Screening analysis of Dechlorane Plus and UV-328 by PY-GC/MS method

Product used：Mass Spectrometer (MS)

1. Introduction

Dechlorane Plus (DP) is widely used to Electronics and Textile products as Chlorinated flame retardants and UV-328 is widely used to Paint and Plastic products as UV absorber. However, these two compounds became regulation target of Persistent Organic Pollutants treaty (POPs) in 2023 due to concerns that their flame resistance, high concentration and long-term toxicity will have a bad influence on the human body. As a screening analysis for judgment of containing/not containing on the same kind regulation target, there is an analysis method of phthalate esters by PY-GC/MS in the IEC62321-8. This method allows direct analysis without sample pretreatment. This study tried to analyze of DP and UV-328 by PY (PY-3030D, FRONTIER LAB)-GC/MS method using the JMS-Q1600GC UltraQuad™ SQ-Zeta. As the result, good reproducibility and detection sensitivity were obtained and It seemed to quite possible to screening analysis.

Gas chromatograph mass spectrometer
JMS-Q1600GC UltraQuad™ SQ-Zeta

2. Experiment

The standard samples for calibration curves of the DP and UV-328 ware prepared in the same way as MSTips No. 290 by using the resin matrix solution and mixed liquid standard samples as described in IEC 62321-8. Acrylonitrile Butadiene Styrene (ABS) was used for resin matrix. Calibration curves were prepared for each compound at concentrations of 100 ppm to 2000 ppm in the resin by varying concentrations of mixed liquid standard samples (addition amount 5 µL) furthermore reproducibility at lower concentration limit (100 ppm) was calculated and Instrument Detection Limit (IDL) was too. Additionally, each compound at concentration of 1000 ppm in Polystyrene (PS) and Polycarbonate (PC) moreover ABS were measured and their recovery rates were calculated by using quantitative value from the calibration curve. Insulating sticky tape and Impact absorption gel sheet ware used for the actual samples. Samples were cut with a knife and measured in put directly in an Eco-cup. The conditions of the instrument used for measuring were shown in Table 1.

Table 1. Measurement Condition

Parameter		Value
PY	Furnace temp.	200 °C(0 min) → 20 °C/min → 300 °C(0 min) → 5 °C/min → 340 °C(1 min)
	Interface temp.	300 °C
GC	Column	ZB-1HT Inferno (Phenomenex), 15 m×0.25 mm id, 0.1 µm film thickness
	Column flow	1.0 mL/min (He)
	Oven temp.	80 °C(0 min) → 20 °C/min → 320 °C(4 min)
	Inlet temp.	320 °C
	Injection mode	split (1/50)
MS	Interface temp.	280 °C
	Ion source temp.	250 °C
	Ionization	EI (70 eV, 50 µA)
	Acquisition mode	SIM/Scan
	Measurement mode	Scan *m/z* 50~700 mith SIM Dechlorane plus : *m/z* 272, 274, 297, 295 UV-328 : *m/z* 322, 323, 351, 352

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3. Results

3-1. Chromatograms and Calibration curves

SIM chromatograms of DP and UV-328 at concentration of 100 ppm in ABS were shown in Figure 1, Calibration curves of each compound draw by measuring pseudo-standard samples at concentration of 100, 200, 500, 1000, 2000 ppm in ABS were shown Figure 2. Incidentally, the area of 2 isomer peaks (syn-DP, anti-DP) were totaled. About linearity of calibration curves, good results were obtained, with coefficient of determination was more than 0.999.

