
**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**

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*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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ISO 24362-1:2014

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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. www.iso.org/directives

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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 WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 38, *Textiles*.

ISO 24362 consists of the following parts, under the general title *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*
- Part 3: *Detection of the use of certain azo colorants, which may release 4-aminoazobenzene*

Introduction

This part of ISO 24362 is based on EN 14362-1:2012 which has been prepared by Technical Committee CEN/TC 248 "Textiles and textile products", the secretariat of which is held by BSI.

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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

1 Scope

This part of ISO 24362 describes a procedure 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 a reducing agent with and without extraction.

Azo colorants accessible to a reducing agent without extraction are those used to dye:

- cellulosic fibres (e.g. cotton, viscose);
- protein fibres (e.g. wool, silk);
- 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, modacrylic, aramid and chlorofibre.

For certain commodities made of cellulose and/or protein fibres blended with man-made fibres it is necessary to extract the dye first.

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

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

3 General

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

Table 1 — Aromatic amines subjected

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. The presence of these colorants should be tested by ISO 24362-3..

4 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 dyes.

The application of the combined methods or 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 relevant, if the test specimen is not discoloured during the application of one of the two methods, the other one is carried out.

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 chlorobenzene 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 chlorobenzene extraction, the specimen is added to the reaction vessel with the methanolic solution of the dispersed dye for combined reduction.

When the method for the other classes of the dyes 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 a solvent appropriate 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.

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5 Safety precautions

WARNING — The substances [amines] listed in [Clause 3](#) are classified as substances known to be or suspected of being human carcinogens.

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

5.2 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.

5.3 Good laboratory practice should be followed. Wear safety glasses in all laboratory areas and a single-use dust respirator while handling powder colorants.

5.4 Users should comply with any national and local safety regulations.

6 Reagents

Unless otherwise specified, analytical grade chemicals shall be used.

6.1 Chlorobenzene.

WARNING — This is a toxic chemical. To handle chlorobenzene, special care is required to prevent skin contact swallowing and aspiration.

6.2 Acetonitrile.

6.3 Methanol.

6.4 *t*-butyl methyl ether.

6.5 *n*-pentane.

6.6 Citrate/sodium hydroxide buffer solution, pH = 6, $c = 0,06 \text{ mol/l}^{1)}$.

6.7 Aqueous sodium dithionite solution, $\rho = 200 \text{ mg/ml}^{2)}$ freshly (daily) prepared.

6.8 Diatomaceous earth.

6.9 Amine substances, amines 1 to 21 (as specified in [Table 1](#)), and aniline and 1,4-phenylenediamine, all of the highest available defined purity standard.

6.10 Standard solutions.

6.10.1 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.

6.10.2 Calibration solution of amines for daily use.

Dilute from the stock solution [6.10.1](#) to a concentration of $\rho = 15,0 \mu\text{g}$ of each amine per millilitre of an appropriate solvent.

6.10.3 Calibration solutions of amines for quantification, concentration range from 2 μg up to 50 μg of each amine per millilitre of an appropriate solvent.

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

6.10.4 Internal standards in solution (IS), $\rho = 1,0 \text{ mg}$ of IS/ml of the appropriate IS solvent.

In case of GC-MS analysis, use one of the following internal standards:

- IS1: benzidine-d8, CAS No.: 92890-63-6;
- IS2: naphthalene-d8, CAS No.: 1146-65-2;
- IS3: 2,4,5-trichloroaniline, CAS No.: 636-30-6;
- IS4: anthracene-d10, CAS No.: 1719-06-8.

NOTE If the confirmation analysis for benzidine is done with DAD or TLC the use of IS1: benzidine-d8, CAS No.: 92890-63-6 is not feasible, because the peak cannot be separated from the none deuterated benzidine.

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

6.12 Grade 3 water, complying with ISO 3696:1987.

1) c is citrate concentration.

2) ρ is the mass concentration.

7 Apparatus

7.1 **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;
- 100 ml round bottom flask NS 29/32;
- heating source.



Figure 1 — Apparatus

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

7.2 **Ultrasonic bath**, capable of ultrasonic power 160 Watt RMS, with controllable heating equipment.

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

7.4 **Heating source**, capable of maintaining the temperature at $(70 \pm 2) ^\circ\text{C}$.

7.5 **Glass or polypropylene column**, inside diameter 25 mm to 30 mm, length 130 mm to 150 mm, packed with 20 g of diatomaceous earth ([6.8](#)), fitted with a 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.

7.6 **Vacuum rotary evaporator** with vacuum control and water bath.

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

7.7 **Pipettes** in required sizes or variable pipettes.

7.8 **Chromatographic equipment** selected from the following:

7.8.1 **Thin layer chromatography (TLC)** or high performance thin layer chromatography (HPTLC) equipment, including relevant detection.

7.8.2 **High performance liquid chromatography (HPLC) equipment**, with gradient elution and diode array detector (DAD) or mass selective detector (MS).

7.8.3 **Gas chromatography (GC) equipment**, with flame ionization detector (FID) or mass selective detector (MS).

7.8.4 Capillary electrophoresis (CE) equipment, with diode array detector (DAD).

NOTE A description of the chromatographic equipment is given in [Annex A](#).

8 Test specimen sampling and preparation

8.1 General

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

- Parts of the textile article;
- Nature of the fibre components (fibre composition);
- Printed materials;
- Colours.

Prepare the test specimen by cutting in order to obtain a total mass of 1 g. For specimens to be submitted to colorant extraction ([9.1](#)) cut into strips (if apparatus described in [7.1](#) is used) or cut into small pieces if other apparatus is used or for specimens to be submitted only to reductive cleavage ([9.3](#)).

8.2 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 that have direct and prolonged contact to skin or mouth, which can be:

- principal fabric(s);
- lining(s);
- pocket fabric(s);
- embroideries;
- label(s) for textile article;
- drawstring(s);
- fastener(s);
- false fur;
- 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 NOTE 2, [Annex C](#).)

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

NOTE If there are omitted portions of sampling because of less than 0,2 g, record the details in the test report.

Embroideries shall be weighed with the ground fabric.