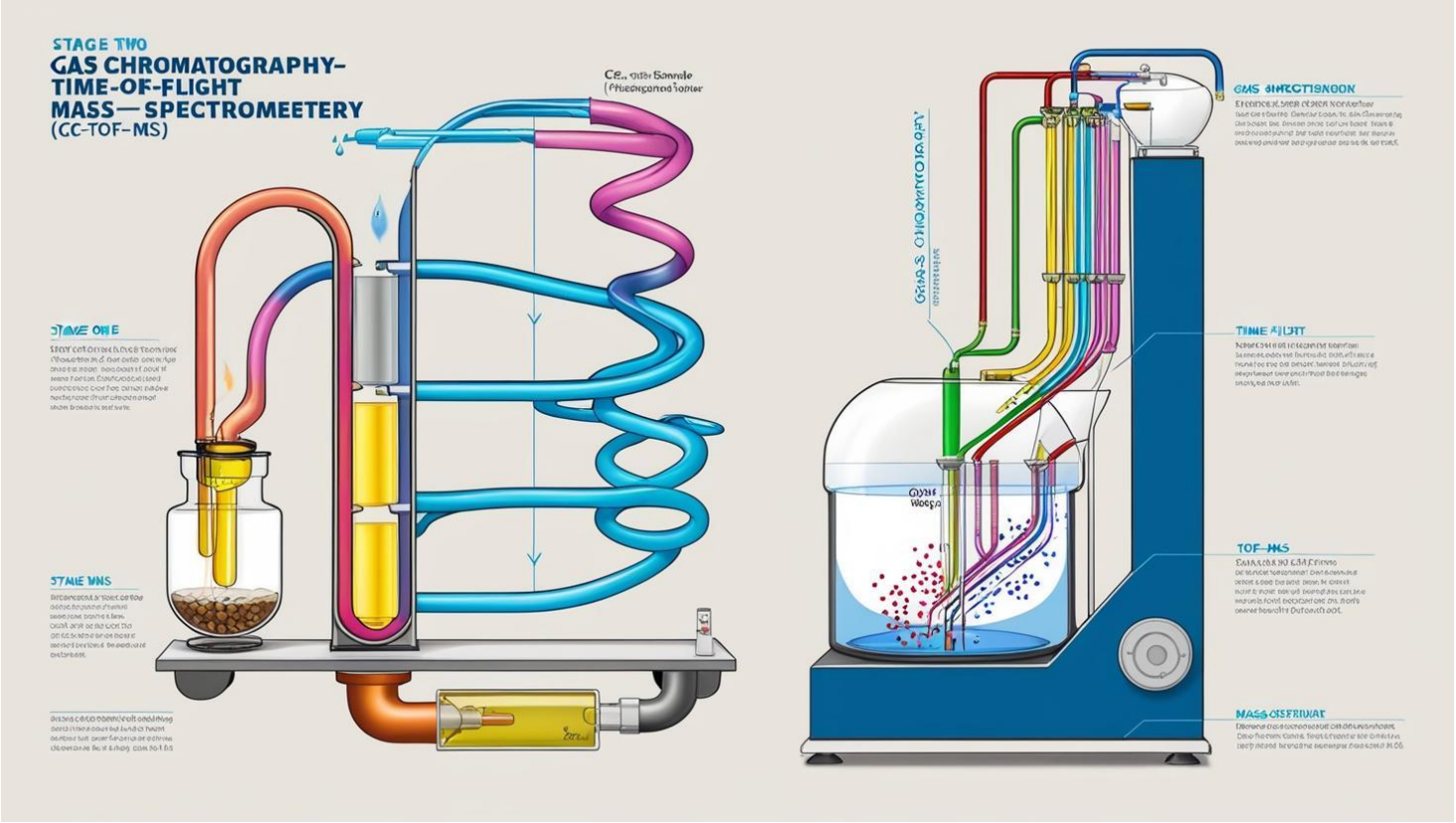


TOF MS – Join the trip beyond the horizon of conventional GC-MS

Tomáš Kovalczuk

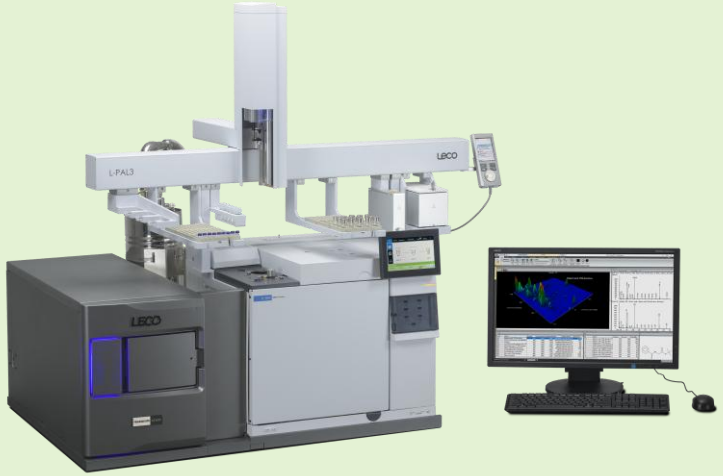
GC with TOF MS detection

What is it in fact?



Well … not that one…. ☺

Current LECO TOFs

