Microplastic Analysis and Additive Screening using Thermal Desorption/Pyrolysis DART-MS

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Introduction

Microplastics are small plastic particles (≤ 5mm) that result from both commercial product development and the breakdown of larger plastics. Microplastics are abundant in our environment and come from variety of sources. Commercial sources include cosmetics, clothing, and other textiles to other pieces of plastics such as water bottles that breakdown with radiation. Microplastics are not a single type of contaminant but a wide variety consisting of flame retardants, plastic stabilizers, and colorants. Currently microplastics have been detected at an alarming level in our marine life and drinking water.

The presented methodology combines direct analysis in real time (DART) ionization with an ionRocket thermal desorption and pyrolysis (TDP) stage (BioChromato Inc., Fujisawa, Japan). The addition of this platform permits for precise control of the temperature (up to 600°C) over a desired time frame. This allows compounds in the sample to be sublimated, vaporized, or pyrolyzed according to their volatility, and then introduced into the DART metastable gas stream. Sample preparation is not required as a small solid cutting of the sample (< 5mg) is placed directly in the heating device. The high-resolution mass spectrometer from Bruker, impact II quadrupole time-of-flight, was used to collect all spectra.

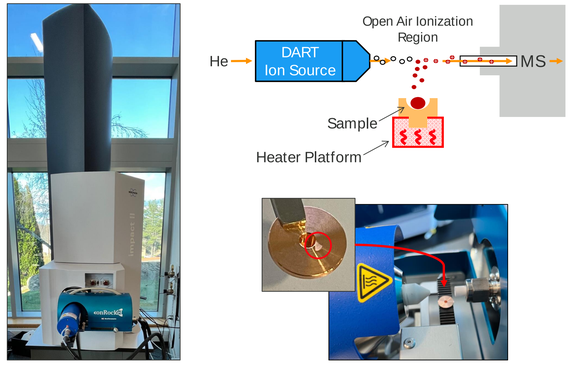


Figure 1. TDP-DART Setup and Schematic on Bruker Impact II QTOF

Methods

The DART source conditions for the experimental study are as follows: 300 °C DART gas heater temperature, 1.5 kV discharge needle voltage, and 350 V grid electrode voltage. High-purity helium (99.998%, 80 psi) was used for ionization.

The temperature profile of the ionRocket was programmed as follows:

Segment No.	Rate (°C/min)	Temperature (°C)	Run Time (min)
Initial	-	30	0.2
1	100	600	6.4

A small amount (< 5mg) of solid samples were loaded onto the copper-pot (fig. 1). Plastics were collected from various sources and cut down to < 5mm in size to mimic particles found in authentic samples. 3 different plastics of known sources and 1 unknown sample were analyzed using autoMS/MS. High-resolution full scan and MS/MS data was collected simultaneously.

Results

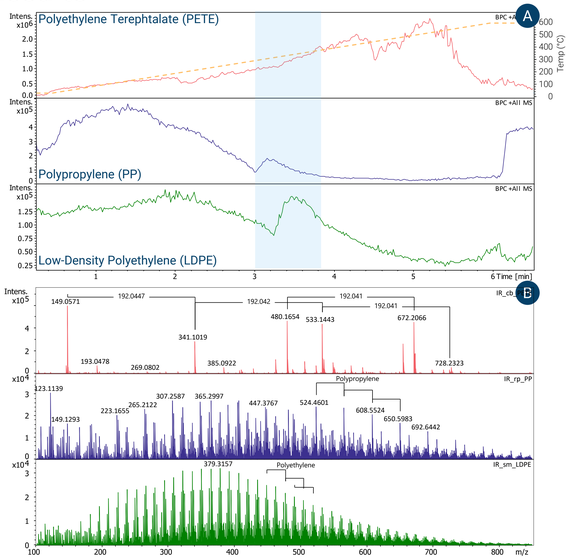
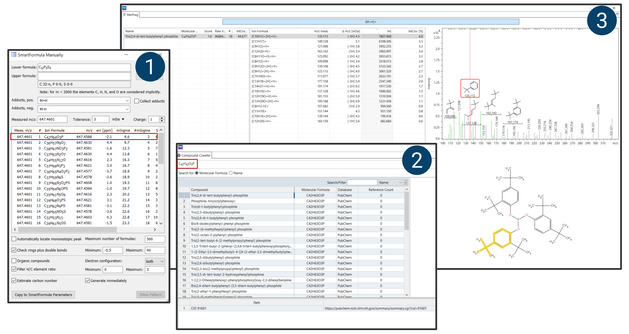


