UNITED STATES
CONSUMER PRODUCT SAFETY COMMISSION
DIRECTORATE FOR LABORATORY SCIENCES
DIVISION OF CHEMISTRY
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Test Method: CPSC-CH-C1001-09

Standard Operating Procedure for Determination of Phthalates*

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This document provides detailed information on test methods that will be used by the U.S. Consumer Product Safety Commission's (CPSC) testing laboratory (LSC) for the analysis of phthalate content in child care items and toys.

CPSC staff has concluded that these test methods are sufficient to determine the concentration of the six regulated phthalates in most consumer products. Adjustments may be necessary for products made from certain materials, and should be based on sound chemistry and materials science knowledge as well as appropriate solvents for the materials. The general approach is to grind the sample to a powder by cryogenic milling, dissolve it completely in tetrahydrofuran, precipitate any PVC polymer with hexanes, filter and then dilute the solution with cyclohexane, and analyze by Gas Chromatography-Mass Spectrometry (GC-MS).

Definitions

1. Sample – An individual consumer product or a group of identical consumer products from a batch to be tested.
2. Component Part – Individual sub-unit within a product.
3. Laboratory Reagent Blank (LRB) – An aliquot of solvents that is treated exactly as a sample including exposure to glassware, apparatus and conditions used for a particular test, but with no added sample. LRB data are used to assess contamination from the laboratory environment.
4. Stock Standard– Phthalate(s) purchased from reputable commercial source at the highest available purity, used to prepare calibration standards. Replace before expiration date.

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*This document was prepared by CPSC staff, has not been reviewed or approved by, and may not necessarily reflect the views of, the Commission.

5. Calibration Standard – Solutions containing between 0.05 to 10 µg/ml of the phthalate(s) of interest in cyclohexane. Each standard should contain 1 µg/ml internal standard. A minimum of 4 calibration standards are used. Calibration standards should be prepared weekly from the stock solution and may be stored at room temperature (record weight of solutions before and after use to monitor for solvent evaporation).
6. Quality Control Sample (QCS) – Solutions containing known amounts of phthalates that are used to evaluate the performance of the analytical instrument system. QCSs are obtained from a source external to the laboratory and are not made from the Stock Standard solutions. For example, certified reference materials (CRMs) are available from the National Institute of Standards and Technology (NIST), such as those listed in the Equipment and Supplies section below.

Equipment and Supplies

The materials used for sampling and analyses are as follows:
1. Tetrahydrofuran (C_4H_8O, THF), GC grade or higher
2. Hexane (C_6H_{12}), GC grade or higher
3. Cyclohexane (C_6H_{12}), GC grade or higher
4. Sealable 25 ml glass vials with PTFE or silicone liner; or similar
5. Cryogenic-mill (or suitable alternative to grind samples to powder)
6. 0.45 µm PTFE filters
7. Agilent 6890 Series Gas Chromatograph with HP-5MS; 30m x .22 mm ID x 0.25 µm column and 5973 Mass Selective Detector, or equivalent
8. CRMs containing phthalates (such as NIST SRM 3074)
9. Benzyl Benzoate ($C_{14}H_{12}O_2$, BB), Analytical grade
10. Dibutyl Phthalate ($C_{16}H_{22}O_4$, DBP), CAS No. 84-74-2. Analytical grade
11. Di-(2-ethylhexyl) phthalate ($C_{24}H_{38}O_4$, DEHP), CAS No. 117-81-7. Analytical grade
12. Benzyl Butyl Phthalate ($C_{19}H_{20}O_4$, BBP), CAS No. 85-68-7. Analytical grade
13. Di-n-octyl phthalate ($C_{24}H_{38}O_4$, DnOP), CAS No. 117-84-0. Analytical grade
14. Diisononyl phthalate ($C_{26}H_{42}O_4$, DINP), CAS No. 28553-12-0/68515-48-0. Analytical grade
15. Diisodecyl phthalate ($C_{28}H_{46}O_4$, DIDP), CAS No. 26761-40-0/68515-49-1. Analytical grade

Measurement of Phthalate Concentration

These methods require the use of hazardous materials. It is paramount to properly handle all hazardous materials safely in a ventilated fume hood with adequate personal protective equipment.

