

GC/MS Analysis of Phthalates in Children's Products

Introduction

Plastic is a well suited material for the manufacture of a wide range of products. Children's products, from plates and cups to mattress liners and diapers and toys, are made of plastic, as a result of its low cost and durability. The manufacture of plastic products often includes additives which are intended to modify the physical properties of the polymer. Common additives are plasticizers, antioxidants and flame retardants. There are a number of different compounds classified as plasticizers – the most common are phthalates (Figure 1).

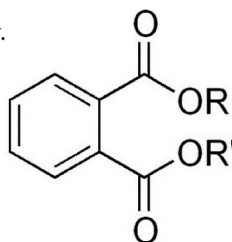


Figure 1.
The base structure of a phthalate molecule.

Phthalates are added to plastics, primarily vinyl, to make the material softer and to increase flexibility. Concerns have been raised over the potential effect of chronic phthalate exposure on human health. This health concern has resulted in the regulation of the type and level of phthalates allowable in toys and other children's products. The European Commission began restricting phthalates in December 1999 and the U.S. government passed the Consumer Products Safety Improvement Act (CPSIA) in August of 2008.

The European regulations specifically limit three phthalates – DEHP, DBP, and BBP – to a level of less than 0.1 % in all toys and articles designed to be put in a child's mouth. This regulation also limits DINP, DIDP, and DnOP to less than 0.1 % in articles designed to be put in a child's mouth.

The U.S. regulations are slightly different – DEHP, DBP, and BBP, have been permanently prohibited at concentration of more than 0.1% in "children's toys" or "child care articles." Three additional phthalates – DINP, DIDP, and DnOP – have been conditionally prohibited at a concentration of more than 0.1 %, in "children's toys" or "child care articles." The condition of the ban on the second three phthalates is on the further study and review by a group of outside experts and the Consumer Product Safety Commission.

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As a result of these regulations, industries which use polymers to produce children's products have to monitor the presence and amount of specific compounds. The identification and quantitation of phthalates requires an analytical technique which can separate each phthalate from other additives and from the plastic matrix itself. Gas chromatography/mass spectrometry (GC/MS) is an excellent instrumental platform for this analysis. The gas chromatograph separates analytes, while the mass spectrometer response is correlated to the amount of phthalate and will confirm the identification. This paper will discuss the sample preparation, demonstrate a calibration for common phthalates, and analyze plastic-toy components.

Experimental

The preparation of a sample is vital to a predictable and reproducible analysis. This analysis has a number of considerations in the sample preparation that will affect the final analytical result. The sample preparation will be different if the measurement is intended to be total where an effort is made to get 'all' of the phthalates out of the material, or surface measurement where only the phthalates on the surface are extracted.

In the case of a surface measurement, phthalates are removed from the surface of the material with a solvent in which they are soluble. In this case, many common organic solvents can be used (hexane, methanol) and many common extraction techniques (ultrasonic, soxhlet) will provide adequate recovery.

If a total phthalate measurement is desired, more care must be taken in the choice of an extraction solvent and technique. Grinding the sample into a very small particle size, increasing its surface area, will improve the extraction efficiency. A solvent (methylene chloride, acetone:hexane), which will either dissolve or dissolve the polymer, will help to extract the phthalates from the entire matrix. The extraction technique will also improve the recovery – ultrasonic-assisted dissolution, microwave-assisted extraction, and heated-soxhlet extraction will assist in the recovery of the analytes from within the polymer. The extracted solution requires a cleanup process that will remove any remaining solid material – centrifugation or filtration is recommended.

Depending on the amount of sample, solvent and the required detection limits, a concentration step may be included to increase the concentration of the analyte in the extract and thus the method detection limit.

Another important consideration in the sample-preparation process is cleanliness of lab ware. Phthalates are very common lab contaminants, thus one of the more difficult aspects of this application is eliminating carry-over and contamination. The solvent stream should be free of plastics, with the exception of PTFE. Glassware will need thorough washing and rinsing with solvent and/or high-temperature bake out. The analysis of method blanks and sample duplicates will allow the laboratory to monitor for contamination in solvents, laboratory equipment and glassware.

For the purpose of this paper, a surface measurement was made on an unused toy (Figure 2). The toy was cut into pieces approximately 1 g in size. A sample was taken from each of the 9 different types of plastic used in the example toy. The extraction of phthalates from each was assisted by 15 minutes of sonication in 10 mL of methylene chloride at 40 °C in a sealed vial. Following extraction, 1 mL of the sample extract was filtered through a 0.45- μm glass-fiber filter into an autosampler vial for analysis.

