

Advancements in Increasing Resolution in Multi Reflecting TOF Mass Spectrometry with Folded Flight Path

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Overview

The recent advancements in HR-TOFMS based on the Folded Flight Path[®] (FFP[®]) mass analyzers are presented. The novel mass analyzer ion optics was coupled with the EI source for GC-HRMS analysis. The experimentally shown resolving power is above 100,000, which allows detecting and unambiguously identified low level analytes of interest in complex environmental and biological matrices.

Introduction

High resolution multi-reflecting time-of-flight mass spectrometry (HRMR-TOFMS) with Folded Flight Path (FFP) (Figure 1) is successfully applied to the analysis of complex mixtures in metabolomics, petroleomics, environmental, and other samples.¹ HRMR-TOFMS with mass resolution up to 50,000 coupled with high speed (up to 200 spectra per second) data acquisition system is compatible with fast separation techniques (GC and GCxGC), and dramatically improves throughput and quality of the results. Simultaneously, challenges faced in modern analytical chemistry demand the need for even higher mass resolution, while improving speed of analysis. This poster describes substantial improvement in resolution and sensitivity of the multi-reflecting analyzers with FFP by reaching higher order focusing using novel ion mirrors in combination with a new signal multiplexing technique.

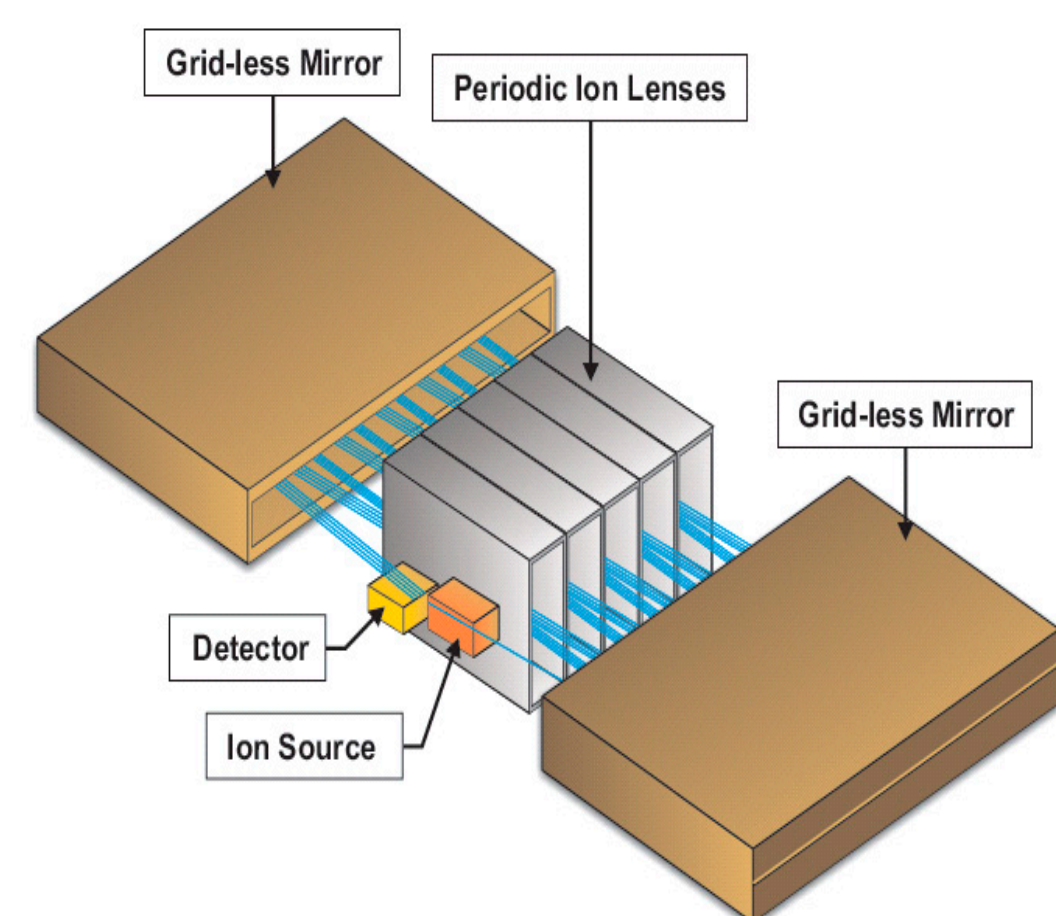


Figure 1. The Concept of the FFP TOF Mass Analyzer.

