Analysis of phthalates in polymeric substrates

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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, and in rubber as a plasticizer.

Although the widespread use of phthalates in the manufacturing 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 U.S., 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.

The U.S. Congress has permanently banned three phthalates (DEHP, DBP, BBP) in any amount greater than 0.1 percent (per plasticized component part of a child’s toy or child care article). There also is an interim ban on DINP, DNOP and DINOP, which only applies to children’s toys that can be placed in a child’s mouth.

Although a number of different analytical techniques can be used to determine the presence of phthalates, most laboratories use solvent-based techniques to extract the phthalates from the polymer matrix. The extract is then analyzed using GC or HPLC to separate and quantify 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 because of 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 in 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.

System configuration
The system configuration is shown in Fig. 1. The vertical micro-furnace technology of the Frontier pyrolyzer allows a continuous-mode analysis while it is connected directly to the GC inlet. Sample introduction is nearly instantaneous. The sample is placed in the sample cup (Eco-cup) and is held at near ambient temperature in helium. The micro-furnace is then preheated to the desired temperature that is precisely measured with a thermal couple sensor. The sample cup then drops into the quartz pyrolysis tube where the sample is pyrolyzed in <20ms/sec. The pyrolyzates are then swept onto the GC analytical column for separation and detection by MS. All surfaces in contact with the sample and pyrolyzates are either quartz or are deactivated using the Frontier Ultra Alloy-brand process.

'Method map'
Using Frontier’s pyrolyzer, multiple analyses can be performed on a single sample. In fact, the multi-mode pyrolyzer can be used to perform evolved gas analysis (EGA), thermal desorption (TD), flash pyrolysis (PY), heart-cutting (HC), and reactive pyrolysis (RxPY).

Frontier Laboratories has developed a series of techniques referred to as the “method map” to chemically characterize samples using the EGA/PY/3030D multi-functional pyrolyzer system in conjunction with a bench top GC/MS. These techniques allow a user to virtually any organic materials from volatiles to high molecular weight polymers and provides the user with two simple steps for determining the composition of any unknown sample.

The first step is the evolved gas analysis. See Phthalates, page 16

Fig. 1: TD-GC/MS system configuration.

Fig. 2: Example of an EGA thermogram.

Fig. 3: 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.

The authors
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William Pipkin has more than 30 years experience in commercializing technology. This includes all aspects: sales, support, marketing, research and development, and management. He has directed inception and development through sales, support and obsolescence. Pipkin received a bachelor’s degree in analytical chemistry from Brigham Young University and an MBA in entrepreneurship and finance from the Wharton School of the University of Pennsylvania. He has been a senior fellow in Wharton’s Emerging Technology Management Research Program.

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ysis. In this technique, a deactivated stainless-steel tube (2.5 M x 0.15 mm i.d.) connects the GC injection port to the MS. The sample is dropped into the furnace, which is at a relatively low temperature (ca. 40-100°C). The furnace is then programmed to a much higher temperature (ca. 600-800°C).

Compounds “evolve” from the sample as the temperature increases. A plot of detector response versus furnace temperature is obtained. The RGA provides a clear picture of the sample complexity and by using extracted ion chromatograms (GC/ MS), one can identify the EGA thermal zone where specific compounds of interest evolve from the sample.

The RGA example in Fig. 2, contains two thermal zones of interest.

The EGA is used to determine the next step in the evolution of the analytical Method Map. From Fig. 2, one can learn about the “volatile” compounds in the sample by simply introducing the sample at 300°C. Only the compounds evolving below 300°C will come out from the sample and be transmitted to the head of the column and analyzed.

If there is interest in both the “volatile” fraction and the higher boiling compounds, this can be done in two steps and it may be necessary to add a micro-cryo trap. The micro-cryo trap refocuses the volatile analytes of interest at the head of the column so that the full separating power of the column can be utilized.

First, the volatile compounds are thermally extracted by dropping the sample into the furnace, which is programmed from 100°C to 300°C.

The volatiles collect at the head of the column and are chromatographically separated. During the GC analysis of the volatiles, the sample is lifted out of the furnace and rests at near ambient temperature.

Upon completion of the GC run, the GC oven is reset and the pyrolyzer furnace temperature is raised to 550°C for performing the second analysis on the sample.

The sample is dropped a second time into the furnace for pyrolysis. The pyrolzates are trapped at the head of the column and subsequently separated.

Sample Preparation

Various 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: processing a non-representative portion of the sample; sample contamination (e.g., glassware, reagents or solvents); and deviations from the procedure prescribed in the method.

It is also important to note that sample preparation represents most of the costs associated with a given analytical procedure. Ideally, the sample should be analyzed “as is.” Direct analysis of the sample is often referred to as a “thin film” method. The entire sample is “as is.” Direct analysis of the sample is referred to as a “thin film” method. The entire sample preparation protocol is summarized in Fig. 3. Each step is described in the Analytical Procedure section.

