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Textiles — Methods for determination of certain aromatic amines derived from azo colorants —

Part 1: Detection of the use of certain azo colorants accessible with and without extracting the fibres

Textiles — Méthodes de détermination de certaines amines aromatiques dérivées de colorants azoïques —

Partie 1: Détection de l'utilisation de certains colorants azoïques accessibles avec ou sans extraction

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Contents

Page

Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by the European Committee Standardization (CEN) Technical Committee CEN/TC 248, *Textiles and textile products*, in collaboration with ISO Technical Committee TC 38, *Textiles*, in accordance with the agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This first edition of ISO 14362-1 cancels and replaces ISO 24362-1:2014, which has been technically revised.

The following is a list of the major technical changes between this edition and ISO 24362-1:2014:

— addition of a new Clause 3 and renumbered;

— changes to Clause 5 "Principle," where the combined method has been removed as it had been found that results were not accurate in certain cases;

— changes to Clause 9 "Test specimen sampling and preparation" to be more explanatory;

— changes to Clause 10 "Procedure" to improve the method, including using xylene as substitute for chlorobenzene (reasons: lower toxicity and lower adverse environmental effect of xylene);

— extension of Annex C "Assessment guide — Interpretation of analytical results" to give examples for false-positive results, suggested procedures and suggested comments in test report;

— addition of Annex G "Pigments."

A list of all parts in the ISO 14362 series can be found on the ISO website.

Textiles — Methods for determination of certain aromatic amines derived from azo colorants —

Part 1:
Detection of the use of certain azo colorants accessible with and without extracting the fibres

1 Scope

This document describes a method to detect the use of certain azo colorants that may not be used in the manufacture or treatment of certain commodities made of textile fibres and that are accessible to reducing agent with and without extraction.

Azo colorants accessible to reducing agent without extraction are those used to colour with pigments or to dye

— cellulosic fibres (e.g. cotton, viscose),

— protein fibres (e.g. wool, silk), and

— synthetic fibres (e.g. polyamide, acrylic).

Azo colorants accessible with extraction are those used to dye man-made fibres with disperse dyes. The following man-made fibres can be dyed with disperse dyes: polyester, polyamide, acetate, triacetate, acrylic and chlorofibre.

The method is relevant for all coloured textiles, e.g. dyed, printed and coated textiles.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at http://www.iso.org/obp

4 General

Certain azo colorants may release, by reductive cleavage of azo group(s), one or more of the following aromatic amines.

Table 1 — Targeted aromatic amines[c]

No.	CAS number	Index number	EC number	Substances
1	92-67-1	612-072-00-6	202-177-1	biphenyl-4-ylamine 4-aminobiphenyl xenylamine
2	92-87-5	612-042-00-2	202-199-1	benzidine
3	95-69-2	612-196-00-0	202-441-6	4-chloro-o-toluidine
4	91-59-8	612-022-00-3	202-080-4	2-naphthylamine
5[a]	97-56-3	611-006-00-3	202-591-2	o-aminoazotoluene 4-amino-2',3-dimethylazobenzene 4-o-tolylazo-o-toluidine
6[a]	99-55-8	612-210-00-5	202-765-8	5-nitro-o-toluidine 2-amino-4-nitrotoluene
7	106-47-8	612-137-00-9	203-401-0	4-chloroaniline
8	615-05-4	612-200-00-0	210-406-1	4-methoxy-m-phenylenediamine 2,4-diaminoanisole
9	101-77-9	612-051-00-1	202-974-4	4,4'-methylenedianiline 4,4'-diaminodiphenylmethane
10	91-94-1	612-068-00-4	202-109-0	3,3'-dichlorobenzidine 3,3'-dichlorobiphenyl-4,4'-ylenediamine
11	119-90-4	612-036-00-X	204-355-4	3,3'-dimethoxybenzidine o-dianisidine
12	119-93-7	612-041-00-7	204-358-0	3,3'-dimethylbenzidine 4,4'bi-o-toluidine
13	838-88-0	612-085-00-7	212-658-8	4,4'-methylenedi-o-toluidine
14	120-71-8	612-209-00-X	204-419-1	6-methoxy-m-toluidine p-cresidine
15	101-14-4	612-078-00-9	202-918-9	4,4'-methylene-bis-(2-chloro-aniline) 2,2'-dichloro-4.4'-methylene-dianiline
16	101-80-4	612-199-00-7	202-977-0	4,4'-oxydianiline
17	139-65-1	612-198-00-1	205-370-9	4,4'-thiodianiline
18	95-53-4	612-091-00-X	202-429-0	o-toluidine 2-aminotoluene
19	95-80-7	612-099-00-3	202-453-1	4-methyl-m-phenylenediamine 2,4-toluylendiamine 2,4-diaminotoluene
20	137-17-7	612-197-00-6	205-282-0	2,4,5-trimethylaniline
21	90-04-0	612-035-00-4	201-963-1	o-anisidine 2-methoxyaniline
22[b]	60-09-3	611-008-00-4	200-453-6	4-aminoazobenzene

