Designation: D8133 – 23

Standard Test Method for Determination of Low Level Phthalates in Poly(Vinyl Chloride) Plastics by Solvent Extraction—Gas Chromatography/Mass Spectrometry[1]

This standard is issued under the fixed designation D8133; 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 quantify six phthalates by solvent extraction of plasticized PVC articles followed by analysis of the extract by gas chromatography/mass spectrometry. Six phthalates, BBP, DBP, DEHP, DNOP, DINP, and DIDP, are used to illustrate how to implement the method.

NOTE 1—The method can be extended to other phthalates in a wide range of polymeric substrates.

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 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

NOTE 2—There is no known ISO equivalent to this standard.

1.5 *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 Guide for Purity of Monomeric Plasticizers by Gas Chromatography

D7083 Practice for Determination of Monomeric Plasticizers in Poly (Vinyl Chloride) (PVC) by Gas Chromatography

D7823 Test Method for Determination of Low Level Phthalates in Poly (Vinyl Chloride) Plastics by Thermal Desorption—Gas Chromatography/Mass Spectrometry

D7993 Guide for Analyzing Complex Phthalates

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:*ADJD7823-EA

Vinyl Plasticizer Library—Total Ion Chromatograms and Mass Spectra

2.3 *CPSC Standard:*[3]

CPSC-CH-C1001–09.3 Standard Operating Procedure for Determination of Phthalates

3. Terminology

3.1 *Definitions:*

3.1.1 For definition of plastic terms used in this standard, see Terminologies D883 and D1600.

3.2 For units, symbols, and abbreviations used in this standard refer to Practices E594, E355, or IEEE/ASTM SI-10.

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

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[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.

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[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 U.S. Consumer Product Safety Commission (CPSC), 4330 East West Hwy., Bethesda, MD 20814, http://www.cpsc.gov.

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

3.3.3 (DBP) 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 CAS #117-81-7

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

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

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

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

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

3.3.11 GC Gas Chromatography

3.3.12 GC/MS Gas Chromatography/Mass Spectrometry

3.3.13 TD-GC/MS Thermal Desorption—Gas Chromatography/Mass Spectrometry

3.3.14 PVC Poly(vinyl chloride)

3.3.15 Heptane GC grade or higher

3.3.16 FTIR Fourier Transform Infrared Spectroscopy

3.3.17 TIC Total ion chromatogram

3.3.18 DQO Data quality objectives

4. Summary of Test Method

4.1 *Test Method A*—100 mg of the plasticized PVC sample along with 10 mL of heptane is extracted for 2 hours with the aid of sonication. One milliliter of the heptane solution is placed in a GC vial and analyzed by GC/MS. Phthalates are identified by their retention times and their mass spectra/SIM ions. Quantification is based on the area of a designated quantitative ion (SIM or full scan) (see Table 1). The amount of each component is determined using a standard addition calibration method.

4.2 *Test Method B*—100 mg of the plasticized PVC sample are dissolved in THF. After the polymer is precipitated by adding 20 mL of hexane, 1.3 mL of the supernatant is filtered and placed in a GC vial and analyzed by GC/MS. Quantification is based on the area of a designated quantitative ion (SIM or full scan) (see Table 1). The amount of each component is determined using an internal calibration method.

NOTE 3—Standard addition calibration will correct for matrix affects (that is, response of the phthalates being different in solvent versus the solvent and sample matrix).

5. Significance and Use

5.1 *Identification and Quantification of Phthalates*—DBP, BBP, DEHP, DNOP, DINP and DIDP are 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 108, Japan—Health, Labor and Welfare Ministry guideline No. 336 (2010) and IEC 62321-8:2017. These test methods provide a procedure to identify and quantify phthalates in PVC.

5.2 Other techniques successfully used to separate and identify phthalates in PVC include TD-GC/MS (ASTM D7823), 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 ensure 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, but is not limited to changing the selectivity of the chromatographic column or the heating profile of the GC column. Calibration by standard addition offers the advantage of correcting for matrix affects.

