Designation: ~~D7823 – 16~~ D7823 – 18

Standard Test Method for Determination of Low ~~Level, Regulated~~ Level Phthalates in Poly (Vinyl Chloride) Plastics by Thermal Desorption—Gas Chromatography/Mass Spectrometry[1]

This standard is issued under the fixed designation D7823; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method provides a procedure to identify and quantify ~~six~~ phthalates by thermal desorption (TD) gas chromatography (GC) mass spectrometry (MS). ~~The phthalates are~~ Six phthalates are used to demonstrate the use of the procedure: BBP, DBP, DEHP, DNOP, DINP and DIDP.

~~NOTE 1—The method can be extended to include other phthalates.~~

1.2 Within the context of this method, "low level" is defined as 1000 ppm.

1.3 The values in SI units are to be regarded as standard.

1.4 This test method includes references, notes and footnotes that provide explanatory material. These notes and footnotes (excluding those in the tables and figures) shall not be considered as requirements of this method.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate ~~safety~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use.*

NOTE 1—The method can be extended to include other ortho-phthalates in a number of polymeric substrates.
NOTE 2—There is no known ISO equivalent to this standard.

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]
D883 Terminology Relating to Plastics
D1600 Terminology for Abbreviated Terms Relating to Plastics
D3465 Test Method for Purity of Monomeric Plasticizers by Gas Chromatography
D7083 Practice for Determination of Monomeric Plasticizers in Poly (Vinyl Chloride) (PVC) by Gas Chromatography
E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
E355 Practice for Gas Chromatography Terms and Relationships
E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
IEEE/ASTM SI-10 Practice for Use of the International System of Units (SI), the Modernized Metric System

2.2 *ASTM Adjuncts:*
Adjunct to D7823 Vinyl Plasticizer Library—Total Ion Chromatograms and Mass Spectra[3]

[1] This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical Methods.
Current edition approved ~~May 1, 2016~~Nov. 1, 2018. Published ~~May 2016~~November 2018. Originally approved in 2013. Last previous edition approved in ~~2014~~2016 as ~~D7823 - 14.~~D7823 – 16. DOI: ~~10.1520/D7823-16.~~10.1520/D7823-18.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from ASTM International Headquarters. Order Adjunct No. ADJD7823S-EA. Original adjunct produced in 2016.

***A Summary of Changes section appears at the end of this standard**

3. Terminology

3.1 *Definitions*—For definition of plastic terms used in this test method, see Terminologies D883 and D1600.

3.2 For units, symbols, and abbreviations used in this test method refer to Practices E594, E355, or SI10.

3.3 *Compounds and Instrumentation:*

3.3.1 *(DOA) Hexanedioic acid, 1,6-bis(2-ethylhexyl) ester* CAS #103-23-1

3.3.2 *(DINCH) 1,2-Cyclohexanedicarboxylic acid, dinonyl ester, branched and linear* CAS #474919-59-0

3.3.3 *(DBP) ~~1,2-Benzenedicarboxylicacid,~~ 1,2-Benzenedicarboxylic acid, 1,2-di-n-butyl ester* CAS #84-74-2

3.3.4 *(BBP) Benzyl butyl phthalate* CAS #85-68-7

3.3.5 *(DEHP) ~~Bis(2-Ethyhexyl) Phthalate~~Bis(2-ethyhexyl) phthalate* CAS #117-81-7

3.3.6 *(DNOP) Di(n-octyl) phthalate* CAS #117-84-0

3.3.7 *~~(DINP) 1,2-Benzenedicarboxylicacid, di-C8-10-branched alkyl esters, C9-rich (Jayflex)~~ (DINP) 1,2-Benzenedicarboxylic acid, di-C8-10-branched alkyl esters, C9-rich (Jayflex)* CAS #68515-48-0

3.3.8 *(DINP) ~~1,2-Benzenedicarboxylicacid,~~ 1,2-Benzenedicarboxylic acid, 1,2-diisononyl (Palatinol)* CAS #28553-12-0

