

Phthalate Esters Screening in Toys and Childcare Articles Using Py-Screener™ Ver 2

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User Benefits

- ◆ Simple and time-saving program for screening of phthalate esters in toys and childcare articles
- ◆ Easy determination of pass, fail and inconclusive results by colored flagging system in LabSolutions Insight™

Introduction

Phthalate esters are a group of compounds formed from esterification of phthalic acid and alcohol¹. They are commonly used as plasticizers in polyvinyl chloride (PVC) materials to increase flexibility². However, some phthalate esters may cause endocrine disruption and reproductive problems². This has led to concerns over the use of phthalate esters in toys and childcare articles as the health of infants and children who are at higher risk of exposure due to their biting and mouthing activities³. The European Union (EU) regulation concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) imposes restrictions on the use of four phthalate esters namely bis(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP) and diisobutyl phthalate (DIBP) in toys and childcare articles. According to Commission Regulation (EU) No 2018/2005, toys or childcare articles that contain more than or equal to 0.1 % w/w (equivalent to 1000 mg/kg) of DEHP, DBP, BBP and DIBP, individually or in any combination, are not allowed to be placed on the market after 7 July 2020⁴. Screening and semi-quantitation of phthalate esters in polymer samples can be accelerated using Py-Screener, an analyzer developed by Shimadzu for phthalate esters and brominated flame retardants using pyrolyzer coupled with a GCMS system. In this application news, a fast simultaneous Scan/SIM method from Py-Screener Ver. 2 is used for screening of seven phthalate esters (DIBP, BBP, DNOP, DIDP, DBP, DEHP and DINP) in toys and childcare articles.

Experimental

Instrumental and Analytical Conditions

Py-Screener consists of Py-GCMS, i.e. a multi-shot pyrolyzer and its auto-shot sampler from Frontier Lab, Japan which is coupled with a single quadrupole GCMS system from Shimadzu Corporation, Japan. The details of the instrumentation are shown in Table 1. It also contains choices of optimized method files and sequence tables for ease of analysis. In this application, the fast method for phthalate esters was selected. SH-1MS column with integrated guard column is utilized in Py-Screener Ver. 2 to increase the lifetime of column from dirty matrices.

Besides that, Py-Screener provides standard samples and sample preparation toolkit for convenience of sample preparation.

Standards and Sample Preparation

1 µl of 500 µg/mL of C8 – C40 saturated alkanes standard (Merck KGaA, Germany) was used for predicting phthalate

Table 1: Instrumentation

Instrumentation	
GCMS	GCMS-QP2020 NX
Multi-Shot Pyrolyzer	EGA/PY-3030D
Auto-Shot Sampler	AS-1020E
Column	SH-1MS with Guard Column (P/N: 227-36346-01) (15 m x 0.25 mm x 0.10 µm + 2 m Integrated Guard)

esters standard retention times using Shimadzu AART (Automatic Adjustment of Retention Time) function. Polymer standard samples from Shimadzu Corporation (Japan), P/N: 225-31003-91 including a blank, 100, and 1000 mg/kg of seven phthalate esters (DIBP, DBP, BBP, DEHP, DNOP, DINP, and DIDP) were utilized in Py-Screener analysis. These polymer standard sample sheets were punched using a micro-puncher provided in the sample toolkit and placed in the sample cup. The standard samples were weighed (exact weights were recorded for quantitation) and covered with phthalate-free quartz wool before subjecting them to Py-GCMS analysis (Figure 1).