[a] The CAS-numbers 97-56-3 (No. 5) and 99-55-8 (No. 6) are further reduced to CAS-numbers 95-53-4 (No. 18) and 95-80-7 (No. 19).

[b] Azo colorants that are able to form 4-aminoazobenzene generate, under the condition of this method, aniline (CAS-number 62-53-3) and 1,4-phenylenediamine (CAS – number 106-50-3). Due to detection limits, only aniline may be detected. If aniline is detected above 5 mg/kg, then the presence of these colorants should be tested by ISO 14362-3.

[c] The targeted aromatic amines are the proscribed aromatic amines under Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency.

5 Principle

After selection of a coloured test specimen from the textile article, the test specimen is tested according to the method of colorant extraction for disperse dyes and/or the method of direct reduction for the other classes of colorants (pigments and/or dyes).

The application of one of the two methods is based on the nature of the fibre(s) of the test specimen (composed of pure fibre or of fibre blends) and the colour treatment (dyeing or printing process). When the method of the colorant extraction for disperse dyes is carried out, the colorant is first extracted from the fibre in the headspace (see Figure 1) using xylene under reflux. The extract is concentrated and transferred to the reaction vessel with methanol for subsequent reduction with sodium dithionite in a citrate-buffered aqueous solution (pH = 6) at 70 °C.

If the textile specimen is not completely discoloured after xylene extraction, a new test specimen needs to be prepared again and reprocessed with the method for non-extractable classes of the colorants. When the method for non-extractable classes of the colorants is carried out, the test specimen is treated with sodium dithionite in a citrate-buffered aqueous solution (pH = 6) at 70 °C in a closed vessel.

After the reduction, any amine released in the process is transferred to a *t*-butyl methyl ether phase by means of liquid-liquid extraction using diatomaceous earth columns. The *t*-butyl methyl ether extract is then concentrated, and the residue is taken up in an appropriate solvent for detection and determination of the amines using chromatography (see Annex A).

A screening method using liquid-liquid extraction without diatomaceous earth columns is described in Annex E.

If any amine is detected by one chromatographic method, then confirmation shall be made using one or more alternative methods.

6 Safety precautions

WARNING — The substances [amines] listed in Clause 4 are classified as substances known to be or suspected of being human carcinogens.

Any handling and disposal of these substances shall be in strict accordance with the appropriate national health and safety regulations.

It is the user's responsibility to use safe and proper techniques in handling materials in this test method. Consult manufacturers for specific details such as material safety data sheets and other recommendations.

7 Reagents

Unless otherwise specified, analytical grade chemicals shall be used.

7.1 Xylene (mixture of isomers) CAS No 1330-20-7.

7.2 Acetonitrile.

7.3 Methanol.

7.4 *t*-butyl methyl ether.

7.5 Citrate/sodium hydroxide buffer solution, pH = 6, c = 0,06 mol/l[1)].

1) c is citrate concentration.

