

# ionRocket: An innovative Thermal Desorption and Pyrolysis Device for Direct Analysis in Real Time-Mass Spectrometry (DART-MS) for Rapid Characterisation of Difficult Samples

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Direct analysis in real time-mass spectrometry († DART-MS) enables rapid analysis of both solid and liquid samples under ambient (open laboratory) conditions without sample preparation. However, certain samples are difficult to analyse using DART-MS due to the varying volatility of substituents in complex samples. Furthermore, fibres and powders can be challenging to keep in place in the DART gas stream. To overcome these challenges, an innovative sample introduction device called 'ionRocket' has been developed, which gradually heats a sample placed directly beneath the DART gas stream. Gradient heating of the sample before ionisation creates time/temperature resolved mass spectra, separating species both by their thermal desorption profiles and  $m/z$ . Samples are placed in a small single-use copper vessel before heating. This both facilitates thermal transfer and also provides the option to weigh samples prior to analysis. Weighed samples yield reproducible mass spectra intensity, allowing calibration curves of analyte amount vs peak intensity to be calculated. The change in temperature by time separates compounds based on volatility thus providing an additional axis of data similar to a chromatogram, while maintaining minimal sample preparation.

## Introduction:

Direct analysis in real time-mass spectrometry (DART-MS) enables nearly instantaneous determination of sample composition using mass spectrometry. Therefore, DART-MS is a powerful method for analysis of sample mixtures. For example, many polymers are difficult to volatilise using DART because of the thermal energy required to break chemical bonds into smaller fragments. Furthermore, the temperature at which compounds vaporise varies based on volatility. If the DART gas temperature is too low, samples will not vaporise efficiently. However, too much heat transfer risks decomposition of compounds and thus cannot be analysed. Samples containing complex matrices can be difficult to resolve desired peaks due to these differences in volatility between compounds. Analysis of oil additives is one example. To enable analysis of difficult samples by using DART-MS, an innovative device for DART-MS, called 'ionRocket' was developed, which induces thermal desorption and pyrolysis of samples [1-3]. The vapour phase of polymer samples is generated by applying a temperature-controlled heating gradient, then ionised and introduced into the mass spectrometer.

Liquid or solid samples are introduced just below the DART stream in a small copper vessel where they are heated directly using an electronic resistive heater (Figure 1a-c), in a controlled manner, from room temperature to 600°C typically at a rate of 100°C/min. Compounds are then vaporised and ionised using the DART source

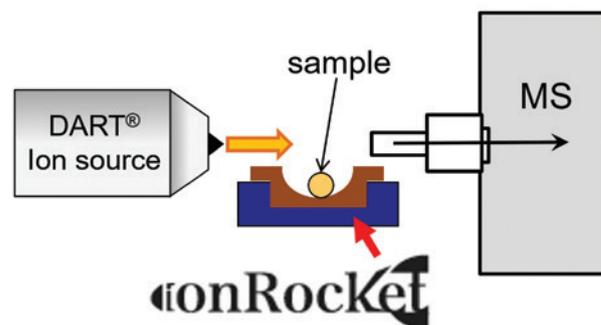


Figure 1a. Diagram of ionRocket between DART ion source and Mass Spectrometer.

and analysed using mass spectrometry. Initially, as the temperature rises, more volatile compounds thermally desorb at relatively low temperatures from around 100-300°C, this can be defined as the thermal desorption region. Then, at higher temperatures around 400-600°C, pyrolysis products of polymers and other compounds can be detected with a specific thermal decomposition pattern based on the material composition, considered the pyrolysis region. Thus, the Thermal Desorption and Pyrolysis (TDP) device 'ionRocket' coupled with DART-MS (TDP/DART-MS) offers detailed information on the sample material composition in minutes without any sample preparation.



Figure 1b. ionRocket coupled with DART placed directly on the Mass Spectrometer front end.

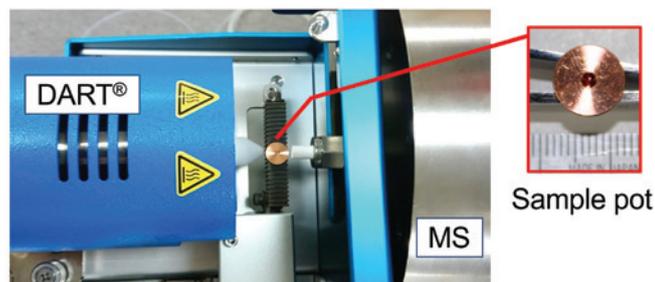


Figure 1c. Top view of the copper vessel 'Sample Pot' inserted into ionRocket heater between the DART source and MS front end.

