TESTING FOR ECOFRIENDLINESS IN DYED TEXTILES

Characterization of eco-friendliness:

- The dyed materials were tested for the presence of heavy metal pesticides and banned arylamines by the methods prescribed as follows:
- Aryl amines by GC and GC-MS
- Pesticide residues by GC and GC-MS
- Heavy metals by AAS/ICP
- Formaldehyde by UV-Vis spectrometer

Aryl amine determination

- Both the Azo dyes and Dyed fabrics release aryl amines on reductive cleavage.
- These are analyzed on GC and subsequently on GC-MS for identification
- 22 banned amines are tested
- The extracted dye and dyed fabric samples were also analyzed for the presence of banned aryl amines after reductive cleavage and isolation of banned amines by GC-MS and HPTLC.

Banned Amines

The GC/MS Analysis of 20 Carcinogenic Amines Banned in Textiles and Consumer Products and of Interest in Environmental Monitoring of Colorization Process Wastes For the analysis of amines from a range of consumer products, a GC/MSD system can be configured and operated in a manner that is most suitable to achieve necessary detection levels. World-class performance with respect to reliability continues to lead commercially available GC/MS instrumentation—an important consideration for laboratories doing routine GC/MS work. Data handling tools previously available for very specific environmental analyses have been expanded for more general use, providing greater ease-of-use in data analysis and customized reporting

Banned amines

- Because the concentration of the amines in products may vary, scan or SIM mode methods have been developed. With split injection of 1-µL aliquots, MS detection in scan mode allows easy detection at 0.1 ppm and ultimate detection down to 0.02-0.04 ppm. The highest sensitivity is obtained by pulsed splitless injection combined with SIM mode, yielding a limit of detection of 5 ppb for injection volumes of 1 µL. For samples with concentrations greater than 10 ppm, split injections are recommended.

According to Commission of the European Communities: Directive 2002/61/EC, there are 22 banned amines substances as below.

4-aminodiphenyl/xenylamine/Biphenyl-4-ylamine (CAS no. 92-67-1) Benzidine (CAS no. 92-87-5)

4-chloro-o-toluidine (CAS no. 95-69-2)

2-naphthylamine (CAS no. 91-59-8)

o-aminoazotoluene/4-o-tolylazo-o-toluidine/4-amino-2',3-dimethylazobenzene (CAS no. 97-56-3)

2-amino-4-nitrotoluol/5-nitro-o-toluidine (CAS no. 99-55-8)

p-chloranilin/4-chloroaniline (CAS no. 106-47-8)

2,4-diaminoanisole/4-methoxy-m-phenylenediamine (CAS no. 615-05-4)

4,4'-diaminodiphenylmethane/4,4-methylenedianiline (CAS no. 101-77-9)

3,3'-dichlorobenzidine/3,3'dichlorobiphenyl-4,4'-ylenediamine (CAS no. 91-94-1)

List of Banned Amines

3,3'-dimethoxybenzidine/o-dianisidine (CAS no. 119-90-4)

3,3'-dimethybenzidine/4,4’-bi-o-Toluidine (CAS no. 119-93-7)

3,3'-dimethyl-4,4'-diaminodiphenylmethane/4,4’-methylenedi-o-toluidine (CAS no. 838-88-0)

p-cresidin/6-methoxy-m-toluidine (CAS no. 120-71-8)

4,4'-methylene-bis-(2-chloro-aniline)/2,2’-dichloro-4,4’methylenedianiline (CAS no. 101-14-4)

4,4'-oxydianiline (CAS no. 101-80-4)

4,4'-thiodianiline (CAS no. 139-65-1)

o-toluidine/2-aminotoluene (CAS no. 95-53-4)

2,4-toluylenediamine/4-methyl-m-phenylenediamine (CAS no. 95-80-7)

2,4,5-trimethylaniline (CAS no. 137-17-7)

4-aminoazobenzene (CAS no. 60-09-3)

o-anisidine/ 2-methoxyaniline (CAS no. 90-04-0)

Toxic heavy metal

- Toxic heavy metal contents in the dye and the dyed fabric were determined by using Inductively Couple Plasma Optical Emission Spectrometer (ICP).

