

Integrated qualitative analysis of polymer sample by pyrolysis - gas chromatography combined high-resolution mass spectrometry: Using accurate mass measurement results both electron ionization and soft ionization

Ueda Y.¹, Ubukata M.¹, Kubo A.¹, Nagatomo K.¹
¹JEOL Ltd., Tokyo, Japan

Introduction:

Electron ionization (EI), which accompanied by extensive fragmentation, is the most popular method used in gas chromatography-mass spectrometry (GC-MS). The compounds are identified by mass spectral database search using with an EI mass spectrum. Sometimes we couldn't obtain the molecular ion in EI data due to EI is one of the hard ionization techniques. **Therefore, it is very hard to do the unknown compounds analysis only with EI mass spectrum.** In that case, **soft ionization is very helpful to obtain and identify the molecular ions.** Recently, we developed an integrated qualitative analysis method coupled with EI and soft ionization (SI) data. We used EI for hard ionization and filed ionization (FI) for soft ionization in this study.

Methods:

The commercially available acrylic resin was used as a sample for GC/EI and GC/FI analysis. The gas chromatography-high mass resolution time-of-flight mass spectrometer (AccuTOF™ GC-Alpha, JEOL) combined with a pyrolyzer (PY-2020iD, Frontier lab) was used for data acquisition.

Table1 Measurement Condition

Method	Pv-GC-HRTOFMS
Sample	Acrylic resin polymer
Heating temp.	600 °C
Column	ZB-5MSi (Phenomenex), 30m x 0.25mm, 0.25µm
Inlet mode	Split100:1
Inlet temp	300 °C
Oven temp.	40 °C(2min)→10 °C/min→320 °C(15min)
Carrier gas	He, 1mL/min
Ion source	EI/FI/FD combination ion source
Ionization	EI+: 70eV/300µA FI+: -10kV/40mA
m/z range	m/z35-800



Fig.1 Latest GC-HRTOFMS and Pyrolyzer system

Integrated qualitative analysis:

Data integration of GC/EI and GC/SI was performed with the following steps.

- The GC peaks were detected from GC/EI and GC/SI data separately.
- The mass spectra were extracted for each GC peak.
- The mass spectra from GC/EI and GC/SI data were linked using retention time information.
- Database search was performed for extracted EI mass spectra using the NIST mass spectral library.
- Accurate mass analyses were performed by using the mass of molecular ions shown in SI spectra and the masses of fragment ions in EI mass spectra.

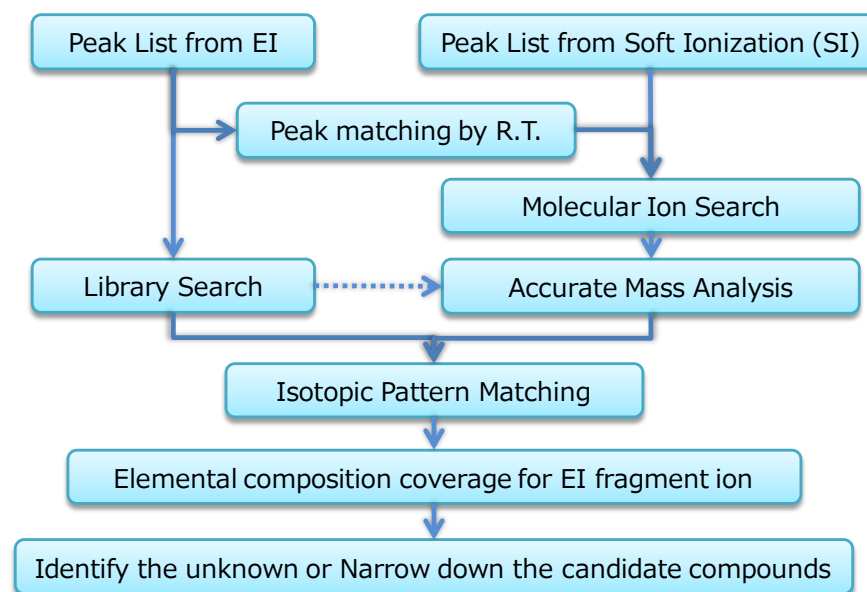


Fig. 2 Integrated qualitative analysis workflow.