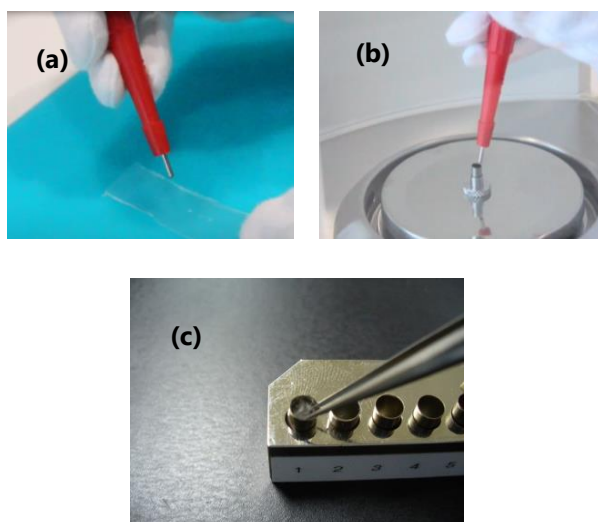


Figure 1. Phthalate ester standard sample preparation: (a) punch the polymer standard sample with a micro-puncher, (b) weigh approximately 0.5 mg in the sample cup, (c) cover the sample cup with wool.

There are 5 samples analyzed, i.e. 3 toys (Toy A, B and C) and 2 childcare articles including a baby milk bottle teat and a pacifier. Approximately 0.5 mg of test samples were obtained from each of the five samples using a cutter and placed in separate Eco-cups. The test samples were weighed (exact weights were recorded for quantitation) in the sample cups and covered with phthalate-free quartz wool before subjecting them to Py-GCMS analysis (Figure 2).

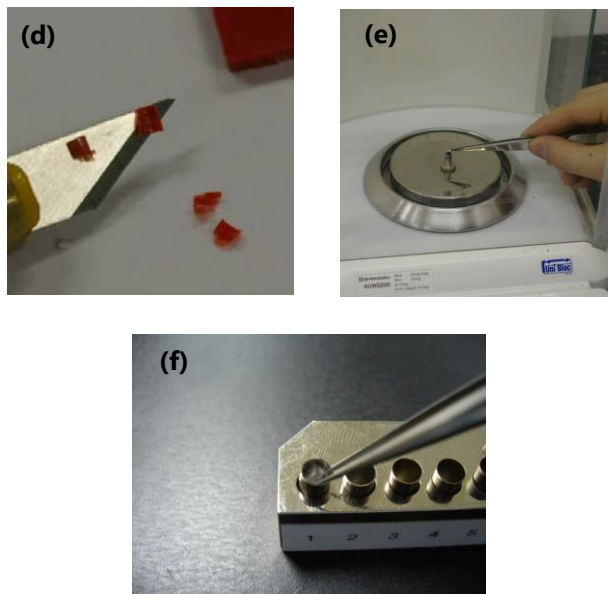


Figure 2. Sample preparation: (d) cut polymer samples (e) weigh samples of approximately 0.5 mg into the sample cup (f) cover the sample cup with wool.

■ Phthalate Esters Analysis Results Using Py-GC/MS

The analysis of phthalate esters in polymer is normally carried out using tedious and time-consuming sample preparation procedure with large amount of solvent. In order to produce high throughput, Py-Screener offers a simple method based on IEC 62321 Part 3-3 method for quick screening and semi-quantitation purpose⁵. As this is a screening method, 1000 mg/kg with $\pm 50\%$ tolerance was utilized in the judgement criteria, which produces 3

categories of screening results depending on the concentration of each phthalate ester concentration (PASS: ≤ 500 mg/kg, INCONCLUSIVE: 500-1500 mg/kg, FAIL: ≥ 1500 mg/kg). Only those samples with INCONCLUSIVE results from Py-Screener analysis should be subjected to a further test using the accurate determination method (e.g. soxhlet sample preparation followed by GCMS). However, the determination method is beyond the scope of this application news. The schematic diagram of judgement criteria of the screening and semi-quantitation in Py-Screener for phthalate esters is displayed in Figure 3.

The REACH regulation requires to monitor 4 phthalate esters: DBP, DIBP, BBP and DEHP, individually or in any combination. However, Py-Screener includes 3 extra phthalate esters: DNOP, DINP and DIDP based on IEC 62321 Part 3-3 method. Therefore, the semi-quantitation in this application news would be done for these 7 phthalate esters. LabSolutions Insight software was used for data processing and analysis. Color-coded flags were applied in LabSolutions Insight to report quality control results and identify data points for review. The flag setting for quality control and screening criteria of the 4 regulated criteria with their summation has been predefined and is included in the Py-Screener Ver. 2.

