanisms for azo dye carcinogenicity were identified; all involving metabolic activation to reactive electrophilic intermediates that covalently bind DNA. These mechanisms are:

1. Azo dyes that is toxic only after reduction and cleavage of the azo linkage to give aromatic amines, mostly via intestinal anaerobic bacteria. The aromatic amines are metabolically oxidized to reactive electrophilic species that covalently bind DNA.
2. Azo dyes with structures containing free aromatic amine groups that can be metabolically oxidized without azo reduction.
3. Azo dyes that may be activated via direct oxidation of the azo linkage to highly reactive electrophilic diazonium salts.

Each mechanism may be compound specific, thus azo toxicity is probably caused by more than one mechanism. Although it is not possible to predict azo dye carcinogenicity with

absolute certainty, it is possible to establish certain guidelines (Brown, 1993).

The European Union, by the Directive 2002/61/EC, reformulated by the Directive 2004/21/CE, has banned the use of these dyes used in the production of textile articles that enter in contact with skin or mouth. These Directives also establish that the referred textile articles cannot contain the 22 amines listed in the legislation, in a concentration higher than 30 ppm and, if the articles are made of recycled fibres, they cannot contain more than 70 ppm (Policy Research Center for Environment and Economy, 1999; ETAD, 2007).

MATERIALS AND METHODS

Reagents and standards

- Acetonitrile and methanol gradient grade from Merck KGaA (Germany), water for chromatography (resistivity min. 18.2 MΩ x cm, TOC max. 50 ppb).
- Analytical standards of 24 aromatic amines from Sigma-Aldrich and Dr. Ehrenstorfer GmbH (Germany).

Instrumentation

- HPLC separation was performed on Agilent 1100 LC System using Agilent Zorbax Eclipse XDB C18 column and MWD detector.
- GC separation was performed on Agilent 6890 GC System coupled with Agilent 5973N transmission quadrupole mass spectrometer (Table 1).

Table 1. Operating condition

Agilent 6890 GC/5973N MS Operating Conditions	
Capillary Column	DB-35MS (J&W), 35 m x 0.25 mm x 0.25 μm;
Injector System	splitless
Injector Temp.	260 °C
Carrier gas	helium
Flow (mL/min)	1 mL/min
Temp. programme	100°C (2 min), 100°C - 310°C (15°C/min), 310°C (2 min)
Injection Volume	1.0 μl
Detection	MS / Full Scan
Acquisition Parameters	EI Positive Ion Mode, 70 eV

Agilent 1100 HPLC/MWD Operating Conditions		
Analytical Column	Zorbax Eclipse XDB C18 150 mm x 4,6 mm x 3.5 μm	
Column Temp.	32°C	
Injection Volume	5.0 μl	
Mobile Phase	Eluent 1: methanol	
	Eluent 2: 0.68 g potassium dihydrogen phosphate in 1000 mL water, 150 mL methanol	
Run time	35 min	
Flow rate	0.6 - 2,0 mL/min (gradient)	
Quantification	at 240 nm, 280 nm, 305 nm and 380 nm	
Gradient profile	Time (minutes)	Gradient (% Eluent 1)
	0.00	10.0
	22.50	55.0
	27.50	100.0
	28.50	100.0
	28.51	100.0
	29.00	100.0
	29.01	10.0
	31.0	10.0
	35.00	10.0

RESULTS AND DISCUSSIONS

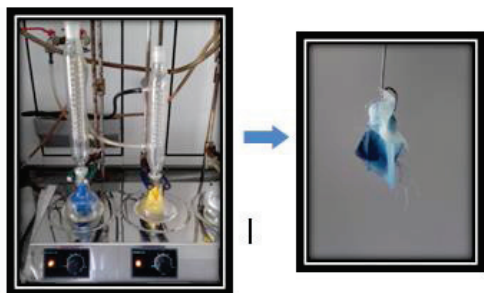
Procedures for extraction of azo dyes from textile materials

To perform procedures for the extraction and purification of azo dyes from painted textiles, we used the standardized method described in ISO/DIS 14362-1:2017.

We used one textile material made of cotton, dyed with Direct Blue 6.

The textile samples were cut in the form of narrow strips and weighed so as to obtain about 1g of material; then hooked with an inert thread and placed into 50 mL round bottom flasks; the painted textile samples were kept in an reflux apparatus over a volume of 25 mL boiling solvent (xylene/methylene chloride) for 40 min; after this time the drops from the textile material became colorless (Scheme 1).

The extract of the dye in the organic extraction solvent was allowed to cool to room temperature and then the solvent was evaporated to concentrate the extract in a rotary evaporator (Figure 1).



Scheme 1. Reflux condenser for extraction of dyes



Figure 1. Rotary evaporator used for evaporation of extraction solvent

In Table 2 below are synthesized factors which were varied for the extraction procedure: the extraction solvent (xylene respectively methylene chloride) and the volume of extraction solvent (25 mL and 50 mL), and two of the samples were carried out in duplicate: 1A, duplicate sample 1A' for reproducibility of results.

