Microplastic Calibration Using EasyPyCal™ Standards

Author:

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Application Note
Microplastics

Abstract
This application note demonstrates the use of a Pyroprobe 6150 with a commercially available mixed microplastics standard to build microplastic calibration curves

Introduction
ASTM D8401-24 defines a calibration-based method for the quantification of microplastics in water, in which polymer concentrations are set so their markers can be reliably quantified with minimal interference between polymers. However, preparing a mixed microplastic standard that contains all 12 microplastics specified is a time-consuming endeavor. It involves preparing 4 solutions of 10 soluble polymers, as well as a solid standard of the insoluble polymers, polypropylene and polyethylene, to be in a solid mineral diluent, which must be homogeneous. It is time-consuming, as well as not environmentally-friendly.

To ease the burden, LabTech CDS Analytical supplies the EasyPyCal™ Py-GC-MS calibration standard: ASTM D8401-24 kit developed by Microplastic Solution to support qualitative and quantitative analysis, allowing for easy calibration curve development. Having the 12 specified polymers evenly dispersed in $CaCO_3$ or SiO_2 helps for easy weighing milligram quantities on a semi-microbalance, in which the polymer themselves are in microgram amounts.

Experiment Setup
The vial containing EasyPyCal™ standard in $CaCO_3$ and 4 stainless steel balls was placed on a vortex blender for 3 minutes. Sample amounts 0.4 to 4 mg (exact weights recorded) were added to DISC tubes in triplicate for each level of 5 calibration levels.

Pyrolysis

Pyroprobe 6150 Autosampler

Pyrolysis: 600°C 40 sec

Interface: 300°C
Transfer Line: 325°C
Valve Oven: 300°C

Thermo Trace 1310 GC ISQ MS

Pre Column:
Rxi-17Sil MS (2m x 0.25mm x 0.25µm)
Column:
5% phenyl (30m x 0.25mm x 0.25µm)
Carrier:
He 1.25mL/min, 75:1 spl
Injector: 360°C
Oven: 40°C for 2 minutes
12°C/min to 320°C (20min)



Results and Discussion
The EasyPyCal™ standard contains Poly(ethylene) PE, poly(propylene) PP, poly(vinyl chloride) PVC, poly(ethylene terephthalate) PET, poly(styrene) PS, poly(carbonate) PC, styrene-butadiene rubber SBR, acrylonitrile-butadiene-styrene ABS, poly(methyl methacrylate) PMMA, Nylon 6 PA6, Nylon 6.6 PA6.6, and an MDI-based polyurethane PU in calcium carbonate, each one at concentrations specified in specified in ASTM Method D8401-24 designed to identify and quantify microplastic particles and fibers in water by Py-GC/MS.

Each polymer was identified and quantified using the an m/z of its specified target compound, provided in Table 1.

Table 1. Polymers and Target Ions.

Microplastic	Abbr.	Target Compound	m/z	R.T.
Polymethyl methacrylate	PMMA	Methyl Methacrylate	100	5.70
Nylon 6.6	N66	Cyclopentanone	84	7.14
Polypropylene	PP	2,4-Dimethyl-1- heptene	126	7.79
Styrene-Butadiene Rubber	SBR	4-Vinylcyclohexene	54	7.78
Polyvinylchloride	PVC	Naphthalene	128	13.58
Nylon 6	N6	Caprolactam	113	14.71
Polycarbonate	PC	4-Isopropenyl phenol	134	14.93
Polyethylene terephthalate	PET	Benzophenone	182	19.07
Polyethylene	PE	1,20-Heneicosadiene	82	22.68
MDI Polyurethane	PU	4-4'-Methylenedianiline	198	24.24
Acrilonitrile butadiene styrene copolymer	ABS	2-Phenyethyl-4-phenylpent-4-enenitrile	170	24.47
Polystyrene	PS	Styrene Trimer	91	28.10

Figure 1 provides Extracted Ion Chromatograms (EICs) of all the Target Ions.