It is important to mention that the accuracy of the measurement is highly dependent upon three factors:

• The homogeneity of the portion of the sample selected for analysis;

• The accuracy of the analytical balance;

• 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 Fig. 4. 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 represent a non-representative portion of the sample.

Experimental

In this experiment, a polyvinyl chloride sample containing DOA (Di(2-ethylhexyl) adipate) was used. The EGA was first performed on the sample by programing the furnace from 100° to 700°C at 20°C/min. The obtained EGA thermogram and the average mass spectra of each peak are shown in Fig. 5.

Using the EGA-MS F-Search interpretation library, each peak was analyzed. Extracted ion chromatograms were then used to delineate the thermal zone over which the phthalates evolve. Ion 149, which is common to all of the phthalates of interest, was used to “identify” the phthalate envelope.

Analysis of the data suggests that the EGA thermogram, DOA, which is a common plasticizer used in the manufacturing of flexible plastic toys, medical devices, and food packaging, desorbs along with the phthalates.

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.

From the EGA thermograms, the thermal desorption for the phthalates of interest was determined as 100° to 320°C.

If the samples are analyzed directly, approximately 100 µg are placed in a sample cup. If the samples are analyzed, the microfilm 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.

To perform the TD-GC/MS analysis, the Frontier Lab EGA/PY-3030D multi-mode pyrolyzer with a 48-position autosampler (Frontier Auto-Shot AS-1020E) interfaced via a split/spitless injection port to a GC/MS were used. The pyrolyzer’s furnace was programmed from 100° to 320°C at 20°C/min. The GC oven was set at 80°C (1 min); 200°C (50°C/min); and 350°C (15°C/min, 2 min hold).

The column was UA-5 (5 percent diethyl, 85 percent dimethyl polysiloxane) (0.25 mm i.d., 0.25 µm film) with helium flow of 1.2 mL/min.

To obtain the TD chromatogram, the cup was dropped into the furnace, which was at 100°C. The temperature increased at 20°C/min until it reached 320°C. The initial column temperature was 80°C, which was low enough to facilitate the condensation of the desorbed vapors into a narrow band at the head of the column.

The TD-GC/MS total ion chromatogram (TIC) and the extracted ion chromatograms (EIC) for the six regulated phthalates are shown in Fig. 6.

The phthalates are identified based on their relative retention time and the presence of the phthalate specific quant ion. The concentration of each phthalate was also calculated using standard addition calibration. Table 1 illustrates the analytical precision based upon the area percentage of each peak.

Fig. 4: Influence of the sample preparation method on analytical precision. Sample: 0.5 mg plastic toy (PVC & DINCH); Thin film: 20 µL THF solution. Direct sampling: powder < 45 mesh.

Fig. 5: Using extracted ion chromatograms to determine the phthalate thermal desorption zone. Sample: PVC + DOA.

Fig. 6: TD-GC/MS of a PVC-DINCH sample spiked with six regulated phthalates.

Table 1: Percent-RSD results for a PVC/DINCH sample for n=6.

% RSD

Phthalates

Replicates

(n=6)

(n=6)

(n=6)

(n=6)

(n=6)

(n=6)

DiBP (Ion 149)

1.35

1.46

2.54

1.60

1.33

2.52

DBP (Ion 223)

DEP (Ion 206)

DNP (Ion 279)

DIDP (Ion 307)
of the phthalate-specific quant ion for six replicates of a PVC/DINCH sample.

Of the four calibration methods most often used for quantitation, standard addi-
tion is the method of choice. Polymeric products are often very complex blends of
additives, copolymers and oligomers. Many different chemical species can be
desorbed along with the phthalates.

For example, Fig. 5 shows that DOA desorbs with the phthalates. Other common plasticizers, such as Mesamoll II (Alkylyphosphonic acid phenyl esters (APE)) and DINCH (1,2-cyclohexane di-
carboxylic acid di-isononyl ester), also desorb with the phthalates. The poten-
tial 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 asso-
ciated with modern day crosslinked stationery phases. While m/z 207 is not an
ion that is associated with any of the phthalates of interest, 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 calibra-
tion protocol when interference is an issue. The calibration is done using the sample
matrix at the same time frame as the sample analysis. Interferences and back-
ground contamination will be constant for all analyses and its effect on the calculat-
ed concentration is negated.

Fig. 7 is a typical set of single point standard addition calibration curves for the six regulated phthalates in PVC containing DOA sample. The number of calibration points can be increased as specified in the laboratory’s data quality objectives (DQO) documents or a proj-
et-specific work plan.

