

Evaluation of a New Comprehensive Two-Dimensional Gas Chromatography – High Resolution Time-of-Flight Mass Spectrometry System (GCxGC-HRTOFMS)

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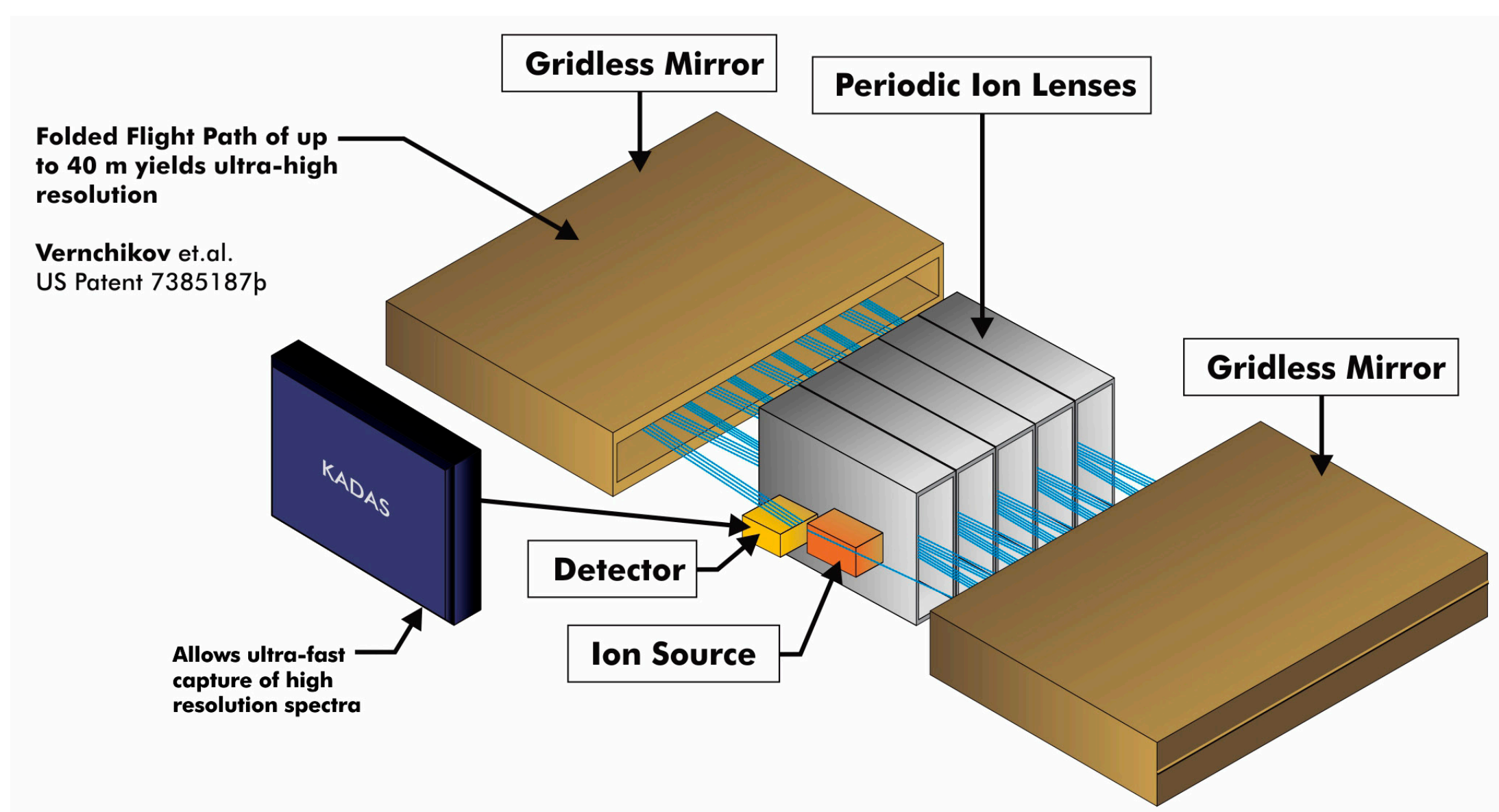
Introduction

