

Analysis of Phthalate Esters in Children's Toys Using GC-MS

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Abstract

As of February 2009, the US Consumer Product Safety Improvement Act, Section 108, mandated that all manufacturers of children's toys analyze their products for Phthalate Esters. The method to be used is in accordance with the US Consumer Product Safety Commission (CPSC). In this study, six phthalate esters in children's toys were measured using the GCMS-QP2010 Ultra. The simultaneous Scan/SIM data acquisition technique was utilized, with the SIM data used for quantitation. The data showed excellent calibration curve linearity and repeatability. In two of the toy samples, unregulated plasticizers were identified by scan data, illustrating the efficiency of simultaneous Scan/SIM measurement.

Keywords: GC-MS, phthalate esters, toys, CPSC method, Scan/SIM

Introduction

"Phthalate esters" is a general term for esterified compounds of phthalic acid and alcohol. Phthalate esters are used as plasticizers to make materials more flexible and elastic. Numerous types of phthalate esters have been developed, differing in the carbon number of the alcohol. The phthalate esters are added based on the desired property, such as insulation, heat resistance, or weatherproofing.

In recent years, regulations on phthalate esters in toys have been investigated in various countries with the aim of protecting the health of infants and children.

EU Directive 2005/84/EC and the US Consumer Product Safety Improvement Act, Section 108, regulate the following 6 phthalate esters: dibutyl phthalate (DBP), butyl benzyl phthalate (BBP), di-2-ethylhexyl phthalate (DEHP), di-octylphthalate (DnOP), diisononyl phthalate (DINP), and di-isodecyl phthalate (DIDP). This article introduces the results of simultaneous Scan/SIM measurements of 6 phthalate esters in children's toys, performed in accordance with analysis method CPSC-CH-C1001-09.3, prescribed by the US Consumer Product Safety Commission (CPSC).

Experiment

Reagents

Phthalate ester standard mixture III (0.1 mg/mL of dibutyl phthalate (DBP), butyl benzyl phthalate (BBP), di-2-ethylhexyl phthalate (DEHP), di-n-octylphthalate (DnOP), diisononyl phthalate (DINP), and di-isodecyl phthalate (DIDP) respectively) was purchased from Kanto Chemical Co., Inc. Benzyl benzoate (BB) was purchased from Wako Pure Chemical Industries, Ltd. for use as the internal standard. The organic solvents used at the preparation stage were all suitable for the analysis of residual agricultural chemicals.

Preparation of Reagents

Phthalate ester standard solutions were prepared by diluting phthalate ester standard mixture III with cyclohexane to create a series of standards with concentrations of 0, 0.25, 0.5, 1, 5, and 10 µg/mL respectively. An internal standard, BB, at a concentration of 1 µg/mL was added to each of the standard solutions.

BB was also diluted to a concentration of 7.5 µg/mL with cyclohexane, for use as an internal standard solution added to the extracted samples.

Sample Preparation

Toys A and B were utilized as samples. Toy A consisted of 2 types of plastic: polyvinyl chloride (PVC) (Toy A-1) and polypropylene (PP) (Toy A-2). Accordingly, preparations were performed separately. Toy B consisted of PVC plastic.

The toys were prepared in accordance with analysis method CPSC-CH-C1001-09.3, prescribed by the CPSC. The samples were cut into 2 mm x 2 mm squares, and 50 mg samples were taken. 5 mL of tetrahydrofuran (THF) was added to each, and they were agitated for 30 minutes.

10 mL of hexane was added to the completely dissolved toy samples A-1 and B (PVC), at which point they were left for 5 minutes to allow the PVC polymers to precipitate. They were then filtered using a PTFE filter (0.45 µm). Then 0.2 mL of internal standard solution (7.5 µg/mL) was added to 0.3 mL of the extracted solution and diluted to a final volume of 1.5 mL using cyclohexane.

The incompletely dissolved Toy A-2 (PP) sample was agitated for 2 hours longer and then filtered with a PTFE filter (0.45 µm). 10 mL of hexane was added to the filtered liquid, at which point it was allowed to settle for 5 minutes before filtering again with a PTFE filter (0.45 µm). 0.2 mL of internal standard solution (7.5 µg/mL) was added to 0.3 mL of extracted solution, and diluted to 1.5 mL final volume using cyclohexane.