3.3.9 *~~(DIDP) 1,2-Benzenedicarboxylicacid, di-C9-11-branched alkyl esters, C10-rich (Jayflex)~~ (DIDP) 1,2-Benzenedicarboxylic acid, di-C9-11-branched alkyl esters, C10-rich (Jayflex)* CAS #68515-49-1

3.3.10 *(DIDP) ~~1,2-Benzenedicarboxylicacid,~~ 1,2-Benzenedicarboxylic acid, 1,2-diisodecyl* CAS #26761-40-0

3.3.11 *TD Thermal Desorption*

3.3.12 *GC Gas Chromatography*

3.3.13 *GC/MS Gas Chromatography/Mass Spectrometry*

3.3.14 *PVC Poly ~~(Vinyl Chloride)~~(vinyl chloride)*

3.3.15 *THF GC grade or higher "Tetrahydrofuran"*

3.3.16 *DCM GC grade or higher "Methylene Chloride"*

3.3.17 *EGA-MS Evolved Gas Analysis-mass spectrometry*

3.3.18 *FTIR Fourier Transform Infrared Spectroscopy*

3.3.19 *TIC Total ion chromatogram*

3.3.20 *DQO Data quality objectives*

~~NOTE 3—DINP and DIDP, when used in various PVC formulations are technical mixtures. Take care, when preparing the phthalate calibration standard to use the technical grade. Here is specific information on DINP and DIDP. For more information, please refer to Appendix X3.~~

~~Jayflex DIDP: 1,2-Benzenedicarboxylicacid, di-C9-11-branched alkyl esters, C10-rich: CAS# 68515-49-1.~~

~~Jayflex DINP: 1,2-Benzenedicarboxylicacid, di-C8-10-branched alkyl esters, C9-rich: CAS# 68515-48-0.~~

4. Summary of Test Method

4.1 200 mg of the PVC sample are dissolved in 10 mL of THF. 10 µL of the THF solution are analyzed using TD-GC/MS. Phthalates are identified by their retention times and their mass spectra. Quantification is based on the area of a designated quant ion (SIM or full scan)—see Table 1. Standard addition is the calibration method.

NOTE 3—Standard addition calibration will negate matrix interference. It also takes into account the overall performance of the instrumentation at the time the samples are analyzed.

5. Significance and Use

5.1 *Identification and Quantitation of Phthalates*—~~Identification and quantitation of phthalates:~~ DBP, BBP, DEHP, DNOP, DINP, and DIDP are ~~required for regulated articles.~~ representative of the phthalates either banned or being monitored by a variety of regulations. Regulations include: EU—Directive 2005/84/EC, US—Consumer Product Safety Improvement Act of ~~2008—section~~ 2008 – section 108, Japan—Health, Labor and Welfare Ministry guideline ~~No.336 (2010). This test method provides~~No. 336 (2010) and IEC 62321-8:2017. These test methods provide a procedure to identify and quantify ~~regulated~~ phthalates in PVC.

TABLE 1 Ions and Ion Ratios Used to Identify Each Phthalate

	DBP	BBP	DEHP	DNOP	DINP	DIDP
Quant ion	223	206	279	279	293	307
Confirm ion 1	149	149	149	149	149	149
Area ratio (±10%) (Quant/ Confirm 1)	<0.04	<0.23	<0.08	<0.06	<0.20	<0.12
Confirm ion 2	167	167	167	167	167	167

5.2 Other techniques successfully used to separate and identify phthalates in PVC include GC/MS, HPLC/UV, HPLC/MS, FTIR, and GC/FID (flame ionization detector).

