Análisis de Microplásticos (MP's) : Técnicas para cuantificar presencia de MP's en muestras

(Soluciones Cromatográficas)

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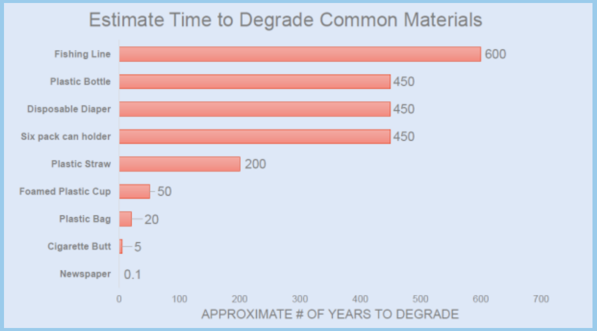
OBJETIVOS

- 1-Definición y Problemática de MP's.
- 2-Posibilidades del Análisis Cualitativo y Cuantitativo de MP's por Cromatografía acoplada a Espectrometria de Masas.
- 3-Pirólisis : Dual/Double Shot y su Versatilidad para la identificación y/o cuantificación de MP's y todos sus posibles componentes.
- 4-Conclusiones

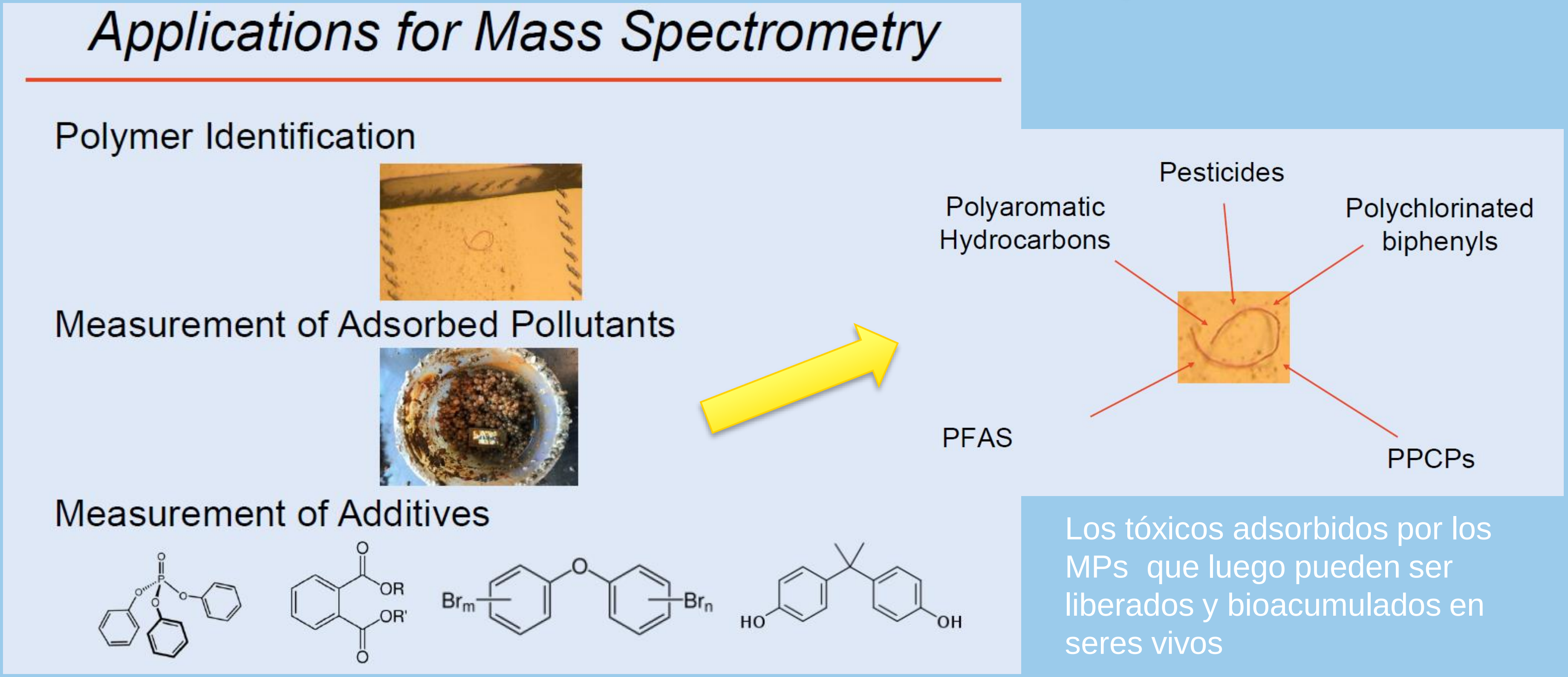
1. Definición y Problemática de MP’s

- Un MP’s se puede definir como cualquier partícula de plástico con tamaño comprendido entre varias micras y hasta alrededor de 5 mm.
- Los MP’s son **contaminantes emergentes** en el medio ambiente, la **PERSISTENCIA** ó tiempo de degradación de los mismos es muy grande y sumado a la **bioacumulación** supone un problema desde el punto de vista medioambiental con incidencia en la seguridad alimentaria.



2. Posibilidades del Análisis Cualitativo y Cuantitativo de MP’s por Cromatografía acoplada a Espectrometria de Masas

- Caracterización de MPs compuestos por un solo tipo de partículas o por mezclas de plásticos



Applications for Mass Spectrometry

Polymer Identification

Measurement of Adsorbed Pollutants

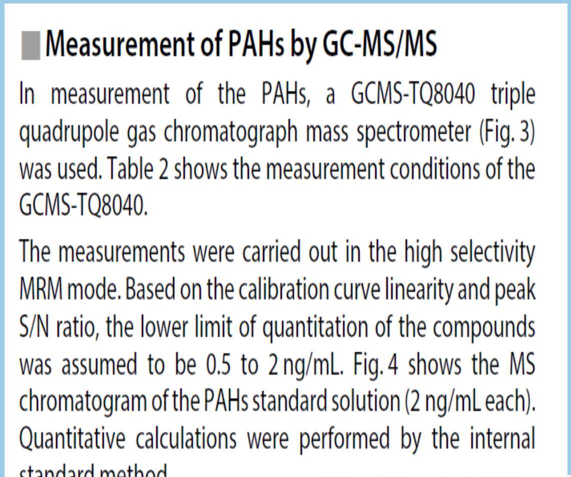
Measurement of Additives

Pesticides
Polyaromatic Hydrocarbons
Polychlorinated biphenyls
PFAS
PPCPs
O
OR
OR'
Br$_m$
Br$_n$
HO
OH
Triphenyl phosphate
Phthalates
Brominated diphenyl ethers (PBDEs)
Bisphenol A

Los tóxicos adsorbidos por los MPs que luego pueden ser liberados y bioacumulados en seres vivos

El estudio de los propios aditivos empleados en la fabricación de los plásticos (MP’s)

2. Posibilidades del Análisis Cualitativo y Cuantitativo de MP’s por Cromatografía acoplada a Espectrometria de Masas



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.

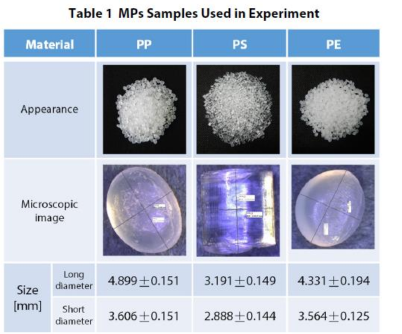


Table 1 MPs Samples Used in Experiment

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

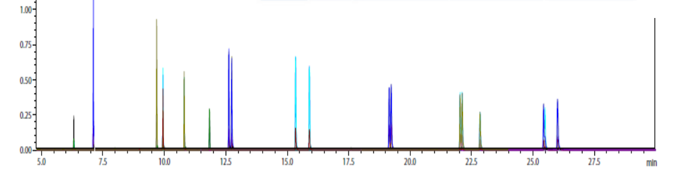


Fig. 4 MRM Chromatogram of PAHs Standard Solution (2 ng/mL Each) (Only Target Substances)