Phthalate Esters Polymer Standard Samples

The blank and 100 mg/kg phthalate ester standard samples were used for quality control checks. Blank phthalate ester standard sample was used to check the background level, while 100 mg/kg phthalate ester standard sample was used for sensitivity checks. The quality control checks criteria for blank standard samples must be less than 30 mg/kg and the signal-to-noise ratio of the seven phthalate esters in 100 mg/kg standard samples must be higher than 30. The flag results for all data points in blank and 100 mg/kg phthalate ester standard samples must be highlighted in green to ensure they pass the quality control criteria. On the other hand, if the quality control item fails, the flag result for blank standard and 100 mg/kg standard samples would be highlighted in red and blue respectively.

The mass chromatograms of seven phthalate esters in 1000 mg/kg phthalate ester standard are shown in Figure 4.

Figure 5 shows that all the seven phthalate esters in the blank and 100 mg/kg standard samples passed the quality control checks (green flags). The 1000 mg/kg phthalate

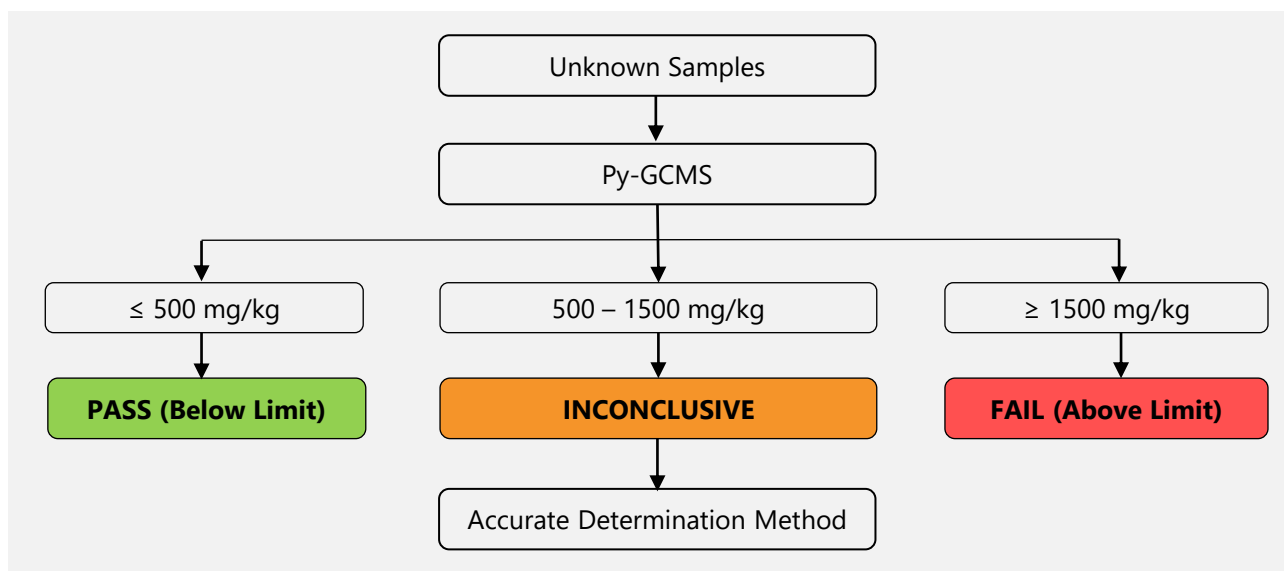


Figure 3. Schematic diagram of judgement criteria for phthalate esters screening results.

