

# Technical Report

## Usefulness of Smart EI/CI Ion Source Which Enables Both EI and CI Mode Measurements with the Same Ion Source

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### Abstract:

Smart EI/CI ion source was newly developed based on the concept of an ion source that can easily switch to CI measurements without compromising the sensitivity of the generally used EI method. This unit can switch between EI and CI measurements without the need to replace the ion source. Measurements can be switched immediately if CI measurements are needed for rapid molecular weight confirmation.

Smart EI/CI ion source is the optimal ion source for users who are using GC-MS mainly for qualitative analysis.

**Keywords:** GC-MS, positive chemical ionization method, PCI, ion source replacement

### 1. Introduction

The Electron Ionization (EI) method is the most generally used GC-MS ionization method. Originally for quantitative analysis to calculate target compounds at trace concentrations in samples, the EI method is also widely used for qualitative analysis as well due to the wealth of mass spectral libraries such as NIST and Wiley.

At the same time, if target compounds are not registered in a mass spectral library, then mass spectral analysis must be performed, and these analysis procedures are very difficult. Additionally, the EI method utilizes characteristics involving the collision of high-energy thermoelectrons to cause fragmentation, so molecular ions might not be detected depending on the structure of the compound.

In the Positive Chemical Ionization (hereinafter, "PCI") method, methane, isobutane, and other reagent gases are ionized within the ion source, and an ion-molecular reaction occurs with the target compound. Because this is an indirect ionization reaction, fragmentation occurs less easily in comparison to the EI method, so this ionization method is suitable for collecting molecular weight information. In particular, when a compound cannot be identified in a mass spectral library with EI measurements, molecular weight information can be very useful for qualitative analysis.

Normally, dedicated ion sources are prepared for each type of ioniza-

tion, in order to obtain the optimal sensitivity with the respective different ionization methods. Fig. 1 shows a schematic of the ion sources for each type of ionization.

With the EI ion source, in order to take in as many thermoelectrons generated from the filament as possible, the port for the thermoelectron incident beam is designed to be large. The diameter of the ion emission port is also designed to be large to ensure that ions are delivered rapidly and efficiently to the quadrupole. With the CI ion source, an ion-molecular reaction occurs with the ionized reagent gases. Accordingly, to ensure that the interior of the ion source is filled with reagent gas, the thermoelectron incident port and the ion emission port are designed to be very small.

With the NCI ion source, the diameters of the thermoelectron incident port and the ion emission port are larger than in a CI ion source. Sub-EI and CI mode can be used to acquire EI and CI with the NCI ion source. However, in sub-EI mode with NCI, many of the thermoelectrons from the filament are not taken into the ion source, so this mode is not intended for analysis at trace concentrations.

Accordingly, to switch between EI and CI, the ion source must normally be replaced. This is quite inconvenient, as the replacement process takes a long time.

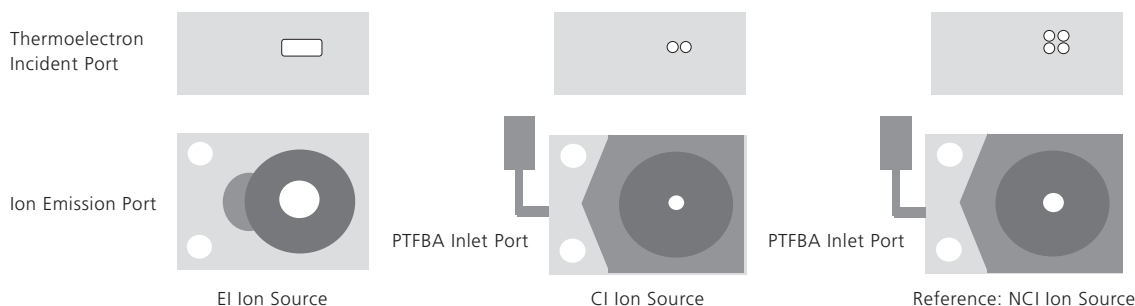


Fig. 1 Schematic Diagram of the Ion Source for Each Type of Ionization

## 2. Smart EI/CI Ion Source

In order to overcome these difficulties, Smart EI/CI ion source was developed based on the following two concepts.

- EI and CI can be acquired with the same ion source.
- The generally used EI sensitivity must not be compromised.

In addition to the GCMS NX series, Smart EI/CI ion source can be used with the GCMS-QP2010 Plus and subsequent GCMS-QP™ series, and GCMS-TQ™ series CI or NCI models.

### 2-1. EI Sensitivity in Smart EI/CI Ion Source

EI sensitivity was compared for pesticides at 10 ng/mL using an EI ion source and Smart EI/CI ion source. Fig. 2 shows the scan mass chromatograms for diazinon and phenthoate.

