Determination of Phthalate Concentration in Toys and Children's Products

Gas Chromatography/Mass Spectrometry

Authors

Yun Zou, Min Cai
Agilent Technologies
(Shanghai) Co.Ltd,
412 YingLun Road
Waigaoqiao Free Trade Zone
Shanghai 200131
China

Abstract

Due to public health concerns, the Chinese government and the US Consumer Product Safety Commission (CPSC) both introduced test methods for the analysis of phthalate content in childcare items and toys using GC/MS in 2008. These regulatory methods require determination of the presence of six regulated phthalate esters including dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), bis(2-ethylhexyl)-phthalate (DEHP), di-n-octyl phthalate (DNOP), di-isononyl phthalate (DINP), and di-isodecyl phthalate (DIDP). These six restricted phthalate esters along with other common phthalates such as dimethyl phthalate (DMP), diethyl phthalate (DEP), dihexyl phthalate (DHP), and bis(2-n-butoxyethyl)phthalate (DBEP) were analyzed with an Agilent 5975C Series GC/MSD and Agilent J&W DB-5ms Ultra Inert column, resulting in accurate calibration coefficients, and excellent reproducibility and recovery.

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Introduction

Phthalates are the most commonly used plasticizers, which are added to soft polyvinyl chloride (PVC) toys and baby products to increase polymer flexibility. This is due to their function as intermolecular "lubricants". Because they are additives and not reagents, they are not chemically bound in the polymer and are therefore able to leach from the matrix. Concerns have been raised over the effect of phthalate exposure from plastic materials because they may disrupt the hormonal development of children and can lead to early puberty, reproductive defects, and other health problems. This health concern has resulted in regulations regarding the type and levels of phthalates allowable in plastic toys and other articles.

In December 1999, the European Union (EU) implemented a restriction on six phthalate esters in toys and childcare products meant to be placed in the mouths of children under the age of three with a maximum concentration (total phthalate content) not exceeding 0.1% (w/w). The phthalate esters of interest include:

- dibutyl phthalate (DBP)
- benzyl butyl phthalate (BBP)
- bis(2-ethylhexyl)phthalate (DEHP)
- di-n-octyl phthalate (DNOP)
- di-isononyl phthalate (DINP)
- di-isodecyl phthalate (DIDP)

China is one of the major exporters of toys and children's products in the world. Chinese regulation GB/T 22048-2008 was issued in June 2008 and came into effect in May 2009 to strengthen the supervision of these harmful compounds. Similar to EU regulation, the identification and quantification of the six regulated phthalate esters were determined using GC/MS with an external standard method [2].

In August 2008, US Congress enacted the Consumer Product Safety Improvement Act (CPSIA 2008), which established a 0.1% (w/w) limit for these six phthalate esters. The US Consumer Product Safety Commission (CPSC) subsequently introduced a test method for the analysis of phthalate content in childcare items and toys using GC/MS with an internal standard method [3].

In addition to these six restricted phthalate esters, different regional regulations imposed provisions on other phthalates such as dimethyl phthalate (DMP), and diethyl phthalate (DEP) according to different regulations. The Statutory Order of Danish Ministry of Environment and Energy defines all diesters of o-phthalic acid as phthalates, indicating that most of the commonly used phthalates in children's products are prohibited by the Danish regulations.

This application note demonstrates the determination of common phthalates in plastic toys using the Agilent J&W DB-5ms Ultra Inert column based on the framework of the original Chinese GB/T 22048-2008 and US CPSC methods.

Experimental

The experiments were performed using an Agilent 7890 Gas Chromatograph System with split/splitless capillary inlet, an Agilent 5975C Mass Spectrometer with triple axis detector, and an Agilent 7683 automatic liquid sampler (ALS). The split/splitless inlets were fitted with long-lifetime septa (Agilent Part No. 5183-4761). Injections were made using a 10-µL syringe (Agilent Part No. 9301-0714).