7.6 Aqueous sodium dithionite solution, ρ = 200 mg/ml[2] freshly prepared (which means to be used within 1 h).

7.7 Diatomaceous earth.

7.8 Amine substances — amines 1 to 4, 7 to 21 (as specified in Table 1), and aniline and 1,4-phenylenediamine — all of highest available defined purity standards.

7.9 Standard solutions.

7.9.1 Stock solution of amines with a concentration of equal to or greater than 300 µg of each amine per millilitre of an appropriate solvent.

NOTE Acetonitrile is an appropriate solvent for this stock solution, resulting in good stability of amines.

7.9.2 Calibration solution of amines for daily use.

Dilute from the stock solution (7.9.1) to a concentration of ρ = 15,0 µg of each amine per millilitre of an appropriate solvent.

7.9.3 Calibration solutions of amines for quantification, concentration range from 2 µg up to 50 µg of each amine per millilitre of an appropriate solvent. If gas chromatography is used, 10 µl of internal standard solution (7.9.4) per millilitre must be added before injection.

NOTE It is the responsibility of each lab to choose appropriate concentrations for the calibration.

7.9.4 Internal standards in solution (IS), ρ = 1,0 mg /ml in the appropriate solvent.

In the case of GC-MS analysis, one of the following internal standards can be used:

— IS1: naphthalene-d8, CAS No.: 1146-65-2;

— IS2: 2,4,5-trichloroaniline, CAS No.: 636-30-6;

— IS3: anthracene-d10, CAS No.: 1719-06-8.

7.9.5 Indicator for later eluting amines: benzidine-d8, CAS No.: 92890-63-6.

ρ = 0,5 mg/ml of benzidine-d8 in solution (7.9.4)

benzidine-d8 (CAS 92890-63-6) is a suitable indicator for interferences in the later part of the GC chromatogram (10.5).

7.10 Sodium hydroxide aqueous solution, a mass fraction of 10 %.

7.11 Grade 3 water, complying with ISO 3696**.**

8 Apparatus

8.1 Extraction apparatus, according to Figure 1, consisting of

— coil condenser NS 29/32,

— a hook, made from an inert material to hold the specimen in place so that the condensed solvent drips onto it,

2) ρ is the mass concentration.

— 100 ml round bottom flask NS 29/32, and

— heating source.

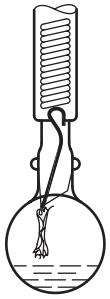

Figure 1 — Apparatus

Similar apparatus may be used, if the same results are obtained.

8.2 Ultrasonic bath.

8.3 Reaction vessel (20 ml to 50 ml) of heat-resistant glass, with tight closure.

8.4 Heating source that generates (70 ± 2) °C.

8.5 Glass or polypropylene column, inside diameter 25 mm to 30 mm, length 130 mm to 150 mm, packed with 20 g of diatomaceous earth (7.7), fitted with glass fibre filter at the outlet.

The diatomaceous earth columns are either bought pre-packed and used as is, or 20 g of diatomaceous earth can be packed into a glass or polypropylene column of the dimensions given.

8.6 Vacuum rotary evaporator with vacuum control and water bath.

Other kinds of evaporation apparatus may be used, e.g. a water bath with a controlled flow of nitrogen over the liquid.

8.7 Pipettes in required sizes or variables pipettes.

8.8 Chromatographic equipment, selected from the following:

8.8.1 Thin layer chromatograph (TLC) or high-performance thin layer chromatograph (HPTLC), including relevant detection.

8.8.2 High-performance liquid chromatograph (HPLC) with gradient elution and diode array detector (DAD) or mass selective detector (MS).

8.8.3 Gas chromatograph (GC) with flame ionization detector (FID) or mass selective detector (MS).

8.8.4 Capillary electrophoresis (CE) with diode array detector (DAD).

8.8.4.1 Membrane filter PTFE (polytetrafluoroethylene), pore size 0,2 µm, adapted for capillary electrophoresis (8.8.4)

NOTE A description of the chromatographic conditions is given in Annex A.