Example Calculation

Equation of the DBP calibration curve is:

\[ y = mx + b \]

where \( y \) = area (ng/mg) corresponding to known pmol of DBP, \( x \) = DBP concentration (ng/mg), \( m \) = 1293.9, \( b \) = 235288 (R^2 = 0.9979)

When \( y = 0 \)

\[ x = \frac{-b}{m} = \frac{-235288}{1293.9} = -181.8 \text{ ng} \]

Concentration in ppm is given by:

\[ \text{Value of DBP} = \frac{\text{Assumed content of PVC-DOA}}{\text{ppm}} = \frac{181.8 \text{ ng}}{200 \text{ mg}} = 0.9092 \text{ ppm} \]

Fig. 8 summarizes the differences in data quality (accuracy and precision) and the thermal desorption/stan-
dard addition and solvent extraction/ex-
ternal standard methods. Wet chemical
methods often result in low values for the concentration of the volatile phthal-
ates. These can be attributed to losses during sample preparation.

High concentration values for DNOP,
DINP and DFD are due to interference from the co-eluting DINCH. The TD stan-
dard addition method gives an almost constant response for all six phthalates with an average precision of 1.8 (per-
cent-RSD).

Extending ASTM D7823-16:

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 phthal-
ates, have implemented in-house phthal-
ate monitoring programs that are able to
report as many as 15 phthalates.

Although ASTM D7823-16 is written specifically for the six regulated phtha-
lates in PVC, it can easily be extended to
include a larger number of phthalates in a number of different polymeric matri-
ces. A simple EGA clearly shows that
thermal desorption (TD-GC/MS) can ef-
ectively "extract" the phthalates.

The solubility and diffusivity of thal-
ates in most non-crystalline polymers is the same. Consequently, the thermal de-
sorption temperature range is indepen-
dent of the polymer substrate. When using
TD to isolate additives that are beyond the scope of ASTM D7823-16 or
are incorporated into a polymeric base that has not been evaluated, it is wise to
verify the thermal desorption zone using EGA-MS.

Fig. 9 shows the EGA thermograms of
four different polymers. The phthalate
thermal desorption zone is the same for
all four polymers (100°C to 320°C). Clear-
lly, 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.

Summary

ASTM D7823-16 is based on TD-GC/
MS. The method is suitable for an ex-
tended list of phthalates in a wide range
of polymeric materials. The entire ana-
alitical 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 conven-
tional sample prep regimes; the sample is
heated to a point that the phthalates de-
sorb 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 interfer-
ence 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 cal-