6.2 When running the GC/MS method, care must be taken to ensure that the vials, septa, and containers are free of any phthalate contamination. Also, all solvents used to prepare standards and sample solutions must be free of contamination.

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 Confirm Ions, and

(3) the ratio of the Quant Ion and the Confirm Ion 1 in Table 1 must satisfy the established guideline.

6.4 Calculating the phthalate concentrations using the areas of compound specific ions significantly reduces interference from non-target compounds, additionally using standard addition corrects for matrix affects.

TABLE 1 Ions and Ion Ratios Used to Identify Each Phthalate

NOTE 1—When DINP and DIDP are both present in a sample or standard, m/z 127 is used as a qualifying ion for DINP and m/z 289 for DIDP. This is because DINP and DIDP partially co-elute and both produce m/z 149 and 167. If 149 qualifier ion ratios are set when DINP and DIDP are at equal concentrations, then any samples with different ratios will produce substantially different 149/167 ratios, potentially leading to a false negative.

	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

7. Safety and Precautions

7.1 Use organic solvents in a well-ventilated space.

TEST METHOD A—HEPTANE EXTRACTION PROCEDURE

8. Apparatus

8.1 *Gas chromatograph/mass spectrometer* capable of operating in the 100-260°C temperature range and equipped with autosampler and injector.

8.2 *GC vials,* glass pipets, 4, and 20-mL vials.

8.3 *Optional Recommended Equipment*—10-mL volumetric flask.

8.4 *GC Capillary Column*—Carbowax capillary column, 30 m by 0.25 mm ID with a 0.25 µm film thickness, or equivalent.

8.5 *Integrator or data handling system,* capable of measuring peak areas and retention times.

8.6 *Analytical balance,* capable of weighing to ±0.00001 g.

8.7 *Pressure regulators,* for all required gas cylinders.

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

9. Reagents and Materials

9.1 Helium carrier gas, chromatographic grade.

9.2 Heptane for preparing the phthalate standard solution (Stock Standard Solution, Standard Solution #1, 10.2 and 10.3; Sample Solution, 10.4), spectral quality or chromatographic grade.

9.3 Standards of the appropriate phthalates for use when preparing the Stock Standard Solution (10.2) and Standard Solution #1 (10.3) used for standard addition. See Note 4.

Note 4—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.

10. Preparation of the Analytical Samples

10.1 Four solutions shall be prepared:

(1) a Stock Standard Solution of the target phthalate standards,

(2) a Standard Solution of the target phthalate standards used to spike the sample,

(3) a solution of the sample, and

(4) the sample solution spiked with the standard stock solution.

10.2 *Stock Standard Solution*—Prepare a stock standard solution of the phthalates by dissolving 0.10 g of each phthalate in 10 mL of heptane (0.10 g/10 mL; this is conveniently performed by weighing the phthalates into a 10 mL volumetric flask and diluting to the mark).

10.3 *Standard Solution #1A*—Prepare a diluted (1:10) solution of the Stock Standard Solution to spike the sample solutions. To test system performance and verify retention times a 10 µL aliquot of Standard Solution #1 is added to 1 mL of heptane and analyzed.

10.4 *Sample Solution*—Cut each plasticized component part 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.

10.4.1 Weigh 100 mg (0.10 g) of the sample in a vial and add 10 mL heptane with a 10-mL volumetric pipet (100 mg/10 mL). The vial with the sample and heptane is placed in a sonication bath and extracted for two hours at room temperature. Into a GC vial, place 1.0 mL of the extracted sample solution (this is conveniently done with a 1 mL volumetric pipet). See Fig. 1 and Fig. 2 for example chromatograms.

10.5 *Spiked Sample Solution*—Place 1.0 mL of the sample solution (10.4) into a GC vial. Add 10 µL of the phthalate Standard Solution #1 (10.3) to the sample solution with a GC syringe.

Note 5—A critical step in the accurate determination of phthalates is sample homogeneity. This is discussed in more detail in Appendix X1.

