SHIMADZU
Excellence in Science

Application News

GC-MS GCMS-QP™2020 NX

Analysis of PIP (3:1) in Plastic by Py/TD-GC-MS

T. Ishii, Y. Kudo, and K. Obayashi

User Benefits

- The pyrolyzer/thermal desorption-GC/MS (Py/TD-GC-MS) enables analysis of PIP (3:1) in plastic using simple operations and no organic solvents.
- By using Fast Automated Scan/SIM Type (FASST), other additives can also be qualitatively analyzed while analyzing PIP (3:1) in high-sensitivity mode.
- Other detected additives are easily identified using the Polymer Additives Library.

■ Introduction

Phenol, isopropylated phosphate (3:1) (PIP (3:1)) (CAS registry no. 68937-41-7) is a phosphate compound with three isopropylated phenyl groups. It is used as a plasticizer or flame retardant in polyvinyl chloride (PVC), polyurethane, and other plastic materials. Due to the wear resistance and compression resistance, the compound is also used in a wide variety of materials, such as hydraulic fluids, lubricating oils, coatings, adhesives, sealants, and plastic articles.

On the other hand, based on Section 6(h) of the Toxic Substances Control Act (TSCA), the United States Environmental Protection Agency (U.S. EPA) addressed PIP (3:1) as a chemical substance that has all three characteristics of persistent, bioaccumulative, and toxic (PBT) chemicals and has started regulating the commercial process and distribution of PIP (3:1) and PIP (3:1)-contained products or articles within United States (Table 1).

The pyrolyzer/thermal desorption-GC-MS (Py/TD-GC-MS) is specified in the international standard IEC 62321-8 as a phthalates screening system.[1] Because this system does not require organic solvents like solvent extraction GC/MS methods, it is currently attracting interest as an environmentally and analytical operator-friendly system. This article describes an example of verifying that Py/TD-GC-MS can be applied to analyze PIP (3:1) in plastic.

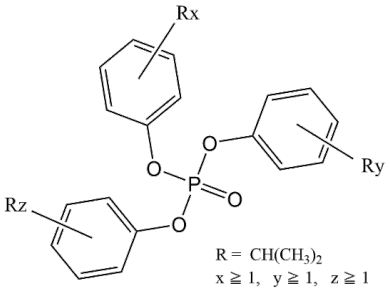

Fig. 1 Structural Formula of PIP (3:1)[2]

Table 1 Overview of PIP (3:1) Regulation in TSCA[3]

Uses	Regulated Activities	Limits	Date of Application
PIP (3:1) and PIP (3:1)-contained products or articles	Commercial process and distribution	Not used	March 8, 2021
Adhesives and sealants	Commercial process and distribution	Not used	January 6, 2025
PIP (3:1)-contained photographic printing articles	Commercial process and distribution	Not used	January 1, 2022

Note: Interpretation of the regulation was performed independently by Shimadzu. For more details, such as the latest trends and exemptions, check the U.S. EPA website (https://www.epa.gov/) or other sources.

■ Analytical Conditions

The instruments, software, and analytical conditions used for this article are indicated in Table 2. Note that except for the monitoring ions to be measured, the analytical conditions are the same as for Py-Screener™.

Table 2 Instruments, Software, and Analytical Conditions

Pyrolyzer:	EGA/PY3030D (Frontier Laboratories)
Analytical Instrument:	GCMS-QP2020 NX
Software:	GCMSsolution™ Ver. 4.53 + Polymer Additives Library
Pyrolyzer	
Furnace Temperature:	200 °C → (20 °C/min) → 300 °C → (5 °C/min) → 340 °C (1 min)
Interface Temperature:	300 °C
GC	
Injection Port Temp.:	300 °C
Control Mode:	Linear velocity (52.1 cm/sec)
Injection Mode:	Split (split ratio 50)
Purge Flowrate:	3.0 ml/min
Carrier Gas:	He
Column:	UA-PBDE (15 m, 0.25 mm I.D., 0.05 µm) (Frontier Laboratories)
GC Oven Program:	80 °C → (20 °C/min) → 300 °C (5 min)
MS	
Interface Temperature:	320 °C
Ion Source Temperature:	230 °C
Ionization Mode:	EI
Measurement Mode:	FASST (Scan/SIM)
Scan Range:	50 - 1,000 amu