- GCxGC has been coupled to a range of detectors including single channel detectors and mass spectrometers. To take advantage of optimized GCxGC, a detector must operate at a high data acquisition rate in order to accurately follow the chromatographic peak. For accurate data processing of narrow GCxGC peaks a data acquisition rate of 200 Hz is required.
- In addition to high data acquisition rates, a mass spectrometer must also be characterized by other criteria including limits of detection (LOD), dynamic range, precision, mass resolution, and mass accuracy.
- Complex applications are typical of GCxGC, and GCxGC-TOFMS with nominal mass resolution has demonstrated proficiency in many areas including environmental, petroleum, and metabolomics for both target and non-target analysis. Identification is often done by spectral matching of EI (electron ionization) spectra.
- Accurate mass information can significantly improve selectivity and identification capabilities for GCxGC-TOFMS.
- A prototype GCxGC-HRTOFMS system (comprehensive two-dimensional gas chromatography – high resolution time-of-flight mass spectrometry system) with electron ionization (EI) is evaluated for its potential as a GCxGC detector. Examples of initial prototype performance including peak shape/width, limit of detection, dynamic range, precision, resolution, and mass accuracy at 200 spectra/sec for narrow GCxGC peaks are presented.

Experimental

- Samples: Octafluoronaphthalene (OFN), dibenzothiophene, crude oil
- Instrument: Prototype GCxGC-HRTOFMS
 - LECO prototype of LECO GCxGC interfaced to LECO Pegasus[®] GC-HRT
 - LECO Pegasus GC-HRT specifications
 - Mass Accuracy: <1 ppm
 - Mass Range: 10 – 1500 m/z
 - Resolving Power: Up to 50,000
 - Detection Limit: Low pg
 - Data Acquisition Speed: Up to 200 spectra/sec
 - Columns (Restek)
 - 10 m x 0.18 mm x 0.2 μm Rtx-5/0.4 m (secondary oven) x 0.1 mm x 0.1 μm Rxi-17 (OFN)
 - 60 m x 0.25 mm x 0.25 μm Rxi-5Sil MS/0.6 m (secondary oven) x 0.25 mm x 0.25 μm Rxi-17Sil MS (crude oil)
 - Conditions
 - GCxGC operated at typical conditions
 - Ion source 250°C, electron ionization at 70 eV
 - Acquisition range, 30 to 510 u at 200 spec/sec, high resolution mode (R = 25,000)

Folded Flight Path™ (FFP™)



Results and Discussion

- The high resolution and mass accuracy achieved by this system is due to the patented mass analyzer design shown above. The Folded Flight Path™ provides a flight path up to 40 m.
- Limit of Detection – Figure 1 shows the XIC (extracted ion chromatogram) of three replicate injections of OFN at ~0.5 pg on column (near detection limit amount) with the observed mass and mass error for each apex spectrum. Mass accuracy of ~1 ppm at 200 spectra/sec was achieved.
- Peak Width/Shape and Range – Figure 2 shows the peak shape and width of OFN over a range of 5 to 500 pg. The peak width is consistently narrow over this range with a FWHH of approximately 35 msec. From 0.5 pg in Figure 1 to 500 pg is 3 orders of magnitude.
- Peak Area Precision – Figure 3 shows excellent peak area precision at 3.5% for 15 consecutive replicate injections of 50 pg OFN on column.
- Mass Accuracy – Figure 3 shows that the mass accuracy at 200 spec/sec for a chromatographic peak width of ~35 msec (FWHH) is ±1 ppm for 15 consecutive replicate injections of 50 pg OFN on column. At 200 spec/sec there are 8 spectra across the FWHH of the peak.
- Resolution - Figure 4 shows two contour plots of a crude oil spiked with dibenzothiophene: one for the TIC, and one for the accurate mass of dibenzothiophene. The selectivity of accurate mass shows only a single peak for the dibenzothiophene. Figure 5 shows the spectrum of dibenzothiophene and the inset shows the ¹³C and ³⁴S isotopes for the [M+2]⁺ ion nearly baseline resolved. Note that the peak profile is not the actual mass peak profile, but a representation of the profile based on the data acquired by the high speed data acquisition system at 200 spec/sec.

Conclusion

Initial testing of a prototype GCxGC-HRTOFMS system shows very promising results for high mass accuracy and high mass resolution mass spectra with narrow GCxGC peaks requiring 200 spectra/sec.