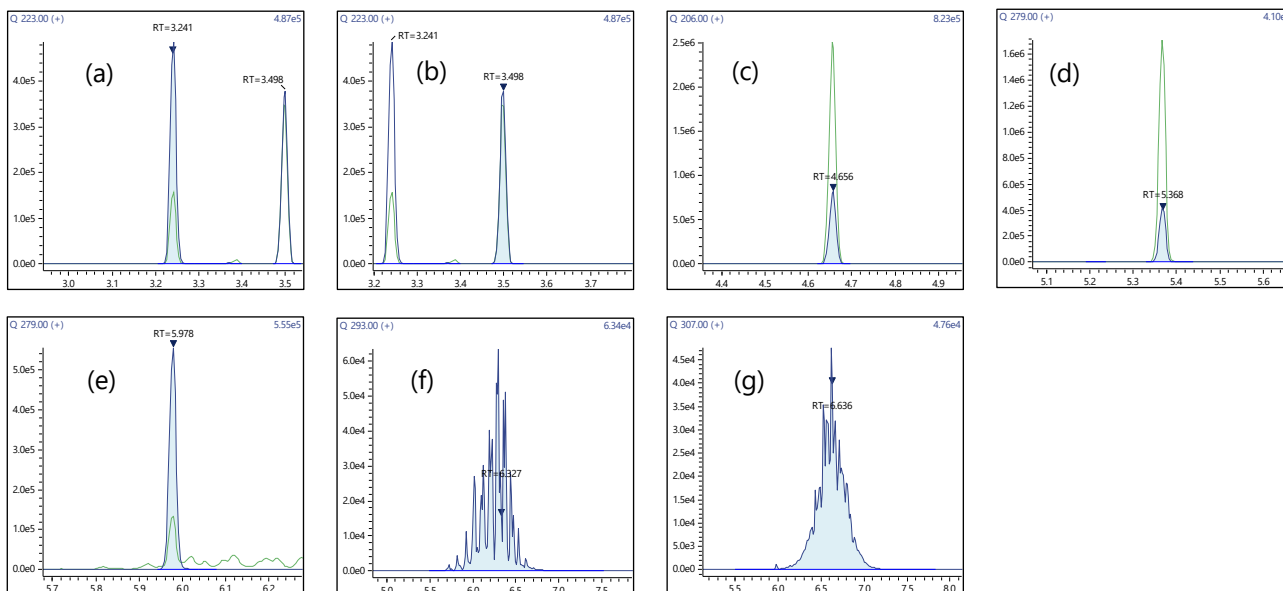


Figure 4. Mass chromatograms of (a) DIBP, (b) DBP, (c) BBP, (d) DEHP, (e) DNOP, (f) DINP, and (g) DIDP in 1000 mg/kg phthalate esters standard sample.

Summary Results													
#	Name	1_2282022_Blank_Cup_01			2_2282022_Phthalate_STD_Blank...			3_2282022_Phthalate_STD_100...			4_2282022_Phthalate_STD_1000...		
		Conc.	S/N	Flag Result	Conc.	S/N	Flag Result	Conc.	S/N	Flag Result	Conc.	S/N	Flag Result
1	DIBP	---	---	█	---	---	█	93.00	3005.86	█	1000.00	23172.14	█
2	DBP	---	---	█	1.44	32.95	█	93.66	3044.73	█	1000.00	17174.91	█
3	BBP	---	---	█	0.18	17.00	█	96.45	5534.85	█	1000.00	45702.83	█
4	DEHP	1.23	76.17	█	1.10	41.33	█	88.77	2101.19	█	1000.00	19520.00	█
5	DNOP	---	---	█	---	---	█	85.90	2687.94	█	1000.00	29204.89	█
6	DINP	---	---	█	---	---	█	84.08	325.88	█	1000.00	4348.88	█
7	DIDP	---	---	█	---	---	█	78.96	381.00	█	1000.00	3269.10	█

Figure 5. LabSolutions Insight summary results for phthalate esters polymer standard samples (blank, 100 mg/kg and 1000 mg/kg). 1000 mg/kg standard was used for one-point calibration curves.

ester standard sample was used to set up one-point calibration curves for all seven phthalate esters. The calibration curves were used for semi-quantitation of phthalate esters in the toys and childcare article samples. Single peak was detected for DIBP, DBP, BBP, DEHP and DNOP, while DINP and DIDP were detected as clusters of peaks due to the presence of multiple isomers.