Phthalate esters

The following phthalate esters were purchased from Sigma-Aldrich and AccuStandard:

- dibutyl phthalate (DBP)
- di-n-octyl phthalate (DNOP)
- di-isodecyl phthalate (DIDP)
- benzyl butyl phthalate (BBP)
- bis(2-ethylhexyl)phthalate (DEHP)
- di-isononyl phthalate (DINP)
- bis(2-butoxyethyl)phthalate (DBEP)
- diheptyl phthalate (DHP)
- dimethyl phthalate (DMP)
- diethyl phthalate (DEP)

Benzyl benzoate was obtained from Restek Corp.

As shown in Figure 1, these phthalates are based on the 1,2-benzenedicarboxylic acid structure. There are an infinite number of possible alkyl side chains (R) and an infinite number of combinations of the side groups (R and R'). For example, the di-isononyl phthalate (DINP) and di-isodecyl phthalate (DIDP) consists of an array of compounds due to the isomeric branched-chain alkyl groups on both side chains. For phthalate esters with saturated alkyl side chains (without oxygen), the most intense peak in the electron impact (EI) ionization mass spectrum at 70 eV is at *m/z* 149, with a signal-to-noise ratio approximately 10–100 times higher than that of other ions in the spectrum. The only exception is for dimethyl phthalate where both R and R' represent CH_3 and so the H on the oxygen is replaced by CH_3. Consequently, *m/z* 163 becomes the base peak. Several less intense ions were selected as application ions in order to eliminate matrix interferences from unwanted phthalates for quantitation, or due to isomeric congeners. For example, the quantitation ions for DINP and DIDP are low abundance ions at *m/z* 293 and *m/z* 307, respectively. Therefore, when preparing the calibration solutions the concentrations for DINP and DIDP normally are quite higher than other phthalates in most of the regulatory

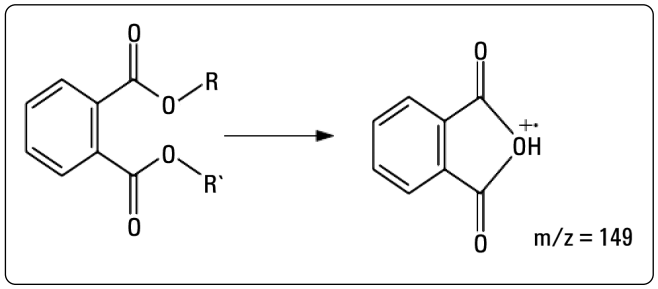

Figure1. Primary structure of phthalates and major fragmentation of phthalate esters in EI ionization (The dominant ion in the EI spectrum is typically m/z 149. The exception is for dimethyl phthalate where both R and R' are CH_3, so the H on the oxygen is replaced by CH_3 and m/z 163 becomes the base peak.)

methods.

Calibration solutions for Chinese GB/T 22048-2008 analytical methods

According to Chinese GB/T 22048-2008 analytical methods, five calibration solutions were prepared by dilution in dichloromethane (DCM). The concentration range of DBP, BBP, DEHP, and DNOP was from 0.5 µg/mL to 10 µg/mL. The concentration range of DINP and DIDP was from 5 µg/mL to 100 µg/mL in calibration solutions.

The experimental conditions are listed in Table 1. Table 2 presents the selected target ion and three qualifying ions.

Table 1. Gas Chromatography and Mass Spectrometers Conditions (GB/T 22048-2008)

GC Conditions	
Column	Agilent J&W DB-5ms Ultra Inert capillary column, 30 m × 0.25 mm, 0.25 µm (p/n 122-5532UI)
Inlet Temperature	Split @ 300 °C, spilt 20:1, split injection liner (Agilent p/n 5188-4647).
Carrier Gas	Helium, constant flow mode, 1.2 mL/min
Injection Volume	1 µL,
Oven Program	180 °C for 0.5 min; to 280 °C at 20 °C/min and hold for 7 min
MS Conditions	
Solvent Delay	4.2 min
MS Temp	230 °C (Source); 150 °C (Quad)
Transfer Line Temp	280 °C
MS	EI, SIM/Scan
Scan Mode	mass range (50-500 amu)
SIM Mode	ions (see Table 2)

