High Dynamic Range Data Acquisition System for TOFMS

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Overview

- High dynamic range data acquisition system reach benchmark of λ=10,000 ion/peak/shot and detection of single ions

- M-ToF detector (El-Mul) fits well; It has 10V linear output signal at SNR=1E+5, and 300 Coulomb output charge longevity;

- Cost-effective single-channel ADC (SA230P, Acqiris) employs time-shared method for high dynamic signal acquisition; data streaming allows for sophisticated signal processing

- Tests on GC MRT MS validated efficiency of the overall data acquisition solution, which opens full potential of compact, highly sensitive, fast, and high-resolution GC-MRT platform.

Introduction

New definition of TOF MS data acquisition system

Continuous improvements in Time-of-Flight (ToF) instrumental sensitivity have resulted in dramatic increase of ion fluxes. Ion currents entering the orthogonal accelerator (OA) easily exceed 1.6 nA, corresponding to:

•10^10 charges/s (10 Bi/s), entering OA

•10^9 ion/s (1 Bi/s), reaching detector at 10% duty cycle of OA

•10^5 ions/shot in spectrum at 10 kHz pulsing rate, and

• λ=10,000 ions/shot/peak.

Consequently, ToF instruments can reach unprecedented dynamic range of analyses … **if** the data acquisition system allows it.

This capability presents challenge for the detector and DAS in:

• Improving detector longevity at >100 C/Year output charge

• Maintaining high detector speed, ideally <0.5ns peak width

• Improving dynamic range of detector and ADC to λ=10,000 i/shot/peak at detection of individual ions

• While allowing for sophisticated signal processing of each waveform

Detector

Under ultimate loads, most of the common ToF detectors degrade rapidly: chevron MCP – 2-3 C/cm²; electron converters – upto 10 C. Moreover, MCPs saturate at 1 million ion/cm²/s. MCP/PIN diode detectors withstand high ion flux better, but lack the required DR and add > 0.5 ns time spread in MCP pores (at 40 μm/ns ion velocity).

Therefore, we believe that "M-ToF" having both high dynamic range and longevity is an ideal candidate for high performance ToF MS systems. We hope on M-TOF acceleration in the future.

Alternated Single Channel ADC

The dynamic range (DR) of a single-channel ADC is limited by DR of preamplifier and ADC to λ<200 i/shot/peak, **if** using a single setting.

To reach λ=10,000, one can use a more costly solution of dual channel ADC and struggle with a limited bandwidth of ADC bus, or use the described here lower cost solution, employing a single channel ADC, dual gain amplifier and a "Time-shared approach" at 80% duty cycle.

The method is developed and validated in this work. We demonstrate reaching unprecedented GC-MRT parameters, while using the overall detection system with high DR.

Methods

GC Multi Reflecting Time of Flight MS

Having high sensitivity and up to few ng linear DR, GC MRToF MS requires high performance detector and DAS to show its analytical power. Achievable peak intensity is up to λ=10,000 ions/shot/peak at a moderate space-charge effects in the analyzer. Main parameters are:

- resolution ADC ~30k
- mass accuracy <1ppm
- linear DR up to 5ng
- 10kHz sampling
- sensitivity ~10,000 i/pg (on base peak of OFN)

