

# Estimation of Elemental Compositions for Additives in Polymers Using Newly Developed EI/CI Ion Source Without Venting MS

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## Introduction

- We have developed a new combined EI/CI ion source that removes the need of physical exchange between an electron ionization (EI) source and chemical ionization (CI) source. This reduces system downtime and allows uninterrupted analysis using both EI and CI.

### EI Method

Qualitative analysis based on mass pattern information.

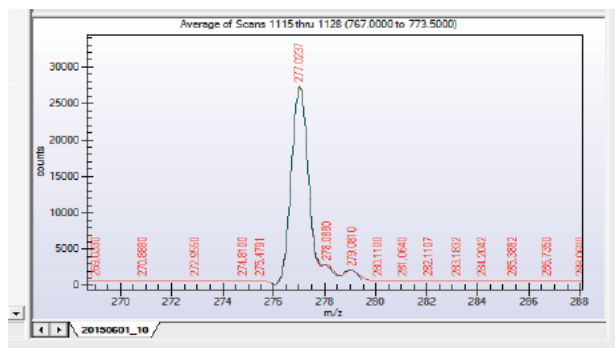
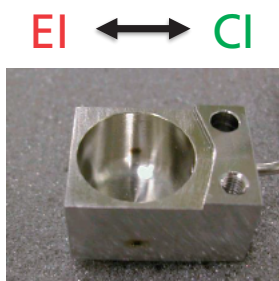
### CI Method

Obtains information about the molecular weights.

- MassWorks software (Cerno Biosciences) allows accurate mass information to be obtained from mass profile data using quadrupole MS. Elemental compositions can be estimated based on molecular-related ions.



	Formula	Mono Isotope	Mass Error (mDa)	Mass Error (PPM)	Spectral Accuracy
1	C <sub>11</sub> H <sub>2</sub> N <sub>8</sub> P	277.0135	10.2450	36.9823	98.6127
2	C <sub>13</sub> H <sub>12</sub> OP <sub>3</sub>	277.0096	14.1490	51.0752	98.6066



## Experimental Procedure

- Evaluating the New EI/CI Ion Source Performance**  
We analyzed a mixed standard solution of phosphate flame-retardant plasticizing agents (10 ppm, solvent: acetone) by liquid injection-GC/MS using three different ion sources (EI-specific ion source, CI-specific ion source, and the new combined EI/CI ion source).
- Evaluating the Elemental Composition of a Standard Sample Estimated by MassWorks**  
A sample of approximately 0.5 mg was cut from a polymer standard sample containing seven phthalate esters (DIBP, DBP, BBP, DEHP, DNOP, DINP, and DIDP, each at 1,000 mg/kg, PE, Shimadzu). The sample was analyzed by spot CI, using a Py-GC/MS system with the new EI/CI ion source installed.

MassWorks was then used to estimate an elemental composition from the molecular-related ions (M+H) detected, and the accuracy of each estimated phthalate ester was evaluated.

- Estimating Chemical Compounds of Unknown Peak Detected by Py-GC/MS Analysis of Polymers**  
A sample of approximately 0.5 mg was cut from a real-world polymer sample (cable sheath). The sample was analyzed using EI and CI by a Py-GC/MS system with the new EI/CI ion source installed. Chemical compound in unknown peak was also estimated using MassWorks to perform elemental composition analysis.

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## Analytical Conditions

Instrument	
Pyrolyzer	: EGA/PY-3030D multi-shot pyrolyzer + AS-1020E auto-shot sampler (Frontier Lab.)
GCMS	: GCMS-QP2020 (Shimadzu)
Pyrolysis	
Analysis Mode	: Heart-Cut EGA (thermal extraction)
Thermal Decomposition Temp.	: 200 °C - 20 °C/min - 300 °C - 5 °C/min - 340 °C (1 min)
ITF Temp.	: 300 °C (manual)
GC-MS	
Column	: UA-PBDE (15 m × 0.25 mm I.D., df = 0.05 μm)
Oven Temp.	: 80 °C -20 °C/min - 300 °C (5 min)
Carrier Gas	: He (linear velocity = 52.1 cm/sec)
Injection Method	: Split (1:50)
Injection Port Temp.	: 280 °C
ITF Temp.	: 320 °C
Ion Source Temp.	: 230 °C
Ionization	: EI, CI (reagent gas isobutane)
Measurement mode	: Scan

### Spot CI

Spot CI is a method where the filament is only turned ON while detecting the target peak (the peak to be analyzed for molecular weight information), but is turned OFF at other times.

