

# 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,

## TECHNICAL NOTEBOOK

Edited by John Dick

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.,<sup>2</sup> 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 children's toy or child care article). There also is an interim ban on DINP, DIDP and DNOP, which only applies to children's toys that can be placed in a child's mouth.<sup>3,4</sup>

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 mo-

tion).

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

## Executive summary

Phthalates have been used as additives in plastic to make them more flexible for many years. Several phthalates are regulated on a global scale, and several analytical techniques can be used for phthalates analysis.

Phthalates have become a hot environmental topic and critical research area for many manufacturers and product consumers. Many analytical laboratories and scientists around the world are seeking new technologies and developments that can analyze phthalates qualitatively and quantitatively. The analysis of phthalates is critical in many industries, such as food safety, children's toys, electronics and consumer products.

All past methodologies for the determination of the regulated phthalates are based on solvent extraction, filtration and concentration. These traditional techniques are cumbersome, time-consuming and suffer from analyst-to-analyst variability while producing data of limited value. Also, polymers often contain many other plasticizers which co-elute with the phthalates of interest. This so-called matrix interference leads to either false positives or false negatives and makes the accurate determination of the co-eluting phthalates impractical.

In response to these analytical challenges and in conjunction with the ASTM, Frontier Lab developed a technique using a multi-mode pyrolyzer coupled with a GC-MS system for analyzing phthalates in polyvinyl chloride. This technique provides the analyst with a "method map" for identifying phthalates both qualitatively and quantitatively.

First evolved gas analysis (EGA)-MS is used for each type of polymer to be analyzed to determine the optimal thermal zone in which the target compounds evolve as the sample is heated. Then thermal desorption (TD)-GC/MS, which is a simple, one-step technique, is used for the analysis. ASTM D7823-16 is based on the thermal desorption (thermal "extraction") of the phthalates from a polymeric substrate.

This article is a discussion of the central factors that influence data quality when using ASTM D7823-16<sup>1</sup> for the determination of phthalates in polymeric substrates.

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 <20msec.

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

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Rojin Belganeh is the technical and marketing director at Frontier Laboratories Ltd.'s North America unit. She graduated from the University of Houston with a bachelor's degree in chemistry.

Belganeh started her career as an analytical chemist in the oil and gas industry. As an analytical chemist, she worked with various analytical instruments and techniques, such as Pyrolysis GCMS, TGA, FTIR, and X-rays for material characterization, polymer identification and contamination analysis.

She also holds an MBA concentrating in strategic marketing from the University of Houston-Victoria. Belganeh joined Frontier in May 2017.

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.

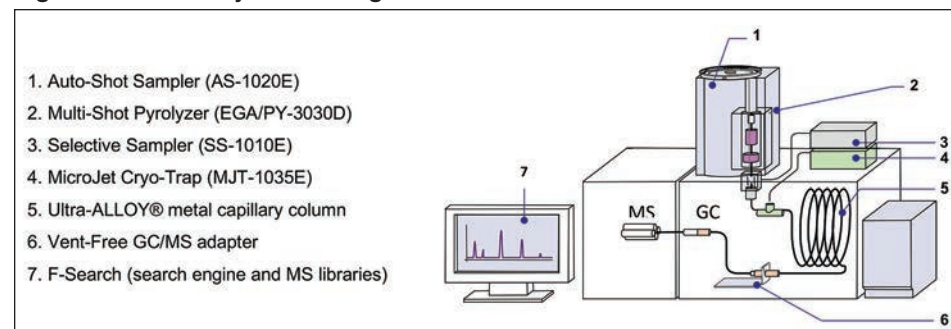
Co-authors included A. Hosaka, C. Watanabe, I. Watanabe I. Iwai, R. Freeman and T. Ramus.

conjunction with a bench top GC/MS. These techniques are applicable for 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.

