

Application Data Sheet

No. 122

GC-MS

Gas Chromatograph Mass Spectrometer

Estimation of Elemental Composition of Additives in Polymers Using Quick-CI and MassWorks™

GC-MS offers a wealth of fragmentation data and a thorough, highly useful mass spectral library, so it is used for identifying unknown compounds. To identify unknown compounds, searches using a mass spectral library are commonly used. However, considerable difficulties with compound identification can be encountered if a compound detected is not registered in the mass spectral library.

The Mass Works™ software from cerno BIOSCIENCE mathematically calculates the accurate mass from the quadrupole MS mass profile. It then outputs candidate composition formulas using the accurate mass and isotopic ratios.

This application sheet introduces the results of composition estimation using MassWorks for data acquired by means of the EI and CI methods with Quick-CI when analyzing additives in polymers.

* MassWorks™ is a trademark of cerno BIOSCIENCE.

Quick-CI

When estimating compositions, it is necessary to make use of molecular ions. However, with some compounds, molecular ions cannot be detected using the EI method. For this reason, in order to acquire information about molecular ions from protonated molecules, the positive chemical ionization (CI) method has been used. However, this requires an exchange of ion sources when switching between the EI and CI methods. By employing Quick-CI, which is included with the GCMS-QP2020, it is now possible to switch between the EI and CI methods without exchanging ion sources. Moreover, it is also possible to acquire data while switching between the EI and CI methods in a continuous analysis situation.

Sample Preparation

The ultrasonic solvent extraction method was used for pretreating the polymer sample. The sample for evaluation was finely pulverized, and approximately 300 mg was weighed and placed in a 40 mL vial. Then, 10 mL THF was added, a stopper was inserted, and it was processed for 60 minutes using ultrasound. The sample was then dissolved in solvent. After acclimatizing to room temperature, 20 mL of acetonitrile was instilled to precipitate the polymer, and then it was left at room temperature for 30 minutes. 1 mL of the supernatant was measured and placed into a GC vial, and then made the sample to be measured using GC-MS.

Output of Mass Profile Data

Mass profile data is required in order to use the MassWorks software. In GCMSsolution Ver4.42, a setting allows the export of mass profile data to be enabled/disabled (Fig. 1) in the analysis method. For the same measurement, both GC/MS data and mass profile data can be exported. By performing a search of the mass spectral library using GC/MS data, and using mass profile data for compounds that are difficult to identify, an estimation of the composition can be accomplished using MassWorks.

GCMS-QP Series

Ion Source Temp.: 230 °C

Interface Temp.: 320 °C

Solvent Cut Time: 4.5 min

Micro Scan Width: 0 u

Profile Export: ON OFF

Detector Voltage: Relative to the Tuning Result Absolute

0.1 kV

Use MS Program: Threshold: 0

Group#1 - Event#1 GC Program Time: 26.60 min

	Start Time (min)	End Time (min)	Acq. Mode	Event Time(sec)	Scan Speed	Start m/z	End m/z	Ch1 m/z	Ch2 m/z	Ch3 m/z	Ch4 m/z
1	5.00	26.50	Scan	0.30	2000	50.00	600.00				
2	0.00	0.00	Scan	0.00	0	0.00	0.00				

Fig. 1: Example of Settings for Profile Export

Analytical Conditions and Settings for Mass Calibration

To use MassWorks, it is necessary to use mass calibration data in order to calculate the theoretical accurate mass. This mass calibration data can be acquired automatically by means of PFTBA, which is used for tuning after analysis of a sample. The analytical conditions pertaining to this Application Data Sheet are shown in Table 1. An oven program was set so that the temperature was lowered to 60 °C to reduce the effect of column bleeding after the column's rise in temperature for the purpose of analyzing the sample (Fig. 2). Also, the MS time program needed to acquire mass correction data was set as shown in Fig. 3. Measurement is possible by setting some additions to the analytical conditions ordinarily used.

