

Technical Report

Comparison of Screening Method (Py-GC/MS) and Quantitative Method (Solvent Extraction–GC/MS) for Phthalate Esters Analysis

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Abstract:

From 2019, four phthalate esters (diisobutyl phthalate (DIBP), *n*-dibutyl phthalate (DBP), benzyl butyl phthalate (BBP) and di(2-ethylhexyl) phthalate (DEHP)) will be added to restricted substances in the amended RoHS Directive (a directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment).

In this technical report, the quantitative results between the solvent extraction-GC/MS method and the Screening System for Phthalate Esters “Py-Screener” (Py-GC/MS method) were compared. The quantitative results using the Py-Screener were equivalent to the results using the solvent extraction-GC/MS method for quantitative measurements in the region of a restricted concentration level of 1000 mg/kg. The Py-Screener was shown to be useful for screening the phthalate esters added to the amended RoHS Directive.

Keywords: RoHS, phthalate esters, Py-GC/MS, Py-Screener

1. Introduction

Phthalate esters are mainly used as plasticizers in polyvinyl chloride (PVC). However, some phthalate esters are suspected of exhibiting reproductive toxicity, which has led to restriction of their use in toys and food packaging.

Effective 2019, four phthalate esters (diisobutyl phthalate (DIBP), *n*-dibutyl phthalate (DBP), benzyl butyl phthalate (BBP) and di(2-ethylhexyl) phthalate (DEHP)) will be added to the six hazardous substances currently subject to restricted use in the amended RoHS Directive, which restricts the use of certain hazardous substances in electrical and electronic equipment ¹⁾.

Phthalate esters are commonly analyzed by GC or GC/MS following extraction from a polymer sample. Extraction methods differ depending on the analytical standard (Table 1).

All of these methods specify the use of organic solvents to extract phthalate esters from the polymer, while only ASTM D7823-14 specifies heating of the polymer to extract the phthalate esters.

However, ASTM D7823-14 is a test method only for determination of low level phthalates in PVC samples, during which the sample must be dissolved in an organic solvent, tetrahydrofuran (THF), prior to thermal extraction. Also, since the standard addition method is used, evaluation must be conducted using the sample and standard solution spiked with multiple concentrations of sample. Furthermore, DIBP, which will be added to the amended RoHS Directive, cannot be analyzed by this analysis standard.

To resolve these issues, Maruyama *et al.* ⁹⁾ developed a quantitative method based on thermal extraction alone using a pyrolysis-GC/MS (Py-GC/MS) method, reporting that it is an effective screening method.

Using the method of Maruyama *et al.*, we conducted measurement of certified reference materials, and examined the percentage recovery as compared with the certified levels. We also conducted measurement of a polymer sample using the Py-GC/MS method and a solvent extraction–GC/MS method, and compared the respective quantitative results to evaluate the efficacy of the Py-GC/MS method for screening of phthalate esters, a method that is compliant with the amended RoHS Directive.

Table 1 Sample Preparation Procedures According to the Analytical Standard

Analytical Standard	Sample Preparation Procedures
Japan's Ministry of Health and Welfare Ministerial Notification No. 370 ²⁾	Solvent extraction by immersion
EN14372 ³⁾	Soxhlet extraction
ASTM D3421-75 ⁴⁾	Soxhlet extraction
CPSC-CH-C1001-09.3 ⁵⁾	Solvent dissolution or precipitation
ISO 8124-6 ⁶⁾	Soxhlet extraction or a solvent extraction
ISO 14389 ⁷⁾	Ultrasonic extraction / dissolution / precipitation
ASTM D7823-14 ⁸⁾	Solvent dissolution and thermal extraction

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2. Experimental

A KRISS CRM 113-03-006 certified reference material and two samples (A and B) of black rubber were used for evaluation.

2-1. Py-GC/MS Method

Seven phthalate ester standards (P/N: 225-31003-91) were prepared by kneading together seven standard phthalate ester samples (diisobutyl phthalate (DIBP), *n*-dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP), di-*n*-octyl phthalate (DNOP), di-isononyl phthalate (DNIP), and diisodecyl phthalate (DIDP)) with polyethylene. A blank, 100 mg/kg and 1000 mg/kg standards were used to check for contamination of the instrument due to carryover, to confirm sensitivity, and to create a single-point calibration curve, respectively.

Standard materials were ribbon-like in shape and of uniform thickness, with two 1.25 mm diameter pieces weighing approximately 0.5 mg. Two pieces of each standard material were obtained using a micro-puncher, then placed inside an Eco-Cup (Frontier Laboratories Ltd., Fukushima, Japan) for pyrolysis, and weighed.

