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**Test Method: CPSC-CH-C1001-09.2  
Standard Operating Procedure for Determination of Phthalates\*  
July 27, 2009**

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.

It has been concluded that in order to protect children from the hazard the Act intended to address, that "concentrations of more than 0.1 percent" must apply per plasticized component part of a children's toy or child care article. This conclusion was determined to be the only reasonable solution to an apparent paradox posed by a hypothetical toy, composed of multiple component parts as described below which illustrates the advantages to this approach based on plasticized component parts.

In a hypothetical case, it is possible for a toy such as a toddler ride-on toy to contain a plasticized part, such as a teether attached to the playing surface, where that teether part could contain a high concentration of one of the prohibited or interim-prohibited phthalates, and yet because of the relative size of that part of the toy compared to the toy as a whole, the toy itself may not contain in excess of 0.1% of the phthalate. If the Act were interpreted to apply to the concentration in the entire article, this hypothetical toy would then meet the standard even though the plasticized part contains a high concentration of the prohibited or interim-prohibited phthalate. Essentially, such an approach would result in a determination that appears contrary to Congressional intent.

It was concluded to be necessary to treat phthalate-testing of toys in a manner analogous to lead testing according to the provisions of Section 101, namely considering the phthalate concentration in each plasticized component part. In this way, the hypothetical toddler ride-on toy (above) with a high concentration of a prohibited phthalate in a plasticized part would be in violation of the standard. This would focus resources on the largest potential exposures to children, in accordance with Congressional intent.

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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.
5. Calibration Standard – Solutions containing the phthalate(s) of interest in cyclohexane. Each standard should contain 20 µg/ml of internal standard. A minimum of four calibration standards are used. Calibration standards should be prepared as needed from the stock solution and may be stored at room temperature. Record weight of solutions before and after use to monitor for solvent evaporation. Standards should be replaced when experimental data demonstrates a decrease in quality or significant loss in solvent weight.
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<sub>4</sub>H<sub>8</sub>O, THF), GC grade or higher
2. Hexane (C<sub>6</sub>H<sub>12</sub>), GC grade or higher
3. Cyclohexane (C<sub>6</sub>H<sub>12</sub>), GC grade or higher
4. Sealable glass vials with PTFE or silicone liner. Size 20 ml or larger
5. Cryogenic-mill (or suitable alternative to grind samples to powder)
6. 0.45 µm PTFE filters
7. Gas Chromatograph-Mass Spectrometer (GC-MS) with an auto-sampler, split/splitless inlet, programmable GC oven, and capable of selective ion monitoring
8. CRMs containing phthalates (such as NIST SRM 3074)
9. Benzyl Benzoate (C<sub>14</sub>H<sub>12</sub>O<sub>2</sub>, BB), Analytical grade
10. Dibutyl Phthalate (C<sub>16</sub>H<sub>22</sub>O<sub>4</sub>, DBP), CAS No. 84-74-2. Analytical grade
11. Di-(2-ethylhexyl) phthalate (C<sub>24</sub>H<sub>38</sub>O<sub>4</sub>, DEHP), CAS No. 117-81-7. Analytical grade or higher

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12. Benzyl Butyl Phthalate (C<sub>19</sub>H<sub>20</sub>O<sub>4</sub>, BBP), CAS No. 85-68-7. Analytical grade or higher  
 13. Di-n-octyl phthalate (C<sub>24</sub>H<sub>38</sub>O<sub>4</sub>, DnOP), CAS No. 117-84-0. Analytical grade or higher  
 14. Diisononyl phthalate (C<sub>26</sub>H<sub>42</sub>O<sub>4</sub>, DINP), CAS No. 28553-12-0/68515-48-0. Analytical grade or higher  
 15. Diisodecyl phthalate (C<sub>28</sub>H<sub>46</sub>O<sub>4</sub>, DIDP), CAS No. 26761-40-0/68515-49-1. Analytical grade or higher

### Measurement of Phthalate Concentration

The procedure to be used for all Compliance Determinations, as described below, consists of three sections: sample preparation, extraction, and analysis. In addition to the procedure described herein, certain alternate extraction and analysis methods, listed below are acceptable to CPSC staff for phthalate content certification testing. Any combination of the listed extraction and analysis methods may be used. However, the CPSC **Sample Preparation** method must be performed prior to the alternative extraction and analysis.