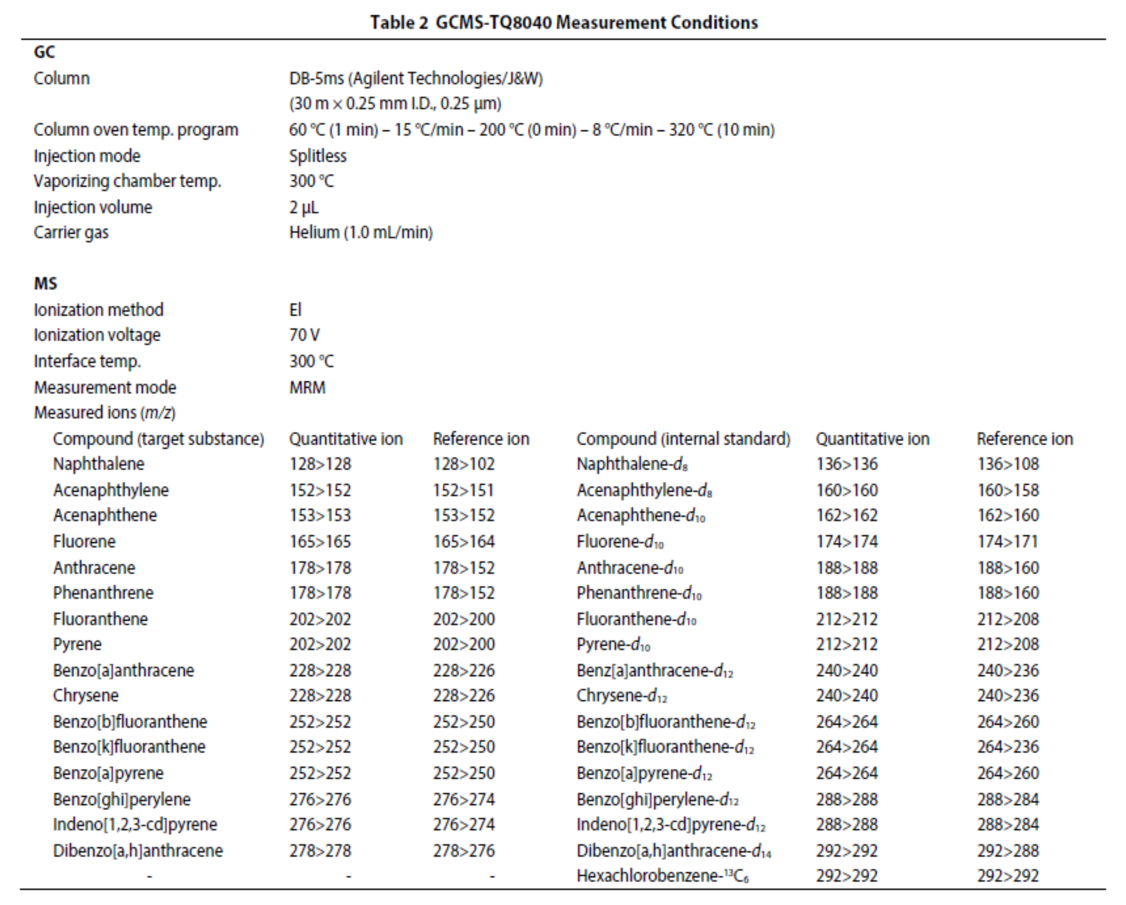
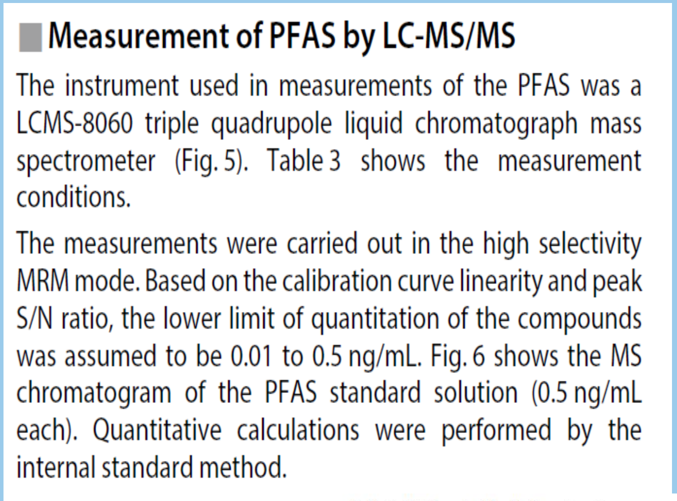


Table 2 GCMS-TQ8040 Measurement Conditions

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

2. Posibilidades del Análisis Cualitativo y Cuantitativo de MP’s por Cromatografía acoplada a Espectrometria de Masas

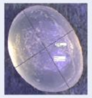
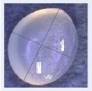


Measurement of PFAS by LC-MS/MS

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.

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

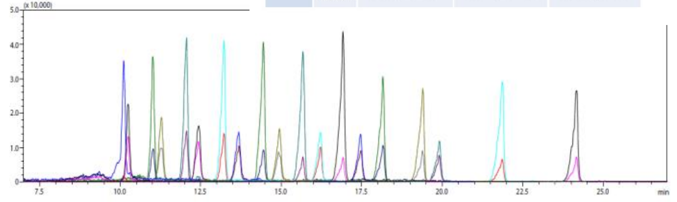


Fig. 6 MRM Chromatogram of PFAS Standard Solution (0.5 ng/mL Each) (Only Target Substances)