	One dimensional		GCxGC
Low Resolution	Pegasus BTX		Pegasus BTX4D
High Resolution	Pegasus HRT+		Pegasus HRT+4D

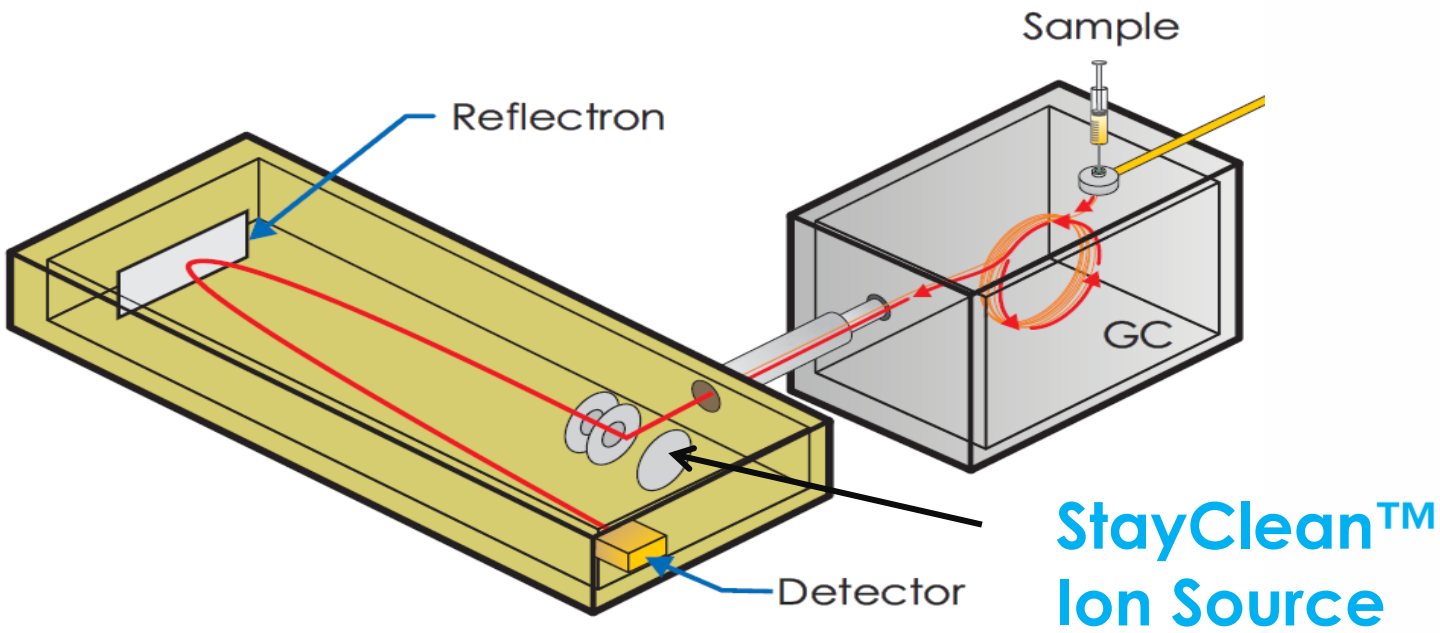
TOF MS “S” Benefits

- Simplicity
- Sensitivity
- Straightforward identification
- Superior Separation

