

A fast, easy and “green” thermal desorption-GC/MS method for the analysis of phthalate esters in PVC

A discussion of the central factors that influence data quality when using ASTM D7823⁽¹⁾ for the determination of phthalates in polymeric substrates

**D. Randle, R. Freeman, A. Hosaka and C. Watanabe
Frontier Laboratories Ltd.**

1. Introduction

Phthalates, which are esters of phthalic acid, have been used in the manufacture of a wide range of consumer products. They are added to plastics to make them more flexible and harder to break. Although the wide-spread use of phthalates in the manufacture of polymeric products has been largely discontinued, they continue to pose a risk to human health. Phthalates are easily released into the environment because they are not covalently bonded to the polymer. Consequently, exposure can be through direct contact, food, water and the atmosphere.

Several phthalates are tightly regulated on a global scale. The United States⁽²⁾, Canada, the European Union, Japan and many other nations have banned the use of and passed regulations designed to monitor for the concentration of phthalates in consumer products. In the US, Congress has permanently banned three phthalates (DEHP, DBP, BBP) in any amount greater than 0.1 percent (per plasticized component part of a children’s toy or child care article). There is also an interim ban on DINP, DIDP and DNOP, which only applies to children’s toys that can be placed in a child’s mouth^(3,4).

Although a number of different analytical techniques can be used to determine the presence of phthalates, most laboratories use wet chemical techniques to extract the phthalates from the polymer matrix. The extract is then analyzed using GC or HPLC chromatographic methods to separate and quantitate the individual phthalates. "Traditional" sample preparation is, at best, cumbersome, time consuming, costly and does not always completely isolate the phthalates from the polymer matrix. Thermal desorption (TD) is a viable alternative to traditional solvent-based sample preparation.

Thermal desorption is based on the fact that there is free volume within the polymer structure through which small molecules (e.g., phthalates) are free to “move”. The motion is due to intermolecular collisions (i.e., Brownian motion). Random motion from regions of high concentration to regions of lower concentration is called diffusion. Factors affecting the rate of diffusion are the solubility and diffusivity of the small molecules in the polymer. Increasing the temperature of a polymer causes the small molecules on the surface to vaporize and the concentration gradient across the polymer to increase. In addition, the permeability of the polymer increases with temperature. These two factors result an even greater flux of small molecules to the surface.

The phthalate vapors are analyzed using GC/MS. Phthalates are identified using both retention data and compound specific ions. The entire process can be automated.

2. Overview of ASTM D7823

ASTM D7823 describes the quantitative analysis of six regulated phthalates in polyvinylchloride (PVC). This analytical method uses thermal desorption (TD) in which phthalates in PVC are thermally desorbed and introduced into GC/MS for separation and analysis. In this method, the sample preparation is simple and easy and the amount of organic solvent required is as small as 10 mL for a single sample.

Also, the standard addition used in this method provides quantitative values with the highest accuracy and the results are virtually not influenced even by high concentrations of non-regulated plasticizers contained up to several tens of percents.

Although ASTM D7823 is written specifically for the six regulated phthalates in PVC; it can easily be extended to include a variety of other phthalates in a number of different polymeric matrices.

3. Sample preparation

ASTM D7823 is based on the thermal desorption (thermal “extraction”) of the phthalates from a polymeric substrate. The method specifically calls for the dissolution of the polymer in a suitable solvent such as THF; however, subsequent studies have shown that meaningful data can also be obtained when the polymer is analyzed directly. Analysis of the solid is often referred to as a “direct” method. Analysis of a microliter aliquot of a quantitative solution of the sample is referred to as a “thin film” method. The entire sample preparation protocol is summarized in Figure 1. Each step is described in the ASTM method.

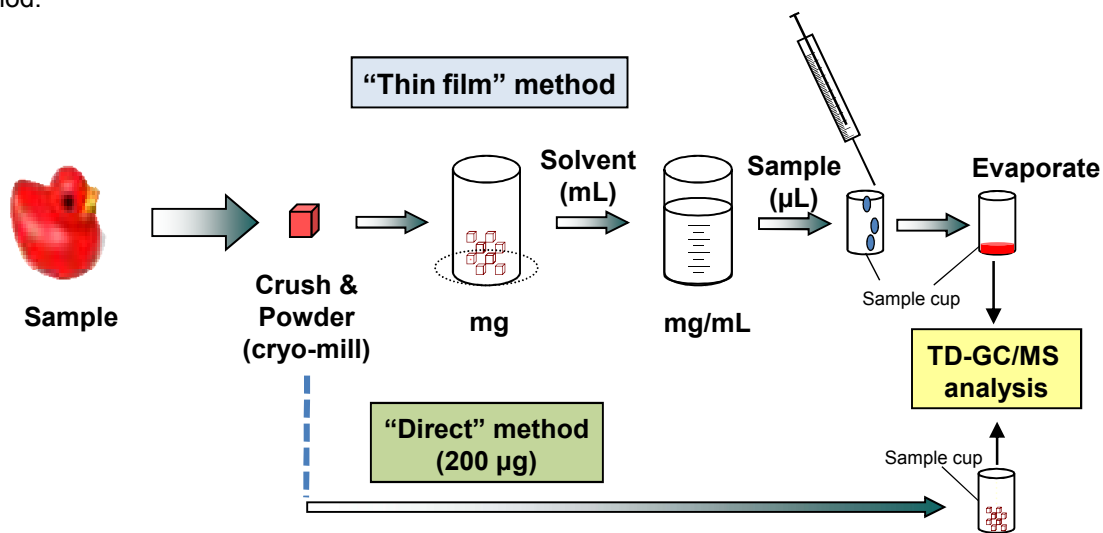


Figure 1. Quick, simple and “green” sample preparation. The “thin film” method requires that a quantitative solution of the sample be prepared. An aliquot of the THF solution is placed in the sample cup.