Methods

The geometry of the ion mirror electrodes and applied voltages have been optimized using novel ion-optical concepts with the aid of a custom simulation software package Axion.

The properties of the optimized HRMR-TOF ion mirrors have been analyzed with the aid of the software package SIMION, and of a custom simulation software Ion Tracer (Figure 2).

The experimental prototype was built based on the selected geometry providing 4th order energy focusing of TOF. The mass analyzer voltages and dimensions were chosen to optimize ion transmission and increase the ions time-of-flight. The analyzer was coupled to an EI source as the part of the GC-HRMS experimental prototype.

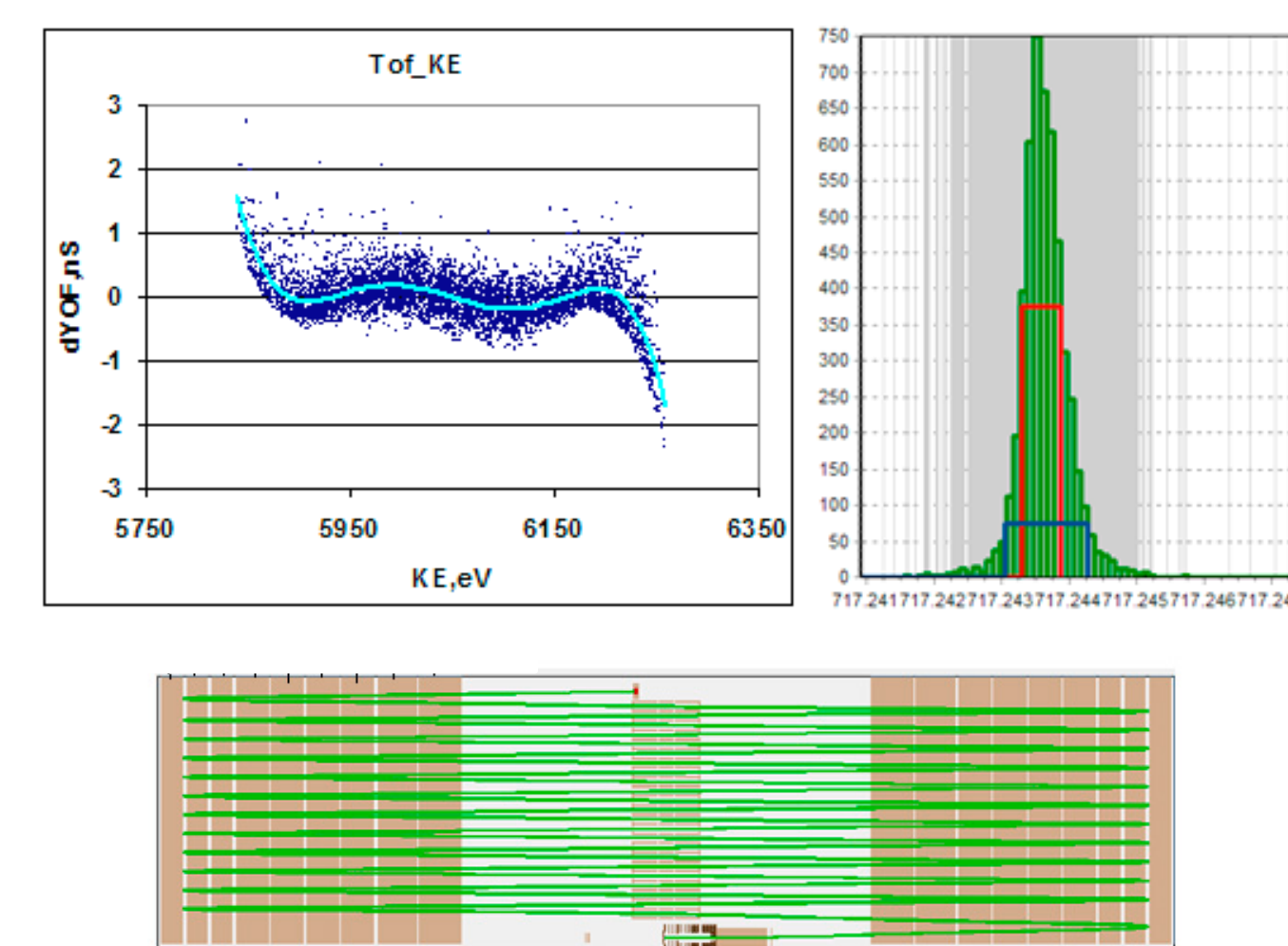


Figure 2. Novel FFP Optics: Achieving 4th order TOF Energy Focusing.

The multiplexing method, with a novel encoding/decoding algorithm, Encoded Frequent Pulsing[™] (EFP[™])², was also implemented with the novel GC-HRMS prototype with FFP to improve duty cycle of the ion beam sampling. The EFP method increased duty cycle 10-100 times in various experiments, improving detection limit and dynamic range proportionally, and ideally fit to the HRMR-TOFMS with FFP analyzer.

The experimental testing was performed using crude oil and urine matrix spiked with various analytes at about 1 ppm level.

Results: Resolving Power

The experimental data were obtained using HRMR-TOFMS with FFP prototype equipped with an Electron Impact source. In this configuration we were able to achieve 4th order TOF focusing, with respect to energy spread, simultaneously with the full third order TOF focusing with respect to the spatial, angular, and energy spread including cross terms. The experimental resolving power was demonstrated reaching greater than 100,000 for the full mass range (m/z 10-1500) (Figure 3).