Phthalates are a common contaminant. Even low levels of contamination can impact quantitative results. Avoid plastic materials and use only scrupulously cleaned glassware and equipment. All solvents should be tested for any phthalate content. Solvent blanks should be run through the GC-MS periodically to monitor for potential contamination. Disposable glassware is recommended where practical.

The procedure described below shall be used for all Compliance Determinations. In addition to the procedure described herein, the following three methods are acceptable to

CPSC staff for certification testing as acceptable alternative methods to measure phthalate concentration. However, the Sample Preparation method described below must be performed prior to the alternative analysis:

- ASTM D 7083-04[1]
- EPA 8061[2] (http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/8061a.pdf) in conjunction with one of the following extraction methods:
  - EPA 3540C, Soxhlet Extraction (http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3540c.pdf)
  - EPA 3541, Automated Soxhlet Extraction (http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3541.pdf)
  - EPA 3545A, Pressurized Fluid Extraction (http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3545a.pdf)
  - EPA 3546, Microwave Extraction (http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3546.pdf)
  - EPA 3550C, Ultrasonic Extraction (http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3550c.pdf)
- Health Canada Method C-34[3] (http://www.hc-sc.gc.ca/cps-spc/prod-test-essai/_method-chem-chim/c-34-eng.php)

Sample Preparation

Prior to analysis, the sample must be converted from its initial state to a representative, uniform sample (i.e., a homogeneous mixture of component parts). Due to the potentially complex nature of toys and children's articles, two approaches may be used to prepare the sample:

A. Basic Sample Preparation

1. Remove any batteries, other power sources, or compressed gas canisters from the sample – these will not be tested or considered part of the sample. (Testing batteries could present environmental and safety hazards due to the internal components of some batteries.) Weigh sample.

2. Grind, mill or otherwise comminute the entire sample. For large samples or certain inhomogeneous components such as printed circuit boards, motors, etc., grind samples down in stages (e.g., grind sample in cutting mill with relatively large sieve, re-grind sample in mill with smaller sieve).
Sample may be cooled in a liquid nitrogen bath prior to milling/grinding to increase effectiveness.

3. Ensure particle size of sample is minimized. An apparatus such as a cryogenic mill or a ball mill should reduce the particle size to a fine powder (<500 µm). Thoroughly mix sample.

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[1] Standard Practice for Determination of Monomeric Plasticizers in Poly (Vinyl Chloride) (PVC) by Gas Chromatography

[2] Phthalate Esters by Gas Chromatography with Electron Capture Detection (GC/ECD)

[3] Determination of Phthalates in Polyvinyl Chloride Consumer Products

B. Sum of Component Parts

1. Detach easily separable parts from the toy.
2. Weigh each part*.

   **Note:* Certain parts, such as unpainted metal, glass or ceramic parts would be considered as phthalate-free and would need only to be weighed for inclusion in the overall toy weight.
3. Grind each component part (or groups of inhomogeneous parts that cannot be easily separated) to a powder using the Basic Sample Preparation procedure listed above.
4. After following the analysis method for each part, mathematically combine the results for the various parts to determine the overall phthalate concentration in the toy.

Phthalate Extraction Method

Method should be performed in triplicate. Prepare LRB concurrently with samples.

1. Weigh out a minimum of 0.05±0.005 g of sample into a sealable glass vial (weighed to an accuracy of ±0.5% relative); if sample is not uniform, collect more to reduce sample variance.
2. Add 5 ml of THF to the sample. For samples larger than 0.05 g, add 10 ml of THF for every 0.1 g of sample (or a reasonable amount to dissolve sample*). Shake sample for at least 30 minutes to allow dissolution*.