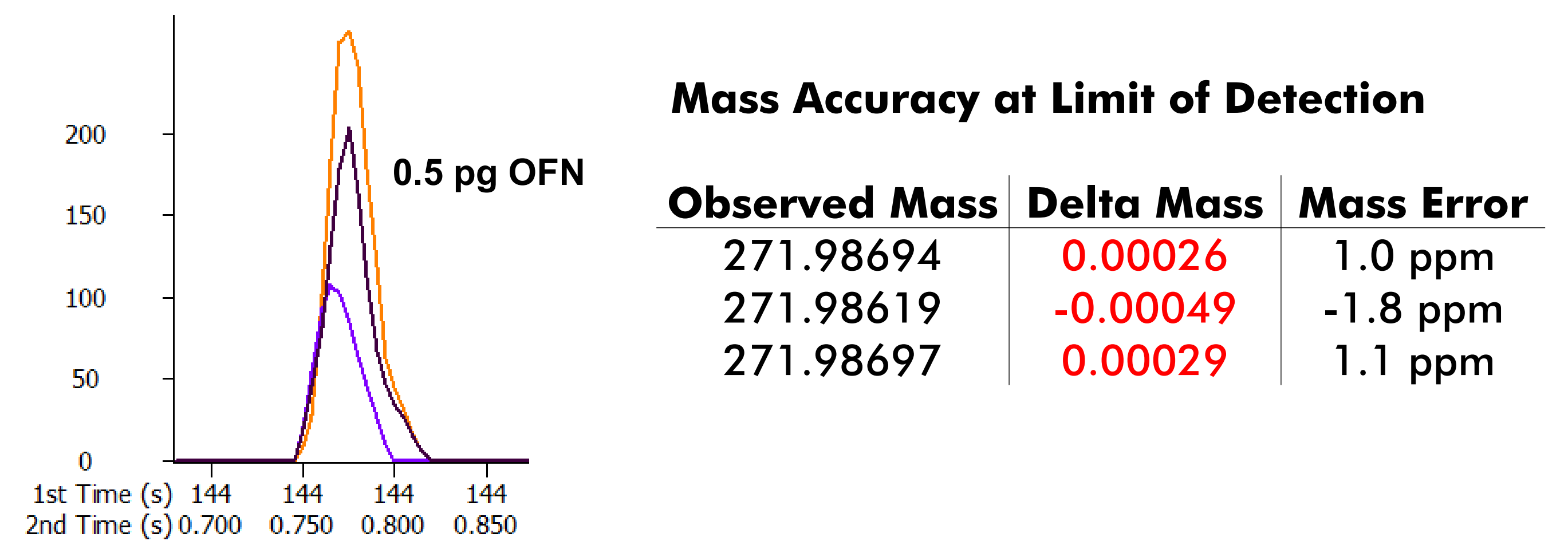


Figure 1. Limit of Detection. Three replicate injections of 0.5 pg of OFN on column in high resolution mode. XIC for 271.9867 ± 0.0005 u is shown. Theoretical accurate mass is 271.986677 u for M⁺ ion.

