

Molecular characterization of petroleum mixtures using multiple ionization modes and GC × GC-HRTOFMS

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Key points

The GC × GC field is ongoing a paradigm shift in which the MS dimension is even further contributing than before.

→ The implementation of softer ionization approach opens the doors of full exploitation of HRMS information, especially for high boiling molecules.

→ The different strength of ionization offers complementary information at the molecular level.

→ The combination of the soft ionization-HRMS with the structured separation of GC × GC is providing additional identification information.

→ The selectivity of PI for some oxygenated compounds offers new way of characterization for oxidation products.

Context

Comprehensive two-dimensional gas chromatography (GC × GC) has become a method of choice for complex mixture characterization, especially in the petroleum industry. Indeed, the high resolving power of the 2D separations offers structured separation allowing pattern recognition and group type classification of sample composition.

For years, the technique was relying on electron ionization (EI) fragmentogram and chromatographic-based identification due to practical limitations on the detector side, mainly the high acquisition frequency required. The development of **high-speed high-resolution time-of-flight mass spectrometers (TOFMS)** offers opportunities to go deeper in the sample characterization.

To obtain the most of the HRMS dimension, there is a growing interest to combine EI with **softer ionization techniques, which can preserve the molecular ion.**

Results & Discussion

Aim of the study

1. Develop an analytical strategy for heavy petroleum mixtures
2. Compare different ionization approaches in order to allow molecular characterization
3. Exploit the additional molecular information

Method and Instrumentation

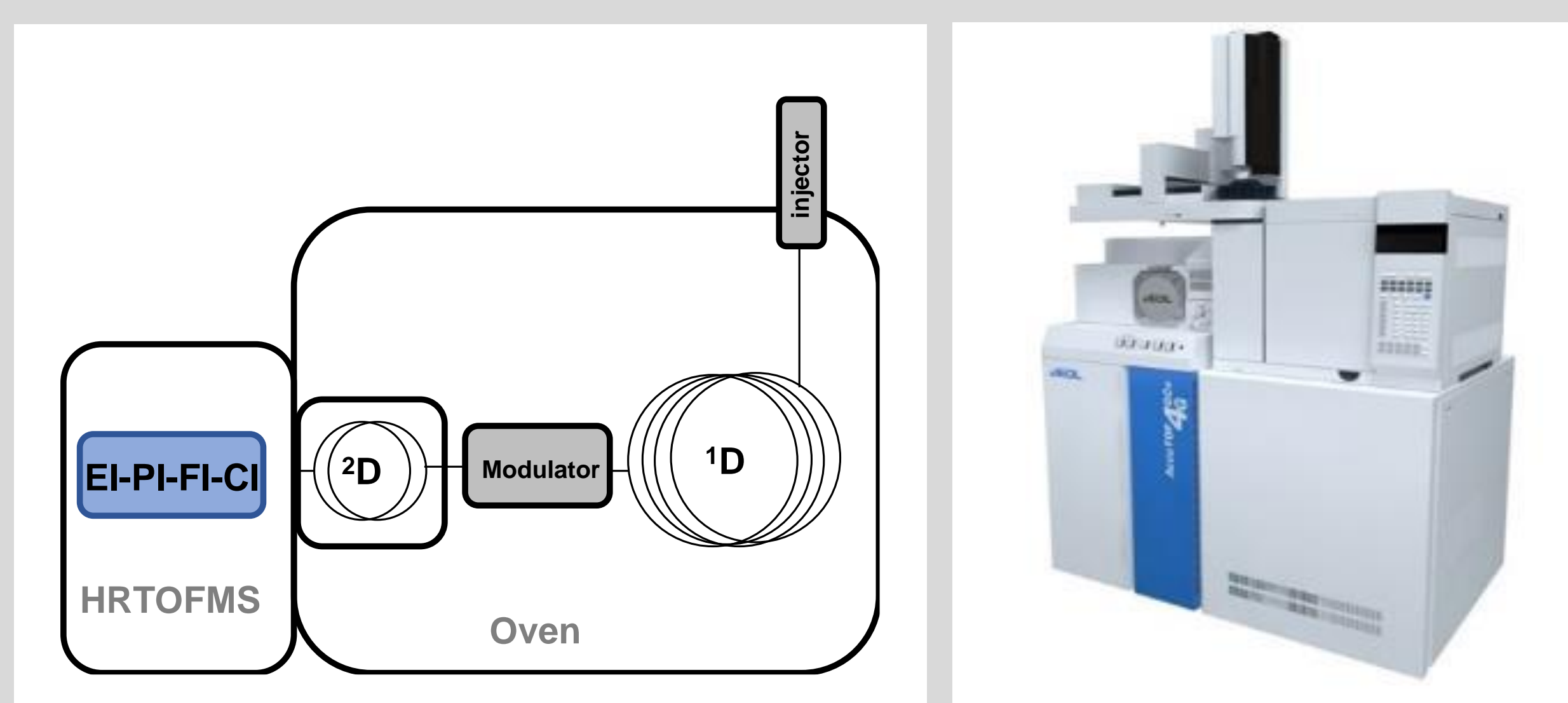


Figure 1: The study was conducted on a unique GC × GC-HRTOFMS instrument: JEOL AccuTOF GCv 4G with modular ionization technologies.