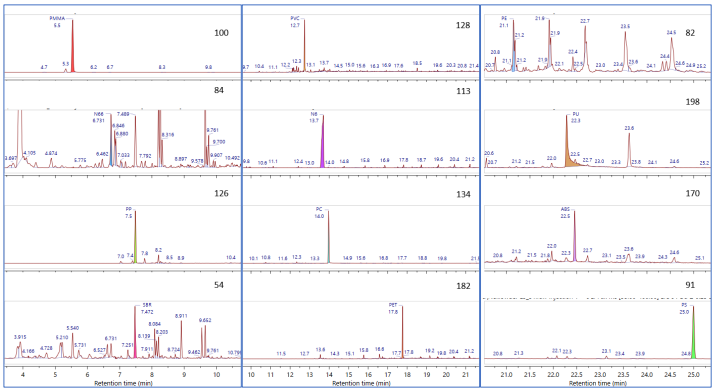


Figure 1. Extracted Ion Chromatograms of Target Ions.

The average calibrations yielded r^2 of 0.99 for every microplastic Target Ion.

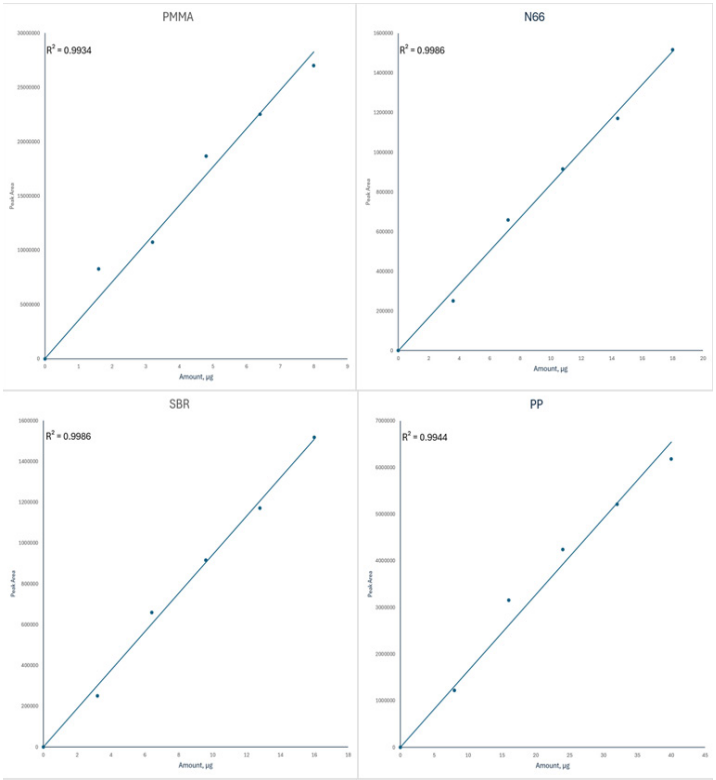


Figure 2. Target Ion Calibration Curves.