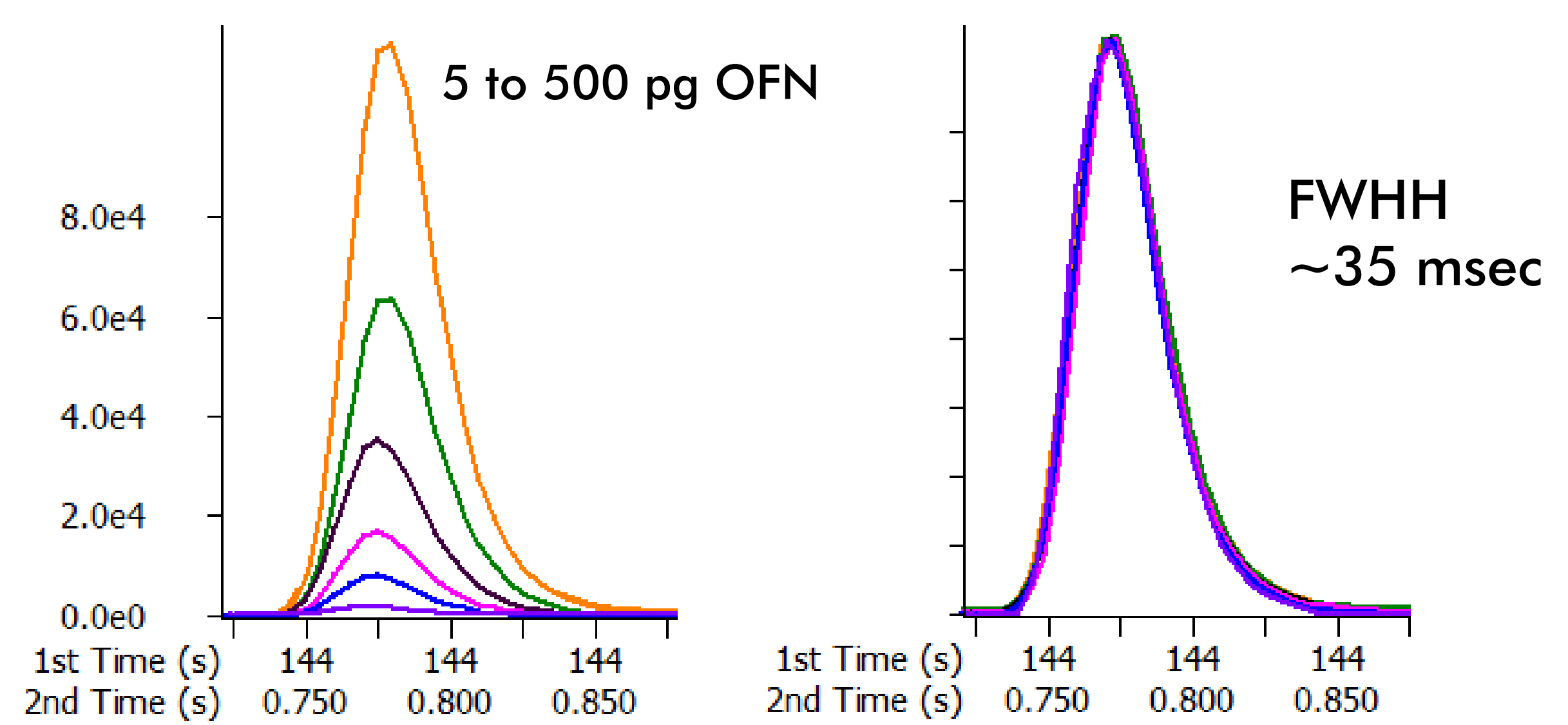


Figure 2. Left. Overlay of OFN peak from 5 to 500 pg for mass window 271.9867 ± 0.0005 u. Right. Same peaks as on left, but normalized to the same height.