Table 2. Typical quantitation ions for phthalate plasticisers

No	Compounds	CAS No.	Tgt ion	Q1	Q2	Q3
1	Dibutyl phthalate (DBP)	84-74-2	149	150	223	205
2	Benzyl butyl phthalate (BBP)	85-68-7	149	091	206	238
3	Bis(2-ethylhexyl)phthalate (DEHP)	117-81-7	149	167	279	150
4	Di-n-octyl phthalate (DNOP)	117-84-0	279	149	150	261
5	Di-isononyl phthalate (DINP)	28553-12-0	293	149	127	167
6	Di-isodecyl phthalate (DIDP)	26761-40-0	307	149	141	150

Calibration solutions for CPSC Analytical Method

The CPSC analytical method was used for determination of six restricted phthalate esters in childcare items and toys:

- DBP
- BBP
- DEHP
- DNOP
- DINP
- DIDP

Benzyl benzoate was adopted as an internal standard. In addition to these six restricted phthalate esters, dimethyl phthalate (DMP), diethyl phthalate (DEP), dihexyl phthalate (DHP) and bis(2-butoxyethyl)phthalate (DBEP) were included in this study because they are prohibited by regulations in other geographical locations.

Five calibration solutions including DBP, BBP, DEHP, DNOP, DINP, DIDP, DMP, DEP, DHP and DBEP at 0.25, 0.5, 1, 2, 5 and 10 µg/mL were prepared by dilution in cyclohexane, along with one calibration blank (cyclohexane). Each standard solution contained 5 µg/mL of benzyl benzoate as the internal standard. The experimental conditions are listed in Table 3. Suggested quantitative ions are in bold in Table 4.

Table 3. Gas Chromatography and Mass Spectrometery Conditions (CPSC Analytical Method)

GC Conditions	
Column	Agilent J&W DB-5ms Ultra Inert capillary column, 30 m × 0.25 mm, 0.25 µm (p/n 122-5532UI)
Inlet Temperature	290 °C
Carrier Gas	Helium at 1 mL/min
Injection Mode	Splitless, pulse injection at 35 psi for 0.5 min, splitless injection liner (Agilent p/n 5188-3316).
Injection Volume	1 µL
Oven Program	50 °C for 1 min to 280 °C at 30 °C/min to 310 °C at 15 °C/min hold for 4 min
MS Conditions	
Solvent Delay	5 min
MS Temp	230 °C (Source); 150 °C (Quad)
Transfer Line Temp	280 °C
MS	EI, SIM/Scan
Scan Mode	mass range (50-500 amu)
	For other parameters, see Table 4

Table 4 Phthalate Esters, CAS Number, Molecular Weights (mol wt) and Corresponding Ions

Compound Name	CAS No	Mol wt	Corresponding Ions (m/z)
Dimethyl phthalate (DMP)	131-11-3	194	194, **163***
Diethyl phthalate (DEP)	84-66-2	222	222, 177, **149**
Benzyl benzoate (BB)**	120-51-4	212	212, 91, 194,**105**
Dibutyl phthalate (DBP)	84-74-2	278	149, 167, 205, **223**
Dihexyl phthalate (DHP)	84-75-3	334	251, 233, **149**
Benzyl butyl phthalate (BBP)	85-68-7	312	91, 149, **206**
Bis(2-n-butoxyethyl)phthalate (DBEP)	117-83-9	366	176,193, **149**
Bis(2-ethylhexyl)phthalate (DEHP)	117-82-8	390	149, 167, **279**
Di-n-octyl phthalate (DNOP)	117-84-0	390	149, 167, 261, **279**
Di-isononyl phthalate (DINP)	28553-12-0	418	149, 167, **293**
Di-isodecyl phthalate (DIDP)	26761-40-0	446	149, 167, **307**

* Suggested quantitative ions are in bold.

