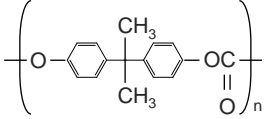# FRONTIER LAB

NEW

Microplastics Calibration Standard set
for MPs analysis using Py-GC/MS

The Microplastics (MPs) Calibration Standard (MPCS) is used to identify and quantify MPs using Py-GC/MS. It allows the user to easily create calibration curves for quantification of MPs. Two MPCS with different diluents (SiO_2 or $CaCO_3$) are available. Both MPCS contain a few µg each of commonly used 12 polymers which are homogeneously dispersed with a solid diluent for easy weighing on semi-microbalances.

MPCS information (12 polymers)

Diluents : Calcium Carbonate ($CaCO_3$) or Silicon dioxide (SiO_2)

$-(CH_2CH_2)_n$ Polyethylene (PE)	Polycarbonate (PC)	Acrylonitrile-butadiene-styrene resin (ABS)
$-[CH_2CH(CH_3)]_n$ Polypropylene (PP)	Poly(methyl methacrylate) (PMMA)	styrene-butadiene rubber (SBR)
$-(CH_2CH)_n$ Polystyrene (PS)	Polyethylene terephthalate (PET)	Polyurethane (PU)
$-(CH_2CH)_n$ Cl Polyvinyl chloride (PVC)	Nylon 6 (N6)	Nylon 66 (N66)

Selection of a MPCS from the two types of products

In most studies on Py-GC/MS analysis of environmental MPs, MPs are extracted from various matrices. After pretreatment processes, collected particles are put in a sample cup for pyrolysis. To enable easy weighing for the quantitative analysis of MPs, use of fine particles (SiO_2) as a diluent (Method-A) was reported, but PU showed unfavorable pyrolytic behavior for quantification (Ref.1).

When $CaCO_3$ was used as a diluent instead of SiO_2, the problem on PU quantification was eliminated due to the weak catalytic activity of $CaCO_3$ at a pyrolysis temperature of 600 ºC (Method-B, Ref. 2). With the MPCS, two types of diluents are available (A: MPs-SiO2 and B: MPs-CaCO3) so that one can select either method-A or method-B depending on the target polymers.

References
1) M. Matsueda et al., *J. Anal. Appl. Pyrolysis* 154 (2021) 104993.
2) T. Ishimura et al., *J. Anal. Appl. Pyrolysis* (in press).
3) K. Matsui et al., *J. Anal. Appl. Pyrolysis* 149 (2020) 104834.

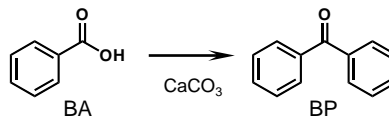# Use of catalytic action of CaCO$_3$ in the pyrolysis of polymers

● Polyurethane (PU)

One of major pyrolyzates of PU is methylenediphenyl diisocyanate (e.g., MDI). However, it is hard to quantitate PU using the MDI GC peak due to the high reactivity of MDI. Therefore, the more stable pyrolyzate, diamine (MDA), is preferred for quantitation of PU. CaCO$_3$, which has weak catalytic activity, reacts with MDI to form MDA in the pyrolyzer.

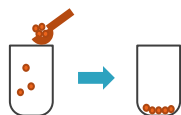OCN — MDI — NCO →(CaCO$_3$)→ H$_2$N — MDA — NH$_2$
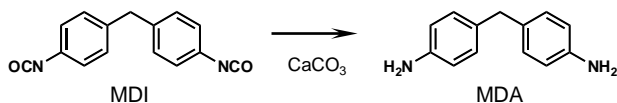
● Polyethylene terephthalate (PET)