6. Interferences

6.1 Retention times for GC are dependent on several variables and it is possible to have two or more components with identical retention times. The analyst shall take the necessary steps to ~~insure~~ make certain that adequate separation of the plasticizer components is achieved ~~and~~ or the ions used to monitor for a target phthalate are free of interference. This ~~includes,~~includes but is not limited to changing the selectivity of the chromatographic ~~column.~~ column and the thermal profile of the column during analysis. Calibration by standard addition ~~offers the advantage of minimizing~~ helps to minimize interferences.

6.2 When using a TD-GC/MS method, care must be taken to ensure that the sample cups are ~~inert and clean.~~ clean. Recent experimentation indicates that equivalent results are obtained using sample cups made of clean "untreated" stainless steel, glass or deactivated stainless steel. The cleanliness of the cup surface is more important than the chemistry of the cup material itself. Any and all solvents and chemware used to prepare standards and sample solutions must be free of ~~contamination.~~ phthalate contamination. Avoid using plastic labware.

6.3 The presence or absence of each phthalate is based upon three criteria: (*1*) the relative retention time of the peak (*2*) the presence or absence of the quant ion and the two confirming ions and (*3*) the ratio of the quant and the confirming ion one must satisfy the established guideline (see Table 1).

6.4 Calculating the phthalate concentrations using the areas of compound specific ions and standard addition significantly reduces interference from non-target compounds.

7. Apparatus

7.1 Gas chromatograph/mass spectrometer capable of operating in the 75 to 350°C range.

NOTE 4—Optional but recommended: Vent-free GC/MS Adapter. This facilitates the rapid conversion between detailed analysis and evolved gas analysis.

7.2 Thermal desorption unit capable of heating the sample from 100 to 350°C at 20°C/min.

7.3 Inert, reusable or disposable sample containers or cups.

7.4 GC capillary column: 5 % diphenyl-95 % poly (dimethylsiloxane) stainless steel, 30 m by 0.25 mm ID with a 0.25 µm film thickness, or equivalent.

7.5 Integrator or data handling system, capable of measuring peak areas and retention times to four significant figures.

7.6 Analytical balance, capable of weighing to ±0.000001 g (1 µg). If using a balance capable of weighing to ±0.00001 g (10 µg), weight used in the sample and standard preparation must be scaled accordingly in order to ensure that the data are accurate to three significant figures.

7.7 Pressure regulators, for all required gas cylinders.

7.8 Flow meter, or other means of measuring gas flow rates ±0.1 mL/min.

8. Reagents and Materials

8.1 Helium carrier gas, chromatographic grade.

8.2 Methylene chloride (DCM) or n-hexane for preparing the phthalate standard solution (Solution #1, 10.2), spectral quality or chromatographic grade.

8.3 Tetrahydrofuran (THF), or a solvent suitable for preparing the PVC sample (Solution #2, 10.3), spectral quality or chromatographic grade.

8.4 Standards of the appropriate phthalates for use when constructing an external calibration curve or when preparing Solution #3 (10.4) that is used for the standard ~~addition. See~~addition procedure. ~~Note 3.~~Use technical grade DINP and DIDP when preparing the calibration standard.

NOTE 5—DINP and DIDP, when used in various PVC formulations are technical mixtures. Here is specific information on DINP and DIDP. For more information, please refer to Appendix X3.
Jayflex DIDP: 1,2- Benzenedicarboxylic acid, di- C9- 11- branched alkyl esters, C10- rich: CAS# 68515- 49- 1.
Jayflex DINP: 1,2- Benzenedicarboxylic acid, di- C8- 10- branched alkyl esters, C9- rich: CAS# 68515- 48- 0.

9. Safety and Precautions

9.1 Use THF and methylene chloride in a well-ventilated space.

10. Preparation of the Analytical Samples (based upon using a 1 µg balance) Weights must be scaled up if using a 10-µg balance.

10.1 Three solutions must be prepared: (*1*) a stock solution of the target phthalate standards, (*2*) a solution of the sample and (*3*) the sample solution spiked with the standard stock solution.

