UNITED STATES
CONSUMER PRODUCT SAFETY COMMISSION
DIRECTORATE FOR LABORATORY SCIENCES
DIVISION OF CHEMISTRY
10901 DARNESTOWN RD
GAITHERSBURG, MD 20878

Test Method: CPSC-CH-C1001-09.3
Standard Operating Procedure for Determination of Phthalates
April 1st, 2010

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 children's toys and child care articles covered by the standard set forth in the Consumer Product Safety Improvement Act Section 108.

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[1].

CPSC staff has determined that using an appropriate combination of the methods of extraction and analysis presented herein is 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 dissolve the sample completely in tetrahydrofuran, precipitate any PVC polymer with hexane, 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.

[1] Statement of Policy: Testing of Component Parts with respect to Section 108 of the CPSIA, August 7, 2009 (http://www.cpsc.gov/ABOUT/Cpsia/componenttestingpolicy.pdf)

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 when running a 20:1 split injection, or 1 µg/ml for splitless injection. 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_4H_8O, THF), GC grade or higher.
2. Hexane (C_6H_{14}), GC grade or higher.
3. Cyclohexane (C_6H_{14}), 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. PTFE filters, 0.45 µm.
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 ($C_{14}H_{12}O_2$, BB), analytical grade or higher.
10. Dibutyl Phthalate ($C_{16}H_{22}O_4$, DBP), CAS No. 84-74-2, analytical grade or higher.
11. Di-(2-ethylhexyl) phthalate ($C_{24}H_{38}O_4$, DEHP), CAS No. 117-81-7, analytical grade or higher.
12. Benzyl Butyl Phthalate ($C_{19}H_{20}O_4$, BBP), CAS No. 85-68-7, analytical grade or higher.
13. Di-n-octyl phthalate ($C_{24}H_{38}O_4$, DnOP), CAS No. 117-84-0, analytical grade or higher.
14. Diisononyl phthalate ($C_{26}H_{42}O_4$, DINP), CAS No. 28553-12-0/68515-48-0, analytical grade or higher.
15. Diisodecyl phthalate ($C_{28}H_{46}O_4$, DIDP), CAS No. 26761-40-0/68515-49-1, analytical grade or higher.

Measurement of Phthalate Concentration

The procedure to be used for all CPSC 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 ten extraction and five analysis methods listed may be used. However, the CPSC staff's

Sample Preparation method must be performed prior to the alternative extraction and analysis methods.

Sample Preparation	Extraction Method	Analysis Method
CPSC-CH-C1001-09.3	CPSC-CH-C1001-09.3	CPSC-CH-C1001-09.3
	Health Canada Method C-34[2] (http://www.hc-sc.gc.ca/cps-spc/prod-test-essai/_method-chem-chim/c-34-eng.php)	
	EN 14372:2004[3]	Health Canada Method C-34
	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)	EN 14372:2004
	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 8270D[4] (must be modified appropriately to include DINP and DIDP)
	EPA 3550C, Ultrasonic Extraction (http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3550c.pdf)	California Dept. of Toxic Substances Control Method
	ASTM D 2124-99 (2004)[5]	
	California Dept. of Toxic Substances Control Method[6]	

Precautions

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.

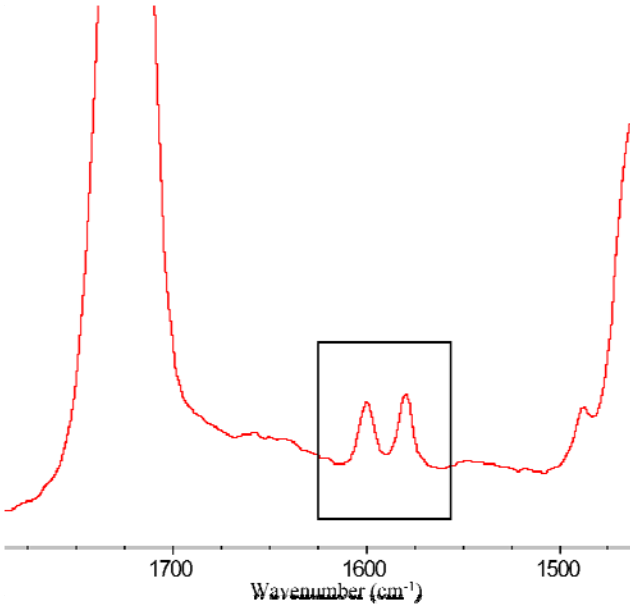
Phthalates are a common contaminant. Even low levels of contamination can impact quantitative results. Avoid plastic materials and use only scrupulously cleaned glassware and equipment. All solvents should be tested for any phthalate content. Solvent blanks should be run through the GC-MS periodically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