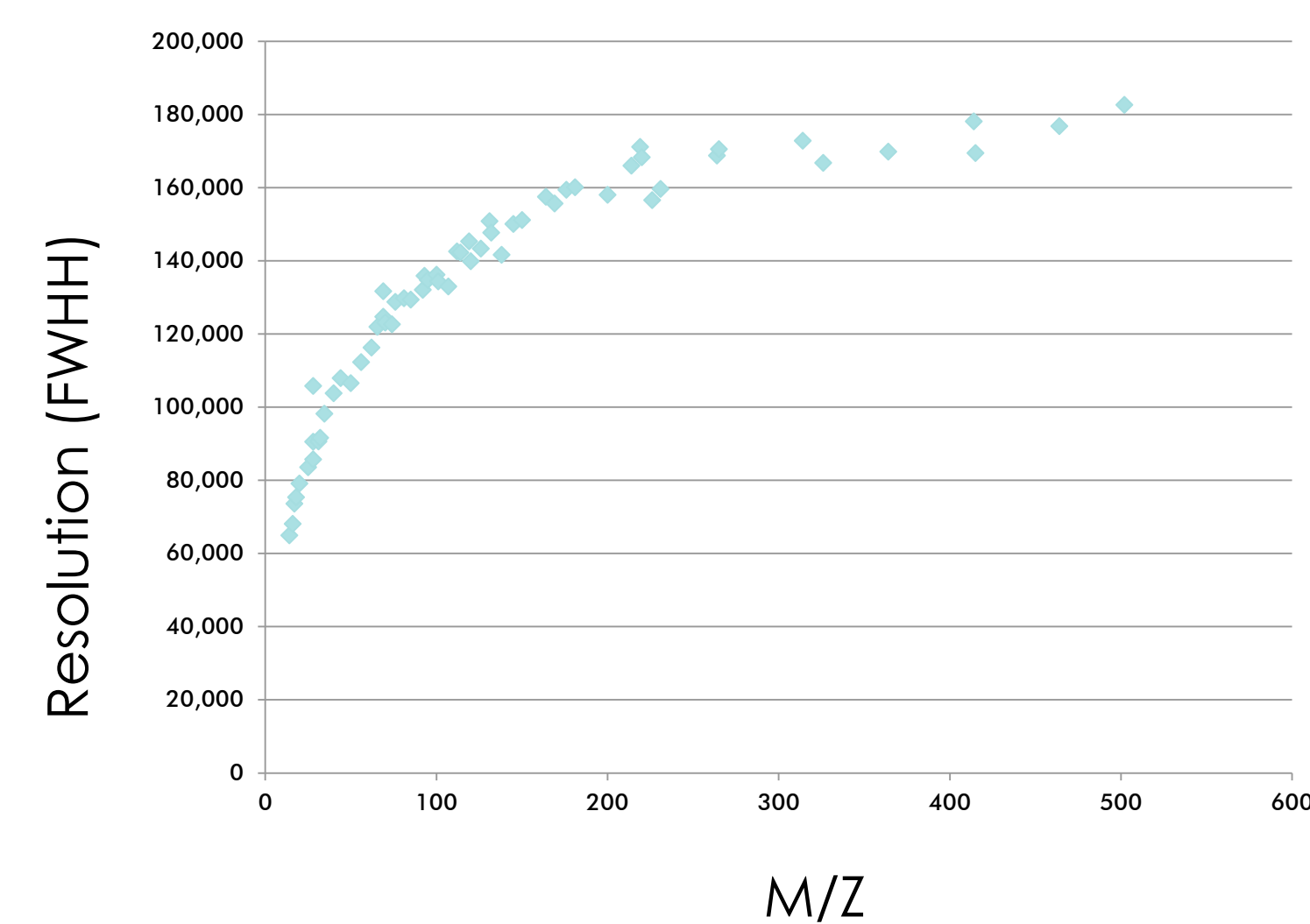


Figure 3. Experimental data on Resolution vs M/Z.

Results: C₃/SH₄ Resolution

As an experimental demonstration of high resolution, a very challenging doublet of C₃/SH₄ was successfully resolved, while analyzing a petroleum sample (Figure 4).