Comment 1: The accuracy of the measurement is highly dependent upon three factors: (1) the homogeneity of the portion of the sample selected for analysis, (2) the accuracy of the analytical balance and (3) the accuracy and/or precision of the device (e.g., syringe) used to transfer the dissolved sample into the sample cups. Sample homogeneity is accomplished using a variety of methods including cryo-milling, grinding and sieving, averaging the results from the analysis of multiple samples and/or dissolving the entire sample in a known volume of solvent. Regardless of how the sample is homogenized, microgram quantities are actually analyzed. The ability of the balance to accurately weigh microgram quantities will directly affect the accuracy of the phthalate determination.

The analytical precision obtained using the thin film and direct sampling methods is compared in Figure 2. The thin film method is an aliquot of a solution that is, by definition, homogeneous, whereas the direct method is a random sampling of particles, which will inherently lack sample-to-sample reproducibility.

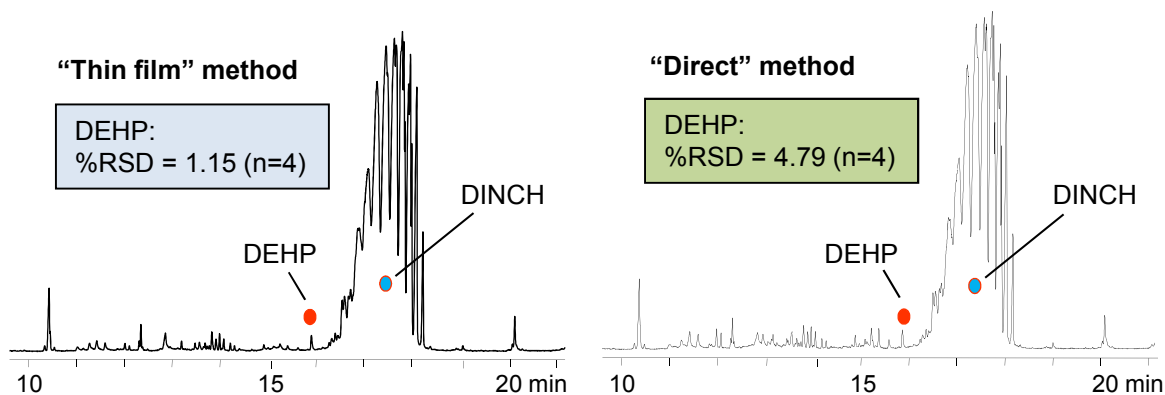


Figure 2. Influence of the sample preparation method on analytical precision. Sample: 0.5 mg plastic toy (PVC & DINCH); Thin film: 20 μ L THF solution. Direct sampling: powder < 45 mesh.

4. Determination of the EGA thermal desorption zone

Evolved gas analysis (EGA) – MS^(5,6) is used to define the thermal desorption zone for the phthalates. This is a simple method that utilizes the temperature programmability of the Frontier EGA/PY-3030D (or 2020iD) pyrolyzer. A deactivated stainless steel tube (2.5 m x 0.15 mm i.d.) connects the injection port to the MS. The sample is heated from a low temperature to a high temperature. As the temperature increases, constituents in the sample vaporize, pass through the tube and are detected by the MS. A plot of sample temperature vs. detector signal is referred to as an EGA thermogram.

The EGA thermogram of a polyvinyl chloride sample is presented in Figure 3. Extracted ion chromatograms are used to delineate the thermal zone over which the phthalates evolve. Ion 149, which is common to all of the phthalates of interest, is used to “identify” the phthalate envelope: 100 to 320°C. In this example, DOA (Di(2-ethylhexyl)adipate) which is a common plasticizer used in the manufacturing of flexible plastic toys, medical devices and food packaging desorbs along with the phthalates. In order to identify and quantitate the phthalates in the sample, it is necessary to either chromatographically separate the DOA isomers from the phthalates of interest or use ions that are present in the phthalate mass spectra and not found in the DOA spectra.