■ Analysis of Standard Solution

A standard solution of PIP (3:1) was prepared by diluting a standard reference material of PIP (3:1) (ChironAS, P/N8777.27) with acetone. Then, an appropriate amount of the PIP (3:1) standard solution and PVC solution was added to a sample cup so that the PIP (3:1) concentration in plastic was 1,000 mg/kg. After drying the mixture at room temperature, it was measured by Py/TD-GC-MS. Fig. 2 is a SIM chromatogram of PIP (3:1), which has three isopropyl groups. Though multiple peaks were detected, they are presumably due to isopropyl group isomers with different bonding positions.

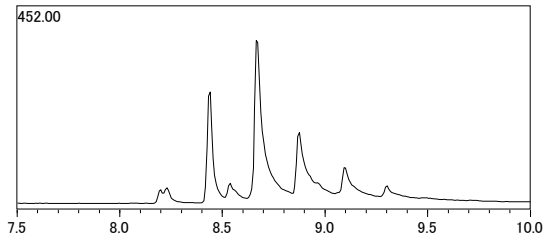

Fig. 2 SIM Chromatogram of Standard Solution (1000 mg/kg)

■ Confirmation of the Detection Limit and Carryover

To confirm the detection limit of PIP (3:1) in plastic and the occurrence of carryover, successive dilution levels of the standard solution of PIP (3:1) were added to sample cups together with the PVC solution, dried at room temperature, and then measured by Py/TD-GC-MS. The results shown in Fig. 3 confirmed that PIP (3:1) can be detected in plastic even at a concentration of 10 mg/kg. On the other hand, measuring 10,000 mg/kg of PIP (3:1) resulted in carryover. That means a blank sample must be measured after detecting high concentrations of PIP (3:1).

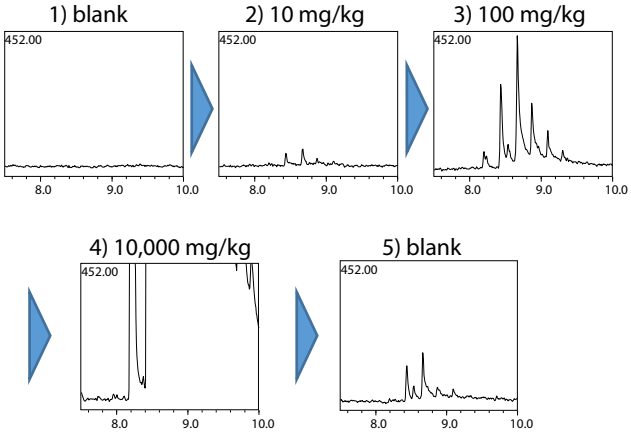

Fig. 3 Standard Solution Dilution Series Measurement Results
(SIM Chromatograms)
Measured in Order from 1) to 5).

■ Analysis of Real Samples

Lastly, plastic articles using PIP (3:1) were measured. About 0.5 mg of PVC cap shavings obtained with a cutter were placed in a sample cup and measured. A polyurethane sponge was also measured by the same procedure. As a result, peaks from PIP (3:1) were detected at the same retention times as the standard solution for all samples, as shown in Fig. 4 and 5. The peak at 6.58 min was identified with a similarity of 95 as Tris(1,3-dichloro-2-propyl) phosphate (TDCPP), one kind of phosphorus-based flame retardant, using Polymer Additives Library as shown in Fig. 5.

