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Application News

No. M293A

Gas Chromatography Mass Spectrometry
Liquid Chromatography Mass Spectrometry

Analysis of Toxic Chemical Substances Adsorbed on Microplastics

The possibility that toxic chemical substances adsorbed on microplastics (MPs) in the environment may impact the ecosystem by desorbing from the MPs, migrating to the bodies of living organisms, and concentrating in those organisms has been pointed out.

The Shimadzu Group has been involved in evaluations of the adsorption characteristics of chemical substances on MPs as part of analysis of MPs (1), (2).

Here, we introduce an example of an evaluation of the MPs adsorption characteristics of polycyclic aromatic hydrocarbons (PAHs) and per- and polyfluoroalkyl substances (PFAS), which are known to have toxicity and bioaccumulation properties. Using commercially-available particulate polypropylene (PP), polystyrene (PS), and polyethylene (PE) as MPs samples, the amount of adsorption of PAHs and PFAS in water on the various plastics was evaluated quantitatively by GC-MS/MS and LC-MS/MS.

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MPs Samples

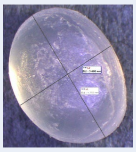
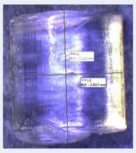
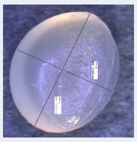
The following three types of plastic particles were used as the MPs samples.

1) Polypropylene (PP)
2) Polystyrene (PS)
3) Polyethylene (PE)

The long and short diameters of each type of particle were calculated from stereoscopic microscope images to confirm that the size of the materials used was less than 5 mm, which is the definition of MPs. Table 1 shows the appearance and microscopic images of the above-mentioned plastic particles 1) to 3), together with the average size of 10 particles sampled at random. The following instruments were used in the measurements.

- Microscope digital camera system : Moticam 1080
- Stereoscopic microscope : STZ-171-TP

Table 1 **MPs Samples Used in Experiment**

Material		PP	PS	PE
Appearance				
Microscopic image				
Size [mm]	Long diameter	4.899±0.151	3.191±0.149	4.331±0.194
	Short diameter	3.606±0.151	2.888±0.144	3.564±0.125

Test Method

First, an adsorption test of PAHs and PFAS (per- and polyfluoroalkyl substances)(*) on the MPs samples was conducted. Fig. 1 shows an outline of the adsorption test system. The MPs were immersed in water, to which PAHs or PFAS had been added, and the water was stirred gently for 24 h to promote adsorption. The amounts of added to MPs were 100 ng of PAHs and 8 ng of PFAS in 300 mL of ultrapure water.

Fig. 2 shows an outline of the test flow. After the adsorption test, the MPs were removed from the test system and dried. With some of the samples, ultrasonic extraction by hexane was used as a pretreatment for the PAHs, and ultrasonic extraction by methanol was used as a pretreatment for the PFAS. The extracts obtained here were injected into the GC-MS/MS and LC-MS/MS, respectively, for quantitative analysis of the PAHs and PFAS.

