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Determination of certain phthalate esters in toys and children's products

玩具及儿童用品中特定邻苯二甲酸酯增塑剂的测定

(ISO 8124-6:2018, Safety of toys - Part 6: Certain phthalate esters in toys and children's products, MOD)

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Determination of certain phthalate esters in toys and children's products

1 Scope

This document describes the determination methods for the plasticizer requirements in 5.3.7 of GB 6675.1-2014.

This document describes the determination methods for 7 kinds of phthalate esters (according to the specifications in Table A.1) in toys and children's products, i.e., di-iso-butyl phthalate (DIBP), di-n-butyl phthalate (DBP), benzyl butyl phthalate (BBP), bis-(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DNOP), di-iso-nonyl phthalate (DINP) and di-iso-decyl phthalate (DIDP).

This document is applicable to toys and children's products containing polymers and similar materials, textiles, coatings and liquid materials, and applicable to 5.3.7 of GB 6675.1-2014. This document has been validated for polyvinyl chloride (PVC), polyurethane (PU) and some representative paint coatings, see Annex B. Other materials for toys and children's products can be determined with reference to this document after validation.

The test of other phthalate esters can refer to this document after validation.

2 Normative references

The contents of the following documents constitute the essential provisions of this document through normative references in the text. Among them, for dated references, only the version corresponding to the date applies to this document; for undated references, the latest version (including all amendments) applies to this document.

GB/T 454 *Paper - Determination of bursting strength* (GB/T 454-2020, ISO 2758:2014, MOD)

GB 6675.1-2014 *Toys safety - Part 1: Basic code*

GB 6675.2-2014 *Safety of toys - Part 2: Mechanical and physical properties* (ISO 8124-1:2000, MOD)

GB 6675.4-2014 *Safety of toys - Part 4: Migration of certain elements* (ISO 8124-3:2010, MOD)

prepare a series of standard working solutions (prepare at least 5 standard working solutions, of which the mass concentration of DIBP, DBP, BBP, DEHP, DNOP is 0.4 mg/L ~ 10 mg/L, and the mass concentration of DINP, DIDP is 2 mg/L ~ 50 mg/L), each of the working solutions contains 10 mg/L of the internal standard.

The mass concentration of the internal standard can be adjusted according to the mass concentration of the test portion, but the mass concentration of the internal standard in the final sample solution (8.3.3) shall be consistent with the mass concentration of the internal standard in the standard working solution. The standard working solution containing the internal standard should be stored at a temperature of 0 °C ~ 8 °C, and the validity period is 1 month.

6 Instruments and equipment

6.1 For normal laboratory glassware, phthalate esters are common contaminants, and even a small amount can affect quantitative results. It is recommended to avoid the use of any plastic equipment that may contaminate the analysis. Glassware and equipment should be cleaned before use.

6.2 Gas chromatography/mass spectrometry (GC-MS): equipped with a quartz capillary column and a mass spectrometer detector (EI source).

6.3 Soxhlet extractor: see Figure C.1. When necessary, with a cooling circulation device.

6.4 Solvent extractor (also known as fat extractor), see Figure C.2. When necessary, with a cooling circulation device.

6.5 Extraction thimble: made of cellulose.

6.6 Cotton wool.

6.7 Analytical balance: an accuracy of 1 mg.

6.8 Concentration apparatus: such as a rotary evaporator, etc.

6.9 Solid phase extraction cartridge (SPE): 1 g silica gel/6 mL tubes, or equivalent.

6.10 Volumetric flasks: of 5 mL, 10 mL, 25 mL, 50 mL and 100 mL capacity.

6.11 Pipettes: of 0.2 mL, 0.5 mL, 1 mL, 2 mL, 5 mL and 10 mL capacity.

6.12 Organic phase microporous membrane filter: of pore size 0.45 μm, recommended to use polytetrafluoroethylene (PTFE) microporous membrane filter.

6.13 Ultrasonic extractor: thermostatically controlled internally or externally, with the effective ultrasonic power density ranging from 0.25 W/cm^2 to 2.0 W/cm^2.

