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Application News

No. GCMS-1504

Gas Chromatograph Mass Spectrometer

A Pyrolysis-GC/MS Screening System for Analysis of Phthalate Esters and Brominated Flame Retardants

■ Introduction

The Restriction of Hazardous Substances (RoHS) Directive controls six hazardous substances commonly used in electronic and electrical equipment [(1)]. Two of the restricted substances are compound classes commonly used in flame retardants: polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE), both known to cause serious health concerns due to their high halogen content. Beside brominated flame retardants, phthalate esters have also been controlled by a number of regulatory authorities. The United States congress has prohibited the use of six specified phthalate esters (DBP, DEHP, BBP, DINP, DIDP and DnOP) in children's toys at concentrations higher than 0.1% under the Consumer Product Safety Improvement Act of 2008 (CPSIA) [(2)]. The European commission has identified DBP, DEHP and BBP as reproductive toxicants under directive 2005/84/EC [(3)]. The Environmental Protection Agency (EPA) has proposed adding eight phthalates to the list of chemicals of concern under the Toxic Substances Control Act (TSCA), including DIBP, DBP, BBP, DEHP, DnOP, DINP, DnPP and DIDP [(4)]. The Food and Drug Administration (FDA) Center for Drug Evaluation and Research (CDER) recommends avoiding the use of DBP and DEHP as excipients in CDER-regulated drug and biologic products, including prescription and nonprescription products [(5)].

To quantitate these substances in a polymer matrix, the traditional approach involves solvent extraction of PBBs, PBDEs and phthalate esters from the sample matrix, followed by detection and quantitation by gas chromatography/mass spectrometry (GC/MS). This method is time consuming and poses the risk of exposure to multiple toxic solvents.

Pyrolysis followed by GC/MS has been well established for detection of volatile and semi-volatile compounds in both natural and synthetic polymers. Using the pyrolysis technique described here, a temperature programed micro-furnace provides thermal desorption processes at two temperature ranges, releasing the PBBs, PBDEs and phthalate esters from the polymer matrix for subsequent analysis by GC/MS.

In this application note, a PY-GC/MS method has been used to screen for seven phthalate esters and 11 brominated flame retardants. A commercially available method package was used, which includes phthalate ester and PBDE standards, pre-registered instrument methods with acquisition and data processing parameters, and calibration curves for semi-quantitative calculation of compound concentration. Quantitation results were generated with minimal sample preparation, requiring no organic solvents. A software program for efficient multi-analyte data confirmation and QAQC review is also discussed.

■ Experimental

Py-Screener Package

This study was conducted using the Shimadzu GCMS-QP2010 Ultra, Frontier Multi-Shot EGA/PY-3030D pyrolyzer, and AS-1020E Auto-Shot sampler, as shown in Figure 1.

Figure 1: Frontier Multi-Shot EGA/PY-3030D pyrolyzer and AS-1020E Auto-Shot sampler installed on the Shimadzu GCMS-QP2010 Ultra

The Frontier Multi-Shot EGA/PY-3030D pyrolyzer and AS-1020E Auto-Shot sampler were installed on the Shimadzu GCMS-QP2010 Ultra, with a UA-PBDE metal capillary column (15 m x 0.25 mm x 0.05 µm). A method package called Py-Screener has been developed and applied in this application. Py-Screener is a method package targeting seven phthalates and 11 brominated flame retardants. It contains pre-registered instrument acquisition methods for the Pyrolyzer and the GC/MS, as well as a data processing analysis method including quantitation parameters and calibration curves developed using phthalate and PBDE standards. Refer to Table 1 and Table 2 for experimental details and complete compound list.

Analytical standards used for this project were included with the Py-Screener package. The phthalate standards were comprised of three thin polymer films, which contain seven phthalates at 0, 100 ppm, and 1000 ppm, and one flame retardant standard containing 11 PBBs and PBDEs. All standards and samples were prepared by slicing off small pieces of the polymer using the knife from the sampling tool kit. Approximately 0.5 mg of standards and samples were weighed using an electronic balance with accuracy of 0.01 mg before loading into the sample cups. For ease of the application, the Py-Screener package also includes sample preparation videos, illustrated troubleshooting procedures and routine maintenance.

