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National Standard

of People's Republic of China

GB 19601-2013

Replacing GB 19601-2004

Limit and determination of 23 harmful aromatic amines in dye products

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Standardization Administration of the People's Republic of China, SAC

Table of Contents

Foreword

All the technical content of this Standard is mandatory.

This Standard is drafted in accordance with the rules of GB/T 1.1-2009.

This Standard replaces GB 19601-2004 "Limit and determination of 23 harmful aromatic amines in dye products". Compared with GB 19601-2004, except editorial changes, the major technical changes are as follows:

- DELETE the analysis methods of gas chromatographic (4.4.3.2 in 2004 edition);
- Quantitative methods have been transformed from the external-standard method into the internal-standard method (see 5.5.3, 4.4.4.2 in 2004 edition);
- DELETE the column extraction from the sample-preparation methods (4.4.1 in 2004 edition);
- MODIFY the sample-preparation methods (see 5.5.1, 4.4.1 in 2004 edition);
- COMBINE qualitative parts and quantitative parts to analysis steps (see 5.5.2, 4.4.3 in 2004 edition);
- REMOVE the reserved time from Appendix A (Appendix A in 2004 edition);
- DELETE the recovery-rate table (Table 2 in 2004 edition).

This Standard is proposed by China Petroleum and Chemical Industry Federation.

This Standard is administered by the National Technical Committee of Dye Standardization (SAC/TC 134)

This Standard is drafted by organizations: Shenyang Chemical Institute Co., Ltd., Xuzhou Kaida Fine Chemical Co., Ltd., State-Key Laboratory of Fine Chemicals of Dalian University of Technology, Jiangsu Yabang Dye Co., Ltd., Beijing Institute of Clothing, Institute of Product Quality Supervision and Inspection of Taizhou City, and National Dye Quality Supervision and Inspection Center.

Chief drafters of this Standard: Ji Hao, Piao Kezhuang, Fu Ping, Peng Xiaojun, Zheng Junliang, Shen Rijong, Ji Lanqin, Zhou Yongkai, and Li Xinggen.

The standard of previous version replaced by this Standard is:

—GB 19601-2004.

Limit and determination of 23 harmful aromatic amines in dye products

Warning: Personnel using this Standard shall have practical working experience in qualified laboratory. This Standard does not point out all possible safety problems. Users are responsible for taking appropriate safety and healthy measures, and to ensure compliance with the relevant conditions of the national regulations.

1 Scope

This Standard specifies the allowable limit and determination methods of harmful aromatic amines in dye products (see Appendix A).

This Standard is applicable to all kinds of commercial dyes, dye products, dye intermediates and textile-dye auxiliaries.

2 Normative references

The following documents are indispensable for the application of this document. For dated references, only the dated edition is applicable for this document. For undated documents, the latest version (including all amendments) applies to this document.

GB/T 6682-2008 Water for analytical laboratory use. Specification and test methods (ISO, 3696:1987, MOD)

GB/T 8170-2008 Rules of rounding off for numerical values & expression and judgment of limiting values

3 Requirements

The content of harmful aromatic amines (see Appendix A) in dye products shall be less than 150mg (aromatic amines)/kg (product), in which the limit of harmful aromatic amines in dye products, such as solution dyes and pigment paste, shall be converted according to the solid content.

4 Principles

In dielectric of citrate buffer solution (pH=6.0), The dye sample uses sodium hyposulfite to achieve the reductive decomposition, and then uses the organic solvent to directly extract the aromatic amines from the lysis solution. After concentration, it uses gas chromatography-mass spectrometry instrument to detect.

5 Experimental methods

5.1 General provisions

Unless otherwise specified, it shall only use the reagents confirmed as analytical reagents and grade 3 water specified by GB/T 6682-2008. Judgment of the inspection results shall be conducted according to 4.3.3 rounding-value-comparison method in GB/T 8170–2008.

5.2 Reagents and materials

5.2.1 Standard sample of aromatic amines: 23 kinds of known-content harmful aromatic amines (see Appendix A).

5.2.2 Standard sample of internal standard: known-content internal standard (see Appendix B).

5.2.3 Chloroform.

5.2.4 Glacial acetic acid.

5.2.5 Citrate buffer solution: 0.06 mol/L aqueous solution, pH = 6 (TAKE 12.526g citric acid and 6.320g sodium hydroxide, DISSOLVE them in water, and then DILUTE to 1000 mL).