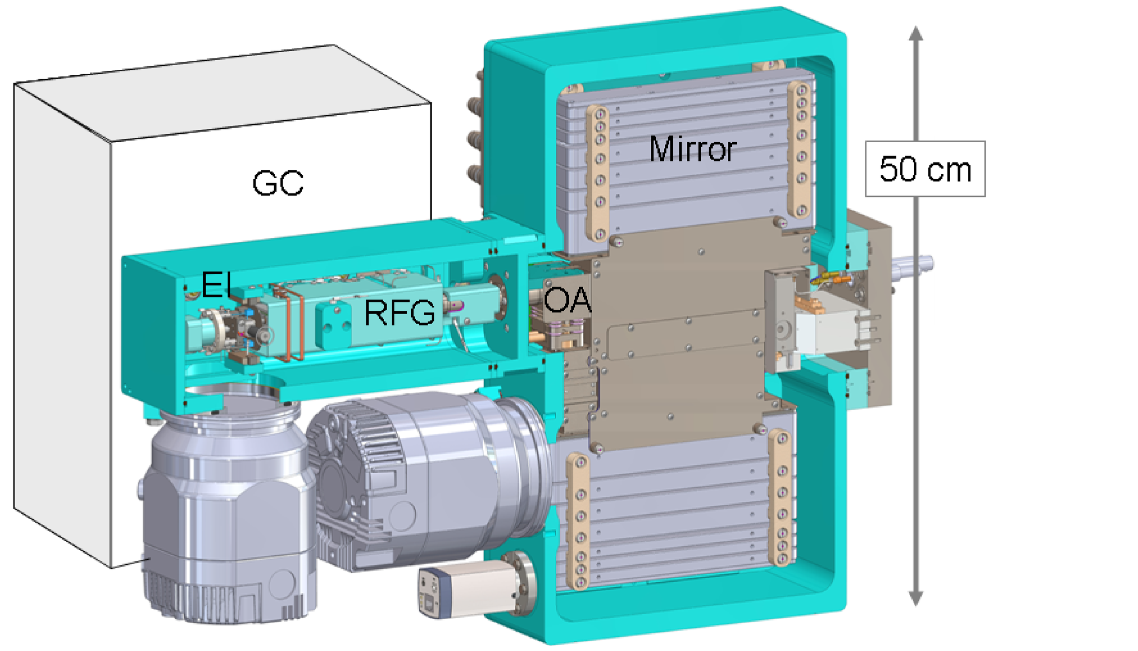


Fig 1. High performance GC MR ToF MS

Detector "M-TOF" by El-Mul

The linear signal range of the M-TOF detector with PMT was extended to 10V on 50 Ohm load, reaching SNR=1E+5 above the most and external electronic noise. The time response is better then 1ns. The detector gain remains constant after two years of operation (lifetime is ~300 Coulomb of output charge).

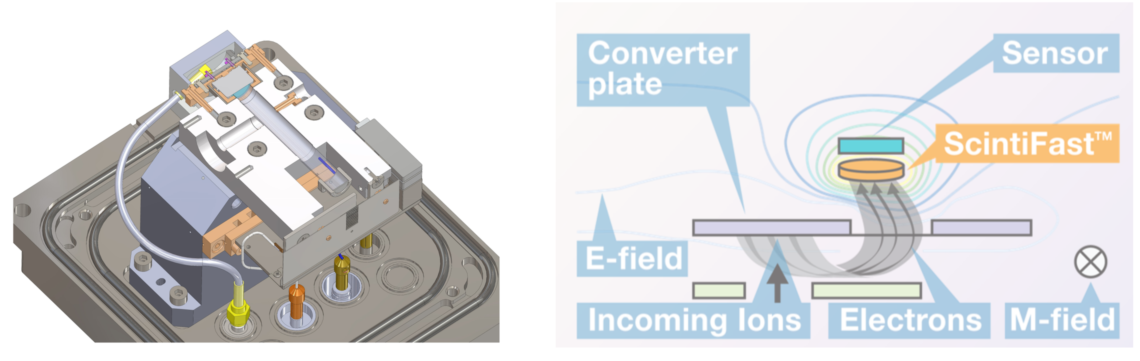


Fig 2. (Left) "Agate" detector prototype (photo). (Right) Principle of operation

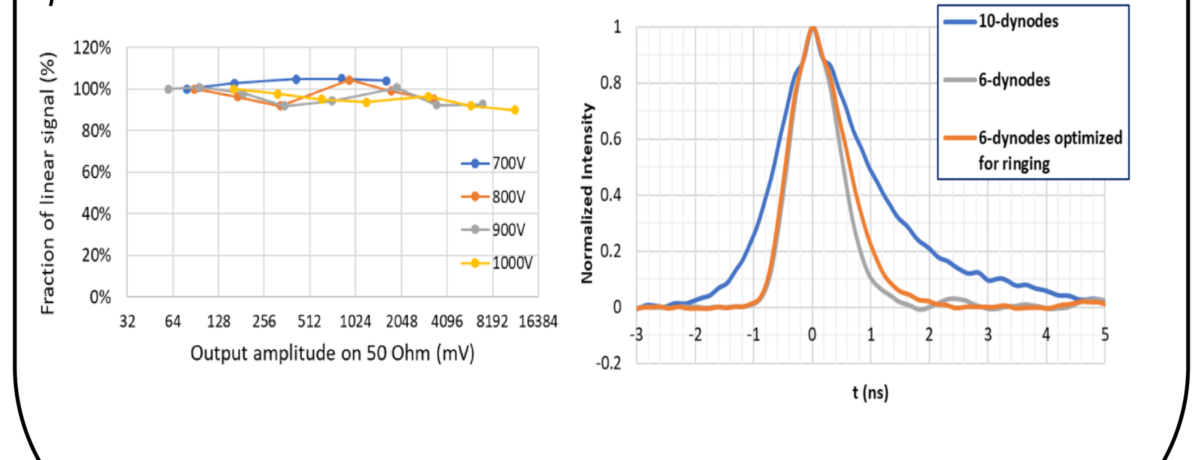
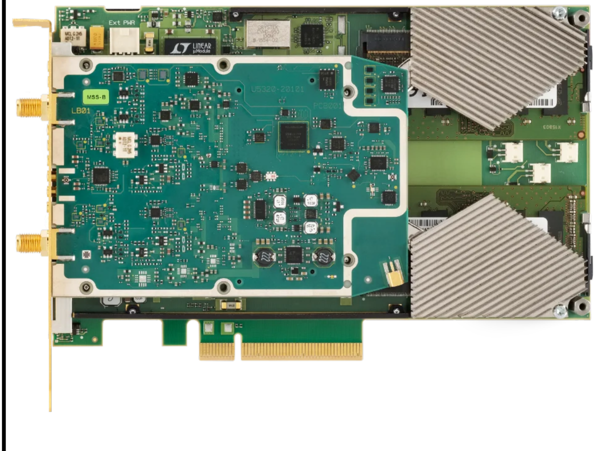