The instrumental analysis was carried out on a PerkinElmer® Clarus® 600 GC/MS system; complete instrumental conditions are presented in Table 1 (Page 3). The GC was fitted with a programmable split/splitless injector; the injector-port temperature was maintained at 280 °C. The injector-port liner was packed with glass wool to improve vaporization and provide a surface for the collection of any dissolved plastic. A PerkinElmer Elite-5MS (30 m x 0.25 mm x 0.25 μm) GC column was temperature programmed from 100 °C to 260 °C at 8 °C/min, then to 320 °C at 35 °C/min. The carrier gas, helium, was set to 1 mL/min with 25 mL/min split at the injector port.



Figure 2. Example toy analyzed in this application note.

Table 1. Gas Chromatograph Conditions.

Gas Chromatograph: PerkinElmer Clarus 600 GC			
Analytical Column:	Elite-5MS (30 m x .25 mm x 0.25 µm)		
Injection Port Type:	Programmable Split/Splitless		
Injector Temperature:	280 °C		
Injection Type:	Split (25 mL/min)		
Syringe Volume:	5 µL		
Injection Volume:	1 µL		
Injection Speed:	Normal		
Rinse Solvent:	Methylene Chloride		
Carrier Gas Type:	Helium		
Carrier Gas Program:	Flow	Hold Time	
	2 mL/min	0.5 min	
	1 mL/min	Hold	
Oven Program:	Temperature	Hold Time	Rate
	100 °C	0 min	8 °C/min
	260 °C	0 min	35 °C/min
	320 °C	Hold	
Instrument Timed Events:	Split flow 50 mL/min @ 1 min		
	Split flow 20 mL/min @ 5 min		

Table 2. Mass Spectrometer Conditions.

Mass Spectrometer:	PerkinElmer Clarus 600 T MS
GC Inlet Line Temp:	280 °C
Ion Source Temp:	280 °C
Function Type:	Full Scan
Full Scan Range:	<i>m/z</i> 45-300
Full Scan Time:	0.15 sec
InterScan Delay:	0.05 sec
Solvent Delay:	3 min

The Clarus 600 Mass Spectrometer was operated in full-scan mode for this analysis. The scanning parameters used achieve 5 scans per second across a range of *m/z* 45-300. The scanning speed is such that approximately 12-15 scans are collected across each peak, this will result in accurate and reproducible peak shape. The heated zones were set at 280 °C to prevent condensation of analytes in either the transfer line or ion source.

Phthalate calibration standards were prepared in methylene chloride across a range of 1-160 µg/mL; the calibration standards contained 16 phthalates. The isomeric mixtures of diisononyl phthalate and diisodecyl phthalate were analyzed in single component solutions.

Table 3. Phthalate Calibration Data.

Standard Concentration (µg/mL)	1	5	10	20	40	80	160	Correlation Coefficient (r²)
Compound Name	Peak Area							
Dimethyl Phthalate	56005	2608024	547773	1153890	2261780	4854921	9936435	0.9996
Diethyl Phthalate	61241	273898	547792	1161504	2331919	5117585	10362640	0.9995
Diisobutyl Phthalate	70882	358650	742955	1611529	3223889	7156851	14708002	0.9992
Di-n-butyl Phthalate (DBP)	82624	439134	871727	1898820	3921153	8603199	17507356	0.9994
Bis (2-methoxyethyl) Phthalate	49627	282863	568670	1257607	2676481	5909382	12086260	0.9993
Bis (4-methyl-2-pentyl) Phthalate	19139	75322	199359	419082	840928	1816872	3741004	0.9995
Bis (2-ethoxyethyl) Phthalate	33925	192792	373471	829989	1779532	3932335	8054468	0.9993
Diamyl Phthalate	81083	449742	920329	2059990	4343220	9539634	18946628	0.9995
Hexyl 2-ethylhexyl Phthalate	86687	498021	985002	2236423	4796807	10449081	21121394	0.9995
Butylbenzyl Phthalate (BBP)	30437	163324	320945	740505	1618402	3516704	7032140	0.9995
Di-n-hexyl Phthalate	36143	24404	406601	907699	1934048	4075672	8348210	0.9997
Bis (2-butoxyethyl) Phthalate	15330	85904	171096	382022	848890	1856538	3789877	0.9993
Dicyclohexyl Phthalate	59462	338855	664693	1491982	3181306	6855167	13876119	0.9996
Bis (2-ethylhexyl) Phthalate (DEHP)	63441	346838	701072	1579613	3453631	7427999	14666869	0.9996
Di-n-octyl Phthalate (DnOP)	75417	469317	916691	2081996	4477587	9590110	19643412	0.9996
Dinonyl Phthalate	83131	503401	992684	2243901	4771617	10170331	20543020	0.9997
Average Correlation Coefficient								0.9995