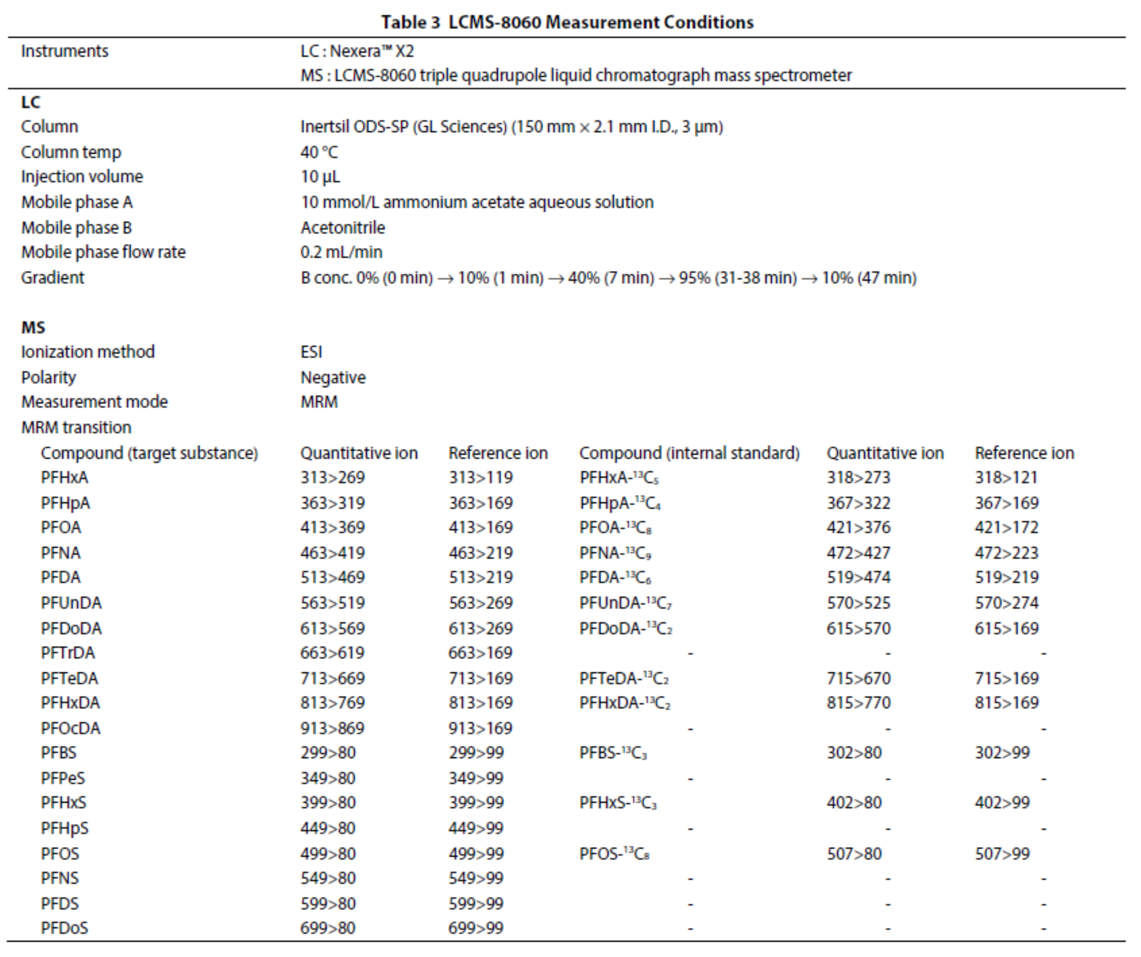


Table 3 LCMS-8060 Measurement Conditions

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	-	-	-

2. Posibilidades del Análisis Cualitativo y Cuantitativo de MP’s por Cromatografía acoplada a Espectrometria de Masas

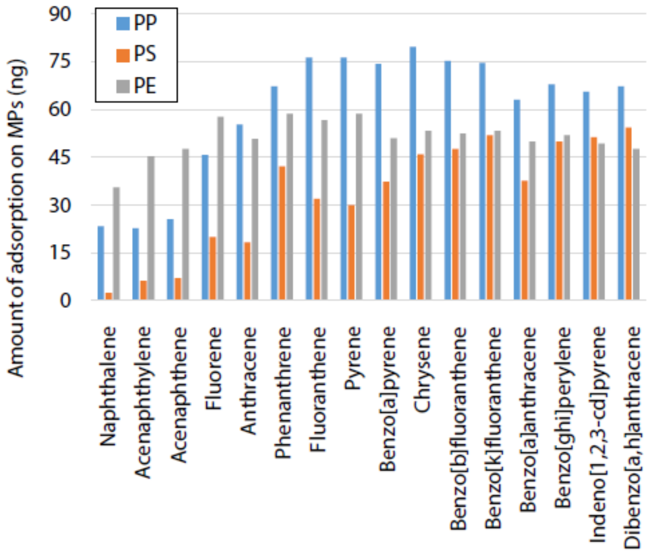


Fig. 7 GC-MS/MS Analysis Results: PAHs

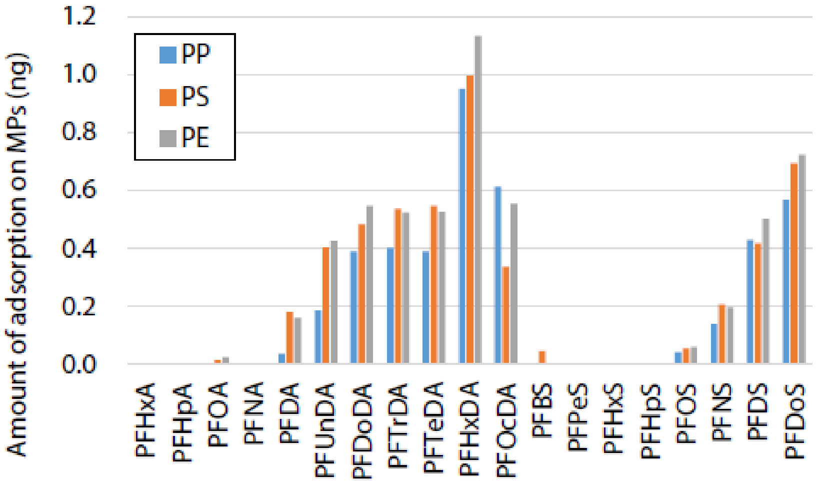
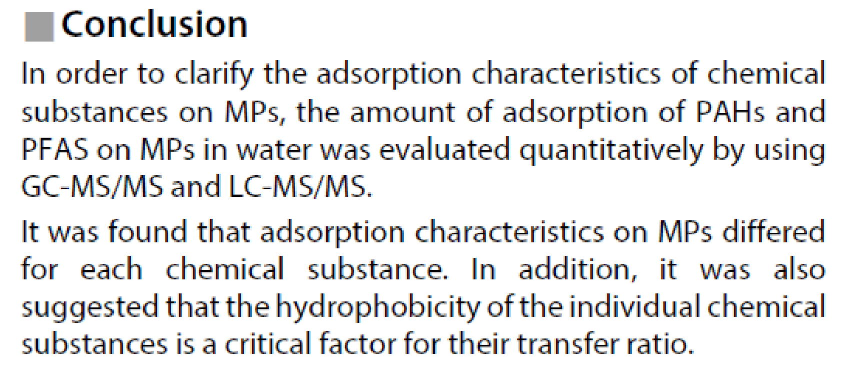


Fig. 8 LC-MS/MS Analysis Results: PFAS



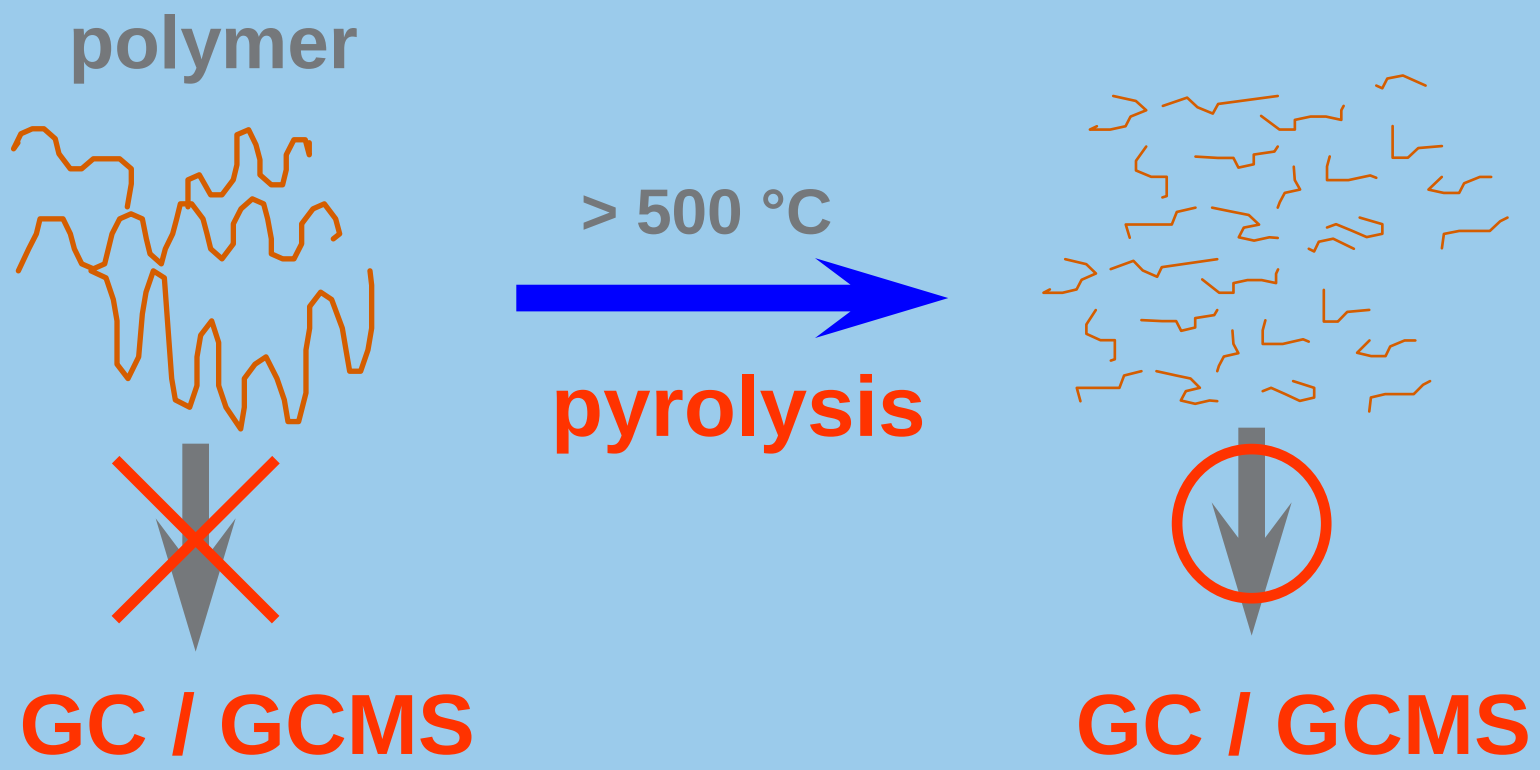
Conclusion

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.

3.Pirólisis : Dual Shot y su Versatilidad para la identificación y/o cuantificación de MP’s y todos sus posibles componentes

- Que sucede en una Pirolisis :



