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DIRECTORATE FOR LABORATORY SCIENCES
DIVISION OF CHEMISTRY
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**Test Method: CPSC-CH-C1001-09.4
Standard Operating Procedure for Determination of Phthalates
January 17, 2018**

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 analyzing phthalate content in children's toys and child care articles covered by the standard set forth in section 108 of the Consumer Product Safety Improvement Act Section and 16 C.F.R. part 1307. In 2017, the Commission at 16 C.F.R. part 1307 issued a rule prohibiting children's toys and child care articles containing specified phthalates. Guidance regarding the law can be found at: <https://www.cpsc.gov/en/Business--Manufacturing/Business-Education/Business-Guidance/Phthalates-Information>.

CPSC staff has determined that using an appropriate combination of the methods of extraction and analysis presented here is sufficient to determine the concentration of the eight 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 dissolved polymer with a second solvent, then 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. These must be replaced before expiration date.
- 5. Calibration Standard** – Solutions containing the phthalate(s) of interest. 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. Standards should be replaced when experimental data demonstrates a decrease in quality.

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 (C₄H₈O, THF), GC grade or higher.
2. Hexane (C₆H₁₄), GC grade or higher.
3. Acetonitrile (C₂H₃N), GC grade or higher.
4. Sealable glass vials with PTFE or silicone liner, size 20 mL or larger.
5. Analytical balance, capable of weighing to ±0.0001 g.
6. Cryogenic-mill (or suitable alternative to grind samples to powder).
7. Ultrasonic Bath.
8. PTFE filters, 0.45 µm.
9. Gas Chromatograph-Mass Spectrometer (GC-MS) with an auto-sampler, split/splitless inlet, programmable GC oven, and capable of selective ion monitoring.
10. GC vials, size 2 mL.
11. Volumetric glassware
12. Volumetric pipettes
13. CRMs containing phthalates (such as NIST SRM 2860 or Korea Research Institute of Standards and Science CRM 113-03-006).
14. Benzyl Benzoate (C₁₄H₁₂O₂, BB), analytical grade or higher.
15. Dibutyl Phthalate (C₁₆H₂₂O₄, DBP), CAS No. 84-74-2, analytical grade or higher.
16. Diisobutyl phthalate (C₁₆H₂₂O₄, DIBP), CAS No. 84-69-5, analytical grade or higher.
17. Di-n-pentyl phthalate (C₁₈H₂₆O₄, DPENP), CAS No. 131-18-0, analytical grade or higher.
18. Di-n-hexyl phthalate (C₂₀H₃₀O₄, DHEXP), CAS No. 84-75-3, analytical grade or higher.
19. Dicyclohexyl phthalate (C₂₀H₂₆O₄, DCHP), CAS No. 84-61-7, analytical grade or higher.
20. Di(2-ethylhexyl) phthalate (C₂₄H₃₈O₄, DEHP), CAS No. 117-81-7, analytical grade or higher.
21. Benzyl Butyl Phthalate (C₁₉H₂₀O₄, BBP), CAS No. 85-68-7, analytical grade or higher.
22. DINP (C₂₆H₄₂O₄):
 - 1,2-Benzenedicarboxylic acid, 1,2-diisononyl; CAS No. 28553-12-0, analytical grade or higher.
 - 1,2-Benzenedicarboxylic acid, di-C₈₋₁₀ branched alkyl esters, C₉-rich; CAS No. 68515-48-0, technical grade.

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 here, certain alternative methods listed below are acceptable to CPSC staff for phthalate content certification testing. Note that some methods require adaptation to be sufficient. Most notably, some methods do not specifically include all of the phthalates that are regulated in use in children's toys and child care items in the United States. As such, the methods must be modified to ensure including all phthalates of interest.

Standalone methods: These methods are acceptable to CPSC staff for phthalate content certification testing, as written, and they require no adaptations beyond including all phthalates of interest:

- CPSC-CH-C1001-09.4 and CPSC-CH-C1001-09.3
- Health Canada Method C34 and C34.2
- EN 14372:2004
- EN 71-5:1993/A1:2006
- ASTM D7823-16
- ASTM D8133-17
- GB/T 22048-2015
- ISO 8124-6 2014
- ISO 14389:2014 (*for textiles only*)
- California Department of Toxic Substances Control Method¹

Extraction only: The following methods are only suitable for the extraction portion of certification testing. They must be combined with an analysis method from a standalone method listed above, or an *analysis only* method listed in the following section.