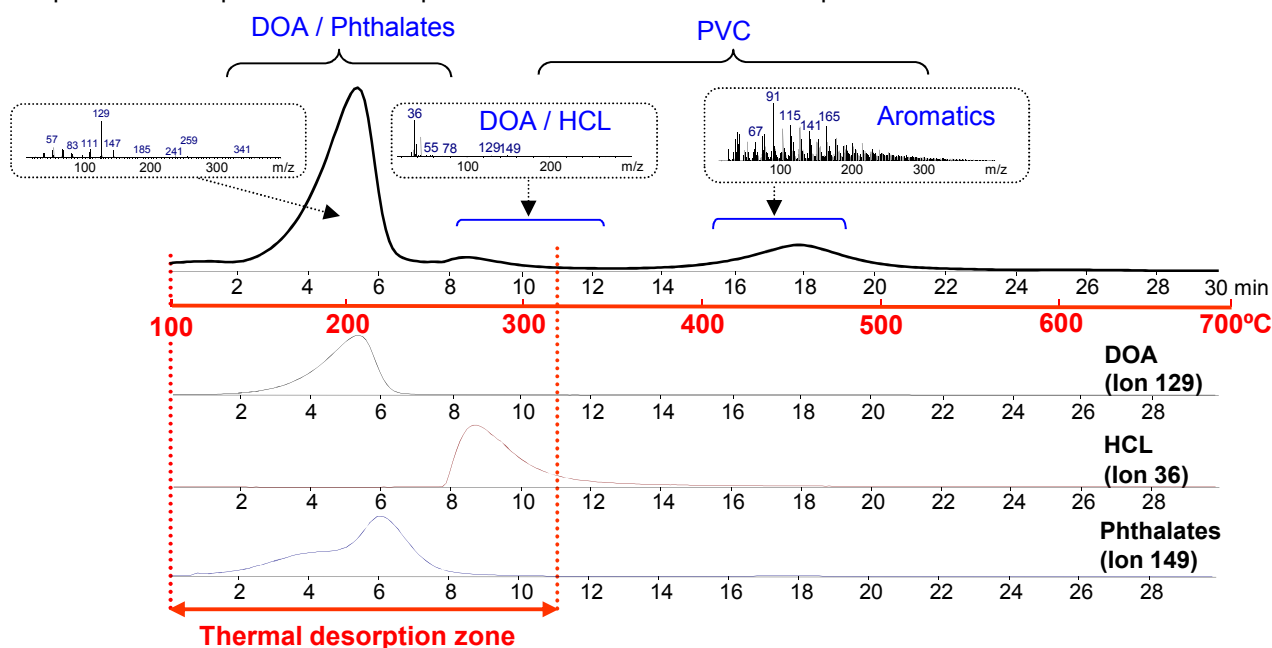


Figure 3. Using extracted ion chromatograms (EIC) to determine the phthalate thermal desorption zone. Sample: PVC + DOA.

5. Advantages of thermal desorption over conventional method (solvent extraction)

Virtually all analytical methods consist of four steps: sample preparation, method calibration, sample analysis and data processing.

Most of the actual sample manipulation occurs during sample preparation and it is during this process that there is the highest probability of introducing error into the determination. Potential sources of errors include: (1) processing a non-representative portion of the sample. (2) sample contamination (e.g., glassware, reagents or solvents) and (3) deviations from the procedure prescribed in the method. Also, it is important to note that sample preparation also represents most of the costs associated with a given analytical procedure. Ideally, the sample should be analyzed “as is”. Direct analysis of the sample increases laboratory productivity and improves the overall data quality.

One of the most important advantages that thermal desorption has over samples prepared using conventional solvent-based techniques is that only that portion of the sample that is desorbed is transported to the column. At 320°C, the highest thermal desorption temperature prescribed in ASTM D7823, any of the polymers is virtually not decomposed and the polymer remains in the sample cup and is therefore not introduced into the GC inlet, column, or MS. Because only the volatile fraction of the sample is “injected,” there is no need for a post-run bake out, more samples can be analyzed per unit time and sample-to-sample carry over is virtually non-existent. This has a major positive impact on both data quality and laboratory productivity.

6. Analysis

In practice, the samples are prepared as previously discussed. If the samples are analyzed directly, approximately 100 µg are placed in a sample cup. If the samples will be analyzed using the thin film method, 10-20 µL of the quantitative solution are added into a sample cup. The solvent is evaporated leaving a thin film of the sample on the cup surface.

TD-GC/MS combines the sample preparation (i.e., TD) with GC/MS analysis. This work was done on using a Frontier Lab EGA/PY-3030D or 2020iD multi-functional pyrolyzer with a 48 position auto-sampler (Frontier Auto-Shot AS-1020E) interfaced via a split/splitless injection port to a GC/MS. The cup is dropped into the furnace, which is at 100°C. The temperature increases at 20°C/min until it reaches 320°C. The initial column temperature is 80°C, which is low enough to facilitate the condensation of the desorbed vapors into a narrow band at the head of the column. A typical total ion chromatogram (TIC) and the extracted ion chromatograms (EIC) for the six regulated phthalates are shown in Figure 4. The analytical precision (n=6) obtained for each phthalate is shown in Table I.