11. Procedure

11.1 Establish that the analytical system has an acceptable background of phthalate contamination by analyzing a heptane solvent blank. Acceptable background contamination will be determined by the data quality specific objectives.

11.2 Establish the relative retention time and mass spectrum/SIM ions of each phthalate by analyzing a solution of 10 µL of Standard Solution #1 (10.1(*3*)) added to 1.0 mL of heptane. The conditions in Table 2 were used to obtain the example chromatograms shown in Figs. 1 and 2.

TABLE 2 Gas Chromatography/Mass Spectrometry Analysis Conditions

Column:	Carbowax (Polyethylene glycol) stationary phase, 30 m × 0.25 mm i.d, 0.25 µm film thickness
Carrier Gas:	Helium or other acceptable gas
Carrier Flow Rate:	1.0 mL/min
Oven Temperature Program:	150°C (0 min hold) to 250°C (at 10°C/min) (45 min hold)
Injector Temperature:	250°C
Injection Conditions:	Split or splitless injection depending on the sensitivity of the instrument. 20:1 split is recommended as a starting point for those wishing to run split.
Injection Volume:	1 µL
MSD Transfer Line Temp.:	250°C
Ion Source (EI) Temp.:	230°C
MS Mode:	SIM (scan mode is employed if sufficient detection sensitivity is met)

11.2.1 The mass spectrometer is run in scan mode for general identification of phthalates and other sample components.

11.3 Analyze the sample (Sample Solution – 10.4) and Spiked Sample (Spiked Sample Solution – 10.5) using the conditions outlined in 11.2. A typical chromatogram is shown in Fig. 1 and Fig. 2.

