Identification of fine plastic materials by Thermal Desorption and Pyrolysis Combined with DART-MS (TDP/DART®-MS)

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Introduction

Evidentiary materials in criminal cases come in many forms, and many aspects, such as fine segments of fiber or bits of resin, are difficult to find with the naked eye. Adhesive sheets are often used in cases where collecting such materials directly using instruments like tweezers proves difficult. In addition, fine materials to be used as evidence collected using adhesive sheets are most commonly used for distinguishing purposes, such as identifying differences among the materials attached to the sheet. When attempting to identify distinctions in materials collected with adhesive sheets, a search operation is performed to locate fine particles for close examination under stereoscopic microscopy. Locating the target object is the most important task during this operation after distinguishing the various attached fine materials, and is highly labor-intensive. The difficulty of the search task can increase if the attached fine materials are of similar color to the adhesive sheet. Moreover, even if a fine particle can be collected from the adhesive sheet, the instrumental analysis such as FT-IR analysis is affected by the adhesive compound adhered to a fine particle slightly, so the difficulty of distinguishing task can also further increase [1].

Recently, we have reported some plastic materials analysis results using Thermal Desorption and Pyrolysis combined with DART- MS (TDP/DART®-MS), and it is a useful analysis method for complex mixture samples without any requirement for sample pre-treatment, since TDP device enables simple sample separation using gradient heating. And it is also a useful for a fragment of synthetic fibers.

In this study, we performed a direct examination of segments of adhesive tape affixed with fine plastic materials. As the results of our subsequent analysis using the Kendrick Mass Defect (KMD) analysis [2,3] suggested the feasibility of identifying and qualifying fine plastic materials without confounding influence from the adhesive tape.

Materials and Methods

◆ Samples :

Samples were consisted by adhesive tape and “fine plastics” (Fig.1).

Adhesive tape
- scotch tape

Model of “fine plastics”
- nylon-6
- polylactic acid (PLA)
- polyethylene glycol (PEG)

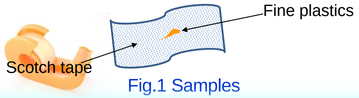
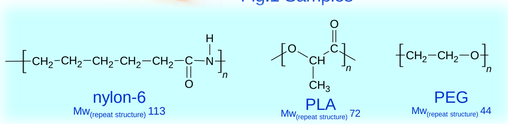


Fig.1 Samples

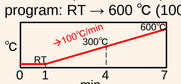


◆ Analytical methods :

TDP/DART-MS (Fig.2)

Small pieces (0.5 mm x 0.5mm) of sample were put into the POT. Mass spectra were measured as the samples were heated. For KMD analysis, the software named Spectra Scope (BioChromato) were used.

Mass Spec.: micrOTOF-Q III (Bruker)
Mass range : *m/z* = 100 - 2000
Ion Source: DART®-SVP (IonSense)
Ionization gas : Helium
Helium gas temperature : 400 ℃
TDP device: ionRocket (BioChromato)
Temperature program: RT → 600 ℃ (100 ℃/min)



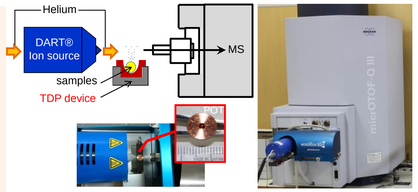


Fig.2 TDP/DART-MS system

◆ Data processing procedure of KMD Analysis:

KMD analysis is a method of analyzing the elemental distribution of constituents based on high resolution mass spectra. In this method, an accurate observed mass is defined as the Kendrick Mass (KM), which is standardized with a "repeat structure" as a basic unit (Equation 1).

$$KM = \text{Observed accurate mass} \times \frac{\text{Nominal mass of “repeat structure”}\ (^{12}C^{1}H_2 = 14)}{\text{IUPAC mass of “repeat structure”}\ (^{12}C^{1}H_2 = 14.01565)} \quad \cdots (1)$$

※As an example, the repeat structure is CH_2

Although the KM value of a compound composed only of a “repeat structure” theoretically assumes an integer value, the KM value of a real compound may not, a deviation from the integer value i.e.,
deviation = KM – observed accurate mass).
By plotting this deviation (the KMD) versus the observed accurate mass (*m/z*), it is possible to confirm the chemical composition of various compounds contained in the sample through a scatter diagram.

Example of KMD analysis ~ blended polymers ~

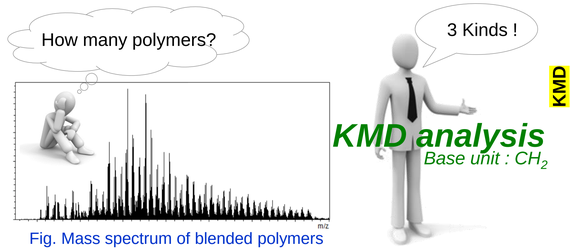


Fig. Mass spectrum of blended polymers

Fig. KMD plot

Results and discussions

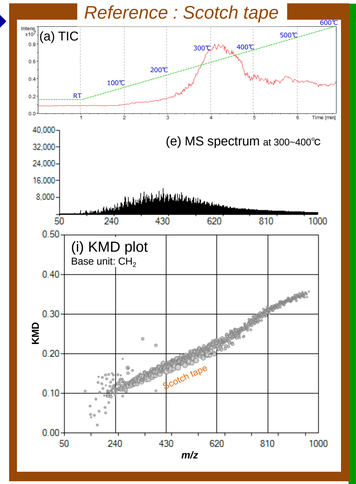
◆ The total ion current gram (TIC) of each sample is shown in Fig. 3(a)~(d). With temperature gradient heating, thermal desorption and a pyrolytic reaction were detected through changes in the signal intensity.