Blank samples (Laboratory Reagent Blank (LRB)) were prepared along with both Toys A-1 and B, and for A-2.

Instrument

The GCMS-QP2010 Ultra was used for the analysis and GCMSsolution was used for data processing. The CPSC analysis method specifies scan mode for qualitative analysis, and SIM mode for quantitative analysis. The GCMS-QP2010 Ultra is equipped with FASST (Fast Automated Scan/SIM Technique), which simultaneously acquires Scan and SIM data in a single analysis. Accordingly, measurements were performed in FASST mode for this analysis. The SIM ions of the various compounds are shown in Table 1, and the analytical conditions are shown in Table 2.

Table 2 GC-MS Analytical Conditions

Instruments

GC-MS : GCMS-QP2010 Ultra
 Autoinjector : AOC-20i + s
 Column : Rxi®-5Sil MS (30 m x 0.25 mm I.D. df=0.25 µm, Restek Corporation)

Analytical Conditions

GC

Injection Temp. : 290 °C
 Column Temp. : 50 °C (1min) – (30 °C /min) – 280 °C – (15 °C /min) – 310 °C (4 min)
 Injection Mode : Splitless
 Carrier Gas : He (Constant Linear Velocity)
 Linear Velocity : 36.3 cm/sec
 Purge Flow : 5 mL/min
 Injection Volume : 1 µL

MS

Ion Source Temp. : 230 °C
 Interface Temp. : 280 °C
 Acquisition Mode : Scan/SIM
 Tuning Mode : Normal
 Emission Current : 60 µA
 Scan
 Scan Range : *m/z* 50 – 450
 Event Time : 0.1 sec
 Scan Speed : 5000 *u/sec*

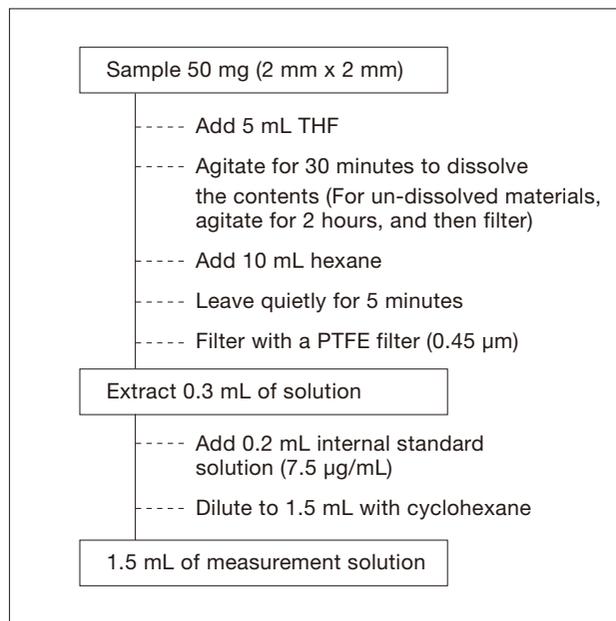


Fig. 1 Preparation Flowchart

Table 1 Monitoring Ions for SIM Measurements

	Monitoring Ion
BB (ISTD)	: <i>m/z</i> 91.1, 105* , 194, 212
DBP	: <i>m/z</i> 149, 167, 205, 223
BBP	: <i>m/z</i> 91.1, 149, 206
DEHP	: <i>m/z</i> 149, 167, 279
DnOP	: <i>m/z</i> 149, 167, 261, 279
DINP	: <i>m/z</i> 149, 267, 293
DIDP	: <i>m/z</i> 149, 167, 307

*The figures in bold show quantitative ions.

Results and Discussion

Fig. 2 shows the total ion current chromatograms for the 6 phthalate esters (DBP, BBP, DEHP, DnOP, DINP, and DIDP) and the internal standard BB (1 µg/mL). Fig. 3 shows the mass spectra for the phthalate esters.

With DINP and DIDP, a number of peaks were detected due to the presence of numerous isomers. DnOP partially co-eluted with the DINP and DIDP peaks in the total ion current chromatogram, but had unique mass chromatograms. Excellent linearity ($R^2 = 0.9991$ min.) was obtained for all the phthalate esters across the range of 0, 0.25, 0.5, 1, 5, and 10 µg/mL (Table 3).