[2] Determination of Phthalates in Polyvinyl Chloride Consumer Products
[3] Child use and care articles – Cutlery and feeding utensils
[4] Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)
[5] Standard Test Method for Analysis of Components in Poly(Vinyl Chloride) Compounds Using an Infrared Spectrophotometric Technique
[6] Ting et al.; GC/MS Screening Method for Phthalate Esters in Children's Toys, Journal of AOAC International, Vol. 92, No. 3, 2009

Optional Sample Pre-Screen Using Infrared (IR) Spectroscopy
A broad estimate of phthalate concentration can be obtained by scanning the sample to be tested with an IR spectrometer. This information can be used when deciding the dilution factor and analysis method later in the procedure. This step is optional.

A doublet peak at 1600 and 1580 cm^{-1} can be observed when phthalate(s) are present in amounts of ~10% or greater (see Figure 1). If this doublet is not observed, the sample should be treated as containing a low concentration of phthalates. If the doublet is present, the sample can be treated as concentrated, and a higher dilution factor may be used.
The absence of the doublet peak does **not** indicate that phthalates are not present in the sample, and that the item is compliant. Conversely, the presence of the double peak does **not** indicate that regulated phthalates are present in restricted amounts.

Figure 1. IR spectrum of PVC plastic containing ~30% phthalates.



Sample Preparation
Prior to analysis, each plasticized component part should be cut into small pieces (no dimension larger than 2 mm), or milled/ground into a representative powder. Each cut/milled plasticized component part will be considered a sample for testing as described below. At minimum, prepare the amount required to constitute a sufficient sample size.

Phthalate Extraction Method
Testing lab shall determine how many replicate samples are necessary to meet their quality assurance requirements. 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, stir,

or otherwise mix sample for at least 30 minutes to allow dissolution*. Sample may be sonicated and/or gently heated to expedite dissolution.

**Note:* Some materials may not dissolve completely. In this case, add an additional 2 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. Shake and 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 µm PTFE filter. Collect a few ml of filtered solution in separate vial. This step is optional, but recommended.
5. Combine 0.3 ml* of the THF/hexane solution with 0.2 ml of internal standard (BB, 150 µg/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 ~5% phthalate, increase the amount of filtered THF/hexane solution from 0.3 to 1.0 ml). For very low concentrations (~0.1%), use 1.3 ml of filtered solution. *A pre-screen of the sample by IR spectroscopy can provide a broad estimate of phthalate concentration.*

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 µm
Flow Mode	1 ml/min, constant flow (He gas)
Inlet Mode	20:1 Split or Splitless
Injection Amount	1 µl
Inlet Temperature	290° C
Solvent Delay	5 min
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 min or longer

The 20:1 split mode injection should be used when the phthalate concentration is expected to be ≥5%. All other samples are run in splitless mode. *A pre-screen of the sample by IR spectroscopy can provide a broad estimate of phthalate concentration.*
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*[7]**
SIM Group 1:	*5 - 9.5 Minutes*		
BB (Internal Standard)	7.9	91.1, **105**, 194, 212	
DBP	8.5	149, 167, 205, **223**	**223**: 4
SIM Group 2:	*9.5 - 10.8 Minutes*		
BBP	9.8	91.1, 149, **206**	**206**: 27
DEHP	10.4	149, 167, **279**	**279**: 10
SIM Group 3:	*10.8 - End*		
DnOP	11.2	149, 167, 261, **279**	**279**: 12
DINP	11.6	149, 167, **293**	**293**: 26
DIDP	12.1	149, 167, **307**	**307**: 27

