

## Analysis of commercially available polypropylene products combining pyrolysis GC/EI and GC/PI (2) - Introduction of an example of differential analysis using msFineAnalysis iQ -

Product: Mass Spectrometer (MS)

The gas chromatograph quadrupole mass spectrometer (GC-QMS) is widely used as a qualitative / quantitative analyzer for volatile compounds. Qualitative analysis by GC-QMS is generally performed by searching the library database (DB) using the measurement data of the Electron Ionization (EI). However, if qualitative analysis is performed using only the similarity with the library spectrum as an index, several significant candidates may be obtained depending on the compound, or erroneous candidates may be selected as the identification result. In such cases, confirmation of molecular ions by the soft ionization (SI) such as the photoionization (PI) is effective.

In 2018, JEOL Ltd. released "msFineAnalysis", an integrated qualitative analysis software that automatically combines the analysis results of EI and SI measured by a gas chromatograph time-of-flight mass spectrometer (GC-TOFMS). msFineAnalysis is software that analyzes the exact mass data of GC-TOFMS, but the usefulness of integrated qualitative analysis can be expected for integer mass data as well.

Therefore, we have newly developed the integrated qualitative analysis software "msFineAnalysis iQ" that supports integer mass data obtained by GC-QMS. In MSTips No. 347, we reported an example of analysis of commercial polypropylene products using msFineAnalysis iQ, especially on the usefulness of integrated qualitative analysis. msFineAnalysis iQ is also equipped with a two-sample comparison (differential analysis) function, which is widely used in the field of material analysis these days. In this MSTips, we have reported on an example of differential analysis of commercial polypropylene products using this function.

### Experiment

Non-woven mask and lunchbox antibacterial sheet, which are commercially available polypropylene products, were used as samples. A GC-QMS "JMS-Q1600GC UltraQuad™ SQ-Zeta (JEOL Ltd.)" equipped with a pyrolyzer "PY-3030D (Frontier Labs)" and the EI/PI combination ion source was used for the measurements. In order to conduct statistical analysis, GC/EI measurements were performed for n=5. Table 1 shows the measurements condition details. The GC/MS data were analyzed using the integrated qualitative analysis software "msFineAnalysis iQ (JEOL Ltd.)" dedicated to JMS-Q1600GC



JMS-Q1600GC UltraQuad™ SQ-Zeta

Table 1 Measurement condition

Pyrolysis condition		MS condition	
Sample amount	EI: 0.4mg, PI:0.5mg	Ion source	EI/PI combination ion source
Pyrolysis temperature	400°C	Ion source temperature	250°C
GC condition		Interface temperature	280°C
Column	ZB-5Msi (Phenomenex) 30 m×0.25 mm I.D., d <sub>f</sub> =0.25 μm	Ionization mode	EI (70 eV, 50 μA), PI (8 - 10eV)
Injection port temperature	320°C	Measurement mode	Scan (m/z 35 - 700)
Oven temperature	40°C(2 min)→20°C/min→320°C (20min)		
Injection mode	Split 100:1		
Carrier gas	He, 1.0 mL/min (Constant Flow)		

## Overview of the differential analysis function in msFineAnalysis iQ

Two-sample comparison (differential analysis) in msFineAnalysis iQ can extract characteristic components and common components of each sample. For example, it is possible to confirm the component that increases or decreases by comparing the reference product and defective product, or to confirm the components that are characteristic in a new material by comparing it with an existing material. In the differential analysis, the reproducibility of the detected compounds mass spectrum and the difference in the area values (intensity ratio) of the detected peaks are checked between samples. A component with reproducibility and differences in area values are classified as characteristic components of each sample, and a component with reproducibility but no differences in area values are classified as components common to each sample. After classification, the integrated qualitative analysis is automatically performed for all detected components.

