Structural Analysis of Polyethylene Terephthalate Film by using a Py-GC-HRTOFMS and msFineAnalysis AI

Product used：Mass Spectrometer (MS)

Introduction

Electron ionization (EI) is one of the most popular ionization methods used in gas chromatography-mass spectrometry (GC-MS). Consequently, compounds are typically identified by mass a spectral database search using EI mass spectra. Because molecular ions are often weak or absent in 70 eV EI mass spectra, identification of unknowns can be difficult by EI alone. In these cases, soft ionization (SI) can be very helpful for producing and identifying molecular ions. Recently, JEOL began developing an integrated qualitative analysis workflow that automatically combines and interprets the information from EI and SI data. And then in 2018, we introduced our integrated qualitative analysis software “msFineAnalysis” which uses both EI and SI data to improve compound identification for GC-MS applications.

Despite the fact that msFineAnalysis was automatically able to determine the molecular formula and partial structure information from EI fragment ion formulas, the actual structural formulas still required manual analysis using chemical compositions. To address this, we then developed an automated structure analysis software package entitled “msFineAnalysis AI” which uses artificial intelligence (AI) to predict EI mass spectra from chemical structures. We have used our newly-developed AI model to create a database of predicted EI mass spectra for around 100 million compounds. In this work, we introduce a polymer materials application that uses msFineAnalysis AI for structural analysis.

AI Structural Analysis

The AI structural analysis workflow is shown in Figure 1. In this method, we used deep learning to construct an AI model that can predict the EI mass spectrum from a structural formula. We then submitted approximately 100 million compound structure formulas to our AI model in order to generate predicted EI mass spectra. The structural formula and the predicted EI mass spectra associated with each compound are included with the software as an “AI library” database that also includes database search function based on the mass spectral pattern. Additionally, msFineAnalysis AI uses the molecular formulas uniquely determined during automatic integrated qualitative analysis in order to narrow down the possible candidate structural formulas.

The predicted EI mass spectrum narrowed down by molecular formula and the actual EI mass spectrum are used to then calculate a score from the similarity of their spectral pattern, and the candidate structural formulas are then listed in order of high similarity to low similarity.

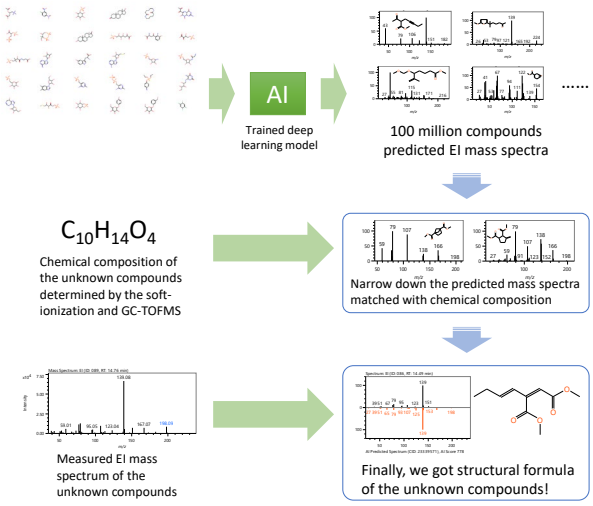

Figure 1: Workflow for structural analysis of unknowns using msFineAnalysis

Experimental

A commercially-available polyethylene terephthalate film was used as a test sample in this study. We performed Py-GC-HRTOFMS measurements using both EI and field ionization (FI) modes with a combination EI/FI ion source. The qualitative data processing was performed with msFineAnalysis AI (JEOL). Measurement conditions are shown in Table 1.

Table 1: Measurement and analysis conditions

Pyrolysis conditions	
Pyrolyzer	EGA/PY-2020D(Frontier Lab)
Pyrolysis Temperature	600°C
GC conditions	
Gas Chromatograph	7890 GC (Agilent Technologies)
Column	ZB-5MSi (Phenomenex) 30 m x 0.25 mm, 0.25 µm
Oven Temperature	40°C (2 min) - 20°C/min -320°C (30 min)
Injection Mode	Split mode (100:1)
Carrier flow	He:1.0 mL/min

MS conditions	
Spectrometer	JMS-T200GC (JEOL Ltd.)
Ion Source	EI/FI combination ion source
Ionization	EI+:70 eV, 300 µA
	FI+:-10 kV
Mass Range	*m/z* 29 - 600
Data processing condition	
Software	msFineAnalysis AI (JEOL Ltd.)
Library database	NIST20, AI Library (JEOL Ltd.)

Results and Discussion

Comparison of AI structural analysis results and references

Among the observed polyethylene terephthalate (PET) pyrolysis products, AI structural analysis was performed for four components not registered in the NIST library database and for which structural formulas were proposed in reference [1]. Figure 2 shows the TIC chromatograms obtained from the Py-GC-EI and FI measurements. The peaks with IDs [058], [059], [115], and [159] in Figure 2 are the four components analyzed in this study. Figure 3 shows the measured EI mass spectra for these four components (upper, black), the structural formula proposed in the reference literature (right side of the spectrum), and its predicted EI mass spectrum (lower, red).