Table 1: Analytical Conditions

GC-MS	: GCMS-QP2020
Workstation	: GCMSsolution Ver4.42
Glass insert	: Deactivated splitless glass insert with wool (PN: 221-48876-03)
[GC]	
Column	: SH-Rxi™-5Sil MS (length 30 m, 0.25 mm I.D., df=0.25 µm)
Injection temp.	: 300 °C
Column oven temp.	: 110 °C (0.5 min) → (20 °C/min) → 110 °C (1 min) → (20 °C/min) → 320 °C (5 min) → (-100 °C/min) → 60 °C (7 min)
Injection mode	: Splitless
Flow control mode	: Linear velocity (45.8 cm/sec)
Initial column flow	: 1.5 mL/min
[MS]	
Interface temp.	: 300 °C
Ion source temp.	: 230 °C
Acquisition mode	: Scan
Scan event time	: 0.3 sec
MS program	: Refer to Fig. 3
EI	
Scan range	: <i>m/z</i> 50 to 600
CI	
Scan range	: <i>m/z</i> 120 to 600
Reagent gas	: Isobutane (80 kPa)

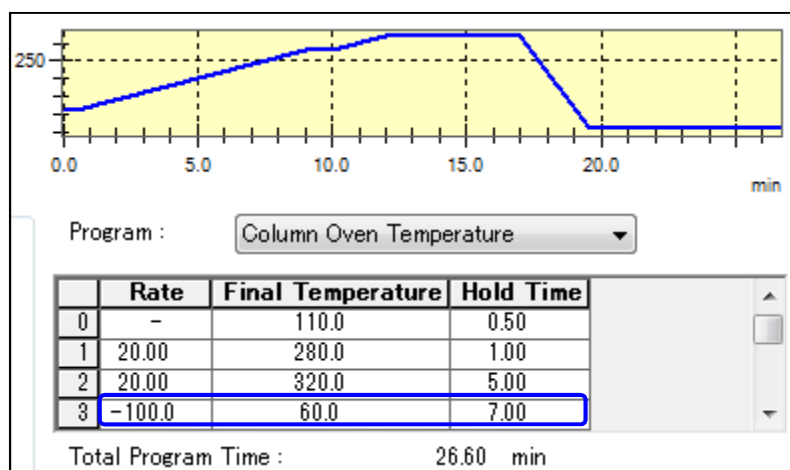


Fig. 2: Setting Example of Column Oven Program

	Time (min)	Command	Value
1	20.10	FilamentOFF	
2	20.60	PFTBAOpen	
3	20.60	DetectorGain=	1.2
4	21.10	FilamentON	
5	26.10	FilamentOFF	

Fig. 3: Setting Window for MS Program to Acquire Mass Calibration Data

Analysis Results

The total ion current chromatogram (TICC) for polymer sample A acquired using the EI and CI methods with Quick-CI is shown in Fig. 4. Concerning peak A, even though the mass spectral library was searched, identification was difficult. An observation of the mass spectrum (Fig. 5) acquired using the EI and CI methods reveals that the molecular weight of the compound is 410. The results of the analysis of an EI method mass profile using MassWorks is shown in Fig. 6. The first candidate was this composition formula: C₂₄H₂₇O₄P (mass error 6.8527 mDa). In that vicinity, phosphoric acid triisopropyl phenyl ester, which has similar fragment ions, was detected; therefore, it could be assumed that it was phosphoric acid diisopropyl (phenyl) ester.