◆ The MS spectra at 300 ~ 400 ℃ (the pyrolysis reaction starting temperature of each sample) is shown in Fig. 3 (e)~(h). The complicated MS spectra of each sample shows that fine plastics were mixed in the reference scotch tape, making it difficult to distinguish them.

◆ KMD plots (base unit: CH_2) were plotted from the aforementioned MS spectra as shown in Fig. 3(i)~(l). In the KMD plot of each sample, the scotch tape and fine plastics are shown separately. When the fine plastic was Nylon-6, a plot of the 113 Da interval derived from their repeat structure was plotted at a position different from the scotch tape. In the same way, plots with a 72 Da interval in PLA and with a 44 Da interval in PEG were observed at positions different from that of the scotch tape.

◆ Subtracted mass spectra (reference from each sample) were shown in Fig. 3(m)~(o). And KMD plots (base unit: $C_6H_{11}O$, $C_3H_4O_2$, and C_2H_4O) were shown in Fig. 3(p)~(r). Scotch tape and the fine plastics were clearly recognized and identified.

◆ Fine foreign substances collected with Scotch tape can be identified without detaching them from the tape by a combination of TDP/DART-MS and KMD analysis.



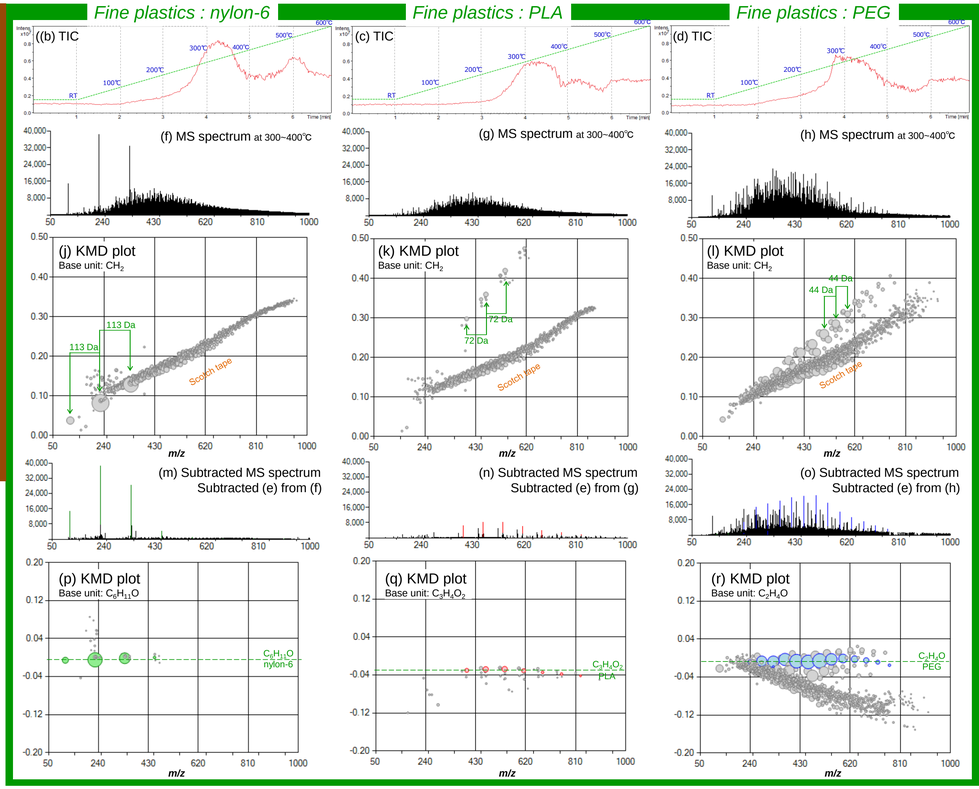


Fig.3 Analysis results using TDP/DART-MS of reference scotch tape and samples ;
(a) ~ (d) : TIC, (e) ~ (h) : Mass spectra of at 300 ~ 400℃, (i) ~ (l) : KMD plot (base unit : CH_2),
(m) ~ (o) : Subtracted Mass spectra (subtracted reference from sample), (p) ~ (r) : KMD plot (base unit : depends on plastics)

Conclusion

◆ TDP/DART-MS enables the direct and rapid analysis of plastic samples.

◆ A combination of TDP/DART-MS and KMD analysis enables the identification of fine plastics without detaching the foreign matter collected from adhesive tape.

◆ A combination of TDP/DART-MS and KMD analysis can be used for material identification of evidence in criminal cases.

References

[1] Nojima, H., Shimoda, O., Sakayanagi, M., Ito, M., and Iwamoto, T.: The 22nd Annual Meeting of Japanese Association of Forensic Science and Technology, 2016, Abstract G-01, p183
[2] Kendrick, E.: Analytical Chemistry. 35, 2146-2154 (1963)
[3] Sato, H., Nakamura, S., Teramoto, K., Sato, T.: Journal of the American Society for Mass Spectrometry, 25(8), 1346-1355 (2014)