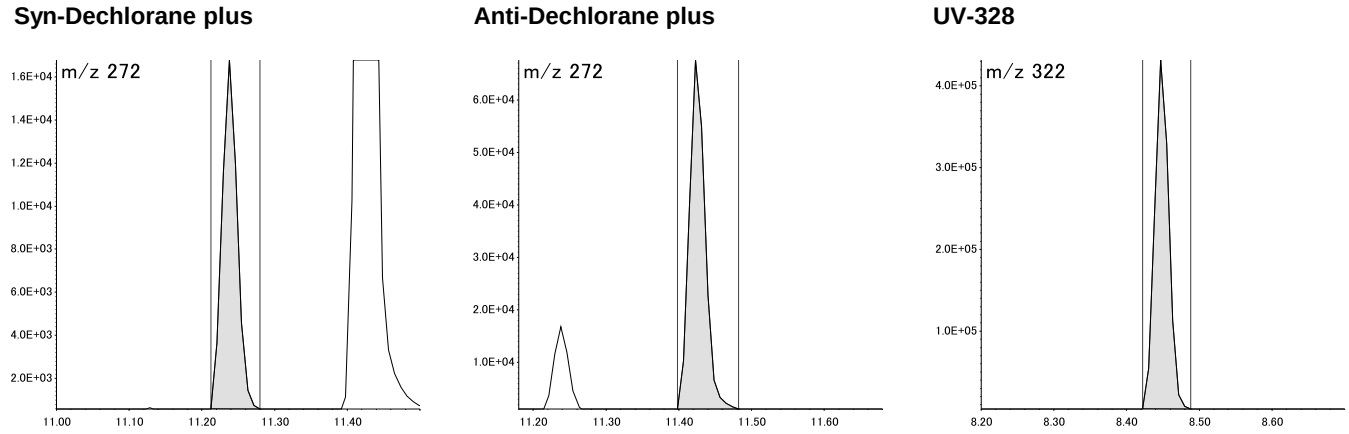

Figure 1. SIM chromatograms of each compound at 100 ppm

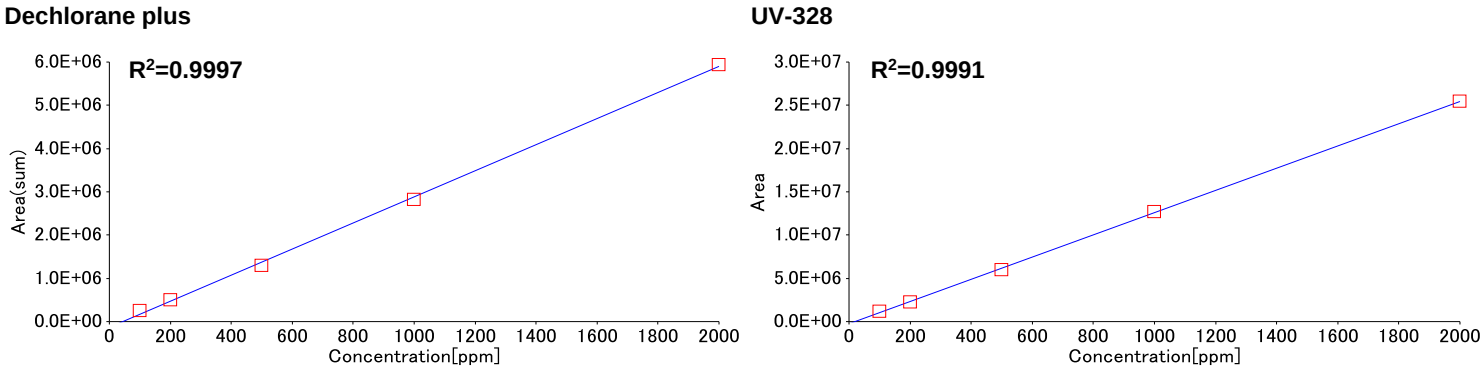

Figure 2. Calibration curve of each compound

3-2. Reproducibility and Instrument Detection Limit

The relative standard deviation (%RSD) of quantitative values obtained by measuring sample in number of trials n=8 at concentration of lower limit in resin (100 ppm) and the calculated IDL were shown in Table 2. At each compound, good results were obtained, with %RSD was less than 5% and IDL was 10 ppm or less. Incidentally, IDL was calculated with t-value of t-test.

Table 2. Relative standard deviation of each compound and Instrument Detection Limit of each compound

Compound name	Quantitation value (ppm)								%RSD	IDL (ppm)
	#1	#2	#3	#4	#5	#6	#7	#8		
Dechlorane plus	108	107	105	107	112	108	106	105	1.8	5.5
UV-328	129	131	130	132	130	131	131	129	0.7	2.2

3-3. Recovery rates of each compound in each resin matrix

TIC chromatograms of DP and UV-328 at concentration of 1000 ppm in ABS were shown in Figure 3. Recovery rates of each compound were evaluated by quantitative values obtained by measuring sample in number of trials n=8 at concentration in resin 1000 ppm were shown in Table 3. Average recovery rate of DP is 88～102 % and of UV-328 is 87～101 %, the result indicated that a screening analysis was adequate.