## Application challenges

Lubricating oil is composed of base oil and additives. Synthetic base oils and various functional additives (e.g. antioxidants, detergent-dispersants, etc.) are used in the development of lubricants for machinery, automobiles, and other industries. Thus, it is important to obtain detailed information on base oils and additives, for market research, research and development, and quality control. In order to analyse the base oils and additives of lubricating oils, in traditional analysis, complicated pretreatment may be required, which takes time and effort. Thermal Desorption and Pyrolysis combined with Direct Analysis in Real Time- Mass Spectrometry (TDP/DART-MS), is a useful method for qualitative and quantitative analysis of lubricating oil.

Polymers and resins (e.g. Nylon-6) present a unique challenge for many mass spectrometry systems. MALDI permits the direct characterisation of repeating units, but requires identifying a solvent/matrix system which allows both the polymer and the matrix to first dissolve and then subsequently co-crystallise. Furthermore, polymers with higher polydispersity ( $M_w / M_n > 1.2$ ) can be extremely difficult to analyse, due to both MS ionisation and instrumentation limitations.

Traditional pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) obviates the need for compatible solvents, but frequently depends on the searching of spectra from py-GC/MS databases for identification of unknowns. Molecular weight distribution data can also be lost, since only pyrolysis products are seen. (TDP/DART)-MS does not require dissolution or other preparation of the sample prior to introduction to the Mass Spectrometer. It also permits the individual measurement of both low molecular weight pyrolysis products and thermally desorbed (but not pyrolysed) products, as well as potential for molecular weight distribution analysis. This combination provides valuable information for elucidating the chemical structure of unknown compounds, including polymers with higher dispersity and mixtures containing reactants and degradants. Both TDP/DART-MS and MALDI-MS can also be used for examining terminal functional groups in unknown polymer samples.

As a comparison with other analytical techniques for polymers, we outline 3 methods, namely 1) py-GC/MS, 2) MALDI-MS, and 3) TDP/DART-MS, for analysis of the homopolymer Poly (butyl acrylate), PBA. In this work, the resulting data from these analytical approaches are compared by looking at the repeating unit, molecular weight distribution, and terminal functional groups for a sample of PBA.

## Results and Discussion

### Nylon-6

As an illustration of analysis using TDP/DART-MS, a small sample of nylon-6 was placed in the copper sample vessel. The sample was heated from room temperature to 600°C at a rate of 100°C/min. and the total ion current (TIC) was measured over time.

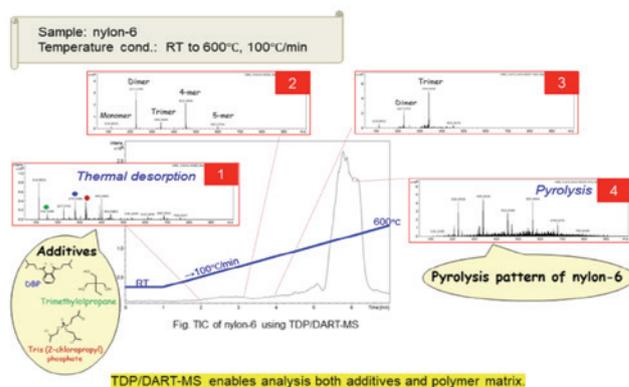


Figure 2.

Mass spectra was separated by time (temperature). The additives Dibutyl Phthalate (DBP), Trimethylolpropane, and Tris (2-chloropropyl) phosphate could be detected at relatively lower temperatures (~200-300°C) in the thermal desorption range. Then, as the temperature increased, polymer fragments of nylon could be detected at higher temperatures, along with a specific pyrolysis pattern of nylon-6 (Figure 2).

## Determination of Polymers

Polymer materials can quickly be identified using TDP/DART-MS. As an example of this, various polymer samples were separately placed in the copper vessel, where they were heated from room temperature to 600°C at a rate of 100°C/min.

## Identification of polymers using TDP/DART-MS

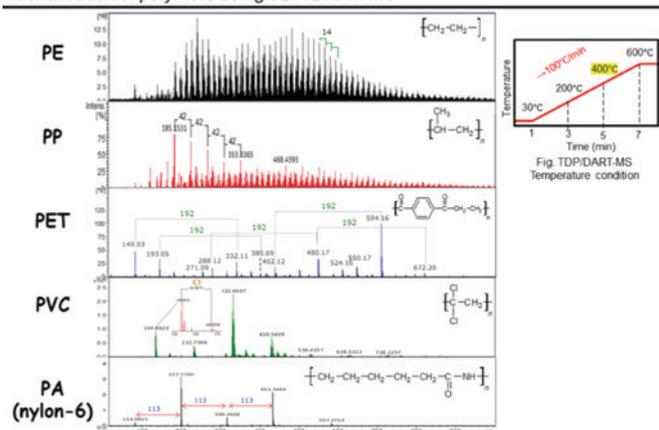


Figure 3. Mass Spectra of Polymers Using TDP/DART-MS at 400°C

Mass spectra taken at 400°C was compared, and each polymer (PE, PP, PET, PVC, nylon-6) could be differentiated based on the repeating units (Figure 3). Thus, TDP/DART-MS is a simple and rapid method for identification of polymers.