** Benzyl benzoate is internal standard

Sample preparation for Real Samples

Sample #1 was a PVC toy and sample #2 was an infant pacifier. Both samples were ground or cut into pieces sized at less than 3 mm × 3 mm. One gram of cut pieces was Soxhlet extracted in 120 mL of dichloromethane for 6 h at 60-80 °C. The extract was concentrated to about 10 mL using a rotary evaporator and then diluted with DCM to 25 mL. For samples having very large amounts of phthalates (for example, 45%), further dilution may be needed to reduce concentration levels into the calibration range.

The spiked samples were treated according to the procedure described above.

Results and Discussion

Chinese GB/T 22048-2008 analytical methods

Calibration standards

The total ion chromatogram (TIC) of the six phthalate esters (DBP, BBP, DEHP, DNOP, DINP and DIDP) is shown in Figure 2. While DBP, BBP, DNOP and DEHP appeared as single peaks in the chromatogram, DINP and DIDP each appeared as typical finger peaks because of an array of possible isomers. The extracted ion chromatogram (EIC) of DINP at *m/z* 293 and DIDP at *m/z* 307 is shown in Figure 3 where area summation integration was used for the quantitation of these compounds.

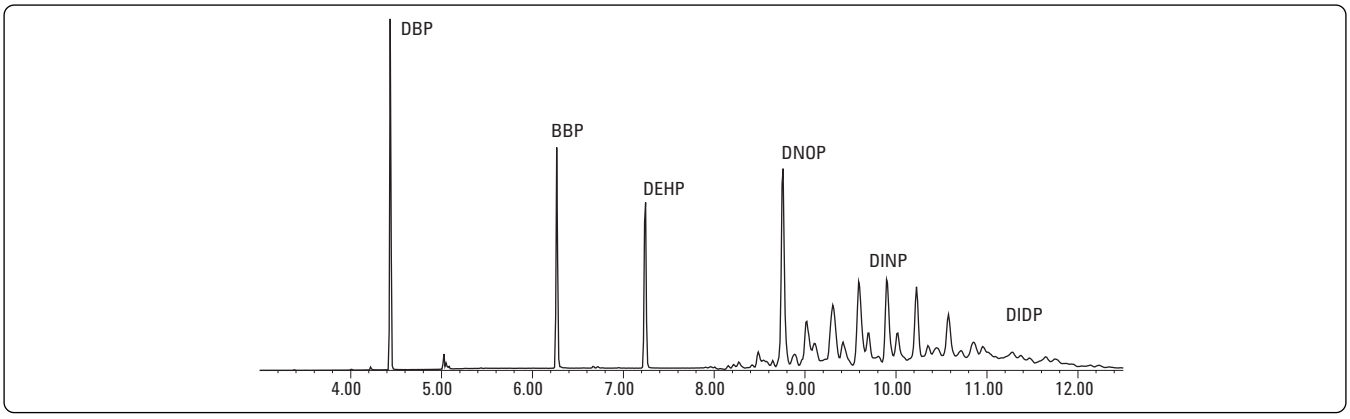

Figure 2. TIC of six regulated phthalates (DBP, BBP, DEHP and DNOP, 5 ppm each; DINP and DIDP 50 ppm each).