Fig 3. (Left). Linear detector (6-dynodes) respond up to 10V (Right) Detector time respond is below 1ns.

Methods

Acqiris SA230P for ToF mass spectrometry

MS signals were recorded on a single channel SA230P ADC at 4GS/s. Waveforms are drift corrected and compressed to 10-bits matching the ENOB=9.3bits of ADC. The shot-by-shot data are streamed via the 6.5GB/s PCIe bus with a possibility of mapping spectra via I/O port to apply any complex recording methods and sophisticated data processing algorithms on-the-fly.



- *14-bit ADC (1 channel)*
- *4GS/s sampling*
- *2Ghz bandwidth*
- *voltage range 0.5V and 2.5V*
- *9.3 bit ENOB*
- *3 I/O channels*
- *10bit compression on board*

Fig 4. SA230P ADC card

Dual Channel switching Preamp

We use dual gain Amplifier. The high-gain x12 channel allows detecting individual ions above a threshold at average SNR>5. It gracefully clamps strong signals above 3V at ADC entrance. Low gain x0.3 channel passes strong signals without saturation. The intra-channel delay and gain ratio are calibrated and stay stable for months.

Time shared approach for high dynamic range

The gains are time-alternated in 1 ms cycles at 8:2 shot pattern, i.e. at 80% duty cycle. Low gain spectra were marked via I/O port.

