Evaluation of HR-TOFMS with the Multi-Mode Ion Source and the Automated Direct Inlet Probe

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Overview

- **Direct Inlet Probe (DIP) is an efficient sample introduction tool for the express analysis of pure samples and for the analysis of analytes with high boiling point that are not admissible for GC-MS analysis**
- **To ensure high confidence in detection and identification of the analytes when using DIP, high resolution and high mass accuracy mass spectrometry are required.**
- **Complimentary ionization methods should also be considered for improving confidence in the analysis results.**
- **The automated DIP was coupled with a Multi-Mode Ionization Source (MMS) and High-Resolution Time-of-Flight Mass Spectrometer.**
- **Preliminary data of testing the DIP-MMS combination are presented.**

Introduction

Direct Inlet Probes (DIP) coupled with Mass Spectrometry are widely used in various applications [1], including analysis of low volatile analytes not admittable to GC-MS analysis and express analysis of pure substances and mixtures, etc. No chromatographic separation is possible when using DIP, and due to the rich matrices, the resultant mass spectra can be extremely complex. This places an increased emphasis on the mass resolving power of the instrument used and extended array of ionization methods as the main tools assisting in the analytes identification. In this work we present the results of combining DIP and High-Resolution Mass Spectrometry equipped with the novel multi-ionization ion source.

Mass Spectrometer

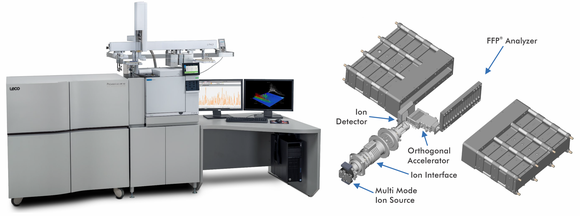
An R&D prototype of the Pegasus® GC-HRT+ 4D mass spectrometer (LECO Corporation, St. Joseph, MI) was used in this work. The ions, originated in the ion source, are introduced orthogonally into the **Folded Flight Path® (FFP®)** TOF mass analyzer [2] providing long (up to 40 m) flight path for ions inside the 75 cm long analyzer vacuum chamber. The LECO ChromaTOF®-HRT software performed the MS hardware control and operation, spectra acquisition, and data processing. The DIP operation was controlled by SIM DIP software.

Ion Source

A novel **Multi-Mode Source™ (MMS™)** recently was made available to operate with a new family of Pegasus GC-HRT+ instruments [3]. The *MMS* can generate ions in three ionization modes (electron ionization and positive and negative chemical ionization) without replacing any hardware parts. The source is intended for use in LECO's GCxGC-HR-TOFMS systems. An *MMS* was modified to accommodate Direct Inlet Probe.

LECO *Pegasus* GC-HRT+ 4D

- *FFP* High-Resolution Time-of-Flight Mass Analyzer
- Mass Accuracy: <1 PPM
- Acquisition Speed: 200 sps
- Enhanced Chromatographic Resolution: GCxGC
- Resolving Power up to 50,000 (FWHH @ m/z 219)



Methods

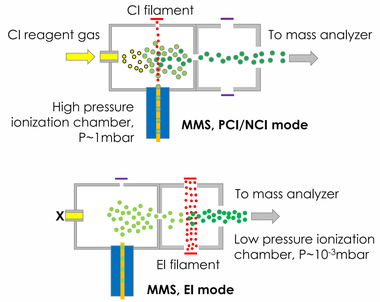
The *MMS* was modified for operation with the automated DIP (SIM GmbH, Germany) and installed on the R&D prototype of the high-resolution TOFMS (LECO Corporation). The *MMS* can operate in the standard EI and soft ionization (PCI and NCI) modes while coupled to a GCxGC. Switching between ionization modes is done via software; no hardware changing is required. To expand the analytical capabilities of the instrument, the *MMS* was modified to work with DIP while leaving the transfer line coupling the ion source to gas chromatograph in the standard position.

The samples, in the form of powder or liquid, were loaded into the standard SIM vials and placed in the holder on the tip of the probe. Data were collected in all three ionization modes: EI, PCI, and NCI. An example of the corresponding parameters is shown in the table below.