polymer

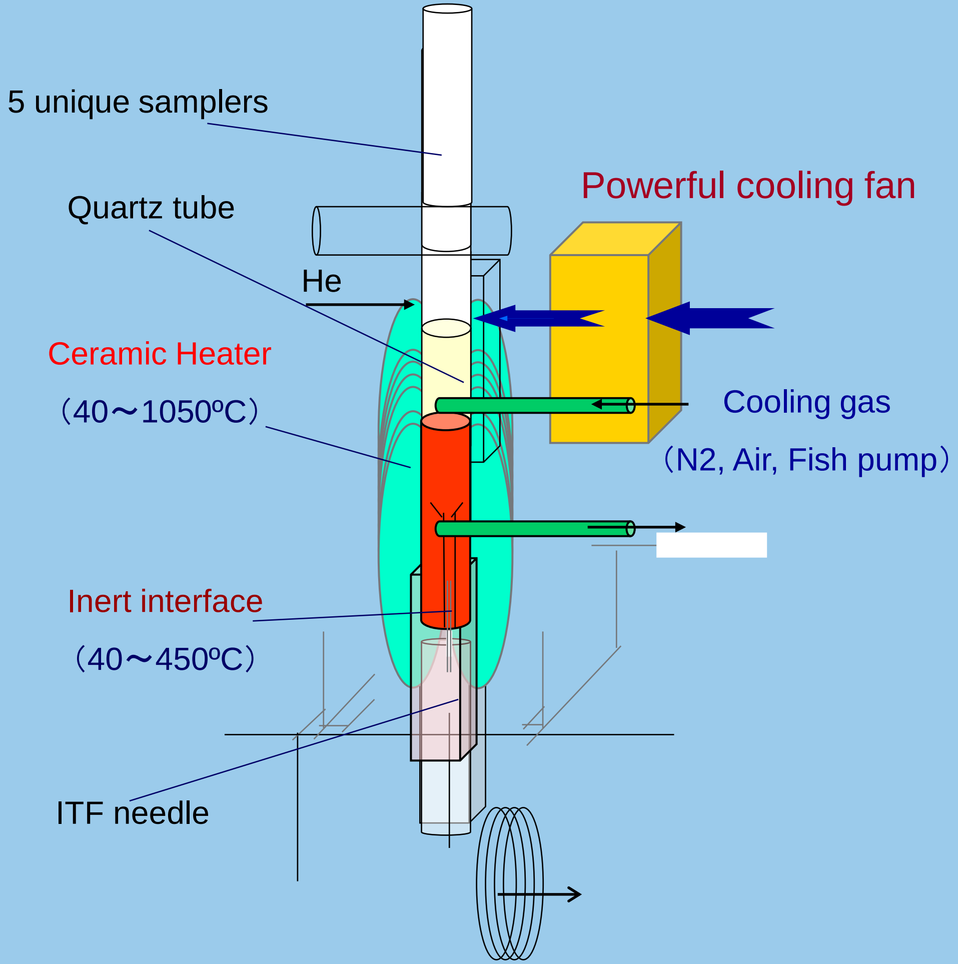
> 500 °C

pyrolysis

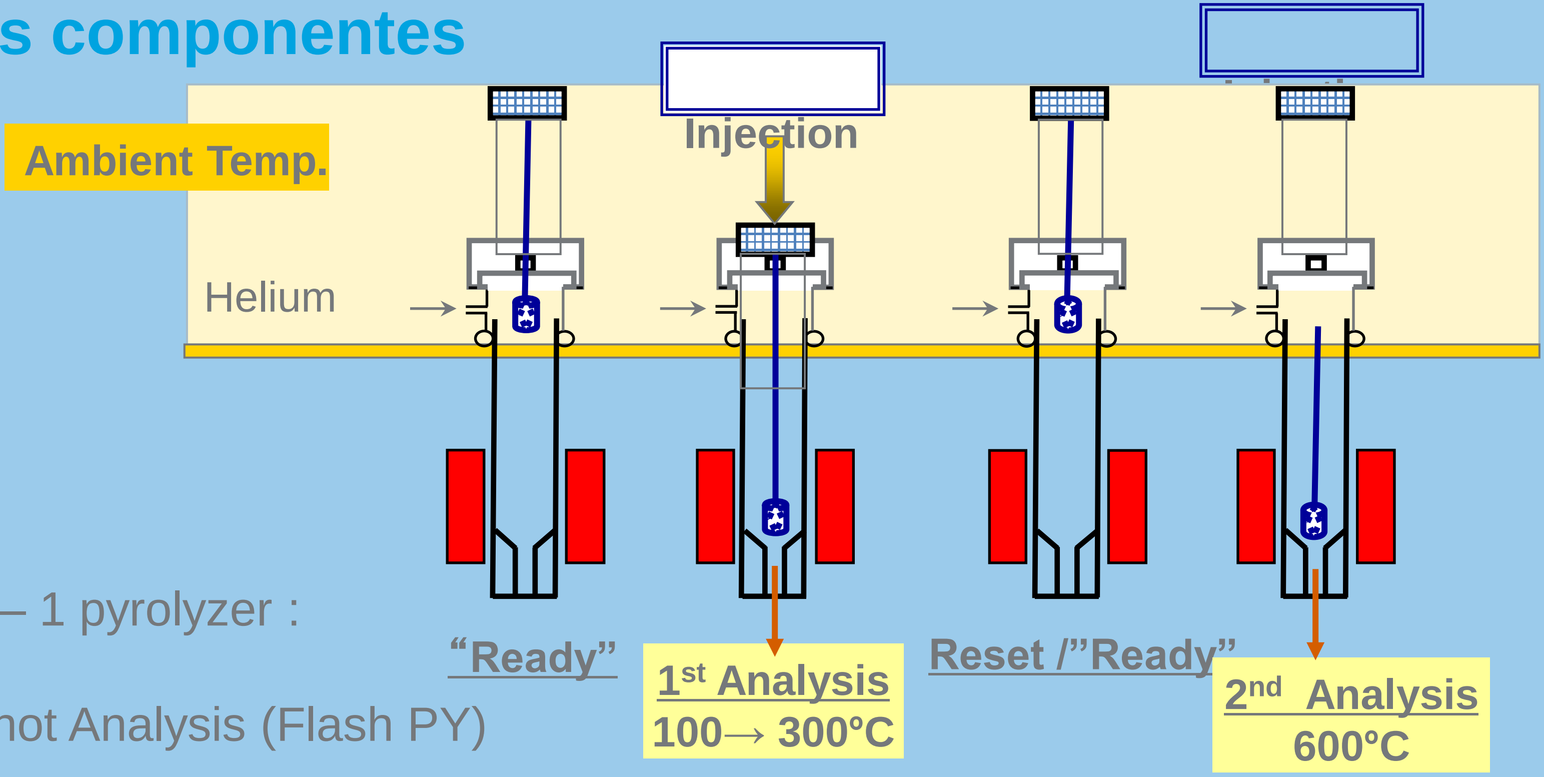
GC / GCMS

GC / GCMS

3.Pirólisis : Dual Shot y su Versatilidad para la identificación y/o cuantificación de MP's y todos sus posibles componentes


5 unique samplers
Quartz tube
He
Ceramic Heater
（40～1050ºC）
Powerful cooling fan
Cooling gas
（N2, Air, Fish pump）
Inert interface
（40～450ºC）
ITF needle

3.Pirólisis : Dual Shot y su Versatilidad para la identificación y/o cuantificación de MP's y todos sus posibles componentes


Ambient Temp.
Helium
Injection
"Ready"
1st Analysis
100→ 300ºC
Reset /"Ready"
2nd Analysis
600ºC

4 techniques – 1 pyrolyzer :

Single-Shot Analysis (Flash PY)

Double-Shot Analysis (TD & Flash PY)

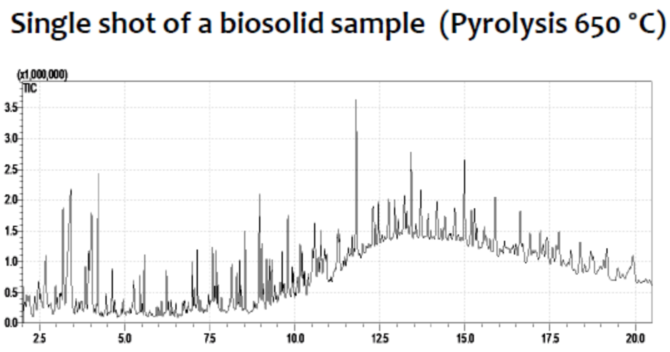
Evolved Gas Analysis (EGA)

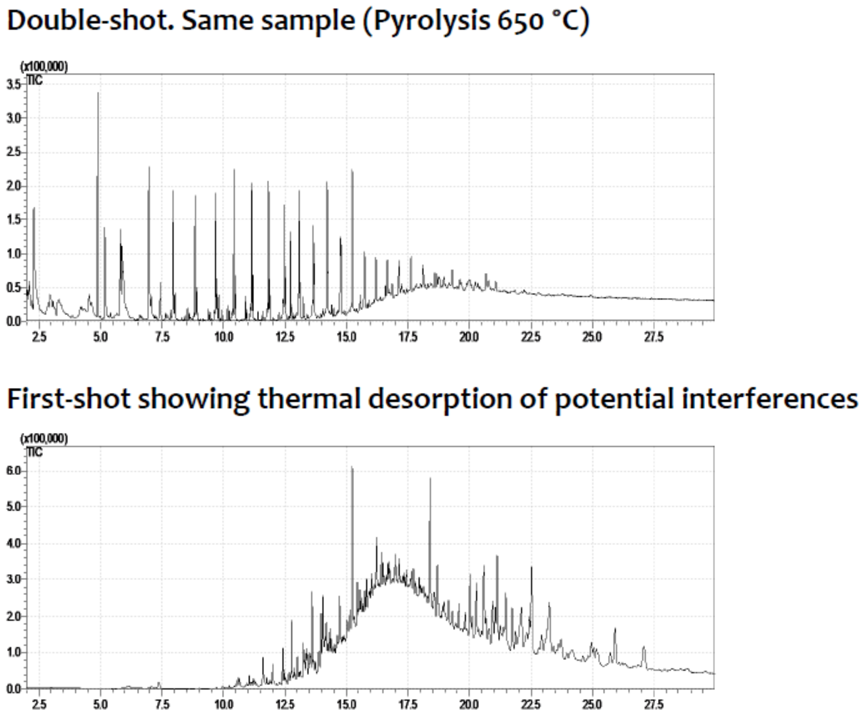
Heart-Cut EGA GC/MS Analysis (HC EGA-GC/MS)

3.Pirólisis : Dual Shot y su Versatilidad para la identificación y/o cuantificación de MP’s y todos sus posibles componentes

En la mayoría de los análisis de MPs, nos encontramos con mezclas complejas compuestas por múltiples plásticos.

Un (Py-GC/MS), nos ofrece la posibilidad de detectar e identificar los componentes de mezclas complejas con elevada sensibilidad.