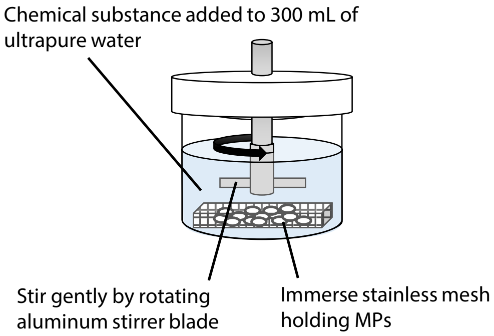


Fig. 1 **Outline of Adsorption Test System**

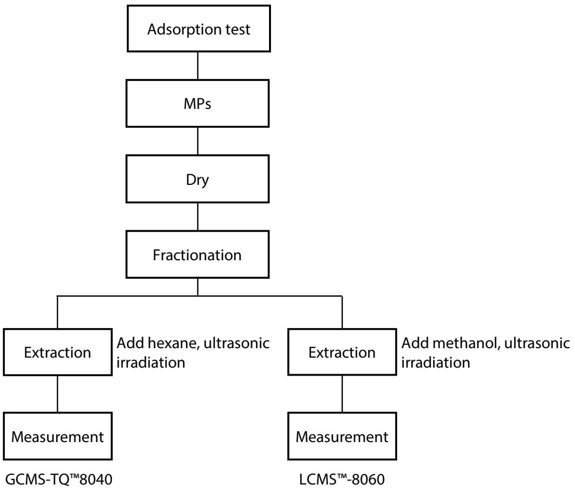


Fig. 2 **Outline of Test Flow**

(*) For analogs, refer to EPA Method 537.1 and EPA Method 533.

Measurement of PAHs by GC-MS/MS

In measurement of the PAHs, a GCMS-TQ8040 triple quadrupole gas chromatograph mass spectrometer (Fig. 3) was used. Table 2 shows the measurement conditions of the GCMS-TQ8040.

The measurements were carried out in the high selectivity MRM mode. Based on the calibration curve linearity and peak S/N ratio, the lower limit of quantitation of the compounds was assumed to be 0.5 to 2 ng/mL. Fig. 4 shows the MS chromatogram of the PAHs standard solution (2 ng/mL each). Quantitative calculations were performed by the internal standard method.

Fig. 3 **GCMS-TQ™8040 Triple Quadrupole Gas Chromatograph Mass Spectrometer**

Table 2 **GCMS-TQ8040 Measurement Conditions**

GC	
Column	DB-5ms (Agilent Technologies/J&W) (30 m × 0.25 mm I.D., 0.25 µm)
Column oven temp. program	60 °C (1 min) – 15 °C/min – 200 °C (0 min) – 8 °C/min – 320 °C (10 min)
Injection mode	Splitless
Vaporizing chamber temp.	300 °C
Injection volume	2 µL
Carrier gas	Helium (1.0 mL/min)
MS	
Ionization method	EI
Ionization voltage	70 V
Interface temp.	300 °C
Measurement mode	MRM
Measured ions (*m/z*)	

Compound (target substance)	Quantitative ion	Reference ion	Compound (internal standard)	Quantitative ion	Reference ion
Naphthalene	128>128	128>102	Naphthalene-d_8	136>136	136>108
Acenaphthylene	152>152	152>151	Acenaphthylene-d_8	160>160	160>158
Acenaphthene	153>153	153>152	Acenaphthene-d_{10}	162>162	162>160
Fluorene	165>165	165>164	Fluorene-d_{10}	174>174	174>171
Anthracene	178>178	178>152	Anthracene-d_{10}	188>188	188>160
Phenanthrene	178>178	178>152	Phenanthrene-d_{10}	188>188	188>160
Fluoranthene	202>202	202>200	Fluoranthene-d_{10}	212>212	212>208
Pyrene	202>202	202>200	Pyrene-d_{10}	212>212	212>208
Benzo[a]anthracene	228>228	228>226	Benz[a]anthracene-d_{12}	240>240	240>236
Chrysene	228>228	228>226	Chrysene-d_{12}	240>240	240>236
Benzo[b]fluoranthene	252>252	252>250	Benzo[b]fluoranthene-d_{12}	264>264	264>260
Benzo[k]fluoranthene	252>252	252>250	Benzo[k]fluoranthene-d_{12}	264>264	264>236
Benzo[a]pyrene	252>252	252>250	Benzo[a]pyrene-d_{12}	264>264	264>260
Benzo[ghi]perylene	276>276	276>274	Benzo[ghi]perylene-d_{12}	288>288	288>284
Indeno[1,2,3-cd]pyrene	276>276	276>274	Indeno[1,2,3-cd]pyrene-d_{12}	288>288	288>284
Dibenzo[a,h]anthracene	278>278	278>276	Dibenzo[a,h]anthracene-d_{14}	292>292	292>288
-	-	-	Hexachlorobenzene-$^{13}C_6$	292>292	292>292