It is evident that the EI method sensitivity with Smart EI/CI ion source was almost equivalent to the sensitivity with a dedicated EI ion source.

The S/N ratios were calculated using the peak-to-peak method.

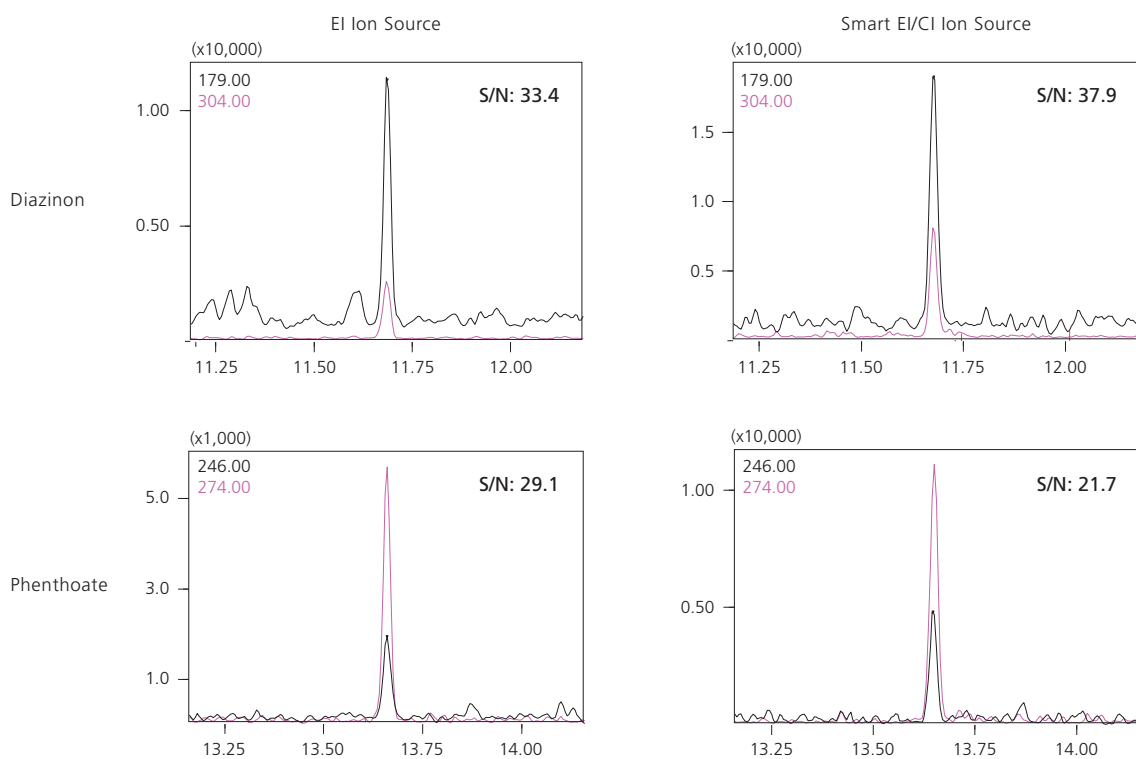


Fig. 2 Typical Pesticide Mass Chromatograms (at a Concentration of 10 ng/mL) Measured with an EI Ion Source and Smart EI/CI Ion Source

Table 1 Results of a Comparison of S/N Ratios with an EI Ion Source and Smart EI/CI Ion Source for Pesticides at 10 ng/mL

Compound Name	EI Ion Source S/N Ratio	Smart EI/CI Ion Source S/N Ratio	Compound Name	EI Ion Source S/N Ratio	Smart EI/CI Ion Source S/N Ratio
Ethoprophos	113.4	52.3	Tolclofos-methyl	253.1	220.7
Salithion	178.0	145.3	Pirimiphos methyl	197.2	94.8
Thiometon	104.6	102.2	Chlorpyrifos	40.9	66.7
Diazinon	33.4	37.9	Fenthion	315.4	549.4
Etrimfos	56.3	30.8	Phenthoate	29.1	21.7
Iprobenfos	47.5	25.2	Bromophos-ethyl	117.1	142.3
Dichlofenthion	174.5	93.0	Prothiofos	35.4	61.3
Chlorpyrifos-Methyl	201.7	343.5	EPN	66.3	112.8

## 2-2. CI Mass Spectra and Sensitivity with Smart EI/CI Ion Source

The CI mass spectra were compared for caffeine and triazolam using a CI ion source and Smart EI/CI ion source (Fig. 3). While some fragment ions were detected in the CI method mass spectra with Smart EI/CI ion source, protonated molecules ( $M+H^+$ ) were confirmed.