The merits of this method are a reduced loss of ion source sensitivity and reduced attrition of the filament.

EGA/PY-3030D + AS-1020E or AOC-20i+s



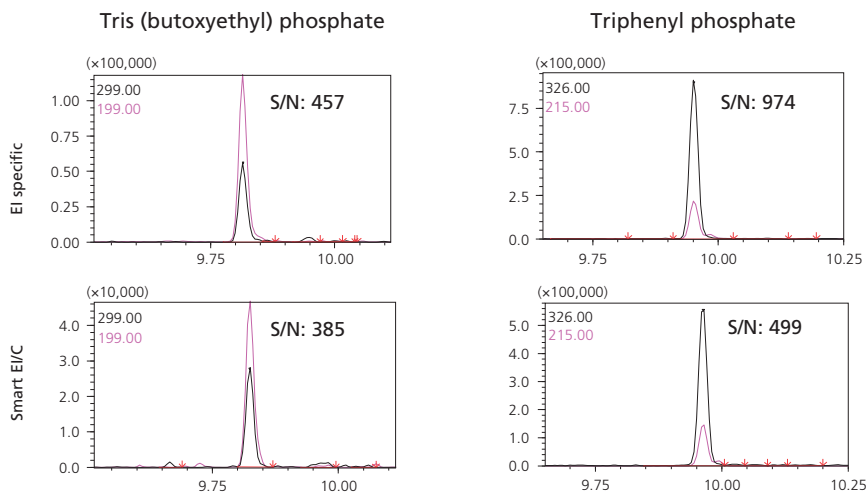
GCMS-QP2020

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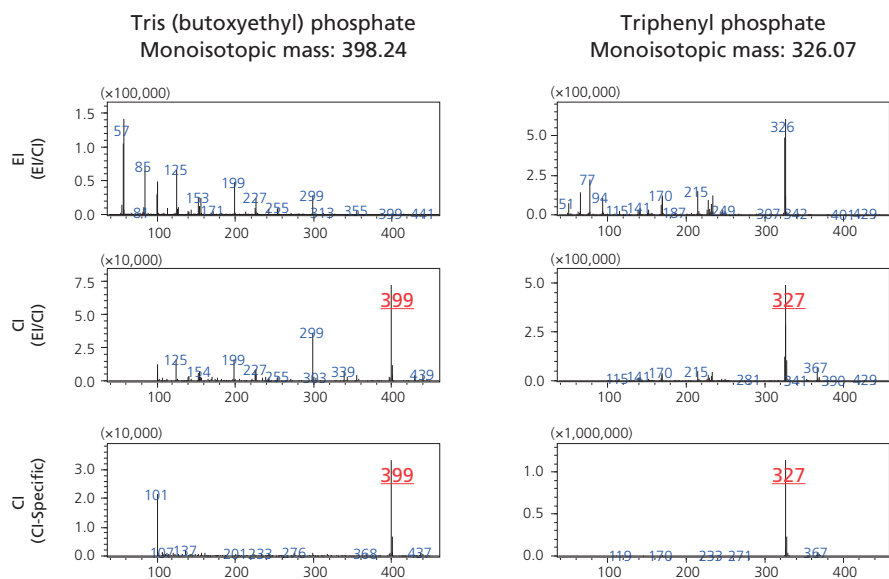
## Analysis Results