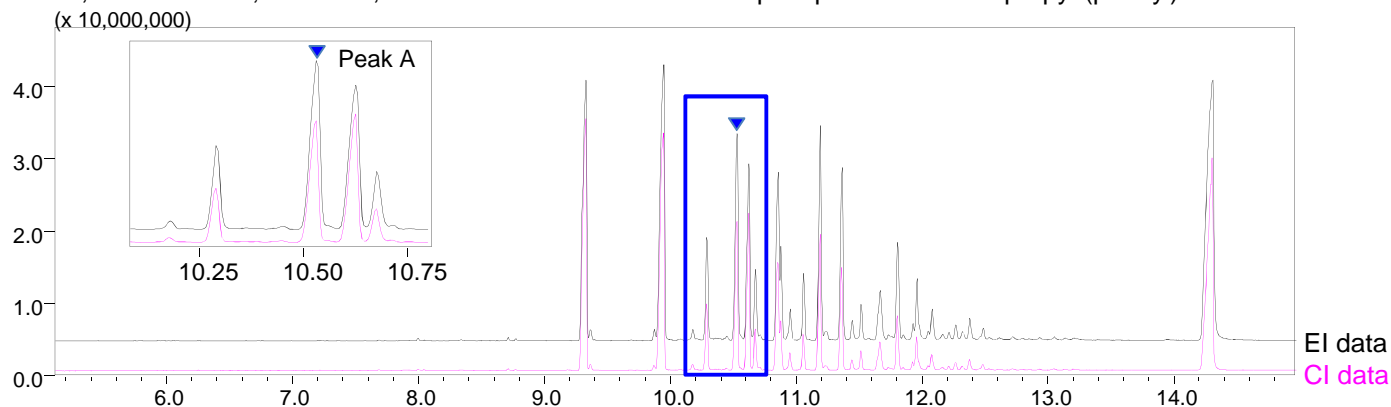


Fig. 4: Total Ion Current Chromatogram for Polymer Sample A Acquired with EI and CI Methods

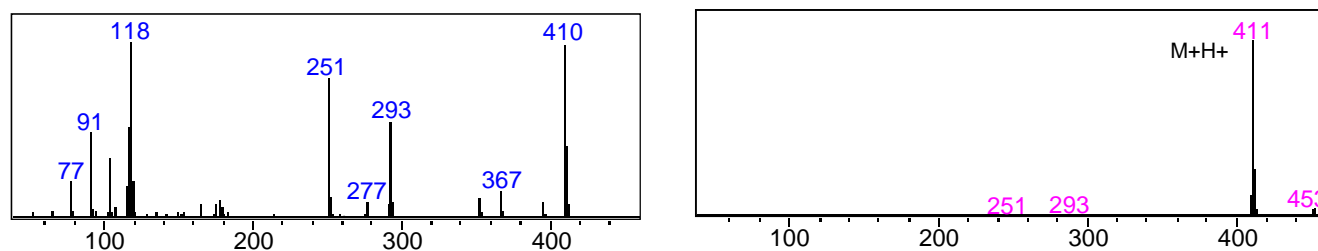


Fig. 5: Peak A Mass Spectrum (Left: EI Mass Spectrum, Right: CI Mass Spectrum)