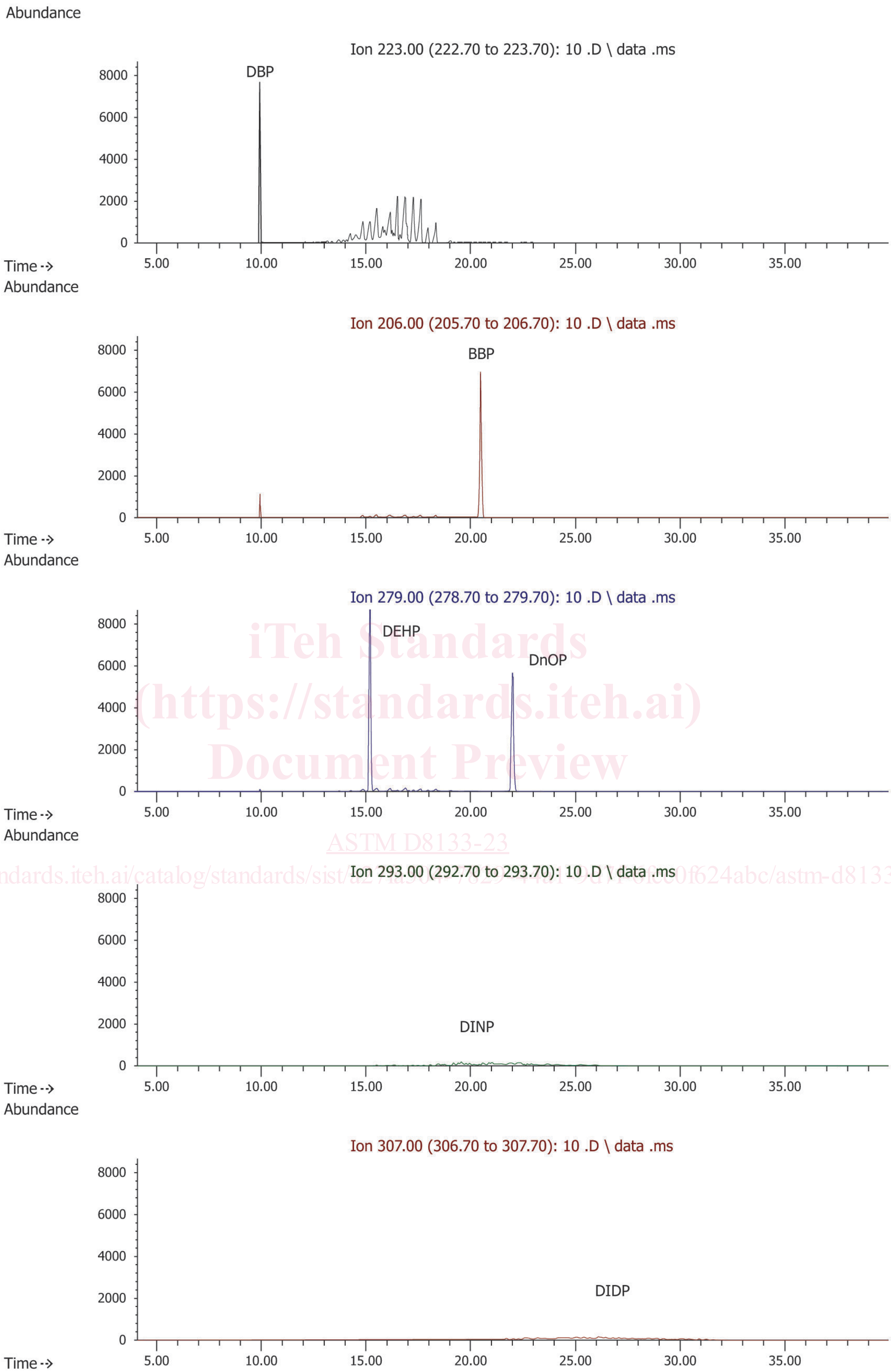

FIG. 1 Sample Solution—Ion Extracted Chromatogram of DINCH Plasticizer with About 1000 ppm of Each Phthalate (see 10.4 and 11.3)