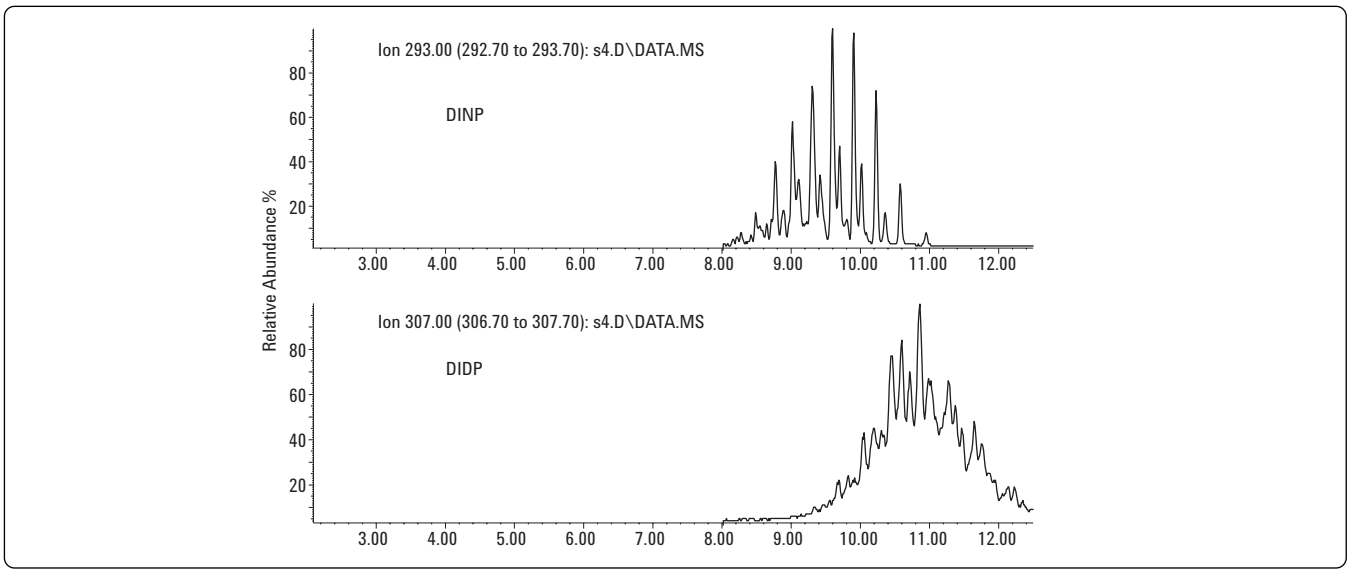

Figure 3. Extracted ion chromatogram of DINP at m/z 293 and DIDP at m/z 307.

Calibration curves were constructed from data obtained by 1-µL injections of standards. All the phthalate esters had excellent calibration coefficients as indicated in Table 5. Table 6 presents the recovery data for spiked samples, which were treated according to the procedure described in the sample preparation. The DINP and DIDP recoveries were determined at concentration levels of 50 mg/L and 100 mg/L, whereas the recoveries of other phthalates were determined at concentration levels of 5 mg/L and 10 mg/L. Excellent recoveries were obtained for all the compounds, ranging from 92% to 107% with relative standard deviations (RSD) being less than 7%.

Table 5. Calibration of Phthalate Esters

	Compound Name	Range of linearity (mg/L)	Correlation coefficient (R^2)
1	Dibutyl phthalate	0.5 ~10	0.9992
2	Benzyl butyl phthalate	0.5 ~ 10	0.9991
3	Bis(2-ethylhexyl)phthalate	0.5 ~ 10	0.9990
4	Di-n-octyl phthalate	0.5 ~ 10	0.9990
5	Di-isononyl phthalate	5 ~ 100	0.9986
6	Di-isodecyl phthalate	5 ~ 100	0.9979

Table 6. Recovery Data of Phthalate Ester Spikes in Sample

Compound Name	Spiked amount (mg/L)	No of replicates	Recovery mean,%	RSD%
Dibutyl phthalate	5	5	98.78	5.09
	10	5	102.76	4.05
Benzyl butyl phthalate	5	5	93.27	3.35
	10	5	99.38	4.03
Bis(2-ethylhexyl)phthalate	5	5	102.16	3.75
	10	5	106.21	5.29
Di-n-octyl phthalate	5	5	103.19	4.58
	10	5	98.43	4.42
Di-isononyl phthalate	50	5	104.81	5.01
	100	5	101.78	3.99
Di-isodecyl phthalate	50	5	104.48	6.11
	100	5	92.12	5.33

Real Sample

The chromatogram for sample #1 is provided in Figure 4 along with the chromatogram for the calibration standard. DEHP and DINP were detected in this particular PVC toy. However, the total % weight of phthalates was 0.037 %, which is well below the regulatory limits of 0.1% (w/w).

