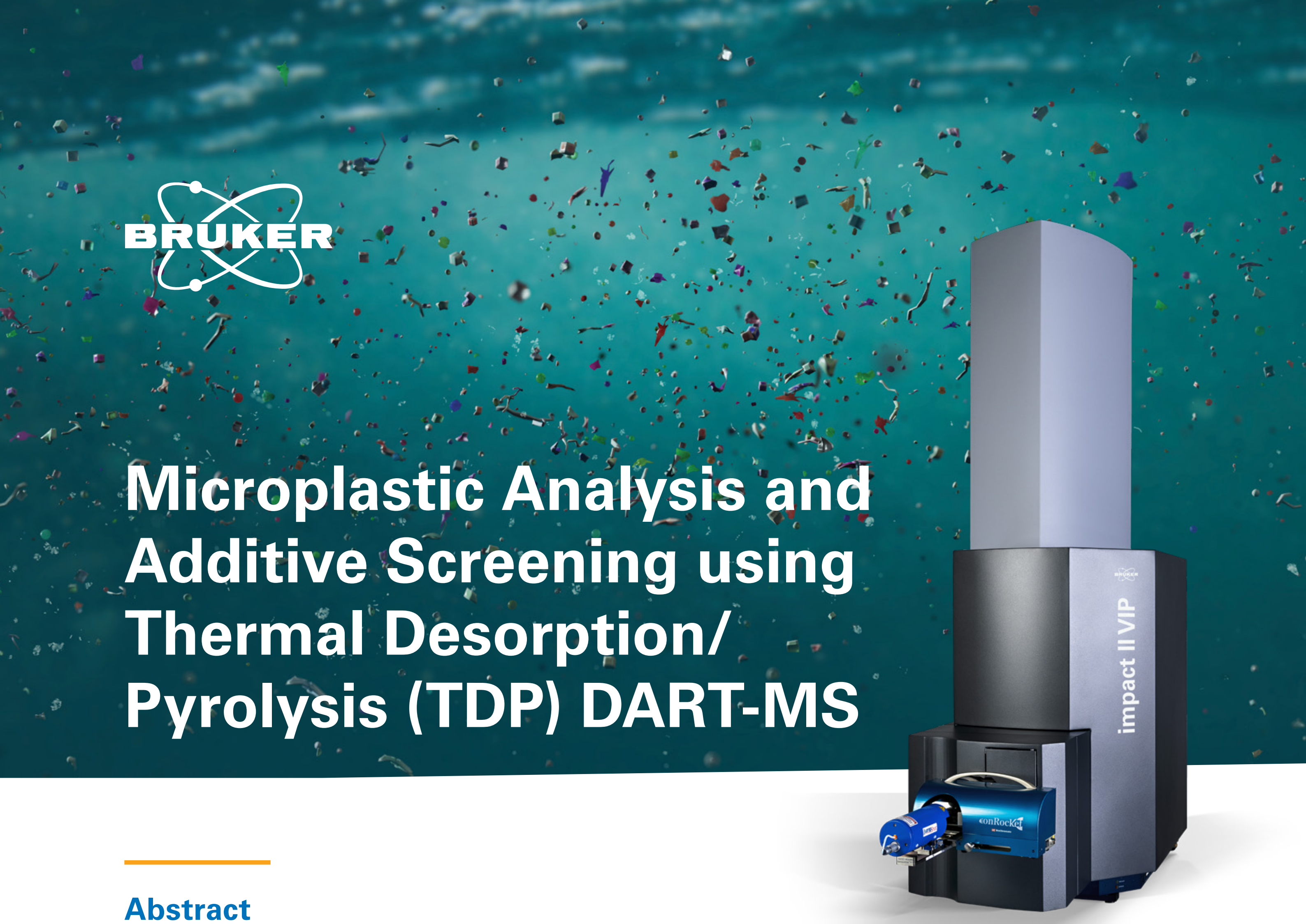

Microplastic Analysis and Additive Screening using Thermal Desorption/ Pyrolysis (TDP) DART-MS

Abstract

Microplastics are more often appearing as contaminants in important water sources including our oceans and drinking supply. As threats to human and animal health, these particles require accurate and flexible methods of detection so they can be monitored and minimized. For this purpose, we present a novel and unique technology combination of thermal desorption/pyrolysis (ionRocket), Direct Analysis in Real-Time (DART) and high resolution mass sprectrometry HRMS. With technology now available in the form of DART ionization source with an IonRocket stage using the process of thermal desorption/pyrolysis (TDP-DART-MS), it is possible to examine samples based on their volatility and generate high resolution MS and MS/MS results for improved detection and characterization of these concerning contaminants.