DIP	SIM DIP adapted for *Pegasus* GC-HRT+ with *MMS*
Injection	SIM vials loaded with samples
Carrier Gas	He @ 1.0 mL/min (not necessary for operation with DIP)
Temperature Program	Initial Temperature 40 °C (0.2 min) to 340 °C @ 2 °C/min hold at 340 °C (20 min)
Mass Spectrometer	**LECO *Pegasus* GC-HRT+ 4D**
Transfer Line	300 °C
Ion Source Temperature	250 °C (EI Mode), 165 °C (PCI Mode), 165 °C (ECNI Mode)
Acquisition Mode	High Resolution, R ≥ 25,000 for m/z 219, Mass Accuracy ≤ 1 ppm
Ionization Mode	EI, ECNI (Moderation Gas: CH_4) and PCI (Reagent Gas: CH_4)
Mass Range (m/z)	EI: 10 – 1,000; ECNI: 20 – 1,000; PCI: 50-1,000
Acquisition Rate	10 spectra/sec

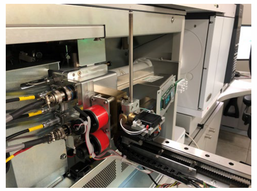
MMS Features

- Single source for EI, PCI, and NCI
- High performance for all three ionization modes
- No hardware changes necessary when switching modes

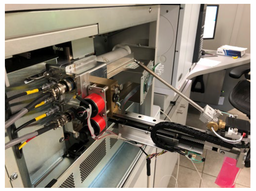


DIP

The Direct Inlet Probe was provided by SIM GmbH (Oberhausen,Germany) and installed on the R&D prototype of the *Pegasus* GC-HRT+ instrument with the modified *MMS*. Sample loading into the vial and inserting of the vial into the probe tip was done manually. All the rest of operation steps—inserting the probe into the vacuum chamber, engaging with *MMS*, programmable heating and cooling, and removing the vial back to atmosphere and setting it to the loading position—were done automatically via SIM-provided software. Automated operation significantly simplified the analysis process and reduced chances of incorrect sequences or operator mistakes when working with the probe when compared to all-manual operations.

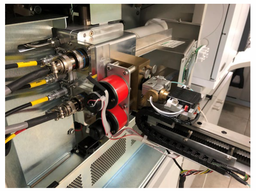


DIP loading position

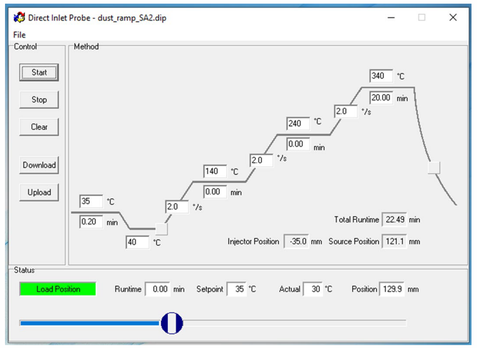


DIP starts moving in inserting position

DIP is ready to be inserted into the vacuum chamber



DIP is fully inserted

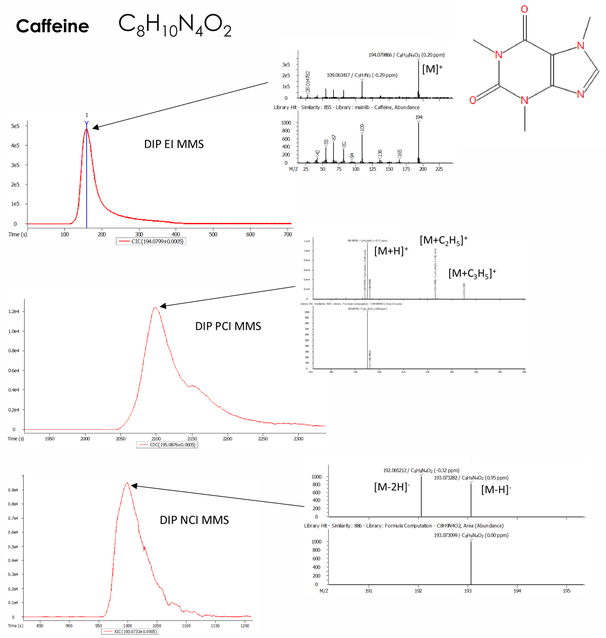


SIM DIP software displaying temperature program and operational progress

Results

The *MMS* was confirmed to operate with DIP in all three ionization modes while using various standards and samples. The preliminary data show no memory effect, which allows the user to easily switch between the projects without extra ion source maintenance procedures. Below are examples of the data from the DIP-*MMS* analysis of caffeine.

Caffeine $C_8H_{10}N_4O_2$



Summary

- The Multi-Mode Ionization Source (MMS) was modified to work with the Direct Inlet Probe (DIP).
- The preliminary data using standards have confirmed satisfactory operation of the modified *MMS* with DIP in all three modes of ionization: EI, PCI, and NCI.

References

[1] Introduction To Mass Spectrometry: Instrumentation, Applications, and Strategies for Data Interpretations by J. Throck Watson, O. David Sparkman, **ISBN-13:** 978-0470516348

[2] https://info.leco.com/folded-flight-path

[3] https://www.leco.com/product/mms

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