Table 1: Experimental conditions for the instrument acquisition method

Gas Chromatograph	**CG-2010 Plus**	
Column	UA-PBDE, 15 m x 0.25 mm x 0.05 µm (Shimadzu PN 220-94824-20)	
Oven Program	80 °C, no hold 20 °C/minute to 300 °C, hold 5 minutes	
Injector	Split mode, split ratio 50:1 300 °C Split Liner w/ wool (Shimadzu PN 220-90784-00)	
Carrier Gas Carrier Gas Flow	Helium Constant linear velocity mode, 52.1 cm/second Total Flow 54 mL/minute, Column Flow = 1.00 mL/minute Purge Flow 3.0 mL/minute	
Interface Temperature	320 °C	
Mass Spectrometer	**GCMS-QP2010 Ultra**	
Ion Source Temperature Solvent Cut Time Detector Voltage	230 °C 0.5 minutes Relative to tune + 0.1 kV	
MS Operating Mode	Acquisition mode: Scan/SIM Total loop time 0.45 second	
	Scan event time 0.15 second Mass range: 50-1000 amu	SIM event time 0.3 second SIM method details listed in table 2
Pyrolyzer	**PY-3030D (Frontier Labs)**	
Sample amount Furnace Temp PY-GC Interface Temperature	0.5 mg TD1 200 °C to 300 °C @ 20 °C/minute, total 5 minutes TD2 300 °C to 340 °C @ 5 °C/minute, total 9 minutes Furnace temperature plus 100 °C, up to 300 °C	
Analysis Time		
PY program GC/MS program Total Cycle Time per sample	14 minutes 16 minutes 30 minutes	

Table 2: Compound list and selected ions for the SIM method

Compound Name	Abbreviation / Congeners	Selected Ions for the SIM Mode		
		Quantitation	Reference #1	Reference #2
Diisobutyl phthalate	DIBP	223.0	205.0	149.0
Dibutyl phthalate	DBP	223.0	205.0	149.0
Butyl benzyl phthalate	BBP	206.0	91.0	149.0
Di(2-ethylhexyl) phthalate	DEHP	279.0	167.0	149.0
Di(*n*-octyl) phthalate	DnOP	279.0	167.0	149.0
Diisononyl phthalate	DINP	293.0	167.0	149.0
Diisodecyl phthalate	DIDP	307.0	167.0	149.0
Hexabromocyclododecane	HBCDD	238.9	560.6	
2,2',4,4'-tetrabromodiphenyl ether	BDE-47	325.8	483.6	
2,2',3,4,4'-pentabromodiphenyl ether	BDE-99	403.8	561.6	
2,2',4,4',6-pentabromodiphenyl ether	BDE-100	403.8	561.6	
2,2',4,4',5,5'-hexabromodiphenyl ether	BDE-153	483.6	643.5	
2,2',4,4',5,6'-hexabromodiphenyl ether	BDE-154	483.6	643.5	
2,2',3,4,4',5,6'-heptabromodiphenyl ether	BDE-183	561.6	721.4	
2,2',3,3',4,4',6,6'-Octabromodiphenyl ether + 2,2',3,4,4',5,6,6'-Octabromodiphenyl ether	BDE-197+204	641.5	643.5	
Nonabromodiphenyl ethers	BDE-206+207+208	719.4	879.2	
Decabromodiphenyl ether	BDE-209	799.3	959.1	
Decabrominated biphenyl	BB-209	783.3	785.3	

PY-GC/MS Method

In the micro-furnace of the pyrolyzer, the sample undergoes a two-step thermal desorption process, where the temperature increases from 200 °C to 300 °C at 20 °C per minute, followed by a second temperature ramp from 300 °C to 340 °C at 5 °C per minute. PBBs, PBDEs and phthalate esters are released in the temperature controlled micro-furnace and are transferred to GC/MS for chromatographic separation and analysis.

A simultaneous selected ion monitoring (SIM) and full scan acquisition method (Scan/SIM) was used on the GCMS-QP2010 Ultra. Using a Scan/SIM method provides enhanced sensitivity of the target compounds by monitoring their signature fragments, while simultaneously screening for the unknown analytes in the full mass range at the same time. Because analysis takes place by rapidly alternating between the two modes, a fast scan rate is essential to assure adequate sensitivity for both SIM and full scan modes.