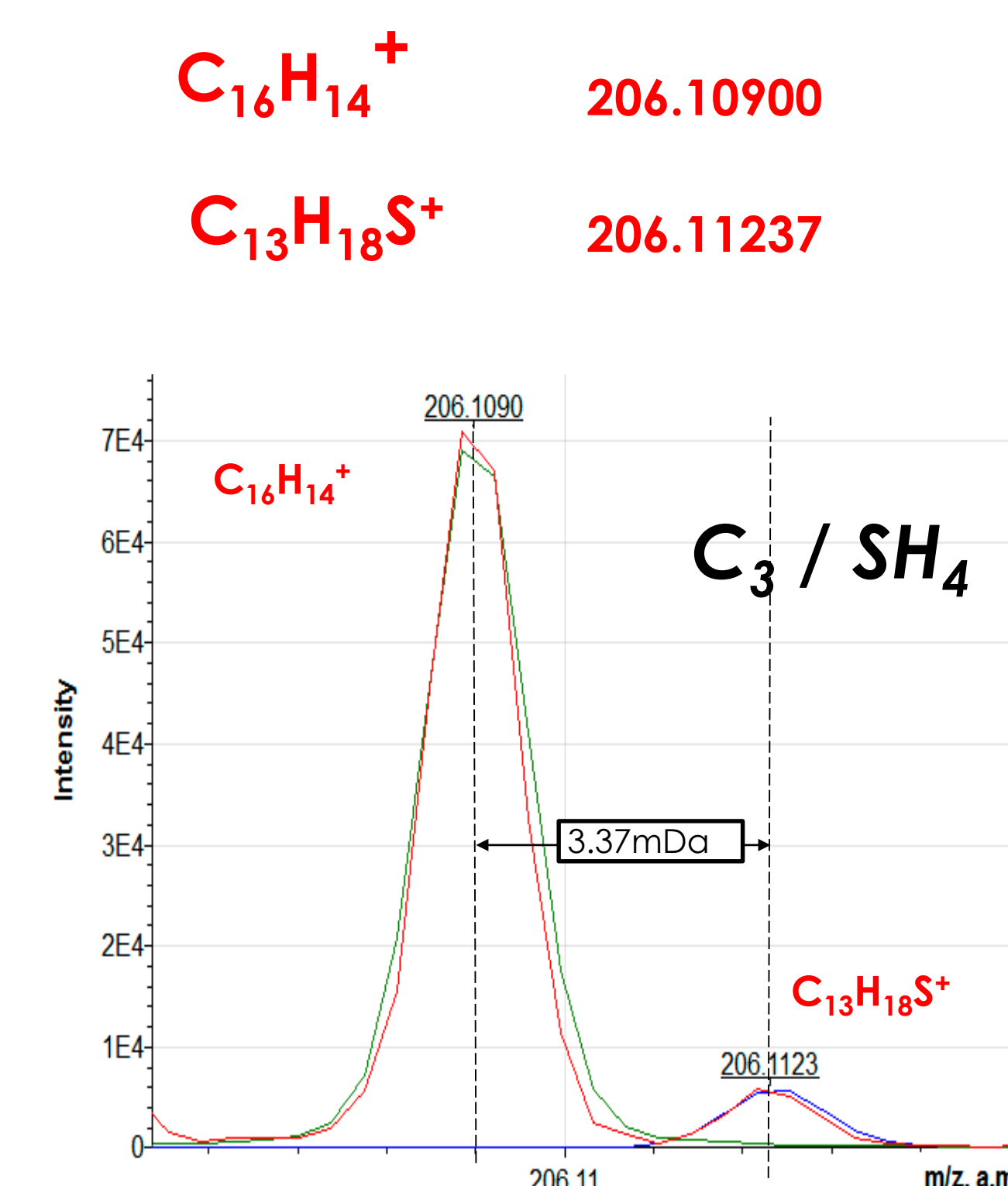


Figure 4. C₃/SH₄ doublet resolution at resolving power of the prototype 150,000 (at FWHH).

Results: Selectivity and Mass Accuracy

The urine samples spiked with various analytes at 0.5 ng/μl level were analyzed using the experimental prototype with a novel ion optics and EFP multiplexing (Figure 5).