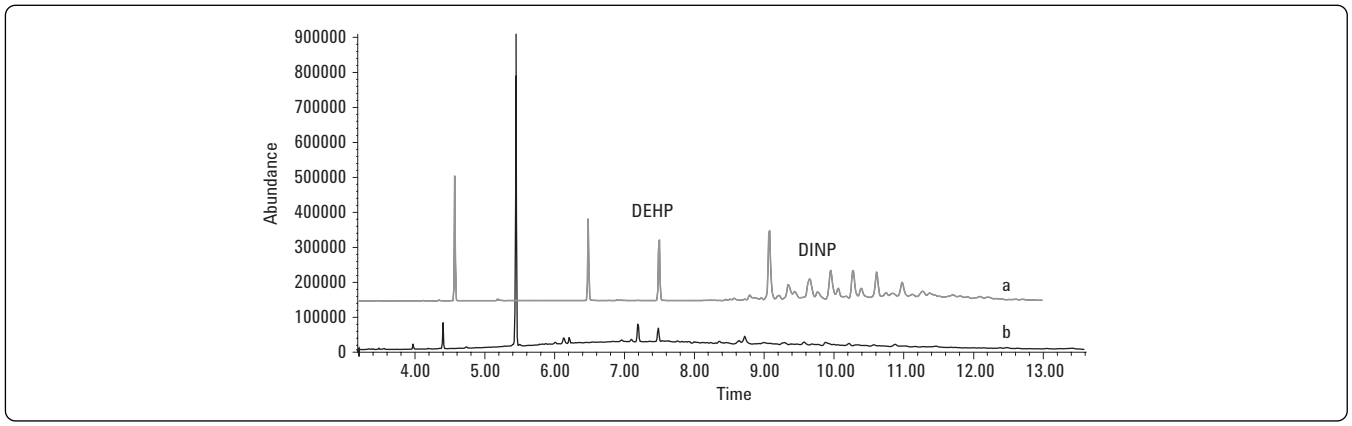

Figure 4. Chromatographic results for the GC/MS analysis of one PVC toy sample. (a) TIC of phthalates standards, (b) TIC of real sample.

CPSC Analytical Method

Calibration Standard

The total ion chromatogram of 10 phthalate esters (DMP, DEP, DBP, DHP, BBP, DBEP, DEHP, DNOP, DINP and DIDP) and internal standard benzyl benzoate at 5 ppm is shown in Figure 5. DNOP, DINP and DIDP were partially co-eluting because of isomeric congeners. As discussed earlier, in order to eliminate interferences, less intense ions at *m/z* 279, *m/z* 293 and *m/z* 307 were chosen as the quantitation ions for DNOP, DINP and DIDP, respectively.

According to the CPSC method, the calibration range is from 0.25 to 10 mg/L for each phthalate. The concentration range of DINP and DIDP in this method is lower compared to that for most other regulatory methods. As indicated in Table 7, all of the phthalates achieved excellent linearity with the linear coefficient R^2 being greater than 0.999. Figure 6 demonstrates an excellent injection-to-injection reproducibility of DIDP at 1 ppm.