9 Test specimen sampling and preparation

9.1 General

The test specimen shall be selected based on the following criteria:

— parts of the textile article (9.2);

— nature of the fibre components (fibre composition) (9.3 and 9.4);

— coloured materials (9.6), especially when pigments are used (9.5).

Prepare the test specimen by cutting the textile article into strips or pieces (see below) in order to obtain a total mass of 1 g.

For specimens to be submitted to colorant extraction (10.1),

— cut the textile article into strips if the apparatus described in 8.1 is used, or

— cut the textile article into small pieces if another apparatus is used or if the specimens will only be submitted to the reductive cleavage procedure (10.3).

9.2 Textile article

If the textile article is a semi-manufactured product, such as yarns, fabrics, etc., cut out test specimens from it.

If the textile article is composed of several parts of textile products, such as a garment, cut out test specimens from all the parts of the textile article, which can be

— principal fabric(s),

— lining(s),

— pocket fabric(s),

— embroideries;

— label(s) for textile article,

— drawstring(s),

— fastener(s),

— false fur, or

— sewing threads.

If the mass of some parts (e.g. labels, sewing threads, embroideries of small size) does not reach the mass (1 g) to be tested, gather identical parts when possible. If the total mass of material is below 0,5 g, this material is defined as a minor component. (See C.1.)

Below 0,2 g of material, the analysis is omitted.

Embroideries shall be weighed with the ground fabric.

9.3 Fibre composition

As the application of this document is partly based on the extraction of colorants, identify the nature of the textile components so that the possible use of disperse dyestuffs can be determined.

Table 2 summarizes the four cases:

Table 2 — Application of colorant extraction for disperse dyes (10.1) in relation to the fibre nature

Nature of fibre	Use of disperse dye-stuffs	Cases	Colorant extraction for disperse dyes (10.1) necessary?
Natural fibre	No	A	No
Man-made fibre	No	B	No
	Undetermined	C	Yes
	Yes	D	Yes
If a fibre is not dyed, the fibre shall not be tested.			

Categories of dyestuffs used in either natural or man-made fibres are explained in Annex D.

9.4 Case of the fibre blends

In the case when fibres of different types are mixed, refer to Table 3 in order to decide if application of the colorant extraction for disperse dyes (10.1) shall be applied.

Table 3 — Application of colorant extraction for disperse dyes (10.1) or other dyes (10.2) in relation to the fibre blends

Which procedures shall be applied?		Other component of the blend			
		A	B	C	D
Component of the blend	A[b]	10.2	10.2	both 10.1, 10.2	both 10.1, 10.2
	B[b]	10.2	10.2	both 10.1, 10.2	both 10.1, 10.2
	C[b]	both 10.1, 10.2	both 10.1, 10.2	both 10.1, 10.2	both 10.1, 10.2
	D[b]	both 10.1, 10.2	both 10.1, 10.2	both 10.1, 10.2	10.1[a]

[a] When pigments are used or when their presence is undetermined, apply 10.2 as well (see 9.5).

[b] See Table 2 for meanings of A, B, C and D.

9.5 Coloured materials with pigments

If material is printed or dyed with pigments (Annex G) as well as any material where the usage of pigments is uncertain, the method in 10.2 shall be carried out.

9.6 Colours

9.6.1 General

All colours shall be tested.

"White" and uncoloured fibres, threads or fabrics are not considered to contain azo colorants and therefore, these parts do not have to be tested. On the other hand, attention should be paid to "pale printed" materials as they can contain azo colorants.

9.6.2 Case of colour gathering

Up to three colours may be tested together.

In order to gather three colours, the following rules shall be applied. The rules have been listed in order of preference:

— Select the three colours from the same part of the textile article;

— If the three colours do not come from the same part of the textile article, select these three colours from textile parts made of the same type of textile fibre;