1.9 The requirements of phthalates for “plasticized material” in toys

The requirements of 1.9 shall apply to the following toys;

(1) Toys specified in Article 78 (1) of the Enforcement Regulations of the Food Sanitation Law (hereinafter referred to as “Designated Toys”).

(2) Non-Designated Toys which are intended for children under 6 years of age.

For the purpose of this standard, “polyvinyl chloride,” “polyurethane” and “rubber” shall be tested as “plasticized material.”

The applicable testing method is specified in 2.10.

1.9.1 Bis(2-ethylhexyl) phthalate(DEHP), dibutyl phthalate(DBP) or butyl benzyl phthalate(BBP) shall not be used at concentrations of greater than 0.1% by mass of the plasticized material in Designated Toys (toys specified under 1.9 (1) above).

1.9.2 Regarding Designated Toys that are intended to come into direct contact with infants’ mouths (excluding pacifiers and teethers made of synthetic resin containing polyvinyl chloride),

(1) Di-isononyl phthalate(DINP), di-isodecyl phthalate(DIDP) or di-n-octyl phthalate(DNOP) shall not be used at concentrations of greater than 0.1% by mass of plasticized material in parts (of toys) that are intended to come into direct contact with infants’ mouths, or

(2) Di-isononyl phthalate(DINP) shall not be used at concentrations of greater than 0.1% by mass of synthetic resin mainly composed of polyvinyl chloride in parts (of toys) that are not intended to come into direct contact with infants’ mouths.

1.9.3 Synthetic resin containing polyvinyl chloride shall not be used in pacifiers and teethers.

1.9.4 For the toys specified under 1.9 (2) above, the requirements for bis (2-ethylhexyl) phthalate(DEHP) in 1.9.1 and di-isononyl phthalate(DINP) in 1.9.2 shall be applied to synthetic resin containing polyvinyl chloride.

2.10 Test method for 6 phthalates for “plasticized material” in toys

Regarding the tests hereof, other test methods may be employed provided that they are recognized to be equal or better ones in specificity, detection limit or clearance of interference peaks.

1. Apparatus

Gas chromatograph/mass spectrometer (GC/MS)

or

Gas chromatograph equipped with hydrogen flame ionization detector（GC-FID）

2. Reagent, Reagent solution

(1) Standard substances of phthalates

Dibutyl phthalate (DBP) $C_6H_4[COO(CH_2)_3CH_3]_2$

Containing 97.0% or more dibutyl phthalate (DBP)

Benzyl butyl phthalate (BBP) $C_6H_4(COOCH_2C_6H_5)COO(CH_2)_3CH_3$

Containing 95.0% or more benzyl butyl phthalate (BBP)

Bis (2-ethylhexyl) phthalate (DEHP) $C_6H_4(COOCH_2CH(C_2H_5)C_4H_9)_2$

Containing 97.0% or more bis (2-ethylhexyl) phthalate (DEHP)

Di-n-octyl phthalate (DNOP) $C_6H_4(COO(CH_2)_7CH_3)_2$

Containing 97.0% or more di-n-octyl phthalate (DNOP)

Di-isononyl phthalate (DINP) $C_6H_4(COOC_9H_{19})_2$

Containing 96.0% or more di-isononyl phthalate.(DINP)

Di-isodecyl phthalate (DIDP) $C_6H_4(COOC_{10}H_{21})_2$

Containing 97.0% or more di-isodecyl phthalate(DIDP)

(2) Standard solution

① “Standard stock solution” of dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), bis (2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DNOP), di-isononyl phthalate (DINP) or di-isodecyl phthalate (DIDP)

Dissolve 10.0 mg of each “standard substance” in acetone to obtain 100 ml of solution for each phthalate. (100 μg/ml)

② “Phthalates standard solution (for GC/MS)”

Mix 1ml of each “standard stock solution” of 6 phthalates and add acetone to obtain 100 ml of solution. (1 μg/ml each)

③ “Phthalates standard solution (for GC-FID)”

Obtain the following 3 solutions (10 μg/ml each)

(a) Mix 1ml of each “standard stock solution” of dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), bis (2-ethylhexyl) phthalate (DEHP) and di-n-octyl phthalate (DNOP), and add acetone to obtain 10 ml of solution.

(b) Add acetone to 1 ml of “standard stock solution” of di-isononyl phthalate (DINP) to obtain 10ml solution.

(c) Add acetone to 1 ml of “standard stock solution” of di-isodecyl phthalate (DIDP) to obtain 10ml solution.

3. Preparation of test solution

Cut the test portion into pieces or pulverize the test portion. Weigh accurately 1.0 g of them and put them into the Erlenmeyer flask of 100 ml with ground-in stopper.

Add 50 ml of mixed solution of acetone and hexane (3:7) and seal the flask tightly.

After shaking, allow to stand it for one night while maintaining the temperature at 40° C.

After cooling, filter the solution using filter paper and put the filtrate and washings (acetone) into the volumetric flask of 100 ml, then add acetone to obtain 100 ml of test solution for GC-FID.

Dilute this GC-FID test solution with acetone to one tenth (1/10) of the amount to obtain GC/MS test solution.

4. Operation

(1) Characterization Test

Using 1 μl of “test solution” and 1μl of “phthalates standard solution”, characterize the test solution under the operation condition on GC/MS or GC-FID as described below. Compare the retention time of peak and peak pattern in chromatograph for “test solution” with the retention time of each peak and peak pattern of dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), bis (2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DNOP), di-isononyl phthalate (DINP) or di-isodecyl phthalate (DIDP) in chromatograph for “phthalates standard solution.”