Three different soft-ionization techniques were used:

- photo ionization (PI)
- chemical ionization (CI),
- field ionization (FI)

→ They were compared to electron ionization (EI) to elucidate their relative capabilities to reveal different base oil hydrocarbon classes.

Column configuration:

¹D: low-polar (ZB-XLB-HT Inferno, 15.0 m, 0.25 mm ID, 0.1 μm, Phenomenex)

²D: polar (ZB-50HT, 2.0 m, 0.1 mm ID, 0.1 μm, Phenomenex)

→ This particular column configuration was used for high boiling base oil analysis

Results and discussion

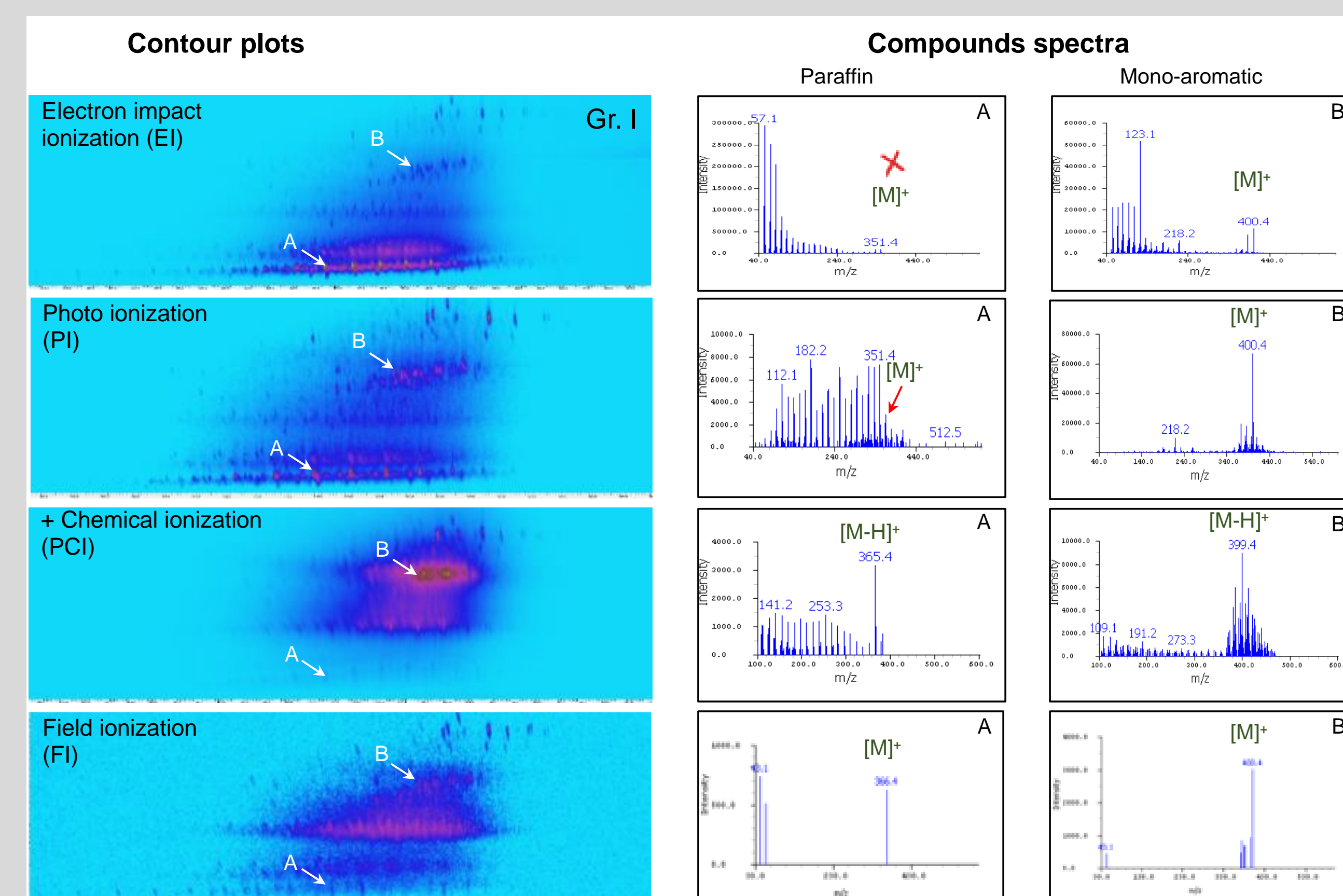


Figure 2: Effect of the different ionization techniques on Group I base oil sample.