- For analysis, 1000-ppm solution (0.1 g sample digested in conc. hydrochloric acid and made up to 100 ml by adding distilled water) was used.

- **Metals** The heavy metal content in the extracted dyes were determined by using Inductively Coupled Plasma Spectrophotometer and it was found that their concentrations are much below the stipulated limits.

- The dye extract if it shows presence of Zn and Hg in less than 0.005%. This will be considered safe, because use of red listed heavy metal based mordants have been avoided thus the dyeing process is ecofriendly.

Pesticide analysis

- Contamination of pesticides is also likely to occur during growing of plants from soil or from preservatives during storage. For analysis, 20 g sample in 150 ml n-hexane was extracted by soxhlet.
- Extraction, clean up and detection by GC/ECD.
- After 6 – 7 hours the hexane evaporated to dryness and a pinch of sodium sulphate is added to this 5 ml of hexane (HPLC grade) was added. It was then filtered and injected in GC.

Formaldehyde content

- The extracted dyes and dyed fabric samples were also tested for presence of formaldehyde by using UV-Visible spectrophotometer.

Health effects of Formaldehyde:

- Although formaldehyde is less toxic than most reactive compounds,certain factors make formaldehyde a particular problem to human health.Firstly, it is a gas that can spread throughout the work and living space.Secondly, most of the formaldehyde resins and their end-use products are potential to liberate formaldehyde.

- The risk of adverse reaction to formaldehyde depends on the sensitivity of an individual, the time of exposure, and the type of contact. On breathing formaldehyde vapor, formaldehyde can result in irritation of nerves in the eyes and nose, which may cause burning, stinging sensation,a sore throat, teary eyes, runny nose and sneezing.

Formaldehyde

- Skin contact with formaldehyde can cause skin rashes and allergic skin reactions. Formaldehyde is well known sensitizer for dermatitis and instances of dermatitis resulting from wearing clothing containing high levels of formaldehyde have been documented.

- The International Agency for Research on Cancer, a World Health Organization panel of 26 scientists has concluded that the formaldehyde is a human carcinogen.

Formaldehyde Release from Textiles

The formaldehyde-containing chemicals are most effective cross linking agents for wrinkle resistance, dimensional stability and flame retardant properties of textiles.

During the finishing process, the N-methylol compounds in formaldehyde containing reagents can react with hydroxyl groups of cellulose, resulting in the preferable cross linking reaction; they may also react with themselves or with NH groups, which occupy there action places on cross linking agents .

Formaldehyde from cross linking agents

- The formaldehyde can simply be released from the N- methyl ol compounds which come from the excess finishing agents or by hydrolysis of cross linking agent

Formaldehyde

- The formaldehyde released from a treated fabric will depend on number of factors including the following:
- The type and quantity of formaldehyde resin used
- Environmental temperature and relative humidity
- The degree that the formaldehyde resin has been cured
- The after-treatment of finishing such as washing

Trace Elements (in ppm)

Details	Cu	Zn	Cd	Co	Pb	As	Hg	Ni	Cr
In the dye	0.03	Absent	Absent	Absent	0.05	1.30	Absent	Absent	0.20
In the dyed fabric	0.02	Absent	Absent	Absent	0.01	0.69	0.67	Absent	0.05

Pesticides (in ppm)

Pesticides	In the dye	In the dyed fabric
1. BHC	0.10	Absent
2. Malathion	0.25	Absent
3. Methylparathion, **4.** Endosulfan, **5.** DDT, **6.** DDE, **7.** DDD, **8.** 2, 4 D, **9.** 2, 4, 5 T, **10.** Aldrin, **11.** Dieldrin, **12.** Ethion, **13.** Dimethoate	Absent	Absent

Use of SEM for pesticides on Textiles

- Backscattered electron imaging (BEI) and x-ray analysis have been beneficial in studying the distribution patterns of pesticides on various fabrics. In order to analyze the samples, pesticides were labeled with osmium tetroxide solution, but there was a possibility of inaccurate results because the pesticide on the surface of the fabric could be dislocated in the aqueous medium.

- A new technique has been developed for labeling the pesticide on the textile material with osmium tetroxide in vapor form, which could produce more accurate results