Application for Forensic Analysis: Discrimination of Fibers using Trace Organic Additive and Pyrolyzate Marker

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Introduction

Scientific examination of miscellaneous evidence collected at the crime scene is required to extract information during a criminal investigation.

The direct analysis in real time (DART) ion source is one of the ambient ionization methods reported by Robert B. Cody et al. in 2005 [1]. It is excellent in versatility and speed, as ionization occurs easily by holding the sample over an ion source. However, when a product consisting of a polymer material such as cloth or plastic is to be analyzed, it is difficult to observe the peak of the target compounds. Therefore, we developed a thermal desorption/pyrolysis (TDP) unit for DART-MS, which consists of a device capable of directly heating the sample from room temperature to 600 °C. Besides, it has been confirmed to be usable for identification of additives and polymer matrices in polymer material products.

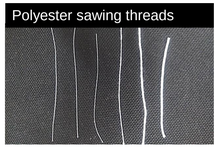
In this presentation, it is shown that TDP/DART-MS can be used for both identification and comparison of polymer material products.

1) R. B. Cody, J. A. Laramée & H. D. Durst, Anal. Chem., 77, 2297-2302 (2005)

Materials and Methods

Samples

6 kinds of white polyester sawing threads (commercial products)



Analytical methods: TDP/DART-MS (Fig. 1)

Sample (ca. 0.2 mg) were used for measurement.

Mass Spec. : compact (Bruker)
Ion Source : DART®-SVP (IonSense)
Ionization gas : Helium
Gas temperature : 400℃
TDP device : ionRocket (BioChromato)
Temperature : RT → 600℃ (100℃/min)

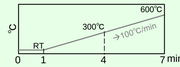


Fig.2 Temperature program of TDP device

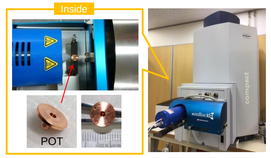
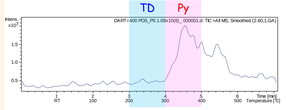


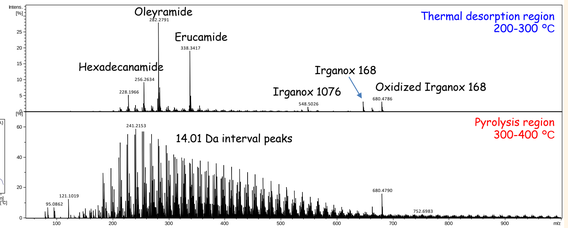
Fig.1 TDP/DART-MS system

Introduction for TDP/DART-MS data

This method enables acquisitions both additives and polymer pyrolyzates, respectively, without sample pretreatment.



TIC of sample using TDP/DART-MS



Mass spectra of sample at thermal desorption/pyrolysis region

This analytical method is powerful tool for rapid & easy identification.

Results and discussions

Reproducibility of TDP/DART-MS

Overwriting of TIC and EIC shows good reproducibility.

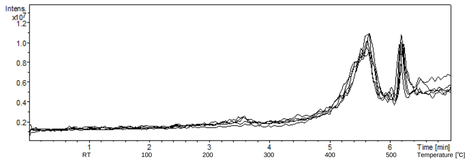


Fig.2 Overwriting of TIC using TDP/DART-MS

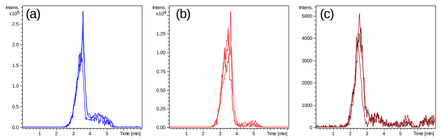
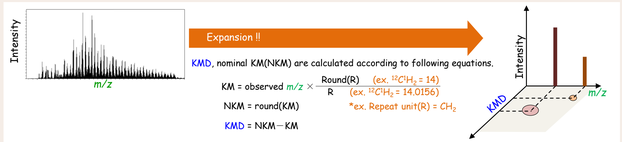


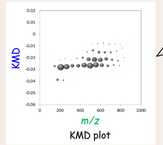
Fig.3 Overwriting of EIC using TDP/DART-MS;
(a) *m/z* 291.11; phosphate ester type additive, (b) *m/z* 600.52; fatty acid amides (FAAs) ,
(a) (c) *m/z* 350.32; polyethylene glycol ethers of tridecyl alcohol.