The Py-Screener method package includes pre-registered retention indices for all the target compounds. Retention time for the target compounds are determined using the retention indices and the retention time for the homologous series of hydrocarbons under the same acquisition conditions using Automatic Adjust of Retention Time (AART) function. A mixture containing saturated hydrocarbon n-isomers from Octane (C8) to Tetracontane (C40) comes with the package and is used in the AART function. Retention time of all 18 target compounds is predicted and is used to adjust the acquisition and data processing retention time parameters in the method.

■ Results and Discussion

Calibration Standards

Four standards were analyzed using the Scan/SIM method, which include three standards with phthalates at 0 ppm, 100 ppm and 1000 ppm, and one with PBDEs at various concentration between 26 ppm and 780 ppm. Total ion chromatograms (TIC) for two standards are shown in Figure 2. Figure 3 shows the SIM chromatographic profiles for the individual target compounds. DIBP, DBP, BBP, DEHP, and DnOP present as narrow sharp chromatographic peaks, while the profiles for DINP and DIDP present as a broad cluster of chromatographic peaks due to their multiple isomeric components. The area count of mass chromatogram in SIM mode for each compound was determined, and applied to the calibration curve in the quantitation method.

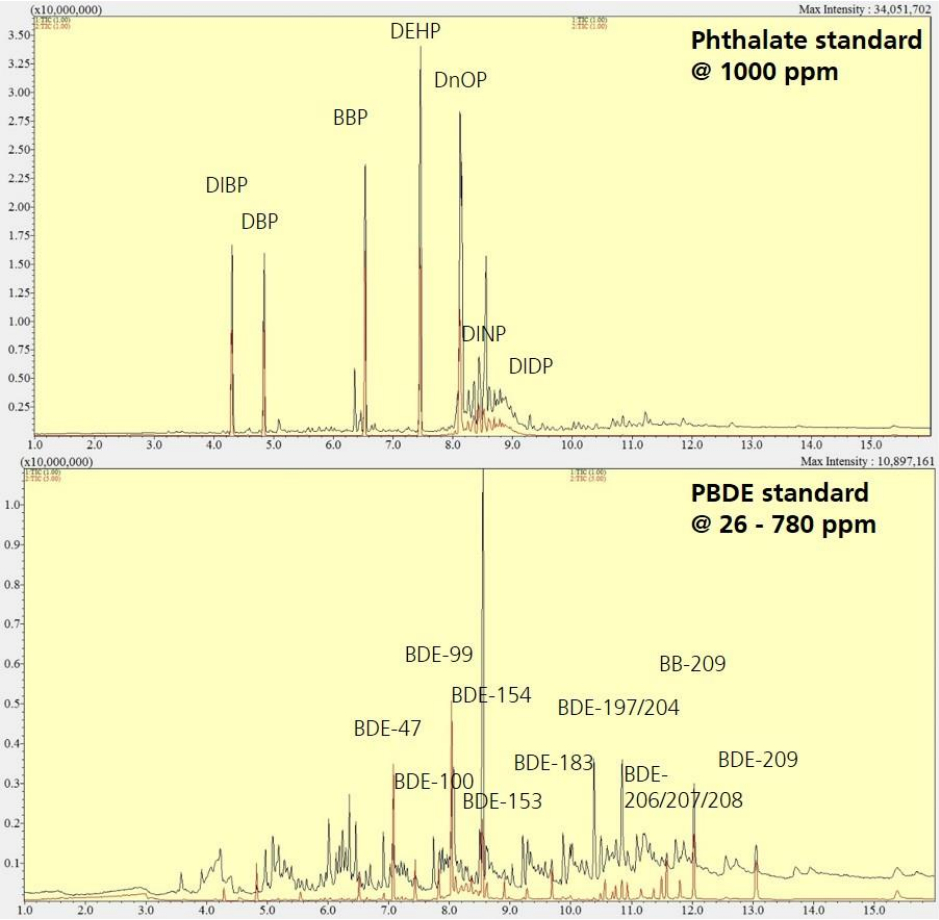

Figure 2: Total ion chromatograms (TIC) for the phthalate and PBDE standards, with full scan mode shown in black and SIM mode shown in red. Phthalate standard contains seven phthalates at 1000 ppm. The PBDE standard contains PBDEs and PBBs at various concentrations between 26 and 780 ppm.

