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Application News

GC-MS GCMS-QP™ 2020 NX

Analyzing UV-328 and Dechlorane Plus in Plastic by Pyrolyzer/Thermal Desorption-GC-MS

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User Benefits

- Pyrolyzer/thermal desorption–GC-MS enables simultaneous screening analysis of UV-328 and dechlorane plus in plastics with a simple operation without the use of organic solvents.
- Fast Automated scan/SIM Type (FASST) enables qualitative and quantitative analysis in a single measurement.

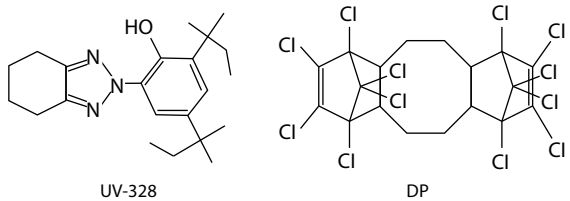
■ Introduction

UV-328 is an ultraviolet (UV) absorber and dechlorane plus (DP) is a fluorinated flame retardant. Two compounds are used as an additive in plastics. UV-328 is used in automobile paints and coatings that must be resistant to light exposure, and DP is used in various industrial products such as electric cabling and wire insulation that must be flame retardant and have insulating properties.

The Stockholm Convention on persistent organic pollutants (POPs) considers UV-328 and DP to be highly environmentally persistent, bioaccumulative, and toxic to humans and other organisms, and identifies them as chemicals of concern for long-range environmental transport. As a result, there is an increasing need to test products and molded articles that contain these substances.

Solvent extraction-GC-MS can quantitate both components accurately but has issues such as a need for large amounts of organic solvent, a long time-consuming for extraction step, and high levels of analyst skills. On the other hand, pyrolyzer/thermal desorption-GC-MS (Py/TD-GC-MS), which has been adopted in the international standard IEC 62321-8, can analyze plastic samples directly without the solvent extraction and provides a very effective analytical technique for analyzing additives in plastics.

In this article, a rapid and simple screening method for UV 328 and DP in polymers was investigated using Py/TD-GC-MS.



UV-328 DP

Fig. 1 Structural Formulae

■ Sample Preparation and Analytical Conditions

Standard solutions of UV-328 and DP were prepared by diluting each with toluene. Next, appropriate amounts of UV 328 and DP standard solutions and plastic solutions were added to a sample cup so that the UV 328 and DP concentrations in plastic were 0, 100, 500, 1000, and 2000 mg/kg. After drying it at room temperature, these were measured by Py/TD-GC-MS.

Liquid crystal module and coated wire were prepared as real samples. About 0.5 mg of the shavings obtained with a cutter were placed in a sample cup and measured by Py/TD-GC-MS.

Table 1 shows the equipment and analytical conditions used.

Table 1 Analytical Conditions

Pyrolyzer:	EGA/PY-3030D Multi-Shot Pyrolyzer and AS-1020E Auto-Shot Sampler (Frontier Laboratories)
GC-MS System:	GCMS-QP 2020 NX
Column:	SH-1MS with integrated guard (Length: 15 m, I.D.: 0.25 mm, film thickness: 0.1 µm + 2 m column guard) (P/N S227-36346-01)
[Pyrolyzer]	
Analysis Mode:	Heart-cut EGA (thermal extraction)
Heating Furnace Temp.:	200 °C - 20 °C/min - 300 °C - 5 °C/min - 340 °C (1 min)
Interface Temp.:	300 °C (manual)
[GC]	
Sample Injection Unit Temp.:	300 °C
Carrier Gas:	He
Control Mode:	Linear velocity control (52.1 cm/sec)
Injection Mode:	Split (1:50)
Oven Temp.:	80 °C - 20 °C/min - 320 °C (4 min)
[MS]	
Ion Source Temp.:	230 °C
Interface Temp.:	320 °C
Ionization Method:	EI
Scanning Mode:	Synchronous scan/SIM (scan: *m/z* 50 to 1000)
Event Time:	Scan 0.15 sec/SIM 0.1 sec

■ Investigation of Quantitative Ions

Standard samples (base plastic: PVC, PS, ABS, and PET) containing 1000 mg/kg of UV-328 and DP were analyzed. Fig. 2 shows the results of the standard samples (1000 mg/kg in PVC). Both additives were separated and detected with almost no interference from other plastic-derived components. Two peaks were detected in DP. It was considered to be isomer. The ions at *m/z* 351.2 (UV-328) and *m/z* 271.8 (DP) were selected as quantitative ions based on their high signal intensity and minimal interference from each plastic.

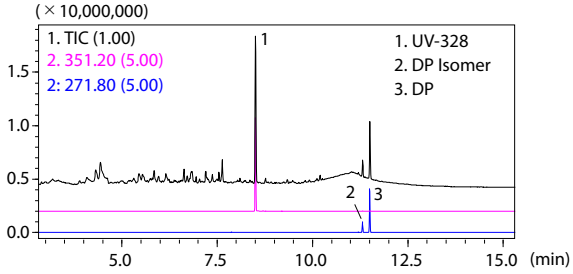


Fig. 2 Total Ion Current Chromatogram (TICC) and SIM Chromatogram for a Standard Sample (1000 mg/kg in PVC)

■ Checking the Calibration Curve

Standard samples with UV-328 and DP concentrations in PVC 0, 100, 500, 1000, and 2000 mg/kg were analyzed and the calibration curve were created. DP was calculated by combining the two peaks (DP and DP isomer) area.