Part I - Simplicity

- Thanks to:
  - Easy & user-friendly SW
  - Automated Peak Finding
  - No clean ion source
  - Multigas (He & H2) without HW change

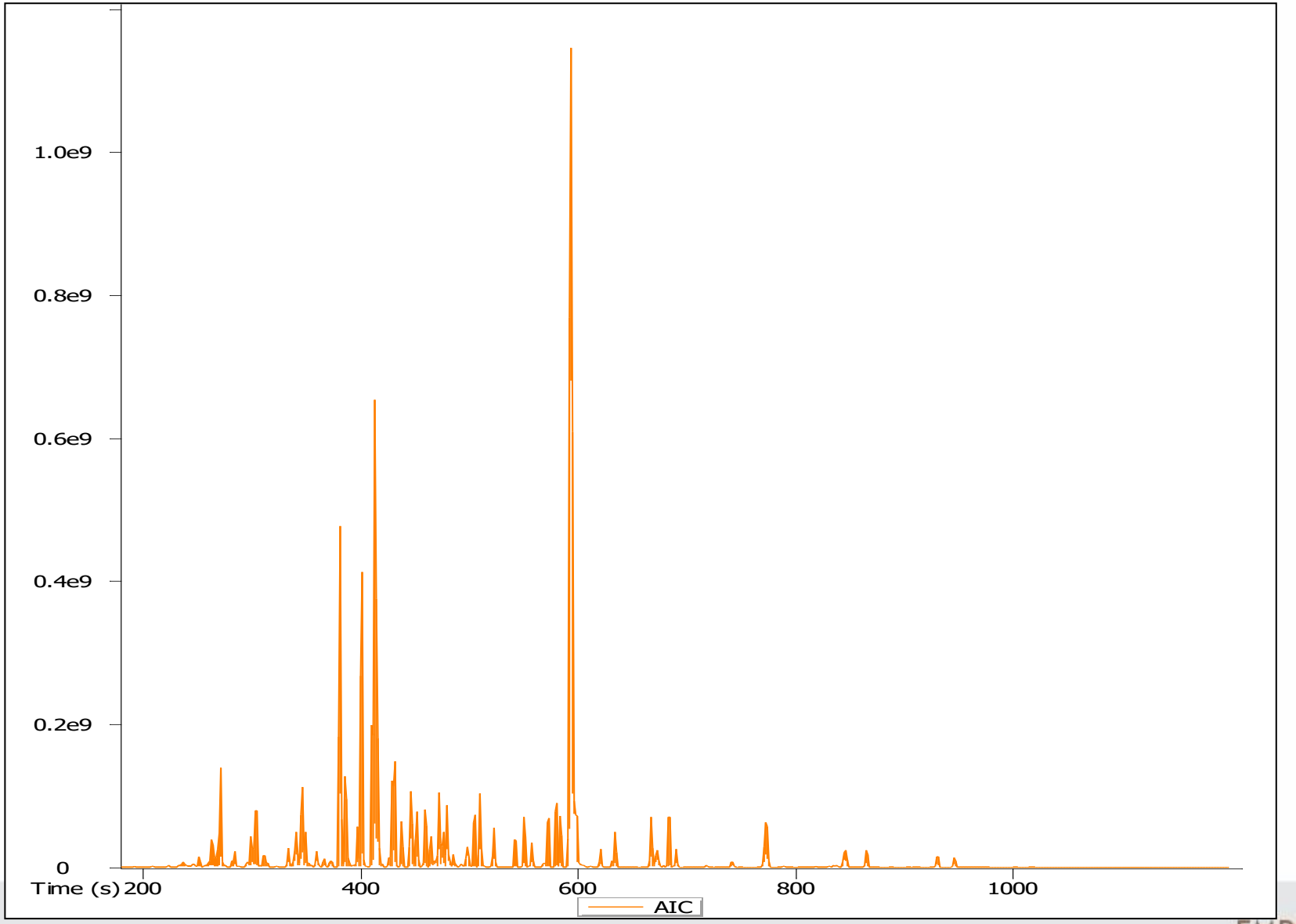
Pegasus BTX schematics



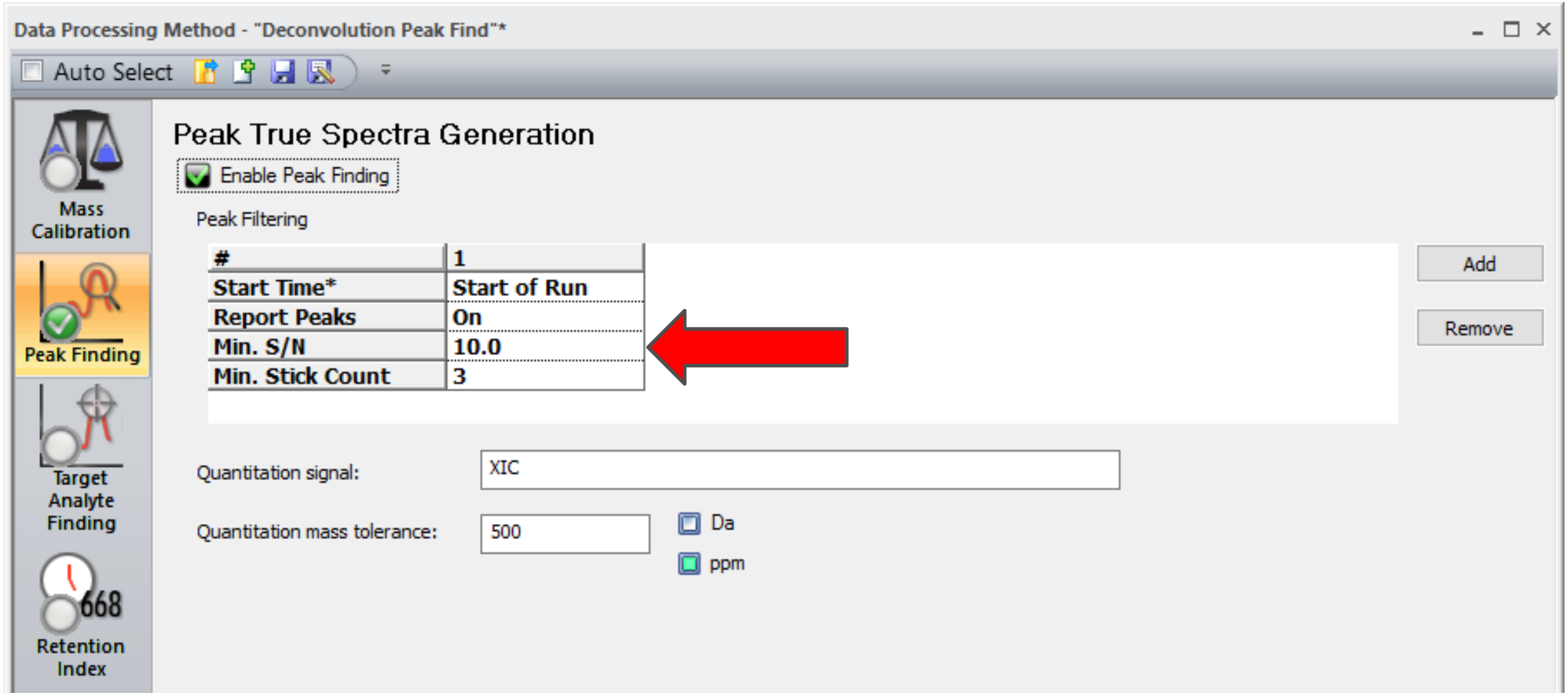
StayClean™ Ion Source

- Analytes enter the ion source and are ionized by EI mechanism
- Push pulse plate samples the ions into the flight tube at frequency upto 35000/sec
- Ions have equal kinetic energies when entering flight tube
- Ions are separated in the flight tube based on equation $E_k = 1/2\ m\ v^2$