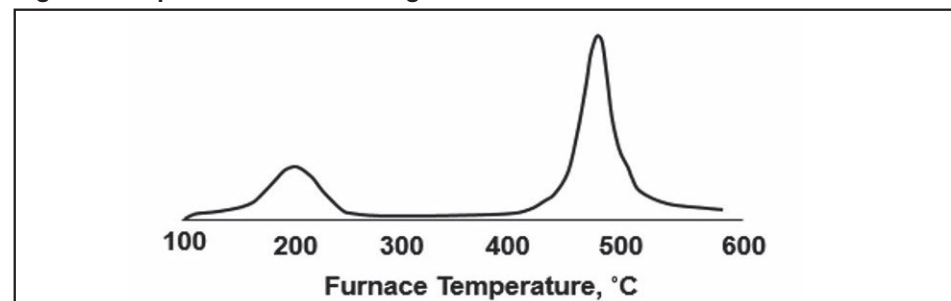
The first step is the evolved gas anal-

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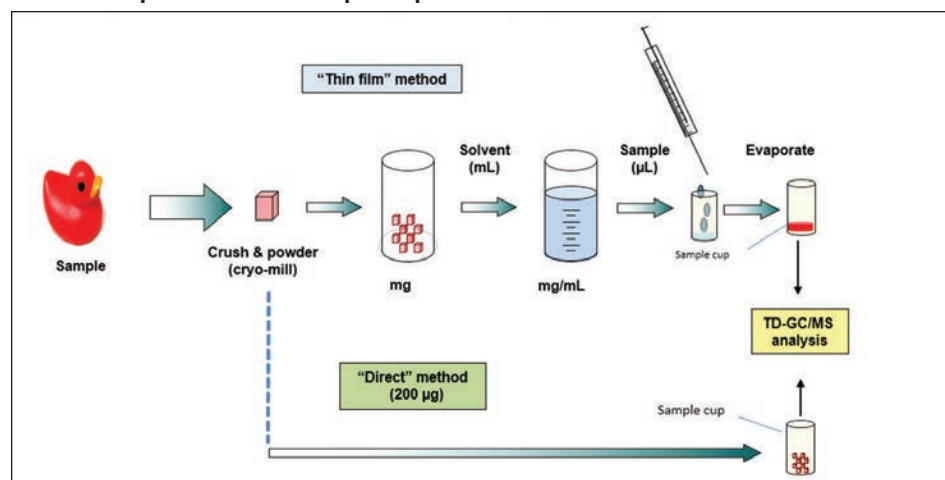
**Fig. 1: TD-GC/MS system configuration.**



**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.**



# Phthalates

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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 EGA 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 EGA 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 “volatiles” 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 transported 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. 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 pyrolyzates are trapped at the head of the column and subsequently separated.

## Sample preparation

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: 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 also is 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 increases laboratory productivity and improves the overall data quality.

Sample preparation using the TD-GC/MS is very simple and straightforward. There is no need for any solvent extraction or sample pretreatment prior to the analysis. In fact, any sample including solids can be analyzed using this technique without any solvent.

ASTM D7823-16 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 solu-

tion 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 ASTM method.

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; and
- 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 lack some sample-to-sample reproducibility.

## 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 programming 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.

As shown from 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 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.

To perform the TD-GC/MS analysis, the Frontier Lab EGA/PY-3030D multi-mode pyrolyzer with a 48-position auto-sampler (Frontier Auto-Shot AS-1020E) interfaced via a split/splitless 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).

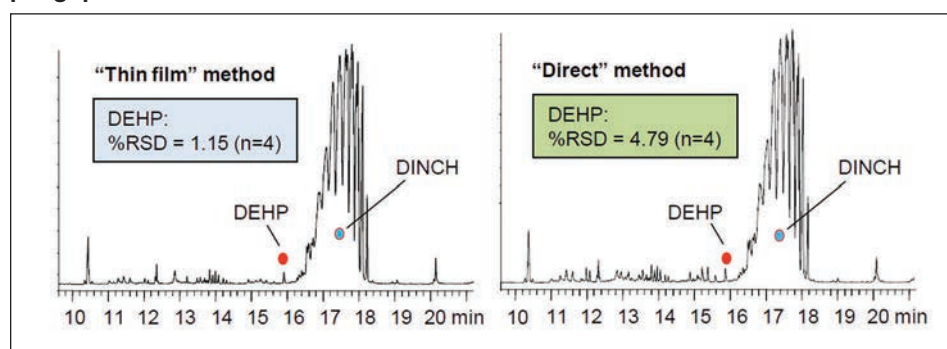
The column was UA-5 (5 percent diphenyl, 95 percent dimethyl polysiloxane) 30 m, 0.25 mm i.d., 0.25 µm film) with helium flow of 1.2 mL/min.

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.

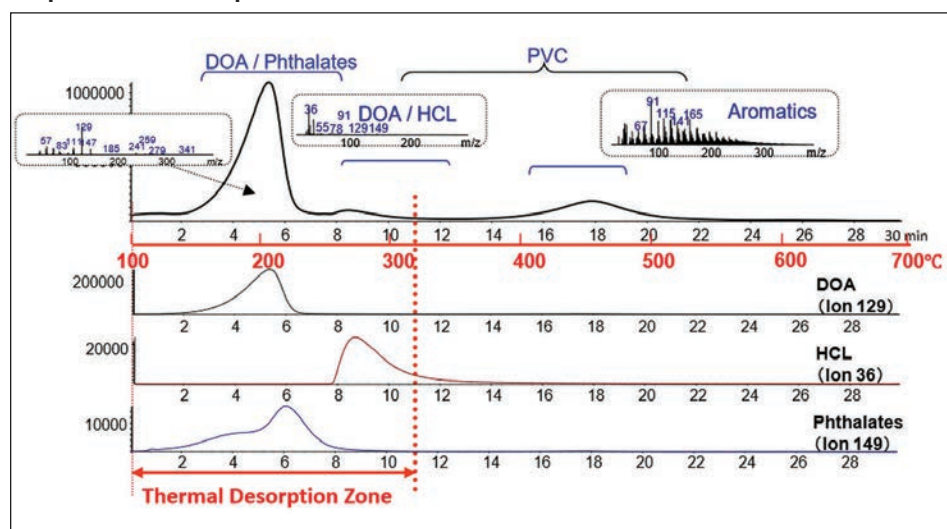
A typical TD-GC/MS total ion chromatogram (TIC) and the extracted ion chromatograms (EIC) for the six regulated phthalates are shown in **Fig. 6**.