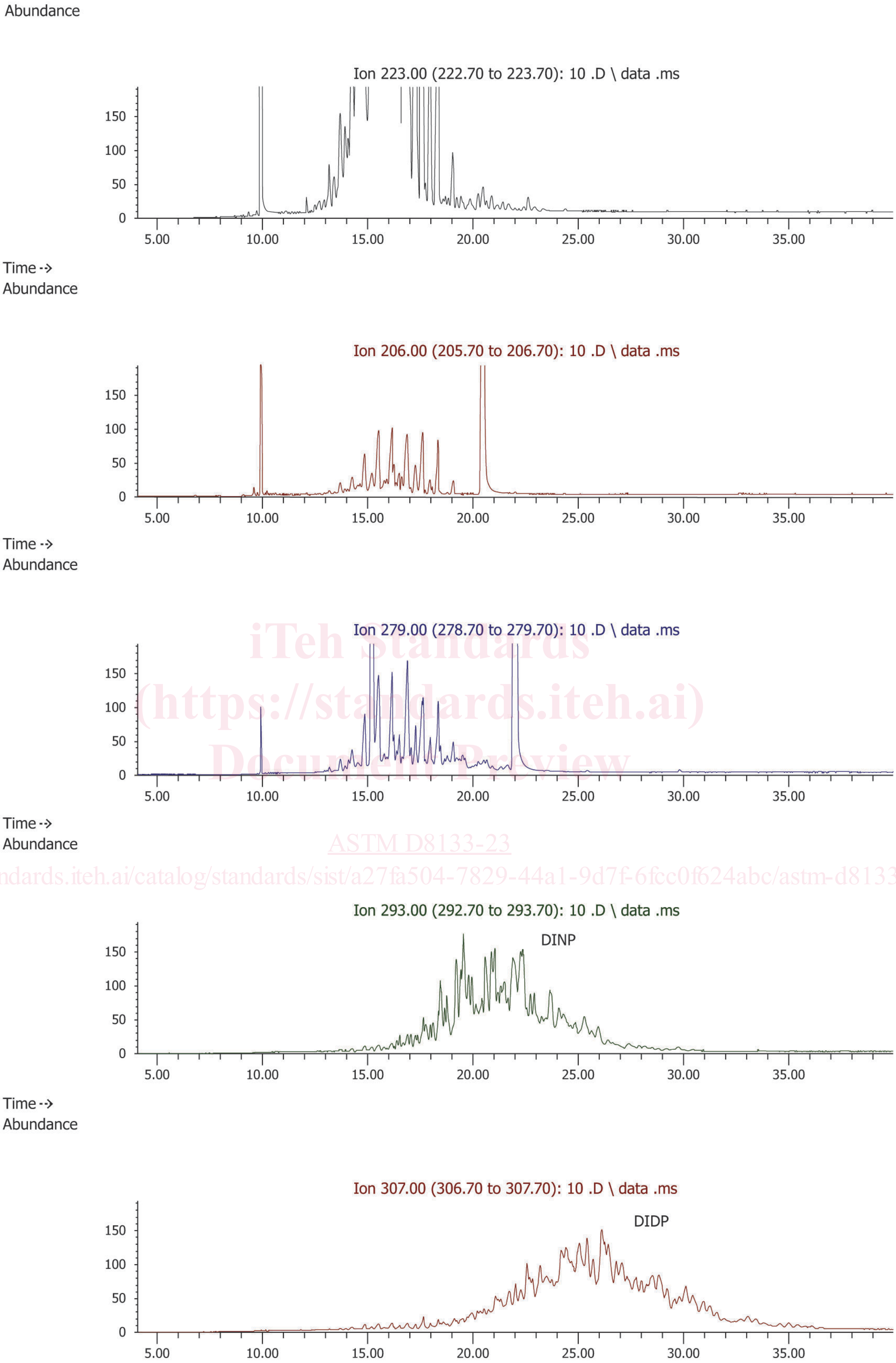

FIG. 2 Sample Solution—Ion Extracted Chromatogram of DINCH Plasticizer with About 1000 ppm of Each Phthalate (see 10.4 and 11.3)—Expanded TIC

11.4 Peak identifications are based on relative retention data, Scan mode (extracted ion) or single ion monitoring (SIM) mode of the quant and confirming ions and the ion area ratios as indicated in Table 1. Phthalate quantification is based upon the peak areas of the quant ions listed in Table 1. The assumption being made is that the sole source of the quant ion at a predetermined retention time is the phthalate. Use the peak area of the quant ion to accurately determine the amount of the phthalate.

11.4.1 Peak identification is based solely on the presence or absence of the quant ion and the two confirming ions at a predetermined retention time. Quantification is based on the area of the quant ion.

NOTE 6—A typical ion extracted chromatogram obtained using the conditions specific in 11.2 is shown in Fig. 1. Because the absolute retention times are dependent upon the entirety of the GC system; relative retention times are used to identify each phthalate.

11.5 Quantification is done using standard addition. Analyze a Sample Solution. A typical ion extracted chromatogram is shown in Fig. 1 and Fig. 2. Standard addition is very useful to correct for difference in response of the analyte in the sample matrix. This is often the case when analyzing PVC where DINCH, Mesamoll or both are present.

NOTE 7—A good overview of standard addition is found on page 476, LCGC North America, Volume 27, number 6, June 2009.

12. Example Calculations

12.1 The amount of each phthalate in the samples are determined by a single-point standard addition method. The amount of the analyte spiked into the sample (in µg) is plotted versus the peak area (see Fig. 3). The line is used to calculate the amount of phthalate in the sample. As only one-tenth of the sample solution is spiked (the weight of sample is about 0.100 g / 10 = 0.01 g).

12.1.1 To determine the amount of the analyte in the sample, determine the point where the line crosses the x-axis (this is the amount of the analyte in the sample solution, DBP in this case).

$y = 12202.3x + 116113.0 = 0$

x (µg of analyte in sample solution) = 116113.0 / 12202.3 = 9.52

Amount of analyte in sample (ppm) = µg of analyte in sample solution / weight of sample in spiked sample

Weight of spiked sample = weight of sample / 10 = 0.1002 / 10 = 0.01002

Amount of BBP in sample (ppm) = 9.52 / 0.01002 = 947

13. Quality Control

13.1 Perform the quality checks outlined in Table 3.

13.2 Ensure that the system is free of phthalate contamination before analyzing samples. Prior to sample analysis the ability of the system to perform properly shall be verified.