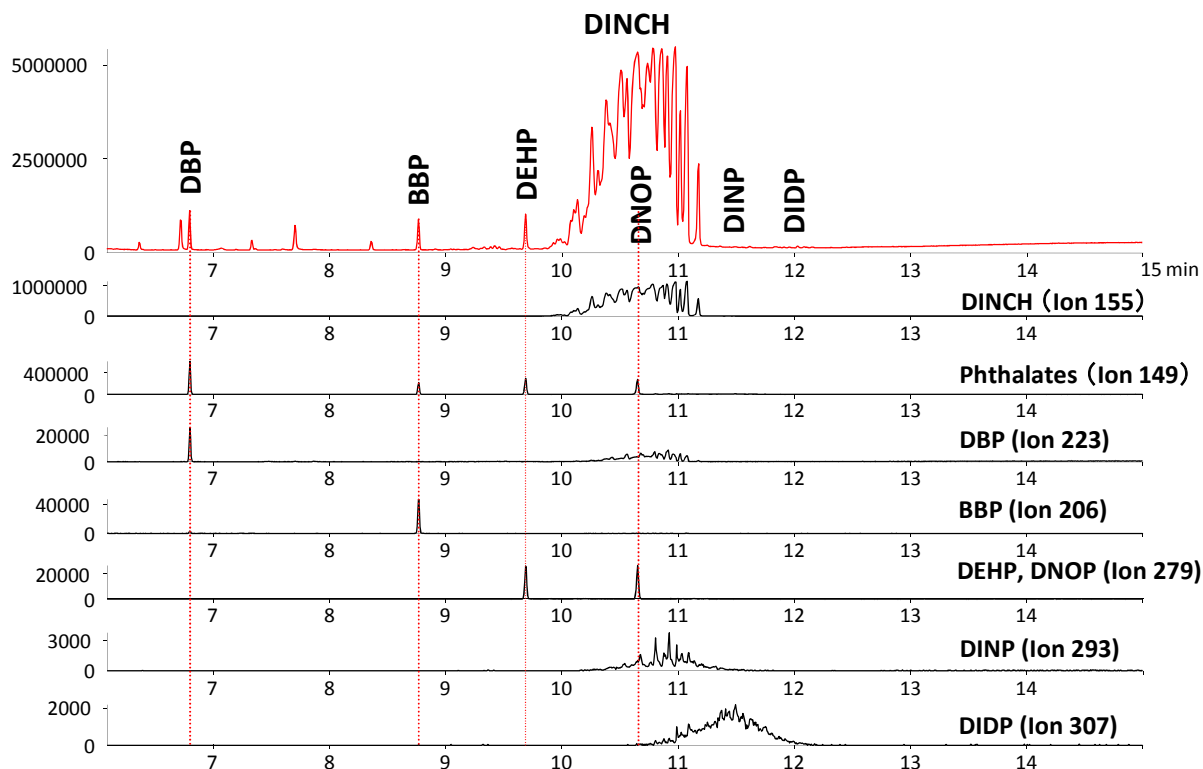


Figure 4. TD-GC/MS analysis of a PVC-DINCH polymer spiked with the six regulated phthalates. The phthalates are identified based upon their relative retention time and the presence of the phthalate-specific quant ion. The thin film sample preparation as described in D7823 was used for this analysis.

Phthalate Quant ion	DBP m/z=223	BBP m/z=206	DEHP m/z=279	DNOP m/z=279	DINP m/z=293	DIDP m/z=307
Replicates	(n=6)	(n=6)	(n=6)	(n=6)	(n=6)	(n=6)
% RSD	1.35	1.46	2.54	1.60	1.33	2.52

Table I. Analytical precision based upon the area of the phthalate-specific quant ion for six replicates (n=6) of a PVC/DINCH sample.

7. Instrument and analytical conditions

Frontier Laboratories' EGA/PY-3030D or 2020iD Pyrolyzer; thermal desorption zone: 100 to 320°C at 20°C/min. PY interface: 320°C (Auto mode); GC injector: 300°C, GC oven: 80°C (1 min) – 200°C (50°C/min) – 350°C (15°C/min, 2 min hold); Solvent delay: 6 min.; Column: UA-5 (5% Diphenyl-95%dimethyl polysiloxane) 30m, 0.25mm i.d, 0.25 µm film); Column He flow: 1.2 mL/min; Split ratio: 1/20; Mass range: 29-600 m/z; Scan speed: 2.57 scans/sec; Threshold: 50; MS transfer line Temp.: 300°C; Ion Source (EI) Temp.: 230°C; Sample wt.: ca. 200 µg.

8. Calibration

Of the four calibration methods most often used for quantitation, standard addition is the method of choice. Polymeric products are often very complex blends of additives, co-polymers and oligomers. Many different chemical species can be desorbed along with the phthalates. For example, Figure 4 shows that DOA desorbs with the phthalates. Other common plasticizers, such as Mesamoll II (Alkylsulphonic acid phenyl esters (ASE)) and DINCH (1,2-Cyclohexane dicarboxylic acid di-isononyl ester), also desorb with the phthalates. The potential for interference is significant. Another issue that must be considered is that it is not unusual for a GC/MS to struggle with long term contamination, most of which is inconsequential to the analysis being performed. For example, m/z 207 is a common polysiloxane associated with modern day cross-linked stationary phases. m/z 207 is not an ion that is associated with any of the phthalates on interest; however, very often the system contamination is, in fact a phthalate; standard addition will help mitigate the error associated with the phthalate background.

Standard addition is the best calibration protocol when interference is an issue. The calibration is done using the sample matrix in the same time frame as the sample analysis. Interferences and background contamination will be constant for all analyses and its effect on the calculated concentration is negated.