The calibration curve was generated using the 1000 mg/kg standard material. About 0.5 mg of the materials cut with a cutter were placed in an Eco-Cup for pyrolysis and weighed for evaluation. The measured weight was used to calculate the quantity of phthalate ester in the polymer.

2-2. Solvent Extraction-GC/MS Method

Mixed standard solutions of seven phthalate esters (DIBP, DBP, BBP, DEHP, DNOP, DINP and DIDP) were prepared at concentrations of 0.5, 1.0, 2.5, 5.0 and 10.0 µg/mL, respectively. An anthracene-d10 internal standard was also added to each mixed standard solution to a concentration of 1.0 µg/mL. These mixed standard solutions were used to generate a 5-point calibration curve with internal standards at constant concentration.

Evaluation samples were prepared as described below. First, samples were frozen using liquid nitrogen and then crushed, and approximately 300 mg was weighed out and placed in a 40 mL vial to which 10 mL of THF was added. The vial was stoppered and the sample was subjected to ultrasonic dissolution in solvent for 60 minutes. Once the mixture returned to room temperature, 20 mL of acetonitrile was added dropwise to precipitate the polymer, and the mixture was left for 30 minutes at room temperature while the polymer precipitated. Finally, 1 mL of supernatant was transferred to a GC vial, and 10 µL of an internal standard was added. If a result exceeded the upper limit of the calibration curve, an aliquot of the top layer in the vial was diluted until the result was within the range of the calibration curve. Then, 10 µL of internal standard was added, and the measurement was conducted again using the diluted sample mixture as the GC/MS sample.

2-3. Analytical Conditions

Py-GC/MS measurements were conducted using the Py-Screener phthalate ester screening system (Shimadzu). The Py-Screener consists of the EGA/PY-3030D multi-shot pyrolyzer (Frontier Laboratories Ltd.), the GCMS-QP2010 Ultra (Shimadzu) GC-MS system, and dedicated software for instrument control and data Processing. For the separation column, the Ultra ALLOY-PBDE (length 15 m, 0.25 mm I.D., $df = 0.05 \mu\text{m}$, Frontier Laboratories Ltd.) column was used. The detailed analytical conditions are shown in Table 2.

The GCMS-QP2010 Ultra was used for solvent extraction-GC/MS measurements, along with an HP-5MS (length 30 m, 0.25 mm I.D., $df = 0.25 \mu\text{m}$, Agilent) column. Detailed analytical conditions are shown in Table 3.

Table 2 Analytical Conditions for the Py-GC/MS Method

Pyrolyzer	
Furnace Temp.	: 200 °C → (20 °C/min) → 300 °C → (5 °C/min) → 340 °C (1 min)
Interface Temp.	: Manual (300 °C)
GC	
Injection Temp.	: 300 °C
Column Oven Temp.	: 80 °C → (20 °C/min) → 300 °C (5 min)
Injection Mode	: Split
Carrier Gas	: He
Flow Control Mode	: Linear velocity (52.1 cm/sec)
Purge Flow	: 3.0 mL/min
Split Ratio	: 50
MS	
Interface Temp.	: 320 °C
Ion Source Temp.	: 230 °C
Measurement Mode	: FASST (Scan/SIM mode)
Scan Mass Range	: m/z 50–1000
Scan Event Time	: 0.15 sec
Scan Speed	: 10000 u /sec
SIM Event Time	: 0.3 sec
SIM Micro Scan Width	: 0.3 u

Table 3 Analytical Conditions for the Solvent Extraction-GC/MS Method

GC	
Injection Temp.	: 300 °C
Column Oven Temp.	: 110 °C (0.5 min) → (20 °C/min) → 280 °C (1 min) → (20 °C/min) → 320 °C (5 min)
Injection Mode	: Splitless
Carrier Gas	: He
Flow Control Mode	: Linear velocity (45.8 cm/sec)
MS	
Interface Temp.	: 320 °C
Ion Source Temp.	: 230 °C
Measurement Mode	: FASST (Scan/SIM mode)
Scan Mass Range	: m/z 50–500
Scan Event Time	: 0.3 sec
Scan Speed	: 1666 u /sec
SIM Event Time	: 0.3 sec

3. Results and Discussion

The results obtained from measurement of the KRIS CRM 113-03-006 certified reference material using the Py-Screener are shown in Table 4. Good quantitative results were obtained, with recoveries in

the range of 92.9 – 109.0 % of the certified values, confirming that phthalate esters can be extracted using the Py-GC/MS method with good recovery.

