Using Hydrogen as Carrier Gas for GC/MS Analysis: GCxGC-HR-TOFMS with Multi-Mode Ion Source

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EMPOWERING RESULTS

Overview

GCxGC-HR-TOFMS with the Multi-Mode Ion Source (EI/PCI/NCI) successfully operates with hydrogen as GC carrier gas.

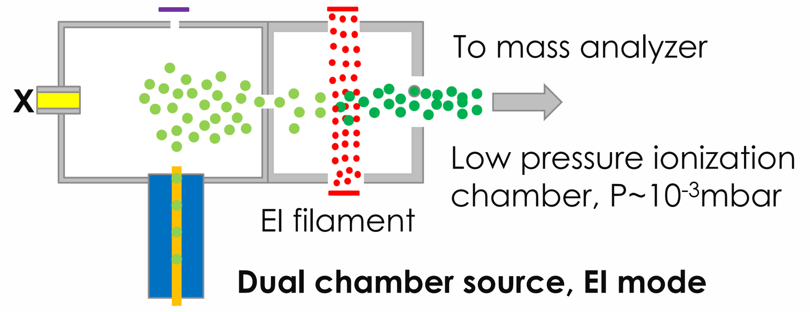
Introduction

Recent shortages of helium and its rising cost have presented challenges for GC/MS laboratories around the world and has increased interest in looking for alternative carrier gases. For GC/MS, hydrogen can be considered as an alternative to helium. When converting to hydrogen carrier gas—as a reactive gas—hydrogen may lead to spectral deviation from the "classical" library resulting in low library matching scores, excessive background, and in some cases peak tailing.

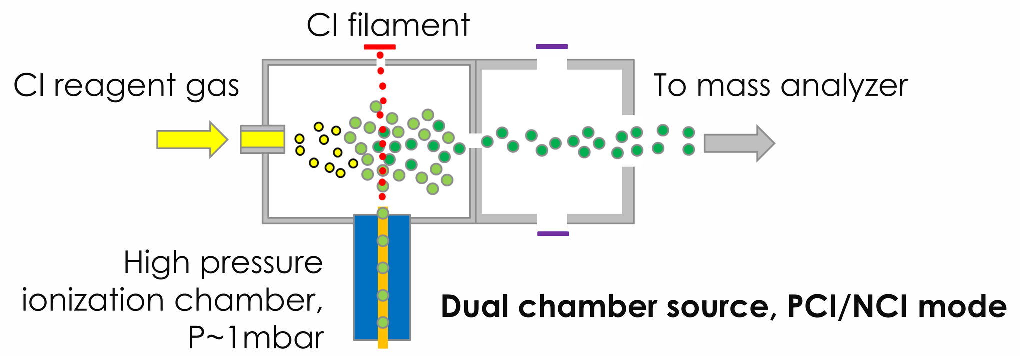
LECO has recently introduced a multi-mode ion source[1](MMS™), which can generate ions via EI, and Positive or Negative CI. *MMS* is a perfect addition to the GCxGC-HR-TOFMS. It enhances the GCxGC-HR-TOFMS's ability in non-target screening applications by combining increased separation capacity of GCxGC, high mass accuracy at full mass range, and high speed of HR-TOFMS with expanded ionization options of *MMS* for confident analytes detection and assignment. Ions are created in CI through ion-molecular reaction steps and the unknown effects of hydrogen as a carrier gas was a concern. In this work we report the evaluation of the GCxGC-HR-TOFMS with *MMS* while using hydrogen as a carrier gas.

Ion Source

A novel, dual chamber, ion source was developed to operate in any of three ionization modes (electron ionization, positive chemical ionization, and electron capture negative ionization) without replacing any hardware parts. The source is intended for use in LECO's GCxGC-HR-TOFMS systems, which achieves the full mass range resolving power of 25,000 or higher with better than 1 ppm mass accuracy with spectra acquisition rate up to 200 full spectra/s without any data loss.