14. Report

14.1 The amount of each target phthalate in ppm.

14.1.1 Analyze 10 % of the samples in triplicate, report the standard deviation for each target compound. If the sample batch is less than 10 samples, then analyze one sample in triplicate and report the standard deviation. The standard deviation must be calculated using N-1 (2 rather than 3). No outlier detection is allowed.

14.1.2 If a sample batch is analyzed over more than two days, the percent difference between the first and last Laboratory control sample must be less than 10. Use the average in the denominator for calculating the % difference.

14.2 Report the concentration (ppm) of each target phthalate in the method blank.

14.3 Report the chromatographic conditions and note any deviations from those specified in 11.2.

15. Precision and Bias

15.1 A round robin is in progress to develop precision and bias data.

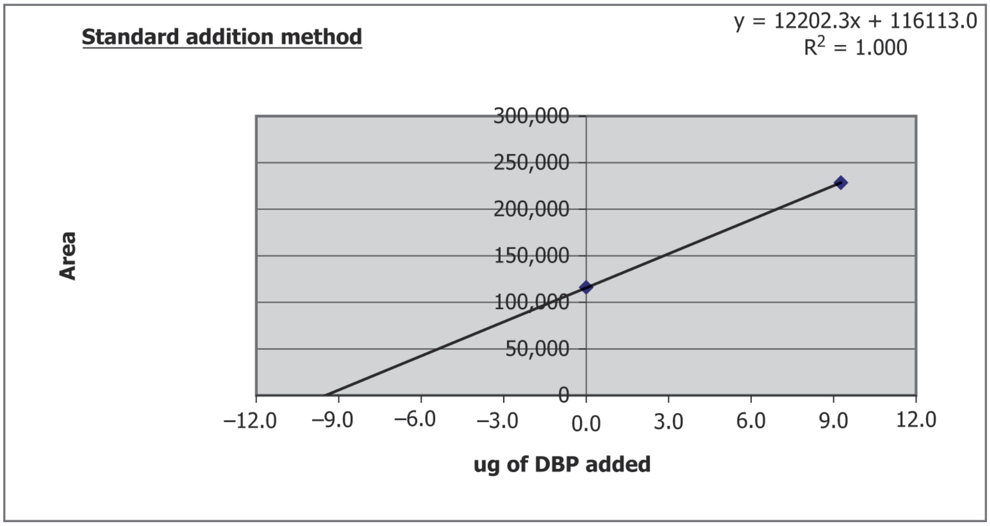

FIG. 3 Plot of Micrograms of Phthalate Added to the Sample Solution Versus Phthalate Peak Area

TABLE 3 System Performance Verification

Sample Description	Frequency	Rationale
Method Blank 1.0 µL Heptane	Prior to sample analysis and after the analysis of 10 samples	Verifies that the phthalate background is below the maximum level of phthalate set by the project's DQO
Laboratory Control Sample 1.0 µL of Sample	Prior to sample analysis and after the analysis of 10 samples	Verifies the stability of the chromatographic system and the stock solution

TEST METHOD B—THE DISSOLUTION AND PRECIPITATION WITH HEXANE PROCEDURE

16. Apparatus

16.1 *Gas chromatograph/mass spectrometer,* capable of operating in the 100-310°C with autosampler and injector.

16.2 *GC Capillary Column*—5 % diphenyl, 95 % dimethyl polysiloxane capillary column, 30 m by 0.25 mm ID with a 0.25 µm film thickness, or equivalent.

16.3 *Integrator or data handling system,* capable of measuring peak areas and retention times.

16.4 *Analytical balance,* capable of weighing to ±0.00001 g.

16.5 *Pressure regulators,* for all required gas cylinders.

17. Reagents and Materials

17.1 Helium carrier gas, chromatographic grade.

17.2 Standards of the appropriate phthalates for use when preparing the Stock Standard Solution and Internal Standard (Section 18). See Note 4.