Example:

One of the following methods can be selected for extraction according to the actual situation.

8.2.1 Method A

Place the test portion in the extraction thimble (6.5) of a 250 mL Soxhlet extractor (6.3). In order to prevent the test portion from floating, cotton wool (6.6) can be placed on the upper layer of the extraction thimble.

Add 120 mL of dichloromethane (5.1) into a 250 mL round-bottom flask, extract for 6 h, and reflux at least 4 times per hour. If necessary, use a cooling circulation device for cooling and refluxing.

The volume of the dichloromethane can be adjusted according to the extraction equipment.

After cooling, use a suitable concentration apparatus (6.8) to concentrate until about 10 mL of the extract remains, and take care to prevent it from being completely evaporated to dryness.

It is recommended to control the temperature of the water bath of a rotary evaporator at 40 °C ~ 50 °C, while maintaining the pressure at 30 kPa ~ 45 kPa.

Care shall be taken to control the temperature of reflux and concentration to prevent the loss of phthalate esters.

8.2.2 Method B

Place the test portion in the extraction thimble (6.5) of a solvent extractor (6.4). In order to prevent the test portion from floating, cotton wool (6.6) can be placed on the upper layer of the extraction paper tube.

Add 80 mL of dichloromethane (5.1) into the extraction bottle, set a suitable temperature (such as 80 °C), make the dichloromethane boil and reflux, extract for 1.5 h, then rinse for 1.5 h; if necessary, use a cooling circulation device for cooling and refluxing. Finally, concentrate the extract to about 10 mL.

The volume of the dichloromethane can be adjusted according to the extraction equipment.

Care shall be taken to control the temperature of reflux and concentration to prevent the loss of phthalate esters.

8.2.3 Method C

8.2.3.1 Solid materials

Place the test portion in an airtight glass reaction vessel (6.15), and add 25 mL of dichloromethane. Place the container in an ultrasonic extractor (6.13), the liquid level in the ultrasonic tank shall be higher than the liquid level of the dichloromethane in the reaction vessel, start at (60 ± 2) °C, and continue ultrasonication for 60 min. The ultrasonic extractor performance check shall be carried out according to Annex E.

NOTE: If the material does not dissolve or swell in dichloromethane, Method A or Method B might be preferable.

8.2.3.2 Liquid materials

Place the test portion in an airtight glass reaction vessel (6.15), and add 15 mL of dichloromethane. Place the container in the ultrasonic extractor (6.13), the liquid level in the ultrasonic water tank shall be higher than the liquid level of the dichloromethane in the reaction vessel, start at (60 ± 2) °C, and continue ultrasonication for 60 min. The ultrasonic extractor performance check shall be carried out according to Annex E.

8.3 Preparation of analytical solutions

8.3.1 General

If the extract obtained in 8.2.1, 8.2.2 or 8.2.3 is turbid, it can be centrifuged with a centrifuge (6.16) at a centrifugal force of 5000 g before filtration. If necessary, the extract can be purified with a solid phase extraction cartridge (6.9). Before purification, pre-wash and activate with 10 mL of dichloromethane, discard the activation solution, and then load the test portion, rinse with 3 mL of dichloromethane for 3 times and collect the eluate.

The extract or the eluent, at room temperature, can be made up to the mark by 8.3.2 external standard method or 8.3.3 internal standard method according to the actual situation.

8.3.2 Constant volume (external standard method)

8.3.2.1 Method A and Method B

Transfer the extract or the eluent into a 25 mL volumetric flask, make up to the mark with dichloromethane, filter through the organic phase microporous membrane filter (6.12), for GC-MS (6.2) analysis.

The final constant volume can be adjusted according to the mass and concentration of the test portion. Care should be taken not to affect the limit of quantification (10.1).

8.3.2.2 Method C

8.3.2.2.1 Solid materials

f) Determination method: identification by full scan mode (full scan), quantification by selected ion monitoring (SIM).