Fig. 4 shows 5 overlaid mass chromatograms for DIDP (0.5 µg/mL) to illustrate the excellent repeatability.

Table 4 shows the calibration curve area repeatability ($n = 5$) for the phthalate esters at 0.5 µg/mL. The area repeatability was within 2.86 %.

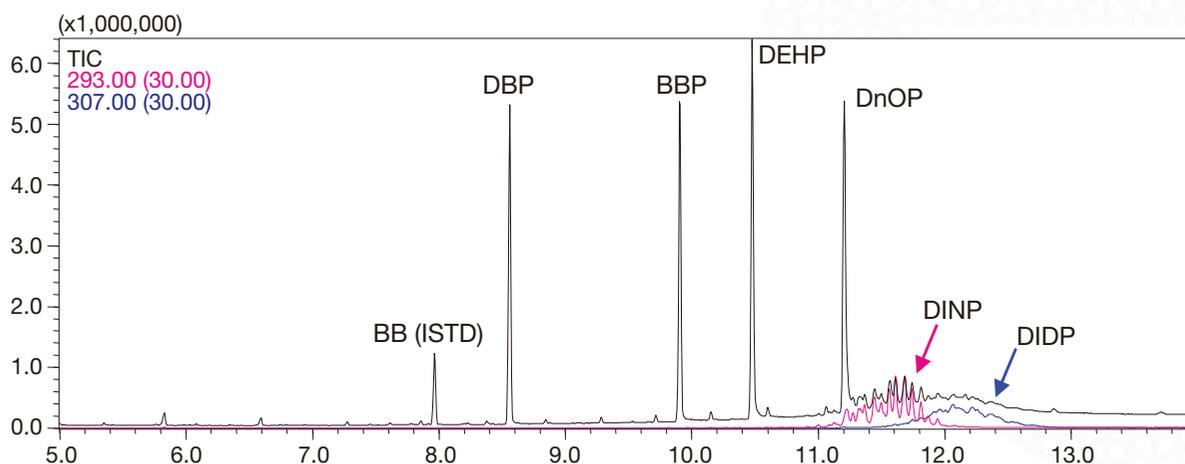


Fig. 2 Total Ion Current Chromatograms for Phthalate Esters (5 µg/mL Each) and BB (Internal Standard, 1 µg/mL)