10.2 *Solution #1*—Prepare a stock standard solution of the phthalates by dissolving 0.30 mg of each phthalate in 10 mL of methylene chloride (0.30 mg/10 mL). N-hexane has also been used with success. See Fig. 1 for a typical chromatogram.

10.3 *Solution #2*—Dissolve 200 mg of the sample in 10 mL THF (200 mg/10 mL). Shake (or sonicate) the solution for five minutes—see Note 6. The solution is likely to range from clear to slightly cloudy. Place 10 µL of the sample solution in a clean sample cup. Evaporate the solvent; the sample is ready to analyze. See Figs. 2 and 3 for example chromatograms.

NOTE 6—A critical step in the accurate determination of phthalates is sample homogeneity. This is discussed in more detail in Appendix X2.

NOTE 7—It is possible that the solution will contain inorganic material. Studies have shown that the presence of insoluble inorganic material will not affect either the accuracy or precision of the phthalate determination.

10.4 *Solution #3*—Place 10 µL of the sample solution (#2) into a clean sample cup. Add 10 µL of the phthalate standard solution (#1). Evaporate the solvent.

NOTE 8—To expedite the evaporation process, pass a steady stream of a high purity inert gas using clean, (plasticizer- and additive-free) tubing over the sample cup.

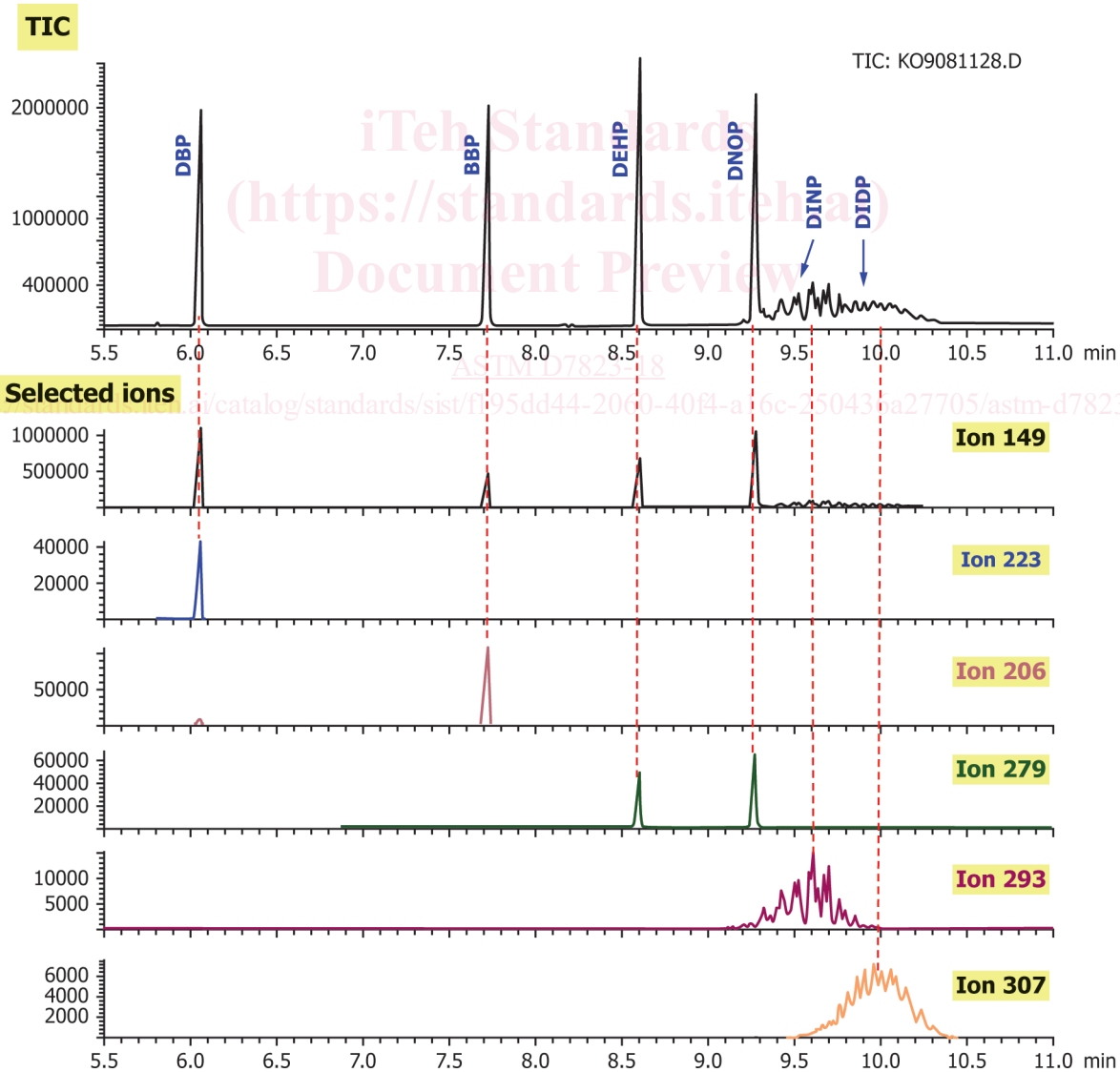


FIG. 1 Solution #1—Phthalates Standard Mixture in DCM (see 10.2)