Fig. 4 shows the mass chromatograms for caffeine and methyl stearate. The CI ion source is structured to make it easy to fill with reagent gases, which leads to peak tailing. With Smart EI/CI ion source, how-

ever, the structure is close to that of an EI ion source, so the peaks are sharp, which contributes to an improved S/N ratio. Accordingly, it is evident that the CI method sensitivity with Smart EI/CI ion source is almost equivalent to the sensitivity with a dedicated CI ion source.

Smart EI/CI ion source is the optimal ion source for customers who are using GC-MS for qualitative analysis.

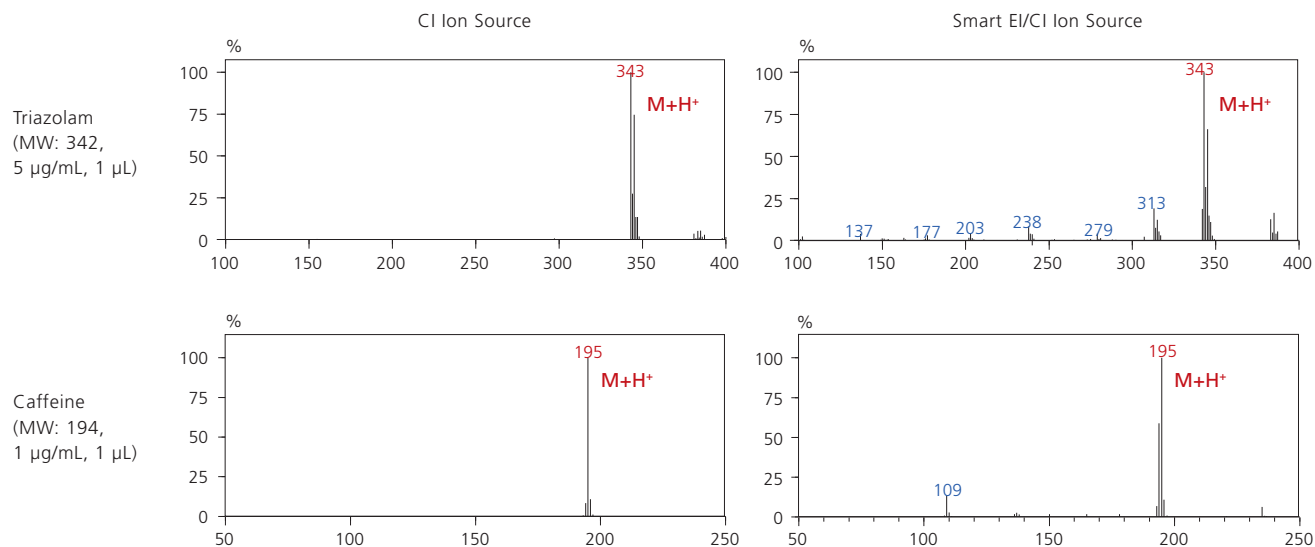


Fig. 3 Mass Spectra for Caffeine and Triazolam Measured with a CI Ion Source and Smart EI/CI Ion Source