A useful feature of the software is the confirmation of database search results with EI mass spectra by molecular information from SI spectra. Additionally, the soft ionization data supports analysis of compounds that are not identified in the database search. Both elemental compositions of molecular ion and fragment ions, which represent substructures, can be determine by accurate mass information from SI and EI mass spectra, respectively.

Results and Conclusion:

Many detected thermal decomposition compounds of acrylic resin were not listed in the library database and the molecular ions were not observed in GC/EI data. We estimated the chemical formulas for both listed and un-listed compounds with accurate mass analysis results using the molecular ion in FI mass spectra and fragment ions in EI mass spectra. **For the acrylic resin sample were analysed by using the integrated qualitative analysis work flow shown in Figure 4. In total, 154 components were identified with only one chemical formula candidate.**

This integrated qualitative analysis method coupled with EI and soft ionization is powerful tool for the unknown compound analysis.

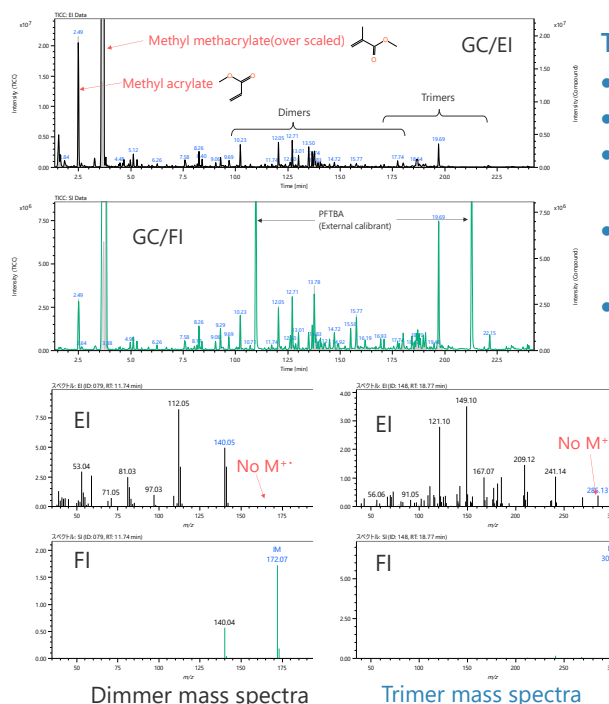


Fig. 3 Py-GC-TOFMS measurement results

TIC result

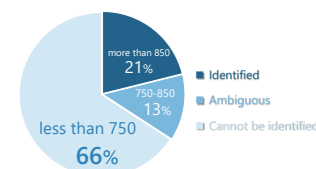
- Py temp. at 600 °C
- Measured by GC/EI and GC/FI
- Methyl acrylate and Methyl methacrylate were detected as monomers

- Many kinds of Dimers and Trimers which have polymer structure information were detected

- In total 120 compounds (Height threshold 0.05%) were detected using deconvolution peak detection

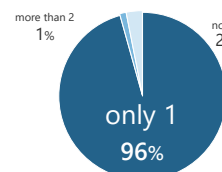
Mass spectrum result

- Molecular ions were not observed in EI data for a lot of thermal decompositions of acrylic resin polymer
- Many detected compounds were not listed in the DB
- Soft ionization technique and accurate mass measurement are necessary to identify them



Library Database Search

- Classification with highest M.F. score
- 66%(106) components were not identified by the library database search



Integrated Qual. Analysis

- Classification with number of the chemical formula candidate
- 96%(154) components were identified with only one chemical formula candidate

Fig. 4 Comparison of qualitative analysis results.