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Application News

GC/MS

No. M284A

Identification of Phthalate Esters Using the SMCI Method

Commercially available foods and beverages come into contact with a variety of substances during their production and storage process. The materials in contact with foods leach into the products and could have an impact on the health of consumers. Phthalate esters, for example, are used as plasticizers for polyvinyl chloride. They are a concern with respect to endocrine disruption effects, developmental toxicity, reproductive toxicity, and tissue damage.

Phthalate esters share the same basic structure, and their mass spectra are similar when the electron ionization (EI) method is used, which can make the identification of target phthalate esters difficult. Conventionally, in such cases, the molecular weight is confirmed via the positive chemical ionization (PCI) method, using methane, isobutane, and other flammable, high pressure gases. In contrast, if the use of flammable, high pressure gases is problematic, the molecular weight can be confirmed via the solvent mediated chemical ionization (SMCI) method using organic solvents.

This article reports on the results of an analysis of phthalate esters using the SMCI method.

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Samples and Analytical Conditions

A standard solution of phthalate esters was prepared to a concentration of 1.0 ng/mL. The solution was measured using the EI and SMCI methods under the conditions in Table 1.

EI and SMCI Mass Spectra

The EI and SMCI mass spectra for Di-n-octyl phthalate and other phthalate esters are shown below.

When a similarity search was performed from the EI mass spectrum for Di-n-octyl phthalate (Fig. 1, top), phthalate esters with different molecular weights but with a high degree of similarity were identified, as shown in Fig. 2. Since compound identification with the EI mass spectrum only was difficult, the number of candidate compounds was narrowed down by confirming the molecular weights with the SMCI mass spectrum (Fig. 1, bottom).

Additionally, Fig. 3 shows the mass spectra for typical phthalate esters when the EI method and SMCI method are used respectively, and Table 2 shows the capability of confirmation of molecular derived ions. It shows that with the EI method, the molecular ions for many of the phthalate esters cannot be confirmed. In contrast, with the SMCI method, the protonated molecular ions for all of the phthalate esters can be confirmed, which provides strong support for compound identification.

Table 1 Instruments Used and the Analytical Conditions

Instruments Used		
GCMS	:	GCMS-TQ™ 8040 NX
Autosampler	:	AOC-20i+s
Analysis Column	:	SH-5MS (30 m × 0.25 mm I.D., 0.25 µm) *1
Glass Insert	:	Topaz Liner, Splitless Single Taper w/Wool
GC Conditions		
Injection Unit Temp.	:	280 °C
Injection Mode	:	Splitless (High pressure injection, 250 kPa, 1 min)
Carrier Gas Control	:	Constant linear velocity (43.8 cm/sec)
Column Oven Temp.	:	80 °C (1 min) → (10 °C/min) → 320 °C (5 °C/min)
Sample Injection Volume	:	1 µL
MS Conditions		
Interface Temp.	:	300 °C
Ion Source Temp.	:	230 °C
Ionization Method	:	SMCI (methanol), EI
Measurement Mode	:	Scan (SMCI: *m/z* 100 to 500, EI: *m/z* 45 to 500)
Event Time	:	0.3 sec

*1 P/N: 221-75855-30

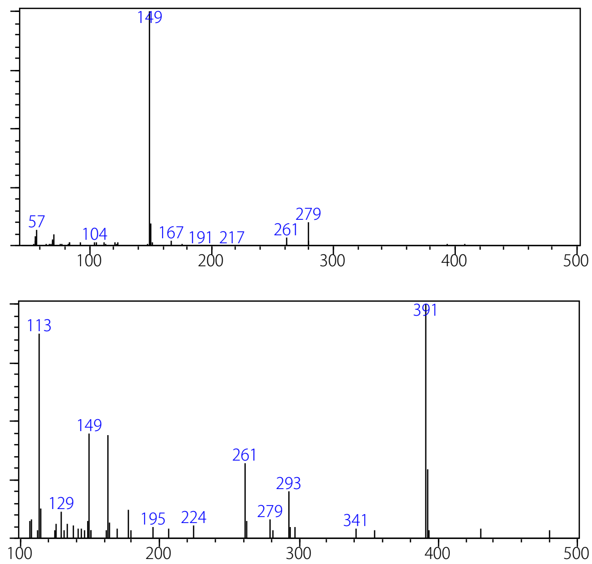
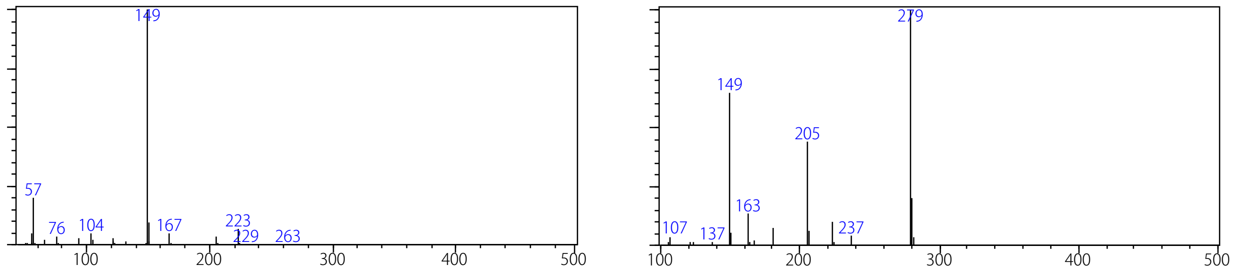