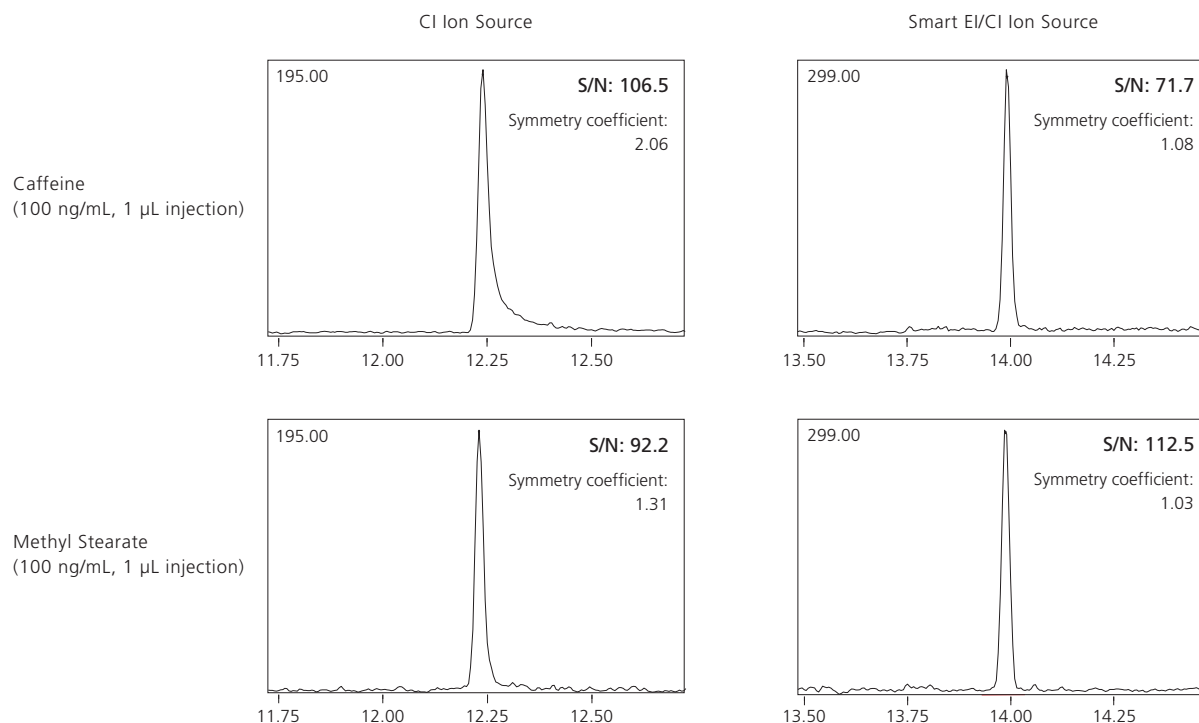


Fig. 4 Mass Chromatograms for Caffeine and Methyl Stearate Measured with a CI Ion Source and Smart EI/CI Ion Source

### 3. Application Examples

#### 3-1. Analysis of Additives in Resin Materials

Various additives are kneaded into resin materials in electrical products and everyday commodities, in order to improve their stability and durability. In recent years, RoHS, REACH, and other restrictions on chemical substances that are harmful to human health have been strengthened, and additives in resin materials are now strictly controlled. In many cases, molecular ions of additives do not appear with EI, so using EI in combination with CI increases the efficiency of the analysis process and improves the reliability of component identification.

Fig. 5 shows the Total Ion Current Chromatograms (TICC) obtained from measurements of a resin material with Py-GC/MS. The stars indicate peaks for which molecular ions could not be confirmed with EI. Fig. 6 shows the EI and CI mass spectra for three typical peaks detected (A to C). Using Smart EI/CI ion source in this way, EI and CI data can be acquired easily by switching between the methods.

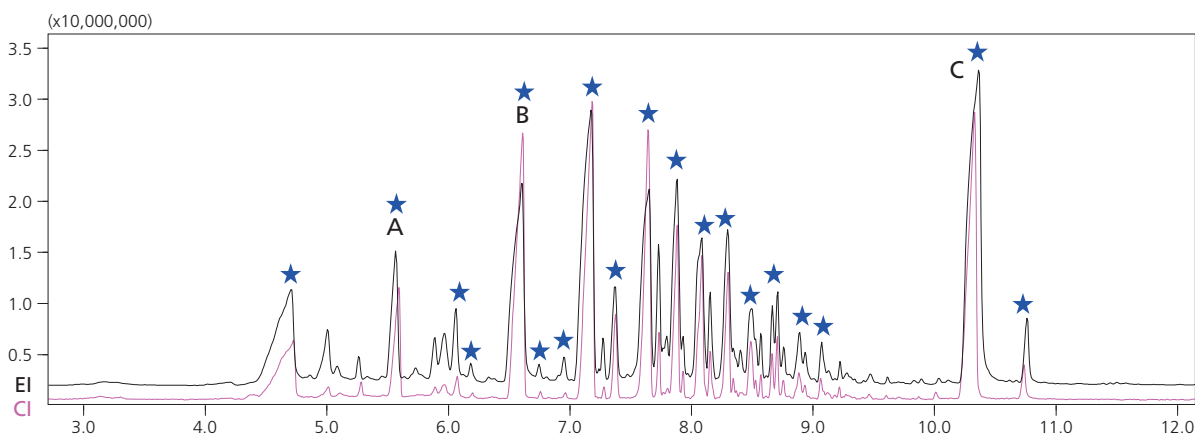
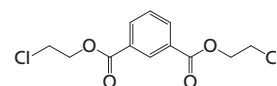
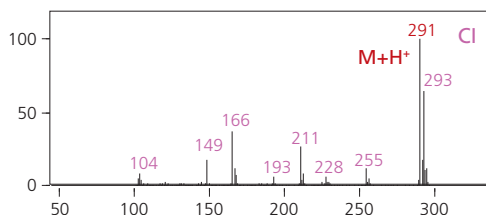
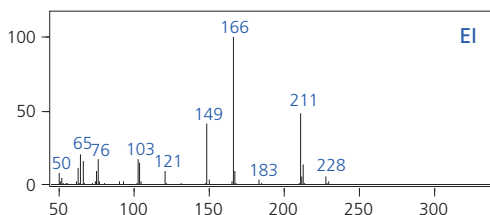
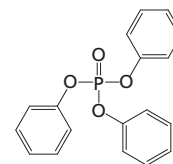
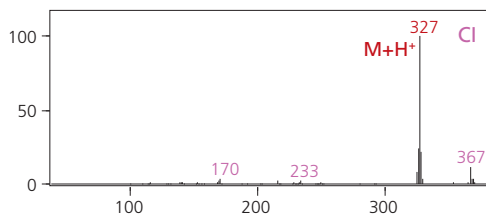
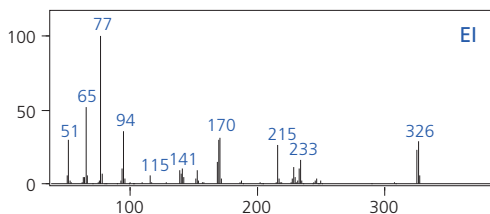


