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Determination of Migratable Chromium (VI) in Toy Materials - Ion Chromatography

玩具材料中可迁移六价铬的测定 离子色谱法

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WARNING: Persons using this Document shall have practical experience working in formal laboratory. This document does not address all possible security issues. It is the user's responsibility to take appropriate safety and health measures and to ensure compliance with the conditions stipulated by relevant national regulations.

1 Scope

This Document describes the use of ion chromatography to determine the migratable chromium (VI) in toy materials.

This Document is applicable to the achievable toy materials:

--- Category-1: dry, brittle, powdery or pliable toy materials;

--- Category-2: liquid or sticky toy materials;

--- Category-3: scratchable toy materials.

2 Normative References

The provisions in following documents become the essential provisions of this Document through reference in this Document. For the dated documents, only the versions with the dates indicated are applicable to this Document; for the undated documents, only the latest version (including all the amendments) is applicable to this Document.

GB/T 6682 Water for Analytical Laboratory Use - Specification and Test Methods

EN 71-3 Safety of Toys – Part 3: Migration of Certain Elements

3 Terms and Definitions

For the purposes of this Document, the terms and definitions given in EN 71-3 apply.

4 Principle

Migratable chromium (Ⅵ) is a Cr (Ⅵ) leachate extracted from the toy material under the condition that the toy material is continuously in contact with gastric acid for a period of time after being swallowed. In this Document, Cr (VI) was separated by anion exchange column and reacted with post-column derivatizing agent under certain pH conditions to form a purple-red complex, which can be determined by ultraviolet-visible (UV-Vis) detector; and quantify by the external standard method.

5 Reagents

Unless otherwise stated, only reagents confirmed to be analytically pure are used in the analysis.

5.1 Water, at least meet the requirements of Class-3 water specified in GB/T 6682.

5.2 0.07mol/L hydrochloric acid solution, c(HCl) = (0.07±0.005) mol/L.

5.3 Ammonia water, the mass fraction is 25%~28%.

5.4 Ammonia water (1+4), take 20mL of ammonia (5.3) and dilute to 100mL with water (5.1).

5.5 For 0.7mol/L ammonia solution, take 5.3mL of ammonia water (5.3) and dilute it with water (5.1) to 100mL.

5.6 For 0.035mol/L ammonium chloride solution, take 500mL of hydrochloric acid solution (5.2); titrate ammonia water (5.4); adjust the pH value to 7~8; and make constant volume to 1000mL by water (5.1).

5.7 1,5-Diphenylcarbazide, $C_{13}H_{14}N_4O$ (CAS number: 140-22-7).

5.8 Methanol, CH_3OH (CAS number: 67-56-1).

5.9 Sulfuric acid (ρ=1.84g/mL), the mass fraction is 98%.

5.10 Post-column derivatization agent: Accurately weigh 0.5g of 1,5-diphenylcarbazide (5.7) and dissolve it in 100mL of methanol (5.8); add 25mL of sulfuric acid (5.9) to about 500mL of water (5.1). After the sulfuric acid solution is cooled, transfer the above two solutions to a 1000mL volumetric flask; make constant volume to the mark with water (5.1); and filter with a membrane filter.

5.11 Potassium dichromate ($K_2Cr_2O_7$) standard substance, dried in an oven at (102±2) ℃ for (16±2) h before use.

5.12 Cr (Ⅵ) standard stock solution (1mg/mL): Take 2.829g potassium dichromate (5.11); dissolve, transfer, wash and make constant volume to a 1000mL volumetric flask with water

(5.1); each 1mL of solution contains 1mg of Cr (VI).

5.13 Cr (VI) standard solution (10μg/mL): Accurately pipette 1mL of Cr (VI) standard stock solution (5.12) into a 100mL volumetric flask; dilute and make constant volume with water (5.1) to the mark; each 1mL of solution contains 10μg of Cr (VI).