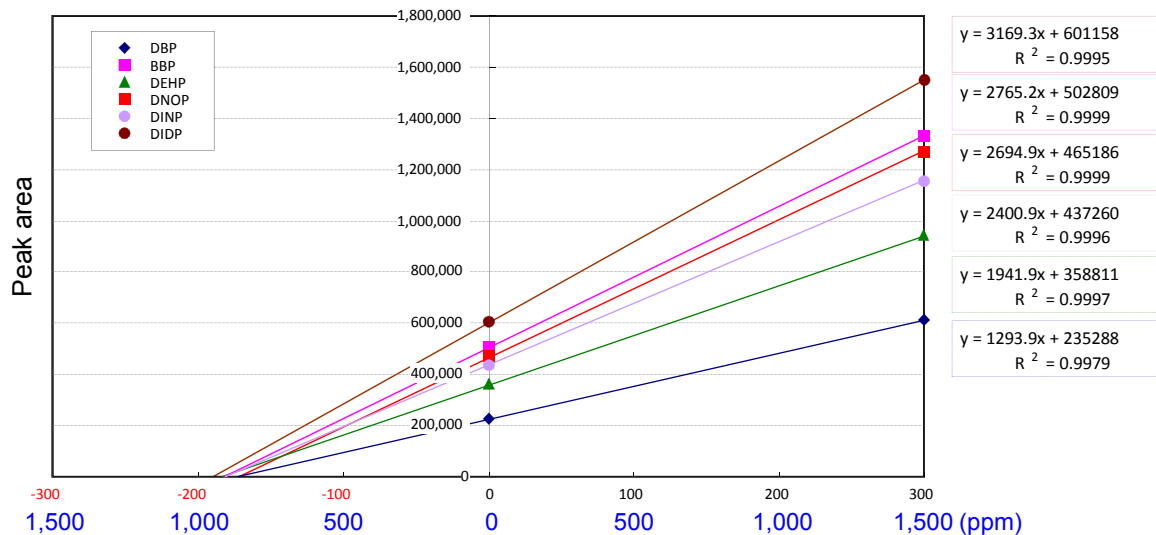


Figure 5. A typical set of single point standard addition calibration curves for the six regulated phthalates in PVC - DOA. The number of calibration points can be increased as specified in the laboratory's data quality objectives (DQO) documents or a project specific Work Plan.

PVC – DOA Quant ion	DBP m/z=223	BBP m/z=206	DEHP m/z=279	DNOP m/z=279	DINP m/z=293	DIDP m/z=307
ng	181.8	181.8	184.8	172.6	182.1	189.7
ppm	909	909	924	863	911	948
%RSD (n=6)	2.08	0.76	1.42	0.85	2.03	2.07

Table II. Calculated amounts of the six regulated phthalates determined using the standard addition calibration method.

Example calculation: Equation of the DBP calibration curve is: $y = mx + b$
 $y = 1293.9x + 235288$ ($R^2=0.9979$).
When $y=0$ then $x = -235288/1293.9 = -181.8 \therefore 181.8$ ng.
Concentration in ppm is given by :
Value of DBP \div Assumed content of PVC-DOA = 181.8 (ng)/ 200 (μg)
= 0.909 (ng/ μg) = 909 (ng/mg) = 909 (ppm).

Comment 2: A list of the most commonly encountered phthalates is shown in Table III. The regulated and monitored phthalates are in red. Note that both DIDP and DINP are technical mixtures because of the isomeric nature of the alcohols used to prepare the phthalates. *The peaks in the mixtures need to be integrated and summed together.*

Comment 3: Suitable in-matrix calibration standards are difficult to find from a commercial provider. They must be prepared by the laboratory. Making a quantitative mixture of primary phthalate commercial standards in a suitable solvent is straightforward. However, if microliters of the standard are injected into a sample cup, which is then analyzed using TD, the precision for the most volatile phthalates will be very poor. Because they are dispersed on the cup surface in a thin film, losses due to evaporation are significant. In addition, the phthalate standards should be in-matrix in order to more accurately represent what truly happens during the desorption process. This is another benefit of using standard addition where the standards are spiked into the actual sample prior to analysis.

9. Extending ASTM D7823

Although ASTM D7823 is written specifically for the six regulated phthalates in PVC; it can easily be extended to include a larger number of phthalates in a number of different polymeric matrices.

Figure 6 shows EGA thermograms of common polymers containing phthalates. It is shown that for any of the polymers, phthalates are desorbed in similar temperature zone. ASTM D7823 prescribes only for PVC, however, the results shown in Figure 6 suggest that this method can be used for a number of other common polymeric matrices.

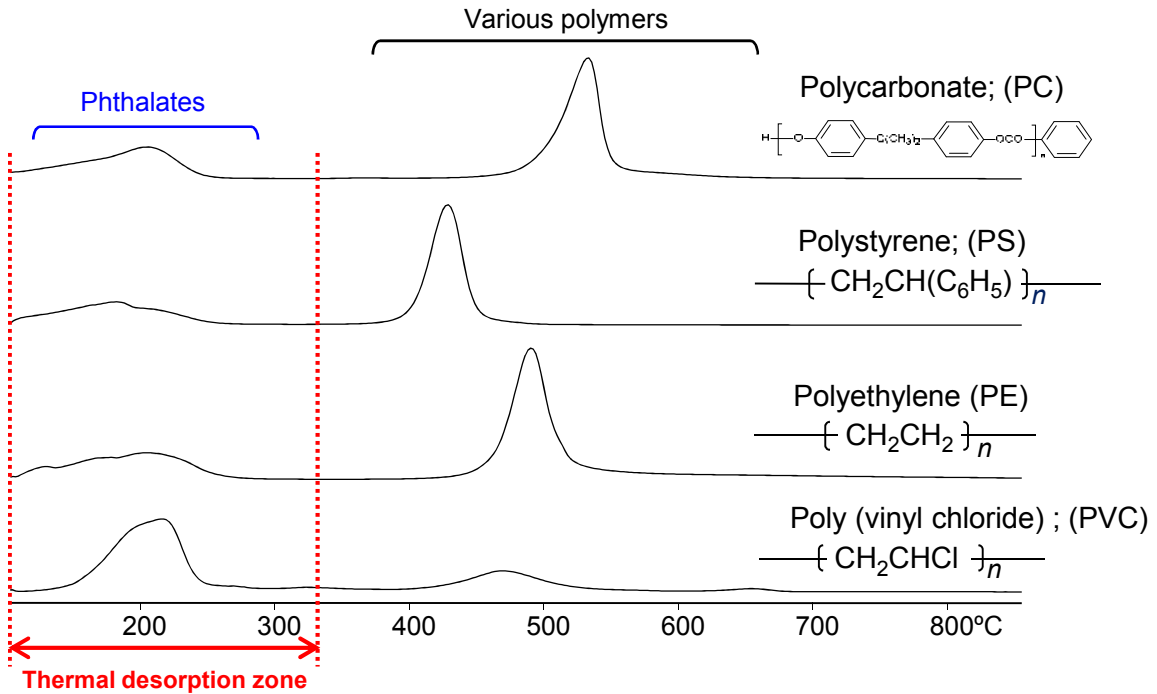


Figure 6. Phthalate thermal desorption zone for four different polymers.