## Lubricating Oil

Samples of automotive engine oil were taken at different driving distances: 0 km, 1,000 km, and 5,000 km. Samples were compared using FT-IR and TDP/DART-MS. As a result of FT-IR, no significant difference was detected among samples (Figure 4).

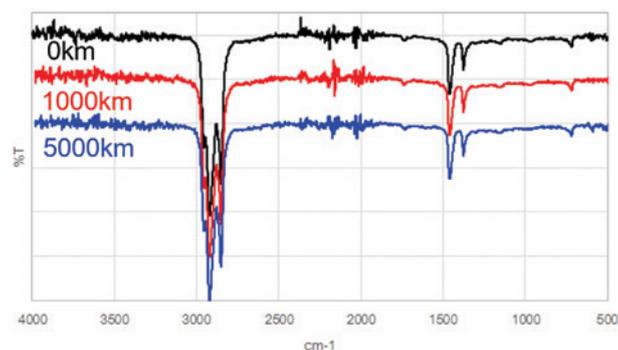


Figure 4. FT-IR of engine oil samples after 0, 1,000, and 5,000 km use.

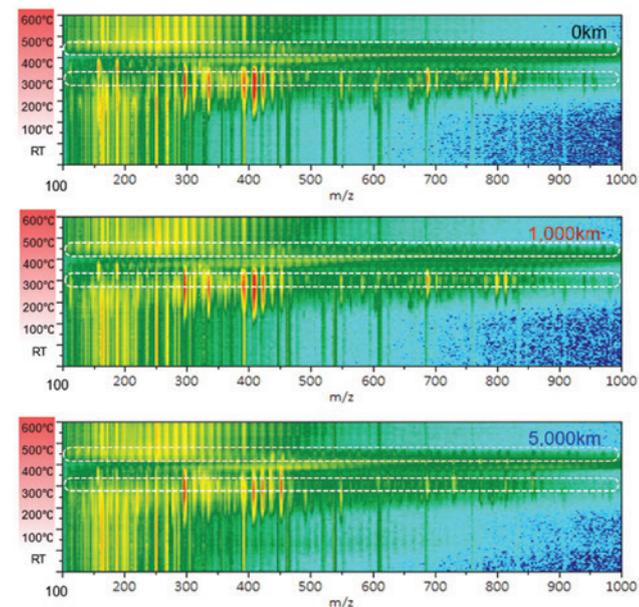


Figure 5. Heat Map

A heat map (horizontal axis: m / z, vertical axis: temperature) of each sample was shown from all the samples (Figure 5).