Table1 . Reproducibility for EIC peak area by TDP/DART-MS

	Peak area value (n=4)				Average	Standard deviation	Coefficient of variation
m/z 291.11 ±0.001	9045346	8662186	9411450	8470357	8897334.8	417862.3	4.7 %
m/z 600.52 ±0.001	438070	490901	482518	474295	471446.0	23260.6	4.9 %
m/z 350.32 ±0.001	151063	156313	165768	153401	156636.3	6455.5	4.1 %

Kendrick mass defect (KMD) plot [2,3]





Horizontally aligned plots show that terminal group, side chain are same, but the number of R are different.

Horizontally aligned plots lines show that R is same, but terminal group, side chain are different.

2) E. Kendrick, *Anal. Chem.* 35, 2146-2154, 1963
3) H.Sato, S.Nakamura, K.Teramoto, T.Sato; JASMS, 2014, 25(8), 1346-1355

Results of Discrimination

Characteristic mass peaks of additives were observed in each sample, at thermal desorption region.
Polyester type were identified by analyzing pyrolysis mass spectra.
KMD plot was useful for finding the difference among samples.

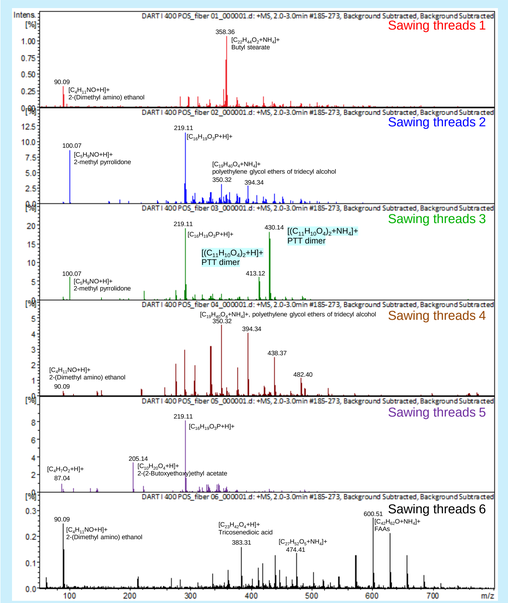


Fig.4 Mass spectra of at thermal desorption region using TDP/DART-MS

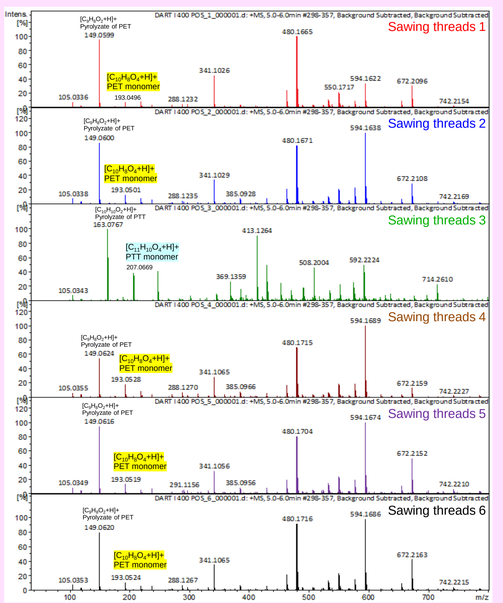


Fig.5 Mass spectra of at pyrolysis region using TDP/DART-MS

Expansion !!

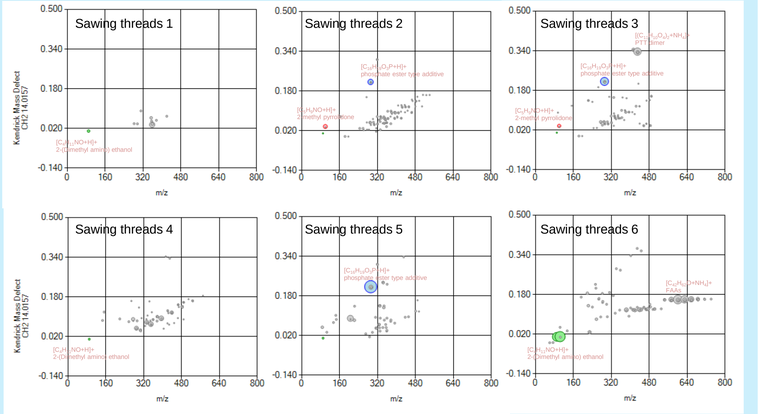


Fig.6 KMD plots converted from mass spectra at thermal desorption region, (base unit: CH_2)

Conclusion

By using TDP/DART-MS, additives contained in sawing threads and polyesters pyrolyzates were detected at thermal desorption region and pyrolysis region, respectively. Moreover, all the samples were distinguished by using additives and pyrolyzates as marker. This analysis method is useful for discrimination of not only sawing threads but also plastic products.