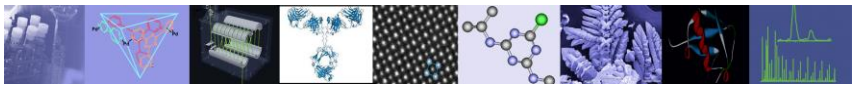

Phthalates Impurity Analysis of PVC Resin Made with Alternative Plasticizers

Product: JMS-Q1500GC GC/MS System

Introduction

The phthalates used as plasticizers in polymer resins are endocrine-disrupting substances that are a risk to human health. Therefore, the use of phthalates is limited by various government agencies. In the field of electrical equipment manufacturing, diisobutyl phthalate (DIBP), dibutyl phthalate (DBP), butyl benzyl phthalate (BBP), and di-2-ethylhexyl phthalate (DEHP) are regulated by the European Union's Restriction of Hazardous Substances (RoHS) Directive. The use of DBP, BBP, DEHP, di-n-octyl phthalate (DNOP), diisononyl phthalate (DINP), and diisodecyl phthalate (DIDP) in toys and baby care products is regulated in Europe, the United States, China, and Japan. Phthalates subject to regulation are being replaced with alternative substances. However, it is known that phthalates tend to contaminate the manufacturing process and storage areas. Some alternative materials (e.g., tris-2-ethylhexyl trimellitate [TOTM]) may contain regulated components (e.g., DEHP) as impurities. In this report, PVC cables for commercial products using alternative substances as plasticizers were analyzed by the pyrolysis/thermal desorption–gas chromatography–mass spectrometry (Py/TD-GC-MS) method described in IEC 62321-8: 2017 [1]. Any phthalates discovered were quantified, and spectral information was collected for other detected compounds.

Experiment

About 0.5 mg sample of PVC electrical conduit without metal conducting wire was measured by Py/TD-GC-MS. NIMJ CRM 8152-a is a PVC pellet containing about 1000 ppm of DIBP, DBP, BBP, DEHP, and DNOP, and is certified as a standard substance manufactured by the National Institute of Advanced Industrial Science and Technology. The standard sample was dissolved in tetrahydrofuran (THF) and adjusted to a concentration of 50 mg/mL. Next, 10 µL of THF solution was dispensed into a sample cup using a micropipette, and 5 µL of n-hexane solution containing 0.1 mg/mL of DINP and DIDP was added. The measurement conditions of the sample and the standard sample are shown in Table 1.

Table 1. Measurement conditions.

Pyrolyser	EGA/PY-3030D (Frontier Laboratories, Ltd.)
Furnace temp.	50˚C (1 min) → 10˚C/min → 340˚C (10 min)
Interface temp.	300˚C
GC column	UA-PBDE, 30m x 0.25 mm, 0.05µm
GC inlet temp.	320˚C
Oven temp.	50˚C (0 min) → 30˚C/min → 200˚C (0 min)→ 20˚C/min → 300˚C (5 min)
Inlet mode	Split 50:1

*1: Bold and underlined *m/z* values are used as quantification ions; other *m/z* values are used as reference ions.

GC-MS	JMS-Q1500GC
Ion source temp.	230˚C
Interface temp.	320˚C
Ionization mode	EI+: 70 eV, 50µA
Relative EM voltage	+300V
Measurement mode	SIM/SCAN simultaneous acquisition
SIM monitoring ion (*1)	DIBP (*m/z* 223, 205,149), DBP (*m/z* 223, 205, 149) BBP (*m/z* 206, 91,149), DEHP (*m/z* 279, 167, 149) DNOP (*m/z* 279, 167,149), DINP (*m/z* 293, 167, 149) DIDP (*m/z* 307, 167,149)
Scan range	*m/z* 50 – 1000