Discussion

The chromatographic result of the analysis of a standard including 16 phthalates is pictured in Figure 3; each phthalate can be identified by its retention time and spectral characteristics. The spectral data of most phthalates are very similar (Figure 4). The dominant fragment measured in electron impact ionization MS is at m/z 149 – this is a result of the loss of the alkyl ester groups and the formation of a furan ring¹.

In this paper, the instrument was calibrated across the range of 1-160 $\mu\text{g/mL}$ for each of the phthalates. The response for each compound was linear with R^2 greater than 0.999 for all compounds. Detailed calibration data for each of the phthalates analyzed is presented in Table 3 (Page 3). Applying the calibration range to a 1-g sample extracted in 10 mL of solvent relates a % weight calibration range of 0.001 to 0.16% weight of each phthalate in solution.

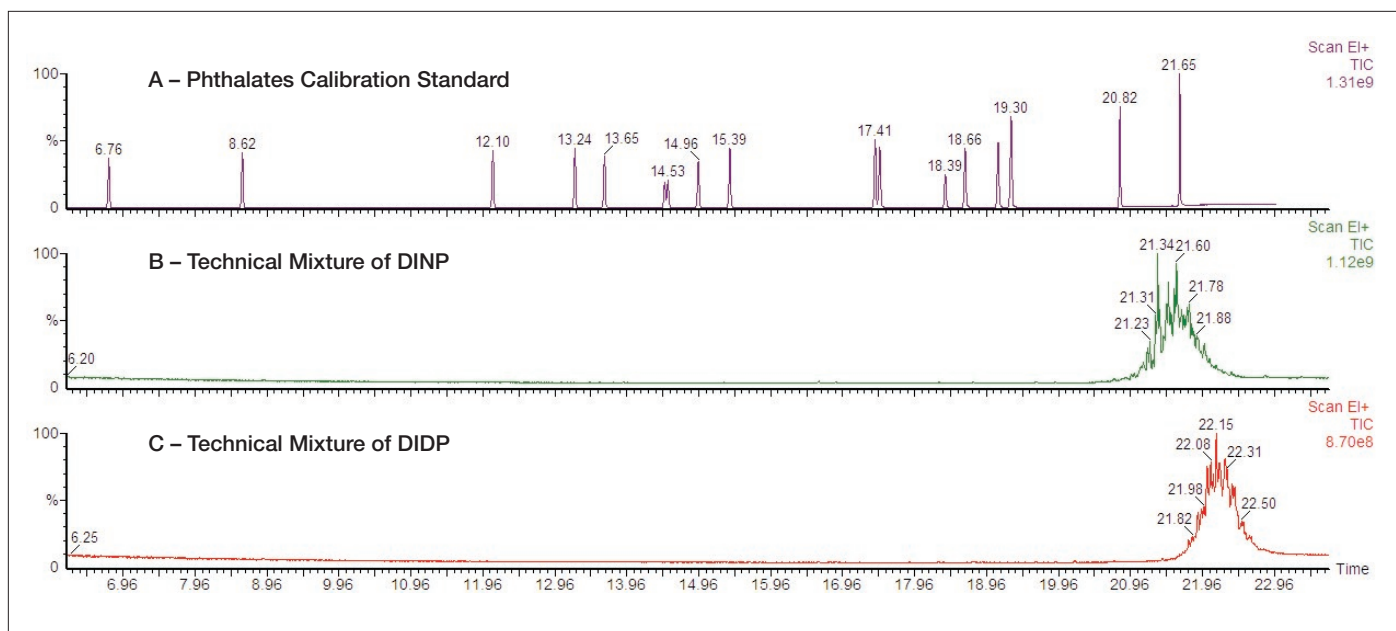


Figure 3. The chromatographic result of the GC/MS analysis of a phthalate standard.