Dual chamber source, EI mode



Dual chamber source, PCI/NCI mode

LECO Pegasus® GC-HRT+ 4D

Methods

Two *Pegasus* GC-HRT+ 4D (LECO, USA) mass spectrometers coupled with Agilent 7890B GC and equipped with Multi-Mode Source™ (*MMS*) were used with helium and hydrogen carrier gases, respectively. The hydrogen with >99.99999% purity was provided from COSMOS MF.H2 generator (FDGSi, France) and set to 100 psi supply pressure. The *MMS* can operate in the standard EI and soft ionization (PCI and NCI) modes while coupled to a GCxGC with QuadJet™ thermal modulator (LECO). Typical carrier gas flowrate was 1 ml/min for Helium and 1.2 ml/min for hydrogen. The presented results were obtained by analyzing EPA Method 8270 MegaMix Standard (76 components, Restek Catalog #3180) combined with the SV Internal Standard Mix (6 components, Restek Catalog #3126) while running GCxGC-HR-TOFMS with *MMS* in 1D and 2D GC modes using helium and hydrogen as carrier gases and operating the *MMS* in EI, PCI, and ECNI ionization modes.

Gas Chromatograph	**LECO GCxGC (Dual Stage *QuadJet* Modulator) in 7890B GC**
Injection	1µL Split 100:1, 250 °C
Carrier Gas	**He** @ 1.0 mL/min, Corrected Constant Flow
Column 1	Rxi-5ms, 30 m x 0.25 mm ID x 0.25 µm film
Column 2	Rxi-17SilMS, 1.4 m x 0.25 mm ID x 0.25 µm film
Temperature Program	Primary Oven: 40 °C (1.0 min) to 280 °C @ 12 °C/min (0.0 min) to 320 °C @ 5 °C/min (1.0 min) Secondary Oven: Temperature Offset +5 °C
Modulation	1.2 s with temperature maintained +15 °C relative to the secondary oven; Hot Pulse Duration - 0.36 s; Cool Time Between Stages – 0.24 s
Mass Spectrometer	**LECO *Pegasus* GC-HRT+ 4D**
Transfer Line	320 °C
Ion Source Temperature	165 °C (ECNI and PCI Modes); 250 °C (EI Mode)
Acquisition Mode	High Resolution, R ≥ 25,000 for m/z 219, Mass Accuracy ≤ 1 ppm
Ionization Mode	EI, ECNI (Moderation Gas: CH_4), PCI (Reagent Gas CH_4)
Mass Range (m/z)	PCI: 50 – 1,000; ECNI: 30 – 1,000; EI: 10 – 1,000
Acquisition Rate	1D – 12 spectra/s; 2D - 200 spectra/s

Gas Chromatograph	**LECO GCxGC (Dual Stage *QuadJet* Modulator) in 7890B GC**
Injection	1µL Split 100:1, 250 °C
Carrier Gas	**H_2** @ 1.2 mL/min, Corrected Constant Flow
Column 1	Rxi-5ms, 40 m x 0.18 mm ID x 0.18 µm film
Column 2	Rxi-17SilMS, 2 m x 0.18 mm ID x 0.18 µm film
Temperature Program	Primary Oven: 40 °C (1.0 min) to 280 °C @ 12 °C/min (0.0 min) to 320 °C @ 5 °C/min (1.0 min) Secondary Oven: Temperature Offset +5°C
Modulation	1.2 s with temperature maintained +15 °C relative to the secondary oven; Hot Pulse Duration - 0.36 s; Cool Time Between Stages – 0.24 s
Mass Spectrometer	**LECO *Pegasus* GC-HRT+ 4D**
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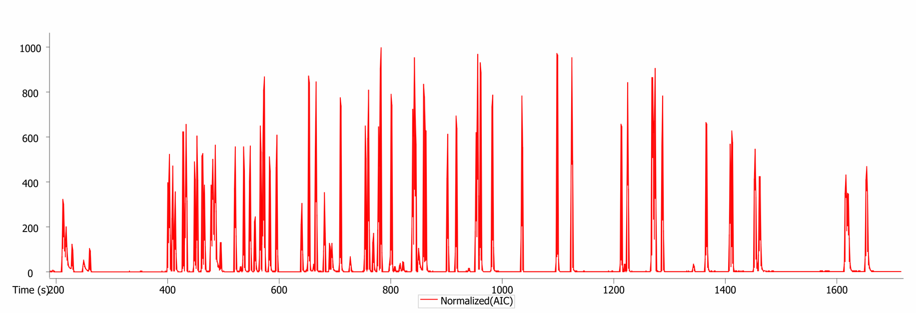
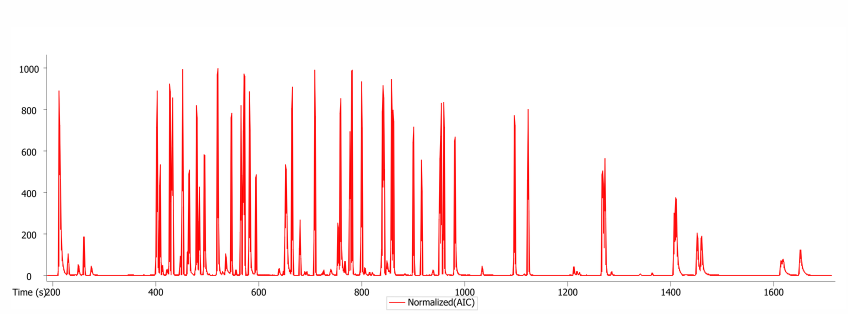
Results: MegaMix 1D and 2D GC-HRT Runs with He and H_2 Carrier Gas

