Application Note
100-RF-0261

Simplified evaluation method of phthalates

Introduction

Effective 22 July, 2019, the revised RoHS directive (EU) 2015/863 restricted the use of 4 types of phthalates (see Figure 1) in mechanical parts as well as toys. This new directive is very strict, especially regarding the 3 types of phthalates (DEHP, BBP and DBP) in toys, their total concentration should be less than 1000 ppm (0.1%). The recommended evaluation method for phthalates is either GC/MS or Py/TD-GC/MS as used in IEC 62321-8. However, it is complicate to set up and handle these instruments, and simpler cheaper alternative is required. JASCO has collaborated with "Kankyo Assist Co., Ltd" to develop a simplified evaluation method using FTIR. This application note offers a detailed evaluation procedure for the controlled phthalates.

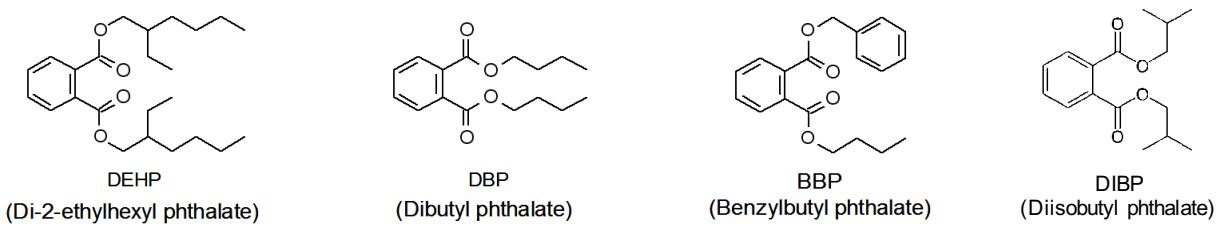

Figure 1. 4 types of phthalate (restricted by RoHS)

Extraction-Condensation Method

Conventionally, an FTIR spectroscopic method with ATR method has been used for evaluating phthalates (App Note: 100-AT-0230). Since the ATR method does not require complicated sampling, it offers easy sample measurement. However, the ATR method does not have sufficient sensitivity to reach the 1000 ppm (0.1%) levels required by the new directive. Therefore, JASCO has developed a new high-sensitivity Extraction-Condensation method.

Using this method phthalates are solvent extracted from the sample, and then made into a thin film for measurement (Figure 2). The LOQ (limit of quantitation) of this method is approximately 700 ppm, and the LOD (limit of detections) is approximately 300 ppm[*1]). If the phthalates are not detected using this method, it can be concluded that the revised RoHS directive is met. Since the measurement time is approx. 40 min/sample, it is estimated that more than 40 samples/day can be analyzed, if multiple samples are extracted at the same time.

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An extraction solvent should be used that dissolves the phthalates without dissolving the resin in the substrate. In the case of PVC resin, a mixed organic solvent (acetone : hexane = 3 : 7) was used. The extracted solution is dropped onto a custom-made substrate*2), which can make uniform thin film of the sample, and then the solvent is volatilized. The a spectrum is measured of the substrate using a reflection-absorption method.

The solvent for extraction should be used which can dissolve the phthalates, but not to dissolve the resin of substrate. In the case of PVC resin, the mixed organic solvent (acetone : hexane = 3 : 7) was used. The extracted solution is dropped on the custom-made (substrate*2) which can make uniform thin film of sample, and then the solvent is volatilized. The substrate is evaluated by spectrum (reflection-absorption method).

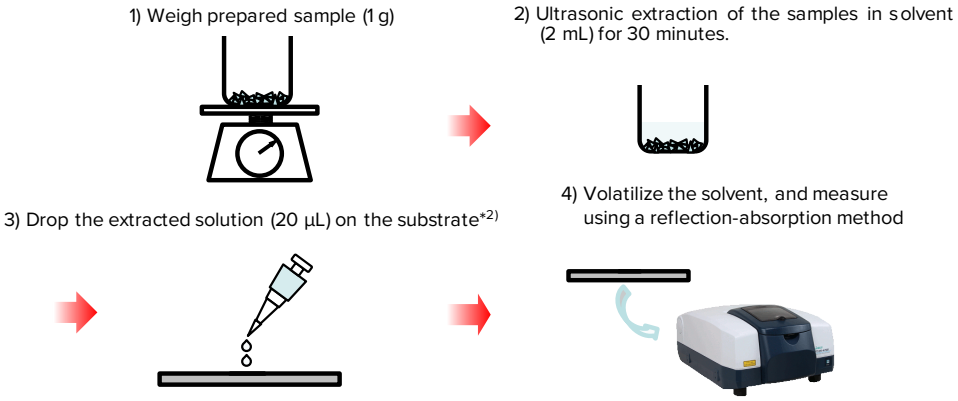

Figure 2. Measurement procedure of extraction-condensation method

*1 If the extraction efficiency of PVC resin is 70%, in the case of other resin except for PVC resin, the verification of the extraction efficiency is required.
*2 This substrate is made by Kankyo Assist Co., Ltd.