Figure 6 shows the EGA thermograms of four different polymers. The phthalate thermal desorption zone is the same for all four polymers: 100 – 320°C. Clearly, it is not necessary to perform an EGA on each batch of samples. Samples arrive in the laboratory essentially ready for analysis. The instrument configuration and GC method will be the same for a wide variety of sample types.

There is near universal interest in monitoring phthalates in a number of consumer products. Many private sector companies, in anticipation of regulations directed at a number of common phthalates, have implemented in-house phthalate monitoring programs that are able to report as many as 15 phthalates – see Table III.

RT	Name	Acronym	CAS No.
7.805	Dimethyl phthalate	DMP	131-11-3
8.7	Diethyl Phthalate	DEP	84-66-2
9.915	Di-n-propyl phthalate	DRPR	131-16-8
10.6	Diisobutyl phthalate	DIBP	84-69-5
11.34	Dibutyl phthalate	DBP	84-74-2
12.957	Di-n-pentyl phthalate	DPP	131-18-0
14.686	di-n-Hexyl phthalate	DHP	84-75-3
14.778	Benzyl butyl phthalate	BBP	85-68-7
15+	Diisoheptyl phthalate	DIHP	71888-89-6*
16.328	Dicyclohexyl phthalate	DCHP	84-61-7
16.509	Bis(2-ethylhexyl) phthalate	DEHP	117-81-7
17+	Diisooctyl phthalate	DIOP	27554-26-3 *
18.056	Di-n-octyl phthalate	DNOP	117-84-0
18 +	Diisononyl phthalate	DINP	68515-48-0 *
19 +	Diisodecyl phthalate	DIDP	26761-49-1*

Table III. These 15 phthalates have been determined using ASTM D7823.

The six regulated phthalates are highlighted in red. (* DIHP, DIOP, DIDP and DINP are technical mixtures. Care should be taken to ensure that the correct standards are used). Also note that these mixtures will have multiple peaks that need to be integrated and summed together. The column temperature program specified in D7823 is modified to ensure resolution of the extended list. GC oven: 40 – 200°C (at 40°C/min), 200 – 300°C (at 5°C/min, 1 min hold), 300 – 320°C (at 20°C/min, 2.5 min hold). Retention times are provided to give the reader a sense of the relative retention of each phthalate using a 5% phenyl/methyl stationary phase column.

10. Phthalates identified in a “power cord” sheath using ASTM D7823 (modified)

The outer PVC material of a power cord was analyzed for an extended list of phthalates using ASTM D7823. Other than the change in the initial column temperature, the samples were analyzed as described in D7823. Commercial standard mixtures of 15 phthalates in methylene chloride (10-3000 µg/mL) were used to prepare the standard addition solution. The standard addition method per ASTM D7823 was used.

The extracted ion chromatogram (m/z 149) of the sample is shown in Figure 7. Obviously, there are a number of phthalates present in the sample. However, it is also clear that the level of DEHP exceeds the linear range of the detector and the sample will have to be diluted and re-analyzed. Concentrations as high as this always raise concerns about carryover and strongly suggest that a series of “blank” runs be made, in order to ensure that there is no carryover, before proceeding with sample analysis.

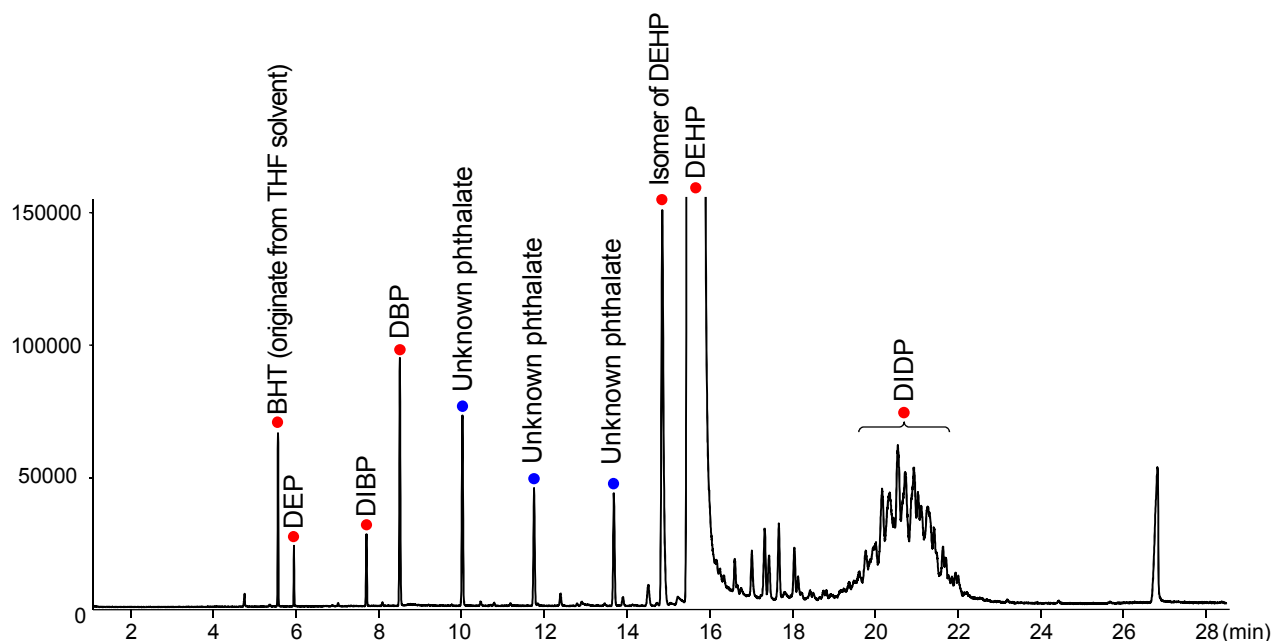


Figure 7. Extracted ion chromatogram (m/z=149) of the power cord sample (200 µg in sample cup).