Fig. 5 EI and CI Total Ion Current Chromatogram for a Resin Material Measured with Py-GC/MS

Peak A: Di(2-Chloroethyl) Isophthalate Ester (MW: 290)



Peak B: Triphenyl Phosphate (MW: 326)



Peak C: Trimellitic Acid Tris(2-Ethylhexyl) Ester (MW: 546)

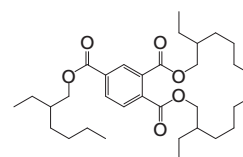
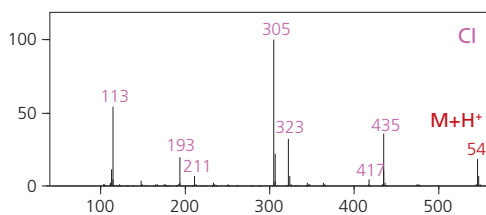
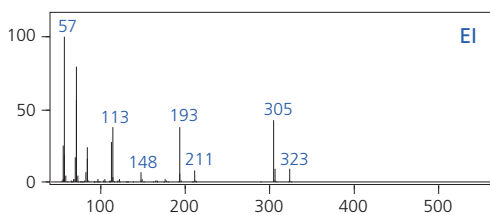


Fig. 6 EI and CI Mass Spectra for Typical Peaks Detected

### 3-2. Mass Spectral Confirmation of Synthetics

In the injection of general samples, the samples are injected from an injection unit and separated in a column. However, some compounds might not be vaporized or eluted from the column depending on their boiling point or polarity, making measurements with GC-MS difficult.

In the direct sample injection method (DI), the sample is injected directly into the ion source without passing through the injection unit or column. The DI probe can be heated up to 500 °C, and the compound is injected directly into the ion source for ionization under vacuum conditions. As a result, the mass spectra can easily be obtained even for high polarity or high boiling point compounds.

The preparations for measurement consist simply of placing the sample in a sample cup and then placing the cup in the probe (Fig. 7).



Fig. 7 Direct Sample Injection (DI) Unit and Operations to Prepare for Measurements

As an example of a qualitative analysis combining DI with Smart EI/CI ion source, the results are shown for a measurement of clarithromycin, a nonvolatile antibiotic (Fig. 8). This compound has a molecular weight in excess of 700, and has multiple hydroxyl groups (-OH) that contribute to its high polarity. Accordingly, GC/MS measurements with general sample injection are very difficult. However, the mass spectrum can easily be obtained using DI.

In the EI mass spectrum, molecular ions from clarithromycin (MW: 747) were not detected. In such a case, if Smart EI/CI ion source is used, the CI method mass spectrum can easily be obtained by switching to the CI method, but without replacing the ion source. With CI measurements using Smart EI/CI ion source, protonated molecules ( $M+H^+$ ) at an  $m/z$  of 748 could be detected.

Clarithromycin (MW: 747)

