

Prescreening of Phthalic Esters Contained in PVC Products by FTIR

Phthalic esters are used as plasticizers for polyvinyl chloride (PVC) and other plastic products, but are a suspected cause of endocrine disruption in the human body. In the revised RoHS Directive (RoHS2.0), the four types of phthalic esters shown in Fig. 1 were added to the list of regulated substances, in addition to the original RoHS 6 substances (lead, mercury, cadmium, hexavalent chromium, PBB, PBDE). Under RoHS2.0, the maximum allowable contents of these four phthalic esters in all electrical and electronic devices except medical equipment and monitoring/control devices is 0.1% (1,000 ppm). Therefore, gas chromatograph-mass spectrometer (GC-MS) is generally used in analyses to determine compliance with the RoHS Directive.

However, soft PVCs and certain other products include materials with high concentrations of phthalic esters, which may place an excessive load on the column used in GC-MS analyses of those materials. Because the Fourier transform infrared spectrophotometer (FTIR) does not require pretreatment and enables spectrum measurement in a short time of about 1 min, it is suitable for prescreening of phthalic esters in samples. If samples with high concentrations of phthalic esters can be prescreened in advance by FTIR, carryover of high-concentration analytes to subsequent analyses in the GC-MS analysis process can be reduced, resulting in more efficient analysis.

This article introduces a prescreening analysis technique for phthalic esters in PVC products using FTIR for efficient GC-MS analysis.

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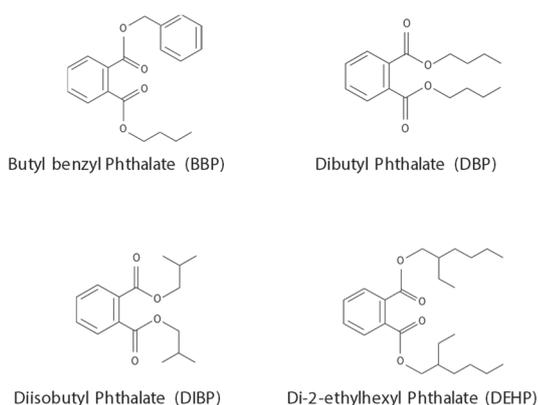


Fig. 1 Structures of RoHS-Regulated Phthalic Esters

ATR Spectra of RoHS-Regulated Phthalic Esters

Fig. 2 shows the ATR (attenuated total reflection) spectra of the RoHS-regulated phthalic esters. The phthalic esters all have distinctive peaks at around 1,600 and 1,580 cm^{-1} (C=C stretching: benzene ring). In addition, peaks in the vicinity of 740 cm^{-1} (C-H in-plane bending vibration) and others can be seen. Differences can also be observed in the peaks at around 3,000 cm^{-1} (C-H asymmetric/symmetric stretching), but these are overlapped with the peaks of PVC and other plastics. However, discrimination is possible if complicated pretreatment processes such as extraction and concentration are applied.

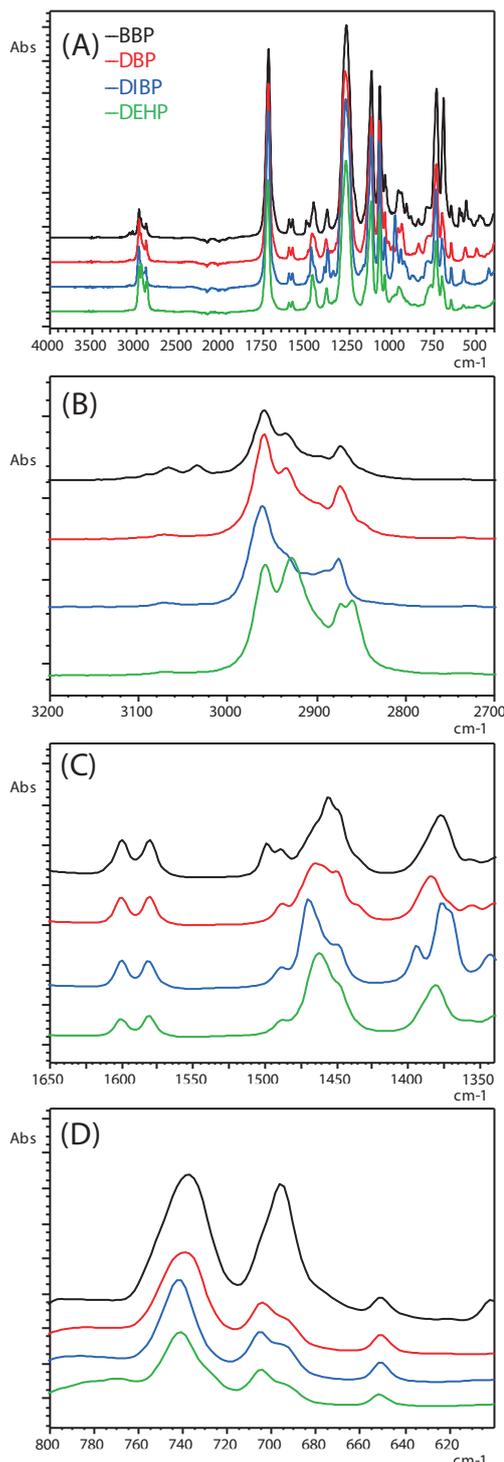


Fig. 2 ATR Spectra of RoHS-Regulated Phthalic Esters
(A) Total Measurement Region, (B) Enlargement of 3,200 to 2,700 cm^{-1} Region, (C) Enlargement of 1,650 to 1,350 cm^{-1} Region, (D) Enlargement of 800 to 600 cm^{-1} Region

■ Prescreening by FTIR

It is difficult to detect phthalic esters at the 0.1% concentration level specified in the RoHS Directive by FTIR, and it is not possible to determine whether a phthalic ester contained in a sample is a regulated phthalic ester or not without pretreatment. However, a simple determination of whether the phthalic ester concentration is high (roughly no less than 1%) or low (roughly no more than 1%) is possible. In a GC-MS analysis, carryover of several 100 ppm occurs in some cases if the phthalic ester content exceeds 1 to 2%. Therefore, the above-mentioned determination of high or low concentration is extremely useful information in a GC-MS analysis.