- EPA 3540C, 3541, 3545A, 3546 and 3550C
- ASTM D2124-99 (2011)

Analysis only: The following methods must be combined with a sample preparation and extraction method from a standalone method or extraction only method.

- EPA 8270D (must be modified appropriately to include all phthalates of interest).

References: The following standard guide is recommended to assist users interpreting results.

- ASTM D7993-15.

Precautions

These methods require the use of hazardous materials. It is of paramount importance 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

¹ Ting et al.; GC/MS Screening Method for Phthalate Esters in Children's Toys, Journal of AOAC International, Vol. 92, No. 3, 2009.

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

Before 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. Add benzyl benzoate directly to the precipitation solvent (choice of acetonitrile or hexane) to yield a concentration of 30 µg/mL for use as an internal standard.

- 1.** Weigh out a minimum of 0.05 ± 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 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 acetonitrile or hexane for every 5 mL of THF used in Step 2. Shake vigorously and allow at least 5 minutes for polymer to settle.
- 4.** Transfer supernatant solution to GC vial for analysis. If hexane was used for Step 3, it is recommended to filter the supernatant solution through a 0.45 µm PTFE filter before transferring.

Instrument Parameters

A GC-MS system with an auto-sampler is suggested for the sample analysis. Related instrumentation, such as GC or liquid chromatography (LC) with advanced MS options (*e.g.*, ion trap or tandem mass spectrometry) can be used for qualitative assessment. 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 μ m
Flow Mode	1 mL/min, constant flow (He or H ₂ gas)
Inlet Mode	20:1 Split
Injection Amount	1 μ l
Inlet Temperature	290° C
Solvent Delay	4.5 minutes
Initial Oven Temp, Hold Time	150° C, 1 min
Ramp 1	30° C/min, 280° C
Ramp 2	15° C/min, 310° C
Final Hold Time	3 minutes or longer

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, 249, 279, and 293 m/z). The retention times listed are based on CPSC data using helium gas, 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 . An example chromatogram is shown in Figure 1.

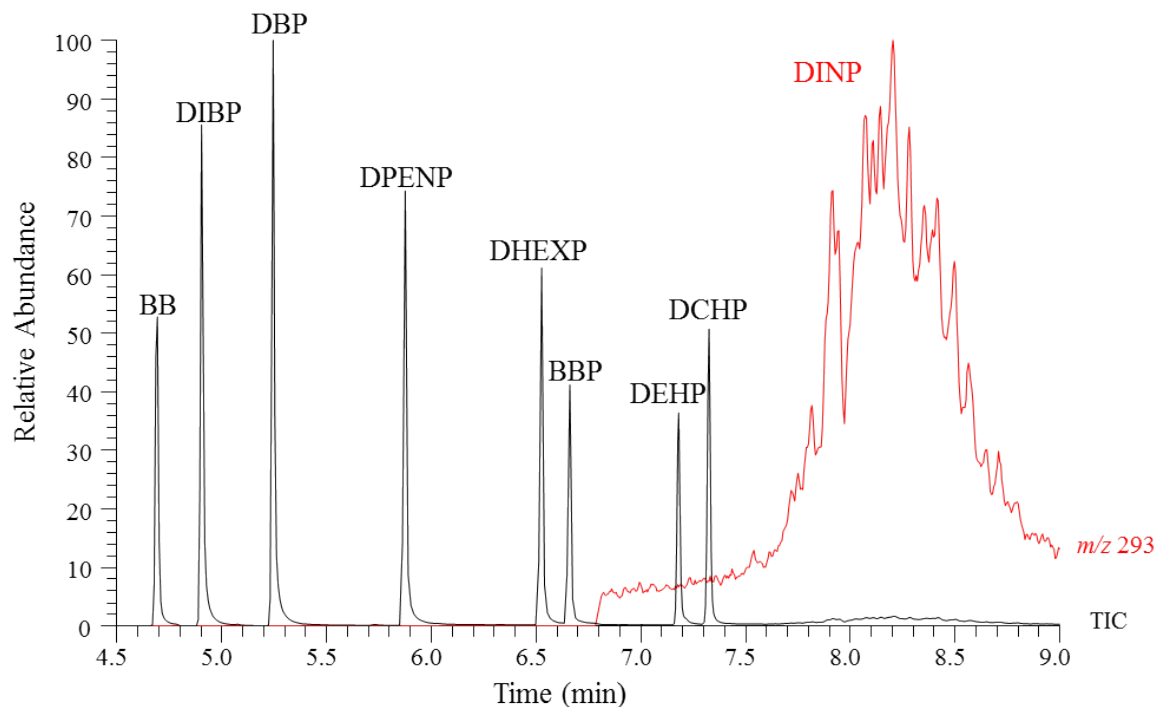
If the instrument to be used has limited SIM abilities, monitor for only those ions in **bold**.