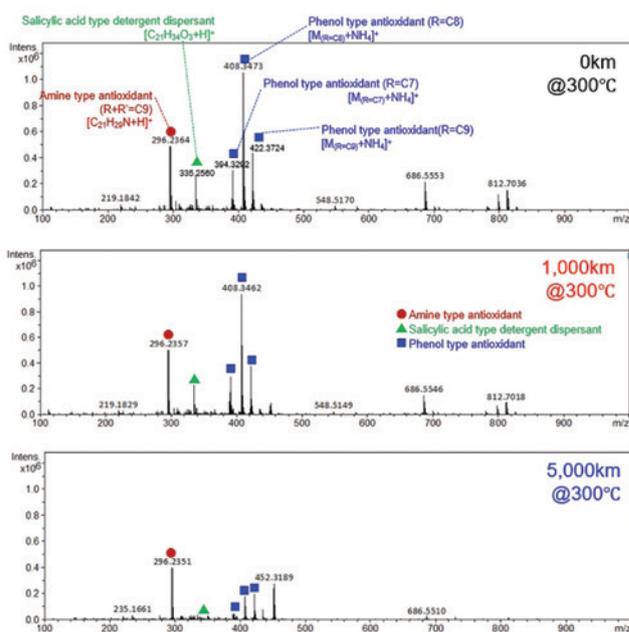


Figure 6. Mass Spectra at 300°C

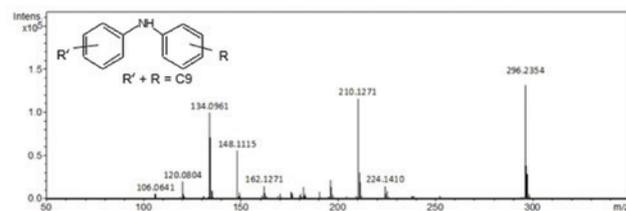


Figure 6a. MS/MS Spectra of m/z 296.23

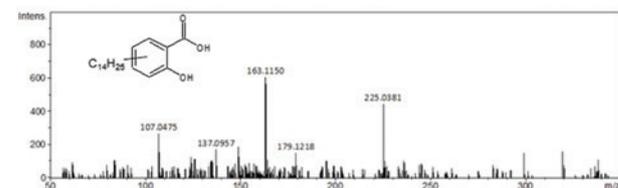


Figure 6b. MS/MS Spectra of m/z 335.25

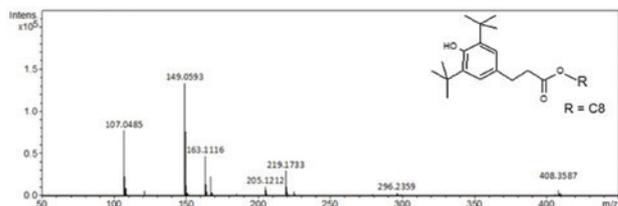


Figure 6c. MS/MS Spectra of m/z 408.34

MS spectra at 300 deg. C (Figure 6) and MS/MS spectra of select compounds (Figures 6a-6c) are shown. By analysing these spectra, additives were characterised including a phenol type antioxidant, an amine type antioxidant, and a salicylic acid type detergent-dispersant. There was no significant difference in the ratio of additive components at 0 km and 1,000 km running, but at 5,000 km, salicylic acid detergent-dispersant and the phenolic antioxidant were significantly decreased. MS spectra at 450 are shown in Figure 7.

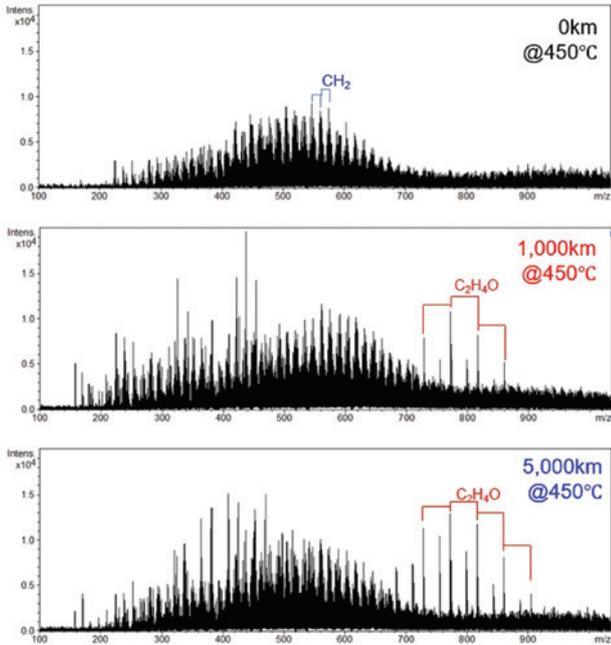


Figure 7. Mass Spectra at 450°C

In the mass spectra of the 0 km sample, the base oil was mainly detected. At 1,000 km, glycol compounds were also detected, and at 5,000 km, the glycol compounds were remarkably increased. In addition, the spectral pattern of the base oil compounds changed with the increase in mileage. Thus, these spectra provide information on the degradation state of base oil. By using this analysis method, it is clear that structural information for additives and base oil in automotive engine oils can be detected without any pretreatment of the samples. In addition, since it is possible to analyse structural information of additives and base oils in degraded automotive engine oils, this technique can be applied to evaluate the degradation degree of automotive engine oils and maintenance of machinery equipment.

Polymer Poly(butyl acrylate), PBA (Sigma Aldrich) was analysed by Py-GC/MS (Pyrolyzer: PY-2020iD, Frontier Lab, GC/MS: QP2010, Shimadzu, 6890GC/5975MSD, Agilent), MALDI-MS (autoflex speed, Bruker), and TDP/DART-MS (TDP: ionRocket, BioChromato, Ion Source: DART-SVP, IonSense, MS: Compact, Bruker) for the characterisation of the repeating unit, molecular weight distribution, and terminal functional groups.