In this experiment, three types of PVC tubes with phthalic ester contents of (a) 12%, (b) 3%, and (c) 500 ppm, respectively, were prepared and measured by FTIR.

Table 1 shows the measurement conditions. A system consisting of a Shimadzu IRSpirit™-T and a QATR™-S single-reflection ATR measurement attachment was used. Fig. 3 shows the appearance of the measurement system. The IRSpirit has a portable, compact body with dimensions of 390 (W) × 250 (D) × 210 (H) mm, and thus has a footprint smaller than an A3 sheet of paper.

Table 1 Measurement Conditions

Instruments	: IRSpirit-T (KBr window plate)
	: QATR-S (wide-band diamond disk)
Resolution	: 4 cm ⁻¹
Accumulation	: 40 times
Apodization function	: Sqr-Triangle
Detector	: DLATGS



Fig. 3 Appearance of IRSpirit™-T + QATR™-S

Fig. 4 shows the ATR spectra of the PVC tubes. The upper part (A) shows the total measurement region of 4,000 to 400 cm⁻¹, and the lower part (B) shows an enlarged view of the 1,750 to 700 cm⁻¹ region. The peak originating from PVC, which is the main component of the tubes, can be seen at around 609 cm⁻¹ (C-Cl stretching).

First, in the spectrum for (a) 12% phthalic ester, distinctive peaks are clearly visible at around 1,600, 1,580, and 740 cm⁻¹. Next, in the spectrum for (b) 3%, the peaks at around 1,600 and 1,580 cm⁻¹ can no longer be seen, but the peak at around 740 cm⁻¹ can be confirmed. On the other hand, in (c) 500 ppm, no peaks originating from phthalic ester can be observed.

From these results, if a GC-MS analysis can be conducted in the order of the lowest concentration (c), followed by (b) and (a), carryover is reduced and retesting can be eliminated.

As a point to note in the measurement described above, in the case of hard samples and samples with an irregular surface shape, measurements are sometimes carried out by cutting off part of the sample to secure good adhesion with the prism. Moreover, since there may be variations depending on the measurement position in some cases, measurement at several different positions is effective in such cases.

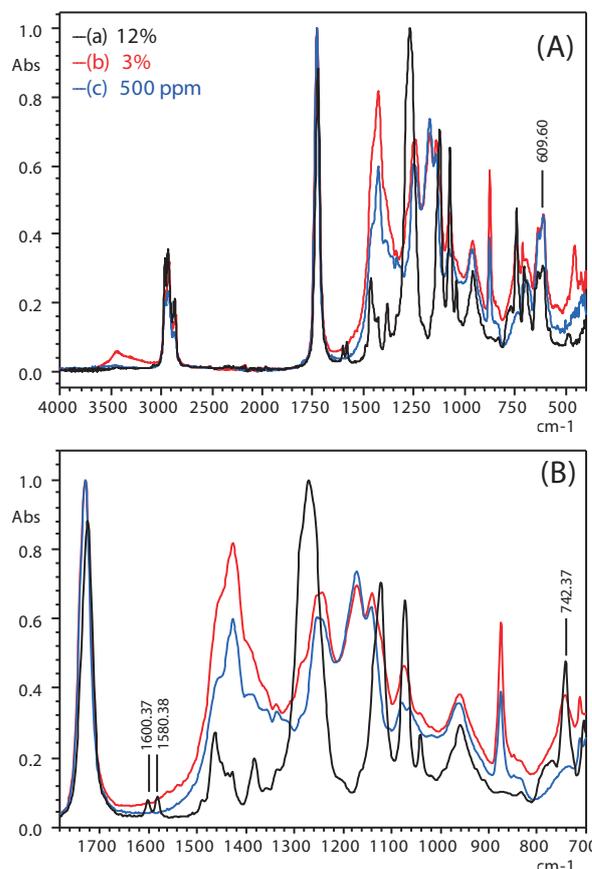


Fig. 4 ATR Spectra of PVC Tubes
(A) Total Measurement Region, (B) Enlargement of 1,750 to 700 cm⁻¹ Region

■ Conclusion

Quick judgment of whether a sample contains a high concentration of phthalic esters or not was possible by prescreening of phthalic esters by FTIR. FTIR has a low running cost, and operation of the instrument is simple and easy. If analysis of a sample of unknown concentration is begun directly from the GC-MS analysis, remeasurement may be necessary, requiring additional time and work. However, efficient GC-MS analysis is possible if the analysis sequence is decided by first classifying the sample as high or low concentration by FTIR.

For best results, we recommend using a combination of a Shimadzu FTIR and Py-Screener™ phthalic ester screening system for GC-MS.

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First Edition: Nov. 2019



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