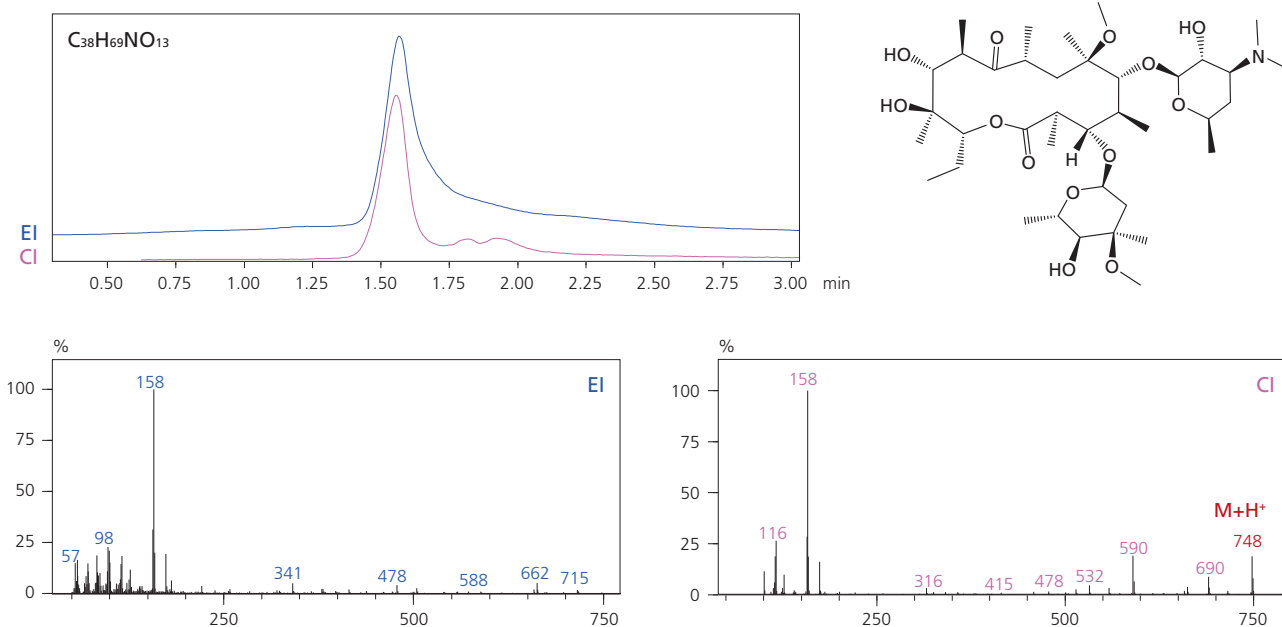


Fig. 8 Example of the Analysis of the Antibiotic Clarithromycin Using Direct Sample Injection (DI) and Smart EI/CI Ion Source

### 3-3. Analysis of Forensic Toxicological Substances

The circulation of drugs that have been structurally modified to avoid regulations on drugs of abuse has become a major social problem. The identification of new drug compounds is now an important mission for crime laboratories.

In analyzing these drugs, identification through the comparison of results obtained from the measurements of standards is indispensable. However, when the chemical structure of drugs has been partially modified, there may not even be analysis data, let alone standards available.

LC-MS(/MS) and GC-MS(/MS) are used as procedures for compound identification. However, while molecular weight information is easily obtained with LC-MS, fragment ions are obtained with GC-MS, so partial structure information can be obtained by reading and analyzing the mass spectrum.

Effective information for compound identification can thus be obtained by combining the analysis results from both instruments.

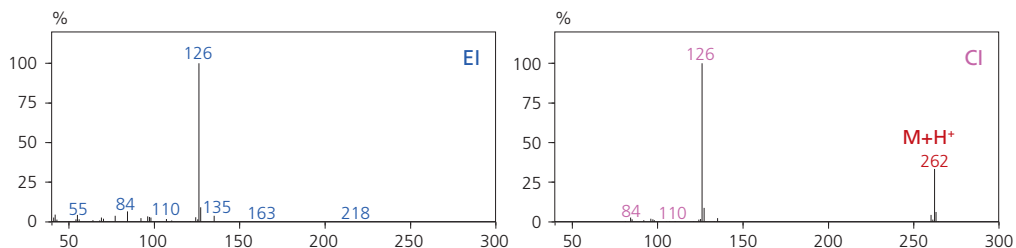
However, because the chromatographic separation is different, when a sample contains multiple compounds, it is necessary to check whether the peaks detected with each instrument are from the target compound.

Using Smart EI/CI ion source, EI and CI data can be acquired under the same analysis conditions without switching the ion source, so confirmation of peaks from each data set can easily be performed.

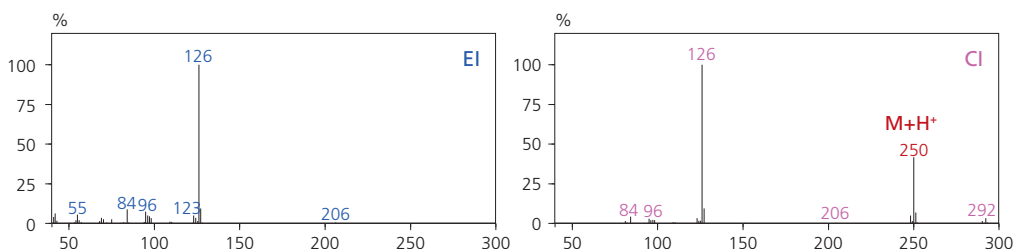
Fig. 9 shows the EI and CI mass spectra for cathinone, including 4-Methoxy- $\alpha$ -PVP, 4-Fluoro- $\alpha$ -PVP and 4-Chloro- $\alpha$ -PVP, obtained with Smart EI/CI ion source.