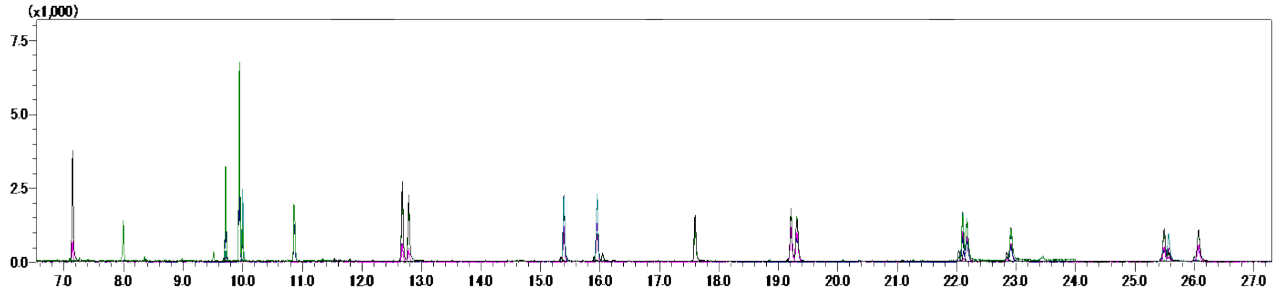


Fig. 4 **MRM Chromatogram of PAHs Standard Solution (2 ng/mL Each) (except internal standards)**

Measurement of PFAS by LC-MS/MS

The instrument used in measurements of the PFAS was a LCMS-8060 triple quadrupole liquid chromatograph mass spectrometer (Fig. 5). Table 3 shows the measurement conditions.

The measurements were carried out in the high selectivity MRM mode. Based on the calibration curve linearity and peak S/N ratio, the lower limit of quantitation of the compounds was assumed to be 0.01 to 0.5 ng/mL. Fig. 6 shows the MS chromatogram of the PFAS standard solution (0.5 ng/mL each). Quantitative calculations were performed by the internal standard method.

Fig. 5 **LCMS-8060 Triple Quadrupole Liquid Chromatograph Mass Spectrometer**

Table 3 **LCMS-8060 Measurement Conditions**

Instruments	LC : Nexera™ X2				
	MS : LCMS-8060 triple quadrupole liquid chromatograph mass spectrometer				
LC					
Column	Inertsil ODS-SP (GL Sciences) (150 mm × 2.1 mm I.D., 3 µm)				
Column temp	40 °C				
Injection volume	10 µL				
Mobile phase A	10 mmol/L ammonium acetate aqueous solution				
Mobile phase B	Acetonitrile				
Mobile phase flow rate	0.2 mL/min				
Gradient	B conc. 0% (0 min) → 10% (1 min) → 40% (7 min) → 95% (31-38 min) → 10% (47 min)				
MS					
Ionization method	ESI				
Polarity	Negative				
Measurement mode	MRM				
MRM transition					
Compound (target substance)	Quantitative ion	Reference ion	Compound (internal standard)	Quantitative ion	Reference ion
PFHxA	313>269	313>119	PFHxA-$^{13}C_5$	318>273	318>121
PFHpA	363>319	363>169	PFHpA-$^{13}C_4$	367>322	367>169
PFOA	413>369	413>169	PFOA-$^{13}C_8$	421>376	421>172
PFNA	463>419	463>219	PFNA-$^{13}C_9$	472>427	472>223
PFDA	513>469	513>219	PFDA-$^{13}C_6$	519>474	519>219
PFUnDA	563>519	563>269	PFUnDA-$^{13}C_7$	570>525	570>274
PFDoDA	613>569	613>269	PFDoDA-$^{13}C_2$	615>570	615>169
PFTrDA	663>619	663>169	-	-	-
PFTeDA	713>669	713>169	PFTeDA-$^{13}C_2$	715>670	715>169
PFHxDA	813>769	813>169	PFHxDA-$^{13}C_2$	815>770	815>169
PFOcDA	913>869	913>169	-	-	-
PFBS	299>80	299>99	PFBS-$^{13}C_3$	302>80	302>99
PFPeS	349>80	349>99	-	-	-
PFHxS	399>80	399>99	PFHxS-$^{13}C_3$	402>80	402>99
PFHpS	449>80	449>99	-	-	-
PFOS	499>80	499>99	PFOS-$^{13}C_8$	507>80	507>99
PFNS	549>80	549>99	-	-	-
PFDS	599>80	599>99	-	-	-
PFDoS	699>80	699>99	-	-	-