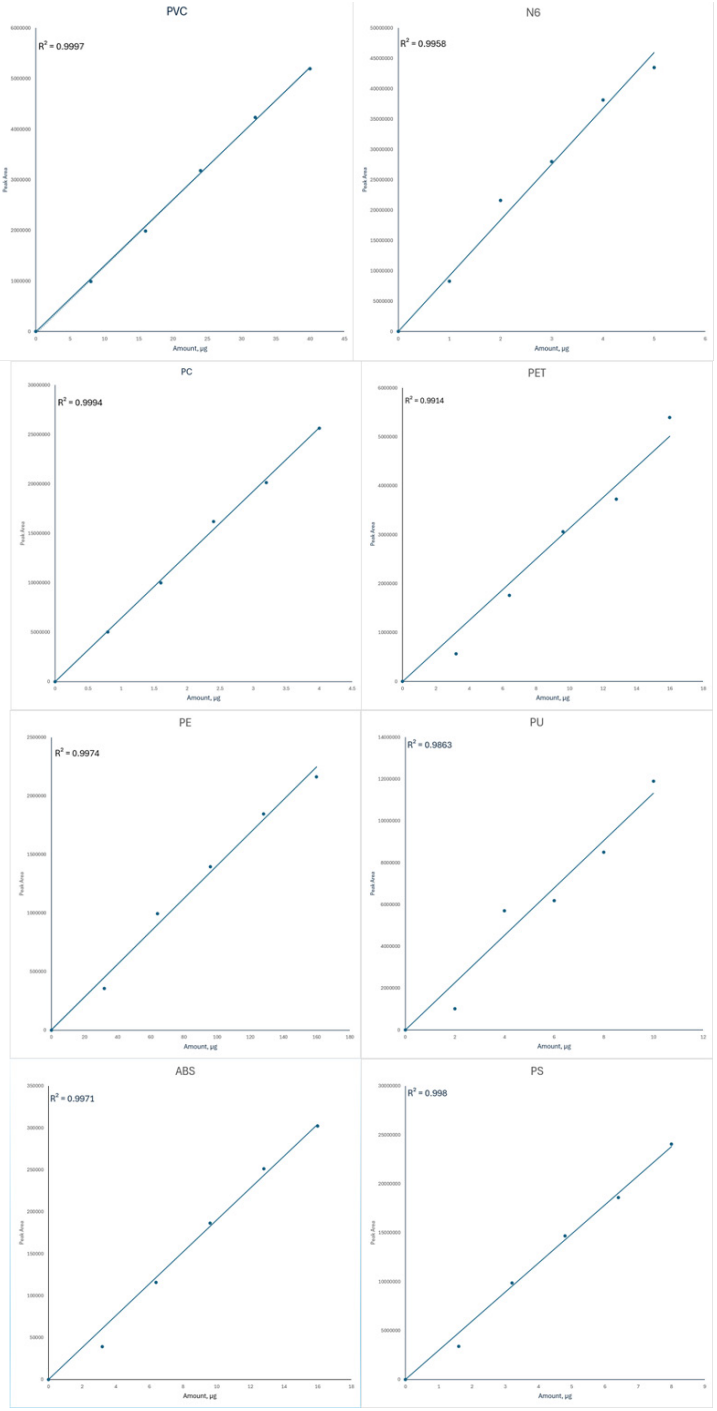


Figure 2 (cont'd). Target Ion Calibration Curves.

Conclusion

The powerful combination of an EasyPyCal™ Py-GC-MS microplastic calibration standard and a Pyroprobe from LabTech CDS Analytical assists productivity for quantitative microplastic analysis.

Microplastic Calibration Using the Expanded Capacity 6400 Pyroprobe Autosampler

Author:

Karen Sam





Application Note
Microplastics

Abstract
This application note demonstrates the use of a Pyroprobe 6400 that allows for larger sample sizes, with the EasyPyCal™ PY-GC-MS calibration standard, to build calibration curves for 12 commonly analyzed microplastics.

Introduction
In applications such as microplastics analysis, analytes may only be present in small amounts of the entire sample. For example, microgram quantities of microplastics could be deposited on a larger filter. The increased capacity (50µL) of the Pyroprobe 6400 allows for larger amounts of sample to be analyzed, therefore increasing the sensitivity of the technique. Here, the Pyroprobe 6400 was used to create calibration curves using the EasyPyCal™ PY-GC-MS calibration standard of 12 commonly analyzed microplastics in $CaCO_3$(CDS p/n 6203-5095), as a verification of the new design's precision and accuracy in the field of microplastics analysis.

Experiment Setup
The vial containing EasyPyCal™ standard in $CaCO_3$ and 4 stainless steel balls was placed on a vortex blender for 3 minutes. Sample amounts ranging from 0.4 to 4 mg (exact weights recorded) were added to 6400 DISC tubes in triplicate for each level of 5 calibration levels.