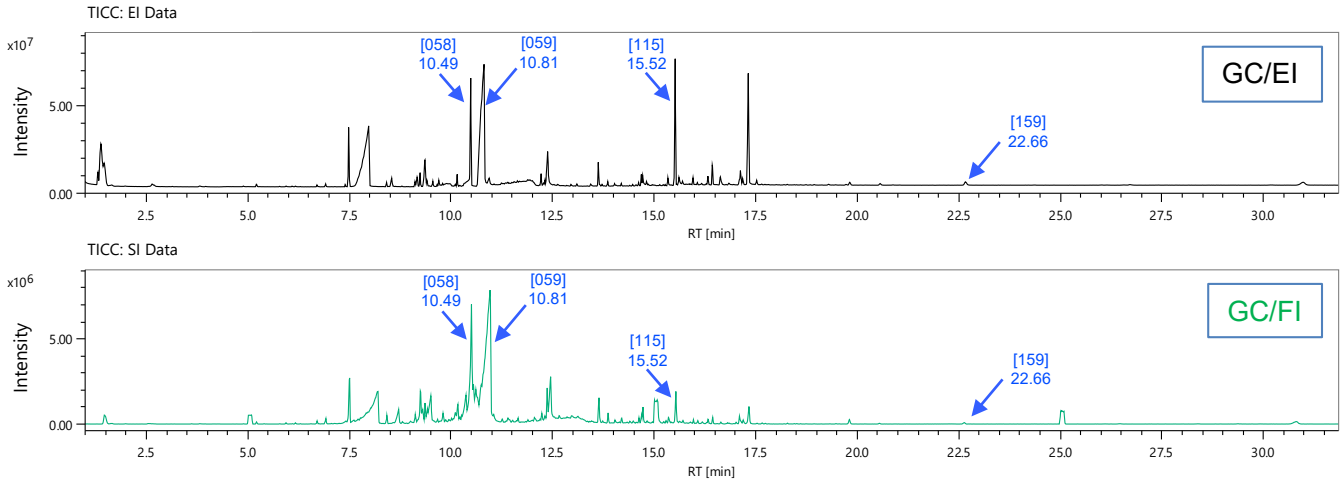

Figure 2: Py-GC-EI and FI TIC chromatograms for Poly(ethylene terephthalate)