8.4.2 Qualitative analysis

Qualitative analysis is performed by comparing the retention time of target substance and the relative abundance of characteristic ions in the test portion and the standard working solution.

The following conditions can be used to determine whether the sample contains the corresponding phthalate esters:

a) The deviation between the retention time of the target substance in the sample and the retention time of the target substance in the standard working solution is within ± 0.5 %;

b) The characteristic ions (see Table F.1) appear at the retention time of the target substance in the standard working solution;

c) The relative abundance of the characteristic ions is consistent with the relative abundance of the target substance in the standard working solution (if the relative abundance > 50 %, a deviation of ± 10 % is allowed; if the relative abundance is between 20 % ~ 50 %, a deviation of ± 15 % is allowed; if the relative abundance is between 10 % ~ 20 %, a deviation of ± 20 % is allowed; if the relative abundance is ≤ 10 %, a deviation of ± 50 % is allowed).

NOTE: Certain isomers of DINP or DIDP can interfere with the qualitative and quantitative determination of DINP or DIDP. For example, dipropyl heptyl phthalate (DPHP, CAS No. 53306-54-0) is one of the isomers of DIDP. It is difficult to separate DPHP from DIDP, but they can be identified by features such as peak shape, retention time and abundance ratio.

8.4.3 Quantitative analysis

8.4.3.1 General

The laboratory can choose the external standard method or internal standard method for quantification according to the actual situation. See G.4 for the selection conditions.

Select at least 5 standard working solutions (5.4 or 5.5.3) with different mass concentrations for determination, and plot a standard curve with peak area versus mass concentration. The linear correlation coefficient of the standard curve is not less than 0.995, and the corresponding value of phthalate easters in the sample solution shall be within the linear range of the instrument. If necessary, it can be diluted with dichloromethane.

Since GC-MS responds differently to DINP and DIDP standard substances with different CAS numbers, the laboratory shall try to select a standard substance similar to

the test portion, and at the same time indicate the CAS numbers of DINP and DIDP in the report, see Clause 12 f).

When integrating the peak area of isomers of DINP and DIDP, the baseline shall be flattened before integration.

NOTE: Due to the existence of inseparable isomers, the peaks of DNOP, DINP and DIDP are partially overlapped. By selecting m/z = 279 (DNOP), m/z = 293 (DINP) and m/z = 307 (DIDP) as quantitation ions, it can minimize the mutual interference.

8.4.3.2 Calibration curve (external standard method)

Calculate the slope and ordinate intercept of the standard curve according to formula (1):

$$A = a_1 \times \rho + b_1 \qquad \cdots\cdots(1)$$

where:

A - the peak area or sum of peak areas of the quantification ions of the certain phthalate esters in the standard working solution;

a_1 - the slope of the calibration curve, in liters per milligram (L/mg);

ρ - the mass concentration of the certain phthalate esters in the standard working solution, in milligrams per liter (mg/L);

b_1 - the ordinate intercept of the calibration curve.

8.4.3.3 Calibration curve (internal standard method)

Calculate the slope and ordinate intercept of the standard curve according to formula (2):

$$\frac{A}{A_{IS}} = a_2 \times \frac{\rho}{\rho_{IS}} + b_2 \qquad \cdots\cdots(2)$$

where:

A - the peak area or sum of peak areas of the quantification ions of the certain phthalate esters in the standard working solution;

A_{IS} - the peak area of the quantification ions of the internal standard in the standard working solution;

a_2 - the slope of the calibration curve;

ρ - the mass concentration of the certain phthalate esters in the standard working solution, in milligrams per liter (mg/L);

w_s - the content of the certain phthalate esters in the test portion, %;

A - the peak area or sum of peak areas of the quantitation ions of the certain phthalate esters in the test solution;

A_{IS} - the peak area of the quantitation ion of the internal standard in the test solution;

b_2 - the ordinate intercept of the calibration curve, which can be obtained from formula (2);

ρ_{IS} - the mass concentration of the internal standard in the sample solution, in milligrams per liter (mg/L);

a_2 - the slope of the calibration curve, which can be obtained from formula (2);

V - the constant volume of the test solution, in milliliters (mL);

m - the mass of the test portion, in grams (g);

D - the dilution factor.