On-line gain stitching

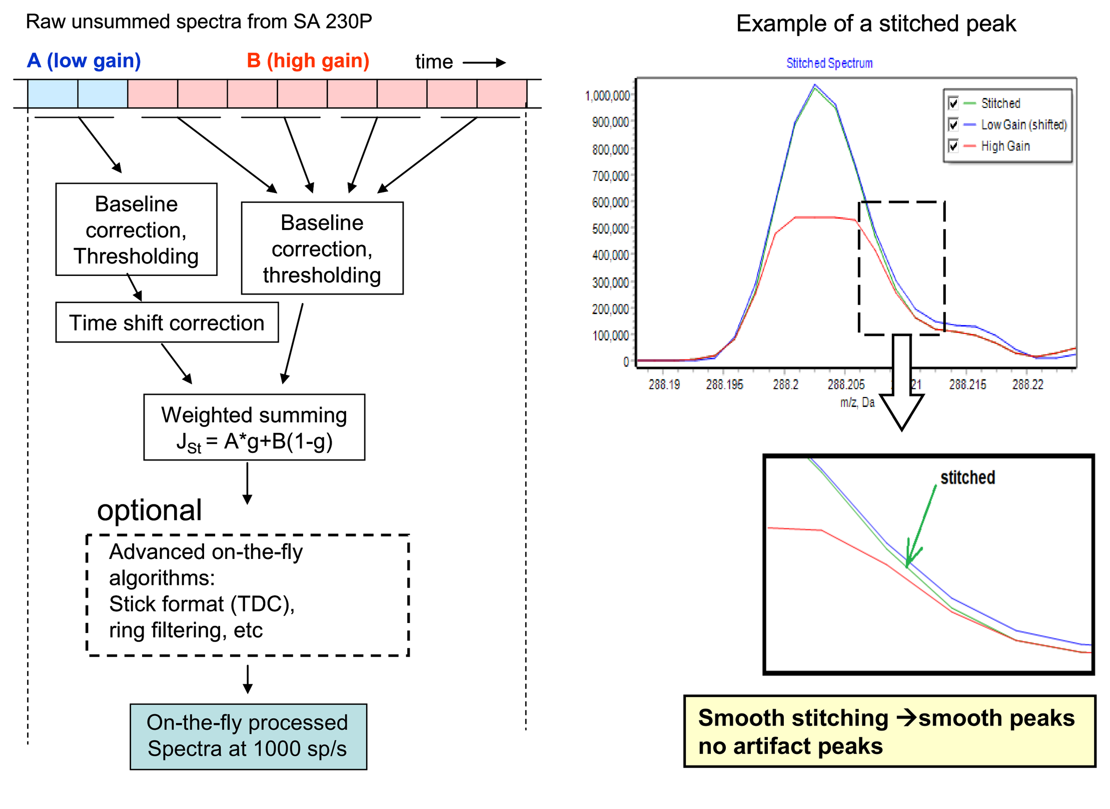


Fig 5. Diagram describing main steps of the time shared method

Methods

Time share approach for high dynamic range

Stitching algorithm operates with ion peaks, not signal points: if peak signal height is above a saturation level – the stitched peak is a weighted sum of high and low channel signal, otherwise is taken from high gain signal.

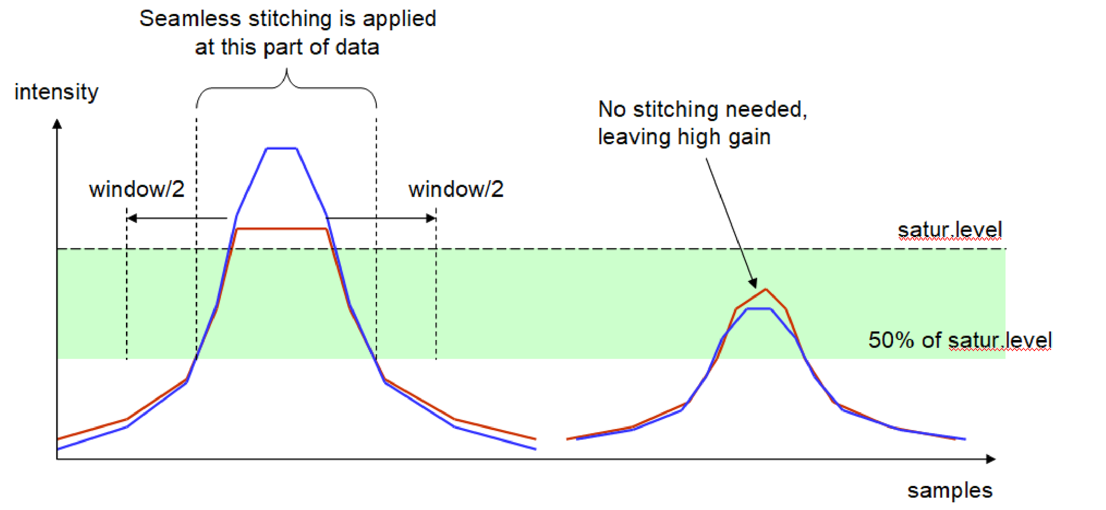


Fig 6. Stitching explanation. (Left) Peak height above saturation level – recording a weighted sum of high and low gain signals. (Right) Peak height is below saturation level – high gain signal is recorded.

Results

Dynamic range

Saturation of the ion peak appears to be at around λ=9000 ion/pk/shot.

At an acquisition rate of 10 Hz (1000 spectra), ion peaks are clearly detectable down to approximately 20 ions or I=0.02 ions/shot/pk.

Therefore, the dynamic range within a spectrum is about 5 x 10^5 at 10 Hz; corresponding to DR/s= 5 x 10^6 /s (at 1 Hz acquisition).