Pyrolysis

Pyroprobe 6400 Autosampler

Pyrolysis: 600°C 40 sec

Interface: 300°C
Transfer Line: 325°C
Valve Oven: 300°C

GC-MS

Column:
5% phenyl (30m x 0.25mm x 0.25µm)
Carrier:
He 1.00mL/min, 30:1 spl
Injector: 300°C
Oven: 40°C for 2 minutes
12°C/min to 280°C (20min)
Ion Source: 230°C
Mass Range: 35-400amu

Results and Discussion
Compared to the Pyroprobe 6150 and 6200 models, 6400 uses larger sample tubes. This helpful for applications in which a high volume is helpful to quantify the polymeric portions in an inorganic matrix, such as micro/nanoplastics on a glass fiber filter. Here, the EasyPyCal™ standard containing 12 commonly used analyzed microplastic polymers in calcium carbonate, each one at concentrations specified in specified in ASTM Method D8401-24, was used to generate calibration curves on the newly designed instrument.

Each polymer was identified and quantified using the an m/z of its specified target compound, provided in Table 1.

Table 1. Polymers and Target Ions.

Microplastic	Abbr.	Target Compound	m/z	R.T.
Polymethyl methacrylate	PMMA	Methyl Methacrylate	100	2.87
Nylon 6.6	N66	Cyclopentanone	84	3.92
Polypropylene	PP	2,4-Dimethyl-1- heptene	126	4.62
Polyvinylchloride	PVC	Naphthalene	128	9.52
Nylon 6	N6	Caprolactam	113	10.40
Polycarbonate	PC	4-Isopropenyl phenol	134	10.90
Styrene-Butadiene Rubber	SBR	4-Phenylcyclohexene	104	11.28
Polyethylene terephthalate	PET	Benzophenone	182	14.40
Polyethylene	PE	1,20-Heneicosadiene	82	17.50
MDI Polyurethane	PU	4-4'-Methylenedianiline	198	18.50
Acrilonitrile butadiene styrene copolymer	ABS	2-Phenyethyl-4-phenylpent-4-enenitrile	170	18.90
Polystyrene	PS	Styrene Trimer	91	20.80

Figure 1 provides Extracted Ion Chromatograms (EICs) of all the Target Ions.

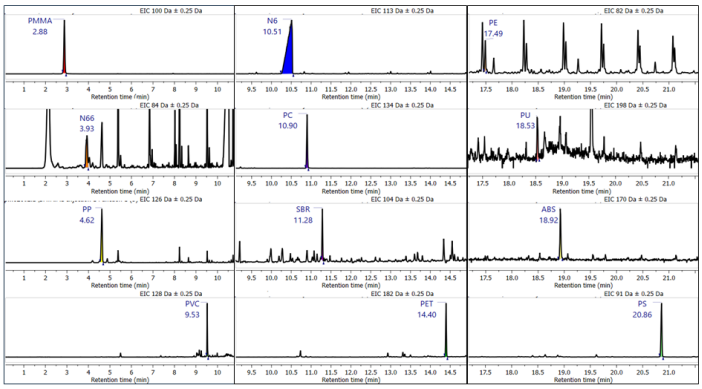


Figure 1. Extracted Ion Chromatograms of Target Ions.

The average calibrations yielded an R^2 of 0.99 or above for every microplastic Target Ion (Figure 2).

