Acquisitions of Molecular-weight Information Using Soft-ionization Techniques (PI and CI)

Product: JMS-Q1500GC GC/MS System

Introduction

Electron ionization (EI), a hard-ionization technique that generates many fragment ions, is the most widely used ionization technique in gas chromatography–mass spectrometry (GC-MS). Since EI mass spectra have good reproducibility, qualitative analysis is possible by comparing an EI mass spectrum of a sample with that of the known compound recorded in the database. However, sometimes EI mass spectra lack molecular ions, which are of key importance to molecular-weight (MW) determination and correct compound assignment. Soft ionization is a useful way to determine MW. The JEOL JMS-Q1500GC offers two soft-ionization techniques: chemical ionization (CI) and photoionization (PI).

In this application note, the MW information of diethyl phthalate and *n*-tetradecane were estimated from measurement results using both of these soft-ionization techniques.

What is Chemical Ionization?

The CI ion source consists of a chamber with higher hermeticity than the EI ion source, as well as a filament and a repeller. The reagent gas introduced into the CI chamber is ionized; ionization of the sample occurs by electrons, protons, and other charged species transferring from the ionized reagent gas to the sample molecule (M). Generally, methane, *iso*-butane, or ammonia is used as the reagent gas. In the case of a proton transfer reaction, we can predict protonated $[M+H]^+$ ion generation based on the proton affinity (*PA*) of both the reagent gas and M. When M has higher *PA* than the reagent gas, a proton transfer reaction occurs. However, CI can be unpredictable, in that generated ion species differ depending on the reagent gas. In the case of methane or *iso*-butane as the reagent gas, $[M+H]^+$ ions are generally produced by proton transfer. Other ions such as $[M-H]^+$, M^+, or $[M + \text{reagent ion}]^+$ may also be detected.

Figure 1. JMS-Q1500GC with PI ion source.

What is Photoionization?

PI is an another soft-ionization technique available with the JMS-Q1500GC. The PI ion source radiates vacuum ultraviolet (VUV) light, which is approximately 8–10 eV, onto sample molecules. The ionization energy of organic compounds in general is between 8 and 11 eV. The similar ionization energy levels provided by the PI technique promote the appearance of the molecular ion M^+, which makes determining the MW a lot easier. In addition, PI is much easier to perform, as it requires VUV lights only—and it does not require reagent gases, which can be flammable or hazardous.

The PI Ion Source

Figure 2 is a schematic of the PI ion source. The PI ion source offers two ionization techniques, normal EI and PI. It has two filaments for EI and a deuterium lamp for PI. The user can easily and quickly switch between hard and soft ionization from the PC without braking vacuum or changing parts.

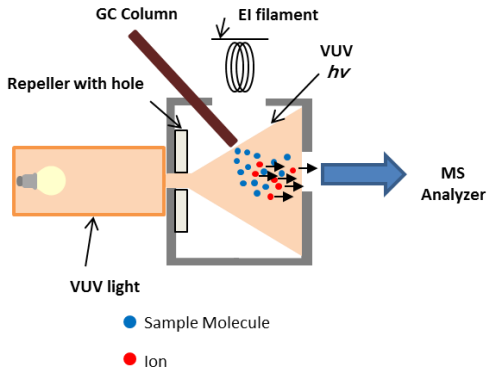


Figure 2. Schematic of the PI ion chamber.

Results

To compare the EI, CI, and PI mass spectra, diethyl phthalate and *n*-tetradecane standards were measured using each technique. Mass spectra results are shown in Figure 3. In the EI mass spectrum, many more fragment ions were detected from both compounds than in the CI and PI mass spectra. The molecular ion was observed as the main peak in CI and PI mass spectra and some fragment ion peaks from each sample.

The CI mass spectra of diethyl phthalate and *n*-tetradecane showed $[M+H]^+$ and $[M-H]^+$, respectively, as MW information. The molecular-ion type obtained from the CI mass spectrum depends on the PA of the compound, of the CI gas, and of other components. To understand the MW information from the detected peak, it is sometimes necessary to measure using two or more CI reagent gases. Molecular-ion assignment also requires experience. On the other hand, only M^+ molecular-ion information was observed, from which it is much easier to estimate MW.

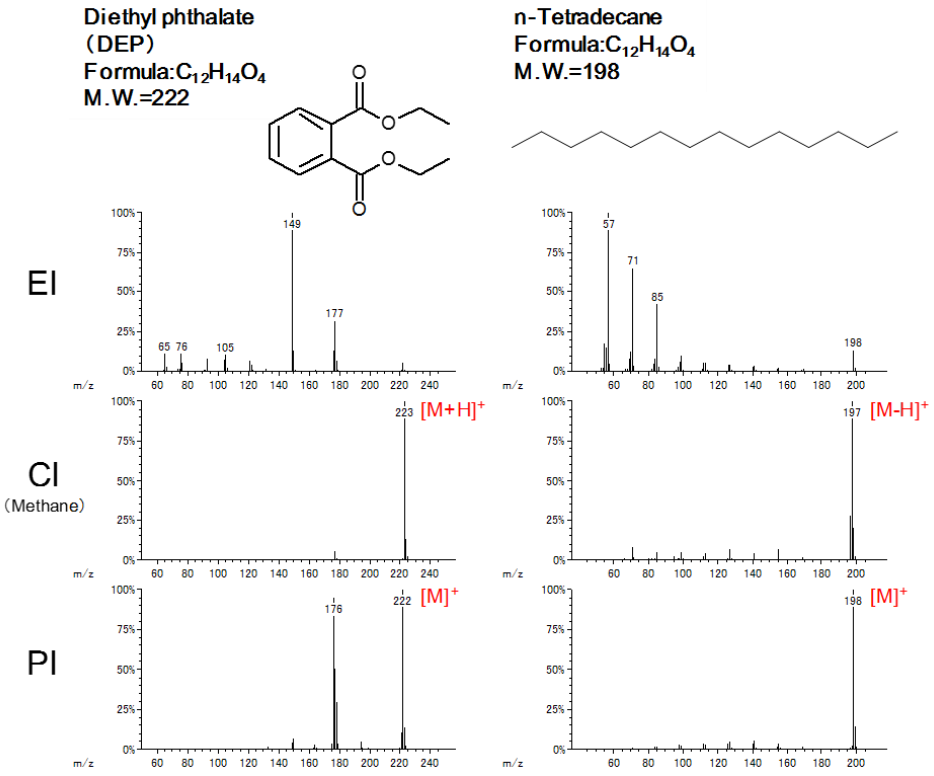
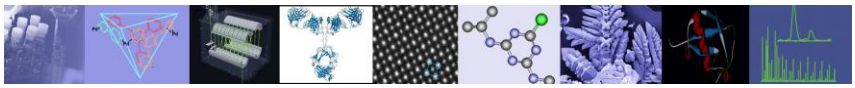


Figure 3. Mass spectra of diethyl phthalate and *n*-tetradecane.



Conclusion

- The CI technique makes it easy to detect $[M+H]^+$ and $[M-H]^+$ ions with high sensitivity. Various compounds can be measured using CI, however, it takes a great deal of time and labor to manage the reagent gas. Another disadvantage is that the mass spectrum becomes complicated by the various ions generated (e.g., $[M-H]^+$, M^+, $[M+H]^+$, $[M+C_2H_5]^+$, $[M+C_4H_9]^+$, $[M+NH_4]^+$).
- The PI ion source allows the user to switch between EI and PI, and it is much safer to handle than CI because there is no need to use flammable gases.
- In addition, PI offers the advantage of easy MW estimation, since primarily M^+ ions are observed in the mass spectrum.

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