5 2.6 Sodium hyposulfite: 200 g/L aqueous solution, when using, TAKE solid sodium hyposulfite (content of $Na_2S_2O_4$ ≥ 85%) and DISSOLVE it in water for preparation.

5.2.7 The solution of sodium carbonate anhydrous: 200 g/L.

5.2.8 Volumetric flask: 10 mL, 25 mL.

5.2.9 Graduated pipettes: 1 mL, 5 mL.

5.2.10 Separating funnel: 60mL.

5.2.11 Grinding-mouth conical flask with stopper: 100 mL.

WEIGH 0.2g of sample (accurate to 0.0002g), PLACE in a 100mL grinding-mouth conical flask, ADD 24mL of citrate buffer solution, ADD 1.0mL of internal standard solution, COVER the stopper. PUT the conical bottle into the water-bath pan in which the temperature is 70°C±2°C to preheat for about 15 min, KEEP shaking from time to time, LET the sample to be completely dissolved as possible. At the same time, PREPARE sodium dithionite. After preheating, TAKE out the erlenmeyer flask, ADD 6.0 mL of sodium dithionite solution in each bottle, COVER with cork immediately, SHAKE well. PUT the conical bottle into the water-bath pan which is 70 °C ± 2°C to maintain for 30 min; SHAKE from time to time to make it fully restored. After restored, TAKE out the conical bottle and USE cool water to make it reach to room temperature quickly, USE anhydrous sodium carbonate solution to adjust to pH 8~9 (add about 5mL). Extract the sample three times with chloroform in a separating funnel, and each time USE 20mL of chloroform. ADD 2~4 drops of glacial acetic acid into the first-extracted solution for acidity. Three-time extracted solution shall be combined in a 125 mL grinding-mouth flat flask and be concentrated to a volume of about 1 mL on a rotating evaporator. REMOVE the concentrated liquid with a suction tube into a 10mL volumetric flask. WASH the flask repeatedly with chloroform, the lotion shall be also added into the volumetric flask, VOLUME to the mark with chloroform. This solution is the sample solution.

Non-water soluble dyes may be added with 3 mL ~ 5 mL of acetone before sample processing, so as to make it disperse in the buffer solution uniformly, then process it according to this Method.

5.5.2 Chromatography

5.5.2.1 Operating conditions of gas chromatography-mass spectrometry

Because test result depends on the instrument to be used, so it is impossible to provide general parameters of chromatography. Using following parameters (refer to Table 2) is proved to be suitable for test.

Table1 Operating conditions of gas chromatography-mass spectrometry instrument

5.5.2.2 Operation

According to the condition of content of tested-substance in the samples, SELECT mixed standard solution with similar concentration to determine. According to the above-mentioned chromatography conditions, TAKE 1.0μL of sample solution and standard solution respectively to determine, the obtained total ion chromatogram of gas chromatography-mass spectrometry refers to Appendix C, USE characteristic ion peak to qualify target compound (confirm target compound with other analysis methods if necessary), USE peak-area internal standard method to quantify.

5.5.3 Result calculation

The content of harmful aromatic amines in sample shall be represented by mass fraction ω_i, the value represented by mg/kg, calculated according to formula (1):

$$\omega_i = \frac{r_i m_s}{r_s m_i} \qquad \cdots\cdots(1)$$

In the formula:

r_i — The ratio of the harmful aromatic amines in sample solution and the response of internal standard;

m_s — The mass value of samples in mixed standard solution, the unit is μg;

r_s — The ratio of the harmful aromatic amines in mixed standard solution and the response of internal standard;

m_i — The mass value of samples in sample solution, the unit is g.

The result shall be represented in the nearest integer.

5.5.4 Spectrum

The total ion chromatogram of gas chromatography-mass spectrometry of harmful aromatic amines determined by this Method refers to Appendix C.

6 Minimum qualitative limit, recovery and precision

6.1 Minimum qualitative limit

The minimum qualitative limit of this Method is 20mg/kg, the determination result is “undetected” when it is below this limit.

6.2 Recovery

USE standard addition method, PUT 1mL of standard mixed solution into 0.2g of dye products that have been determined by this Method not containing harmful aromatic amines, OPERATE according to Chapter 5, the determined recovery of harmful aromatic amines shall be between 70% and 130%.