Table 7. Calibration of Phthalate Esters

Compound Name	Range of linearity (mg/L)	RT (min)	Correlation coefficient (R^2)
Dimethyl phthalate (DMP)	0.25-10	6.56	0.9991
Diethyl phthalate (DEP)	0.25-10	7.13	0.9995
Benzyl benzoate (BB)*	5	7.89	IS
Dibutyl phthalate (DBP)	0.25-10	8.47	0.9993
Dihexyl phthalate (DHP)	0.25-10	9.71	0.9991
Benzyl butyl phthalate (BBP)	0.25-10	9.81	0.9990
Bis(2-n-butoxyethyl)phthalate (DBEP)	0.25-10	10.13	0.9995
Bis(2-ethylhexyl)phthalate (DEHP)	0.25-10	10.34	0.9992
Di-n-octyl phthalate (DNOP)	0.25-10	11.04	0.9994
Di-isononyl phthalate (DINP)	0.25-10	10.92-11.80	0.9987
Di-isodecyl phthalate (DIDP)	0.25-10	11.41-12.20	0.9990

* Benzyl benzoate is internal standard

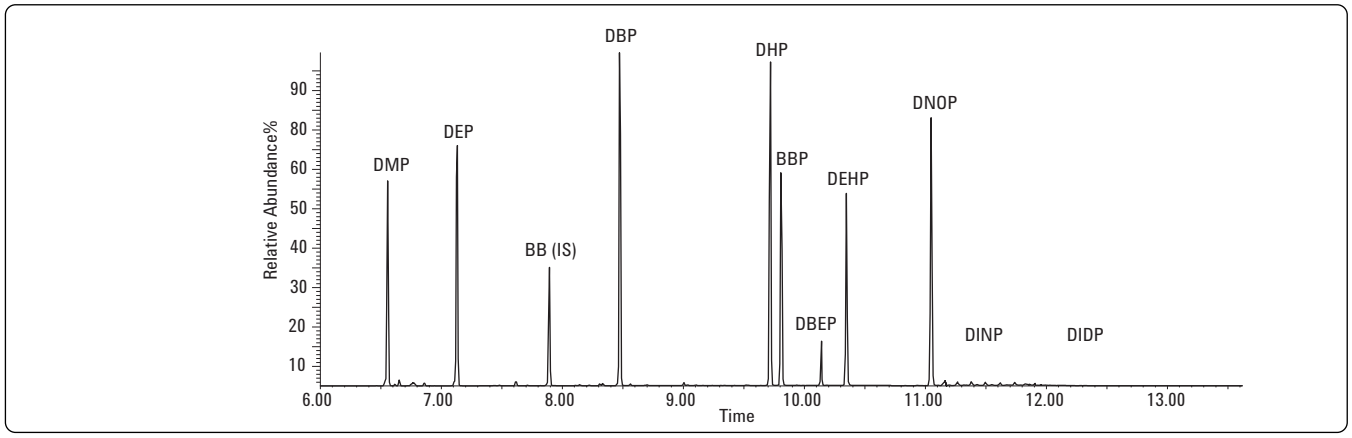

Figure 5. TIC of phthalates at 5 ppm.