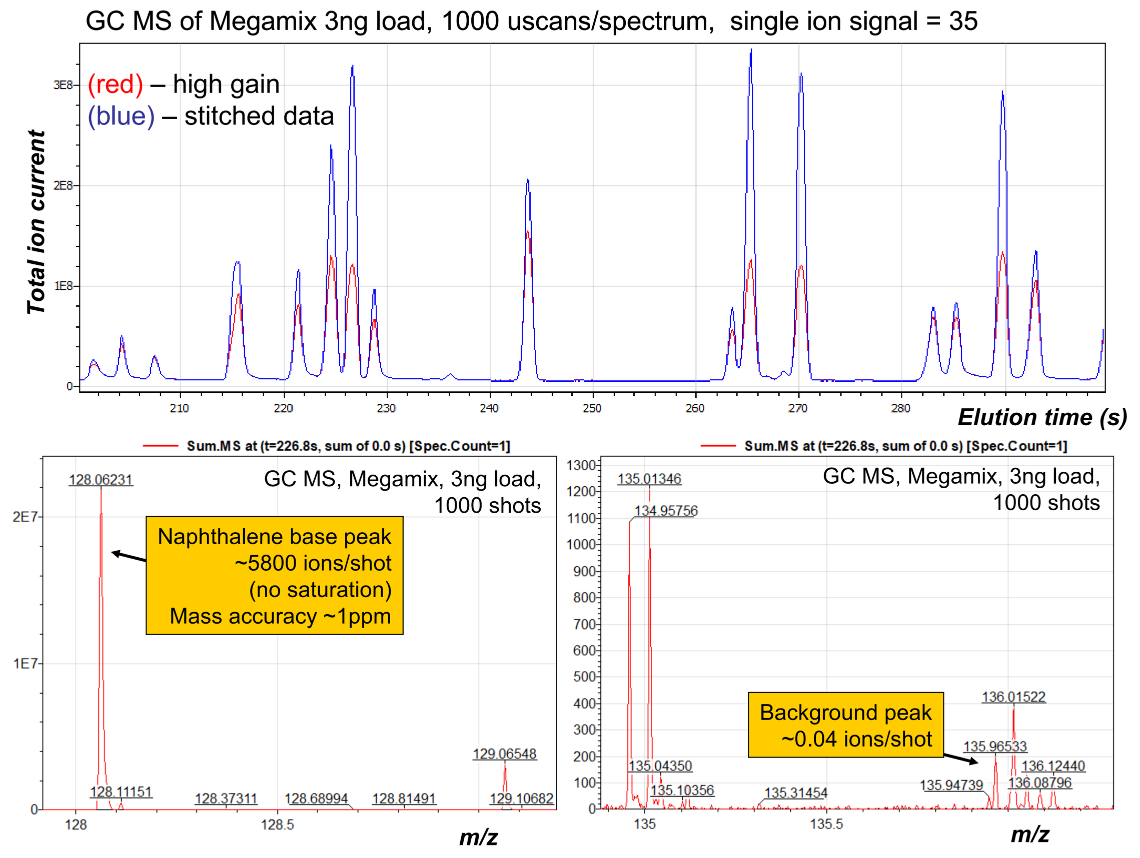


Fig 7. GC MS, Megamix 3ng load, 1000 shots per spectrum (800 at high gain, and 200 at low gain). (Top) Comparison between stitched ion signal and raw ion signal (high gain). (Bottom) Intense peak(left) and minor peak (right) in the same spectrum of naphthalene at maximum of eluted GC peak.

Results

Dynamic range

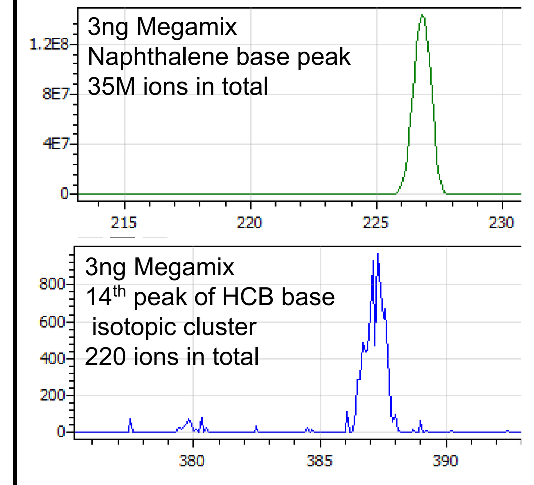


Fig 8. Example of traces for intense (left) and minor (right) ion peaks.