Sample Preparation	Extraction Method	Analysis Method
CPSC-CH-C1001-09.2	CPSC-CH-C1001-09.1	CPSC-CH-C1001-09.1
	Health Canada Method C-34 <sup>1</sup> ( <a href="http://www.hc-sc.gc.ca/cps-spc/prod-test-essai/_method-chem-chim/c-34-eng.php">http://www.hc-sc.gc.ca/cps-spc/prod-test-essai/_method-chem-chim/c-34-eng.php</a> )	
	EN 14372:2004 <sup>2</sup>	
	EPA 3540C, Soxhlet Extraction ( <a href="http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3540c.pdf">http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3540c.pdf</a> )	Health Canada Method C-34
	EPA 3541, Automated Soxhlet Extraction ( <a href="http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3541.pdf">http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3541.pdf</a> )	EN 14372:2004
	EPA 3545A, Pressurized Fluid Extraction ( <a href="http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3545a.pdf">http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3545a.pdf</a> )	
	EPA 3546, Microwave Extraction ( <a href="http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3546.pdf">http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3546.pdf</a> )	
	EPA 3550C, Ultrasonic Extraction ( <a href="http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3550c.pdf">http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3550c.pdf</a> )	EPA 8270D <sup>3</sup> *
	ASTM D 2124-99 (2004) <sup>4</sup>	
	California Dept. of Toxic Substances Control Method <sup>5</sup>	
	California Dept. of Toxic Substances Control Method	

\*EPA 8270D must be modified appropriately to include DINP and DIDP.

<sup>1</sup> Determination of Phthalates in Polyvinyl Chloride Consumer Products

<sup>2</sup> Child use and care articles – Cutlery and feeding utensils

<sup>3</sup> Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)

<sup>4</sup> Standard Test Method for Analysis of Components in Poly(Vinyl Chloride) Compounds Using an Infrared Spectrophotometric Technique

<sup>5</sup> Ting et al.; GC/MS Screening Method for Phthalate Esters in Children's Toys, Journal of AOAC International, Vol. 92, No. 3, 2009

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## Precautions

This method requires 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.

## 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.)
2. Prior to analysis, each plasticized component part should be cut into small pieces, or milled/ground into a representative powder. Each cut/milled plasticized component part will be considered a sample for testing as described below.

## Phthalate Extraction Method

Testing lab shall determine how many replicate samples are necessary to meet quality assurances. Prepare LRB concurrently with samples.

1. Weigh out a minimum of  $0.05 \pm 0.005$  g of sample into a sealable glass vial (weighed to an accuracy of  $\pm 0.5\%$  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, stir, or otherwise mix sample for at least 30 minutes to allow dissolution\*. Sample may be sonicated or gently heated to expedite dissolution.  
*\*Note:* Some materials may not dissolve completely. In this case, add an additional two hours to mixing 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. (*Optional*) Filter THF/hexane solution through a  $0.45 \mu\text{m}$  PTFE filter. Collect approximately 1 ml of filtered solution. Although not mandatory, this step is recommended.
5. Combine 0.3 ml\* of the THF/hexane solution with 0.2 ml of internal standard (BB, 150  $\mu\text{g/ml}$ ) in a GC vial, and dilute to 1.5 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  $\sim 5\%$  phthalate, increase the amount of filtered THF/hexane solution from 0.3 to 1.0 ml). For very low concentrations ( $\sim 0.1\%$ ), it may be more practical to add internal standard directly to the THF/hexane mixture from Step 3 to give an internal standard concentration of 1  $\mu\text{g/ml}$ . Then filter and analyze without additional dilutions.

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## GC-MS Operating Procedures and Quality Control Measures

A GC-MS system with an auto-sampler is suggested for the sample analysis.