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** demonstrates the analytical precision based upon the area

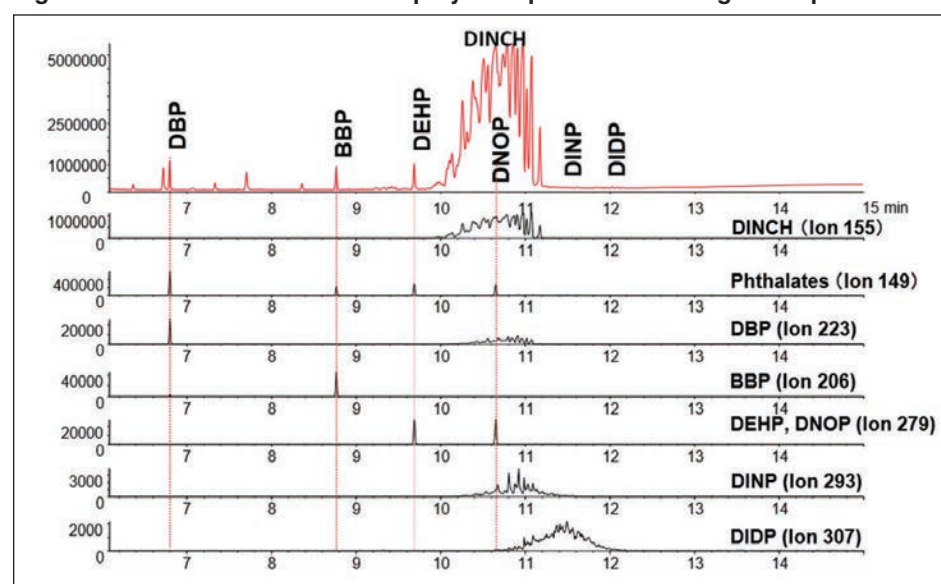
**Fig. 4: Influence of the sample preparation method on analytical precision. Sample: 0.5 mg plastic toy (PVC & DINCH); Thin film: 20 µL THF solution. Direct sampling: powder < 45 mesh.**



**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 polymer spiked with six regulated phthalates.**



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

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

of the phthalate-specific quant ion for six replicates (n=6) of a PVC/DINCH sample.

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, 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 (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 crosslinked stationary 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 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.

**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 project-specific work plan.

### Example Calculation

Equation of the DBP calibration curve is:  $y = mx + b$

$$y = 1293.9x + 235288 \quad (R^2 = 0.9979)$$

When  $y=0$  then  $x = -235288/1293.9 = -181.8 \therefore 181.8 \text{ ng}$ .

Concentration in ppm is given by:

Value of DBP ÷ Assumed content of PVC-DOA =  $181.8 \text{ (ng)}/200 \text{ (}\mu\text{g)} = 909.2$

$$(\text{ng}/\mu\text{g}) = 909 \text{ (ng/mg)} = 909 \text{ (ppm)}$$

One of the obvious advantages of using standard addition to calculate the concentration of the individual phthalates is that it eliminates the need for primary, polymeric phthalate standards. Standard addition calibration plots are essentially generated in the same time frame as the analyses are performed, which minimizes the impact that changes in the chromatographic system may have on the data quality.

To prepare the calibration line:

- Prepare a quantitative solution of the target phthalates in a suitable solvent;

- Combine a volume (e.g., 10 $\mu\text{L}$ ) of the phthalate solution with an aliquot of the sample. The sample amount must be the same in both analysis (analytical and calibration); and

- Vary the spike volume to generate a multi-point calibration line.

The calibration points are, by definition, in-matrix and accurately represent what truly happens during the desorption process. When using the "thin film" method, the analyst must be aware that the volatile components of the sample (e.g. DBP) may evaporate from the surface over time. Evaporation will manifest itself by a decrease in precision (i.e., an increase in the percent-RSD) and higher than expected concentrations.