NOTE: When the internal standard mass concentration of the sample solution is the same as that of the standard working solution, it is usually set the internal standard mass concentration $\rho_{IS} = 1$ in the internal standard method.

10 Quality control

10.1 Limit of quantitation

The limit of quantitation for the content of 7 phthalate esters in this document are:

DIBP, DBP, BBP, DEHP, DNOP: 0.001 %;

DINP, DIDP: 0.005 %.

10.2 Method blank test

A method blank test is required for each batch of samples. Except that no sample is added, it uses the same test procedure as the sample test. The results of the blank test can be used to assess the contamination of the test process. The result of the blank test shall be less than the limit of quantitation (10.1).

10.3 Recovery rate

Take 1 mL of the standard stock solution (5.3) as a sample and operate according to the procedures in Clause 8 and Clause 9. The recovery rate of each phthalate ester is 80 % ~ 120 %.

Annex D

(informative)

Composite test

D.1 Introduction

Composite test of similar materials is an effective screening method to reduce testing costs. However, there are also many difficulties in composite test, such as the complexity of the test matrix, interpretation of the analytical results and unpredictable chemical reactions between different materials. These factors usually lead to wrong conclusions. Therefore, composite test can only be used when a qualitative conclusion is sufficient to determine that the material meets the requirements. The composite test described in this annex is only for screening purposes.

It is worth noting that composite test is not used to solve the lack of mass of a test portion, and composite test cannot get more accurate results. If the mass of a test portion is not enough for a single test, it is also not possible to carry out a composite test either.

D.2 Preparation of composite test portions

Composite test portions shall meet the following conditions:

a) Only a maximum of three test portions can be combined to form a composite test portion.

b) Only similar materials can be combined for composite test. Different types of materials are not suitable for composite test, such as plastics and paint coatings cannot be made into a composite test portion.

c) The mass of each test portion for composite test shall be similar. The difference in mass between any two test portions shall not exceed 10 %. The mass of each test portion in composite test shall be controlled within the range of 100 mg ~ 500 mg.

D.3 Test procedure

The test procedures specified in Clause 8 can be used for composite tests.

D.4 Calculation

The average content of the certain phthalate esters in composite tests and the maximum content of the certain phthalate esters in the individual test portions can be calculated by formula (D.1) and formula (D.2), respectively.

NOTE: Take into account the testing capability, the variability of different laboratories and the diversity of materials, laboratories can select an appropriate safety factor based on their experience and historical data accumulated. This document recommends 60 % as a safety factor, which is based on practical analysis conclusions of phthalate esters.

D.6 Test report

In addition to the information given in Clause 12, the test report shall include the following information:

a) indicate the test portions for the composite test;

b) the average content of the certain phthalate esters in the composite test portion (based on the total amount), the value is expressed in %;

c) the maximum content of the certain phthalate esters in the composite test portion (based on the minimum amount), the value is expressed in %.

D.7 Examples

Assume that a composite test portion consists of a physical mixture of three PVC plastics, labeled A, B, and C, with corresponding masses of 0.3054 g, 0.3125 g and 0.3250 g, respectively. After constant volume, the volume of the composite test portion solution is 25 mL, and the DEHP content in the test result of the composite test portion solution is 5.90 mg/L.

Refer to the formula (D.4) for the calculation of the average content of phthalate esters in the composite test portion:

$$w_{avg} = \frac{5.90 \times 25}{0.305\ 4 + 0.312\ 5 + 0.325\ 0} \times \frac{1}{10\ 000} = 0.015\ 6\% \quad \cdots\cdots\cdots\cdots (D.4)$$

Refer to the formula (D.5) for the calculation of the maximum content of phthalate esters in the individual test portions:

$$w_{max} = \frac{5.90 \times 25}{0.305\ 4} \times \frac{1}{10\ 000} = 0.048\ 3\% \quad \cdots\cdots\cdots\cdots\cdots\cdots (D.5)$$

If the regulated limit of DEHP is 0.1 %; the safety factor is set at 60 %.