Keywords:
microplastics, DART, HRMS, QTOF, thermal desorption/ pyrolysis (TDP)

Introduction

Microplastics are small plastic particles ≤ 5mm in size that result from both commercial product development and the breakdown of larger plastics. These small particles are abundant in our environment and originate from a variety of sources including commercial products such as cosmetics, clothing and textiles, as well 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, and the need to monitor and measure them accurately is important and obvious.

The methodology described here 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 novel platform allows for a precisely controlled temperature increase up to 600°C over a programmed time frame. This facilitates the sublimation, vaporization and pyrolysis of compounds in the sample according to their volatility prior to being introduced into the DART metastable gas stream. Sample preparation is not required as a small solid cutting of the sample of < 5 mg is placed directly in the heating device. The high resolution mass spectrometer from Bruker, impact II VIP quadrupole time-of-flight, was used to collect all spectra.

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Materials and Methods

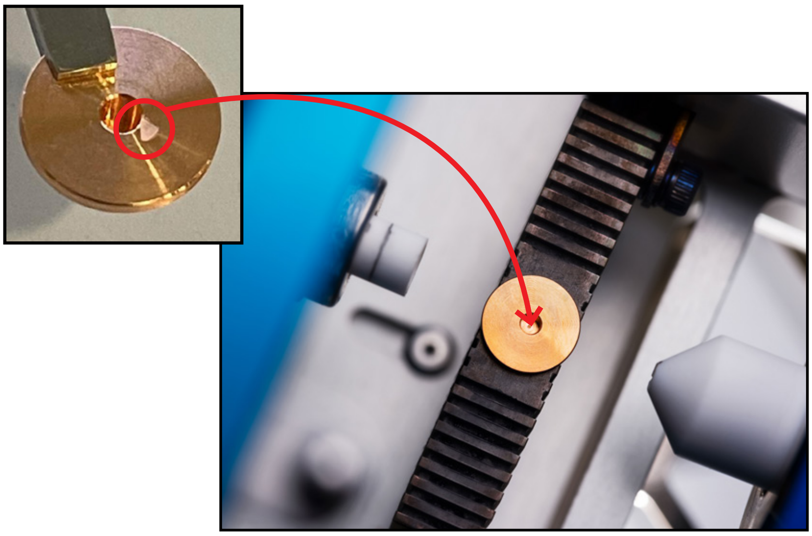
MS and DART Source

MS analysis was performed using the BRUKER impact II VIP QTOF. The DART source conditions for the experimental study were 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

Sample Preparation

Three types of plastics were evaluated: Polyethylene Terephthalate (PET), Polypropylene (PP), and Low- Density Polyethylene (LDPE) from various sources. Additionally, an unknown plastic was analyzed. A small amount of < 5 mg for the solid samples was loaded onto the copper pot as shown in the figure below. Plastics were cut down to < 5mm in size to mimic particles found in authentic samples. The three different plastics of known sources and the unknown sample were all analyzed using autoMS/MS on a BRUKER impact II VIP QTOF system. The high-resolution full scan and MS/MS data were collected simultaneously.



Data Analysis

MetaboScape® (Bruker, Inc.) is an all-in-one software platform for robust data processing, encompassing retention time alignment, deisotoping, and feature extraction. It supports automatic annotation of target compounds through user-defined analyte lists and offers tools for identifying unknown compounds using library matching and *in-silico* fragmentation. The software provides a range of statistical analyses, quality scoring, and pathway mapping. It supports known compound databases, customized data export and a client server architecture for efficient data processing. Unknown ions were identified using search tools built in to MetaboScape. Specifically, **SmartFormula** was used to calculate the elemental composition based on accurate mass and isotope pattern. **CompoundCrawler** was employed to search structures for the elemental composition using online databases (e.g., ChemSpider, ChEBI, and PubChem) as well as user-generated databases (Analyte DB). **MetFrag** was then used to predict ion formation and subsequent fragmentation patterns of arbitrary small molecules and validate putative annotations of tandem mass spectrometry data.