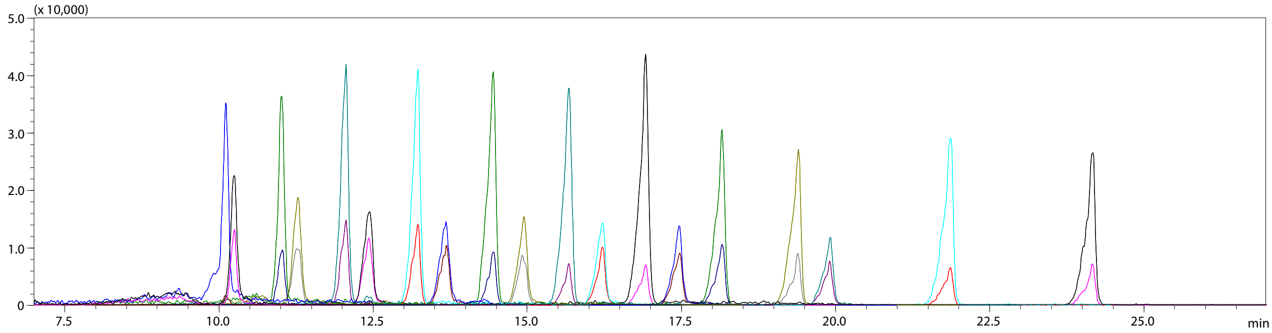


Fig. 6 **MRM Chromatogram of PFAS Standard Solution (0.5 ng/mL Each) (except internal standards)**

Analysis Results

Fig. 7 shows the results of the analysis of the PAHs by GC-MS/MS, and Fig. 8 shows the results of the analysis of the PFAS by LC-MS/MS. Adsorption on the MPs was confirmed for all PAHs substances and for some PFAS substances. Adsorption of the PAHs on PP and PE tended to be large. However, the amount of adsorption of the PFAS tended to differ for each chemical substance. Based on these results, because the adsorption characteristics on MPs differed depending on the chemical substance, it is thought that some are easily affected by the MPs material, in other words, its molecular structure and others are not so.