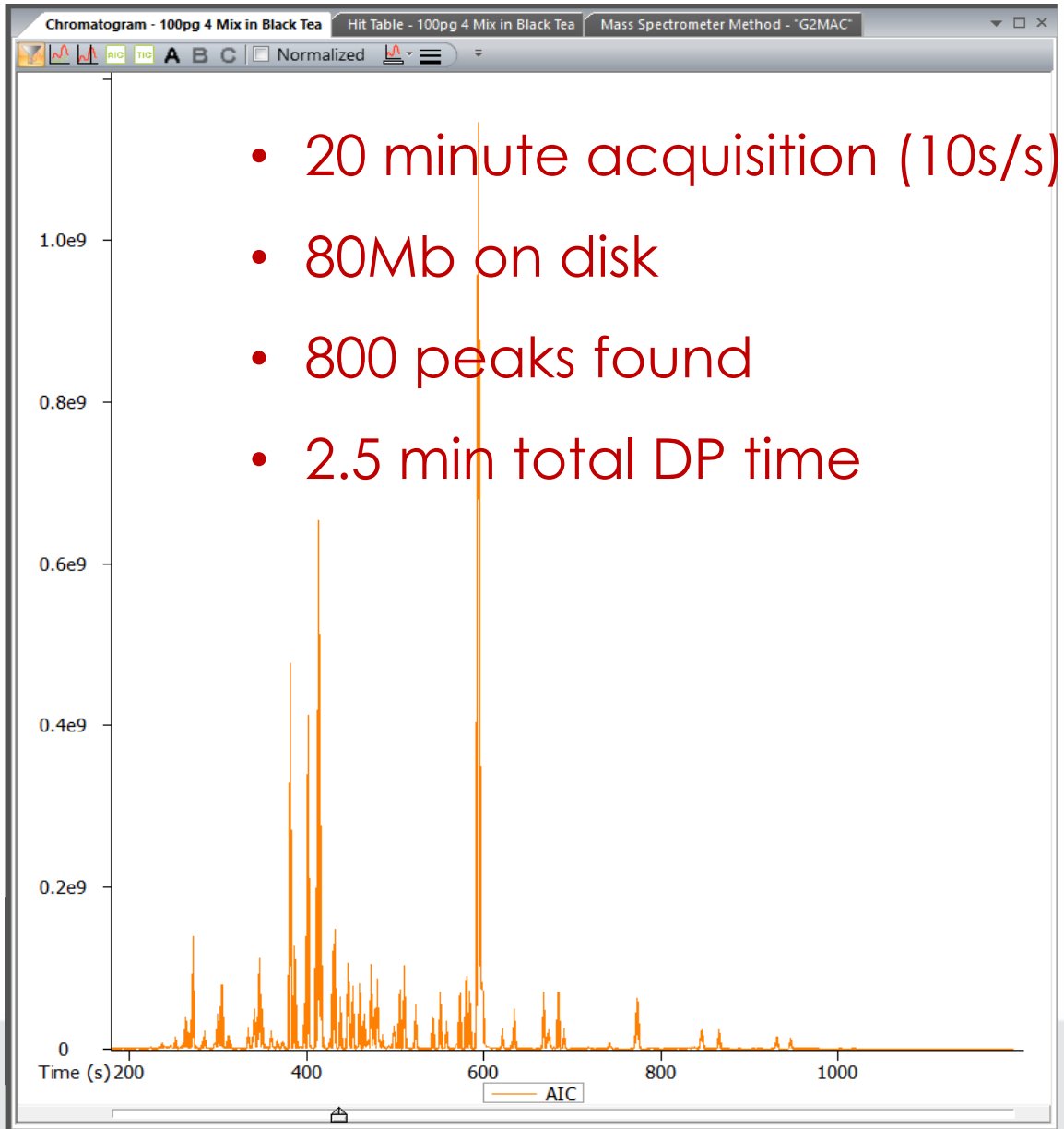
Data file… what next?