Figure 1 shows the workflow of differential analysis and integrated qualitative analysis in msFineAnalysis iQ. In the differential analysis, the reproducibility is calculated for the t-test using the EI measurement data. In the differential analysis function, it is possible to set  $n=1, 3, 5$ , for the number of measurements for each sample. In the case of  $n=1$ , it is not possible to evaluate the statistical reproducibility. However, it is possible to confirm which components are different. This function allows the user to do sample comparisons even when it is not possible to acquire more than one measurement result for each sample.

After the preparation of the measurement data, alignment (identity determination) is performed based on the retention time of the chromatogram and the similarity of the EI mass spectrum, and differential analysis is performed. After the differential analysis, the integrated qualitative analysis is performed as described above. The flow of integrated qualitative analysis is the same as that of Figure 1 of the previously reported MSTips No. 347.

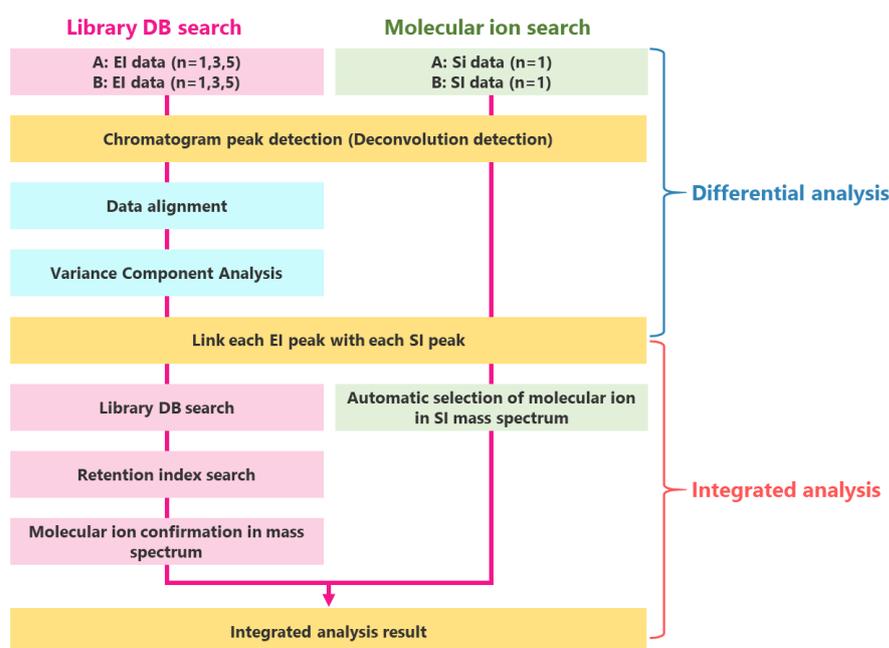


Figure 1 msFineAnalysis iQ workflow for the differential analysis and integrated analysis

## Results

Figure 2 shows the total ion current chromatogram (TICC) of the pyrolysis GC/MS results of the non-woven mask and the lunchbox antibacterial sheet using the EI data. In both samples, many peaks of pyrolysis products, presumably derived from polypropylene, were detected. Figure 3 shows a volcano plot, the result of the differential analysis. The volcano plot is a scatter plot that allows us to visualize the characteristic components among the samples, and shows the intensity ratio ( $\text{Log}_2(B/A)$ ) among the samples on the horizontal axis and the statistical reproducibility ( $-\text{Log}_{10}(p\text{-value})$ ) on the vertical axis. The volcano plot enabled us to visualize the characteristic and common components in non-woven mask and lunchbox antibacterial sheet.

On the next page, we show the results of detailed integrated qualitative analysis of compound 1), which is a characteristic component of non-woven mask in the volcano plot, and compound 2), which is a characteristic component of lunchbox antibacterial sheet (Figure 3).