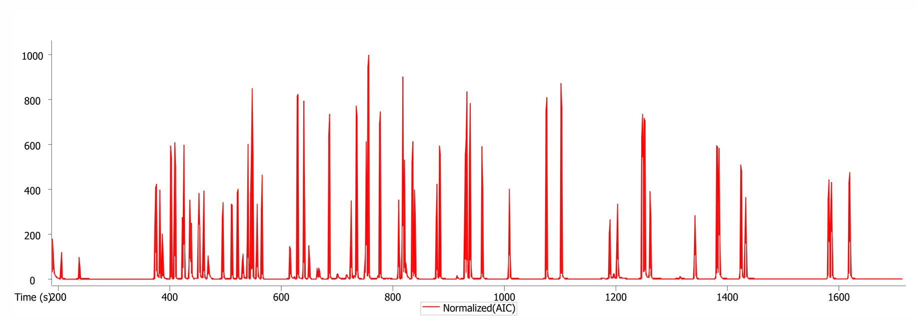
SVOC Mix He Carrier Gas EI 1D GC AIC



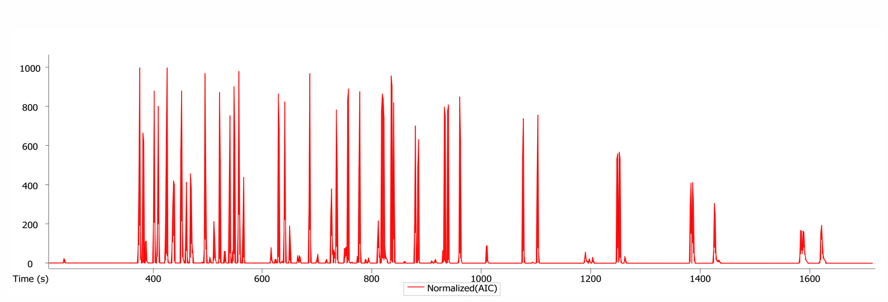
SVOC Mix He Carrier Gas PCI 1D GC AIC



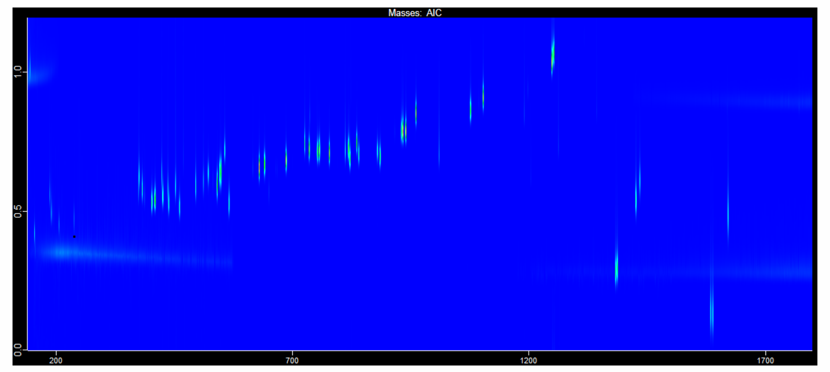
MegaMix H_2 Carrier Gas EI 1D GC AIC



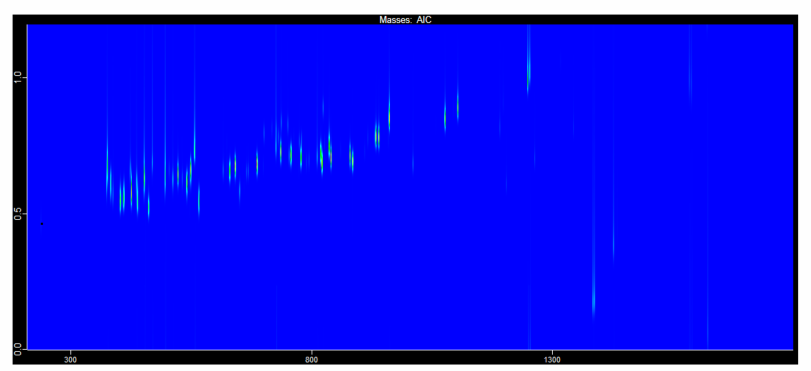
MegaMix H_2 Carrier Gas PCI 1D GC AIC



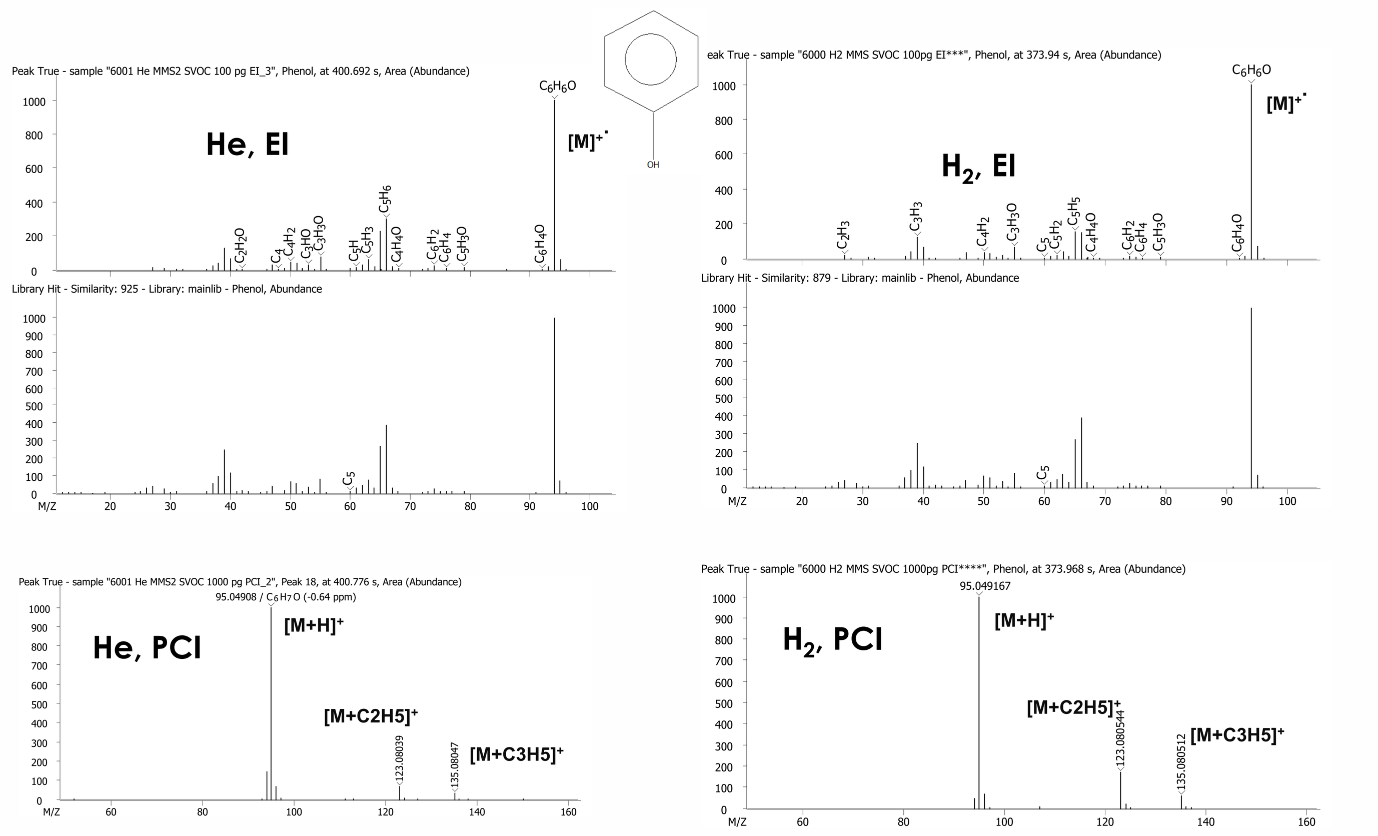
MegaMix H_2 Carrier Gas EI 2D GC AIC



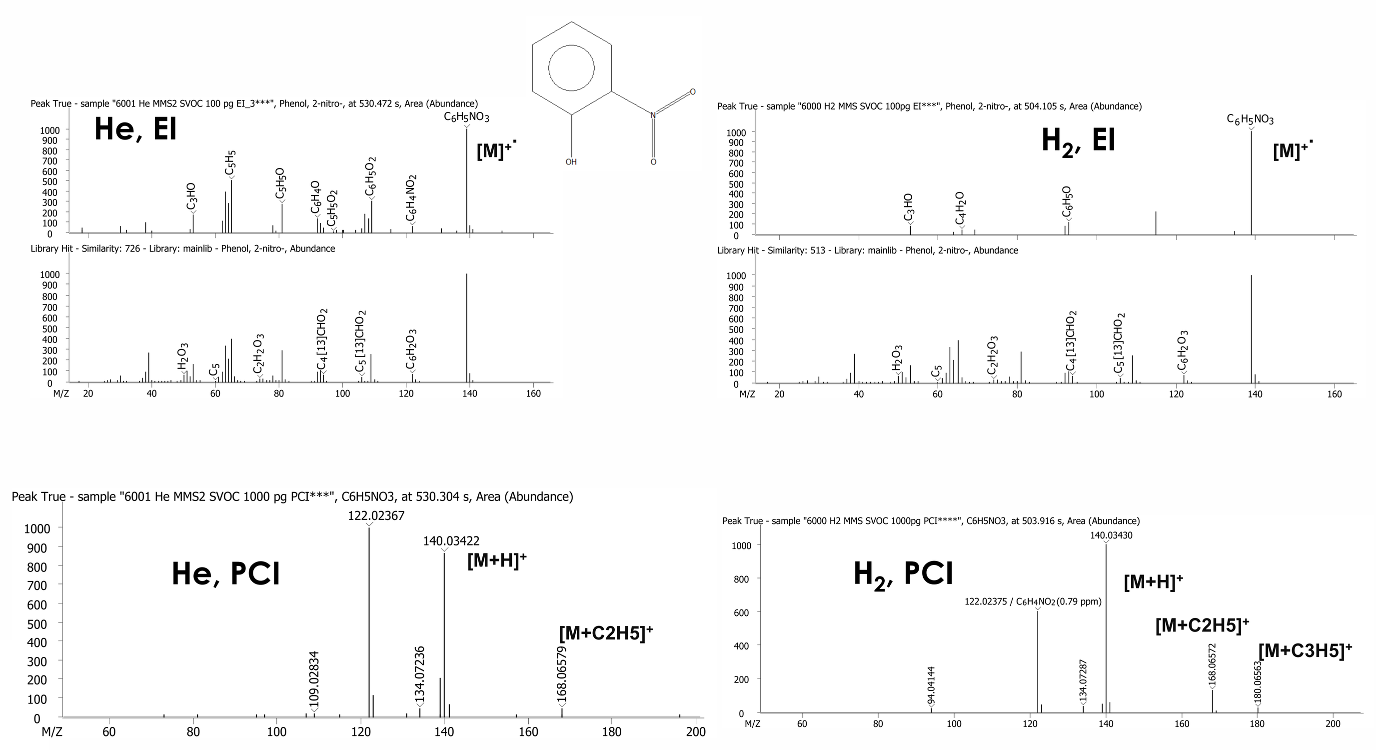
MegaMix H_2 Carrier Gas PCI 2D GC AIC



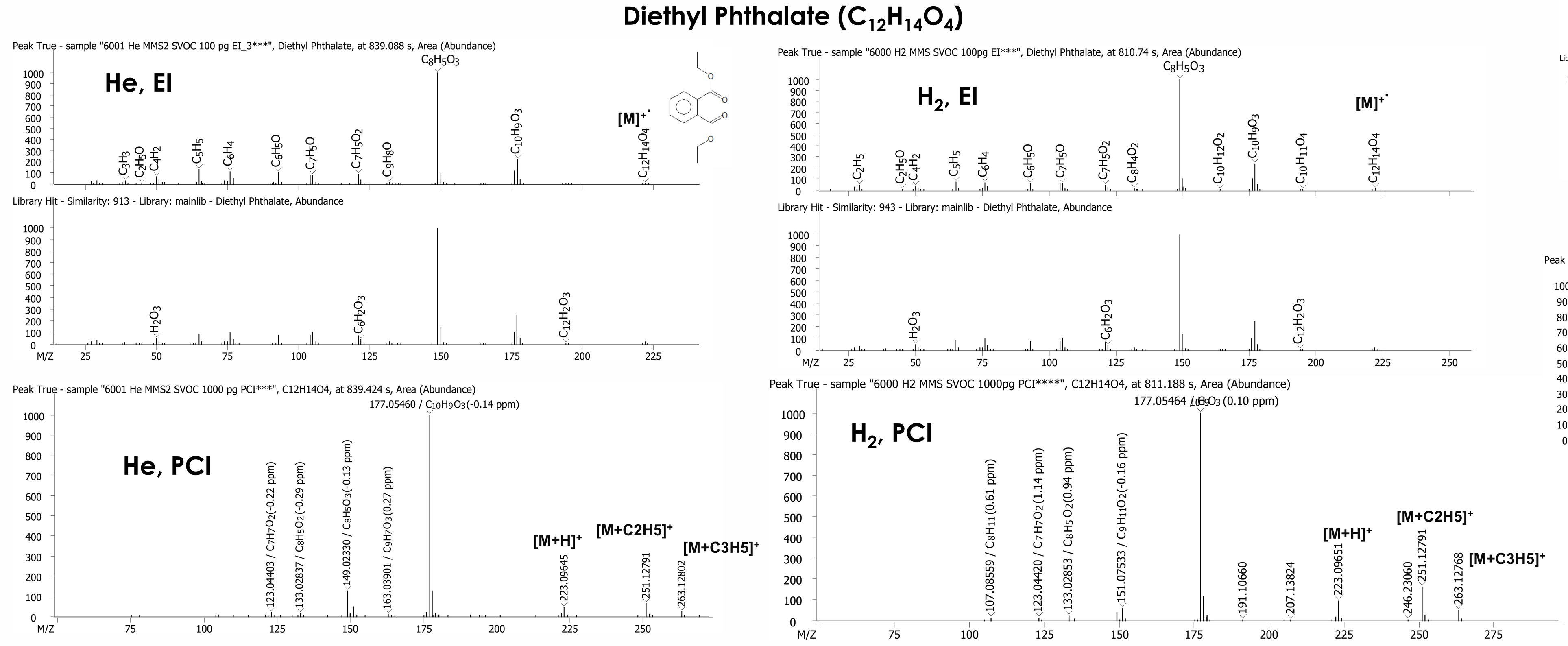