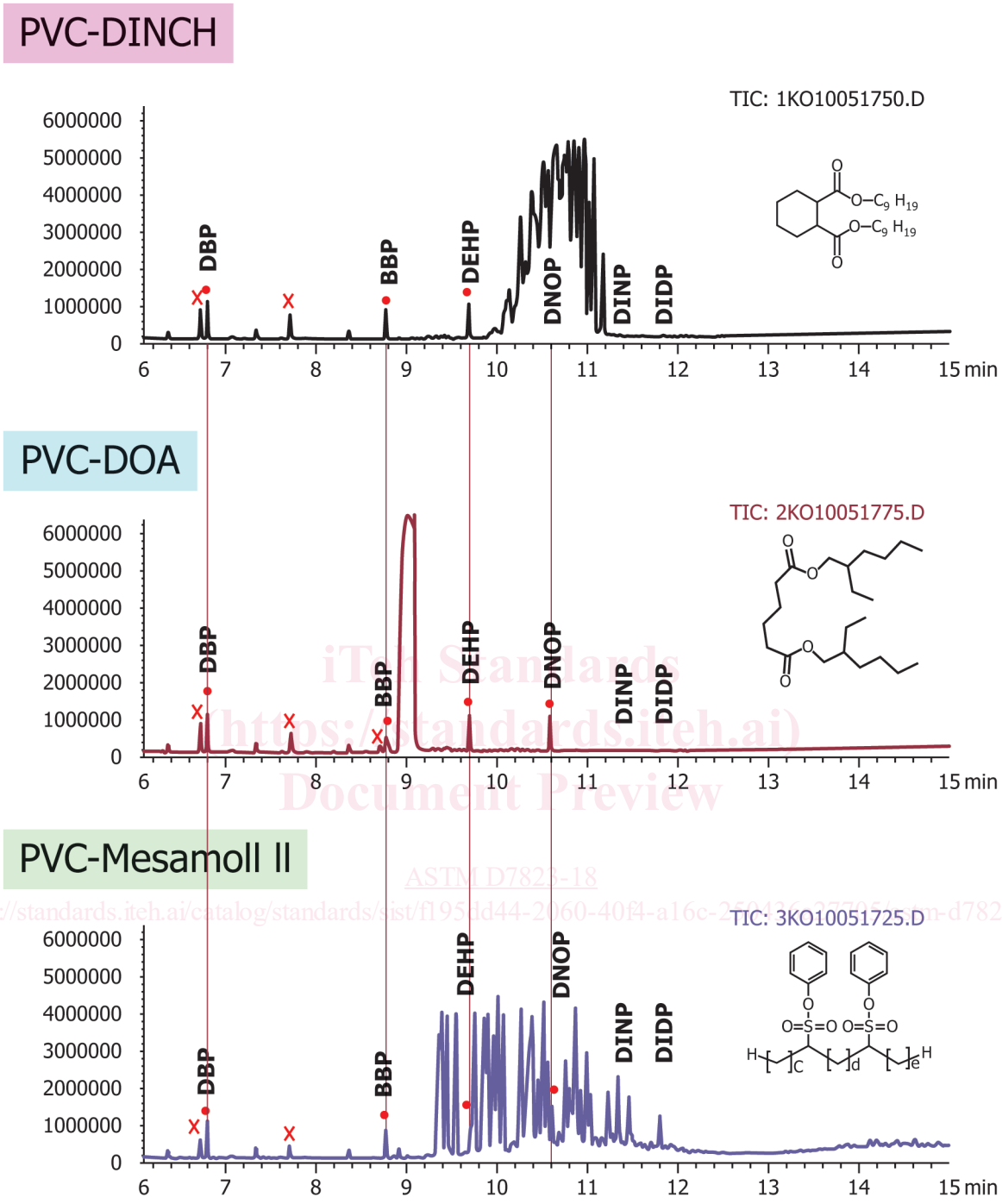


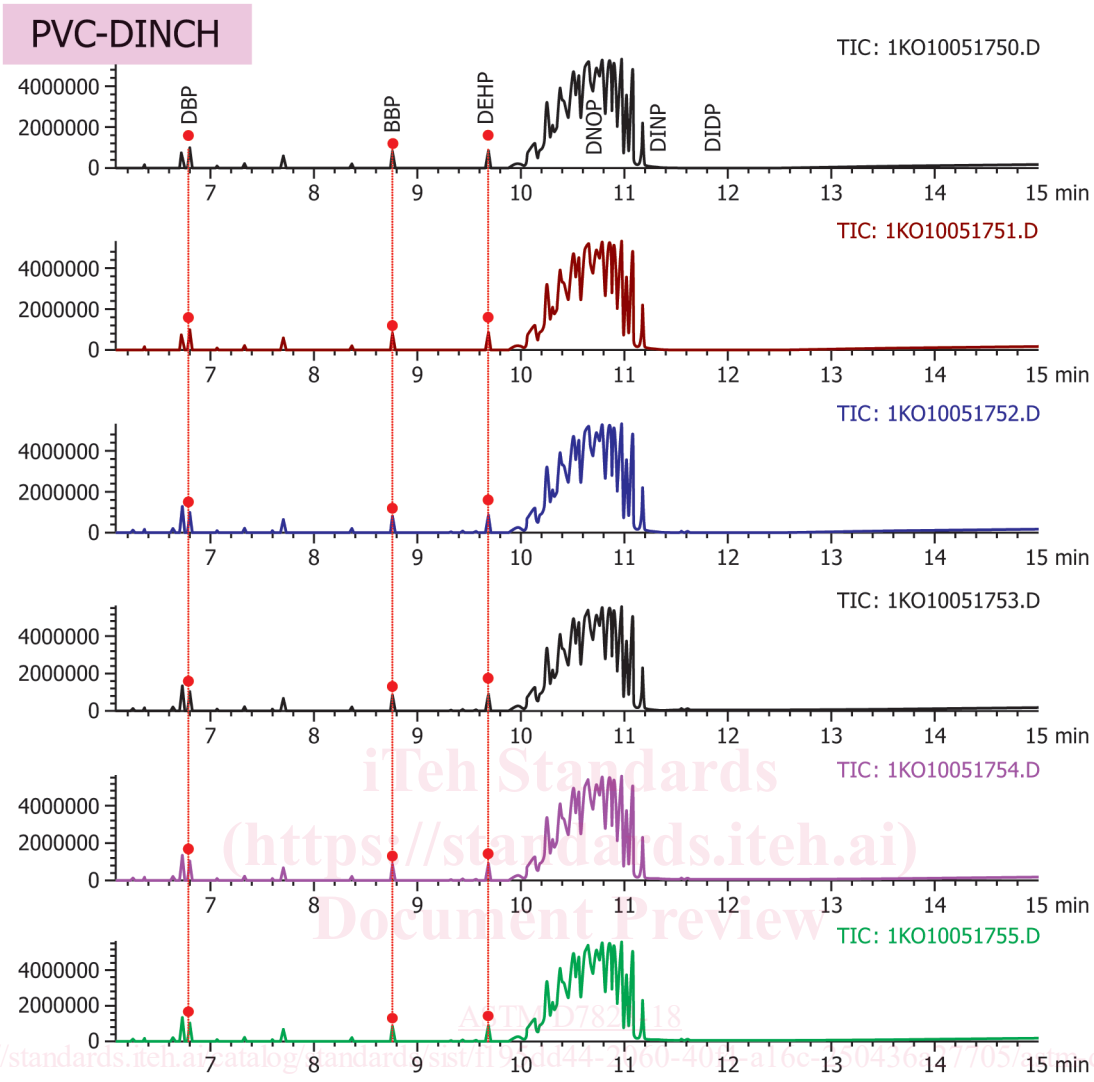
FIG. 2 Solution #2—Chromatograms (TIC) of PVC with Three Different Plasticizers, TD-GC/MS Analysis (see 10.3 and 11.3)