The chromatogram refers to Ion chromatogram in GC/MS and Gas chromatogram in GC-FID.

(2) Content Determination Test

When the retention time of peak and peak pattern for any one or more phthalate in chromatograph for “test solution” is equal to retention time of peak and peak pattern in chromatograph for “phthalates standard solution” in the characterization test, proceed with the following test.

When the peak area of the relevant phthalate in test solution is measured based on the result obtained under the “operation condition” of (1) Characterization Test, the peak area must not be larger than the peak area of the same phthalate in standard solution.

When this is satisfied, the amount of the corresponding phthalate in the test sample is

0.1% or less.

(3) Confirmation Test

When the requirements for “(1) Characterization Test” or “(2) Content Determination Test” conducted by GC-FID have not been satisfied, perform “(1) Characterization Test” using GC/MS and confirm that the retention time of peak and peak pattern of compound in the test solution is equal to those of the phthalates standard solution.

Operation Condition

Column: Fused silicate narrow tube of 0.25 mm in internal diameter and 30 m in length, covered with coating of 0.25μm thickness of methyl silicone (containing 5% phenyl silicone) for gas chromatograph

Column Temperature: From 100°C, increase temperature by 20 °C every minute. After reaching 320 °C, maintain for 10 minutes.

Temperature of Injection Inlet for Test Solution: 250 °C

Detector: Operate at 280 °C.

In case of GC/MS, the following ions shall be used for determination;

Ion of 149 in mass number for dibutyl phthalate (DBP), benzyl butyl phthalate (BBP) and bis (2-ethylhexyl) phthalate (DEHP)

Ion of 279 in mass number for di-n-octyl phthalate (DNOP)

Ion of 293 in mass number for di-isononyl phthalate (DINP)

Ion of 307 in mass number for di-isodecyl phthalate (DIDP)

Carrier gas: Helium or nitrogen shall be used. Adjust the flow speed of carrier gas so that bis (2-ethylhexyl) phthalate (DEHP) may flow out in about 10 minutes.

5. Remarks

(1) As dibutyl phthalate (DBP) and bis (2-ethylhexyl) phthalate (DEHP) can be found in the environment, a blank test should be conducted under the same operation procedure without a test sample.

When the peak of phthalates is detected in the blank test solution, see that the peak area of the blank test solution is less than one-tenth of the peak area of the standard solution of each phthalate. If the peak area of the blank test solution exceeds one-tenth of the peak area of the standard solution of each phthalate, it is recommended the test to be conducted after diminishing the peak area of the blank test solution less than one-tenth of the peak area of the standard solution of phthalates by, for example, using new solvent.

(2) In the analysis using GC-FID, the retention times of di-n-octyl phthalate (DNOP), di-isononyl phthalate (DINP) and di-isodecyl phthalate (DIDP) are so close that some parts of these peaks may overlap.
This is why three kinds of “phthalates standard solutions” are prepared for GC-FID.

(3) When the requirements as for specified test sample relate to only three phthalates (dibutyl phthalate (DBP), benzyl butyl phthalate (BBP) and bis (2-ethylhexyl) phthalate (DEHP)), a standard solution containing only these three phthalates may be prepared.

(4) Attention needs to be paid as there is some possibility of misidentification between bis (2-ethylhexyl) terephthalate (DEHTP) and di-n-octyl phthalate (DNOP), since they have similar retention time and both of them have the same fragment ion of 279 in mass number.

When any peak is detected within the retention time of di-n-octyl phthalate (DNOP), identify whether or not it is di-n-octyl phthalate (DNOP) by comparing the mass spectrum of the standard solution which is measured under “SCAN mode” in GC/MS.

Or, analyze under the modified “operation condition” such as modifying the column temperature so that the retention times of bis (2-ethylhexyl) terephthalate (DEHTP) and di-n-octyl phthalate (DNOP) can be distinguished from each other.

An example of modified “operation condition” is shown below;

Column Temperature: After holding 1 minute at 50°C, increase temperature by 20 °C every minute.
After reaching 200 °C, increase temperature by 10 °C every minute.
After reaching 320 °C, maintain for 10 minutes.

Carrier gas: Helium or nitrogen shall be used.
Adjust the flow speed of carrier gas so that bis (2-ethylhexyl) phthalate (DEHP) may flow out in about 15 minutes.

(5) When interference peaks which prevent from testing are detected in chromatograph, remove impurities which cause the interference peaks by, for example, purifying.
Following the above treatment, conduct “Characterization Test” and “Content Determination Test” by GC/MS. Secure appropriate recovery rates and reproducibility in the purifying.

The following is an example of operation to clear interference peaks for rubber;

Conduct the vacuum concentration on 1 ml of “test solution for GC-FID” at 40° C or lower. Dissolve it by adding 2ml of hexane.

Inject this solution into an “alumina mini-column.”

(The alumina mini-column has been prepared to be run off by “10 ml of mixed solution of acetone and hexane (3:7)” and “10 ml of hexane” respectively.)

After running 10 ml of hexane through the alumina mini-column, inject acetone to obtain 10 ml solution as a test solution.

When interference peaks cannot be cleared by the above operation, remove impurities which cause the interference peaks by florisil-column chromatography, gel permeation chromatography or etc.