Figure 3: Chromatographic profile of the target compounds extracted from SIM chromatogram of the phthalate and PBDE standards. The primary SIM ions are shown in black, and the secondary reference ions are shown in pink.

LabSolution Insight

LabSolution Insight is a software program designed for simultaneously analyzing data sets from multiple samples. With LabSolution Insight, quantitative results for a complete series of data files can be displayed side-by-side for comparison and QC review. All of the chromatograms from a selected target compound can be displayed simultaneously, making it easy to review the detected peaks and confirm the quantitative results. Color-coded QAQC flags quickly identify any outliers that require further examination. Results can be displayed in a variety of ways, allowing users to select the view that is best suited for their workflow, and when necessary, peaks can be re-integrated and re-quantified directly from LabSolution Insight.

For this project three polymer samples were analyzed using the PY-GC/MS method described above; they are labeled Blue Conveyor, White Conveyor, and Gasket. A blank sample cup was also analyzed using the same method for quality control purpose. Figure 4 shows the total ion chromatograms of the three polymer samples. The pre-registered calibration curve from the Py-Screener package was used for quantitation. The calibration is based on a one-point calibration from analysis of the highest phthalate standard at 1000 ppm, and the PBDE standard. The quantitation results are categorized into three groups to comply with multiple regulations: below 500 ppm, between 500 and 1500 ppm, and beyond 1500 ppm. All 7 target phthalate compounds from one standard and the three samples are displayed side-by-side in LabSolution Insight, and the outliers with concentration above 1500 ppm are labeled with flags, as shown in Figure 5.