Single shot of a biosolid sample (Pyrolysis 650 °C)


Double-shot. Same sample (Pyrolysis 650 °C)

First-shot showing thermal desorption of potential interferences

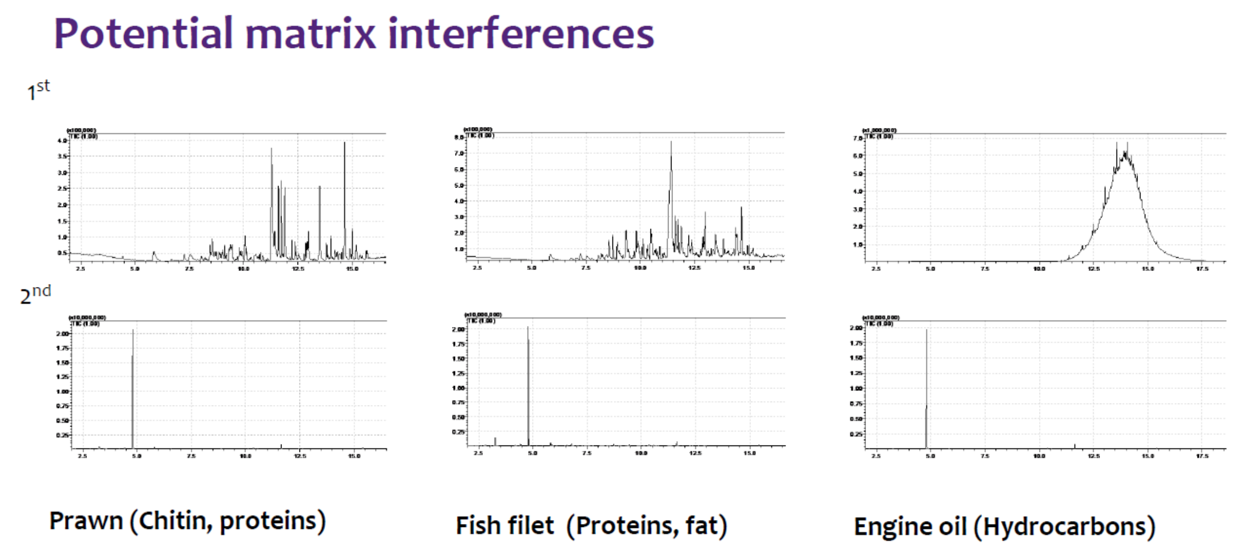
Dual Shot (Desorción Térmica + Pirolisis)

Permite separar los compuestos más volátiles, aditivos y adsorbidos de los propios plásticos (MP’s)

3.Pirólisis : Dual Shot y su Versatilidad para la identificación y/o cuantificación de MP’s y todos sus posibles componentes

Dual Shot (Desorción Térmica + Pirolisis)

Permite separar las interferencias de la matriz dependiendo de la muestra a analizar

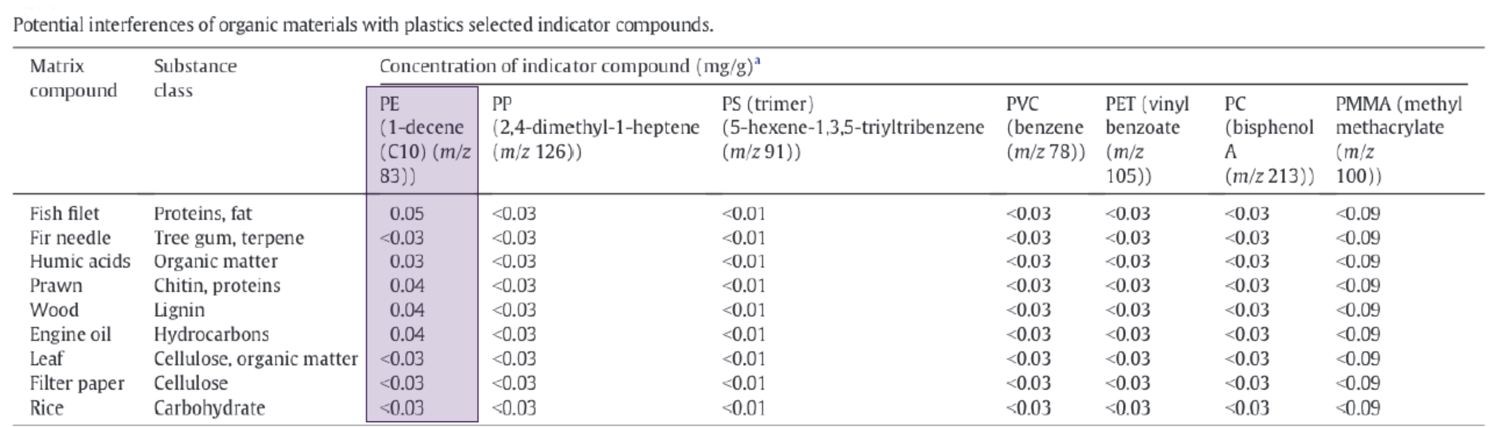


Potential matrix interferences

Prawn (Chitin, proteins)

Fish filet (Proteins, fat)

Engine oil (Hydrocarbons)

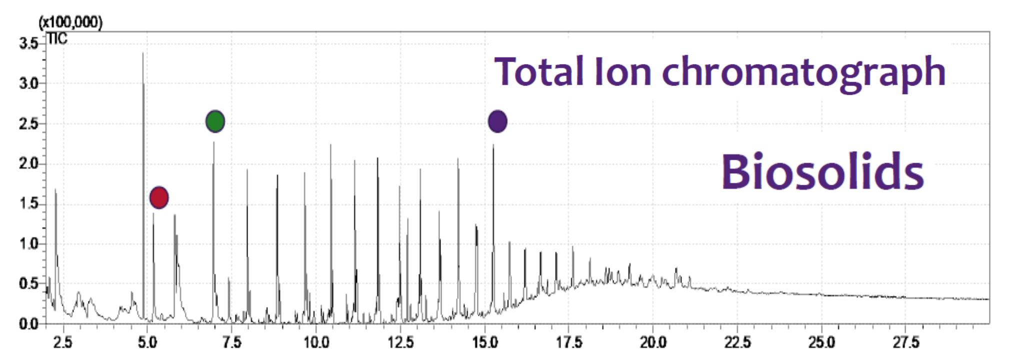


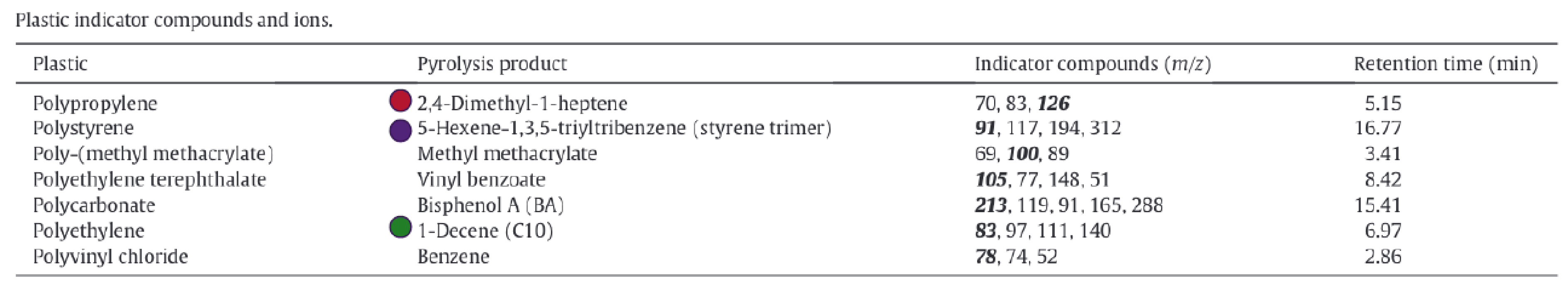
Potential interferences of organic materials with plastics selected indicator compounds.

Matrix compound	Substance class	Concentration of indicator compound (mg/g)[a]						
		PE (1-decene (C10) (*m/z* 83))	PP (2,4-dimethyl-1-heptene (*m/z* 126))	PS (trimer) (5-hexene-1,3,5-triyltribenzene (*m/z* 91))	PVC (benzene (*m/z* 78))	PET (vinyl benzoate (*m/z* 105))	PC (bisphenol A (*m/z* 213))	PMMA (methyl methacrylate (*m/z* 100))
Fish filet	Proteins, fat	0.05	<0.03	<0.01	<0.03	<0.03	<0.03	<0.09
Fir needle	Tree gum, terpene	<0.03	<0.03	<0.01	<0.03	<0.03	<0.03	<0.09
Humic acids	Organic matter	0.03	<0.03	<0.01	<0.03	<0.03	<0.03	<0.09
Prawn	Chitin, proteins	0.04	<0.03	<0.01	<0.03	<0.03	<0.03	<0.09
Wood	Lignin	0.04	<0.03	<0.01	<0.03	<0.03	<0.03	<0.09
Engine oil	Hydrocarbons	0.04	<0.03	<0.01	<0.03	<0.03	<0.03	<0.09
Leaf	Cellulose, organic matter	<0.03	<0.03	<0.01	<0.03	<0.03	<0.03	<0.09
Filter paper	Cellulose	<0.03	<0.03	<0.01	<0.03	<0.03	<0.03	<0.09
Rice	Carbohydrate	<0.03	<0.03	<0.01	<0.03	<0.03	<0.03	<0.09

3.Pirólisis : Dual Shot y su Versatilidad para la identificación y/o cuantificación de MP’s y todos sus posibles componentes

Monitorizando las señales SIM de masas específicas, de ciertos productos de pirólisis de los polímeros de la mezcla se puede confirmar la presencia de cada uno de los polímeros en una muestra.