   **Note:* Some materials may not dissolve completely. In this case, add an additional two hours to shaking time and then proceed.
3. Precipitate any PVC polymer with 10 ml of hexane for every 5 ml of THF used in Step 2. Allow at least 5 minutes for polymer to settle (longer times may be necessary to minimize clogging of filters in subsequent step).
4. Filter THF/hexane solution through a 0.45 µm PTFE filter. Collect at least 2 ml of filtered solution. (If the filter becomes clogged, it may be necessary to change filters repeatedly until sufficient filtered solution has been collected.)
5. Combine 0.1 ml* of the filtered THF/hexane solution with 80 µl of internal standard (BB, 250 µg/ml) and dilute to 20 ml with cyclohexane.

   **Note:*

   Depending on the phthalate concentration, a different dilution ratio may be necessary to produce results in the calibration range. (e.g., if the sample is known to contain <5% phthalate, increase the amount of filtered THF/hexane solution from 0.1 ml to 1 ml).
6. Transfer diluted sample to a GC-MS ready vial for analysis.

GC-MS Operating Procedures and Quality Control Measures

A GC-MS system with an automatic injector is suggested for the sample analysis.
The following GC conditions are used (Table 1):

Table 1. GC Conditions

Column	HP-5MS; 30m x .22 mm ID x 0.25 µm
Initial Flow Mode	1 ml/min, constant flow (He gas)
Injection Mode	Pulsed splitless
Injection Amount	1 µl
Injection Port Temp	290° C
Pulse Pressure & Time	35 psi, 0.5 min
Purge Flow & Time	20 ml/min, 2 min
Solvent Delay	5 minutes
Initial Oven Temp, Hold Time	50° C, 1 min
Ramp Temp 1, Plateau	30° C/min, 280° C
Ramp Temp 2, Plateau	15° C/min, 310° C
Final Hold Time	4 minutes

Samples are analyzed using the Select Ion Monitoring (SIM) program listed in Table 2. Scan for corresponding ions of each compound listed in a particular stage (e.g., set SIM Stage 3 to scan for 149, 167, 261, 279, 293, and 307 *m/z*). Note that retention times and optimal *m/z* scan values may differ between instruments. For many instruments it will be possible to program the detector to scan for the various ions in the different stages within a single run.

Table 2. SIM Settings

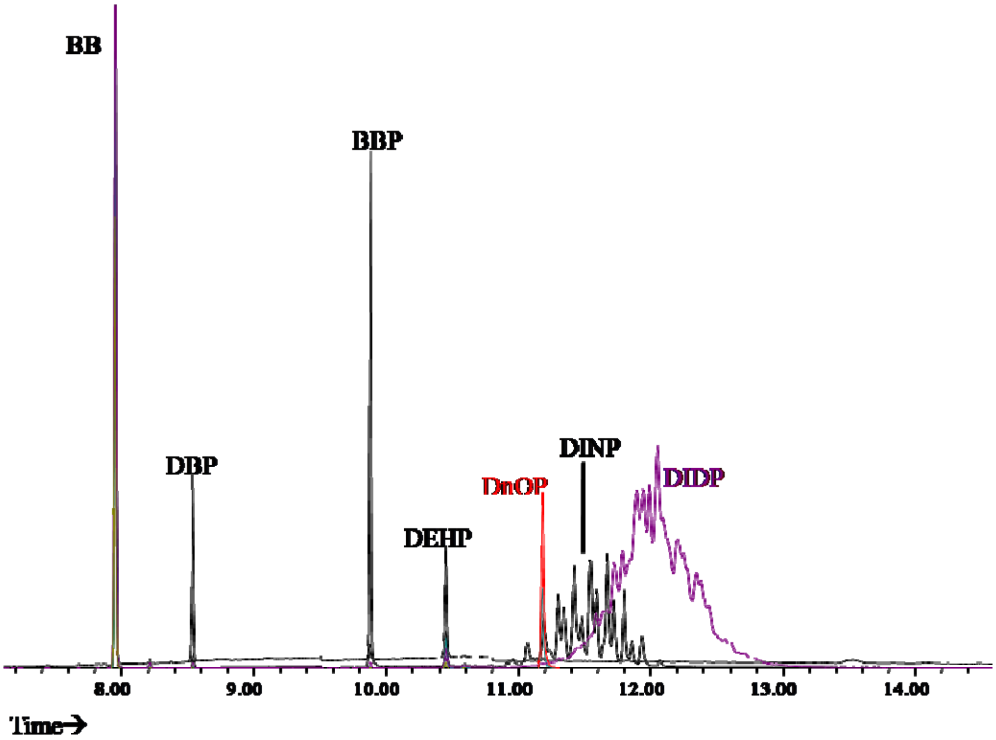
	Retention Time (min)	**Corresponding Ions (*m/z*)**
Scan Stage 1:	*5 - 9.5 minutes*	
BB (Internal Standard)	7.93 – 7.99	91.1, **105**, 194, 212
DBP	8.52 – 8.57	149, 167, 205, **223**
Scan Stage 2:	*9.5 - 10.8 minutes*	
BBP	9.84 – 9.93	91.1, 149, **206**
DEHP	10.42 – 10.49	149, 167, **279**
Scan Stage 3:	*10.8 - End*	
DnOP	11.15 – 11.24	149, 167, 261, **279**
DINP	10.90 – 12.1	149, 167, **293**
DIDP	11.20 – 13.00	149, 167, **307**