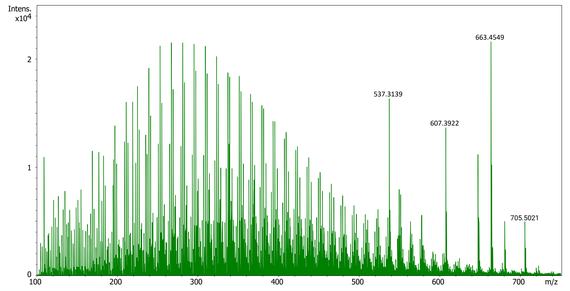
Figure 2. (A) Base peak chromatograms of 3 different types of plastics. ionRocket thermal program outline with the yellow, dashed line. **(B)** Spectra extracted from the portion shaded in light blue.



Unknown ions were identified using search tools built in to MetaboScape

1. SmartFormula calculates the elemental composition based on accurate mass and isotope pattern
2. CompoundCrawler searches structures for the elemental composition determined with online databases (e.g., ChemSpider, ChEBI, and PubChem) as well as user-generated databases (Analyte DB)
3. MetFrag is then used to predict ion formation and subsequent fragmentation patterns of arbitrary small molecules and validate putative annotations of tandem mass spectrometry data.

Figure 3. Mass chromatogram of LDPE highlighting some of the additives observed with TDP-DART-MS



Compound	Formula	$(M+H)^+$	Description
Tris(2,4-ditert-butylphenyl)phosphate	$C_{42}H_{63}O_3P$	663.4549	Oxidized Irgafos 168 (stabilizer)
Tris(4-tert-butyl-2-methylphenyl) phosphate	$C_{33}H_{45}O_4P$	537.3139	Breakdown product of Irgafos 168
(2-Tert-butylphenyl) bis(2,4-ditert-butylphenyl) phosphate	$C_{38}H_{55}O_4P$	607.3922	Breakdown product of Irgafos 168
Tris(nonylphenyl) phosphate	$C_{45}H_{69}O_4P$	705.5021	Oxidized Naugard P (antioxidant/stabilizer)

Summary

MetaboScape® 2023 (Bruker, Inc.) was used for statistical evaluation. Multivariate statistics (PCA) of 3 analyses for each plastic samples resulted in accurate grouping. The loading plot (fig. 4) also displays features that are unique to the different plastic types.

An unknown plastic sample was analyzed and processed under the same conditions as the known samples. Based on the clustering within the PCA plot, results suggest that the plastic is made up of PETE, a common plastic used in the production of beverage bottles and food containers.

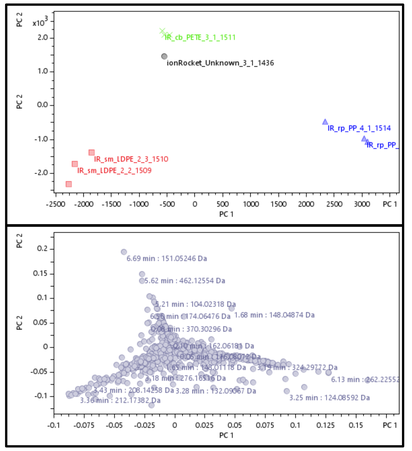


Figure 4. PCA and loading plot of plastic samples

Conclusion

- The presented method requires no sample preparation and allows for quick screening of plastics with TDP-DART-MS,
- Resulting high-resolution MS and MS/MS data can be quickly processed and matched against existing libraries.
- Data can also be identified using tools built into the software thus constantly expanding a user-generated library.
- Continued work will further characterize different plastic materials of various origins.

Thermal Desorption/Pyrolysis DART QTOF-MS