### 1. Evaluating the New EI/CI Ion Source Performance

- Comparison of SIM Sensitivity of EI Methods

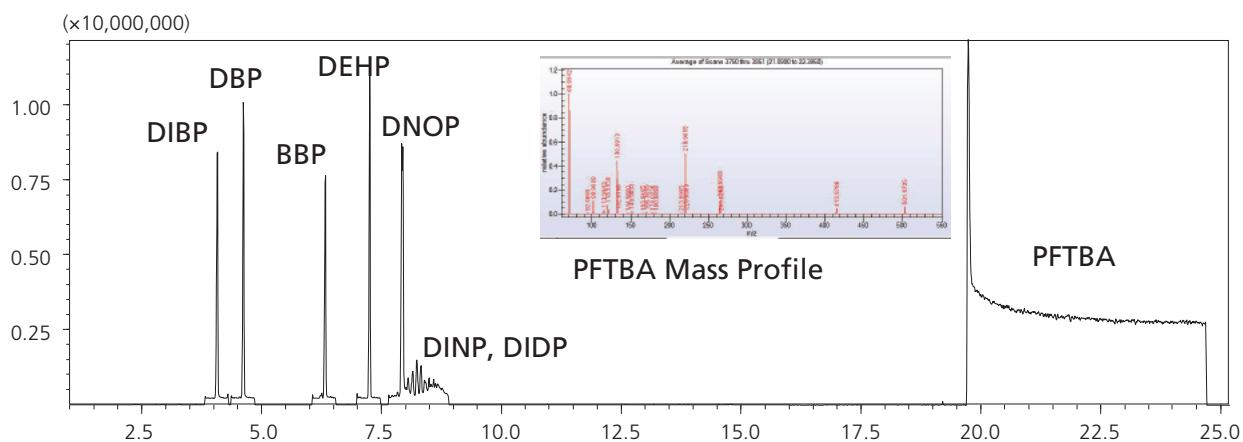


- Comparison of Mass Spectra of CI Methods



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## 2. Evaluating the Elemental Composition of a Standard Sample Estimated by MassWorks



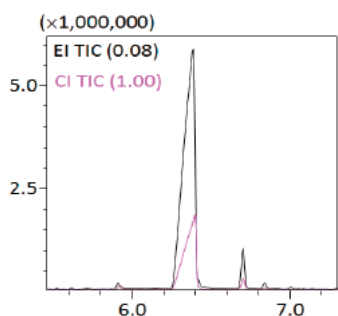
TIC of Polymer Standard Sample Containing Seven Phthalate Esters (1,000 mg/kg, Spot CI)

### • Results of Composition Estimation

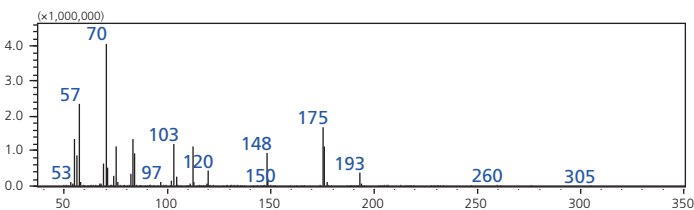
Without consideration of H desorption				With consideration of H desorption		
Ranking	Name of Compound	Formula	Monoisotope	Ranking	Spectral Accuracy	Mass Error (mDa)
10	DIBP	C16O4H23	279.1591	1	96.5385	-1.8856
5	DBP	C16O4H23	279.1591	1	97.2037	-2.8856
6	BBP	C19O4H21	313.1434	1	96.822	18.3644
6	DEHP	C24O4H39	391.2843	1	95.4571	8.6138
5	DNOP	C24O4H39	391.2843	1	95.6035	-0.7862
1	DINP	C26O4H43	419.3156	1	94.7035	3.4137
1	DIDP	C28O4H47	447.3469	1	95.8813	-1.2864

# Estimation of Elemental Compositions for Additives in Polymers Using Newly Developed EI/CI Ion Source Without Venting MS