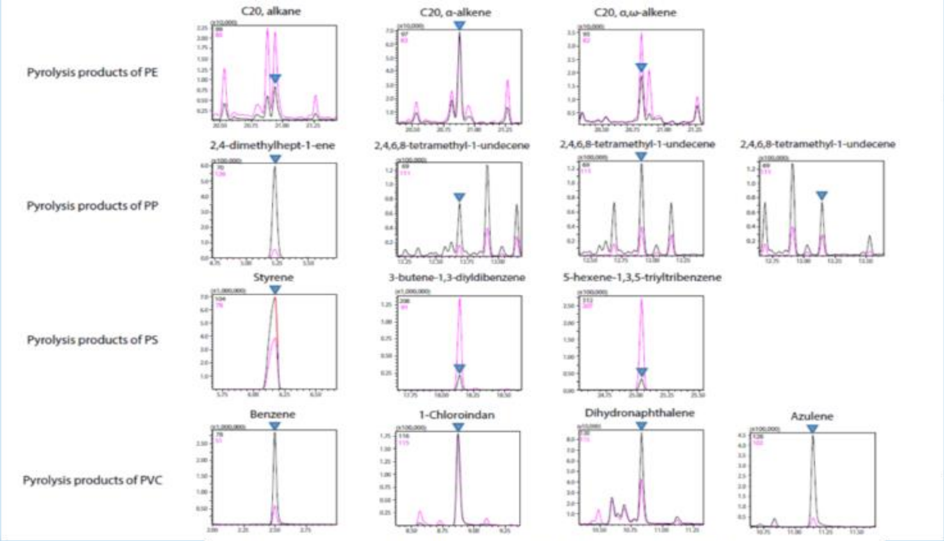


Plastic indicator compounds and ions.

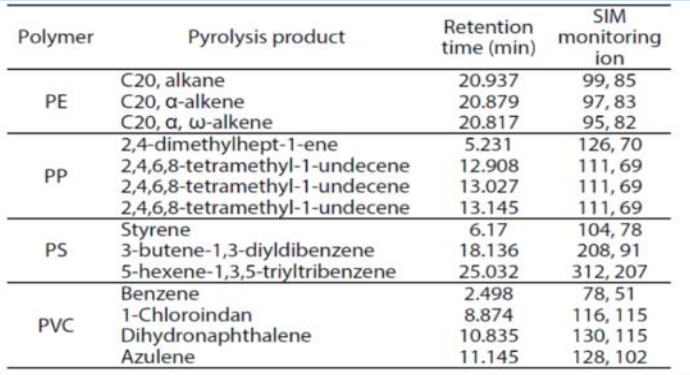
Plastic	Pyrolysis product	Indicator compounds (*m/z*)	Retention time (min)
Polypropylene	● 2,4-Dimethyl-1-heptene	70, 83, ***126***	5.15
Polystyrene	● 5-Hexene-1,3,5-triyltribenzene (styrene trimer)	***91***, 117, 194, 312	16.77
Poly-(methyl methacrylate)	Methyl methacrylate	69, ***100***, 89	3.41
Polyethylene terephthalate	Vinyl benzoate	***105***, 77, 148, 51	8.42
Polycarbonate	Bisphenol A (BA)	***213***, 119, 91, 165, 288	15.41
Polyethylene	● 1-Decene (C10)	***83***, 97, 111, 140	6.97
Polyvinyl chloride	Benzene	***78***, 74, 52	2.86

Italics and bold values used for calibration and quantification.

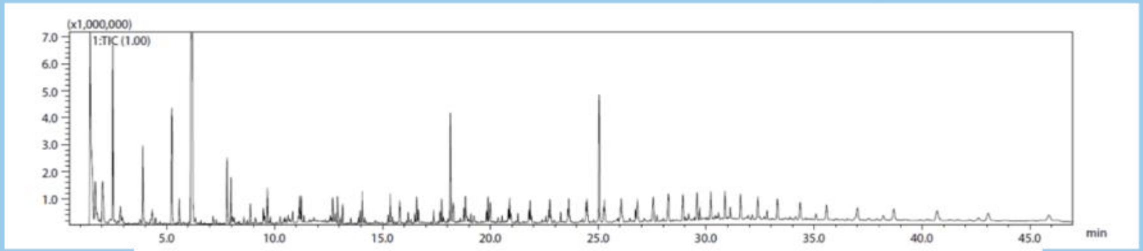
3.Pirólisis : Dual Shot y su Versatilidad para la identificación y/o cuantificación de MP’s y todos sus posibles componentes



SIM Chromatograms of Pyrolysis Products of Polymers in Mixed Polymer Sample



Polymer	Pyrolysis product	Retention time (min)	SIM monitoring ion
PE	C20, alkane	20.937	99, 85
	C20, α-alkene	20.879	97, 83
	C20, α, ω-alkene	20.817	95, 82
PP	2,4-dimethylhept-1-ene	5.231	126, 70
	2,4,6,8-tetramethyl-1-undecene	12.908	111, 69
	2,4,6,8-tetramethyl-1-undecene	13.027	111, 69
	2,4,6,8-tetramethyl-1-undecene	13.145	111, 69
PS	Styrene	6.17	104, 78
	3-butene-1,3-diyldibenzene	18.136	208, 91
	5-hexene-1,3,5-triyltribenzene	25.032	312, 207
PVC	Benzene	2.498	78, 51
	1-Chloroindan	8.874	116, 115
	Dihydronaphthalene	10.835	130, 115
	Azulene	11.145	128, 102



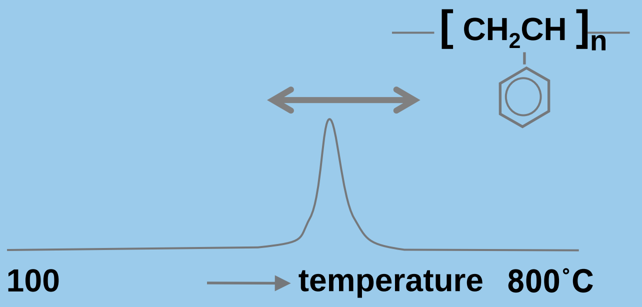
TIC Chromatogram Obtained by Analysis of Mixed Polymer Sample by Py-GC/MS Method

Appearance of Py-GC/MS System

Análisis por Py-GC/MS de una mezcla conocida de polímeros. Cromatogramas TIC (scan entre m/z 29 y 700) y SIM (de productos de pirólisis conocidos)

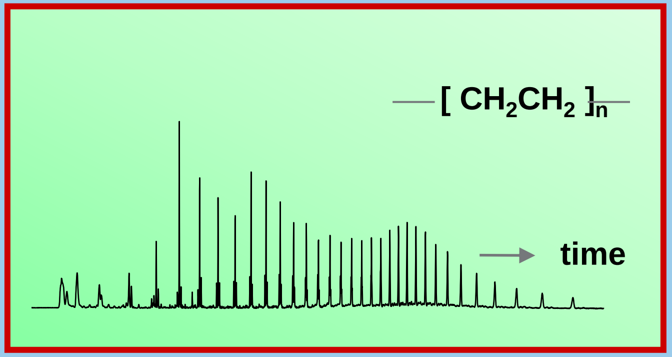
3.Pirólisis : Dual Shot y su Versatilidad para la identificación y/o cuantificación de MP's y todos sus posibles componentes

Polymer EGA-MS Library (1000 polymers)



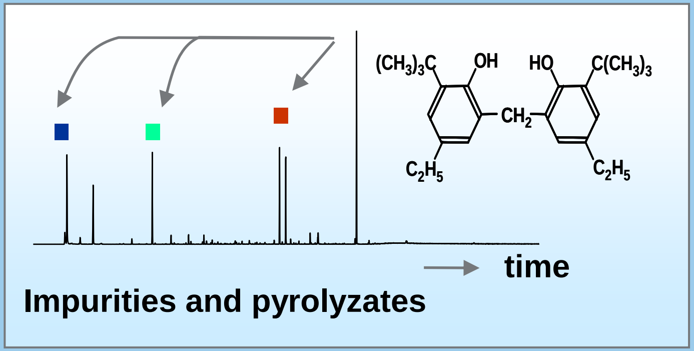
Thermogram (Entire information)

Polymer-PyGC-MS Library (1000 polymers)

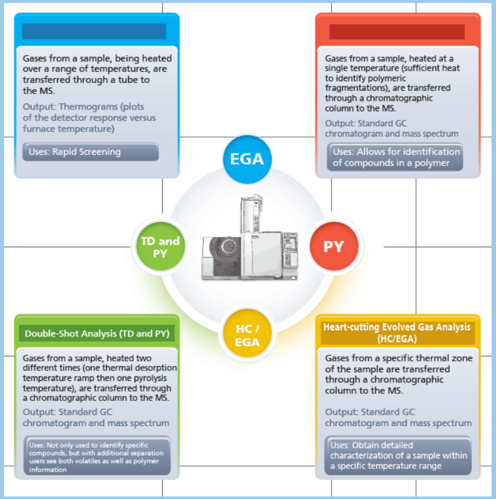


Pyrogram (Entire information)

Additive-MS Library (494 additives)



TD/Py chromatogram (Individual information)



Gases from a sample, being heated over a range of temperatures, are transferred through a tube to the MS.

Output: Thermograms (plots of the detector response versus furnace temperature)

Uses: Rapid Screening

Gases from a sample, heated at a single temperature (sufficient heat to identify polymeric fragmentations), are transferred through a chromatographic column to the MS.

Output: Standard GC chromatogram and mass spectrum

Uses: Allows for identification of compounds in a polymer

Double-Shot Analysis (TD and PY)

Gases from a sample, heated two different times (one thermal desorption temperature ramp then one pyrolysis temperature), are transferred through a chromatographic column to the MS.