Table 4 Quantitative Results from KRIS CRM113-03-006 using the Py-Screener

	Conc. (mg/kg)	Certified Value (mg/kg)	Recovery* (%)
DBP	1059	972	109.0
BBP	894	962	92.9
DEHP	1015	989	102.6
DNOP	993	967	102.7

* The recovery of each detected phthalate ester was calculated based on the certified values.

The quantitative results obtained with the Py-Screener, are shown in Fig. 1. All phthalate esters included in the sample were detected automatically. Further, the dedicated software automatically corrects for the weight of the collected sample, and displays the concentration of phthalate esters in the polymer as a quantitative result. The mass chromatogram and quantitative concentrations can be displayed in different colors based on user-specified QC limits. For example, concentrations under 500 mg/kg may be displayed as color-

less, 500 to 1500 mg/kg may be displayed in orange, and samples greater than 1500 mg/kg in red. This permits visual observation of which quantitative results are within which concentration range.

Two evaluation samples were measured using both the Py-GC/MS method and the solvent extraction-GC/MS method, and the quantitative results were compared. Each sample was measured three times and the mean quantitative results were calculated.

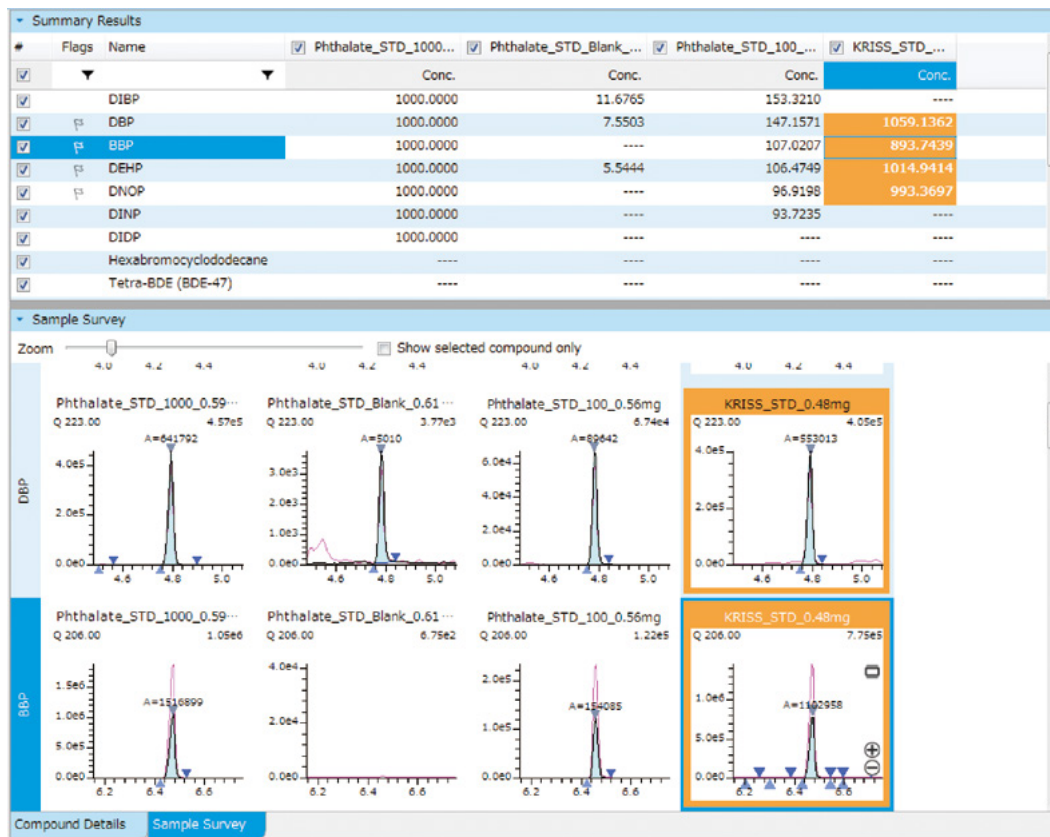


Fig. 1 Summary Screen of Py-Screener with LabSolutions Insight

The results from evaluation sample A are shown in Table 5, with the associated chromatograms shown in Fig. 2. DEHP was detected by both methods. The quantitative results obtained by the Py-GC/MS method were 124 % of those obtained by the solvent extraction-GC/MS method, while the %RSD of the three measurements using the Py-GC/MS method was 5.1 %, which was equivalent to that obtained by the solvent extraction-GC/MS method. Regarding the higher quantitative result obtained with the Py-Screener, the sample used in the measurement by the solvent extraction-GC/MS method was diluted to bring the result below the maximum concentration in the calibration curve. On the other hand, with the Py-Screener, the quantitative value is

calculated using the 1000 mg/kg 1-point calibration method, suggesting that this may be the source of the discrepancy between the detected concentration and the calibration point concentration. However, although the quantitative results substantially exceeded the 1000 mg/kg concentration limit specified in the amended RoHS Directive, from the standpoint of screening, the fact that it exceeded the regulatory value was easily determined.