Table 2. SIM Settings

	<i>Estimated Retention Time (min)</i>	Corresponding Ions (m/z)	Published Relative Abundance of ID Ion to 149 m/z²
<i>SIM Group 1:</i>	<i>4.5 – 5.3 minutes</i>		
BB (Internal Standard)	4.69	91.1, 105 , 194, 212	
DIBP	4.91	149, 167, 205, 223	223 : 9.6
DBP	5.25	149, 167, 205, 223	223 : 4
<i>SIM Group 2:</i>	<i>5.5 – 7.0 minutes</i>		
DPENP	5.88	149, 219, 237	237 : 6.1
DHEXP	6.53	149, 233, 251	251 : 4.5
BBP	6.66	91.1, 149, 206	206 : 27
<i>SIM Group 3:</i>	<i>7.0 – End</i>		
DEHP	7.18	149, 167, 279	279 : 32
DCHP	7.33	149, 167, 249	249 : 4.5
DINP	7.8-8.9	149, 167, 293	293 : 26

² Bolgar, M; Hubball, J; Groeger, J; Meronek, S; *Handbook for the Chemical Analysis of Plastic and Polymer Additives*, CRC Press, Boca Raton, FL, 2008.

Figure 1. Total ion chromatogram (TIC) of the internal standard and all phthalates of interest, overlaid with an extracted ion chromatogram isolating DINP (red, m/z 293).



Analysis

1. Prepare at least four calibration standards for each of the eight phthalates of interest along with one calibration blank. Each calibration standard should have an internal standard concentration of 20 $\mu\text{g/mL}$.
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 $\pm 15\%$ 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. Other chemicals which may have mass ions of interest and/or similar retention times to the phthalates of interest must be qualitatively eliminated from consideration based on their spectra and chromatograms. Examples 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, prepare additional calibration standards or dilute the sample for re-analysis.

Calculations and Results

Results can be reported as follows:

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

Where

C = Concentration of phthalate in GC-MS sample (in $\mu\text{g/mL}$)

V = Total volume of solvents added from steps 2 and 3 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 acetonitrile were added (total of 15 mL of solvent). The GC-MS results found 20 $\mu\text{g/mL}$ of DEHP and 5 $\mu\text{g/mL}$ of DINP. Therefore, the sample contained 0.60% DEHP and 0.15% DINP by weight.

W	C	V	$[(C \times V) / (W \times 1000)] \times 100$
Sample weight	Measured DEHP Concentration by GC-MS	Original Volume	% DEHP (w/w)
50 mg	20 $\mu\text{g/mL}$	15 mL	$[(20 \mu\text{g/mL} \times 15 \text{ mL}) / (50 \text{ mg} \times 1000 \mu\text{g/mg})] \times 100\% = \mathbf{0.60\%}$
	Measured DINP Concentration by GC-MS		% DINP (w/w)
	5 $\mu\text{g/mL}$		$[(5 \mu\text{g/mL} \times 15 \text{ mL}) / (50 \text{ mg} \times 1000 \mu\text{g/mg})] \times 100\% = \mathbf{0.15\%}$

Summary of Changes in Revision CPSC-CH-C1001-09.4

- Page 1; added link to CPSC website for guidance.
- Page 2; updated list to reflect currently prohibited phthalates; additional clarity provided for the definition of DINP.
- Page 3; updated acceptable alternative methods section to improve clarity and include new options, including reference section.
- Page 4; removed optional IR pre-screen due to modification of test method.
- Page 4; added option to use acetonitrile instead of hexane. Acetonitrile was determined to yield a better precipitation, eliminating the need for filtering the solution before analysis.
- Page 4; internal standard is now directly added to precipitation solvent prior to sample preparation.
- Page 4; alternative technical options are listed under **Instrument Parameters**.
- Page 4; new GC parameters are listed in **Table 1** to decrease analysis time.
- Page 5; **Table 2** is updated with new retention times to reflect the updated GC parameters and current prohibited phthalates.
- Page 6; **Figure 1** was updated to reflect the updated GC parameters and current prohibited phthalates.
- Page 7; Example calculation updated to reflect modification of test method.