Toys and Childcare Articles Sample Results

The retention times and peak shapes of phthalate esters present in the samples correspond well with the peaks in standard. The concentration of phthalate esters in the samples were determined using the calibration curves created with the 1000 mg/kg phthalate ester standard sample. TOTM (tris(2-Ethylhexyl) trimellitate), a non-phthalate plasticizer additive, is also monitored because when plastic materials contain TOTM, DEHP might exist as an impurity. Moreover, in high temperature, there is a possibility of TOTM reacting with components in polymer sample to generate trace quantity of DEHP. Although this trace amount of DEHP may not be significant enough to affect the screening results, it can be considered during the results investigation.

The screening results of the samples can be identified based on the colors reflected on the flag column in LabSolutions Insight as indicated in Figure 6. When a green flag is displayed, the phthalate ester, either individually or the summation of the 4 REACH regulated phthalate esters concentration is ≤ 500 mg/kg. If phthalate ester or the summation concentration is ≥ 1500 mg/kg, red flag would

be displayed, indicating that sample fails the screening. Meanwhile, if concentration falls between 500 mg/kg and 1500 mg/kg, this sample should be re-analyzed using the accurate determination method.

The semi-quantitation values and flag results of phthalate esters in toys and childcare article samples are shown in Figure 6. From the summary result table, we can conclude that Toy C failed the screening because the flags results were highlighted in red. The two red flagged phthalate esters are DEHP and DINP with a concentration of 3111.53 mg/kg (0.31%, w/w) and 4447.04 mg/kg (0.44%, w/w) respectively. The summation concentration of DEHP, DBP, BBP and DIBP were also displayed and indicated with red flag. TOTM was not observed in Toy C (refer to the mass chromatogram of TOTM in Figure 7). This implies that there was no contribution of DEHP from TOTM in this sample. Based on this screening result, it is confirmed that Toy C exceeded the 0.1% w/w (equivalent to 1000 mg/kg) limit of DEHP, DBP, BBP and DIBP individually and in any combination as stipulated in Commission Regulation (EU) No 2018/2005.

The mass chromatograms of seven phthalate esters and TOTM additive in Toy C are shown in Figure 7.

Meanwhile, Toy A, Toy B, baby milk bottle teat and baby pacifier passed the screening, indicated by the green flag beside each phthalate ester as well as the summation of 4 regulated phthalate esters. These samples passed the screening test and met the requirements of REACH regulation.

Summary Results																
#	Name	5_Toy A			6_Toy B			7_Toy C			8_Milk Bottle Teat			9_Pacifier		
		Conc.	S/N	Flag Result	Conc.	S/N	Flag Result	Conc.	S/N	Flag Result	Conc.	S/N	Flag Result	Conc.	S/N	Flag Result
1	DIBP	16.84	244.93	Pass	4.30	66.07	Pass	113.25	1021.61	Pass	2.30	10.32	Pass	1.91	22.80	Pass
2	DBP	11.26	71.38	Pass	4.55	35.74	Pass	169.04	299.62	Pass	6.86	59.85	Pass	5.85	57.18	Pass
3	BBP	----	----	Pass	----	----	Pass	3.18	27.61	Pass	----	----	Pass	----	----	Pass
4	DEHP	101.46	951.37	Pass	5.24	43.26	Pass	3111.53	9174.92	Fail	23.08	85.84	Pass	116.74	201.86	Pass
5	DNOP	2.45	60.53	Pass	----	----	Pass	----	----	Pass	----	----	Pass	----	----	Pass
6	DINP	45.91	95.27	Pass	13.28	9.36	Pass	4447.04	3821.14	Fail	20.87	31.87	Pass	41.36	62.76	Pass
7	DIDP	8.56	16.82	Pass	----	----	Pass	128.15	132.47	Pass	----	----	Pass	----	----	Pass
8	TOTM	----	----	Pass	----	----	Pass	----	----	Pass	----	----	Pass	----	----	Pass
9	DIBP, DBP, BBP, DEHP	129.57	----	Pass	14.09	----	Pass	3396.99	----	Fail	32.24	----	Pass	124.50	----	Pass

Figure 6. LabSolutions Insight summary concentration and flag results for phthalate esters in Toy A, B, C, milk bottle teat and baby pacifier individually and in summation for the 4 regulated phthalate esters. Green flag indicates pass, red flag indicates fail, orange flag (not shown here) indicates inconclusive screening result.