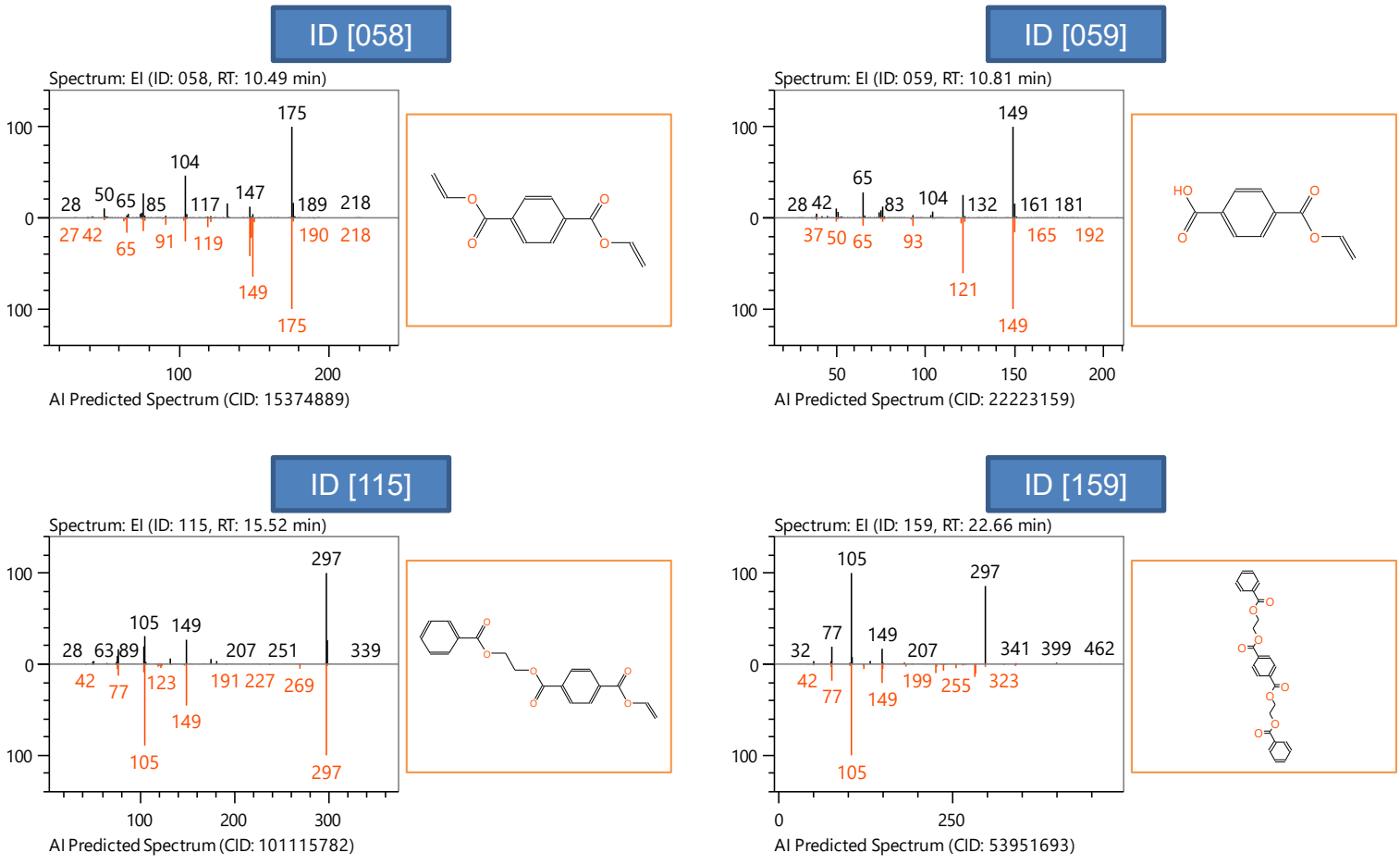

Figure 3: Measured EI mass spectra and predicted EI mass spectra of the proposed structural formula in reference [1] for ID[058], [059], [115], [159] in Figure 2

AI structural analysis results are shown in Table 2. In the table, the “AI Score” is a score (up to 999) calculated by msFineAnalysis AI that represents the cosine similarity between the measured and predicted EI mass spectra. "Rank" indicates the score rank of the structural formulas listed in Figure 3, and "Total" indicates the number of candidate structural formulas. Three of the four components analyzed in this study (ID [058], [059], [115]) obtained over 800 score which means a high degree of similarity, and the fragment ions observed in the measured mass spectra and the predicted mass spectra were in good agreement. The number of candidate structural formulas ware about 970-1400, and the structural formulas proposed in the reference were obtained as within the top two.

For ID [159], the AI Score was calculated at 510 score, and although this score was lower than the other components, the structural formula proposed in the reference literature was obtained at #3 rank in 311 candidates.

As a result, it was found that the structural formulas proposed in the reference literature were obtained in the top three positions for all the components evaluated in this study.

Table 2: AI structual analysis result

Reference [1] data		msFineAnalysis AI result					
Notation	Assignment of Main Peaks	ID	RT(min)	IUPAC name	PubChem CID	AI Score	Rank	Total
C	CH2=CHOCOC6H4COOCH=CH2	058	10.49	bis(ethenyl) benzene-1,4-dicarboxylate	15374889	820	2	1471
D	CH2=CHOCOC6H4COOH	059	10.81	4-ethenoxycarbonylbenzoic acid	22223159	914	2	1013
F	C6H5COOCH2CH2OCOC6H4COOCH=CH2	115	15.52	1-*O*-(2-benzoyloxyethyl) 4-*O*-ethenyl benzene-1,4-	101115782	877	1	975
H	C6H5COOCH2CH2OCOC6H4COOCH2CH2OCOC6H5	159	22.66	bis(2-benzoyloxyethyl) benzene-1,4-dicarboxylate	53951693	510	3	311

Conclusion

In this MSTips, we introduced our newly-developed software msFineAnalysis AI, which contains AI structural analysis functionality to enhance qualitative analysis workflow. Additionally, a polymer application using msFineAnalysis AI to identify components of a pyrolyzed PET film was also presented.

Structural analysis using AI was performed on four components not registered in the NIST library database, and results were compared with structural formulae proposed in the reference literature.

In spectral pattern comparisons, Three of the four components analyzed in this study (ID [058], [059], [115]) cosine similarity scores were over 800, indicating that AI-predicted mass spectra showed a high degree of similarity to measured mass spectra. The number of candidate structural formulas ware about 970-1400, and the structural formulas proposed in the reference were obtained as within the top two. For ID [159], the AI Score was calculated at 510 score, and although this score was lower than the other components, the structural formula proposed in the reference literature was obtained at #3 rank in 311 candidates. The prediction by AI showed high accuracy, indicating that the method is effective for structural analysis of pyrolysis products.

Qualitative analysis of GC-MS data can be greatly assisted by using EI and SI data together with msFineAnalysis AI, especially when trying to identify unknown compounds in complex samples.

Reference

[1]Shin Tsuge, Hajime Ohtani, Chuichi Watanabe (2011), Pyrolysis - GC/MS Data Book of Synthetic Polymers, Elsevier

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