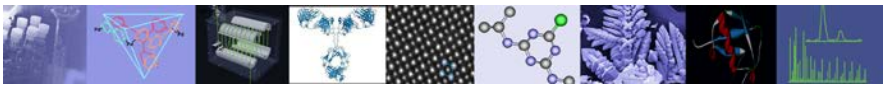

Applications Note

AccuTOF-GCx Series

Comprehensive Analysis + Unknown Component Analysis of Vinyl Acetate Resins Using Pyrolysis GC-MS

Characteristic Component Extraction by Multiple Classification PCA and Component Identification by High Resolution MS

Introduction

Advances in mass spectrometry are enabling analysis of micro samples and unknown components that were not observable before. As the volume of information acquired from mass spectrometry increases, researchers are calling for simple techniques to analyze numerous components observed, and as a result, there is a rise in demand for comprehensive analytical techniques including multiple classification analysis.

In this work, we will introduce a new technique for non-target analysis, which combines comprehensive analysis using high resolution GC-TOFMS and unknown component analysis using soft ionization.

Experiment

As model samples, 6 commercial vinyl acetate resins (adhesives) were used. A gas chromatography time-of-flight mass spectrometer (GC-TOFMS) was used for measurement. Since emulsion samples including adhesives are difficult to analyze without preliminary treatment, the samples were subjected to pyrolysis.

The resulting data was analyzed by AnalyzePro (SpectralWorks) to compare multiple samples by PCA.

Table 1. Measurement conditions

Instruments	JMS-T200GC *AccuTOF GCx* (JEOL Ltd.) EGA/PY-2020iD (Multi-Shot Pyrolyzer: Frontier Laboratories Ltd.)
Pyrolyzer conditions	
Pyrolysis temp.	600˚C
GCTOFMS conditions	
Inlet mode	Split 100:1
Inlet temp.	300˚C
GC column	DB-5msUI (15 m x 0.25 mm, firm thickness 0.25 µm)
Oven temp. program	50˚C (1min) => 30˚C/min => 330˚C (1.7min)
Carrier gas flow	1.0 mL/min (He, Constant flow)
Ionization method	EI(+) : 70 eV, 300 µA FI(+) : -10 kV, 6mA (Carbotec 5µm)
Spectrum recording interval	0.1 sec/spectrum
m/z range	35 ～ 650
Software	AnalyzerPro (Spectralworks Ltd.)

Results

A total of 6 vinyl acetate resin samples were analyzed by pyrolysis GC-EI TOFMS (n=3), and the resulting data was subjected to PCA by AnalyzerPro. The PCA score plot (Figure 1) shows that sample E was clearly separated at the 1st principal component axis and sample B at the 2nd principal component axis, respectively. Components contributing to each principal component were easily detected in the loading plot.

Among the components contributing to the separation at the secondary principal component axis (positive side) , that is, characteristic components of sample B, the component at R.T. 4.55 min was analyzed in detail (data on the right side of Figure 2).

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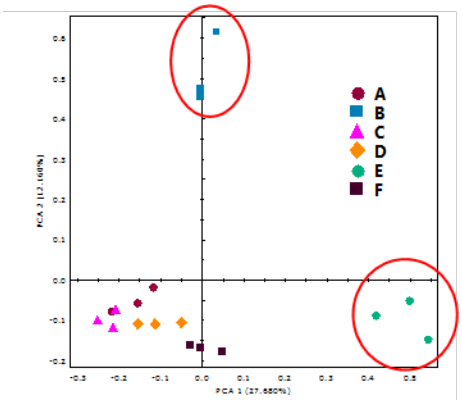
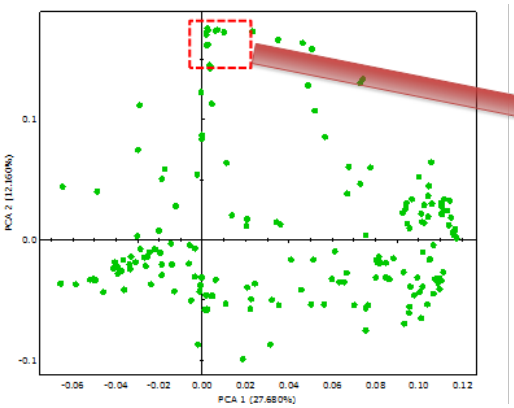