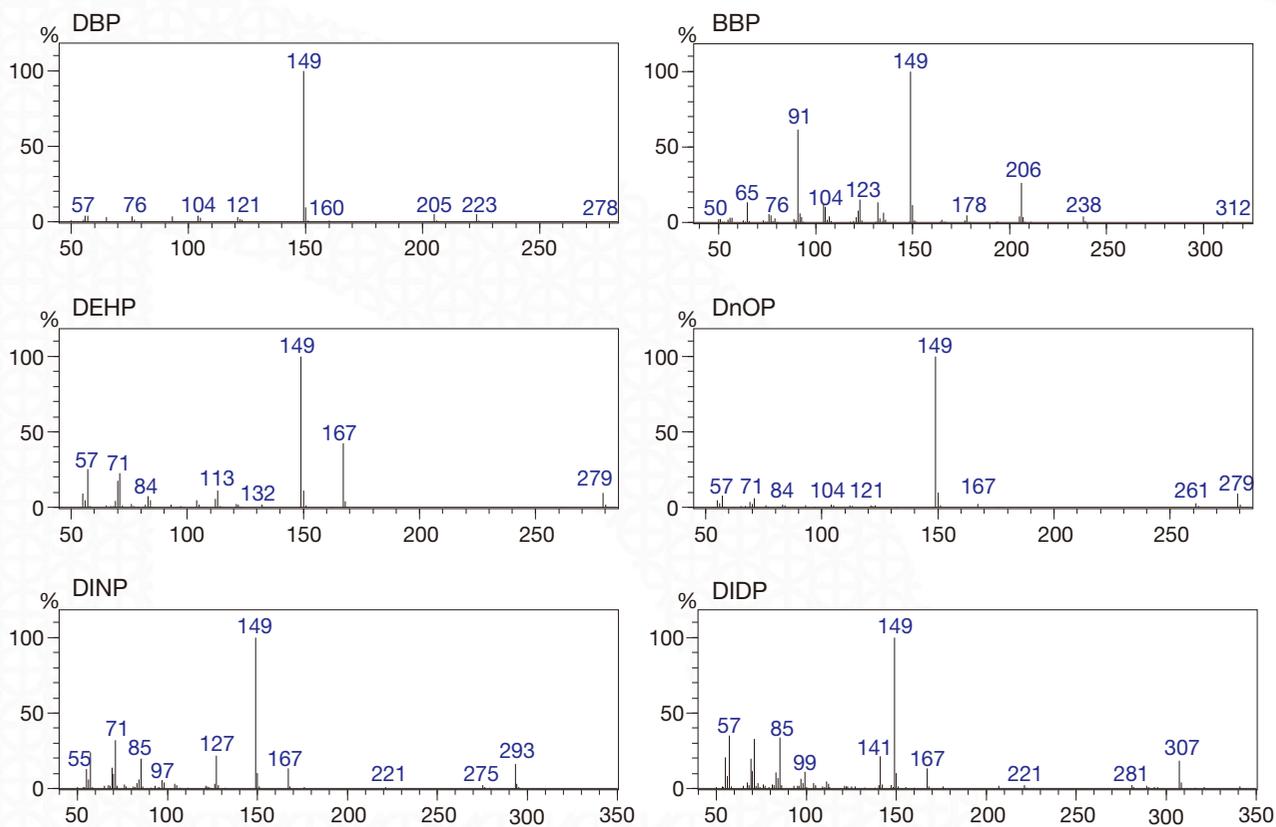


Fig. 3 Mass Spectra for Phthalate Esters

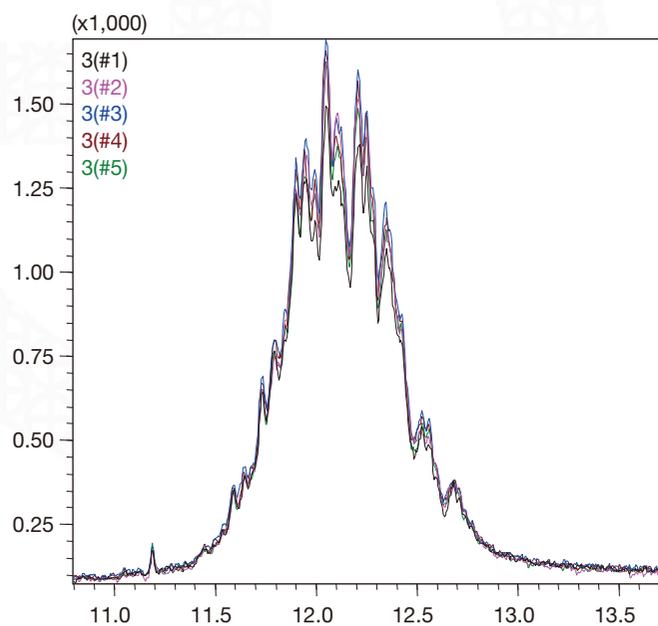


Fig. 4 Repeatability of DIDP (0.5 µg/mL)
Mass Chromatograms (n = 5)

Table 3 Linearity of Phthalate Ester Calibration Curves
(0.25 – 10 µg/mL)

Compound name	Correlation coefficient (R ²)
Benzyl benzoate (BB)	ISTD
Dibutyl phthalate (DBP)	0.9991
Benzyl butyl phthalate (BBP)	0.9999
Bis(2-ethylhexyl) phthalate (DEHP)	0.9998
Di-n-octyl phthalate (DnOP)	0.9999
Diisononyl phthalate (DINP)	0.9992
Diisodecyl phthalate (DIDP)	0.9993

Table 4 Area Repeatability of Phthalate Ester (0.5 µg/mL) Calibration Curves (n = 5)

	Area 1	Area 2	Area 3	Area 4	Area 5	%RSD
Benzyl benzoate (BB)*1	656,139	659,567	671,700	671,570	672,480	1.17
Dibutyl phthalate (DBP)	42,268	42,645	43,999	43,351	43,906	1.77
Benzyl butyl phthalate (BBP)	78,228	80,054	80,307	80,440	81,263	1.40
Bis(2-ethylhexyl) phthalate (DEHP)	35,037	36,332	35,626	36,387	35,770	1.55
Di-n-octyl phthalate (DnOP)	48,885	51,946	51,669	50,906	51,719	2.47
Diisononyl phthalate (DINP)	55,923	56,971	59,762	57,682	56,292	2.65
Diisodecyl phthalate (DIDP)	50,477	53,169	53,638	51,860	50,437	2.86

*1: Benzyl benzoate (BB) is the internal standard. The concentration is 1 µg/mL.