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Rubber groups
Fort Wayne Rubber & Plastics Group: Golf outing, June 13, Fort Wayne Golf Club, Fort Wayne, Ind. (www. fwgrp.org)
Mexico Rubber Group: Courses on Feb. 21, April 13, June 6, July 29, Aug. 20 and Oct. 17 and Nov. 21, Rubber Chamber Auditorium; 53 year anniversary breakfast, Cancun Riviera, Sept. 27, End of your hooch dinne, Dec. 5, Cancun Riviera Base (321-555-161399; 321-555-35289); Francisco Mousko mousko@prosex.net; Miguel Bernal crigdy@prosex.net; Jos Erauskin auto- gkbb@prosex.net
Mid-Atlantic & Rubber & Plastics Group: Spring technical meeting, May 16, ACG, Rixton, Pa., Full technical meeting, Sept. 14, Pennsylvania College of Technology, Mid- atlantic symposium, Nov. 14, Lehagry University, Bethla- mom, Pa. (www.bin.edu/binhamfo@beinsign.com; www.maanrubgroup.org)
New England Rubber Group: Water gala, Feb. 9, Providence Biltmore Hotel, Providence, R.I.; Spring technical meeting, April 23, TRB, central Massachusetts section, Golf outing, Aug. 18, Blackstone National Golf Club, Sutton, Mass.; Full technical meeting or plant tour, Nov. 12, TRB, www.tnr.org
Twin Cities Rubber Group: Technical meetings, March 30, Sept. 29, Nov. 14; Holiday Inn After Lakes, Maple Grove, Minn., June 5, Holiday Inn, Maple Grove Golf Club, Nokomish, Minn. (berg1993@gmail.com; www.twinrubberconferences.org)
Calendar
Three-phased pyrolyzer enables the users to perform multiple analyses on a single sample in addition to flash pyrolysis.
Thermal analyzers can be programmed for thermal desorption (including multi- step TD), evolved gas analysis, and heart-cutting (slicing the EGA thermo- gram into multiple temperature zones and obtaining separate GCMS chro- matograms for each temperature zone).
38th annual meeting and conference on Rubber Roller Group: Annual meeting, May 7-9, Hilton Cincinnati Netherland Plaza, Cincinnati, Ohio. (www.rubberrollergroup.com)
Polyurethane Manufacturers Association: Annual meeting, May 5-7, Crown’s Palace, Las Vegas, Nev. (www. pmahe.org)
Power Transmission Distributors Association: Joint convention and exposition, April 20-22, Hyatt Regency Brooklyn, Brooklyn, N.Y. (www.ptda.org)
TECHL Rubber Americas: Trade show conference, on April 24-26, Centro Banamex, Mexico City. (www.techlatexamerica.com)
World Elastomer Summit: Conference focused on market predictions for butadiene, synthetic and natu- ral rubber, March 27-28, Lona, France. (www.pijegroup.com/event/elastomer-summit)
Trade/technical associations
AC8 Rubber Division: 19th Technical Meeting, April 30-May 2, University of Massachusetts, Amherst, Independent, Ohio; International Elastomer Confer- ence, March 26-28, 2019, Intercontinental Hotel & Conven- tion Center, Pittsburgh, (330-583-5531; www.cab- ber.org)
Adhesive and Sealant Council: 30th annual Spring Conference & Expo, April 8-9, Philadelphia Marriott, Philadelphia, Philadelphia (www.ascouncil.org)
Association for Rubber Products Manufacturers: Environmental, Health & Safety Conference; 2019, Columbia, Ohio; Benchmarking and Best Practices Con- ference, May 22-23, the Renaissance Indianapolis, Indi- anapolis. (317-865-6752; www.arepm.org)
Center for Automotive Research: CAR Manage- ment Summit; Featamurafuture topics impacting the automotive industry, Aug. 5-6, Grand Traverse Resort, Traverse City, Mich. (920-792-0941; Emmity@ carrgery.com; www.cargery.org)
Institute of Scrap Recycling Industries: Annual meeting and trade show, Nov. 18-20, Renaissance Las Vegas Convention Center, Las Vegas, Nev. (www.isri.org)
International Institute of Synthetic Rubber Pro- ducers: 3rd International Rubber Conference, Sept. 13-16, Renaissance Seattle Hotel, Seattle, WA (www.isiprc.org)
International Zinc Association and Zinc Ores Conference, Feb. 24-27, Water Kier- ning, Maynort, France. (www.iza.org)
NAHAD: 39th annual convention, Apr. 5-10, The Bahamas, Las Vegas, Nev. (www.nahad.com)
Polyurethane Foam Association: General meeting, May 22-23, Vanity Renaissance Hotel & Resort, St. Peter- burg, Fla. (www.gfia.com)
Polyurethane Manufacturers Association: Annual meeting, May 5-7, Crown’s Palace, Las Vegas, Nev. (www. pmahe.org)
Power Transmission Distributors Association: Joint conference and exposition, April 20-22, Hyatt Regency Brooklyn, Brooklyn, N.Y. (www.ptda.org)
TEIL Rubber Americas: Trade show conference, on April 24-26, Centro Banamex, Mexico City. (www.techlatexamerica.com)
Rubber Roller Group: Annual meeting, May 7-9, Hilton Cincinnati Netherland Plaza, Cincinnati, Ohio. (www.rubberrollergroup.com)
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Iibration and sample analysis are performed under identical instrument conditions.
Standard addition requires that each sample is processed three times, but the benefits far outweigh the investment in the second analysis, especially given the fact that the entire process is automated.
Conclusion
The three-phased laboratory in plastic, polymer manufacturing, food pack- aging, medical devices and toy industries are becoming increasingly popular, but the benefits far outweigh the investment in the second analysis, especially given the fact that the entire process is automated.
References
3. “A los-ethylhexyl” phthalate (DEHP), dibutyl phthalate (DBP), di(2-ethylhexyl) phthalate (DHEP), Diiodozenyl phthalate (DIP), Diiodocyclohexyl phthalate (DCHP), and Dodecyl phthalate (DOP).
5. Laboratory quality and laboratory productivity.
7. “A los-ethylhexyl” phthalate (DEHP), dibutyl phthalate (DBP), di(2-ethylhexyl) phthalate (DHEP), Diiodozenyl phthalate (DIP), Diiodocyclohexyl phthalate (DCHP), and Dodecyl phthalate (DOP).
9. Laboratory quality and laboratory productivity.
11. Tire Technology Expo: 19th showcase for the tire and automotive industries, and the confer- ence industry, May 5-7, Deutsche Messe, Hanover, Germa- ny. (www.tiretechnology-expo.com)
12. TLPLAS 2019: International Trade Fair for the Plas- tic and Rubber Industries, Sept. 18-21, Bangkok In- ternational Trade and Exhibition Center, Bangkok, Thailand (081-972-5180; info@tlplas.com; www.tlplas.com)
13. UETEC Americas Trade show conference, on April 10-12, Centro Banamex, Mexico City. (www.utealcamerica.com)
14. Worldwide Elastomer Summit: Conference focused on market predictions for butadiene, synthetic and natu-