Fig. 1 Mass Spectra for Di-n-Octyl Phthalate (MW: 390) (Top: EI, Bottom: SMCI)

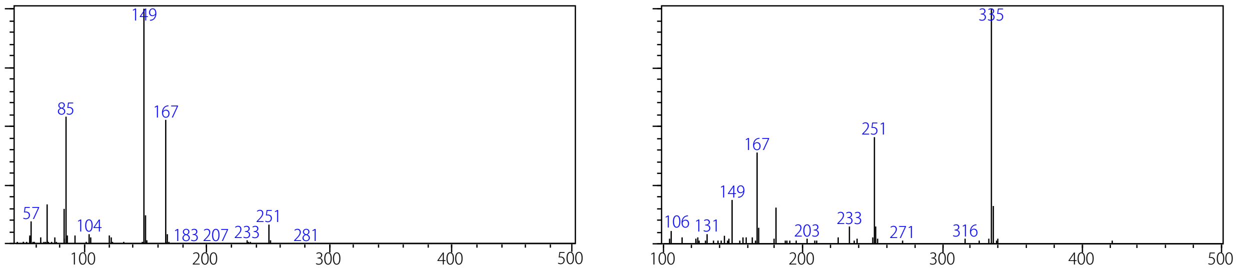
Hit#	Similarity	Register	Compound Name	Mol Wt	Formula	Library Name
1	97	☐	Di-n-octyl phthalate $$ 1,2-Benzenedicarboxylic acid, dioctyl ester	390	C24H38O4	NIST17s.lib
2	96	☐	Phthalic acid, 6-methylhept-2-yl octyl ester	390	C24H38O4	NIST17-1.lib
3	96	☐	Phthalic acid, hept-3-yl octyl ester	376	C23H36O4	NIST17-1.lib
4	95	☐	Phthalic acid, hex-3-yl octyl ester	362	C22H34O4	NIST17-1.lib
5	95	☐	Phthalic acid, 4-methylhept-3-yl octyl ester	390	C24H38O4	NIST17-1.lib
6	95	☐	Phthalic acid, dec-2-yl octyl ester	418	C26H42O4	NIST17-1.lib
7	95	☐	Phthalic acid, hept-4-yl octyl ester	376	C23H36O4	NIST17-1.lib
8	95	☐	Di-n-octyl phthalate $$ 1,2-Benzenedicarboxylic acid, dioctyl ester	390	C24H38O4	NIST17s.lib
9	95	☐	Phthalic acid, hept-2-yl octyl ester	376	C23H36O4	NIST17-1.lib
10	94	☐	Phthalic acid, 5-methylhex-2-yl octyl ester	376	C23H36O4	NIST17-1.lib

Fig. 2 Similarity Search Results Using the EI Mass Spectrum for Di-n-Octyl Phthalate

Diisobutyl phthalate (MW: 278)



Bis(4-methyl-2-pentyl) phthalate (MW: 334)



Dicyclohexyl phthalate (MW: 330)

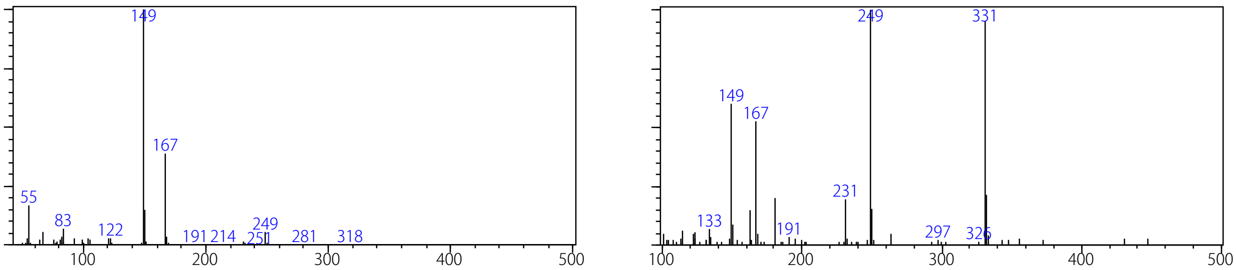


Fig. 3 Mass Spectra for Phthalate Esters (Left: EI, Right: SMCI)

Table 2 Capability of Confirmation of Molecular Derived Ions by the EI Method and SMCI Method

Compound Name	MW	SMCI	EI
Dimethyl phthalate	194	Yes	Yes
Diethyl Phthalate	222	Yes	Yes
Diisobutyl phthalate	278	Yes	No
Di-n-butyl phthalate	278	Yes	Yes
Bis(2-methoxyethyl) phthalate	282	Yes	No
Bis(4-methyl-2-pentyl) phthalate	334	Yes	No
Bis(2-ethoxyethyl) phthalate	310	Yes	No
Dipentyl phthalate	306	Yes	Yes
Di-n-hexyl phthalate	334	Yes	Yes
Benzyl butyl phthalate	312	Yes	Yes
Bis(2-n-butoxyethyl) phthalate	366	Yes	No
Dicyclohexyl phthalate	330	Yes	No
Bis(2-ethylhexyl) phthalate	390	Yes	No
Di-n-octyl phthalate	390	Yes	No
Di-nonyl phthalate	418	Yes	No

Summary

For many phthalate esters, confirmation of molecular weight from the EI mass spectrum is difficult. However, pseudo molecular ions can be confirmed using the SMCI method. Accordingly, even if the use of a flammable, high pressure gas is problematic, it is evident that the SMCI method is effective for the confirmation of molecular weights.

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