Evaporation results in a lower [area/DBP concentration], which results in an artificially higher concentration for DBP. Of course, losses will be lower if the laboratory's temperature is less than 25°C. In addition, Frontier Lab produces polymer coated cups that are Pyrex glass sample cups whose inner walls have been coated with PVC thin film.

When sampling a phthalate solution, the PVC thin film on the inner wall help retain volatile phthalates such as DMP and DEP. The PVC thin film inhibits evaporation of low boiling compounds. It is particularly useful for analysis using auto-shot sampler with which a long-standing time is required. This product is disposable and intended for single use only.

### Results and discussion

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

MS:

**Fig. 8** 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 (percent-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 phthalates, have implemented in-house phthalate monitoring programs that are able to report as many as 15 phthalates.

Although ASTM D7823-16 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. A simple EGA clearly shows that thermal desorption (TD)-GC/MS can effectively "extract" the phthalates.

The solubility and diffusivity of phthalates in most non-crystalline polymers is the same. Consequently, the thermal desorption temperature range is independent 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. 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.

### Summary

ASTM D7823-16 is based on 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.)

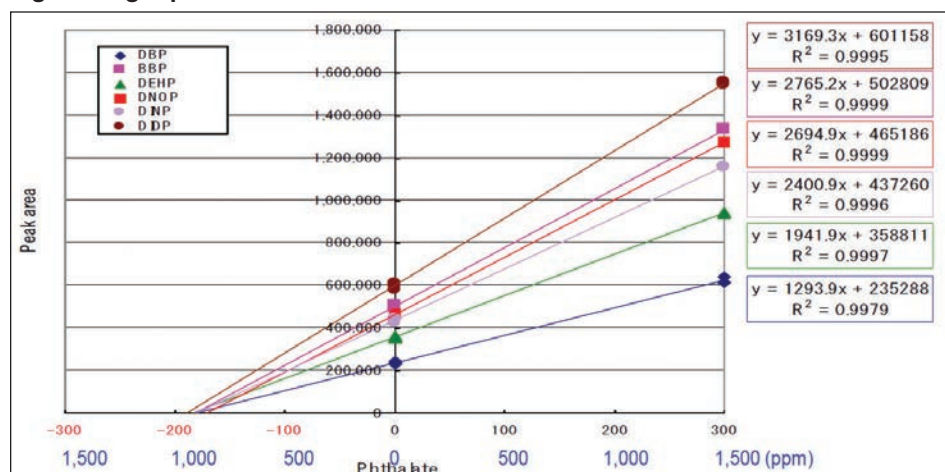
Thermal desorption eliminates conventional sample prep regimes; the sample is heated to a point that the phthalates desorb from the polymer. It is fast, uses a minimal volume of solvent and eliminates the need for expensive glassware.

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 cal-

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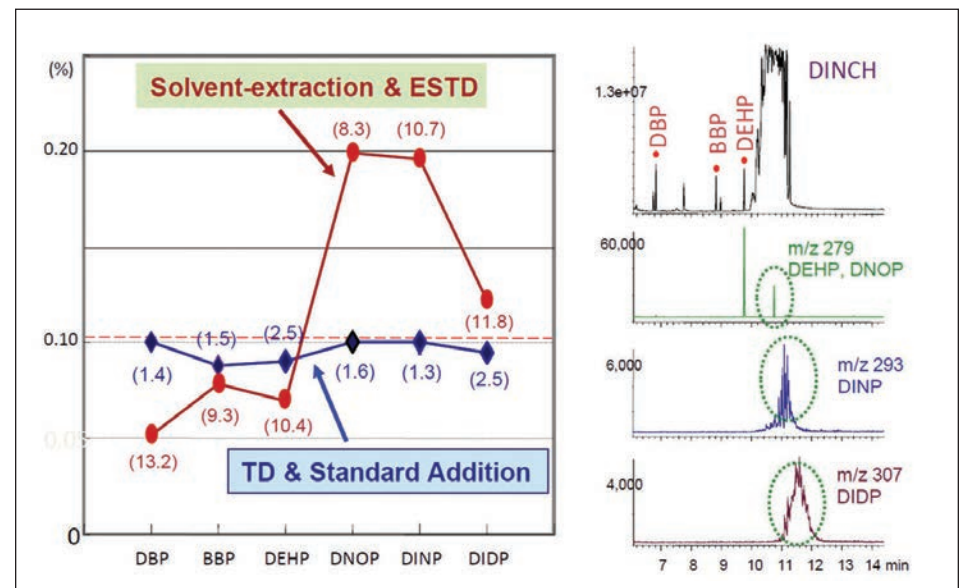
**Fig. 7: Single-point standard addition calibration curves.**