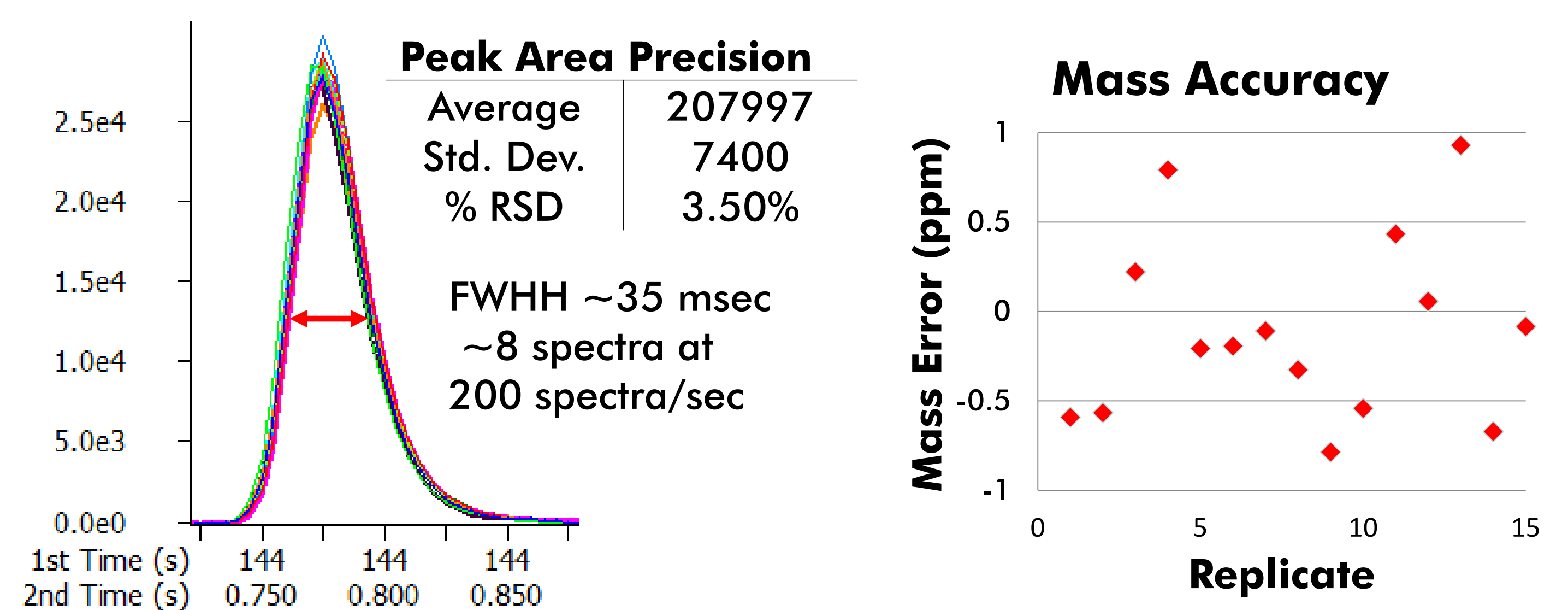


Figure 3. Peak overlay of 15 replicate injections of 50 pg OFN on column in high resolution mode. Mass window is 271.9867 ± 0.0005. On the right is a plot of mass error for same 15 replicates.

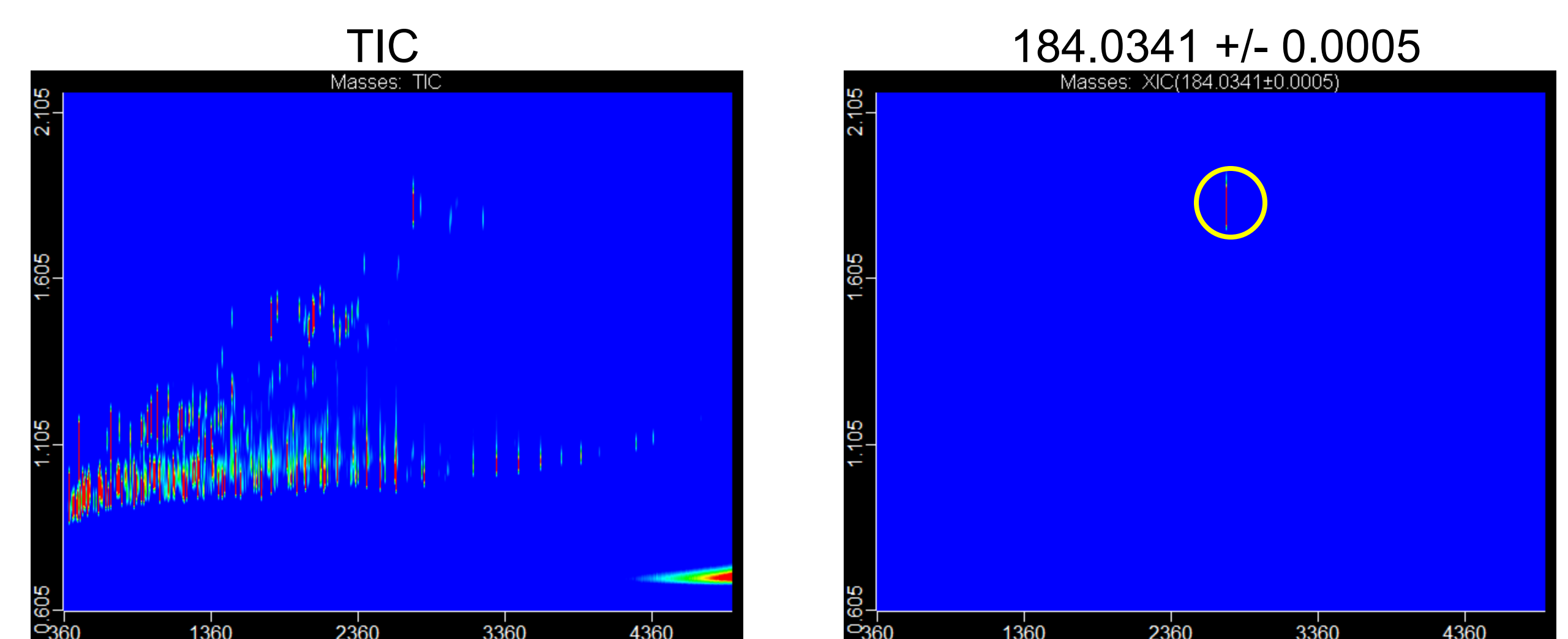


Figure 4. Contour plots of crude oil spiked with dibenzothiophene.