The linearity of the calibration curves (R^2) were 0.998 or higher for both compounds (Table 2). It shows good result.

■ Checking Repeatability and Lower Limit of Detection

A standard sample with concentrations of UV-328 and DP in PVC of 1000 mg/kg was analyzed three times consecutively and repeatability, and %RSD was confirmed. Furthermore, a standard sample of 100 mg/kg in PVC was analyzed eight times consecutively, and the minimum detection limit (MDL) was calculated from a Student's t-test (confidence interval: 99 %) (Table 2).

The repeatability (%RSD) was less than 5 %. The MDL was under 50 mg/kg for both components, which was found to be sensitive enough to be used as a screening analysis to determine inclusion/absence.

Table 2 Calibration Curve Linearity, Repeatability, and MDL

Compound	Linearity R^2	%RSD at 1000 mg/kg	MDL (mg/kg)
UV-328	0.998	1.3	9.3
DP	0.999	4.6	23

■ Evaluating Additive Recovery from Various Plastics

Standard samples with concentration of UV-328 and DP in plastic of 1000 mg/kg (base plastic: PVC, PS, ABS, and PET) were analyzed four times consecutively. Concentrations of two compounds were determined using the calibration curves and recoveries ware evaluated (Fig. 3).

Average recovery rates were between 104 and 111 % for UV-328 and 96 and 134 % for DP, showing the quantitative accuracy of the method is good enough to use in screening analysis.

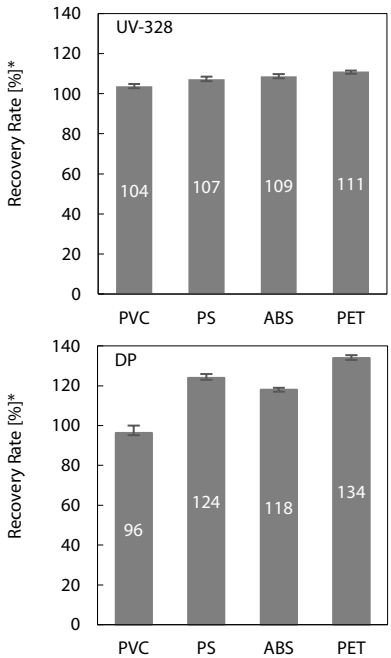


Fig. 3 UV-328 and DP Recovery from Various Plastics

* Error bars show standard deviation.

■ Results from Real Samples

A cutter was used to remove pieces of a liquid crystal module and coated wire, which were analyzed three times consecutively. UV-328 was detected in the second layer of material in the liquid crystal module and DP was detected in the coated wire.

Figs. 4 and 5 show the TICC and SIM chromatogram for the liquid crystal module and coated wire samples, respectively. Tables 3 and 4 show the conc. in plastics and the its repeatability detected in the liquid crystal module and coated wire.

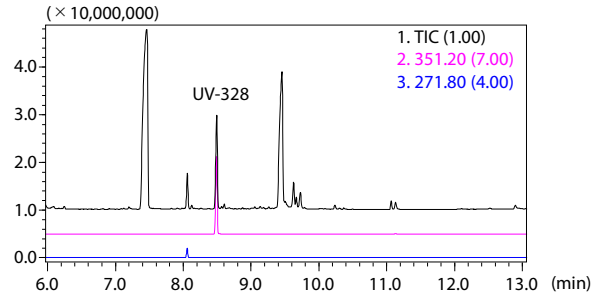


Fig. 4 TICC and SIM Chromatogram of Liquid Crystal Module

Table 3 Similarity, Conc. in Plastics, and Repeatability of Liquid Crystal Module (n = 3)

Compound	Similarity	Conc. in Plastics (mg/kg)	%RSD
UV-328	90	3.8×10^3	5.1

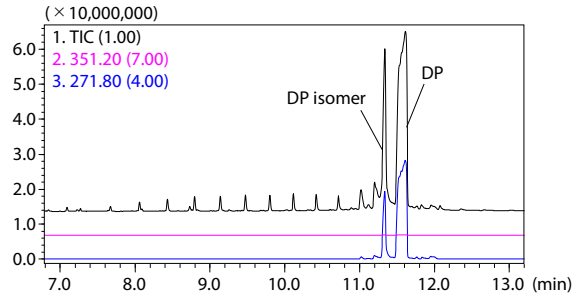


Fig. 5 TICC and SIM Chromatogram of Coated Wire

Table 4 Similarity, Conc. In Plastics, and Repeatability of Coated Wire (n = 3)

Compound	Similarity	Conc. in Plastics (mg/kg)	%RSD
DP	89	8.4×10^4	6.5
DP Isomer	86		

■ Conclusion

In this article, POPs additional components, UV-328 and DP were analyzed by Py/TD-GC-MS. An investigation of calibration curve linearity, repeatability, minimum detection limit, and recovery rates from various plastics showed the Py/TD-GC-MS method is sensitive enough and offers sufficient quantitative accuracy to determine whether the additives are present or not present in samples.

Py/TD-GC-MS can analyze plastic samples directly without solvent extraction and provide a rapid and simple method of screening for UV-328 and DP in plastics.

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