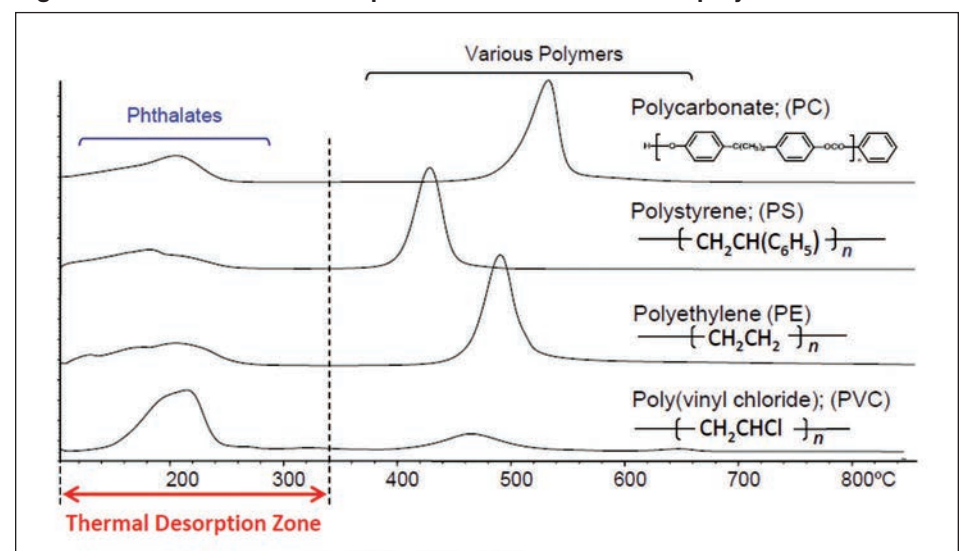
**Table 2: Calculated amounts of the six regulated phthalates determined using the standard addition calibration method.**

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

**Fig. 8: Quantitation and precision using solvent extraction and external standard calibration and thermal desorption and standard addition calibration. Percent-RSD (n=4) values are shown in parenthesis. Phthalate concentrations = 1,025 ppm.**



**Fig. 9: Phthalate thermal desorption zone for four different polymers.**



# Calendar

## IN COMING WEEKS

Ohio Rubber Group: Technical meeting . . . . .Jan. 29

Thermoplastic Concentrates 2019 in Coral Springs, Fla. . . . .Jan. 29

MD&M West: Medical design and manufacturing expo . . . . .Feb. 5

Los Angeles Rubber Group: TIPS meeting and casino night . . . .Feb. 5

New England Rubber Group: Winter gala . . . . .Feb. 9

iLearn Innovation Institute: Recession informative course . . . . .Feb. 12

**Clemson Tire Conference:** Annual event discussing issues impacting the tire industry, April 10-12, Sonesta Resort, Hilton Head, S.C. (Nan Johnston, 864-656-2200; ejohns5@clemson.edu)

**Future Tire Conference:** Bringing together top-level industry leaders to discuss technology and market developments that shape the future of the tire industry, June 11-12, Leonardo Royal Hotel Koeln - Am Stadtwald, Cologne, Germany, organized by *European Rubber Journal*. (dbushell@crain.com; www.tyre-conferences.com)

**Healthcare Elastomer conference:** Inaugural event seeking to provide engineers of the medical community knowledge of new technologies, trends and ideas in elastomers for the health care industry, May 21-22, Renaissance Schaumburg Convention Center Hotel, Schaumburg, Ill., organized by *Rubber & Plastics News*. (bweaver@crain.com; www.rubbernews.com/conferences)

**Hose Manufacturers' Conference:** Symposium for the rubber hose manufacturing industry, Nov. 12-13, Sheraton Suites, Cuyahoga Falls, Ohio, organized by *Rubber & Plastics News*, Beaver Manufacturing and Continental ContiTech. (bweaver@crain.com; www.rubbernews.com/conferences)

**iLearn Innovation Institute:** A division of Ace Products & Consulting L.L.C. February training: Recession-What You need to Know, Feb. 12, Ace Products, Ravenna, Ohio; Rubber for Dummies, Feb. 19, Ace Products, Ravenna, Ohio; Business Law Lunch and Learn, Feb. 20, Ace Products, Ravenna, Ohio. (Christie Robinson, 330-577-4088, christie.robinson@aceprod-con.com)

**ITEC in Focus: Green Tire:** Biennial event spotlighting green tires and their impact on the tire industry, Sept. 25-26, Sheraton Suites, Cuyahoga Falls, Ohio, organized by *Rubber & Plastics News*. (bweaver@crain.com; www.rubbernews.com/conferences)

**ITEC: Tire Manufacturing:** Biennial event spotlighting the tire industry, Sept. 15-17, 2020, John S. Knight Center, Akron, organized by *Rubber & Plastics News*. (bweaver@crain.com; www.rubbernews.com/conferences)