A large peak detected at a retention time of 8.3 minutes was identified as di(2-ethylhexyl) terephthalate based on a mass spectral library search. Using scan/SIM simultaneous measurements, it is possible to identify an unknown peak based on the mass spectrum of the scan.

Table 5 Comparison of Quantitative Results for Py-GC/MS Method and Solvent Extraction-GC/MS Method for Sample A

	Py-GC/MS method (Py-Screener)			Solvent Extraction-GC/MS method			Relative ratio of conc. (%)
	Average Conc. (mg/kg)	SD	%RSD	Average Conc. (mg/kg)	SD	%RSD	
DEHP	3923	199	5.1	3162	196	6.2	124

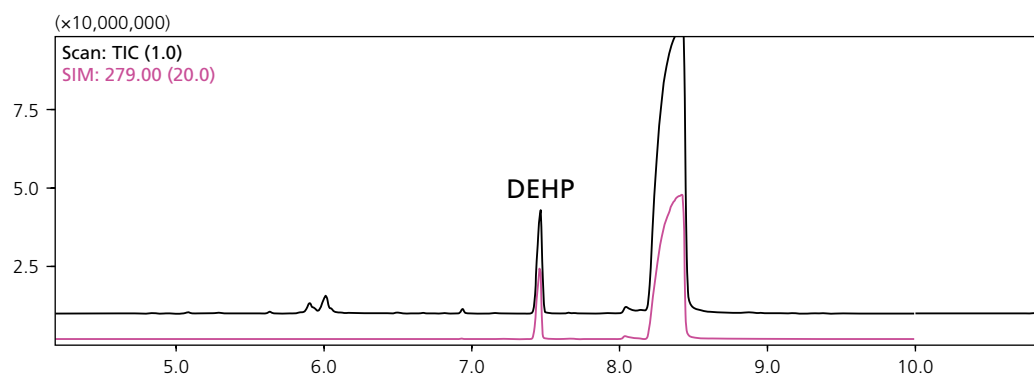


Fig. 2 TIC and Extracted Chromatograms of Sample A Measured using Py-GC/MS Method

The measurement results for sample B are shown in Table 6, with the chromatograms shown in Fig. 3. Five phthalate esters (DBP, BBP, DEHP, DINP and DIDP) were detected by both methods. The quantitative results for each phthalate ester using the Py-Screener were 124, 332, 44041, 2796 and 1516 mg/kg, respectively. The quantitative results were in the range of 68 to 108 % of the quantitative results obtained using the solvent extraction-GC/MS method. Regarding the larger quantitative ratio obtained for DEHP using the solvent extraction-GC/MS method, this was determined to be due to the use of different calibration methods as described above. Regarding the DIDP with its 1500 mg/kg concentration in the vicinity of the 1000 mg/kg Py-Screener calibration point, this quantitative result is considered to be equivalent to that obtained using the solvent extraction-GC/MS method.

This confirmed that when the concentration was in the range of 500 – 2000 mg/kg, such as the 1000 mg/kg obtained here, the calculated concentration was easily compared to the regulatory action level for screening purposes. Analysis precision in terms of repeatability (%RSD) of the Py-Screener was 3.3 to 5.5 %, and analysis precision in terms of repeatability (%RSD) of the solution extraction-GC/MS method was 4.2 to 16.6 %. Analysis precision in terms of repeatability was markedly worse using the solvent ex-

traction-GC/MS method compared to that using the Py-Screener when analyzing phthalate esters of low boiling point: DBP (16.6 %) and BBP (12.7 %). As internal standard correction is used with solvent extraction, this variation is attributed mainly to pretreatment.

Since the amended RoHS Directive sets the regulatory concentration at 1000 mg/kg, tests must be at their most accurate when measuring concentrations in the region of 1000 mg/kg. Therefore, as the Py-Screener demonstrated good recovery at 1000 mg/kg, it is considered effective for the testing described in the amended RoHS Directive, and in particular, for screening when the results are used as the basis for determining the necessity to perform more detailed quantitation. Furthermore, good analytical precision in terms of repeatability is an effective criterion for screening.