About DEHTP and DNOP

Di-2-ethylhexyl terephthalate (DEHTP), a structural isomer of DNOP, has a retention time very close to that of DNOP. Figure 1 shows the mass spectrum of DEHTP detected from the PVC wire and that of DNOP in the standard sample. Both compounds have peaks at m/z 279, which is the quantitative ion for DEHP and DNOP. However, there are two clues to help distinguish each compound. First, m/z 261 is specific to DEHTP, but it was not set as an ion to monitor using SIM. Therefore, in order to distinguish between DEHTP and DNOP, confirmation of mass spectra using scan measurement is important. Second, the intensity ratio between m/z 167 and m/z 279 is largely different. This difference makes it possible to distinguish DEHTP from DNOP using SIM measurement.

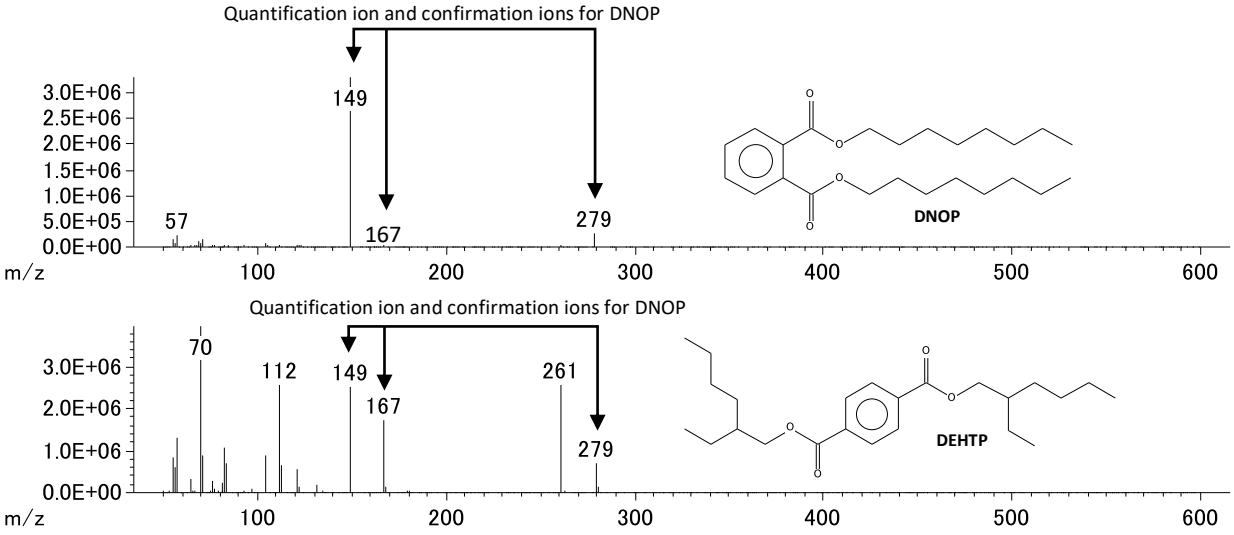

Figure 1. Mass spectra of DNOP and DEHTP.

Results

Figure 2 shows the total ion current chromatogram (TICC) from the scan measurement and the selected-ion chromatograms (SIMs; *m/z* 223, 279, 293, 307) of the PVC conduit. From the scan measurement, DEHTP, DIDP, DINP, and TOTM were detected; from the SIM measurement, DBP and DEHP were also observed. Concentrations of phthalic acid esters were 266 ppm for DBP, 90 ppm for DEHP, and 3650 ppm for DINP, all calculated using a one-point calibration curve. DIDP and TOTM were used as plasticizers because the peak intensities on their TICCs are extremely large. By contrast, the other components are considered impurities because they were detected at ppm-level concentrations.