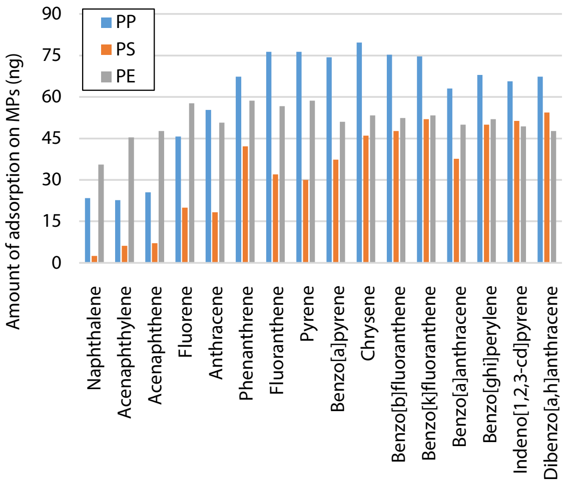


Fig. 7 **GC-MS/MS Analysis Results: PAHs**

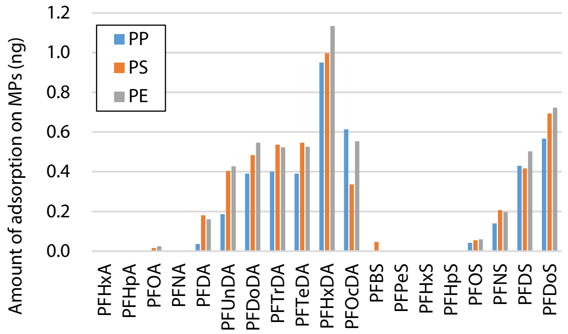


Fig. 8 **LC-MS/MS Analysis Results: PFAS**

Adsorption of chemical substances on MPs is considered to depend mainly on their hydrophobic interaction. Therefore, we examined the correlation between Log Kow (*1) and Log D (*2), which show the hydrophobicity of chemical substances, and chemical substances transfer ratio to MPs. The transfer ratio to MPs was defined as the value obtained by dividing the amount of PHAs or PFAS adsorbed on the MPs by the amount of those substances added to water. Fig. 9 shows the relationship between the hydrophobicity of the chemical substances and the transfer ratio to the MPs. In order from the top, this figure shows the transfer ratios to PP, PS, and PE. In these results, the transfer ratio showed a tendency to increase with higher values of Log Kow and Log D, independent of the type of MPs.

(*1) Log Kow : octanol/water partition coefficient

(*2) Log D : Log Kow is a partition coefficient of a chemical substance which considers the influence of electrolytic dissociation (ionization) in water. Here, this coefficient was calculated for water having pH 6.4 at the time of the test.

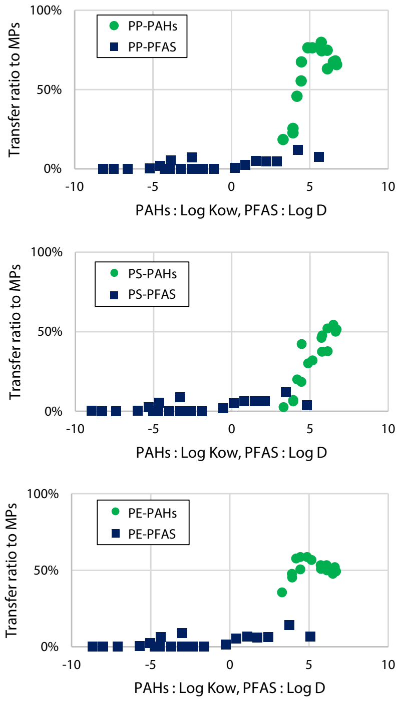


Fig. 9 **Hydrophobicity of Chemical Substances and Transfer Ratios to MPs (Top: PP, Middle: PS, Bottom: PE)**

Conclusion

In order to clarify the adsorption characteristics of chemical substances on MPs, the amount of adsorption of PAHs and PFAS on MPs in water was evaluated quantitatively by using GC-MS/MS and LC-MS/MS.

It was found that adsorption characteristics on MPs differed for each chemical substance. In addition, it was also suggested that the hydrophobicity of the individual chemical substances is a critical factor for their transfer ratio.

<References>

(1) Makoto Yasojima, Haruna Mizuka, Takaki Mine, Hiroaki Takemori, Shinji Takeuchi, Yoshihide Yasui, “Adsorption Characteristics of Chemical Substances on Microplastics,” Proceedings of the 22nd Symposium of the Japan Society on Water Environment (2019)

(2) Makoto Yasojima, Haruna Mizuka, Takaki Mine, Hiroaki Takemori, “Existence of Unknown Chemical Substances Adsorbed on Microplastics Immersed in Rivers and Adsorption Characteristics of Chemical Substances on Microplastics,” Proceedings of the 56th Environmental Engineering Research Forum (2019)

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