Analysis

1. Prepare at least four calibration standards for each of the six phthalates of interest (in the range of 0.5 to 10 µg/ml), along with one calibration blank (cyclohexane). Each calibration standard should have an internal standard concentration of 1 µg/ml.
2. Analyze standards and blank with the GC-MS. Qualitatively analyze the results to ensure proper retention times and no contamination.

3. Integrate the peak area from valley to valley (the time range listed in Table 2) for each standard. Compounds scanned in Stages 1 and 2 can be integrated by Total Ion Current (TIC) or the ion chromatograph (suggested quantitative ions are in **bold**). The phthalates scanned in SIM Stage 3 overlap and **must** be integrated using their quantitative ions (again, in **bold**).
4. Construct a calibration curve from normalized phthalate signals. Normalization is performed by dividing the integrated phthalate signal area by the integrated internal standard signal area.
5. Analyze a CRM to ensure a proper calibration. The analyzed value should be within ±10% of the expected value. If not, prepare new standards and re-run calibration.
6. Analyze the LRB and all samples. Analyze a CRM if time has passed since the last calibration check.
7. Quantitate results. If the results are out of the calibration range, return to step 5 of the phthalate extraction method (perform another dilution to get results in calibration range).

Figure 1. Chromatogram overlay of all phthalates of interest and internal standard.



Calculations and Results

Results can be reported as follows:
Percentage [Phthalate] = % Phthalate (w/w) = [(C x V x D) / (W x 1000)] x 100

Where
C = Concentration of phthalate in GC-MS sample (in µg/ml)
V = Total volume of THF and hexanes added from steps 2 and 3 of phthalate extraction method
D = Dilution factor from step 5 of phthalate extraction method
W = Weight of sample collected (in mg)
Repeat calculation for each phthalate present in sample

Example:

A 50 mg sample was dissolved in 5 ml THF; next 10 ml of hexane were added (total of 15 ml of solvent). Of the filtered solution, 0.1 ml was combined with 80 µl of internal standard and diluted with hexane to 20 ml for GC-MS analysis (200 times dilution factor). The GC-MS results found 2 µg/ml of DINP and 0.5 µg/ml of DIDP. Therefore, the sample contained 12% DINP and 3% DIDP by weight.

W	C	V	D	[(C x V x D) / (W x 1000)] x 100
Sample weight	**Measured DINP Concentration by GC-MS**	**Original Volume**	**Dilution Factor**	**% DINP (w/w)**
50 mg	2 µg/ml	15 ml	20 ml / 0.1 ml = 200	[(2 µg/ml x 15 ml x 200) / (50 mg x 1000 µg/mg)] x 100% = **12%**
	Measured DIDP Concentration by GC-MS			**% DIDP (w/w)**
	0.5 µg/ml			[(0.5 µg/ml x 15 ml x 200) / (50 mg x 1000 µg/mg)] x 100% = **3%**