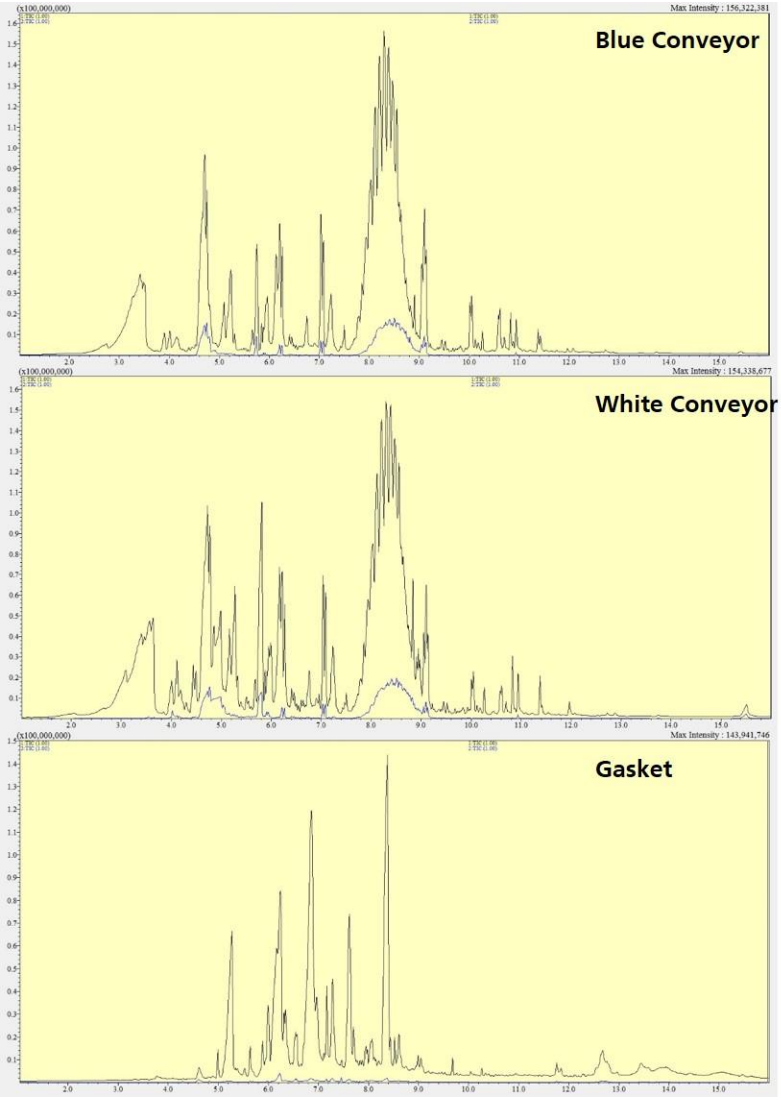

Figure 4: Total ion chromatogram from three samples - *Blue Conveyor*, *White Conveyor*, and *Gasket*, with full scan mode shown in black and selected ion monitoring (SIM) mode shown in blue. Note that the noise level in SIM mode is reduced significantly compared to full scan mode.