11. Procedure

11.1 Establish that the analytical system contains concentrations of phthalate contamination that are lower than the background contamination acceptable to the project specific Data Quality Objectives by analyzing 10 µL of THF.

11.2 Establish the relative retention time and mass spectrum of each phthalate using Solution #1—10.2: The following conditions were used to obtain the example chromatograms shown in Figs. 1-4:

	~~Thermal Desorption (TD) GC/MS Analysis~~ Thermal Desorption (TD) GC/MS Parameters
TD temperature:	100 - 20°C/min - 320°C (5 min hold)
Py interface:	320°C (Auto mode),
GC injector :	300°C



No	File name	DBP m/z=223	BBP m/z=206	DEHP m/z=279	DNOP m/z=279	DINP m/z=293	DIDP m/z=307
1	KO 10051750	243.840	505.044	328.756	332.096	489.945	616.594
2	KO 10051751	242.452	517.461	340.418	321.613	497.762	633.184
3	KO 10051752	240.288	517.972	354.329	331.371	507.979	657.815
4	KO 10051753	246.959	528.137	349.345	327.968	505.853	646.300
5	KO 10051754	238.760	515.500	345.159	336.845	504.904	656.879
6	KO 10051755	246.510	521.102	343.431	333.874	503.383	653.434
Averaged peak area		243.135	517.536	343.573	330.628	501.638	644.034
SD		3293.118547	7556.303832	8729.726158	5296.045748	6684.847213	16242.41879
RSD (%)		**1.35**	**1.46**	**2.54**	**1.60**	**1.33**	**2.52**

FIG. 3 Solution #2—Reproducibility of PVC-DINCH (n=6) (see 10.3 and 11.3)

~~GC oven:~~	~~80 (1 min hold) to 200°C (at 50°C/min) to 320°C (15°C/min, 2 min hold)~~
GC oven:	80 (1 min hold) to 200°C (at 50°C/min). Injection at 80°C avoids thermal shock, which improves analytical precision. The initial ramp rate is not critical and will be a function of the performance of the GC oven. 200°C to 320°C (15°C/min), 2 min hold 320°C
Solvent delay:	6 min
Column:	UA-5 (5 % Diphenyl-95 % dimethyl polysiloxane) 30 m by 0.25 mm i.d, 0.25 µm film) or equivalent
Column He flow:	1.2 mL/min, Split ratio: 1/20
Mass range:	29-600 m/z,