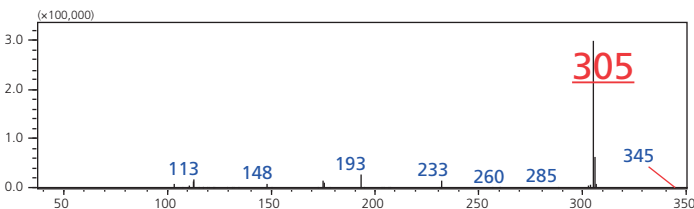
## 3. Estimating Chemical Compounds of Unknown Peaks Detected by Py-GC/MS Analysis of Polymers



EI



CI



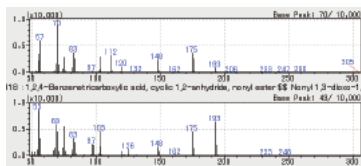
Results of Analyzing a Cable Sheath Using Py-GC/MS (EI and CI Methods)

### • Similarity Search of NIST 14

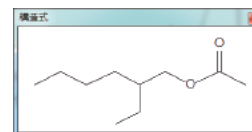
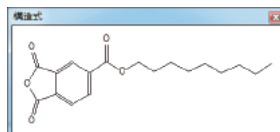
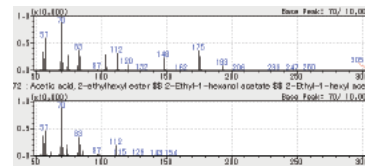
順位	類似度	化合物名	分子量	分子式	メタボ名
1	76	Carbonic acid, propanoyl 2-ethylhexyl ester	212	C12H20O3	NIST14.Jb
2	76	1-Hexanol, 2-ethyl-, acetate	172	C12H22O2	W01.00.Jb
3	75	Carbonic acid, 2-chloroethyl 2-methylhexyl ester	226	C11H21ClO3	NIST14.Jb
4	75	Carbonic acid, ethyl 2-ethylhexyl ester	214	C12H22O3	NIST14.Jb
5	75	Formic acid, 2-methylhexyl ester	158	COH16O2	NIST14.Jb
6	74	Carbonic acid, 2-methylhexyl octyl ester	286	C17H34O3	NIST14.Jb

Similarity of all results is below 80.

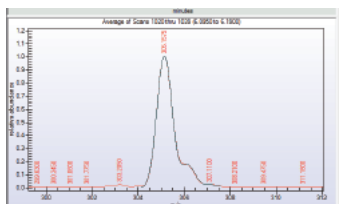
Similarity 76



Similarity 76



### • Composition Analysis with MassWorks

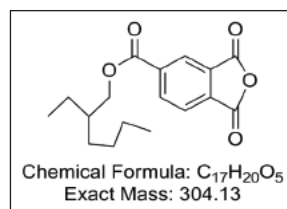


CLIPS search of  $m/z$  305

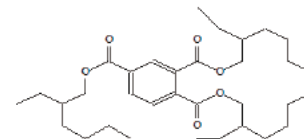
CLIPS Results						
Formula	Mono Isotope	Mass Error (mDa)	Mass Error (PPM)	Spectral Accuracy	RMSE	DBE
1	C17O5H21	305.1384	19.1496	62.7538	99.0777	7.5
2	C16O4N2H21	305.1496	7.9164	25.9420	99.0683	7.5
3	C18O4H25	305.1747	-17.2357	-56.4814	99.0669	7.60

**C17O5H21**

Estimated compositional formula



Estimated chemical compound  
(Probably a degradation product of TOTM)



Tri(2-ethylhexyl) trimellitate (TOTM)

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### Conclusion

1. We have developed a new EI/CI ion source capable of both EI and CI that does not require physical exchange between EI and CI ion sources. The new EI/CI ion source demonstrated almost the same performance with both EI-specific and CI-specific ion source.
2. The composition of seven phthalate esters was estimated using the new EI/CI ion source and MassWorks, and the correct component compositions appeared.
3. A real-world sample was subject to Py-GC/MS using EI and CI methods. MassWorks was used to estimate the composition of peak where the corresponding compound could not be identified, and the unknown chemical compound was estimated to probably be a TOTM degradation product.

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