Measurement of Actual Samples

Fig. 5 shows the total ion current chromatograms and SIM mass chromatogram obtained from the measurement of the samples: Toy A, PVC (A-1) and PP (A-2). With both samples, DnOP monitoring ions m/z 261 and 279 were detected at the DnOP retention time of 11.2 minutes.

However, the library search of the mass spectra obtained from scan measurements in the FASST mode shows that the peak is not DnOP but rather diethylhexyl terephthalic acid (Fig. 6). By utilizing the SIM/Scan data acquisition technique, scan data was used to avoid a misidentification that would have occurred if only SIM data were collected, thus enhancing analysis reliability.

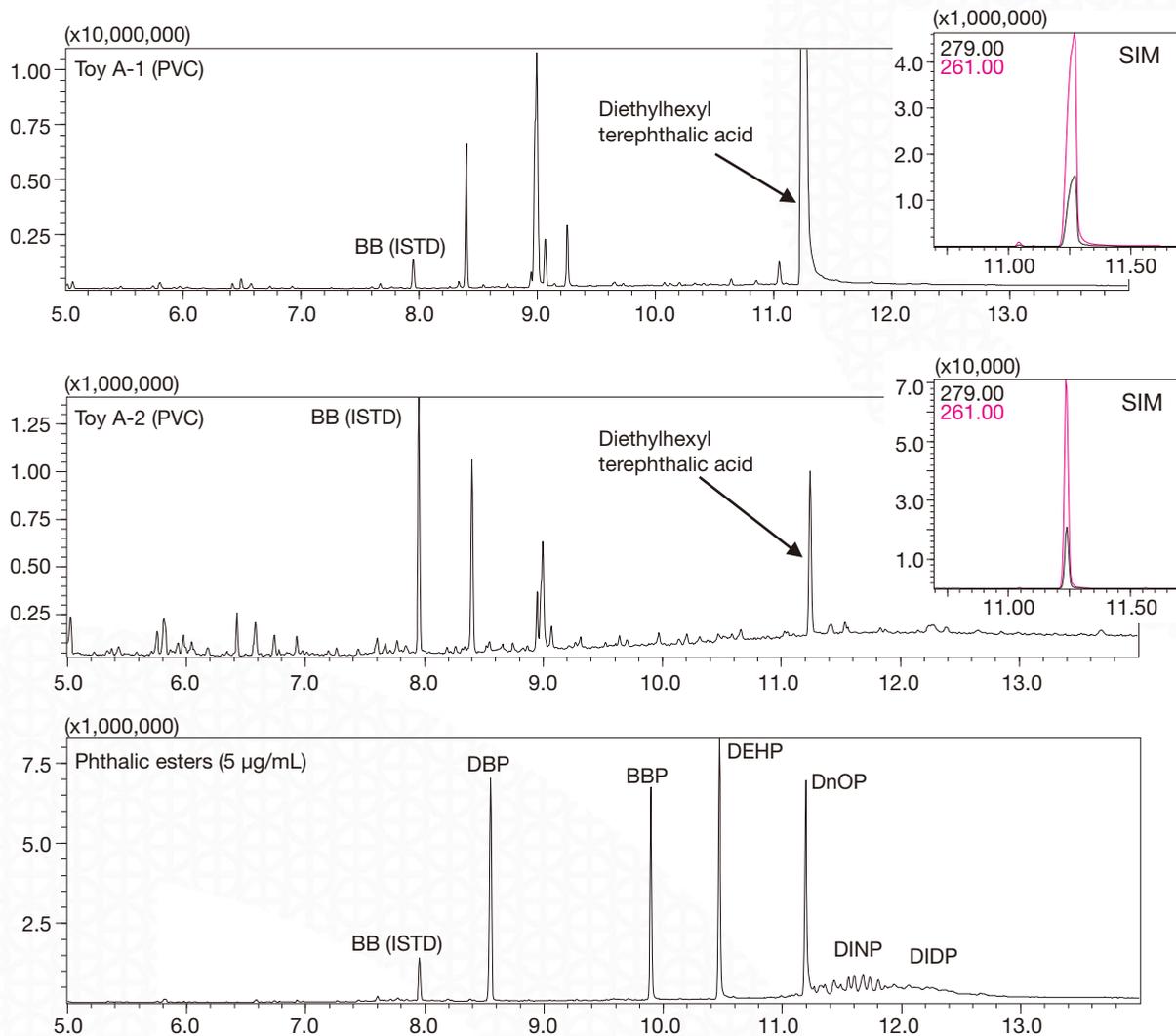


Fig. 5 Total Ion Current Chromatograms and SIM Chromatogram for Solutions Extracted from Toys A-1 and A-2 (Top: Toy A-1 (PVC); Middle: Toy A-2 (PP); Bottom: Phthalate ester standard solution (5 µg/mL))