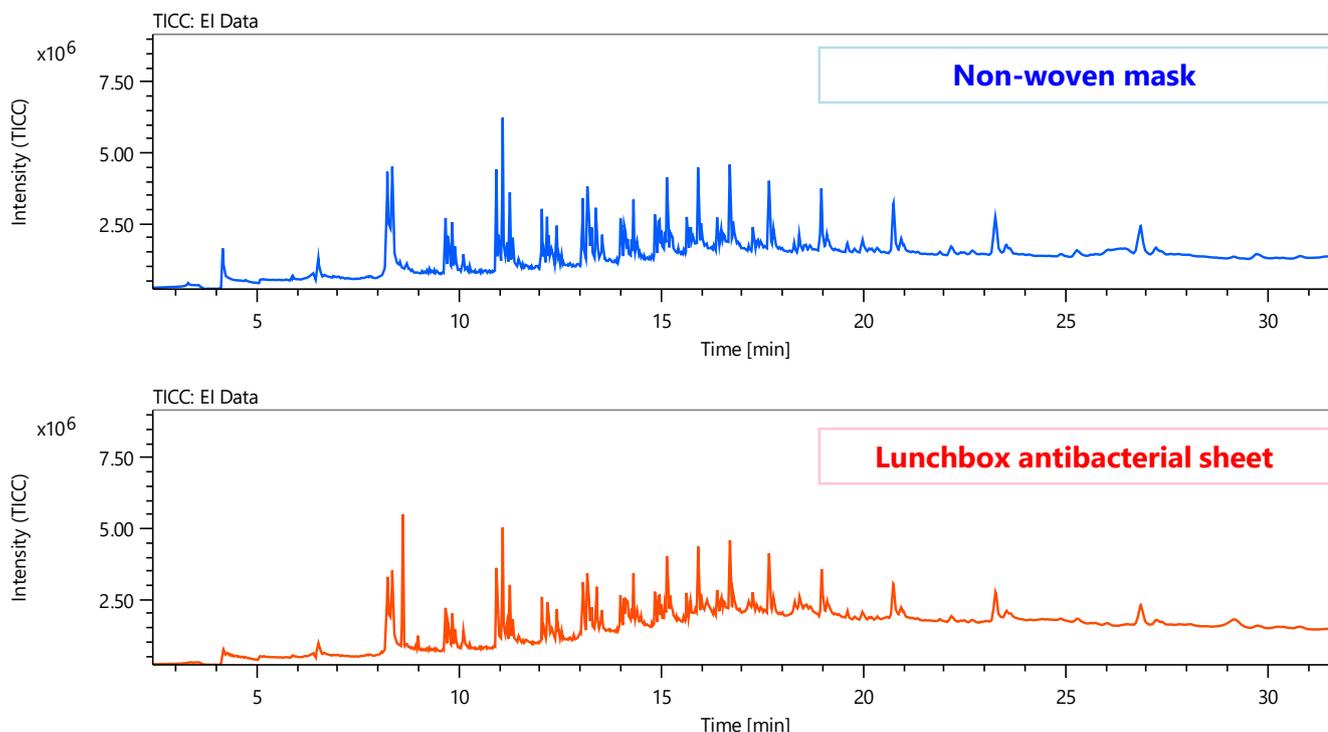


Figure 2 Total ion current chromatograms

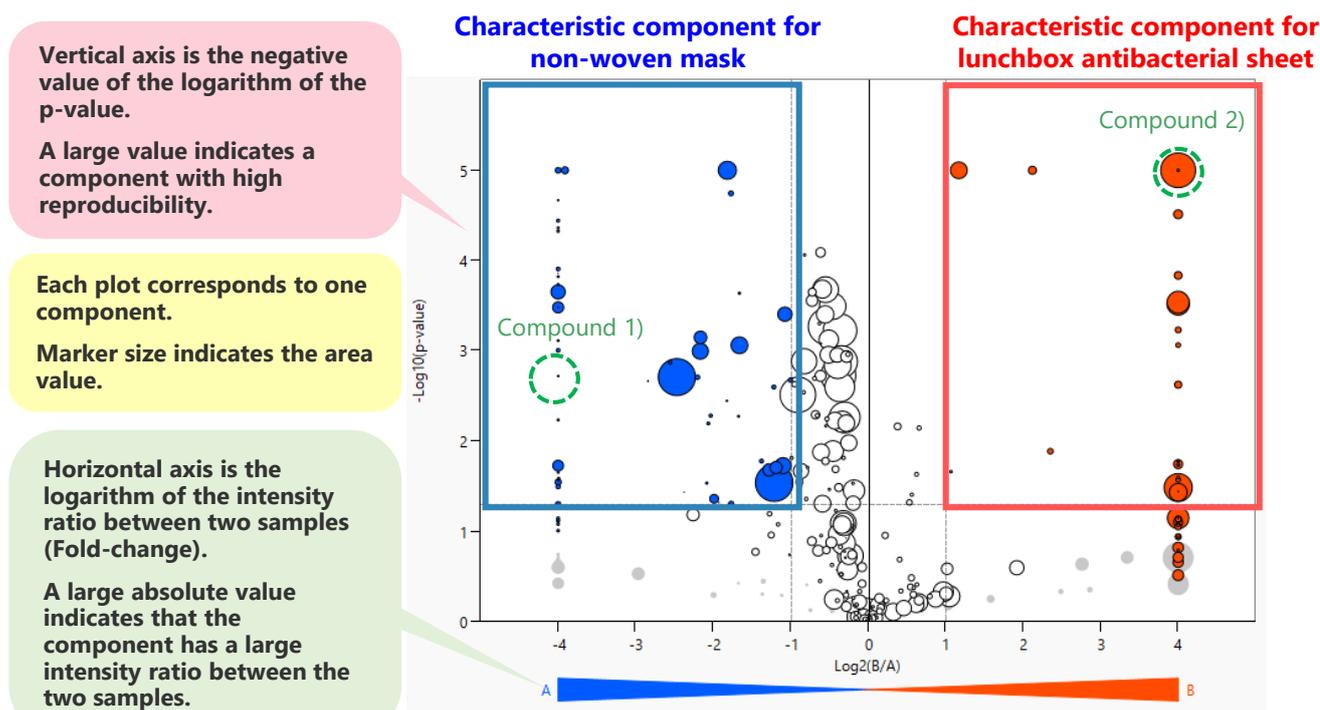


Figure 3 Volcano plot of differential analysis result

The mass spectra of compound 1) are shown in Figure 4.  $m/z$  206, which is presumed to be the molecular ion, was detected in both the EI and PI mass spectra, and the PI mass spectrum showed the molecular ion as the base peak. The integrated qualitative analysis result list (top 5 candidates) by msFineAnalysis iQ is shown in Table 2. From this result, compound 1) was estimated to be "2,4-Di-tert-butylphenol" with 933 similarity score to the library DB. 2,4-Di-tert-butylphenol is a compound known as a raw material for antioxidants, suggesting that antioxidants are added to the non-woven mask.

The mass spectra of compound 2) are shown in Figure 5.  $m/z$  174 ions, which are presumed to be molecular ions, were detected in both EI and PI mass spectra, and a simple mass spectrum with only molecular ions was obtained in the PI. The integrated analysis result list (top 5 candidates) by msFineAnalysis iQ is shown in Table 3. From this result, compound 2) was estimated to be "Benzene, 1,3-diisocyanato-2-methyl- (2,6-TDI)" with 906 similarity score to the library DB. 2,6-TDI is a compound known as a raw material for polyurethane, suggesting that polyurethane is added to the lunchbox antibacterial sheets.

As described above, the differential analysis function of msFineAnalysis iQ made it possible to easily find the differential components in the data where it was difficult to identify the difference on the TICC. In addition, the differential components in each sample could be determined as unique candidates by integrated qualitative analysis.