Table 2. Extraction parameters

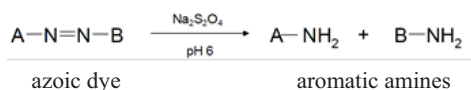
Sample	Solvent [mL]		Sample mass [g]
	Xylene	Methylene chloride	
1 A	25	-	1.0463
1 A'	25	-	1.0578
2 A	50	-	0.9870
3 A	-	25	1.0150

Procedures for reducing azo dyes to aromatic amines

In order for the aromatic amines to be detected from the textile materials, must be performed reductive cleavage of the azo dyes.

This is generally accomplished with sodium dithionite solution, which results in the breakage of the azo -N = N- bond, with the formation of two amine groups, -NH₂.

The reductive cleavage reaction of the dyes is shown schematically below:



The selective reduction was carried out as follows: a volume (15 and 20 mL) of an oxidizing agent - citrate buffer/sodium hydroxide solution preheated to 70°C was added to a reaction vessel, which was kept on the plate at 70°C (± 2°C) for 30 minutes (± 1 min); Subsequently, a volume of sodium dithionite reducing agent (3 mL respectively) was added and kept at 70°C (± 2°C) for 30 minutes (± 1 min).

Subsequently, the reaction vessels were cooled to room temperature (20-25°C) over 2 min (Table 3).

Table 3. Reduction parameters

Sample	Sodium citrate pH=6 [mL]	Sodium hydroxide pH=6 [mL]	Sodium dithionite 200 mg/ml [mL]	Sodium hydroxide 10% [mL]
1 A	15	-	3	0.2
1 A'	15	-	3	0.2
2 A	20	-	3	0.2
3 A	15	-	4	0.5

Separation and concentration of aromatic amines

In the reaction vessel (Figure 2) we added a 10% volume of sodium hydroxide (0.2 and 0.5 mL), and after vigorous stirring, the solution was transferred to a column of diatomaceous earths (Figure 3) - Sigma Aldrich and maintained to be absorbed by the column for 15 minutes.

Meanwhile, 10 mL of t-butyl-methyl ether was added to the reaction vessel, and after vigorous stirring, it was poured into the diatomaceous column (repeated procedure), followed by 60

mL of t-butyl-methyl ether they poured directly into the column.

The extract was collected in a 50 mL round bottom flask and the solvent was evaporated to a minimum volume of 1 mL in a rotary evaporator; this volume of extract from each sample was then taken up with 1 mL of acetonitrile and analyzed by liquid and gas chromatography method.



Figure 2. Dye reduction to amine



Figure 3. Purification of the amine extract

Results of HPLC-MWD and GC-MS analyzes on textile-dyed samples

Sample 1A

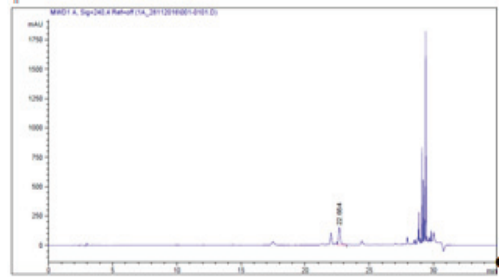


Figure 4. Chromatogram of sample 1A
 HPLC MWD detection at 240 nm

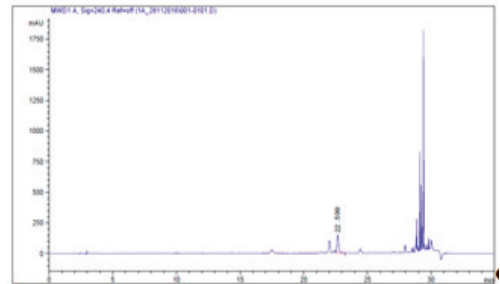


Figure 5. Chromatogram of sample 1A'
 HPLC MWD detection at 240 nm

RetTime [min]	Type	Area [mAU*s]	Amt/Area	Amount [ug/ml]	Grp	Name
22.664	VB	1522.86292	3.35605e-2	51.10811		amina 4
Totals :				51.10811		

RetTime [min]	Type	Area [mAU*s]	Amt/Area	Amount [ug/ml]	Grp	Name
29.196	EV	52.36035	8.09748e-2	4.23987		amina 22
Totals :				4.23987		