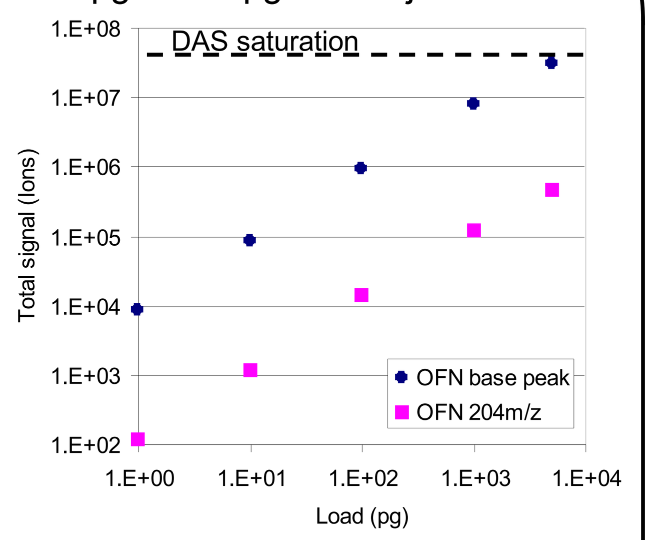


Fig 9. Test of DR by OFN injections.

Mass accuracy

Mass shift due to the time shared stitching approach was found to be below 0.5ppm. Thus, the overall analytical mass accuracy of GC MS prototype of ~ 1ppm is not reduced by the used algorithm, but rather limited by the quality of internal calibration, ion statistics, and analyzer space charge effects.

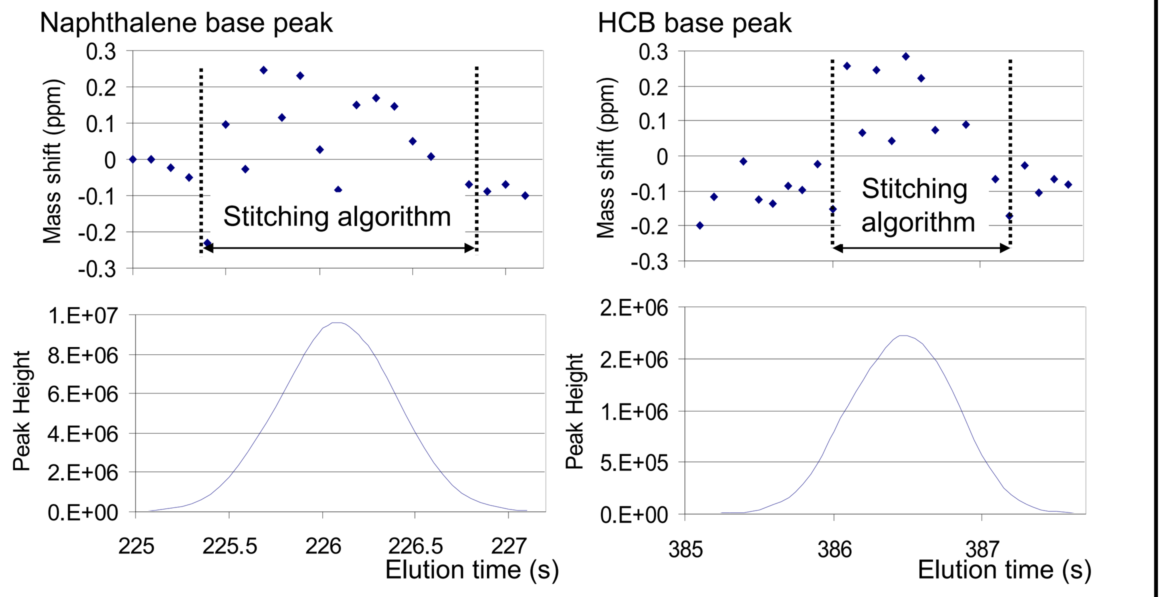


Fig 10. GC MS, Megamix 1ng load, 1000 shots per spectrum (800 high gain, 200 low gain). Elution on Naphthalene (left) and HCB (right). Mass shift due to the algorithm is below 0.5ppm. Internal calibration by PFTBA leak signal is applied after stitching algorithm.

Conclusions

- High-performance GC-MRT-MS combined with an M-TOF detector and SA230P ADC card allows obtaining up to 5x10^6 dynamic range (DR) at a 1-second spectra acquisition time.

- The time-shared stitching algorithm extends the DR range at the expense of a 20% reduction in sensitivity at a 2:8 sharing pattern at 1 ms acquisition cycle, limiting acquisition speed to 1000 spectra/s.

- The time-shared algorithm does not induce any significant mass shift. Therefore, internal calibration of spectra allows maintaining mass accuracy within 1 ppm in GC-MS with dynamic range of 5x10^6.

Conflict of Interest

The authors declare no competing financial interest.