**India Rubber Expo:** 10th event highlighting the opportunities for rubber in India, Jan. 17-19, Bombay Exhibition Centre, Mumbai, India. (ire@indiarubber-expo.in)

**International Fluid Power Exhibition:** Co-located with Conexpo-Con and AGG 2020 with a focus on integration of fluid power with other technologies for power transmission and motion control applications, March 10-14, 2020, Las Vegas Convention Center, Las Vegas. (www.ifpe.com)

**International Latex Conference:** Exploring new applications, changing market dynamics and industry trends, organized by *Rubber & Plastics News* and Akron Dispersions, Aug. 6-7, Hilton Inn, Fairlawn, Ohio. (bweaver@crain.com; www.rubbernews.com/conferences)

**K 2019:** Trade fair for plastics and rubber held every

three years, Oct. 16-23, Messe Duesseldorf, Duesseldorf, Germany. (www.k-online.com)

**Latin American & Caribbean Tyre & Latin Auto Parts Expo:** Joint conference for the tire and automotive parts industries, July 24-26, Amador Convention Center, Panama City, Panama. (786-293-5186; info@LatinTyreExpo.com; www.LatinTyreExpo.com)

**MD&M West:** Medical design and manufacturing expo featuring suppliers to the medical industry, Feb. 5-7, Anaheim Convention Center, Anaheim, Calif. (www.mdmwest.mddionline.com)

**Polymer Foam 2019:** International conference on foam technology and applications in thermoplastic and elastomeric products, June 18-19, Marriott City Center, Pittsburgh. (www.amiplastics.com/events)

**Polymers in Cables 2019:** International conference and exhibition for polymers in cable applications, June 18-19, Sofitel Philadelphia, Philadelphia. (www.amiplastics.com/events)

**Polymers in Footwear 2019:** International conference and exhibition for polymers in footwear applications, March 5-6, Hilton Boston/Woburn, Woburn, Mass. (www.amiplastics.com/events)

**Polyurethanes Technical Conference:** Bringing together industry leaders to discuss and learn about innovations and applications for polyurethane, Oct. 7-9, Gaylord Palms Resort & Convention Center, Orlando, Fla. (<http://polyurethane.americanchemistry.com>)

**RCI International Convention & Trade Show:** March 14-19, Rosen Shingle Creek Resort, Orlando, Fla. (800-828-1902; www.rci-online.org/building-envelope-edu/convention-ts/)

**Techtextil North America:** 15th symposium featuring developments in technical textile and non-wovens, Feb. 26-28, Raleigh Convention Center, Raleigh, N.C. (www.techtextilNA.com)

**Thermoplastic Concentrates 2019:** Examines key issues facing the thermoplastic concentrates industry, Jan. 29-31, Fort Lauderdale Marriott Coral Springs Golf Resort, Coral Springs, Fla. (Stephanie Berchem, 610-478-0800, sb@amiplastics-na.com; www.amiplastics-na.com/events)

**Tire Technology Expo 2019:** 19th showcase for the global tire design, development and manufacturing industry, March 5-7, Deutsche Messe, Hanover, Germany. (www.tiretechnology-expo.com)

**T-PLAS 2019:** International Trade Fair for the Plastics and Rubber Industries, Sept. 18-21, Bangkok International Trade and Exhibition Center, Bangkok. (312-781-5180; info@mdna.com; www.tplas.com)

**UTECH Las Americas:** Trade show, conference on polyurethanes, April 10-12, Cento Banamex, Mexico City. (www.utechlasamericas.com)

**World Elastomer Summit:** Conference focused on market predictions for butadiene, synthetic and natu-

ral rubber, March 27-28, Lyon, France. (www.wplgroup.com/aci/event/elastomers-conference)

## Trade/technical associations

**ACS Rubber Division:** 195th Technical Meeting, April 30-May 2, Holiday Inn Independence (Cleveland), Independence, Ohio; International Elastomer Conference, featuring Rubber Expo, 196th Technical Meeting & Education Symposium, Oct. 9-11, Huntington Convention Center, Cleveland. (330-595-5531; www.rubber.org)

**Adhesive and Sealant Council:** ASC annual Spring Conference & Expo, April 8-10, Philadelphia Marriott, Philadelphia. (www.ascouncil.org)

**Association for Rubber Products Manufacturers:** Environmental, Health and Safety Summit, July 17-18, Columbus, Ohio; Benchmarking and Best Practices Conference, Oct. 2-4, Marriott Downtown Indianapolis, Indianapolis. (317-863-4072; www.arpminc.org)

**Center for Automotive Research:** CAR Management Briefing Seminars featuring topics impacting the automotive industry, Aug. 5-8, Grand Traverse Resort, Traverse City, Mich. (Lisa Hart, 734-929-0465. lhart@cargroup.org; www.cargroup.org)