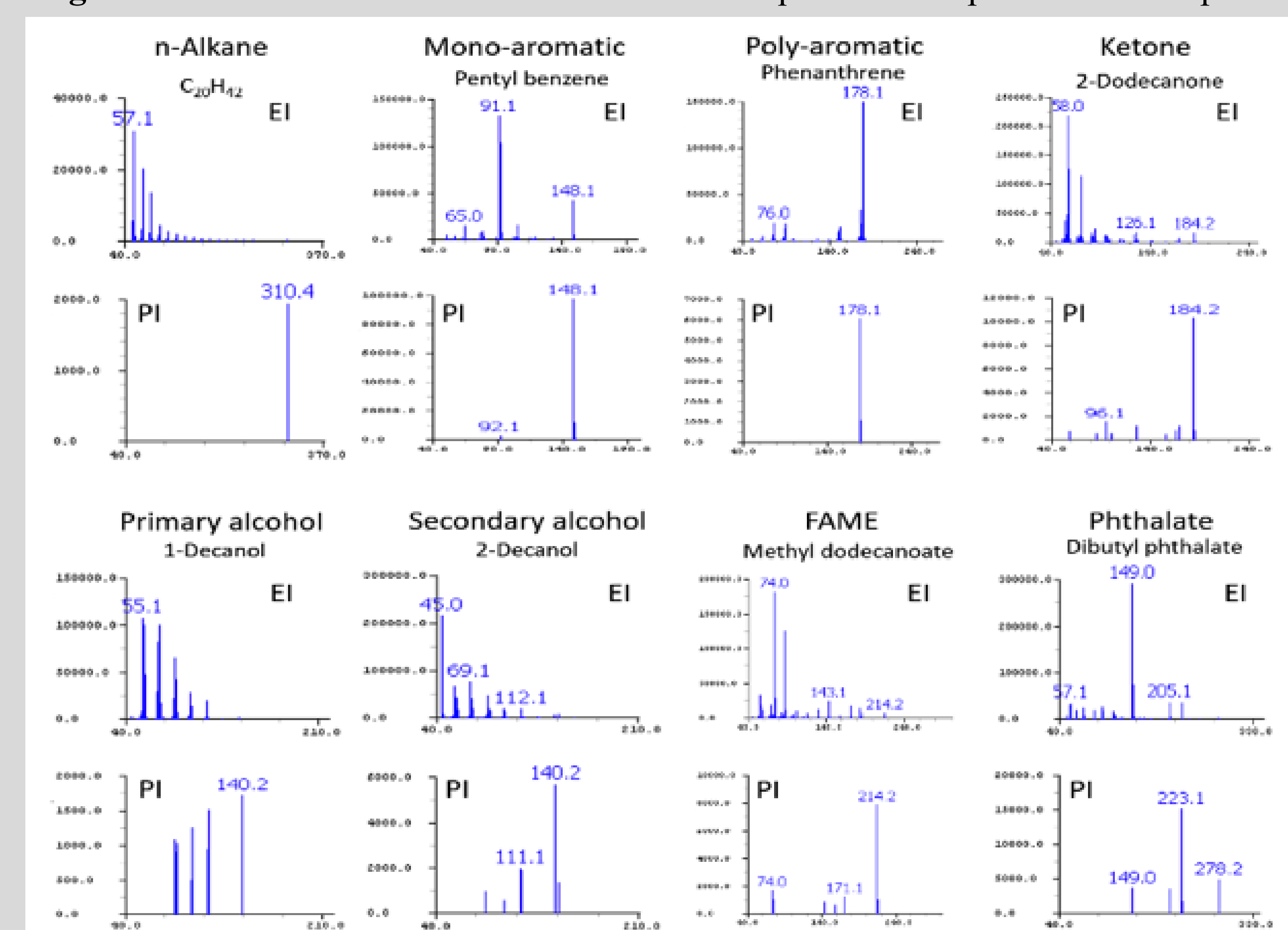


Figure 3: Enhancement of the molecular ion signal with PI for different chemical families

References:

1. Giri et al. Analytical Chemistry 2017
2. Giri et al. Journal of Mass Spectrometry 2019

Acknowledgement:

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