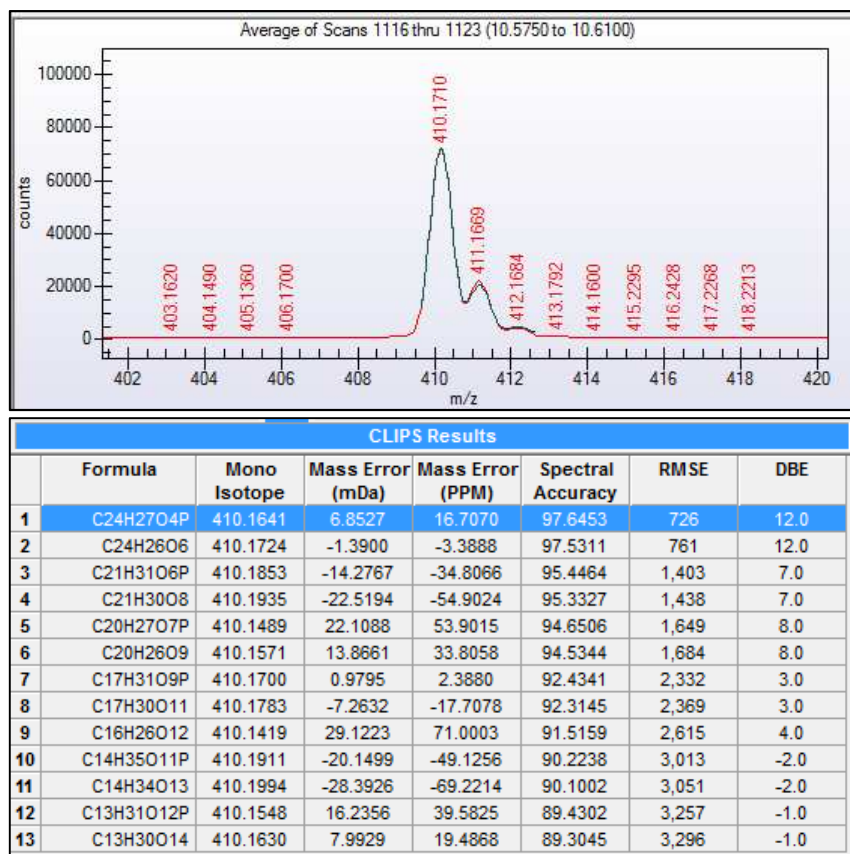


Fig. 6: MassWorks Processed Results for Peak A
(Top: Mass Profile of *m/z* 410 of Peak A, Bottom: List of Candidates for Compositional Formula)

The total ion current chromatogram (TICC) for polymer sample B acquired using the EI and CI methods with Quick-CI is shown in Fig. 7. Concerning peak B, a search of the mass spectral library resulted in a large number of hits for similar compositions, which made identification very difficult. An observation of the mass spectrum (Fig. 8) acquired using the EI and CI methods reveals that no molecular ions were detected using the EI method, and that the molecular weight of the compound is 370, based on protonated molecules of the CI mass spectrum. Since in some cases no molecular ions can be detected using the EI method, it is essential that CI method data be evaluated in order to estimate the composition. The results of the analysis of a CI method mass profile using MassWorks is shown in Fig. 9. The first candidate is this composition formula: C₂₂H₄₃O₄ (mass error -0.7863 mDa). Considering the search results of the library using EI data, it was possible to infer and presume that it was diethylhexyl adipate (C₂₂H₄₂O₄, protonation taken into consideration). Even with detection peaks that cannot be identified with a mass spectral library, the combination of CI molecular weight data and theoretical accurate mass data from MassWorks analysis allows for an expansion of qualitative analysis.

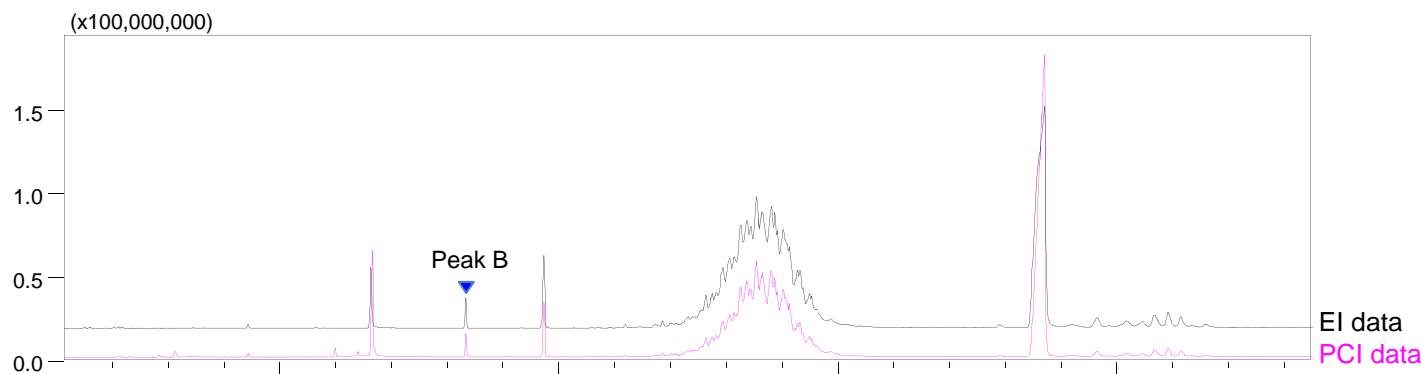


Fig. 7: Total Ion Current Chromatogram for Polymer Sample B Acquired with EI and CI Methods