Sample Measurement

The results for evaluation of phthalates concentration from a polyester polyurethane tube by extraction-condensation method is detailed below.

1) The sample was cut into small pieces of several mm with scissors and weighed (Figure 3). The total sample weight was 1002 mg.

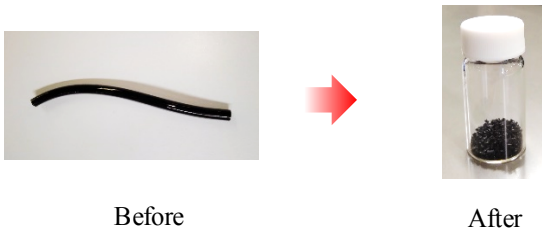

Figure 3. Prepared sample

2) Put the sample into the mixed solvent (2 mL, acetone : hexane = 3 : 7), and use ultrasonic extraction for 30 minutes.
3) Drop the extracted solution (20 µL) onto the substrate, and volatilize the solvent.
4) Measure the thin-film sample using a reflection-absorption method.

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Measurement Condition

Main unit: FT/IR-4700 (left in Figure 4)
Accessory: SMART-400i (right in Figure 4)
Detector: DLATGS
Resolution: 4 cm^{-1}
Accumulation: 50

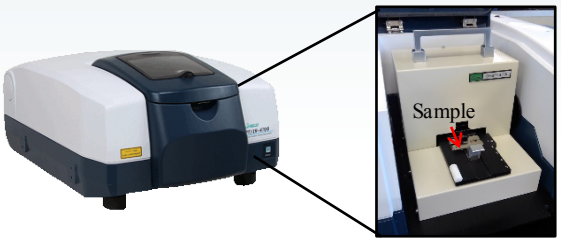

Figure 4. FT/IR-4700 with SMART-400i

Results

The spectrum in Figure 5 on the left side shows the entire spectrum, and the spectrum on the right side shows a zoomed view of key band region of phthalates (benzene ring stretching vibration). The spectra of the actual sample and standard phthalate sample (1000 ppm) are overlaid in a zoomed view. As a result, benzenesulfonamide (plasticizer) was detected, but phthalate was not detected. It means that the sample meets the standard of the revised RoHS directive.

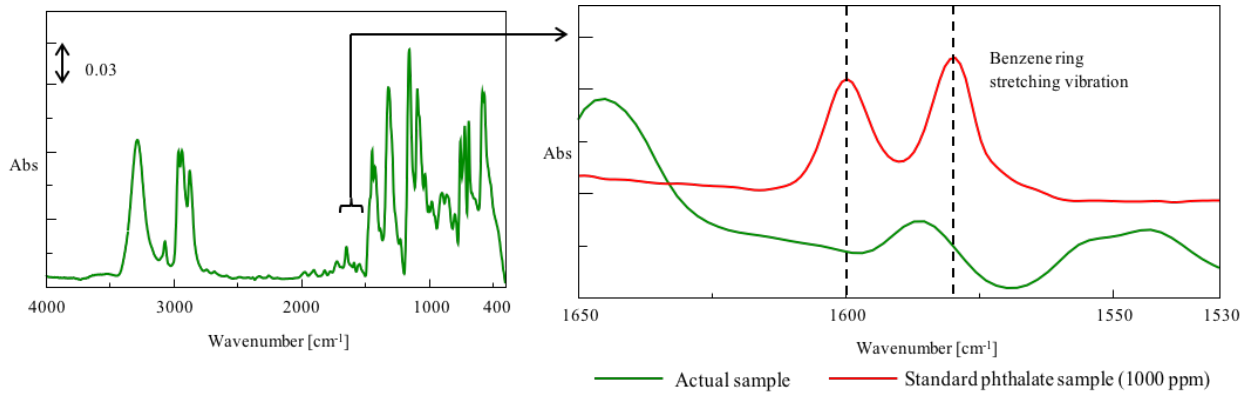

Figure 5. IR spectrum of polyester polyurethane tube (extraction-condensation method)

Conclusions

FTIR cannot be used to quantify each of the restricted phthalates, but it can be used to quantify 'total' phthalates. Since FTIR is much faster and easier than GC/MS and Py/TD-GC/MS, it can be used as a rapid screening techniques to reduce the burden of using the more complex and expensive MS-based techniques.

System Configuration			
	Model	**Description**	**Part Number**
Main Unit	FT/IR-4700	Temperature Interval	7084-J002A *1
Option	SMART-400i	Smart Tech	6909-J142A
Software	N/A		
Others		Sampling cell (substrate for extraction-condensation method) for Smart Tech*2	

*1 FT/IR-4700 and FT/IR-6600/6700 are also available.
*2 JASCO can provide the item as the customized product.

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