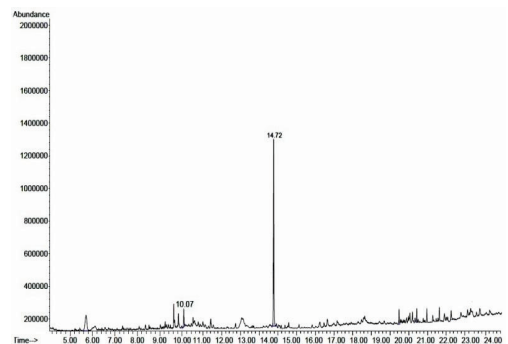


Figure 6. GC-MS Chromatogram of sample 1A

Table 4. Concentration of amines resulting from dye reduction for sample 1A

Component	Name	CAS #	Conc. [ppm]
1.	Amine 4: 2-naphthylamine	91-59-8	53.0021
2.	Amine 22: 4-aminobenzene	60-09-3	4.2561

Table 5. Concentration of amines resulting from dye reduction for sample 1A'

Component	Name	CAS #	Conc. [ppm]
1.	Amine 4: 2-naphthylamine	91-59-8	51.4628
2.	Amine 22: 4-aminobenzene	60-09-3	3.9592

Table 6. Concentration of amines resulting from dye reduction for sample 2A

Component	Name	CAS #	Conc. [ppm]
1.	Amine 4: 2-naphthylamine	91-59-8	1.0938
2.	Amine 22: 4-aminobenzene	60-09-3	4.9751

Table 7. Concentration of amines resulting from dye reduction for sample 3A

Component	Name	CAS #	Conc. [ppm]
1.	Amine 4: 2-naphthylamine	91-59-8	47.3265
2.	Amine 22: 4-aminobenzene	60-09-3	3.3105

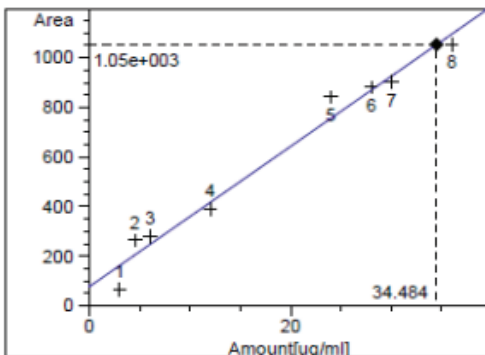


Figure 7. Calibration curve for amine 4

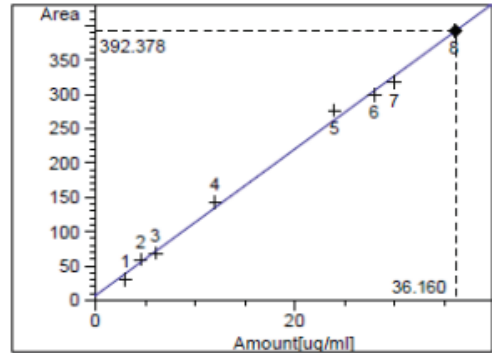


Figure 8. Calibration curve for amine 22

CONCLUSIONS

As a result of analyzes performed by both HPLC and GC, for samples 1A and 1A' respectively, the simultaneous detection of the amines 4 and 22 is observed by the two methods.

The specific structure of the dye has determined, by its splitting the appearance of the two amines.

By changing the volume of xylene (50 mL vs. 25 mL) and the volume of citrate (20 mL versus 15 mL), the decreased sensitivity of the method for determining aromatic amines is noticeable, meaning that amine 4 can no longer be detected.

Modification of extraction parameters (use of 25 mL of methylene chloride versus 25 mL xylene) and reduction parameters (use of sodium dithionite: 4 mL vs. 3 mL and 10% sodium hydroxide: 0.5 mL versus 0, 2 mL) there was also a decrease in the sensitivity of the method proved by lower amounts of amines compared to the standardized method.

ACKNOWLEDGEMENTS

This research work was carried out in Nucleu Programme TEX-PEL-2020, implemented with the support of MCI, project entitled „Exploitation of filamentous fungi for the production of bio-composite materials”.

REFERENCES

- Brown M.A., De Vito S.C., 1993. Predicting azo dye toxicity, *Critical Reviews in Environmental Science and Technology* Vol. 23, Iss. 3.
- ETAD, 2007. Available in: <[http:// www.etad.com/information 6htm](http://www.etad.com/information6htm) > Accessed in: January, 2007.
- Hunger K., 2003. *Industrial Dyes. Chemistry, Properties, Applications*, Wiley VCH.
- International Association of Natural Textile Industry, <https://naturtextil.de/en/ecology/>
- Lavandeira J. G., Salgado-Pentia C., Blanco E., Cela R., 2010. A sensitive and efficient procedure for the high throughput determination of banned aromatic amines in textile and leather products aided by advanced sample composition, *Anal Bioanal Chem.* 397:751-763.
- Nadiger G.S., 2001. Azo ban, eco-norms and testing, *Indian Journal of Fibre & Textile Research*, Vol. 26, March-June 2001, pp. 55-60.
- Policy Research Center for Environment and Economy. 1999. The 3rd Meeting of the 2nd Phase of CCICED Impacts of Environmental Standards and Requirements in EU Countries on Cna's Textile Industry”.