Output: Standard GC chromatogram and mass spectrum

Uses: Not only used to identify specific compounds, but with additional separation users see both volatiles as well as polymer information

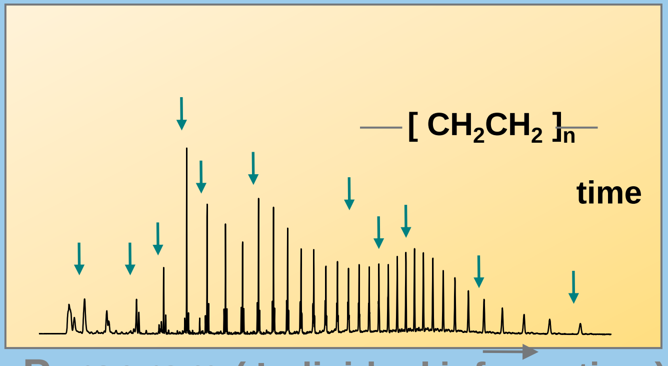
Heart-cutting Evolved Gas Analysis (HC/EGA)

Gases from a specific thermal zone of the sample are transferred through a chromatographic column to the MS.

Output: Standard GC chromatogram and mass spectrum

Uses: Obtain detailed characterization of a sample within a specific temperature range

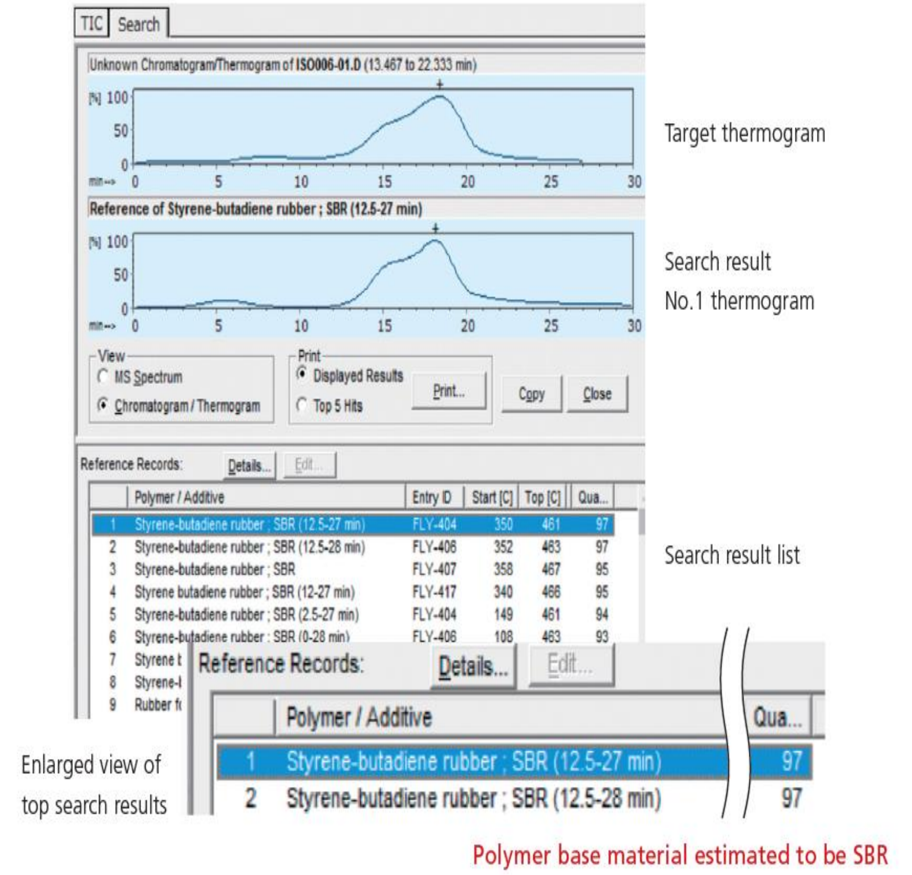
Polymer Pyrolyzate-MS Library (268 polymers/additives)



Pyrogram (Individual information)

Izasa Scientific
A Werfen Company

3.Pirólisis : Dual Shot y su Versatilidad para la identificación y/o cuantificación de MP’s y todos sus posibles componentes


TIC
Search
Unknown Chromatogram/Thermogram of ISO006-01.D (13.467 to 22.333 min)
[%] 100
50
0
min-->
0
5
10
15
20
25
30
Target thermogram
Reference of Styrene-butadiene rubber ; SBR (12.5-27 min)
Search result
No.1 thermogram
View
MS Spectrum
Chromatogram / Thermogram
Print
Displayed Results
Top 5 Hits
Print...
Copy
Close
Reference Records:
Details...
Edit...
Search result list
Enlarged view of
top search results

View: ○ MS Spectrum ● Chromatogram / Thermogram

Print: ● Displayed Results ○ Top 5 Hits

	Polymer / Additive	Entry ID	Start [C]	Top [C]	Qua...
1	Styrene-butadiene rubber ; SBR (12.5-27 min)	FLY-404	350	461	97
2	Styrene-butadiene rubber ; SBR (12.5-28 min)	FLY-406	352	463	97
3	Styrene-butadiene rubber ; SBR	FLY-407	358	467	95
4	Styrene butadiene rubber ; SBR (12-27 min)	FLY-417	340	466	95
5	Styrene-butadiene rubber ; SBR (2.5-27 min)	FLY-404	149	461	94
6	Styrene-butadiene rubber ; SBR (0-28 min)	FLY-406	108	463	93
7	Styrene t				
8	Styrene-l				
9	Rubber fo				

	Polymer / Additive	Qua...
1	Styrene-butadiene rubber ; SBR (12.5-27 min)	97
2	Styrene-butadiene rubber ; SBR (12.5-28 min)	97

Polymer base material estimated to be SBR

Fig. 2 Results from Compositional Analysis of Polymer Base Material Using Evolved GC/MS F-Search Polymer Library

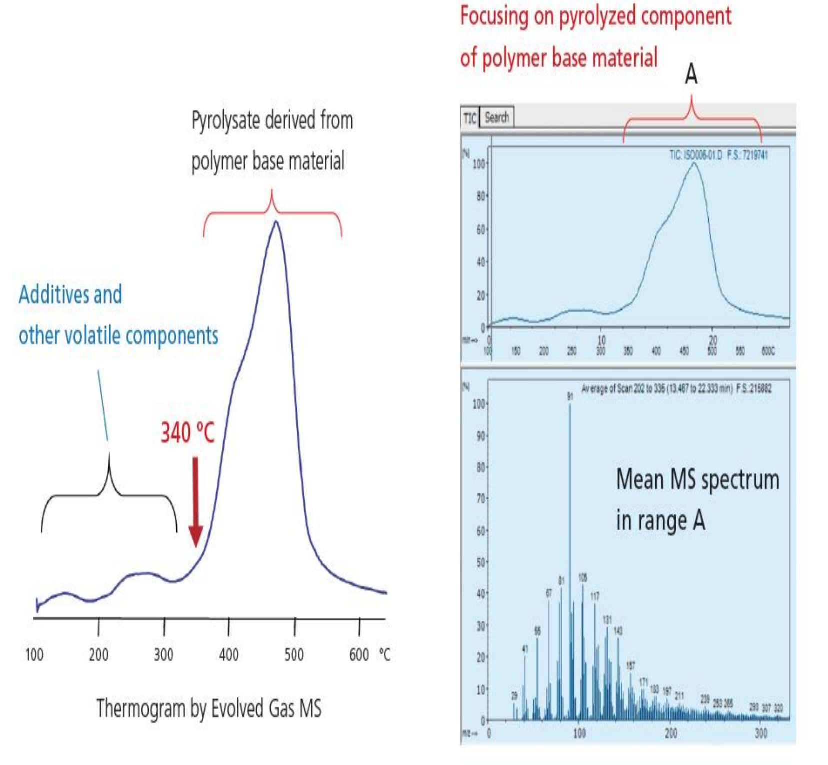
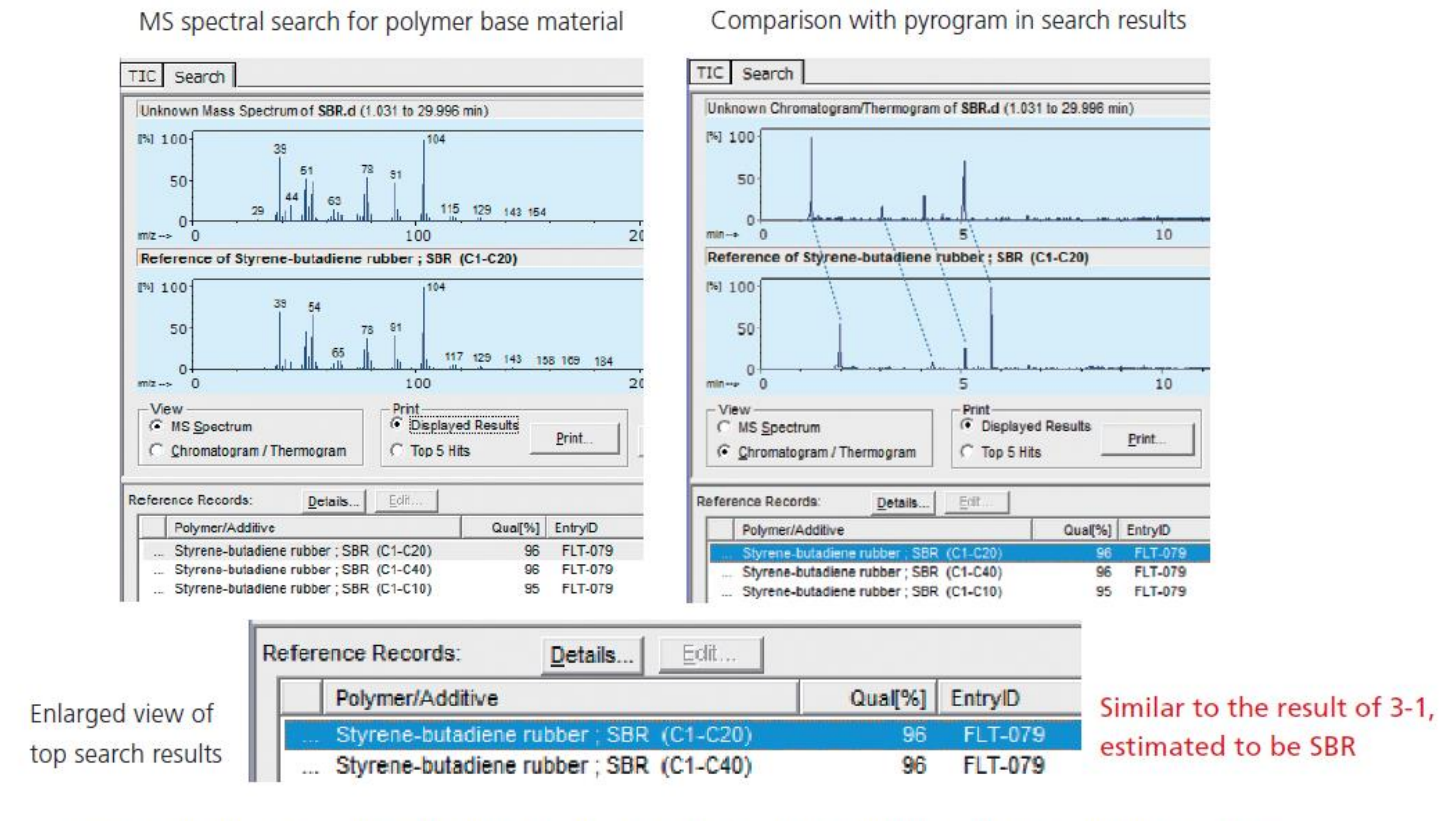