Repeating Unit

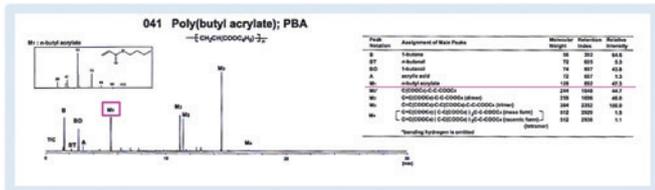


Figure 8. Pyrogram and Peak Assignment Table of PBA using Py-GC/MS

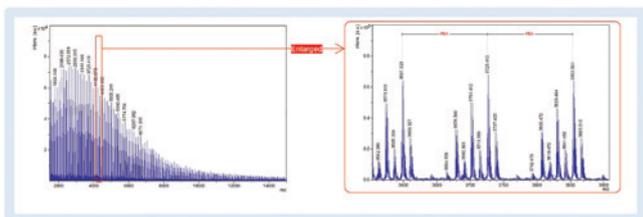


Figure 9. Mass Spectra of PBA Using MALDI-MS (reflector mode)

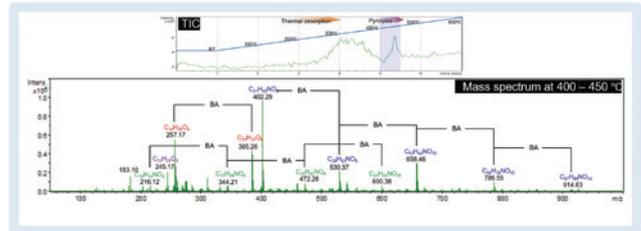


Figure 10. TIC and Mass Spectrum at Pyrolysis Region of PBA Using TDP/DART-MS

Py-GC/MS enables identification of polymer type using the available spectral library of pyrolysis products [4] (e.g. F-Search, Frontier Lab), (Figure 8).

MALDI-MS enables identification of polymer type using the observed mass interval corresponding to the mass of the repeating unit or the elemental compositions calculated from the mass (Figure 9).

TDP/DART-MS enables identification of polymer type without spectral library using the observed elemental compositions of the repeating unit (Figure 10).

Molecular weight distribution

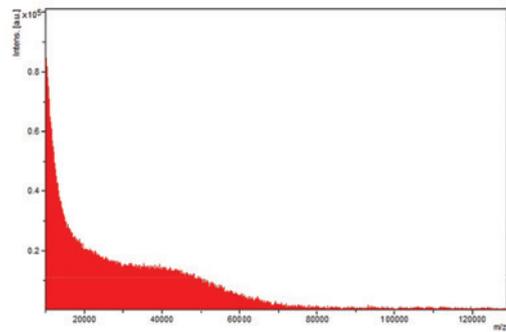


Figure 11a. Mass Spectra of PBA Using MALDI-MS (liner mode)

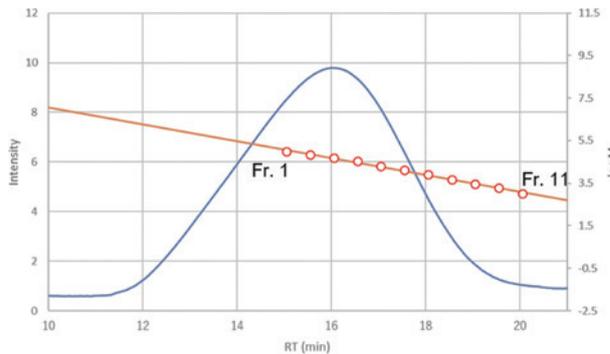


Figure 11b. SEC Curve for PBA

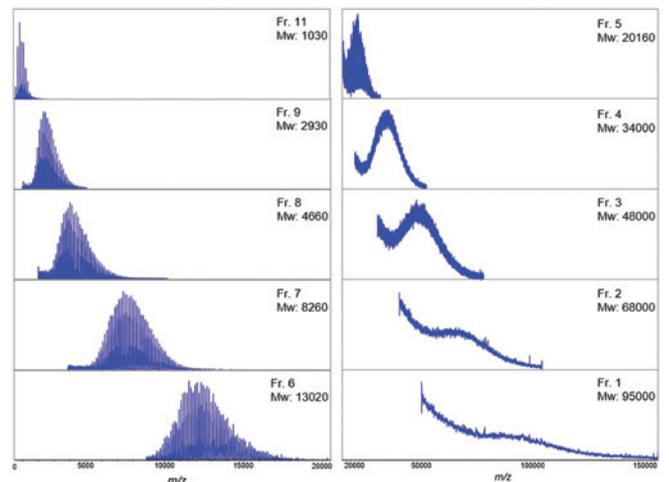


Figure 12. Mass Spectra of PBA Using SEC/MALDI-MS