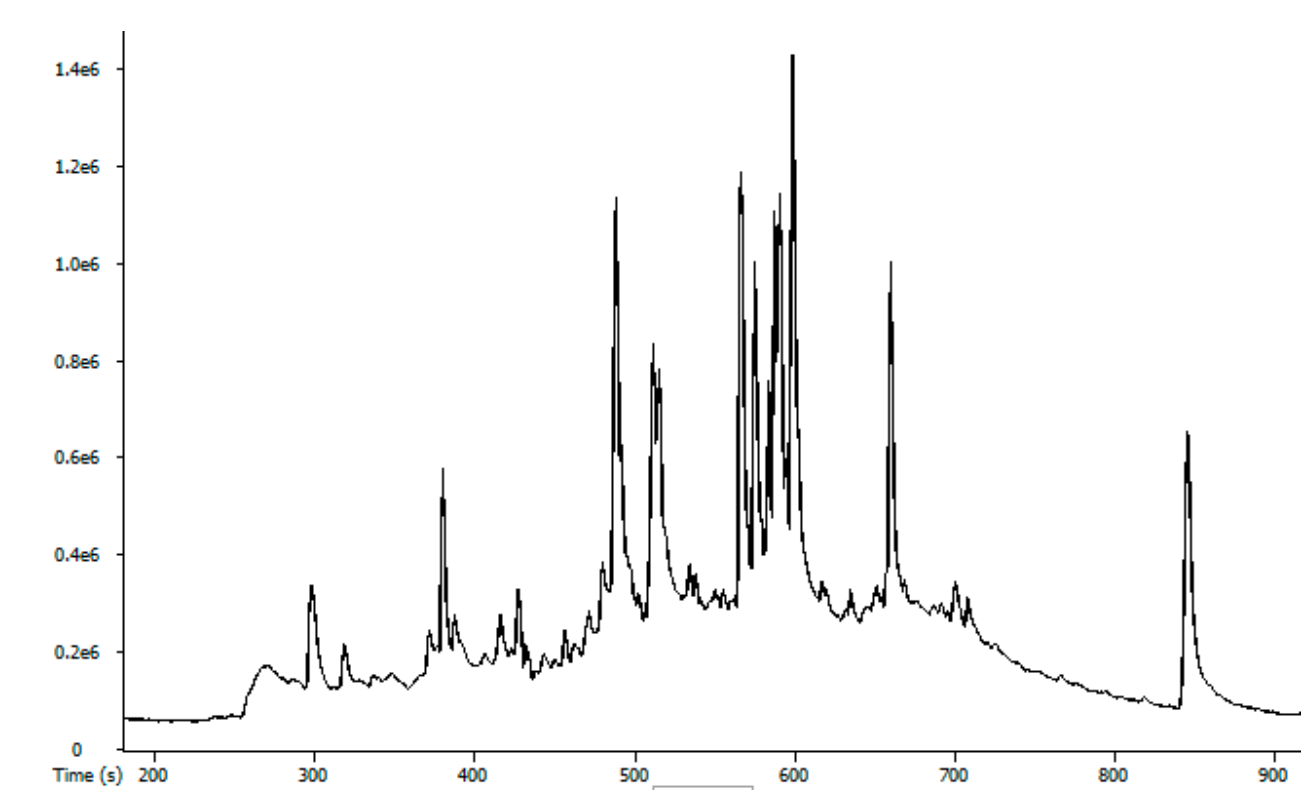


Figure 5. TIC Chromatogram of the urine sample.

