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**NATIONAL STANDARD OF THE
PEOPLE'S REPUBLIC OF CHINA**

GB/T 23344-2009

Textiles - Determination of 4-aminoazobenzene

纺织品 4-氨基偶氮苯的测定

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Foreword

Annex A, Annex B, Annex C and Annex D in this Standard are informative. This Standard was proposed by China National Textile and Apparel Council. This Standard shall be under the jurisdiction of basic standard subcommittee of Technical Sub-Committee on Textiles of Standardization Administration of China (SAC/TC 209/SC 1). Drafting organizations of this Standard. Jiangsu Entry-Exit Inspection and Quarantine Bureau of the people's republic of china, Standardization Research Institute of Textile Industry, and Jiangsu High Hope International Group. Chief drafting staffs of this Standard. Cao Xizhong, Ding Youchao, Xu Xinhua, Feng Quanbing, Qian Kai, Tian Shu, Zhou Jia, and Chen Xiaoding. Textiles - Determination of 4-aminoazobenzene WARNING. The personnel using this Standard shall have practical experiences in regular laboratory work. This Standard does not point out all the possible safety problems. The users shall be responsible for taking appropriate safety and health measures and ensure to comply with the conditions specified in the relevant laws and regulations of the nation.

1 Scope

China's national method for determining 4-aminoazobenzene in textiles. It specifies the method for detecting and quantifying this compound in textile products. This is a short

standard that exists to close a specific gap in the azo dye regulations. Certain azo dyes cleave under reductive conditions to release aromatic amines that are carcinogenic, and the regulation of textiles worldwide bans dyes that release any of a listed set of them. The standard methods for that determination reduce the dye on the fabric with sodium dithionite and then identify the amines released. 4-aminoazobenzene is on the banned list, but it behaves differently from the others in a way that defeats the standard procedure: under the reducing conditions used it is itself cleaved further, into aniline and 1,4-phenylenediamine, so a dye that releases it produces no 4-aminoazobenzene in the analysis at all - and a laboratory following the general method reports a negative result on a fabric that in fact contains a banned dye. Detecting it therefore requires a different treatment: a milder reduction that liberates the compound without destroying it, followed by extraction and determination by chromatography with confirmation by mass spectrometry. That is what this standard specifies, and it is why the determination is a separate document rather than a clause in the general azo dye method. The scope covers the extraction from the textile, the reduction conditions, the chromatographic separation, the confirmation and the quantification, with the detection limit stated. Issued on 19 March 2009 and in force since 1 February 2010.

This Standard specifies test methods for determination of the 4-aminoazobenzene decomposed from some azo dyes in textile products by gas chromatography - mass spectrogram detection method (GC /MSD) and high performance liquid chromatography method (HPLC/DAD). This Standard is applicable to various textile products after dyeing and printing.

2 Normative References

The following documents contain provisions which, through reference in this text, constitute provisions of this Standard. For dated reference, subsequent amendments (excluding correction) or revisions of these publications do not be applied. However, the parties who enter into agreement according to these specifications are encouraged to research whether the latest editions of these references are applicable. For undated references, the latest edition of the normative document is applicable to these specifications.

GB/T 6682 "Water for analytical laboratory use - Specification and test methods" (GB/T 6682-2008, ISO 3696.1987, MOD)

GB/T 7592 "Textiles - Determination of the banned azo colourants"

3 Principles

The samples is reduced with sodium dithionite in alkaline medium; the decomposed 4-aminoazobenzene shall be extracted by appropriate liquid-liquid distribution method;

4 Reagent

Except otherwise specified, the reagents used shall be analytically pure, and water shall be grade 3 water in accordance with those specified in GB/T 6682.

4.1 Sodium chloride

4.2 Tertiary butyl methyl ether (CAS No.. 1634-04-4).

Note. if tertiary butyl methyl ether is not available, fresh ethyl ether may be used to replace it. Preparation method of fresh ethyl ether. take 500mL of ethyl ether and put it in 1000mL separating funnel. Add 100mL of 5% ferrous sulfate solution. Shake it violently. Discard the water layer. Put it in the all-glass device to distill it. Collect the distillate of 33.5°C ~34.5°C.

4.3 Acetonitrile (HPLC Grade).

4.4 Sodium hydroxide solution, 20g/L.

4.5 Sodium dithionite solution (200mg/mL). take sodium dithionite (content of Na₂S₂O₄ ≥ 85%), dissolve it with water. Prepare the fresh solution.

4.6 Standard solution

4.6.4 Anthracene-d₁₀ internal standard working solution (2 mg/L). prepare it with tertiary butyl methyl ether (4.2); this solution shall be prepared when using.

4.6.5 Mixed standard working solution. prepare it with tertiary butyl methyl ether (4.2).

5 Equipment and Instruments

5.1 Reactor. made of hard glass in shape of tubes with airtight plug, about 65mL.

5.2 Thermostatic water-bath. temperature may be controlled at (40±2)°C.

5.3 Mechanical oscillator. oscillation frequency is about 150 times/min.

6 Analytical Procedures

6.1 Preparation and reduction treatment of specimen Take representative samples; cut them into the chips of 5 mmx 5 mm; Mix them well; weigh 1.0g of the mixed sample, accurate to 0.01g;

6.2 Extraction

6.2.1 For gas chromatographic analysis Add accurately 10mL of anthracene - d₁₀ internal standard working solution (4.6.4) in the above reactor; add again 7g of sodium chloride (4.1); seal the reactor well; shaken forcibly for mixing completely; shake for 45min in

mechanical oscillator (5.3); Stand at still; after two-phase layering, take the supernatant liquor for GC/MSD analysis.

6.2.2 For high performance liquid chromatography analysis Add 10mL of tertiary butyl methyl ether (4.2) in above reactor; add again 7g of sodium oxide (4.1); seal the reactor; shake for 45min in mechanical oscillator after it is shaken for mixing; Stand at still; after two-phase layering, take the supernatant liquor through 0.45µm organic filter membrane for HPLC/DAD analysis.

6.3 Gas chromatography - mass spectrometry method

6.3.2 Qualitative and quantitative analysis Isometric cross injection shall be carried out to the mixed standard working solution (4.6.5) and the sample test solution (6.2.1); gas chromatograph (5.4) shall be adopted for its testing and analysis according to the requirements in 6.3.1.

6.4.1 HPLC/DAD analysis conditions As test result depends on the used instrument, so the general parameters of chromatographic analysis are impossible to be provided. It has proved that it is suitable to adopt the following operation conditions in the test. 6

4.2 Qualitative and quantitative analysis Isometric cross injection shall be carried out to 4-aminoazobenzene standard working solution (4.6.3) and sample test solution (6.2.2); high performance liquid chromatograph shall be adopted for its testing and analysis according to the requirements of 6.4.1. Carry out the qualitative analysis through comparison of the retention time between the sample and the standard sample, and ultraviolet spectrogram.

7.1 External standard method

7.3 Expression of results Test results shall be expressed in the concentration of 4-aminoazobenzene. The calculated results shall be expressed to its integer.

8 Detection Lower Limit, Recovery Rate and

8.1 Detection Lower limit The detection lower limit in this method is 5 mg/kg.

8.2 Recovery rate See Annex D.

8.3 Precision The tests are carried out in the same laboratory; in mutual independence; on the same tested object;