**Fluid Sealing Association:** Annual Meeting, Oct. 21-25, Javitz Center, New York. (www.fluidsealing.com)

**Gasket Fabricators Association:** Semi-annual meeting, March 12-14, Saddlebrook Resort, Tampa, Fla.; Semi-annual meeting, Sept. 24-26, Lansdowne Resort & Spa, Leesburg, Va. (www.gasketfab.com)

**Institute of Scrap Recycling Industries:** Annual convention and exposition, April 6-11, Los Angeles Convention Center, Los Angeles. (www.isri.org)

**International Institute of Synthetic Rubber Producers:** 59th Annual General Meeting, May 13-16, Renaissance Seattle Hotel, Seattle. (www.iisrp.com)

**International Rubber Conference Organization:** International Rubber Conference, Sept. 3-5, Kia Oval, London. (www.internationalrubberconference.org)

**International Rubber Study Group:** World Rubber Summit 2019: New paths for the rubber economy, March 18-19, Singapore. (www.wrs2019.rubberstudy.com)

**International Zinc Association:** International Zinc and Zinc Oxide Conferences, Feb. 24-27, Westin Kierland Resort, Scottsdale, Ari. (www.zinc.org)

**NAHAD:** 35th annual convention, April 5-10, The Bellagio, Las Vegas. (www.nahad.org)

**NIBA-The Belting Association:** Annual convention, Sept. 18-21, Gaylord National Resort & Convention Center, Washington. (www.niba.org)

**Polyurethane Foam Association:** General meeting, May 22-23, Vinoy Renaissance Hotel & Resort, St. Petersburg, Fla. (www.pfa.org)

**Polyurethane Manufacturers Association:** Annual meeting, May 5-7, Caesar's Palace, Las Vegas. (www.pmahome.org)

**Power Transmission Distributors Association:** Spring meeting and leadership development conference, March 20-22, Hyatt Regency Savannah, Savannah, Ga.; 2019 Industry Summit, Oct. 23-26, J.W. Marriott Austin, Austin, Texas. (312-516-2100; www.ptda.org)

**Rubber Roller Group:** Annual meeting, May 5-7, Hilton Cincinnati Netherland Plaza, Cincinnati. (www.rubberrollergroup.com)

**Tire Society:** 38th annual meeting and conference on tire science and technology, Sept. 10-11, Hilton Inn, Fairlawn, Ohio. (www.tiresociety.org)

## Rubber groups

**Blue Ridge Rubber Group:** Spring technical meeting, May 16, Olde Beau, Roaring Gap, N.C. (Tony Williams, 302-562-1608, TWilliams@tainsstruments.com; www.rubber.org/blue-ridge-rubber-group)

**Chicago Rubber Group:** Spring technical meeting, May 13, Hawk's View Golf Club, Lake Geneva, Wis.; Chicago Golf Outing, July 18, Village Links, Glen Ellyn, Ill.; Wisconsin Golf Outing, Aug. 14, Hawk's View Golf Club, Lake Geneva, Wis.; Fall technical meeting, Sept. 19, White Pines Golf Course, Bensenville, Ill. (www.chicagorubbergroup.org)

**Fort Wayne Rubber & Plastics Group:** Golf outing, June 13, Maxwellton Golf Club, Syracuse, Ind. (www.fwrpg.org)

**Los Angeles Rubber Group:** TIPS meeting and casino night, Feb. 5, The Phoenix Club, Anaheim, Calif. (www.tlargi.org)

**Mexico Rubber Group:** Courses on Feb. 21, April 11, June 6, July 25, Aug. 29, Oct. 17 and Nov. 21, Rubber Chamber Auditorium; 55 year anniversary breakfast, Concamin Ballroom, Sept. 27; End of year luncheon, Dec. 5, Concamin Ballroom. (52-55-55666199; 52-55-55352266; Francisco Martha cni1@prodigy.net.mx; Miguel Bernal cni1@prodigy.net.mx; Jose Gazano anto-gua@prodigy.net.mx; www.cni1.com.mx)

**Michigan Rubber Group:** Technical meeting, March 6, Grand River Hotel, Grand Rapids, Mich.; Golf outing, May 30, Forest Akers, East Lansing, Mich.; Fishing outing, July 26, Grand Haven, Mich.; Technical meeting, Sept. 11, TBD, Frankenmuth, Mich.; Technical meeting, Nov. 6, University Club at Michigan State, East Lansing, Mich. (Keith Korhals, 989-435-7400, kakorhals@laursilicone.com, www.michiganrubbergroup.com)