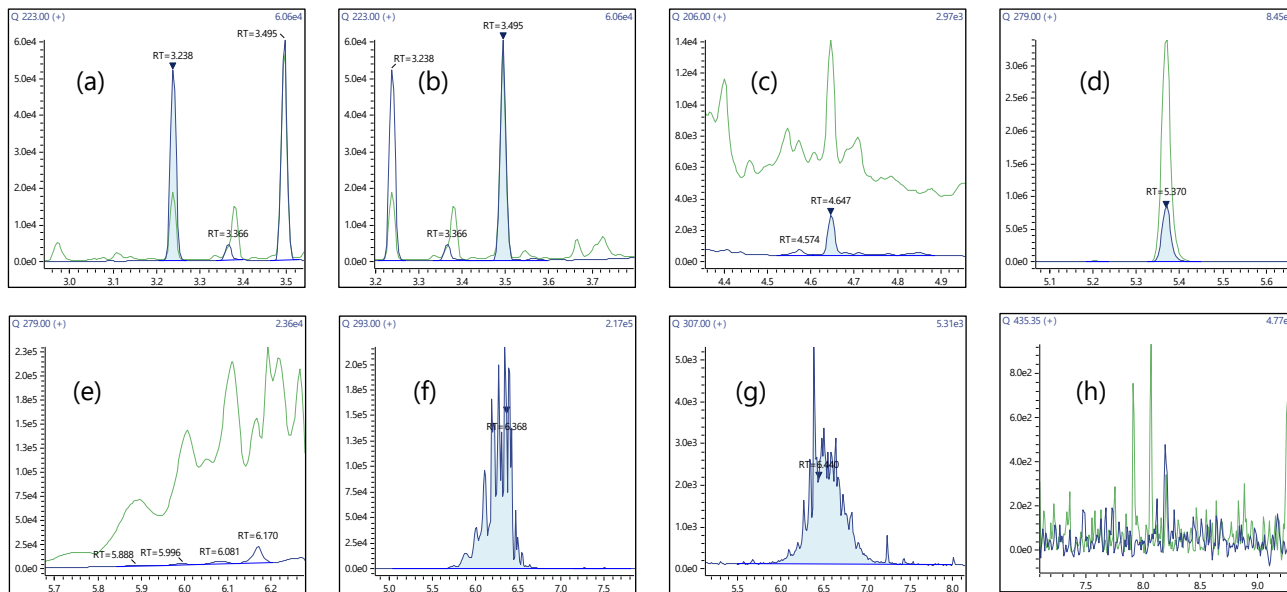


Figure 7. Mass chromatograms of (a) DIBP, (b) DBP, (c) BBP, (d) DEHP, (e) DNOP, (f) DINP, (g) DIDP, and (h) TOTM in Toy C sample.

Conclusion

This application news demonstrates the use of Py-Screener Ver. 2 method package for a fast screening of seven phthalate esters in toys and childcare articles. Sample preparation is simple. It does not require long procedure and the use of organic solvents. The fast phthalate ester method in Py-Screener Ver. 2 allows rapid separation and semi-quantitation of phthalate esters as well as the summation of the 4 REACH regulated phthalate esters. LabSolutions Insight and predefined flag settings were used to determine the screening results in a glance. Overall, Py-Screener is capable of analyzing not only phthalate esters in toys and childcare articles, but also other solid or liquid samples such as rubber, paints, polymers, and many more samples with minimal sample preparation and fast analysis achieving high sample throughput.

Acknowledgement

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