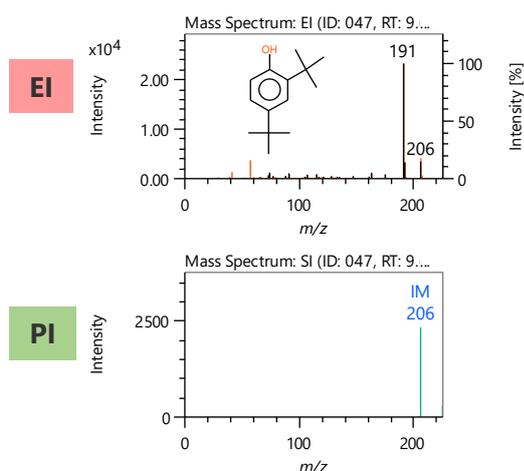


Figure 4 Mass spectra of compound 1)

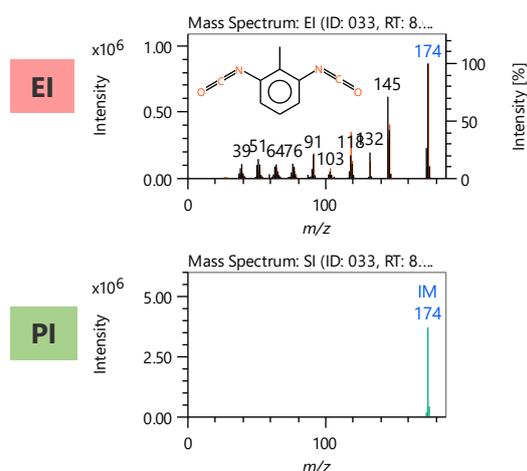


Figure 5 Mass spectra of compound 2)

Table 2 Integrated qualitative analysis result of compound 1)

Library Name	CAS#	Similarity	Reverse Similarity	Lib. RI [iu]	$\Delta$ RI [iu]	Formula	El Base Peak (Lib.)	MW	Molecular Weight Check
★ 2,4-Di-tert-butylphenol	96-76-4	933	933	1514	4	C <sub>14</sub> H <sub>22</sub> O	191	206	✓
Phenol, 2,5-bis(1,1-dimethylethyl)-	5875-45-6	862	862	1514	4	C <sub>14</sub> H <sub>22</sub> O	191	206	✓
Phenol, 3,5-bis(1,1-dimethylethyl)-	1138-52-9	834	834	1255-1855	0	C <sub>14</sub> H <sub>22</sub> O	191	206	✓
Silane, [4-(1,1-dimethylethyl)phenyl]trimethyl-	18412-68-5	761	762	848-1610	0	C <sub>13</sub> H <sub>22</sub> Si	191	206	✓
4'-Diethylaminoacetanilide	5326-57-8	738	755	1399-2109	0	C <sub>12</sub> H <sub>18</sub> N <sub>2</sub> O	191	206	✓

Table 3 Integrated qualitative analysis result of compound 2)

Library Name	CAS#	Similarity	Reverse Similarity	Lib. RI [iu]	$\Delta$ RI [iu]	Formula	El Base Peak (Lib.)	MW	Molecular Weight Check
★ Benzene, 1,3-diisocyanato-2-methyl-	91-08-7	906	906	N/A	N/A	C <sub>9</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>	174	174	✓
Benzene, 2,4-diisocyanato-1-methyl-	584-84-9	875	875	1352	14	C <sub>9</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>	174	174	✓
3-Ethyl-1,2-dihydro-2-oxoquinoline	13297-35-3	763	763	1184-1894	0	C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> O	174	174	✓
4H-Pyrido[1,2-a]pyrimidin-4-one, 2,6-dimethyl-	16867-28-0	739	746	1180-1890	0	C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> O	174	174	✓
Benzo [f]-1,5-diazabicyclo[3.2.2]nonene	7092-76-4	737	760	1177-1887	0	C <sub>11</sub> H <sub>14</sub> N <sub>2</sub>	174	174	✓

## Conclusions

In this MSTips, we reported an example of differential analysis of msFineAnalysis iQ. By using the differential analysis function, it was possible to easily extract the differential components and common components between the two samples. In addition, it was possible to easily perform qualitative analysis of each component. By using this software, it is expected that the qualitative accuracy of qualitative analysis using GC-QMS will be improved and efficient analysis work will be performed.

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