**Mid-Atlantic Rubber & Plastics Group:** Spring technical meeting, May 16, AGC, Exton, Pa.; Fall technical meeting, Sept. 12, TBD, Philadelphia; Technical symposium, Nov. 14, Lehigh University, Bethlehem, Pa. (Bruce Rhoades brhoades@gtweed.com; www.marpg.org)

**New England Rubber Group:** Winter gala, Feb. 9, Providence Biltmore Hotel, Providence, R.I.; Spring technical meeting, April 2, TBD, central Massachusetts area; Golf outing, Aug. 6, Blackstone National Golf Club, Sutton, Mass.; Fall technical meeting or plant tour, Nov. 12, TBD. (www.nerpg.com)

**Ohio Rubber Group:** Technical meeting, Jan. 29, Hilton Garden Inn, Twinsburg, Ohio; Spring technical meeting, Apr. 9, Hilton Garden Inn, Twinsburg, Ohio; Golf Outing, June 18, Yankee Run Golf Course, Brookfield, Ohio; Golf outing, Aug. 26, Silver Lake Country Club, Silver Lake, Ohio; Technical meeting, Sept. 24, Hilton Garden Inn, Twinsburg, Ohio. (www.ohiorubbergroup.org)

**Southern Rubber Group:** Winter technical meeting, Feb. 25, Embassy Suites, Greenville, S.C.; Summer technical meeting, June 24, The King and Prince, St. Simons Island, Ga. (www.southernrubbergroup.org)

**Twin Cities Rubber Group:** Technical meetings, March 7, Sept. 19, Nov. 14, Holiday Inn Arbor Lakes, Maple Grove, Minn.; Golf outing, Aug. 1, Willingers Golf Club, Northfield, Minn. (twrg2013@gmail.com; www.twincities-rubbergroup.org)

## Seminars/conferences

**American Coatings Show and Conference 2020:** Biennial event featuring coatings, paints, sealants, construction chemicals and adhesives, March 30-April 2, 2020, Indianapolis Convention Center, Indianapolis. (www.american-coatings-show.com)

**Chem Show:** Focus on key issues facing today's chemical processing market, Oct. 22-24, Javits Center, New York. (Steve Levine, steve.levine@iecshows.com; www.chemshow.com)

# Phthalates

Continued from page 17

ibration and sample analysis are performed under identical instrumental conditions.

Standard addition requires that each sample be analyzed at least twice, but the benefits far outweigh the investment in the second analysis, especially given the fact that the entire process is automated.

## Conclusion

Today, more laboratories in plastic, polymer manufacturing, food packaging, medical devices and toy industries are integrating the Frontier multi-mode pyrolyzer into their mainstream analytical protocols. The multi-mode pyrolyzer

enables the users to perform multiple analyses on a single sample in addition to flash pyrolysis.

The furnace can be programmed for thermal desorption (including multi-step TD), evolved gas analysis, and heart-cutting (slicing the EGA thermogram into multiple temperature zones and obtaining separate GC/MS chromatograms for each temperature zone).

As demonstrated in this article, no solvent extraction is required when using TD-GC/MS as opposed to traditional GC/MS techniques. The phthalates are thermally extracted from the polymeric mixture instead of using solvent extraction.

One of the most important advantages that thermal desorption has over samples prepared using conventional solvent-based techniques is that only the

portion of the sample that is desorbed is transported to the GC column.

Look closely at the thermal desorption zone for the phthalates in **Figs. 5 and 8**, only the phthalates (and other additives) thermally evolve from the sample at 320°C. This means that the polymer remains in the sample cup and is not introduced into the GC inlet, column or MS. Because the bulk of the sample (i.e. the polymer fraction) remains in the cup, more total sample can be placed in the sample cup.

This improves the signal to noise (S/N) of the target compounds. 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 carryover is virtually non-existent. This has a major positive impact on both data

quality and laboratory productivity.

## References

1. ASTM D7823-13, Standard Test Method for the Determination of Low Level, Regulated Phthalates in Poly (Vinyl Chloride) Plastics by Thermal Desorption—Gas Chromatography/Mass Chromatography.
2. Section 108: Products Containing Certain Phthalates. <http://www.epsc.gov/about/pcsia/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).
4. Consumer product safety commission, Test Method: CPSC-CH-C1001-09.3—Standard Operating Procedure for Determination of Phthalates, April 1, 2010.
5. Applications of a multifunctional pyrolyzer for evolved gas analysis and pyrolysis-GC of various synthetic and natural materials: part 2, S. Tsuge, H. Ohtani, Chu Watanabe and Y. Kawahara, American Laboratory, 35, 32-37, March 2003.
6. Rapid and Simple Determination in Plastic Toys by a Thermal Desorption-GC/MS Method, T. Yuza-wa, Chu Watanabe, R. Freeman and S. Tsuge, Analytical Sciences, Sept. 25, 2009, 1,057-1,058.

# Technical