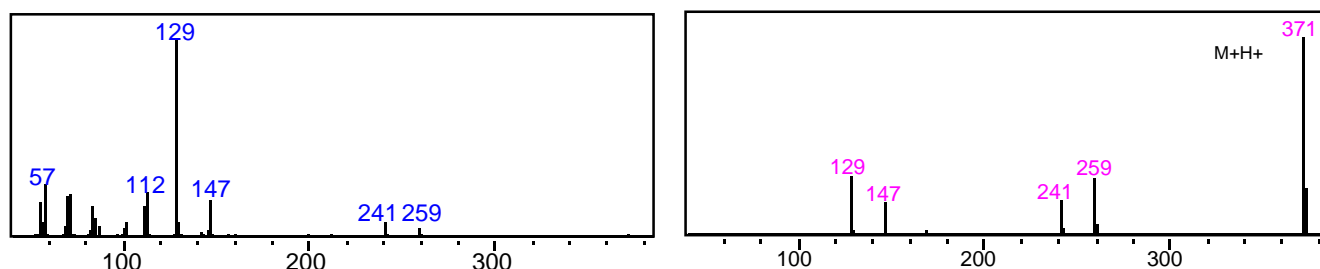
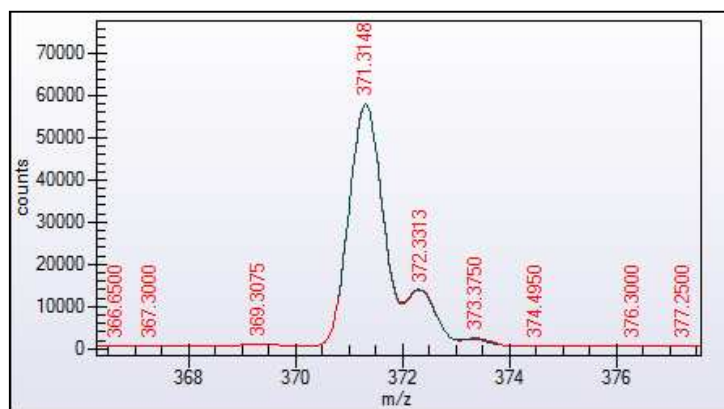


Fig. 8: Peak B Mass Spectrum (Left: EI Mass Spectrum, Right: CI Mass Spectrum)



CLIPS Results							
	Formula	Mono Isotope	Mass Error (mDa)	Mass Error (PPM)	Spectral Accuracy	RMSE	DBE
1	C ₂₂ H ₄₃ O ₄	371.3156	-0.7863	-2.1176	98.9772	256	1.5
2	C ₁₉ H ₅₀ P ₃	371.3120	2.8124	7.5743	98.7149	321	-3.5
3	C ₁₉ H ₄₈ O ₂ PS	371.3107	4.0856	11.0030	97.8758	531	-3.5
4	C ₁₉ H ₄₇ O ₄ S	371.3190	-4.1571	-11.1956	97.6479	588	-3.5
5	C ₁₉ H ₄₉ O ₂ P ₂	371.3202	-5.4303	-14.6244	98.8709	282	-3.5
6	C ₂₂ H ₄₄ O ₂ P	371.3073	7.4564	20.0811	98.8498	287	1.5
7	C ₁₉ H ₄₉ P ₂ S	371.3025	12.3283	33.2017	98.0966	476	-3.5
8	C ₁₉ H ₄₇ O ₂ S ₂	371.3012	13.6014	36.6305	95.1422	1,214	-3.5

Fig. 9: MassWorks Processed Results for Peak B (Top: Mass Profile of *m/z* 371 of Peak B, Bottom: List of Candidates for Compositional Formula)