Fig. 1 Thermogram Obtained by Evolved Gas MS Analysis and MS Spectrum of Pyrolyzed Component of Polymer Base Material

3.Pirólisis : Dual Shot y su Versatilidad para la identificación y/o cuantificación de MP’s y todos sus posibles componentes



MS spectral search for polymer base material

Unknown Mass Spectrum of **SBR.d** (1.031 to 29.996 min)

Reference of Styrene-butadiene rubber ; SBR (C1-C20)

View: ● MS Spectrum ○ Chromatogram / Thermogram

Print: ● Displayed Results ○ Top 5 Hits

Reference Records:

	Polymer/Additive	Qual[%]	EntryID
...	Styrene-butadiene rubber ; SBR (C1-C20)	96	FLT-079
...	Styrene-butadiene rubber ; SBR (C1-C40)	96	FLT-079
...	Styrene-butadiene rubber ; SBR (C1-C10)	95	FLT-079

Comparison with pyrogram in search results

Unknown Chromatogram/Thermogram of **SBR.d** (1.031 to 29.996 min)

Reference of Styrene-butadiene rubber ; SBR (C1-C20)

View: ○ MS Spectrum ● Chromatogram / Thermogram

Print: ● Displayed Results ○ Top 5 Hits

Reference Records:

	Polymer/Additive	Qual[%]	EntryID
...	Styrene-butadiene rubber ; SBR (C1-C20)	96	FLT-079
...	Styrene-butadiene rubber ; SBR (C1-C40)	96	FLT-079
...	Styrene-butadiene rubber ; SBR (C1-C10)	95	FLT-079

Enlarged view of top search results

Reference Records:

	Polymer/Additive	Qual[%]	EntryID
...	Styrene-butadiene rubber ; SBR (C1-C20)	96	FLT-079
...	Styrene-butadiene rubber ; SBR (C1-C40)	96	FLT-079

Similar to the result of 3-1, estimated to be SBR

Fig. 3 Results from Compositional Analysis of Polymer Base Material Using Pyrolysis GC/MS F-Search Polymer Library

3.Pirólisis : Dual Shot y su Versatilidad para la identificación y/o cuantificación de MP’s y todos sus posibles componentes

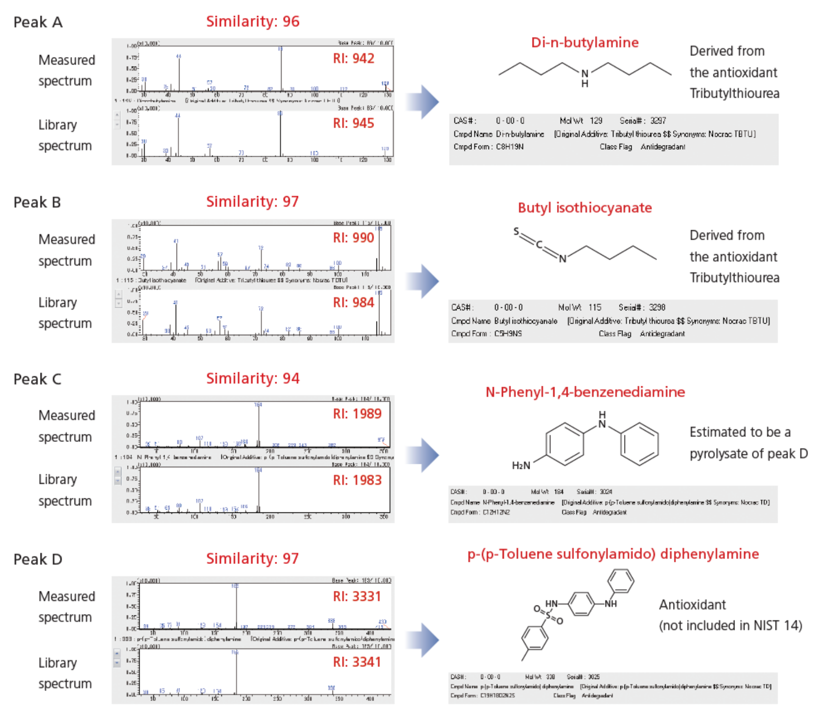


Fig. 5 Results from Qualitative Analysis of Peaks A, B, C, and D Using the Polymer Additives Library

Qualitative Analysis of Additives by Thermal Extraction GC/MS Analysis

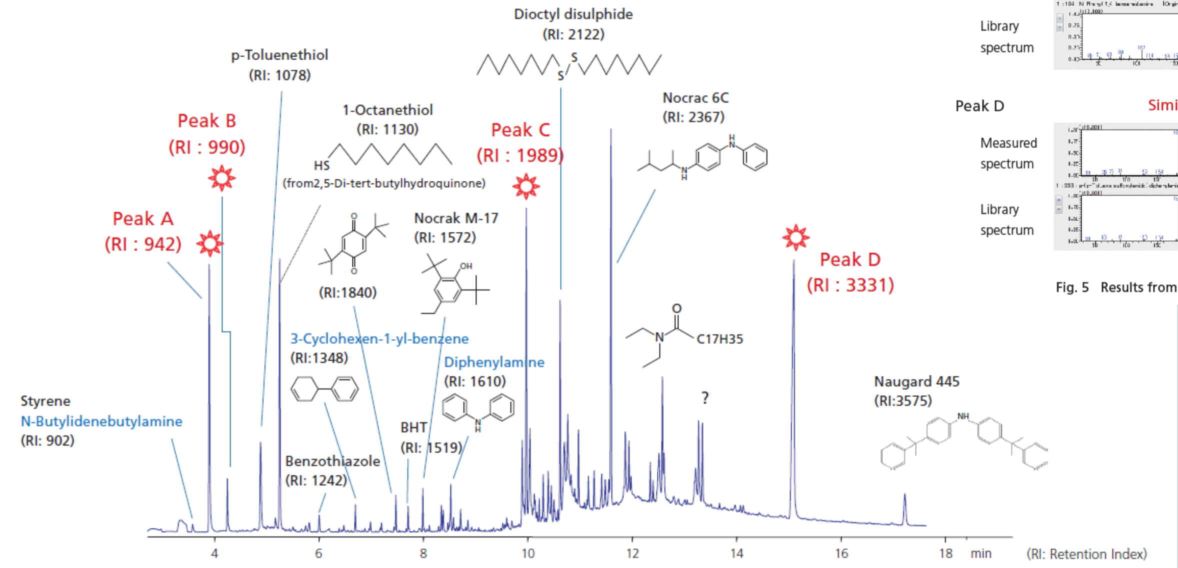


Fig. 4 Total Ion Current Chromatogram Obtained by Thermal Extraction GC/MS Analysis, and Results from Qualitative Analysis of Each Detected Peak

4.Conclusiones

- Las técnicas cromatográficas se presentan como una interesante y potente alternativa para el análisis de MPs.

- La variedad de sistemas de introducción de muestra, así como de analizadores de espectrometría de masas, permiten abordar el estudio de los MPs de interés y de los compuestos presentes en ellos, tales como aditivos del propio plástico y/o contaminantes adsorbidos.

- El desarrollo de métodos de análisis y de herramientas para la fácil identificación de dichas especies, supone un gran avance en la aplicación de las técnicas cromatográficas a la problemática de los MPs.

Gracias por su atención

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