These compounds with molecular ions are difficult to detect with EI. In addition, only characteristic molecular ions, such as  $m/z$  126 of amine-initiated  $\alpha$ -cleavage, can be detected, making it difficult to estimate the modifying functional groups. By switching to CI with Smart EI/CI ion source, molecular weight information can easily be obtained and functional groups can be estimated.

4-Methoxy- $\alpha$ -PVP (MW: 261)



4-Fluoro- $\alpha$ -PVP (MW: 249)



4-Chloro- $\alpha$ -PVP (MW: 265)

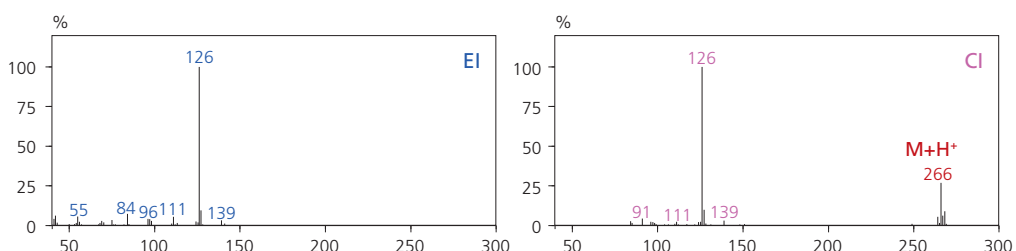


Fig. 9 EI and CI Mass Spectra of  $\alpha$ -PVP with Different Functional Groups

### 3-4. Analysis of Impurities in Container Packaging

In recent years, a transition to a positive list system has been investigated for container packaging in food products due to health concerns. There are a wide range of materials in the synthetic resins used in container packaging, including additives, resin materials, by-products and impurities generated by the synthesis process.

The analysis of impurities starts with qualitative analysis to determine what compounds are contained in, or are leaching from, the target sample.

Sometimes, these compounds are not registered in a mass spectral library, in which case, confirmation of molecular weights with CI gives a hint at the identification of the compound detected.

In the analysis of leachates in container packaging, EI and CI measurements were performed using Smart EI/CI ion source.

A packaging container was cut up into 1 cm<sup>2</sup>, and the material was placed in a vial so as to obtain a surface area of 20 cm<sup>2</sup>. Two vials

were prepared, and 20 mL of an aqueous 20 % ethanol solution and 3 % acetic acid were added respectively.

Then, the vials were heated for 60 minutes at 60 °C. After heating, 20 mL of dichloromethane was added, and two cycles of liquid extraction were performed. The extracted samples were mixed and then enriched using an evaporator under a nitrogen gas flow. The volume was then adjusted to 1 mL using dichloromethane to form the test sample.

Fig. 10 shows the total ion current chromatogram for impurities in container packaging extracted with 20 % ethanol. Additionally, Fig. 11 shows the EI and CI mass spectra for typical peaks detected.

From the EI mass spectra and CI protonated molecular results, peak A can be identified as erucamide, which is used as a lubricant, and peak B can be identified as tris(2,4-di-tert-butylphenyl) phosphite, which is used as an antioxidant.