Results and Discussion

The standard samples and spectra were used to help identify the components of the unknown plastic sample. Fig. 1 shows the base peak chromatograms (BPC) for each plastic with the y-axis on the left reflects the relative intensity. The dotted orange line was superimposed to visualize the previously described temperature program that was applied to the copper pot. This is a temperature ramp from room temperature to 600°C with the x-axis representing the time-scale (minutes) and y-axis (right) the temperature (°C). These plots examine the ionization profile as function of temperature. TDP-DART analysis allows for different compounds to desorb in order of their volatility along the temperature gradient, and thus are separated in time. For example, in polymer analysis, it is possible to observe chemical residues, additives, or vaporized dyes at lower temperatures (< 250°C), the polymer chain at mid-level temperatures (> 300°C), and further breakdown products at high temperatures (> 450°C). Average mass spectra of the light blue shaded portion for each chromatogram can be seen in Figure 2.

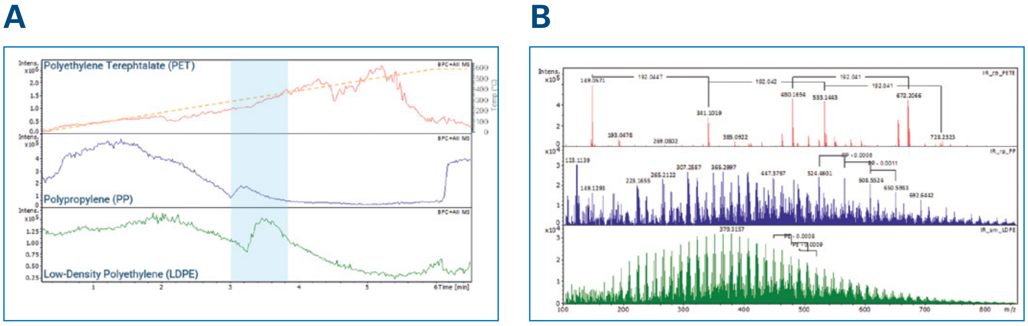


Fig. 1 impact II VIP QTOF chromatograms and mass spectra of plastics
A: Base peak chromatograms for (top) Polyethylene Terephthalate (PET), (middle) Polypropylene (PP), and (lower) Low-Density Polyethylene (LDPE). The unique features in each chromatogram enable the use of these profiles as representative patterns.

B: Spectra were extracted from the portion shaded in light blue for an observation time between 3 and 4 min. All spectra differ significantly for the three standards.

In Figure 2, extracted mass spectra were generated for each plastic when the ionRocket temperature program was between ~300 and 400°C. At this temperature range the polymer structure begins to break down into oligomers. The annotation of the ions observed in the spectra can label the repeating unit within the chain and identify the polymer type (repeating mass units of 192 Da for PET, 42 Da for PP and 28 Da for PE).

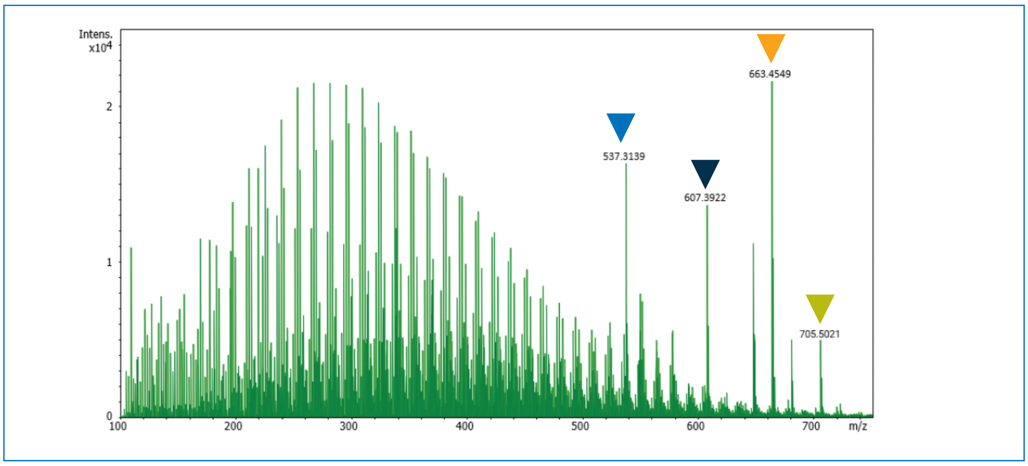
When LDPE was looked at more closely using TDP-DART-MS, some of the additives can be seen clearly as shown in Figure 3 below, and as identified in 1. The mass chromatogram was extracted around 250°C, and at this temperature the polymeric breakdown of LDPE can be observed on the left side of the spectrum whereas the ions observed on the right side were identified using MetaboScape.

