Title – Limit 20 words

Photoionization as a Soft Ionization Source for Comprehensive Two-dimensional GC (GCxGC) and High-Resolution TOFMS

Authors

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Introduction – Limit 120 words

Recently, we developed a photo ionization (PI) ion source as 3rd soft ionization technique for a gas chromatography/high resolution time-of-flight mass spectrometer (GC/HR-TOFMS) system. PI is a soft ionization technique that provides good sensitivity and molecular ion information for compounds with ionization energies below the maximum practical photon energy (10.8 eV) of the deuterium lamp used in our current design. GC/PI MS and GCxGC/PI MS is particularly useful for the analysis of hydrocarbons and aromatic compounds and can be more sensitive than field ionization for certain applications. Because GC/HR-TOFMS can easily give exact mass information for all of the ions generated by photoionization, target compound identification can be very selective and the identification of unknowns is facilitated.

Methods – Limit 120 words

We measured petroleum biomarkers including steranes, triterpenes and adamantanes in several crude oils. The crude oil samples were dissolved in n-hexane without further purification. Afterwards, the sample solutions were analyzed with a JMS-T100GCv "AccuTOF GCv 4G" (JEOL), gas chromatograph / high-resolution time-of-flight mass spectrometer equipped with an Agilent 7890B GC and a Zoex ZX-2 thermal modulator for GCxGC separations. We used electron ionization (EI) as hard ionization, and photo ionization (PI) as soft ionization in this study. All mass spectra were mass-calibrated after the measurements with a one-point drift compensation method using a background ion from the capillary column in EI and PI mode.

Preliminary data – Limit 300 words

In this study, we initially checked several PI mass spectra for hydrocarbons in crude oil samples. We observed molecular ions as the 1st or 2nd most abundant peak for hydrocarbons such as n-Alkanes, PAHs, steranes, triterpenes and adamantanes. No fragment ions were observed in the mass spectra for PAHs.   Molecular ions were observed for other compound classes such as chloroalkanes, ketones, FAMEs, phthalates and phenols with PI technique. Alcohols were the exception: these produced predominantly $[M-H_2O]^+$.

The high-resolution mass spectrometer was easily able to separate biomarkers having identical integer masses but different exact masses from their interferences. However, homologue fragment ions produce interferences that can be complicate the identification of sterane molecular ions in EI mode. For example, if we need to separate the molecular ion of steranes ($C_{27}H_{48}^+$, *m/z* 372.3756) from the isotopic fragment ion of methyl steranes ($^{12}C_{26}^{13}C_1H_{47}^+$: *m/z* 372.3712), a mass resolving power of over 200,000 is required to separate these components. Therefore, the molecular ion extracted ion chromatogram (EIC) for steranes ($C_{27}H_{48}^+$, *m/z* 372.3756) in the GCxGC/EI data also includes the chromatographic peaks of the isotopic fragment ion of methyl steranes ($^{12}C_{26}^{13}C_1H_{47}^+$: *m/z* 372.3712).

Because PI is a much softer ionization method, the interfering fragment ions are not observed and the unwanted peaks can be eliminated. The EIC for sterane molecular ions in the GCxGC/PI data showed that the isotopic fragment ion interferences from the methyl steranes disappeared. The PI EICs made it much easier to interpret the data and correctly assign the biomarker identities in crude oil samples.

Novel aspect – Limit 20 words

The combination of GCxGC with high-resolution mass spectrometry and photo ionization is powerful tool for biomarker identification in crude oils.