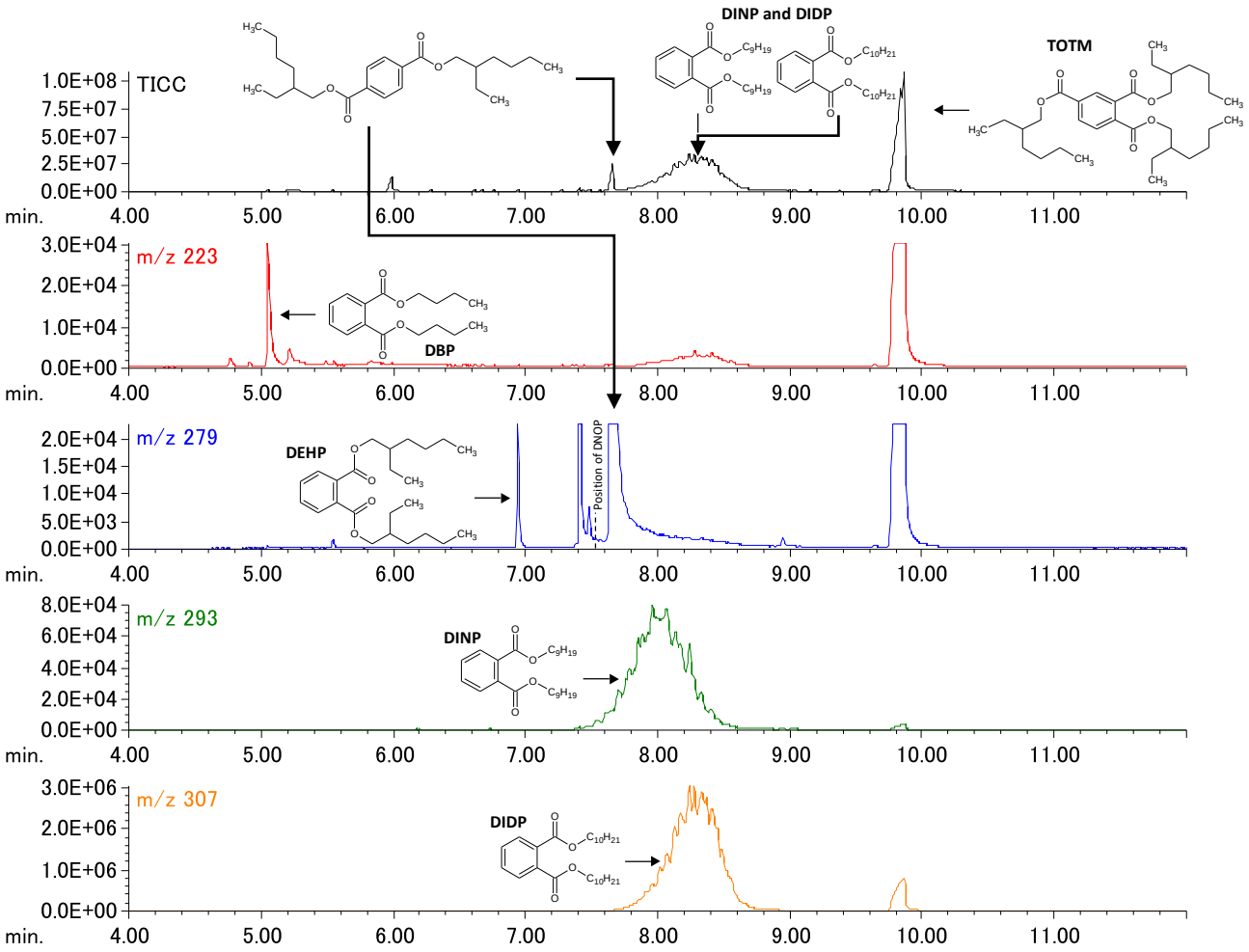

Figure 2. Py/TD-GC-MS measurement results for PVC resin.

Reference

[1] Determination of certain substances in electrotechnical products - Part 8: Phthalates in polymers by gas chromatography–mass spectrometry (GC–MS), gas chromatography–mass spectrometry using a pyrolyzer/thermal desorption accessory (PY/TD–GC–MS), Edition 1.0 2017-03

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