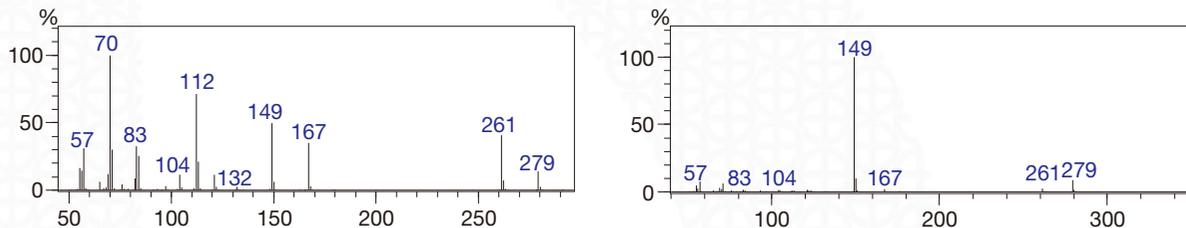


Fig. 6 Mass Spectra of The Peak Detected at Retention Time of 11.2 Minutes and DnOP
Left: Mass Spectra of Diethylhexyl Terephthalic Acid Detected at Retention Time of 11.2 Minutes
Right: Mass Spectra of DnOP

The library search of the mass spectra obtained from scan measurements in the FASST mode shows that the peak is not DnOP but rather diethylhexyl terephthalic acid.

Fig. 7 shows the total ion current chromatogram for the solution extracted from Toy B. DEHP was detected in this solution (Fig. 8), but the mass percent was 0.011 %, a sufficiently low concentration in comparison to the standard value.

Using the mass spectra obtained from the results of the Scan measurement in FASST mode, it was possible to identify substances including the fatty acids hexadecanol and octadecanol, tributyl aconitate, acetyl tributyl citrate, and isononyl cyclohexane dicarboxylic acid.