6.3 Precision

In same laboratory, USE the same instrument by same operator, according to same test method, the absolute difference values of two independent test results obtained from the independent tests of same object in a short period of time, shall not be greater than 30% of the arithmetic mean of these two determined values.

7 Test report

The test report shall provide following contents at least:

a) Description of sample;

b) Standard used;

c) Test result;

d) Difference of deviation standard;

e) Date of test.

Appendix C

(Informative)

Spectrum

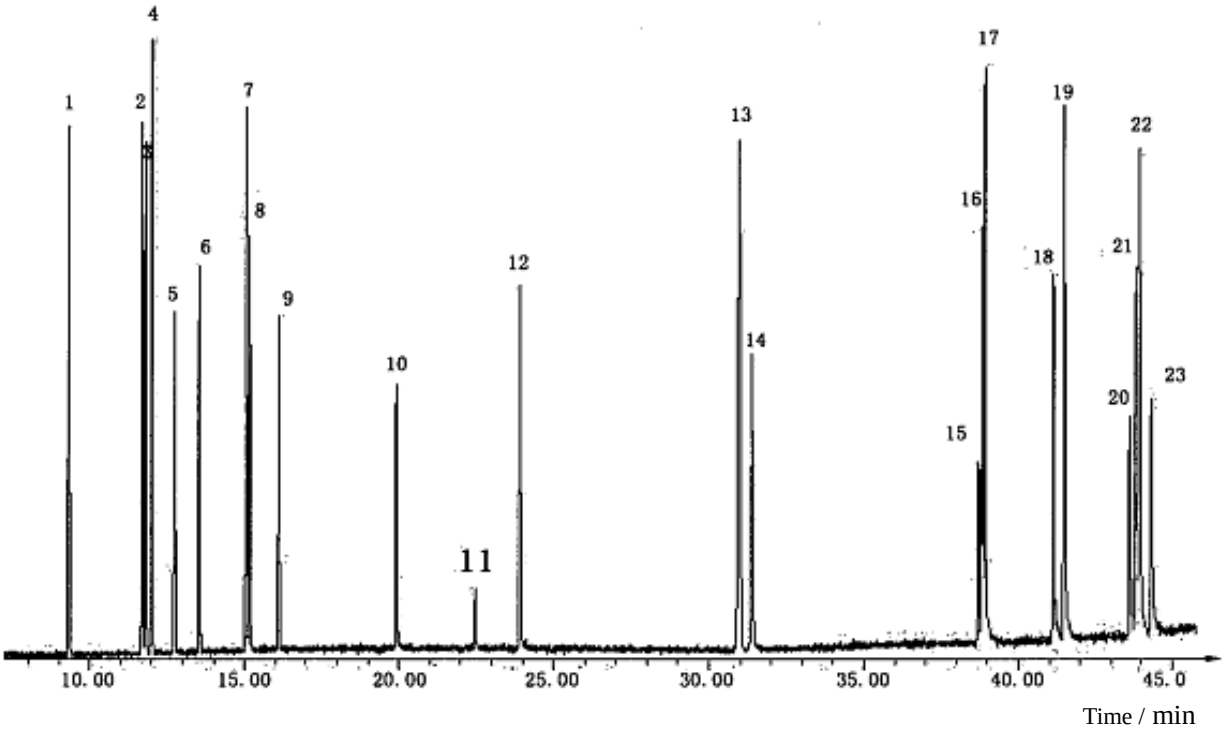

Illustration:

1— o-Toluidine;

2— 2,4-Xylidine;

3— 2,6-Xylidine;

4— Naphthalene;

5— o-Anisidine;

6— p-Chloroaniline;

7— 2,4,5-Trimethylaniline;

8— p-Cresidine;

9— 4-Chloro-2-toluidine;

10— 2,4-Toluylenediamine;

11— 2,4-Diaminoanisole;

12— 2-Napyhthylamine;

13— Anthracene;

14— 4-Aminodiphenyl;

15— 4,4’-Oxydianiline;

16— 4,4’-Diaminodiphenylmethane;

17— Benzidine;

18— 4,4’-Methylene-bis(2-chloroaniline);

19— 3,3’-Dimethylbenzidine;

20— 4,4’-Thiodianiline;

21— 3,3’-Dichlorobenzidine;

22— 3,3’-Dimethyl-4,4’Diaminodiphenylmethane;

23— 3,3’-Dimethosybenzidine.

Figure C.1 The total ion chromatogram of gas chromatography-mass spectrometry of harmful aromatic amines

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