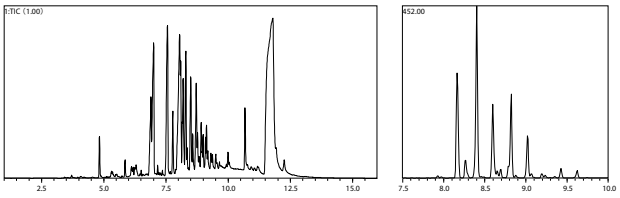

Fig. 4 PVC Cap Measurement Results

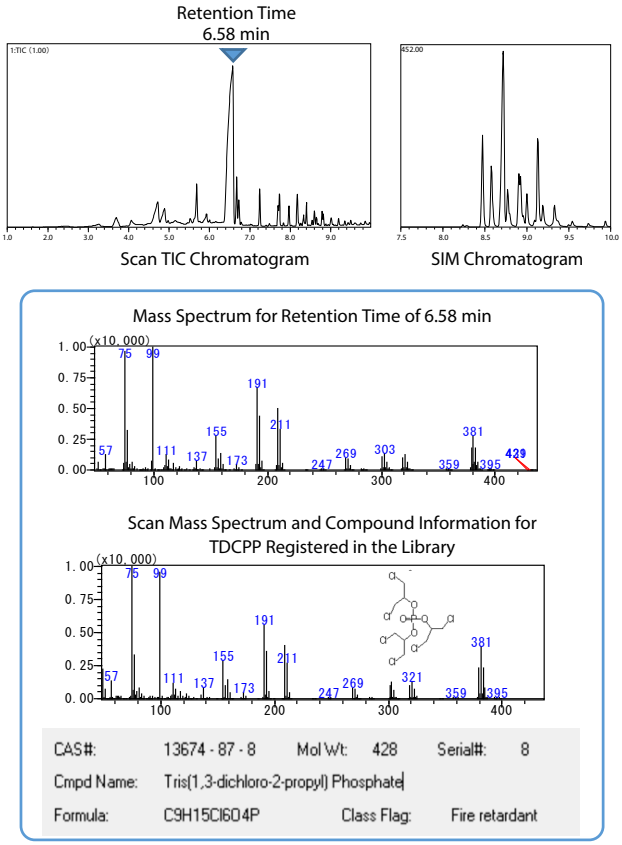

Fig. 5 Polyurethane Sponge Measurement Results

■ Conclusion

Because TSCA regulations do not specify an allowable concentration level of PIP (3:1), ultra-trace sensitivity is required for an analytical instrument. The Py/TD-GC-MS can analyze PIP (3:1) in plastic using simple operations and without any need for organic solvents or complicated pretreatment steps. If the FASST is used, other additives can also be qualitatively analyzed during high-sensitivity analysis of PIP (3:1) (detection limit of 10 mg/kg). With about 4900 scan spectra and types of additives (such as flame retardants and plasticizers) registered in the Polymer Additives Library, additives can be identified even by operators without detailed knowledge on mass spectra.

This example also showed that PIP (3:1) carryover can occur. Therefore a blank sample needs to be analyzed after a high concentration of PIP (3:1) is detected.

■ References

1) IEC 62321-8:2017, 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)

2) U.S. EPA, Preliminary Information on Manufacturing, Processing, Distribution, Use, and Disposal: Phenol, isopropylated, phosphate (3:1)
https://www.epa.gov/sites/production/files/2017-08/documents/pip3-1_-_use_information_8-10-17.pdf

3) U.S. EPA, 40 CFR Part 751, REGULATION OF CERTAIN CHEMICAL SUBSTANCES AND MIXTURES UNDER SECTION 6 OF THE TOXIC SUBSTANCES CONTROL ACT
https://ecfr.federalregister.gov/current/title-40/chapter-I/subchapter-R/part-751

01-00191-EN First Edition: Jul. 2021

SHIMADZU
Shimadzu Corporation
Analytical & Measuring Instruments Division
Global Application Development Center

www.shimadzu.com/an/