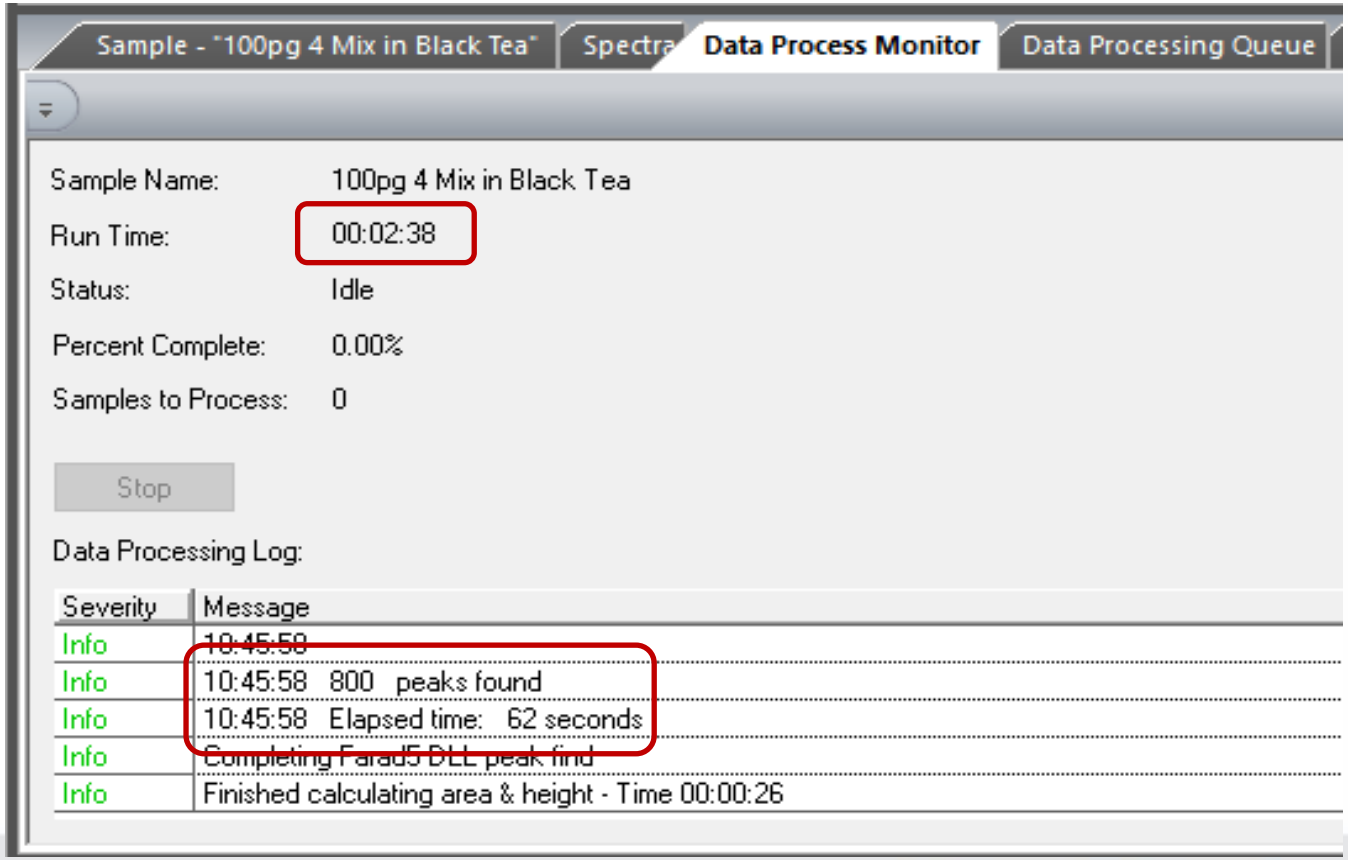
ChromaTOF Data Processing Method



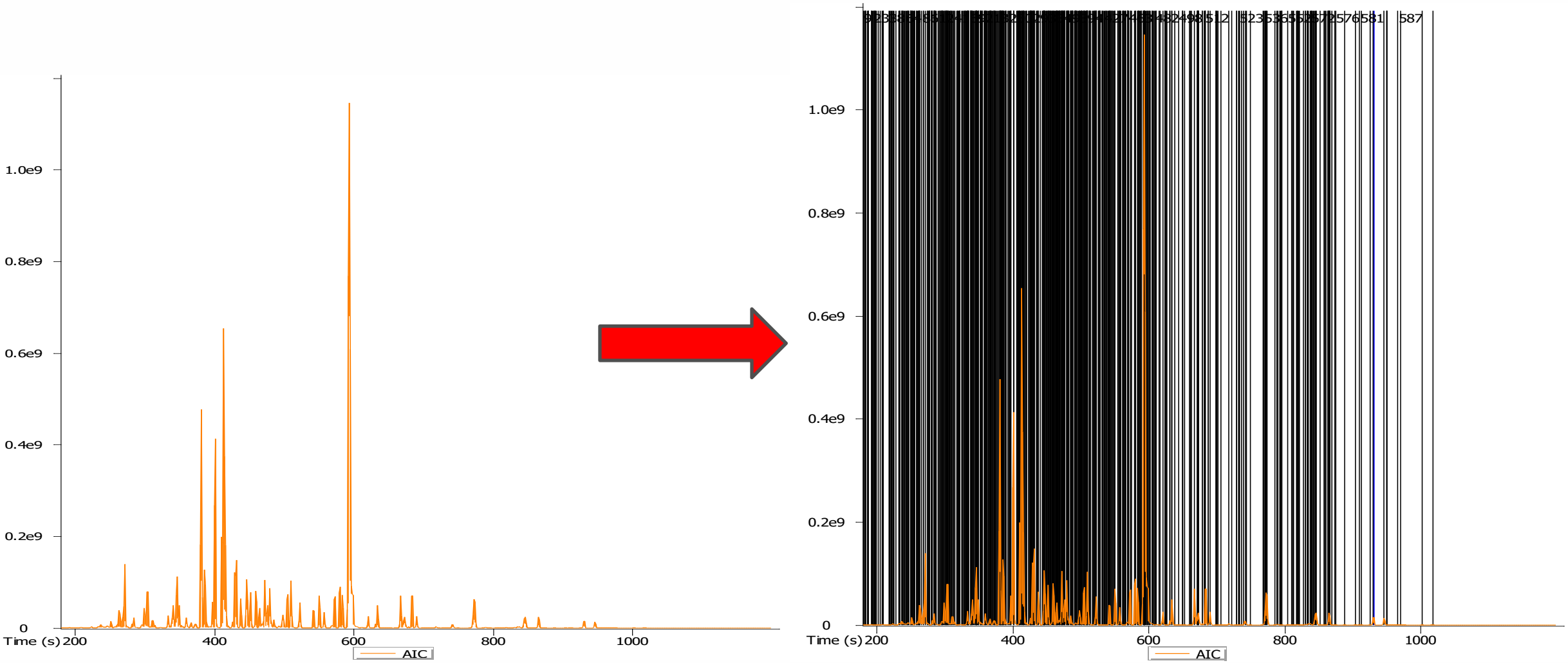
Data Size



- 20 minute acquisition (10s/s)
- 80Mb on disk
- 800 peaks found
- 2.5 min total DP time