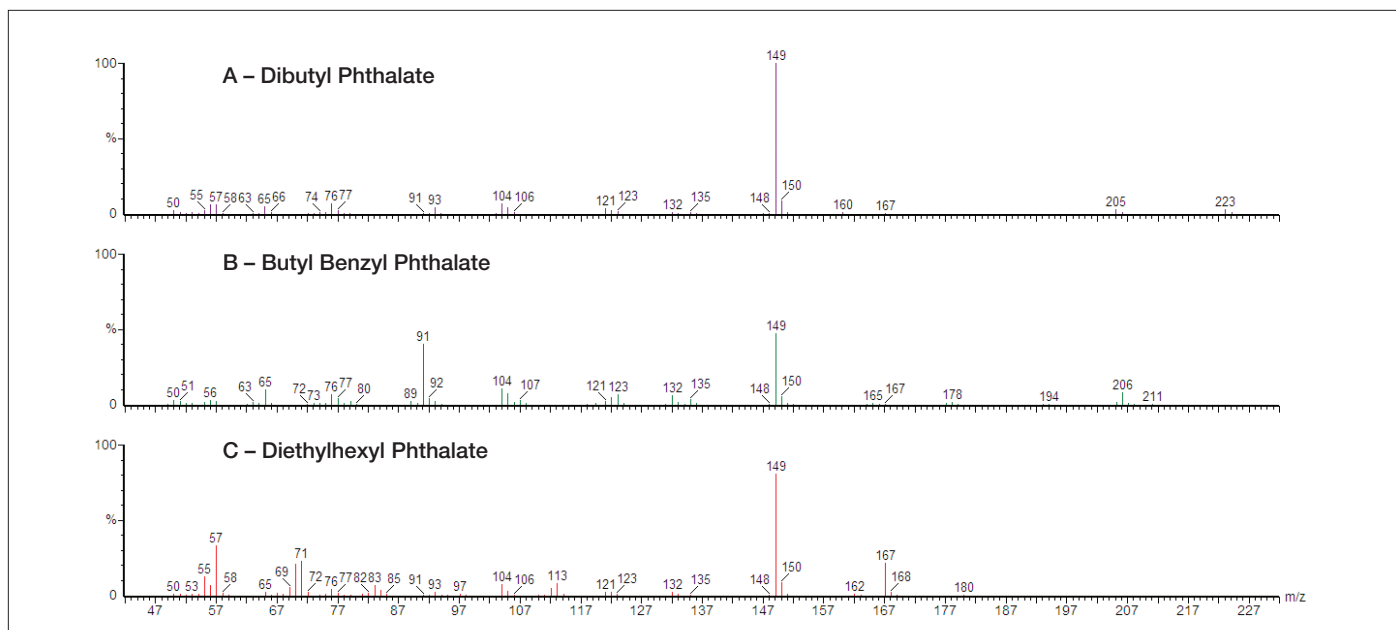


Figure 4. The comparison of the spectral data of three different phthalates.

Depending on the sample-preparation technique and the final volume of the extract, the analysis may require lower instrument detection limits. In that case, two options are available. A splitless injection will increase the amount of sample introduced to the column approximately 25x over the split technique demonstrated here. The negative aspect of a splitless injection is that more sample matrix and solvent will be introduced into the column and detector. This will increase the wear and tear on the system and may require more frequent maintenance. Another means to reaching lower detection limits is the addition of single ion recording (SIR) functions to the MS method. SIR will increase the response of analytes, without changing the GC injection conditions – the improvement in response can be between 20x and 80x. SIR functions can be combined with full-scan analysis, providing both improved sensitivity and full spectral data.

The analysis of the toy samples resulted in detection of phthalates in each of the different plastic materials; however, the phthalate level of all analyses was well below the regulatory limits. A sample analysis is pictured in Figure 5; diisobutyl phthalate, and di-n-butyl phthalate are evident in chromatogram C. The total % weight of phthalates in this component was 0.007%.

In addition to phthalates, other organic species present in the sample are extracted (Figure 5 – chromatogram D). Full-scan MS analysis will detect other expected or unexpected polymer additives and coatings. In this case, butylated hydroxytoluene, a common antioxidant, was also detected in our toy sample (Figure 5 – chromatogram B). The MS data was used to screen the toy samples for polycyclic aromatic hydrocarbons (PAHs). The signature ion for each common PAH was reviewed and no significant peaks with matching spectrum were observed.