Analysis

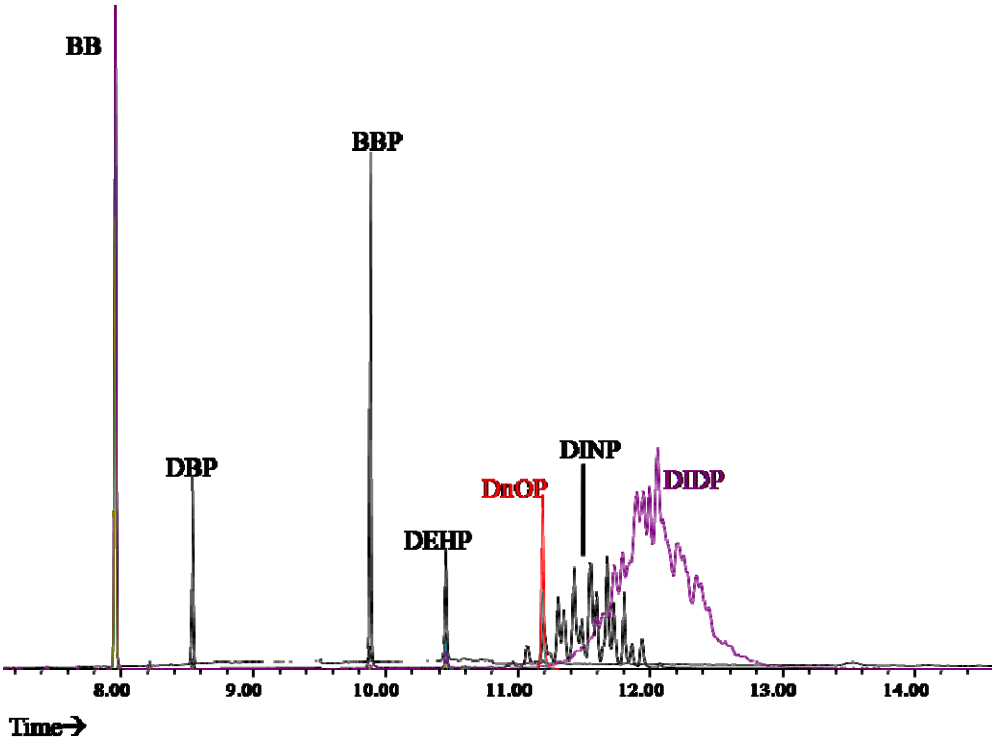
1. Prepare at least four calibration standards for each of the six phthalates of interest along with one calibration blank (cyclohexane). Each calibration standard should have an internal standard concentration of 20 µg/ml (for 20:1 split mode samples) or 1 µg/ml (for splitless mode samples).
2. Analyze 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 quantified 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 quantified 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:
$$Pht_n = \frac{Pht}{ISTD}$$
Where *Pht* is the phthalate response and *ISTD* 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.
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

[7] Bolgar, M; Hubball, J; Groeger, J; Meronek, S; *Handbook for the Chemical Analysis of Plastic and Polymer Additives,* CRC Press, Boca Raton, FL, 2008.

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). If signal is still below quantitation limits when using a splitless injection, the injection amount can be doubled from 1 µl to 2 µl (calculations must be adjusted accordingly).

Figure 2. 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 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 ml 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.

<table>
<tr><td>W</td><td>C</td><td>V</td><td>D</td><td>[(C x V x D) / (W x 1000)] x 100</td></tr>
<tr><td>Sample Weight</td><td>Measured DEHP Concentration by GC-MS</td><td>Original Volume</td><td>Dilution Factor</td><td>% DEHP (w/w)</td></tr>
<tr><td rowspan="3">50 mg</td><td>200 µg/ml</td><td rowspan="3">15 ml</td><td rowspan="3">1.5 ml / 0.3 ml = 5</td><td>[(200 µg/ml x 15 ml x 5) / (50 mg x 1000 µg/mg)] x 100% = 30%</td></tr>
<tr><td>Measured DINP Concentration by GC-MS</td><td>% DINP (w/w)</td></tr>
<tr><td>50 µg/ml</td><td>[(50 µg/ml x 15 ml x 5) / (50 mg x 1000 µg/mg)] x 100% = 7.5%</td></tr>
</table>