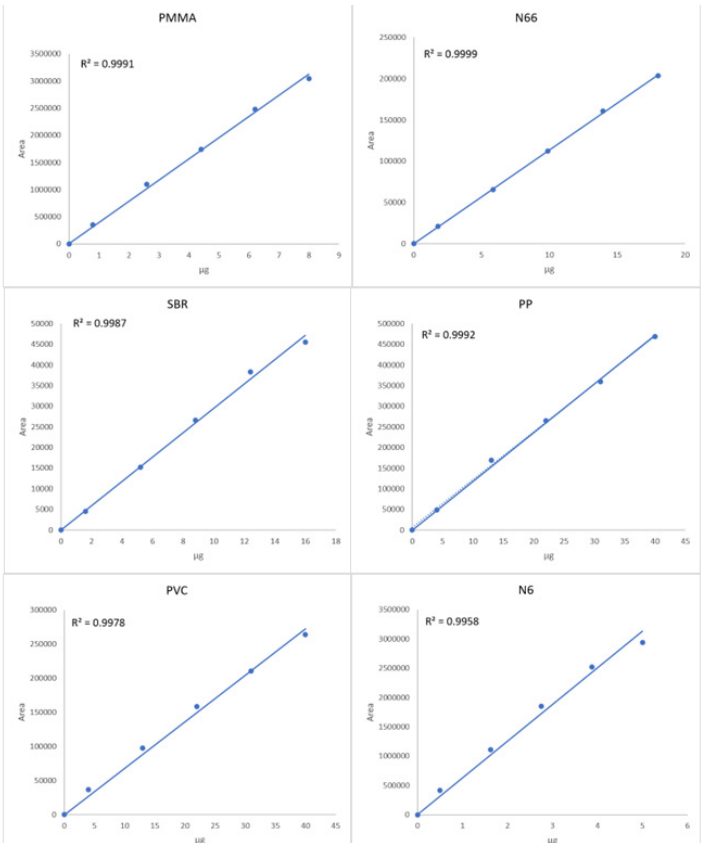


Figure 2. Target Ion Calibration Curves.

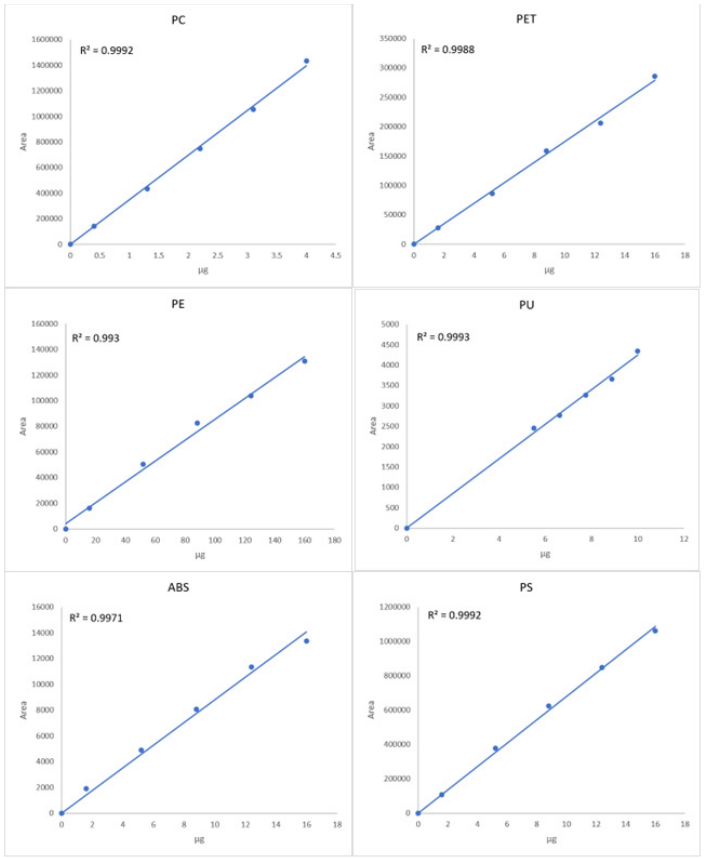


Figure 2 (cont'd). Target Ion Calibration Curves.

Conclusion

The effective combination of the EasyPyCal™ Py-GC-MS microplastic calibration standard and the Pyroprobe 6400 Autosampler with increased sample capacity provides for easy and reliable quantitative analysis in microplastic applications.

References

1. Sam, Karen D. "Chapter 11 - Pyrolysis-gas chromatography " in Gas Chromatography (Second Edition) Handbooks in Separation Science ,2021, Pages 325-342.

2. CDS Application Note #295, Microplastic Calibration Using an EasyPyCal™ Standard.