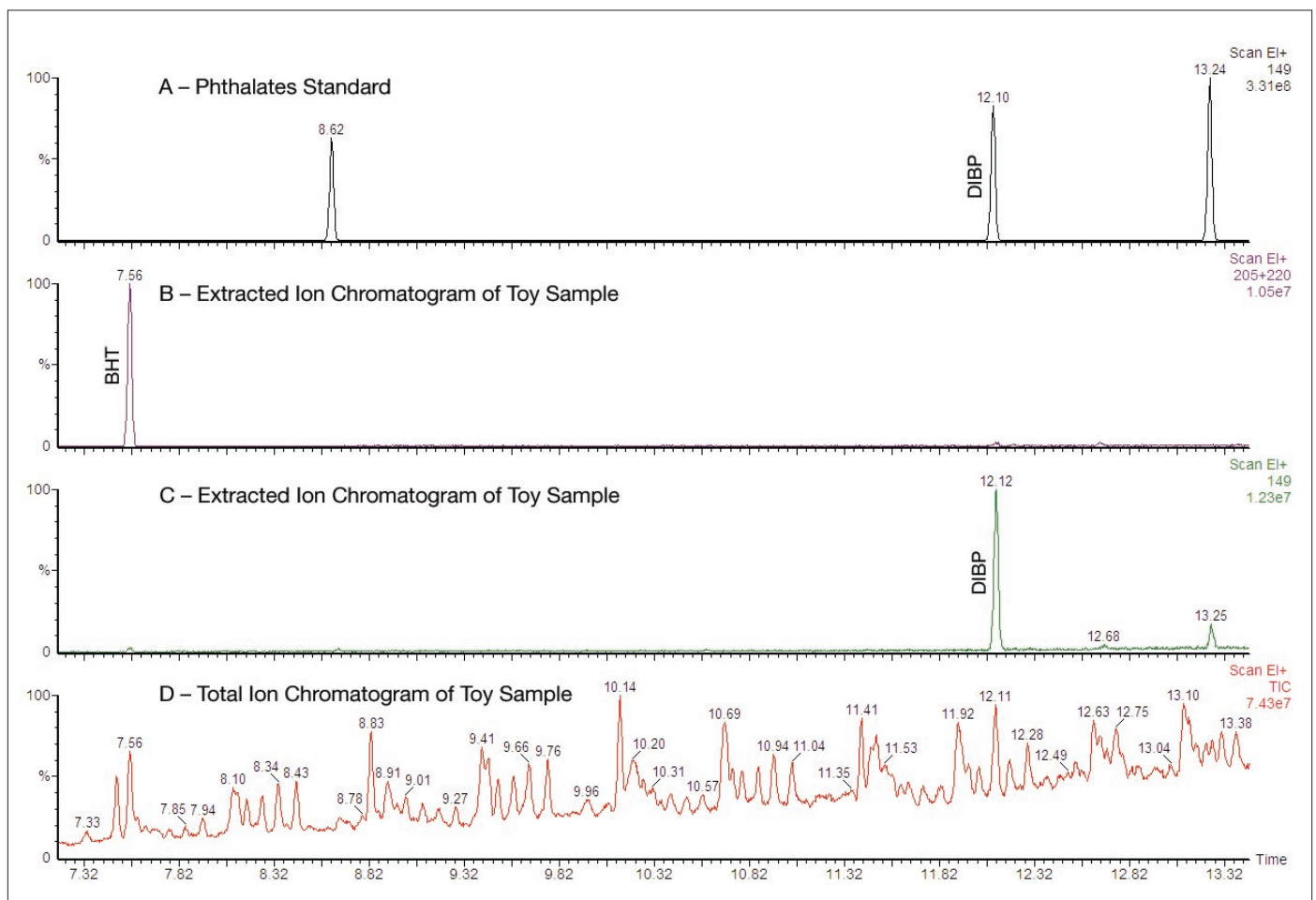


Figure 5. Chromatograms of the analysis of a toy sample for phthalates.

Conclusion

European and North American countries have set regulations on the acceptable level of phthalates in toys. As a result, a reliable technique to determine the phthalate level in toys is necessary. This application note has presented a robust and accurate GC/MS analysis which will determine the phthalate content of plastic-toy components. Important aspects of sample preparation – cleanup and laboratory practices – were presented. Sample preparation for surface and total phthalate measurements were discussed. The GC/MS analysis demonstrates separation and detection of common phthalates. This measurement achieved detection at levels considerably lower than the regulations. Finally, the power of GC/MS analysis was used to screen the samples for other common additives including anti-oxidants and PAHs.

References

1. Staples, C.A., ed. *Phthalate Esters – The Handbook of Environmental Chemistry*. New York: Springer, 2003.

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