Analytical method:

Thermal desorption temperature: 100 - 320°C (20°C/min)

GC Injection port: 300°C

GC Oven: 40 – 200°C (40°C/min) – 300°C (5°C/min, 1 min hold) – 320°C (20°C/min, 2.5 min hold)

Column: Ultra ALLOY-5 (MS/HT)

(5% diphenyl 95% dimethylpolysiloxane, L=30m, i.d.=0.25mm, df.=0.25µm)

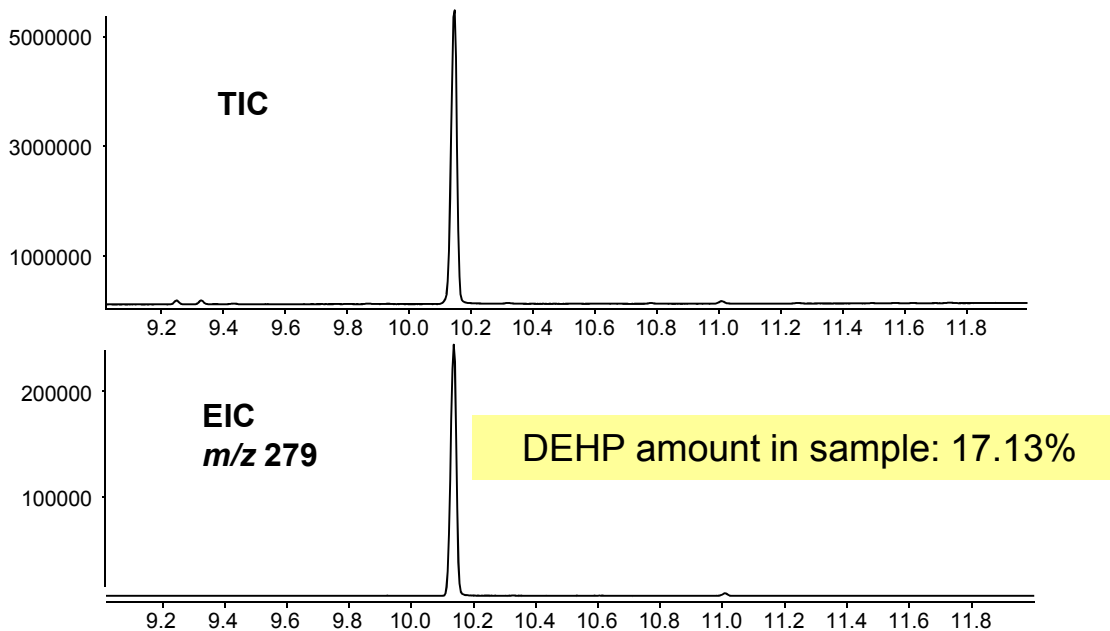
Column Flow: 1.2 mL/min

Split ratio: 1/20

Scan speed: 4 scans/sec

Sample weight: 2.1 & 200 mg dissolved in 10 mL THF ; 2.1- 200 µg in sample cup

The concentration of DEHP is determined by a re-analysis of the sample in which the amount of sample is reduced from 200 to 2.1 μg , or a hundred-fold decrease in the amount of sample analyzed. Figure 8 shows the total ion chromatogram and extracted ion chromatogram ($m/z=279$) used to quantitate DEHP. Note this actual sample contained a whopping 17.13% DEHP!



Standard addition

Sample Name	Sample amount (μg)	Standard addition (ng)	Area
PVC Sample	2.15	0	3059903
PVC Sample + spike	2.15	900	10535796
Quant value (%)			17.13 %

Figure 8. Total ion chromatogram and extracted ion chromatogram ($m/z=279$) of 2.15 μg of the power cord. GC oven profile: 40 – 180°C (at 40°C/min) - 280°C (at 20°C/min) – 320°C (at 10°C/min, 2.5 min hold) to 320°C. DEHP was calculated to be 17.13% using the two point standard addition calibration method.

Comment 4: Samples, such as this power cord sheath, can have an immediate and potentially disastrous effect on the instrumentation. High level system contamination is common and will require time and effort to eliminate. If possible, “unknown” samples should be screened using Infrared (IR) Spectroscopy ⁽⁷⁾. At a minimum, this will flag the sample and it can be initially analyzed at a very high dilution like was done with the power cord sheath.

Comment 5: Although MDL studies yield values for several phthalates in the low ppm range, it may be wise to use the practical quantitation limit (PQL). Other laboratories have selected a reporting limit that be achieved for all targeted phthalates. A value of 50-100 ppm is common. This takes into account changes in the instrument performance and varying levels of contamination that occur as the number of samples analyzed increases. The impact of these changes is somewhat mitigated by using standard addition.