The following GC conditions are used (Table 1):

**Table 1.** GC Conditions

Column	DB-5MS; 30 m x 0.25 mm ID x 0.25 $\mu$ m
Flow Mode	1 ml/min, constant flow (He gas)
Inlet Mode	20:1 Split or Splitless
Injection Amount	1 $\mu$ l
Inlet Temperature	290° C
Solvent Delay	5 minutes
Initial Oven Temp, Hold Time	50° C, 1 min
Ramp 1	30° C/min, 280° C
Ramp 2	15° C/min, 310° C
Final Hold Time	4 minutes or longer

Splitless mode should be used only when phthalate concentration is expected to be near or below the lower limit of quantitation. All other samples are run in 20:1 split mode.

Samples are analyzed using both full scan mode and the Selective Ion Monitoring (SIM) program listed in Table 2. Monitor for corresponding ions of each compound listed in a time segment (e.g., set Group 3 to monitor for 149, 167, 261, 279, 293, and 307  $m/z$ ). The retention times listed are based on CPSC data, and must be confirmed by analyzing stock standards. The last column indicates the identification (ID) ion, and the relative abundance of this ion to 149  $m/z$ .

If the instrument to be used has limited SIM abilities, monitor for only those ions in **bold**.

**Table 2.** SIM Settings

	Estimated Retention Time (min)	Corresponding Ions ( $m/z$ )	Published Relative Abundance of ID Ion to 149 $m/z$ <sup>6</sup>
<i>SIM Group 1:</i>	<i>5 - 9.5 minutes</i>		
BB (Internal Standard)	7.9	91.1, <b>105</b> , 194, 212	
DBP	8.5	149, 167, 205, <b>223</b>	<b>223</b> : 4
<i>SIM Group 2:</i>	<i>9.5 - 10.8 minutes</i>		
BBP	9.8	91.1, 149, <b>206</b>	<b>206</b> : 27
DEHP	10.4	149, 167, <b>279</b>	<b>279</b> : 10
<i>SIM Group 3:</i>	<i>10.8 - End</i>		

<sup>6</sup> Bolgar, M; Hubball, J; Groeger, J; Meronek, S; *Handbook for the Chemical Analysis of Plastic and Polymer Additives*, CRC Press, Boca Raton, FL, 2008.

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DnOP	11.1	149, 167, 261, <b>279</b>	<b>279</b> : 12
DINP	10.9	149, 167, <b>293</b>	<b>293</b> : 26
DIDP	11.2	149, 167, <b>307</b>	<b>307</b> : 27

### Analysis

1. Prepare at least four calibration standards for each of the six phthalates of interest along with one calibration blank (cyclohexane). Each calibration standard should have an internal standard concentration of 20 µg/ml (for 20:1 split mode samples) or 1 µg/ml (for splitless mode samples).
2. Analyze standards and blank with the GC-MS in both full-scan mode and SIM. Qualitatively analyze the results to ensure proper retention times and no contamination.
3. Integrate the peak area from valley to valley (approximate retention times are listed in Table 2) for each standard. Compounds monitored in SIM Groups 1 and 2 can be quantitated by extracted ion chromatograph (EIC) or the ion chromatograph (suggested quantitative ions are in **bold**). The phthalates monitored in SIM Group 3 overlap and **must** be quantitated using their quantitative ions (again, in **bold**).
4. Construct a calibration curve using normalized phthalate responses. The normalized phthalate response ( $Pht_n$ ) is calculated by:

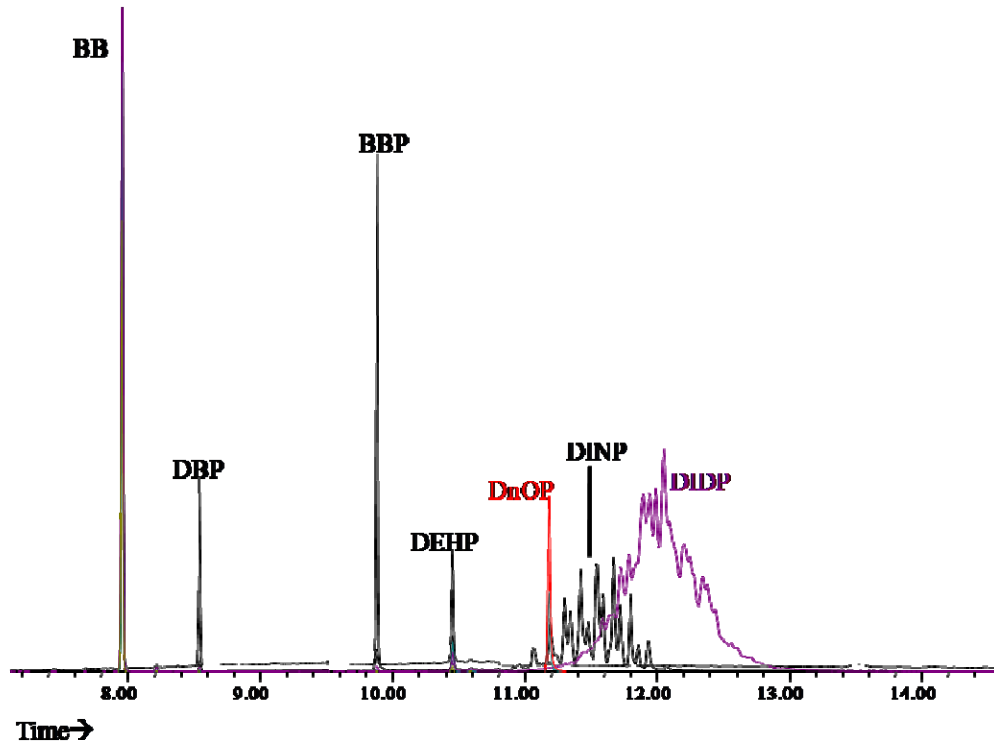
$$Pht_n = \frac{Pht}{IS}$$

Where  $Pht$  is the phthalate response and  $IS$  is the internal standard response.

5. Analyze a CRM to ensure a proper calibration. The analyzed value should be within ±15% 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. Qualitatively evaluate full-scan results. Phthalates of interest should be identified by matching with retention times and mass spectra of standards. Potential non-regulated chemicals which may have mass ions of interest and/or similar retention times and must be qualitatively eliminated from consideration based on their spectra and chromatograms include, but are not limited to, linear C9 and C10 phthalates, and terephthalates.
8. Quantitate SIM 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). If signal is near or below the limit of detection, change the inlet mode to “splitless” injection (when using splitless injection, samples and calibration curves should contain an internal standard concentration of 1 µg/ml).

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



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**Calculations and Results**

Results can be reported as follows:

$$\text{Percentage [Phthalate]} = \% \text{ Phthalate (w/w)} = [(C \times V \times D) / (W \times 1000)] \times 100$$

Where

C = Concentration of phthalate in GCMS 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 small, homogeneous PVC toy was cut into small pieces and ground to a powder. 50 mg of sample powder was dissolved in 5 ml THF; next 10 ml of hexane were added (total of 15ml of solvent). Of the filtered solution, 0.3 ml was combined with 0.2 µl of internal standard and diluted with cyclohexane to 1.5 ml for GC-MS analysis (5 times dilution factor). The GC-MS results found 200 µg/ml of DEHP and 50 µg/ml of DINP. Therefore, the sample contained 30% DEHP and 7.5% DINP by weight.

W	C	V	D	$[(C \times V \times D) / (W \times 1000)] \times 100$
<b>Sample weight</b>	<b>Measured DEHP Concentration by GC-MS</b>	<b>Original Volume</b>	<b>Dilution Factor</b>	<b>% DEHP (w/w)</b>
50 mg	200 µg/ml	15 ml	1.5 ml / 0.3 ml = 5	$[(20 \mu\text{g/ml} \times 15 \text{ ml} \times 5) / (50 \text{ mg} \times 1000 \mu\text{g/mg})] \times 100\% = \mathbf{30\%}$
	<b>Measured DINP Concentration by GC-MS</b>			<b>% DINP (w/w)</b>
	50 µg/ml			$[(50 \mu\text{g/ml} \times 15 \text{ ml} \times 5) / (50 \text{ mg} \times 1000 \mu\text{g/mg})] \times 100\% = \mathbf{7.5\%}$

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