Caliper - sample "Crude Oil + Dibenzothiophene HR 1000 pg on column_2", 2731.82 s to 2731.82 s - 2731.72 s to 2731.72 s

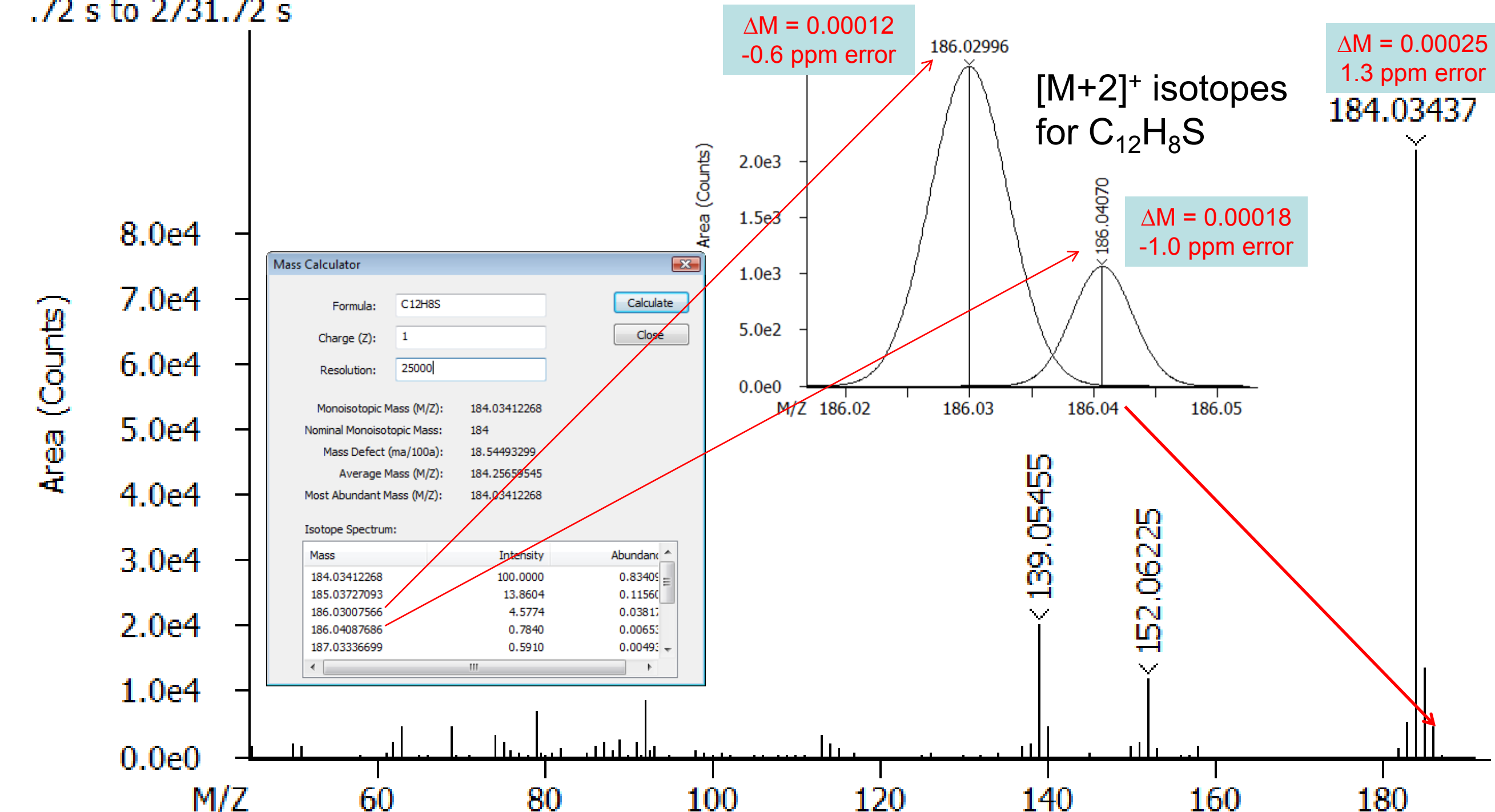


Figure 5. Mass spectrum of dibenzothiophene spiked in crude oil.