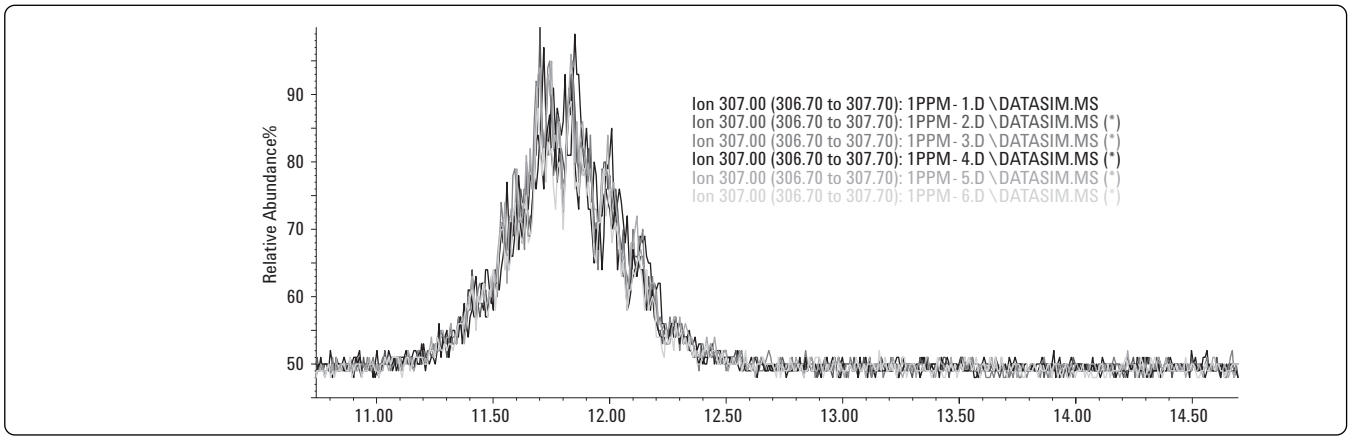

Figure 6. Reproducibility of DIDP from six injections at 1 ppm.

Real Sample

The extract and matrix spiked extract for sample #2 are shown in Figure 7. No regulated phthalates were detected in this sample #2 extract. A peak for butylated hydroxytoluene was evident, which is an antioxidant commonly added to polymers.

The spiked samples were treated according to the sample-preparation procedure described above. The recovery data and their statistics were based on five replicates of matrix spikes with 10 target phthalate esters at the 2-ppm level. Good recoveries were obtained for all investigated phthalates, ranging from 90% to 110% with relative standard deviations (RSD) less than 13.3%. Among these phthalate esters, excellent results for DMP, DEP, DBP, DHP, BBP, DEHP and DNOP were achieved, with the range of recovery at 97–105% and RSD repeatability of less than 5%.

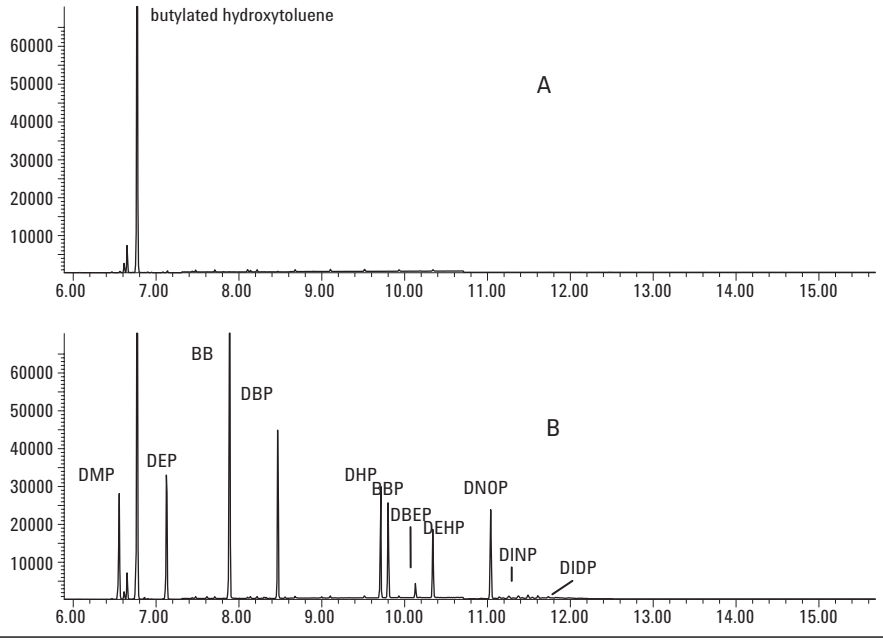

Figure 7. TIC of infant pacifier extract (A) and sample # 2 (pacifier) extract spiked with 2-ppm phthalate mixture (B).

Conclusion

According to the approved China standard and US CPSC method, two GC/MS methods were developed for the determination of phthalate esters in toy and children's products using the Agilent 7890A GC System and an Agilent 5975 Series GC/MSD with an Agilent J&W DB-5ms Ultra Inert column. These methods well meet the requirements of both regulatory methods and have good linearity, repeatability, and recoveries for all target phthalate esters.

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