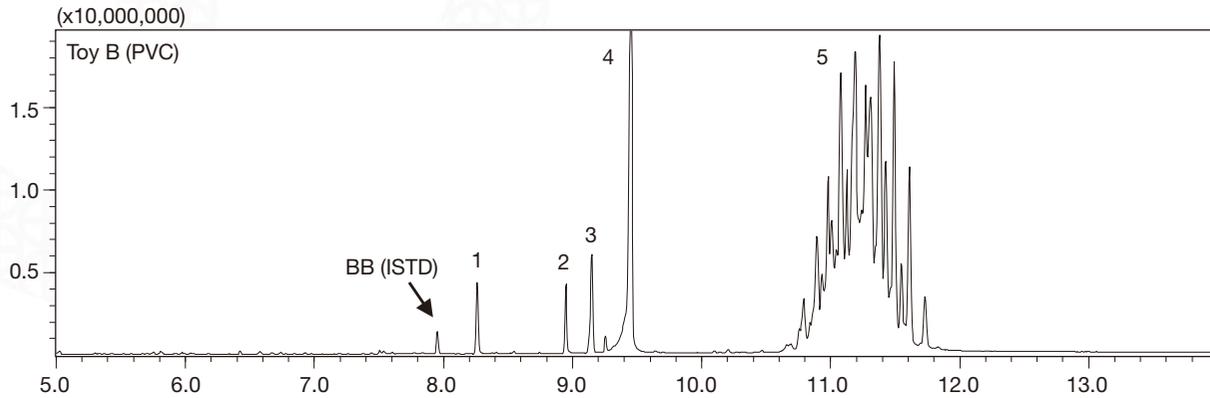


Fig. 7 Total Ion Current Chromatogram for Toy B
 1: Hexadecanol; 2: Octadecanol; 3: Tributyl aconitate;
 4: Acetyl tributyl citrate; 5: Isononyl cyclohexane dicarboxylic acid

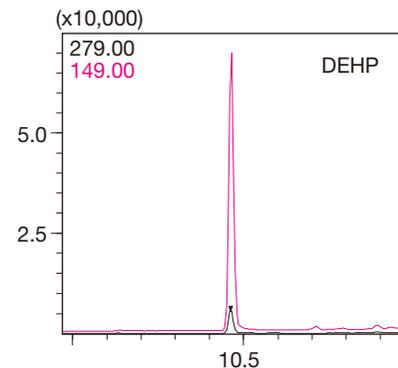


Fig. 8 DEHP SIM Mass Chromatogram Detected from the Solution Extracted from Toy B

Conclusion

FASST measurements (simultaneous Scan/SIM measurements) of phthalate esters in toys were performed in accordance with the analysis methods prescribed by the US Consumer Product Safety Commission (CPSC). Excellent calibration curve linearity and repeatability were observed, with a minimum R^2 value of 0.9991 in the 0.25 to 10 $\mu\text{g/mL}$ range, and %RSD < 3.0 % for 5 measurements repeated at 0.5 $\mu\text{g/mL}$.

From the results of the 2 toy samples, unregulated plasticizers could be identified from the scan data while, with Toy B, it was possible to detect DEHP sufficiently well, even at concentrations approximately 1/10 that of the prescribed value.

References

- [1] Consumer Product Safety Improvement Act of 2008
- [2] Test Method: CPSC-CH-C1001-09.3 – Standard Operating Procedure for Determination of Phthalates, April, 1, 2010
<http://www.cpsc.gov/about/cpsia/CPSC-CH-C1001-09.3.pdf>
- [3] Official Journal of the European Communities, Decision 198/815/EC. 1999, European Commission; European Union Scientific Committee on Toxicology, Ecotoxicology, and the Environment.
- [4] DIRECTIVE 2005/84/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 14 December 2005

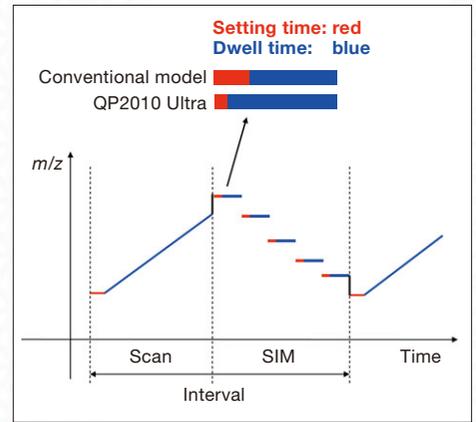
Scan/SIM Measurement Utilizing the GCMS-QP2010 Ultra

Simultaneous Scan/SIM Measurement (Fast Automated Scan/SIM Technique)

FASST mode (Fast Automated Scan/SIM Technique), which simultaneously measures Scan and SIM data, is capable of providing mass spectral measurements with Scan simultaneously with high-sensitivity measurements with SIM. In FASST mode, the respective data is acquired by alternately repeating Scan and SIM measurements. In SIM, settling time (measurement standby) is required prior to measuring each of the configured channels.

From the principles of signal processing, the dwell time (measurement time) must be extended in order to decrease the noise in each measurement mode and thus improve sensitivity.

The GCMS-QP2010 Ultra is designed to shorten the switching time between Scan and SIM in FASST mode, and to shorten the settling time (measurement standby) in comparison to conventional models. As a result, higher sensitivity Scan and SIM measurements are possible in FASST mode in comparison to conventional models.