One of major pyrolyzates of PET is benzoic acid (BA). However, it is hard to quantitate PET using the BA peak due to poor peak shape in pyrograms. Therefore, the more stable pyrolyzate, benzophenone (BP), is preferred for quantitation of PET. CaCO$_3$ reacts with BA to form BP in the pyrolyzer.
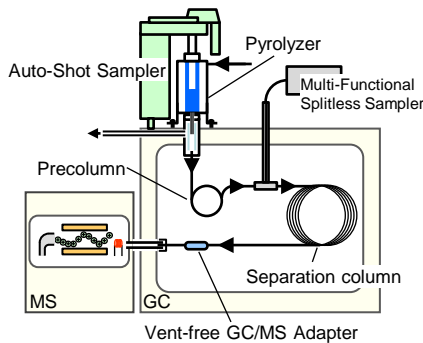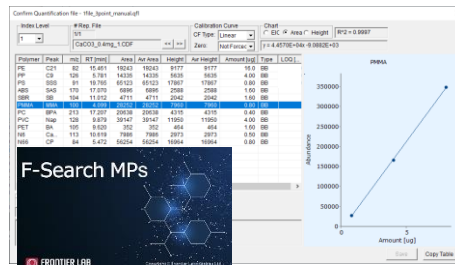
BA —(CaCO$_3$)→ BP

Example

1. Put 4 mg of MPCS into a sample cup

2. Py-GC/MS measurements

Auto-Shot Sampler, Pyrolyzer, Multi-Functional Splitless Sampler, Precolumn, Separation column, MS, GC, Vent-free GC/MS Adapter

3. Making calibration curves and quantitation of polymers in unknown samples based on a software, F-Search MPs 2.0 (Ref.3).

F-Search MPs
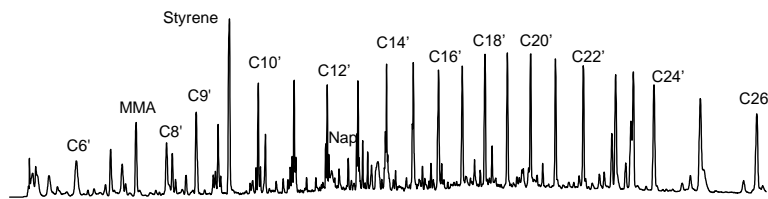
Pyrograms of MPCS

(EGA/PY-3030D, Py temp. 600 ºC)

4 mg of MPCS
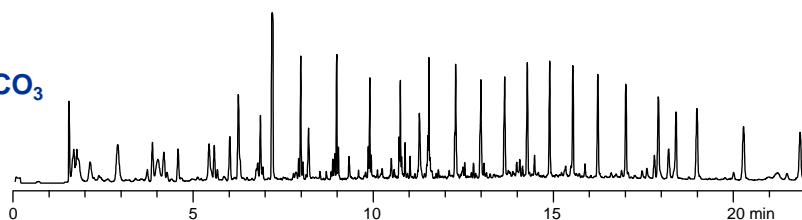(These are reference amounts. Refer to the inspection certificate attached to the product.)
PE: 160 µg, PP: 40 µg, PS: 8 µg, ABS: 16 µg, SBR: 16 µg, PMMA: 8 µg, PC: 4 µg, PVC: 40 µg, PU: 4 µg, PET: 16 µg, N6: 5 µg, N66: 18 µg, Diluent: 3.8 mg
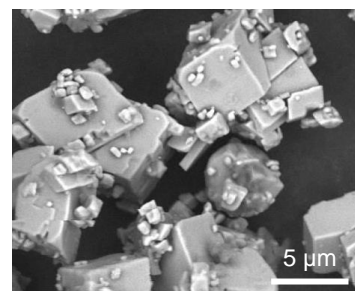
MPs-SiO$_2$

MPs-CaCO$_3$

SEM image of MPs-CaCO$_3$

5 µm

(CaCO$_3$ for cubes, others are MPs)

Contents of package

Microplastics Calibration Standard set (P/N：PY1-4940)			
Product name	Amount (g)	Qty.	Description
MPs-SiO2	1	1	MPCS for Method A, Diluent: SiO$_2$, this can be used for reactive pyrolysis using TMAH* reagent
MPs-CaCO3	1	1	MPCS for Method B, Diluent: CaCO$_3$
Diluent SiO2	3	1	SiO$_2$
Diluent CaCO3	3	1	CaCO$_3$
MPs-Quartz Wool	0.2	1	Use for preventing the scattering of powdered sample from a sample cup by putting some quartz wool on the sample in the cup
Micro Spatula 03	---	1	Sampling tool for small amount of solid sample

* tetramethylammonium hydroxide