5.14 Cr (VI) standard solution (0.1μg/mL): Accurately pipette 1mL of Cr (VI) standard solution (5.13) into a 100mL volumetric flask; dilute and make constant volume with water (5.1) to the mark; each 1mL of solution contains 0.1μg of Cr (VI).

NOTE 1: This solution can be stored at 0 ℃ ~ 4 ℃ for 1 week; and return to room temperature before use.

NOTE 2: It can directly use the commercially available standard solution to prepare Cr (VI) standard solution (0.1μg/mL).

6 Apparatus

6.1 Ion chromatograph

With ultraviolet visible (UV-Vis) detector or diode array (DAD) detector and post-column derivatization device.

6.2 Electronic balance

The accuracy is 0.1mg.

6.3 pH meter

The accuracy is ±0.02 pH units.

7 Classification of Toy Materials

The toy materials can be divided into three categories.

--- Category-1: dry, brittle, powdery or pliable toy materials. Such materials refer to powdered materials that are released during play. These powdered materials can get on hands and may be swallowed.

--- Category-2: liquid or sticky toy material. Such materials are fluid or sticky materials that may be ingested into the body or come into contact with the skin during play.

--- Category-3: scratchable toy materials. Such materials refer to solid materials, whether coated or not, that can be ingested into the body during play, by biting, tearing with teeth, sucking or licking.

standard method for quantification.

If the mass concentration of Cr (Ⅵ) in the specimen solution exceeds the maximum mass concentration of the standard curve, it shall be properly diluted with ammonium chloride solution (5.6) before determination.

12 Blank Test

Blank test does not add sample; take the same amounts of all reagents; and use the same analysis procedures; it shall be determined in parallel with the sample.

13 Calculation of Results

The migratable Cr (VI) content in the specimen is calculated by mass fraction *w*; and the value is expressed in milligrams per kilogram (mg/kg), which shall be calculated according to Formula (1):

$$w = \frac{(\rho_1 - \rho_0) \times V \times V_2 \times d}{m \times V_1 \times 1\ 000} \qquad \cdots\cdots(1)$$

Where:

w – the migratable Cr (VI) content in the specimen, in mg/kg;

ρ_1 – the on-instrument test mass concentration of Cr (VI) in the specimen solution, in μg/L;

ρ_0 – the on-instrument test mass concentration of Cr (VI) in the specimen blank solution, in μg/L;

V – volume of the added simulation liquid, in mL;

V_2 — volume of migration solution after pH adjustment, in mL;

d – dilution factor (see 11.3);

m – mass of specimen, in g;

V_1 – pipetting volume of migration solution, in mL.

NOTE: If the specimen mass is 10mg ~ 100mg, the migratable Cr (VI) content of the specimen shall be calculated according to 100mg of used test specimen.

The calculation results shall be retained for 2 significant figures.

14 Mass Control

14.1 Quantification limit

The quantification limit for this method is 0.0025 mg/kg. The quantification limit for this method is related to the equipment configuration and chromatographic conditions used in the laboratory. The laboratory should confirm the quantification limit when using this method. When using the test results of this method for conformity assessment, the method quantification limit should be no greater than 50% of the limit value.

14.2 Precision

The precision test result data of this method can refer to Appendix B.

15 Test Report

The test report shall at least give the following:

a) specimen;

b) the used standard (including the year of publication or issuing);

c) results, including those covered in the Clause "Calculation of Results";

d) Details of the method used for the preparation of the test specimen (see Clause 8), including but not limited to the following:

--- the specimen is not separated from the matrix material;

---centrifugal separation of the solids in the specimen solution prior to analysis and testing;

--- additionally titrate hydrochloric acid to lower the pH;

--- additionally titrate ammonia water to adjust the pH;

--- the ratio of solid sample to acid extractant exceeds the range of 1:50;

e) any deviations from the specified sample preparation and extraction procedures due to protocol or otherwise;

f) abnormal phenomena observed in the test;

g) test date;

h) quantitation limit.

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