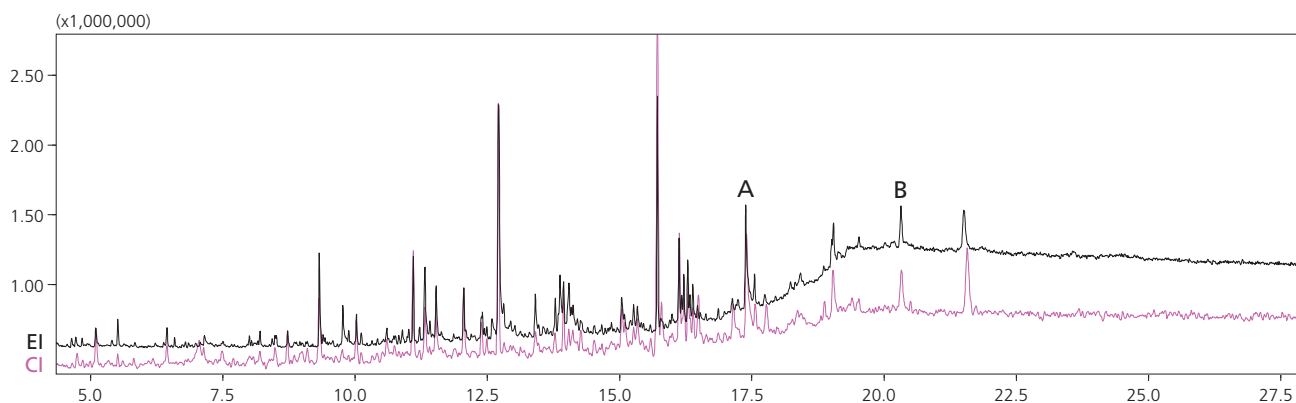
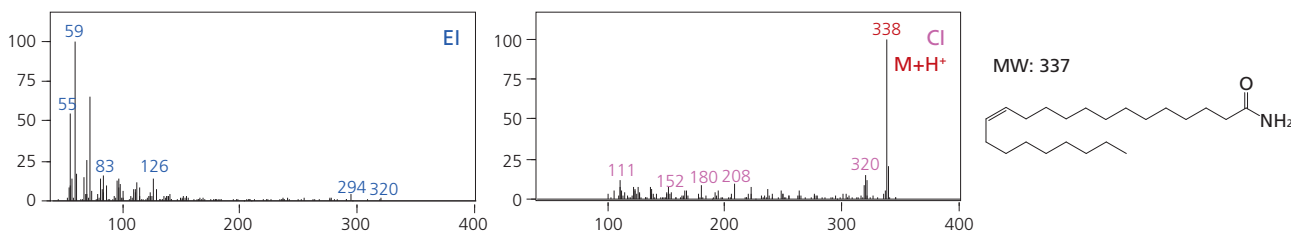


Fig. 10 EI and CI Total Ion Current Chromatogram for Leachates from Packaging Containers in 20 % Ethanol

Peak A: Erucamide (MW: 337)



Peak B: Tris(2,4-Di-Tert-Butylphenyl) Phosphite (MW: 646)

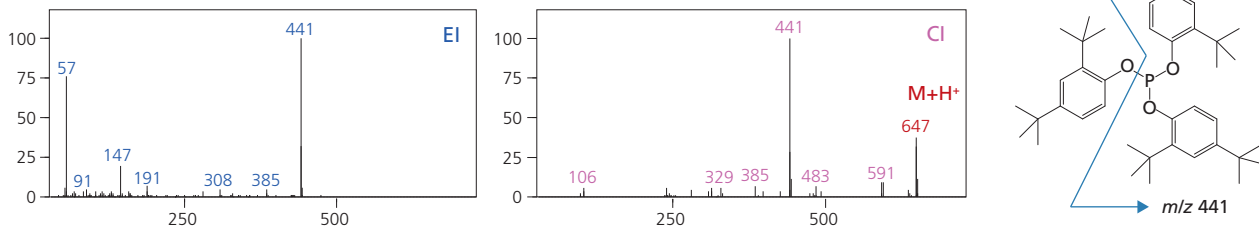


Fig. 11 EI and CI Mass Spectra for Typical Peaks Detected

## 4. Conclusion

Smart EI/CI ion source was developed as a new ion source that can perform CI measurements with the same ion source without compromising the sensitivity of generally used EI.

This ion source will expand CI usage options for analysts who have been reluctant to use CI because of the necessity of replacing the ion source in order to switch between EI and CI.

In addition to EI mass spectral analysis in order to identify unknown compounds, molecular weight information can now be combined, improving the reliability of the analysis.

Smart EI/CI ion source is the optimal ion source for users who are using GC-MS mainly for qualitative analysis.

## Gas Chromatograph Mass Spectrometer GCMS-QP2020 NX

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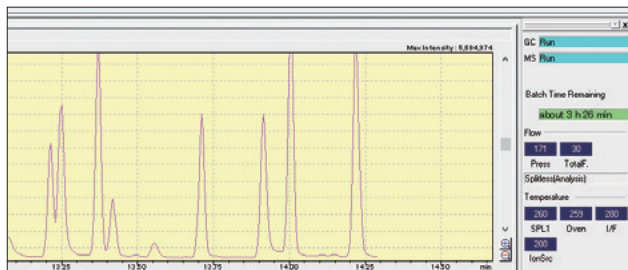


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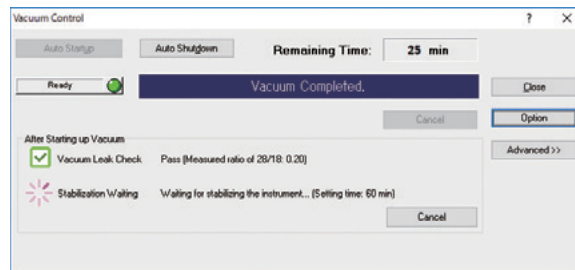
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