A single-point calibration curve is adequate for phthalate ester screening according to the amended RoHS Directive, with a regulatory level of 1000 mg/kg. However, the current 1000 mg/kg single-point calibration method used with the Py-Screener method is not appropriate for performing analysis with respect to a different regulatory concentration level, or when precision across a wide range of concentration measurements is required. In such cases, the Py-Screener must be used in combination with the solvent extraction-GC/MS method for quantitation.

Table 6 Comparison of Quantitative Results Obtained for Sample B using Py-GC/MS Method and Solvent Extraction–GC/MS Method

	Py-GC/MS method (Py-Screener)			Solvent Extraction–GC/MS method			Relative ratio of conc. (%)
	Average Conc. (mg/kg)	SD	%RSD	Average Conc. (mg/kg)	SD	%RSD	
DBP	124	6	5.1	115	19	16.6	108
BBP	332	13	3.8	466	59	12.7	71
DEHP	44041	1456	3.3	64785	2753	4.2	68
DINP	2796	98	3.5	2695	242	9.0	104
DIDP	1516	84	5.5	1511	127	8.4	100

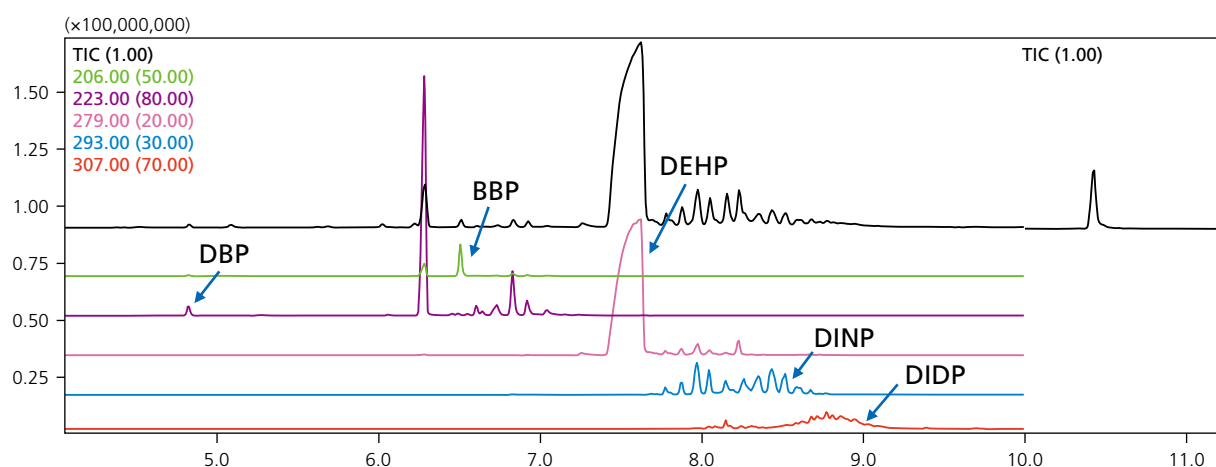


Fig. 3 TIC and Extracted Chromatograms of Sample B Measured using Py-GC/MS Method

4. Conclusion

The quantitative results from analysis of phthalate esters in polymer were compared using the solvent extraction–GC/MS method and the Py-Screener, a dedicated system that utilizes the quick and simple Py-GC/MS method, which requires no pretreatment or organic solvents. The results obtained using the Py-Screener and solvent extraction–GC/MS methods were found to be equivalent for quantitative measurements in the region of the regulatory concentration level of 1000 mg/kg. The Py-Screener was shown to be useful for screening of the phthalate esters that were added to the amended RoHS Directive.

References

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Screening System for Phthalate Esters

Py-Screener

Organics Solvents Are Not Required for Sample Preparation

Analytical standards and test samples can be prepared without using organic solvents. Sample preparation videos provide support so that even novices can easily prepare samples.



Sample Preparation Videos



All Required Items Are Available for Sample Preparation

The analytical standards for this system were developed in cooperation with SGS Japan, the market leader for RoHS tests. Standards for sensitivity confirmation, quantitation, and blank tests can be prepared simply by punching out a portion of a standard material using the micro puncher.



Standards Containing Phthalate Esters for Py-GC/MS

Tabular Display of Concentrations and Criteria Clarifies the Results

The concentrations of target components detected in continuous measurements are displayed in a table and color-coded using criteria based on concentration ranges. The results for continuously measured test samples can be checked at a glance.



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