As TDP-DART-MS is a chromatography-free analysis, retention-time based identification cannot be used. However, given that the experiment was collected on a high-resolution-MS/MS platform, accurate mass, isotopic patterns, and fragmentation patterns can all be used within MetaboScape to identify the selected ions. Specifically, SmartFormula was used to calculate the elemental composition based on accurate mass and isotope pattern. CompoundCrawler was employed to search structures for the elemental composition using online databases (e.g., ChemSpider, ChEBI, and PubChem) as well as user- generated databases (Analyte DB). MetFrag was then used to predict ion formation and subsequent fragmentation patterns of arbitrary small molecules and validate putative annotations of tandem mass spectrometry data.

Compound	Formula		[M+H]$^+$	Description
Tris(2,4-ditert-butylphenyl)phosphate	$C_{42}H_{63}O_4P$	▼	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)

Table 1
Additives of LDPE

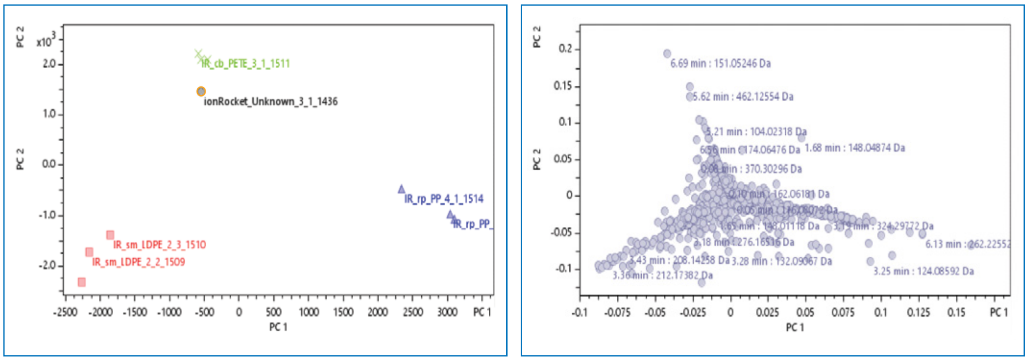
Fig. 3 Mass Spectrum
Collected at 250°C to highlight some of the additives observed with TDP-DART-MS for LDPE (see Table 1).



MetaboScape was also used for the statistical evaluation and identification of the unknown plastic. Multivariate statistics (PCA) of 3 analyses for each of the known plastic samples resulted in accurate grouping. The loading plot (Figure 4) also displays features that are unique to the different plastic types.

The unknown plastic sample was analyzed (orange circle) 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 PET, a common plastic used in the production of beverage bottles and food containers.

Fig. 4 PCA and Loading Plot
Statistical results and the loading plot for the three known sourced plastics and one unknown.



Conclusions

This presented TDP-DART-HRMS method required no sample preparation and allowed for the rapid and direct screening of plastics of known and unknown sources without the need of any chromatographic separation. The unique combination of thermal desorption, direct ionization, high-resolution mass spectrometry and sophisticated post-processing software for compound identification and statistics resulted in a comprehensive investigation. The resulting high-resolution MS and MS/MS data was quickly processed and used to match against existing libraries with successful identification of the components that were present in the unknown sample. With this set of tools, data can also be identified using features that are built into the software. This allows users to constantly expand their own generated libraries as they continue to monitor and identify the contaminating microplastics that are present in critical water sources.

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