Fig 1. PCA score plot of polyvinyl acetate samples



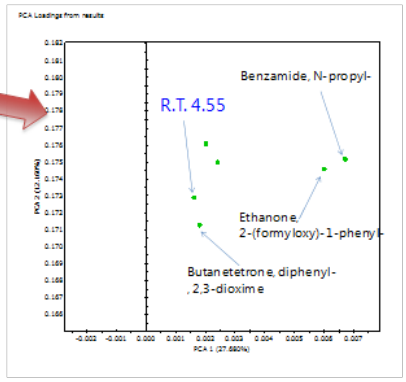
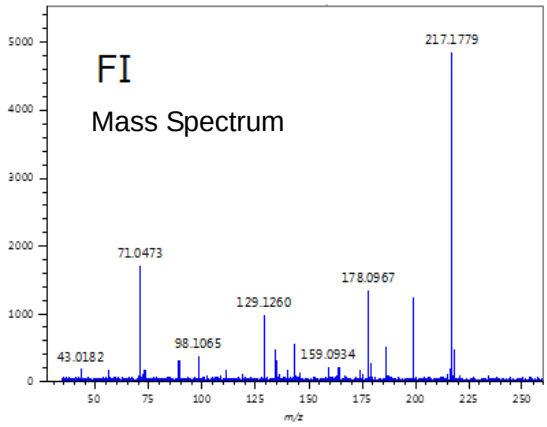
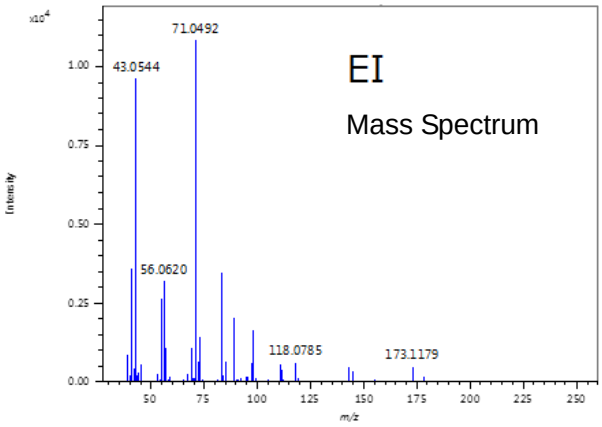


Fig 2. PCA loading plot of polyvinyl acetate samples



Mass	Formula	Calculated Mass	Mass Error [mDa]	DBE
217.178	C12 H25 O3	217.1798	-1.8	0.5



Mass	Formula	Calculated Mass	Mass Error [mDa]	DBE
43.0544	C3 H7	43.0542	0.2	0.5
56.0622	C4 H8	56.0621	0.1	1.0
71.0493	C4 H7 O	71.0491	0.2	1.5
83.0858	C6 H11	83.0855	0.3	1.5
89.0596	C4 H9 O2	89.0597	-0.1	0.5
98.1091	C7 H14	98.1090	0.1	1.0
111.1177	C8 H15	111.1168	0.9	1.5
143.1096	C8 H15 O2	143.1067	2.9	1.5
145.1246	C8 H17 O2	145.1223	2.3	0.5
173.1189	C9 H17 O3	173.1172	1.7	1.5

Fig 3. EI and FI mass spectra and exact mass analysis results for the unknown component (R.T. 4.55 min) in sample B

The NIST library search estimated that the component at R.T. 4.55 min was likely to be 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate (molecular weight 286) with a match factor of 813.

However, the FI mass spectrum of this component detected a base peak at *m/z* 217, and as a result, the molecular weight estimated in NIST library search differed significantly from the molecular weight estimated from the results of FI ionization. While the chemical structure of 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate contains an ester group, FI ionization detected no ion that has an *m/z* equal to that. Ester group containing compounds are generally known to produce protonated molecules by FI ionization. Thus, it is likely that the component at R.T. 4.55 min is not the component estimated in NIST library search but is another component having a similar EI spectrum. Figure 3 shows the mass spectra of the component at R.T. 4.55 min acquired by EI and FI. Figure 4 shows the structural formula of 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate. After examining the EI and FI data in detail, it was estimated that the component at R.T. 4.55 min has the structure shown in Figure 5. None of the major libraries provided by NIST included a component equal to this structure.

Conclusion

PCA is an effective and efficient technique for the comprehensive analysis of GC-TOFMS data. Specifically, for multiple sample comparisons, use of score and loading plots makes it possible to examine the similarities between the samples and the characteristic components of each sample.

Also, while the NIST library search is a powerful tool for identifying characteristic components of samples, combining NIST library searches with molecular weight information acquired by soft ionization such as FI makes it possible to identify components with a higher level of accuracy, preventing false identifications.

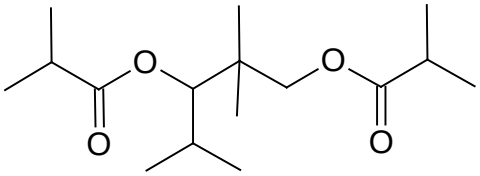


Fig 4. Structural formula of 2,2,4-Trimethyl-1,3-pentanediol diisobuterate

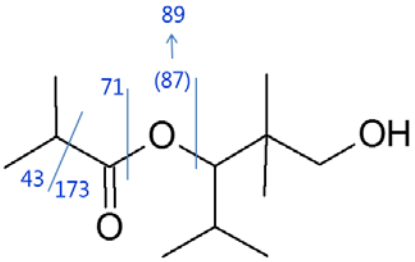


Fig 5. Estimated structural formula for the unknown component (R.T. 4.55 min) in sample B