17.3 Tetrahydrofuran (THF), GC grade or higher.

17.4 Hexane, GC grade or higher.

17.5 Cyclohexane, GC grade or higher.

17.6 Sealable glass vials with PTFE or silicone liner, size 4 mL and 40 mL.

17.7 GC vials, size 2 mL.

17.8 PTFE filters, 0.45 µm.

18. Preparation of the Analytical Samples

18.1 *Stock Standard Solution*—Prepare a 1 mg/mL stock standard solution of the phthalates by dissolving 0.050 g of each phthalate in 50 mL of cyclohexane (this is conveniently performed by weighing the phthalates into a 50 mL volumetric flask and diluting to the mark).

18.2 *Internal Standard*—Prepare a 150 µg/mL internal standard solution by adding 15 mg of neat benzyl benzoate to a 100 mL volumetric flask. Fill with cyclohexane to the mark.

18.3 *Calibration Working Standards*—Prepare working calibration standards in volumetric flasks by adding the appropriate amount of phthalate stock solution (1 mg/mL) to achieve the target calibration standard concentrations. The range of standards needs to cover the expected concentration of the sample to be tested. Add benzyl benzoate (internal standard) to each flask to yield a final concentration of 20 µg/mL, then dilute with cyclohexane to the volumetric mark.

18.4 *Sample Solution*—Cut each sample into small pieces (no dimension larger than 2 mm), or mill/grind into a representative powder. Each cut/milled plasticized component part will be considered a sample for testing as described below.

18.4.1 Weigh out 100 mg of sample into a sealable glass vial. Prepare samples in triplicate.

18.4.2 Add 10 mL of THF to the sample. Shake, stir, or otherwise mix sample for at least 30 minutes to allow dissolution. It is acceptable for the sample to be sonicated and/or gently heated to expedite dissolution. If material does not dissolve completely, add an additional 2 hours to mixing time and then proceed.

18.4.3 Precipitate any dissolved polymer by adding 20 mL hexane. Shake and allow at least 5 minutes for polymer to settle (longer times may will potentially be necessary to minimize clogging of filters in subsequent step).

18.4.4 Filter THF/hexane solution through a 0.45 µm PTFE filter. Collect a few mL of filtered solution in separate 4-mL vial.

18.4.5 Combine 1.3 mL of the THF/hexane solution with 0.2 mL of internal standard (from 17.2) in a GC vial.

19. Procedure

19.1 Establish that the analytical system has an acceptable background of phthalate contamination by analyzing a cyclohexane solvent blank. Acceptable background contamination will be determined by the data quality specific objectives.

19.2 Establish the relative retention time and mass spectrum/SIM ions of each phthalate by analyzing the calibration working standards. The conditions in Table 4 were used to obtain the example chromatogram shown in Fig. 4.

TABLE 4 Gas Chromatography/Mass Spectrometry Analysis Conditions

Column:	5 % Diphenyl, 95 % Dimethyl polysiloxane stationary phase, 30 m × 0.25 mm i.d, 0.25 µm film thickness
Carrier Gas:	Helium or other acceptable gas
Carrier Flow Rate:	1.0 mL/min
Oven Temperature Program:	150°C (1 min hold) to 280°C (at 30°C/min); then to 310°C (at 15°C/min) with a final hold of 5 min[A]
Injector Temperature:	290°C
Injection Conditions:	Split or splitless injection depending on the sensitivity of the instrument. 20:1 split is recommended as a starting point for those wishing to run split.
Injection Volume:	1 µL
MSD Transfer Line Temp.:	250°C
Ion Source (EI) Temp.:	230°C
MS Mode:	Simultaneous SIM/Scan if available; SIM only if not

[A] Slight changes to the oven temperature profile are permissible as needed to allow for different instruments and injection styles. A test with a standard mix is recommended to ensure that all peaks elute and are baseline separated from other peaks sharing the same monitored transitions.

19.2.1 The mass spectrometer is run in scan mode for general identification of phthalates and other sample components.