Phenol (C6H6O)



2-Nitrophenol (C6H5NO3)



Diethyl Phthalate ($C_{12}H_{14}O_4$)



Summary

- The MegaMix standard was analyzed using the following setups: with helium carrier gas – 1D and 2D GC, EI, PCI,and ECNI; with hydrogen carrier gas - 1D and 2D GC, EI, PCI and ECNI
- Majority of the analytes analyzed in EI mode with hydrogen carrier gas provide high matching scores compared to the "classical" spectral libraries with few peculiarities, which will require further studies but can be addressed using the comprehensive nature of the GCxGC-HR-TOFMS with *MMS* data.
- The PCI ionization mode with hydrogen carrier gas and methane reagent gas was exhibiting consistent and expected mass spectral patterns, similar to the mass spectra obtained with helium carrier gas.
- We plan to follow this study with comprehensive evaluation of the obtained results, as well as continue application of this setup for analysis of various samples with the goal of achieving high throughput with a high level of analyte identification confidence
- The comprehensive two-dimensional gas chromatography coupled with HR-TOFMS and the multi-mode source with hydrogen as a carrier GC gas is a powerful tool for non-target screening of the complex samples of various origin.

References

[1]Mazur, D.M. et al. GC-HRMS with Complementary Ionization Techniques for Target and Non-target Screening for Chemical Exposure: Expanding the Insights of the Air Pollution Markers in Moscow Snow. Science of Total Environment, 761(2021) https://doi.org/10.1016/j.scitotenv.2020.144506