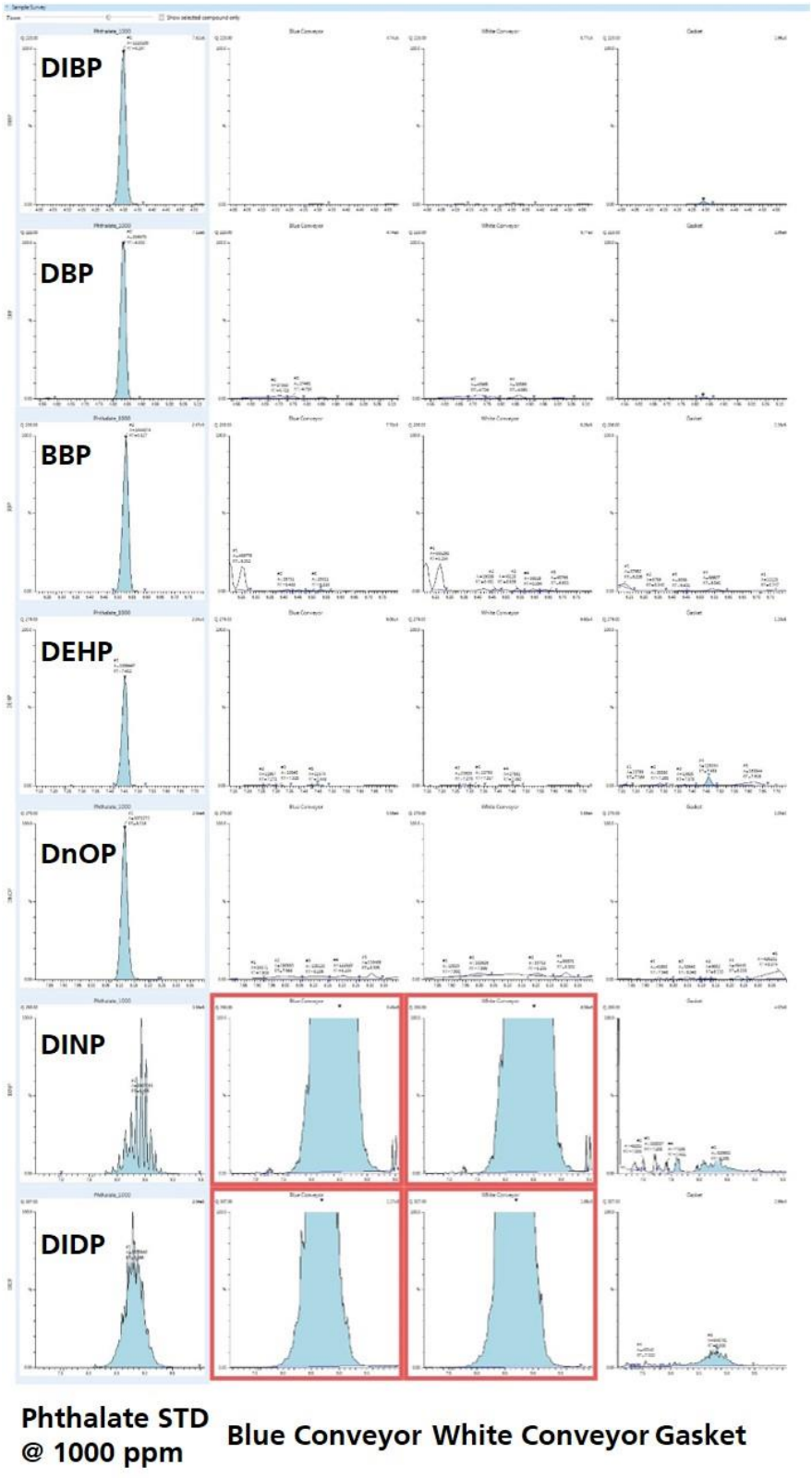

Figure 5: Quantitative analysis of the seven phthalate analytes in one standard and three polymer samples using the LabSolution Insight QAQC software. All the phthalate target compounds from three samples with unknown phthalate concentration are displayed with intensity scaled at the same level as phthalate standard at 1000 ppm. Phthalate content higher than 1500 ppm have been automatically flagged with a red box by the LabSolution Insight software.

The two samples labeled Blue Conveyor and White Conveyor have similar chromatographic profiles, which both show significant phthalate content compared to the Gasket sample. Quantitative analysis results on the blank and the three polymer samples are shown in table 3. DINP and DIDP were detected at around 3% and 0.7% in both Blue Conveyor and White Conveyor samples, which exceed the 0.1% limit in several regulations. The Gasket sample shows only low content of DINP and DIDP at about 0.03% and 0.02%. All the other types of phthalates and PBDEs are either negligible or non-detected in all the three samples.

Table 3: Quantitative analysis result of three polymer samples

Compound Name	Blank (ppm)	Blue Conveyor (ppm)	White Conveyor (ppm)	Gasket (ppm)
DIBP	ND	ND	ND	**23**
DBP	**1**	ND	ND	**11**
BBP	**< 1**	**9**	ND	ND
DEHP	**< 1**	**12**	**11**	**81**
DNOP	ND	ND	ND	ND
DINP	ND	**31489**	**31722**	**297**
DIDP	ND	**7149**	**7860**	**192**
HBCDD	ND	ND	ND	ND
Tetra-BDE (BDE-47)	ND	ND	ND	ND
Penta-BDE (BDE-100)	ND	ND	ND	ND
Penta-BDE (BDE-99)	ND	ND	ND	ND
Hexa-BDE (BDE-154)	ND	ND	ND	ND
Hexa-BDE (BDE-153)	ND	ND	ND	ND
Hepta-BDE (BDE-183)	ND	ND	ND	ND
Octa-BDE (BDE-197+204)	ND	ND	ND	ND
Nona-BDE	ND	ND	ND	ND
Deca-BDE (BDE-209)	ND	ND	ND	ND

QAQC

Phthalate standards at 0 ppm and 100 ppm were analyzed using the same method to support quality control. In LabSolution Insight, QAQC criteria were applied so that the data will be highlighted when either of the following two conditions was met: the concentration of any of the target compounds in 0 ppm standard exceeds 10 ppm, or the signal to noise ratio of 100 ppm standard falls below 30.

Since the Py-Screener package was developed for phthalate and PBDE screening for several regulations, the quantitation is only adequate enough to be categorized in those three groups. To achieve further accuracy, sohexlet extraction followed by liquid injection GC/MS will be required. Regular liquid injection with capillary column Rxi-1HT (15 m x 0.25 mm x 0.1 µm) is recommended instead of pyrolysis. In this case, the Twin Line MS kit can be used to save time on column switching

■ Summary and Conclusion

The Py-Screener method package was used to investigate the phthalates and PBDEs content in three polymer samples. Experimental conditions and data processing method are described in detail. The LabSolution Insight program was used to review multiple data and flag outliers based on defined QAQC parameters.

■ References

1. Directive 2002/95/EC, Official Journal of the European Union
2. Public law 110–314, Consumer Product Safety Improvement Act of 2008
3. Directive 2005/84/EC, Official Journal of the European Union
4. Phthalates action plan, U.S. Environmental Protection Agency
5. Guidance for industry limiting the use of certain phthalates as excipients in CDER-regulated products, U.S. Department of Health and Human Services Food and Drug Administration Center for Drug Evaluation and Research

First Edition: September 2015

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