Phthalates Identified	DEP	DIBP	DBP	DEHP	DINP	DIDP
Phthalate amount	22 ppm	24 ppm	76 ppm	17.13 %	140 ppm	3900 ppm
Sample amount analyzed (µg in sample cup)	200 µg	200 µg	200 µg	2.1 ug	200 µg	200 µg

Table IV. Quantitative results for each phthalate found in the power cord sheath.

11. Comparing the TD-GC/MS method with the traditional liquid extraction-GC/MS method

Figure 9 summarizes the differences in data quality (accuracy and precision) between the thermal desorption/standard addition and solvent extraction/external standard methods. Wet chemical methods often result in low values for the concentration of the volatile phthalates; These can be attributed to losses during sample preparation. High concentration values for DNOP, DINP and DIDP are due to interference from the co-eluting DINCH. The TD/standard addition method gives an almost constant response for all six phthalates with an average precision of 1.8 (%RSD).

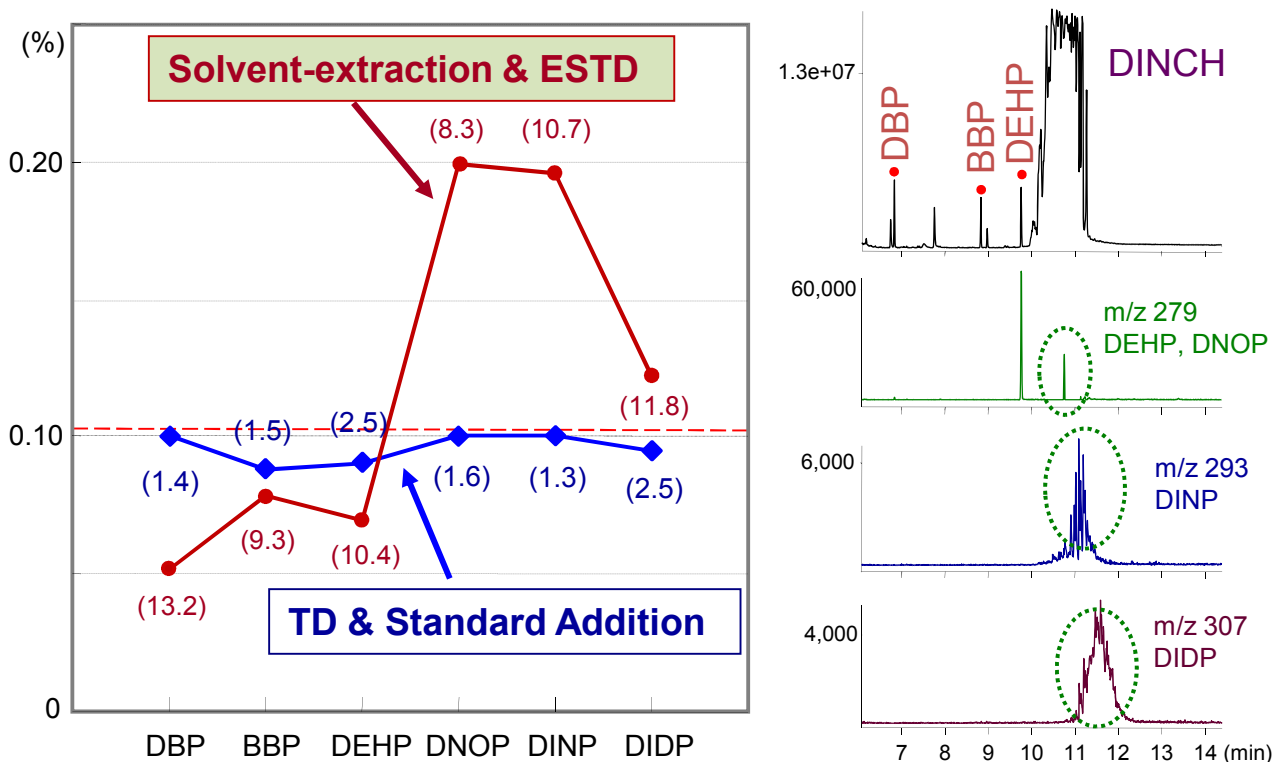


Figure 9. Quantitation and precision using **solvent extraction and external standard calibration** and **thermal desorption and standard addition calibration**. %RSD (n=4) values are shown in parenthesis. Phthalate concentrations = 1,025 ppm

12. SUMMARY

ASTM D7823 is based on thermal desorption (TD) – GC/MS. The method is suitable for an extended list of phthalates in a wide range of polymeric materials. The entire analytical sequence is performed in a single step: a known weight of sample (i.e., a known weight of solid sample or a known volume of a quantitative solution is placed in a sample cup which in turn is placed in the auto sampler carousel.

Thermal desorption eliminates conventional sample prep regimes; the sample is heated to a point that the phthalates desorb from the polymer. It is fast, uses a minimal volume of solvent, and eliminates the need for expensive glassware.

Calibration is based on the areas of specific quant ions for each phthalate which virtually eliminates the interference that may occur from co-eluting non-target chemicals. Quantitation is done using standard addition which takes into account any impact the sample matrix may have on the process. It also ensures that the calibration and sample analysis are performed under identical instrumental conditions. Standard addition does require that each sample be analyzed at least twice, but the benefits far out weigh the investment in the second analysis, especially given the fact that the entire process is automated.

13. References

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<http://www.cpsc.gov/about/cpsia/faq/108faq.html>
3. Di-(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), and benzyl butyl phthalate (BBP). Diisononyl phthalate (DINP), diisodecyl phthalate (DIDP), and di-*n*-octyl phthalate (DNOP).
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