Fast Automated Scan/SIM Technique

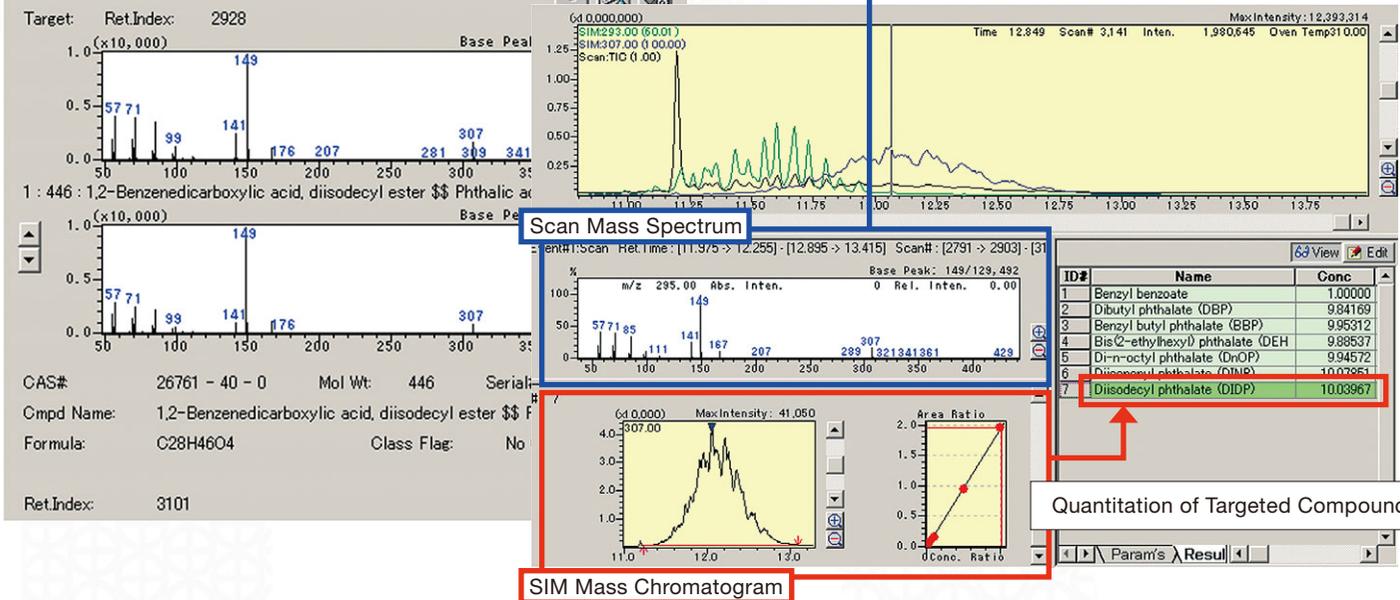
Seamless Analysis of Scan and SIM Data

GCMSsolution Ver. 2.6 is capable of analyzing the 2 sets of data obtained from simultaneous Scan/SIM measurements as a single data set. Even if the target constituents overlap with other constituents in SIM mode, the overlapping constituents can be analyzed with the mass spectra obtained from Scan measurements.

Furthermore, untargeted constituents can easily be identified by subjecting the mass spectra obtained with Scan measurements to a library search of compounds with unknown constituents. Even trace amounts of targeted constituents can be identified utilizing the data obtained with SIM measurements.

Hit#	Simila	Regi	Ret. Inde	Compound Name	Mol Wt
1	92	<input checked="" type="checkbox"/>	3101	1,2-Benzenedicarboxylic acid, diisodecyl ester	446
2	91	<input type="checkbox"/>	3101	1,2-Benzenedicarboxylic acid, diisodecyl ester	446
3	91	<input type="checkbox"/>	3229	Didecyl phthalate \$\$ 1,2-Benzenedicarboxylic	446
4	90	<input type="checkbox"/>	3101	1,2-Benzenedicarboxylic acid, diisodecyl ester	446
5	90	<input type="checkbox"/>	2902	Phthalic acid, bis(7-methyloctyl) ester \$\$ 1,2-	418
6	87	<input type="checkbox"/>	2902	Phthalic acid, bis(7-methyloctyl) ester \$\$ 1,2-	418

Mass spectral confirmation of targeted compounds and identification of detected compounds with untargeted constituents



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