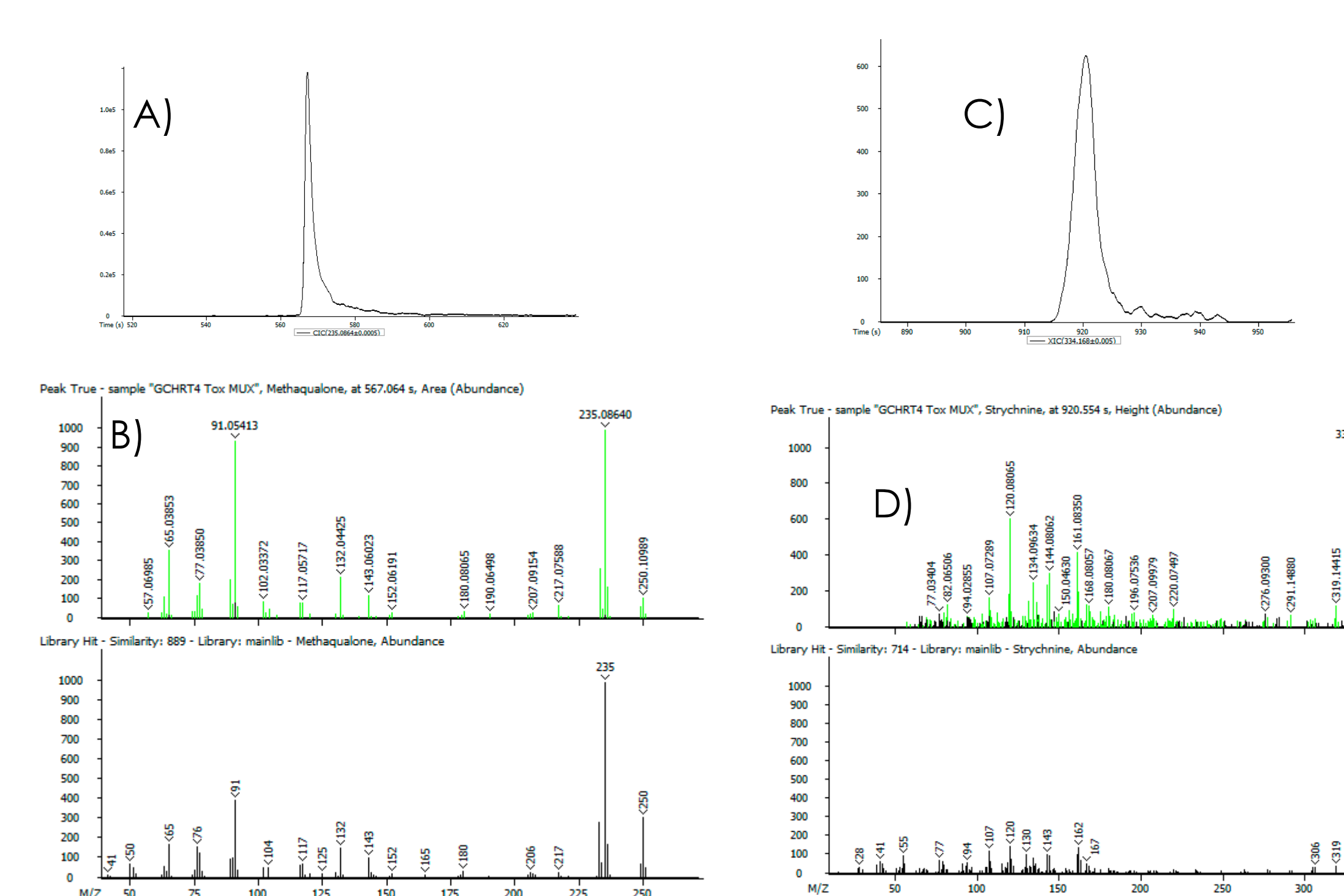


Figure 6. GC peak corresponding to the Methaqualone at 1 ppm (A), and the Peak True and the NIST library mass spectra (B). The ion peaks in Peak True mass spectrum which match the elemental formula within 5 ppm mass accuracy are shown in green. Same as for Strychnine—chromatogram and mass spectra (C and D, correspondingly).

Analyte	Formula	Mol. Ion M/Z	Mass Accuracy, ppm		
			Molecular Ion	RMS Top 10	RMS Top 50
Methaqualone	C ₁₆ H ₁₄ N ₂ O	250.11006	0.7	0.82	0.97
Strychnine	C ₂₁ H ₂₂ N ₂ O ₂	334.16758	-0.19	0.7	1.34

Conclusions

- A novel FFP mass analyzer with 4th order energy and full 3rd order spatial TOF focusing were incorporated into the ultra high resolution GC-TOFMS prototype.
- The resolution >100,000 (@FWHH) was experimentally demonstrated for the full mass range (m/z=100-1500) **and** high acquisition rate (up to 200 sps).
- The FFP ultrahigh resolution technology combined with high data acquisition speed and high duty cycle operation mode, provided by EFP, creates unprecedented combination of characteristics significantly expanding the tool box of the modern analytical laboratory.

References

- www.leco.com
- ASMS 2015 Proceedings, TOA am, P. Willis et al. "High Resolution Multi-Reflecting TOFMS with Multiplexing by Encoded Frequent Pulsing for increasing the duty cycle 10-100 times"

Acknowledgments

The authors would like to thank Dmitry Koluntaev (Interlab, Russia) and Dmitry Alexejchikov (MSC) for preparing samples, as well as analyzing and reviewing the data.