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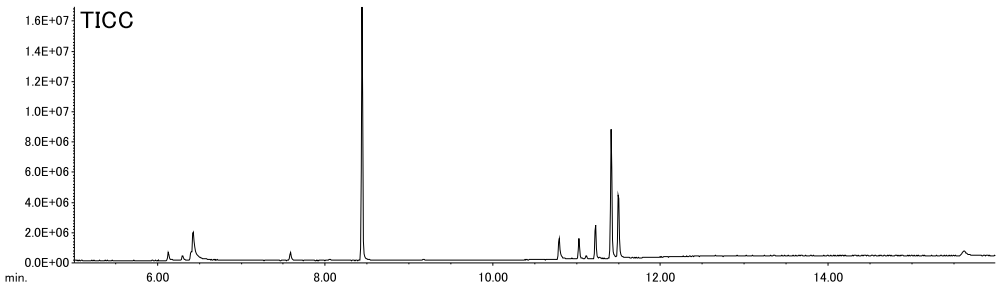

Figure 3. TICC chromatograms of each compound at 1000 ppm in ABS matrix sample

Table 3. Recovery rates in each matrix sample

Matrix name	Compound name	Quantitation value (ppm)						Recovery rate %
		#1	#2	#3	#4	#5	Avg.	
ABS	Dechlorane plus	953	959	964	985	988	970	97.0
	UV-328	879	895	932	939	946	918	91.8
PC	Dechlorane plus	913	864	912	890	868	889	88.9
	UV-328	872	877	883	866	862	872	87.2
PS	Dechlorane plus	990	1037	1013	1016	1051	1021	102.1
	UV-328	978	1009	1019	1011	1041	1012	101.2

3-4 Measurement of Actual samples

Actual samples were measured in number of trials n=5 respectively. SIM chromatogram of DP from Insulating sticky tape and UV-328 from Impact absorption gel sheet were shown in Figure 4. %RSD calculated by using calibration curve were shown in Table 4. %RSD was less than 10 % at over a wide concentration range of approximately 85～1.3×10^5 ppm, the result indicates that a screening analysis was adequate.

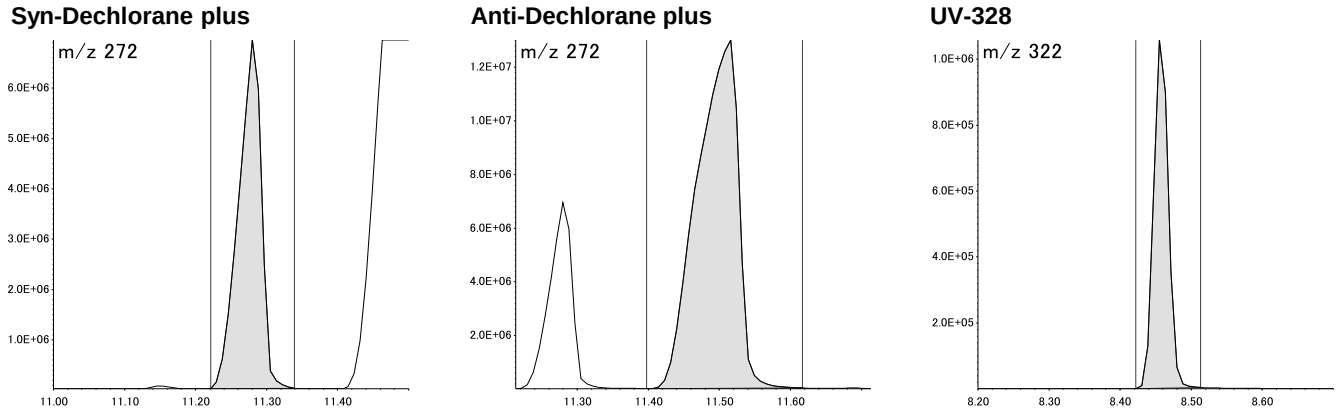

Figure 4. SIM chromatograms of each compound at real sample

Table 4. Relative standard deviation of each compound

Sample name	Compound name	Quantitation value (ppm)						%RSD
		#1	#2	#3	#4	#5	Avg.	
Adhesion tape	Dechlorane plus	128135	119584	137706	144612	148178	135643	7.8
Gel sheet	UV-328	89	84	84	86	84	85	2.2

Conclusion

DP and UV-328 regulated by POPs were analyzed by using PY-GCMS method. Good results of linearity of calibration curve and reproducibility at concentration of lower limit were obtained. It was quite possible to screening analysis. Additionally, Good results of recovery rate of each resin matrix were obtained. So, it could be applied to actual samples.

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