- the maximum DEHP content in an individual test portion is 0.0483 %, which is lower than the safety limit of 0.1 % × 0.6 = 0.06 %, and individual test is not required.

- see Table D.1 for the test result report.

Annex E

(normative)

Ultrasonic extractor performance check

E.1 Introduction

Not all ultrasonic extractors are suitable for extracting phthalate esters from toys and children's products. It shall select a suitable ultrasonic extractor (6.13) and check its performance regularly. This annex describes the performance check procedure.

E.2 Principle

The ultrasonic extractor includes an ultrasonic generator, an ultrasonic transducer and a stainless steel tank. The ultrasonic generator generates a high-frequency oscillation signal, which is converted into high-frequency mechanical oscillation waves by the ultrasonic transducer to act on the liquid in the stainless steel tank, "tearing" the liquid apart, leaving millions of microscopic "voids" or "partial vacuum bubbles" (cavitation). These bubbles release enormous (mechanical) energy, which breaks down the contents in the liquid into pieces. In this method, ultrasonic waves are applied to the aluminum foil, forcing the foil to form small perforated holes. The intensity of ultrasonic waves is related to the perforated rate of the aluminum foil. The performance check of the ultrasonic extractor is carried out by calculating the perforated rate of the aluminum foil during the ultrasonic process, not by measuring the sound intensity.

E.3 Instruments and equipment

E.3.1 Aluminum foil: the purity is not less than 85 %, the thickness is (0.020 ± 0.001) mm, and the bursting strength is (185 ± 10) kPa.

Use a thickness measuring device to measure the thickness of aluminum foil according to 5.10 in GB 6675.2-2014. The thickness is measured at 10 equidistant points across the diagonal.

Use a bursting strength measuring device to measure the bursting strength of aluminum foil according to GB/T 454.

E.4 Analysis procedure

Perform a performance check on the ultrasonic extractor as follows:

a) Spread a piece of aluminum foil on the bottom of the ultrasonic basket and smooth it out, avoiding wrinkles.

b) Hang the hanging basket in the ultrasonic extractor, make sure that the distance between the lower surface of the hanging basket and the bottom of the tank is

Annex G

(informative)

Background and rationale

G.1 Introduction

Plastics, including polyvinyl chloride (PVC), are the main materials for toys and children's products, and are widely used in industrial production. In the production process of PVC, it is often necessary to add some plasticizers (such as phthalate esters) to increase its plasticity. As certain phthalate esters are considered to be estrogens and environmental hormones, and can accumulate in organisms through the food chain, their impact on organisms and the environment has received more and more attention. Therefore, since 1999, some countries and regions have gradually begun to formulate regulations to restrict the use of certain phthalate esters. At the same time, some related test methods have also been proposed, but there are large differences between these methods.

In toys and children's products, in addition to PVC, PU plastics, textiles and paint coatings may also contain phthalate esters. This document aims to provide test methods for phthalate esters in materials that may contain plasticizers in various toys and children's products.

G.2 Other phthalate eaters in toys and children's products

This document has validated 7 phthalate esters, DIBP, DBP, BBP, DEHP, DNOP, DINP and DIDP in toys and children's products. Validated test of other phthalate esters can also refer to this document.

G.3 Extraction and test techniques

When preparing samples, the sample can also be milled or ground into a representative powder, but cross-contamination shall be avoided.

Soxhlet extraction, solvent extraction, microwave extraction and ultrasonic extraction can all be used to extract phthalate esters in toys and children's products. Among them, Soxhlet extraction is a classic and most widely used organic extraction method, and its apparatus is relatively simple and easy to obtain commercially. Solvent extraction is an improvement of the classic Soxhlet extraction method to provide a simpler and faster sample extraction method. Both methods have been validated as effective extraction methods for phthalate esters.

Ultrasonic extraction has been validated as an effective extraction method (see 8.2.3).

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