Processed Data File

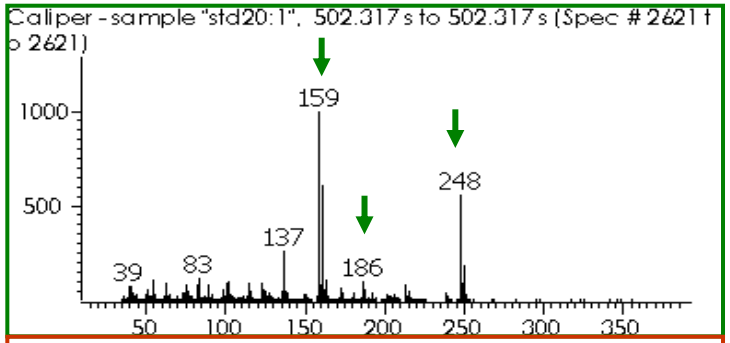


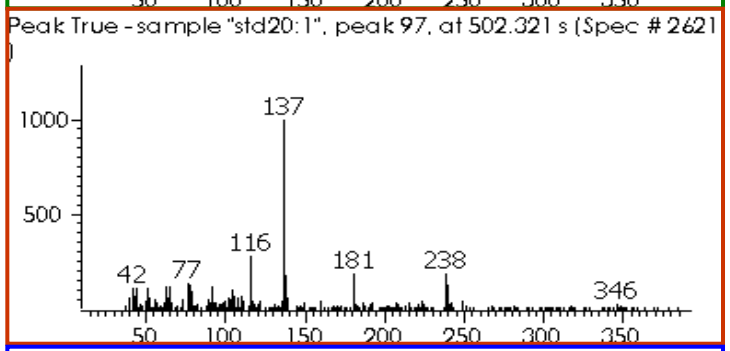
Mass spectral deconvolution

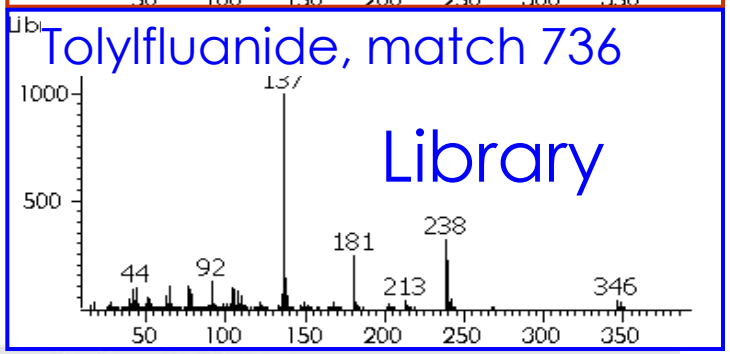
interferences

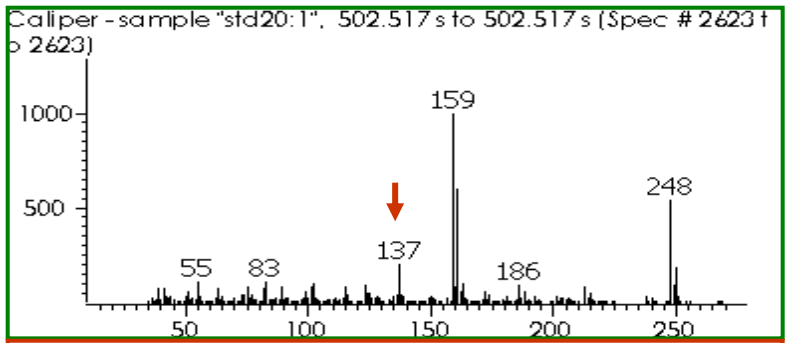
Spectrum from peak apex

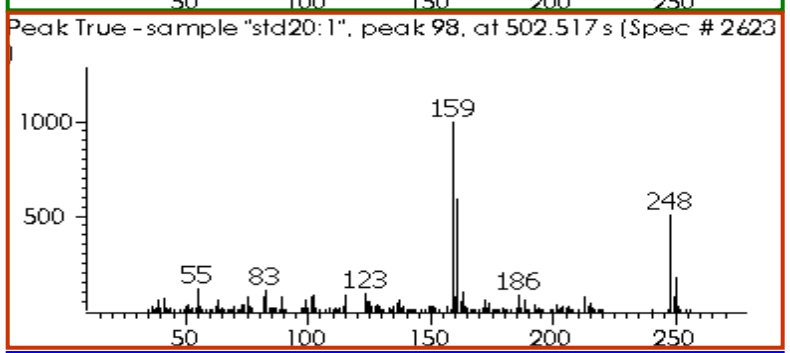
Deconvoluted spectrum

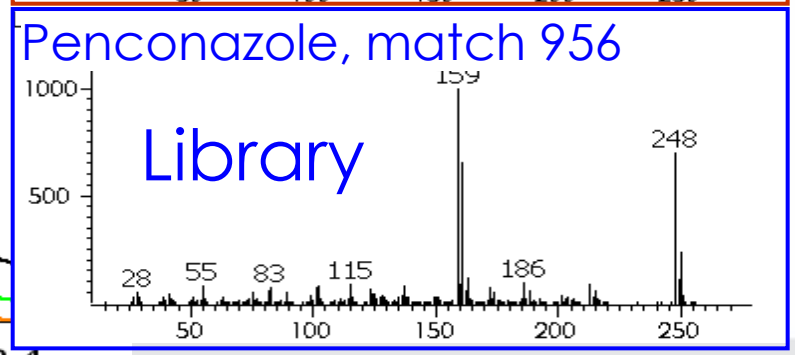


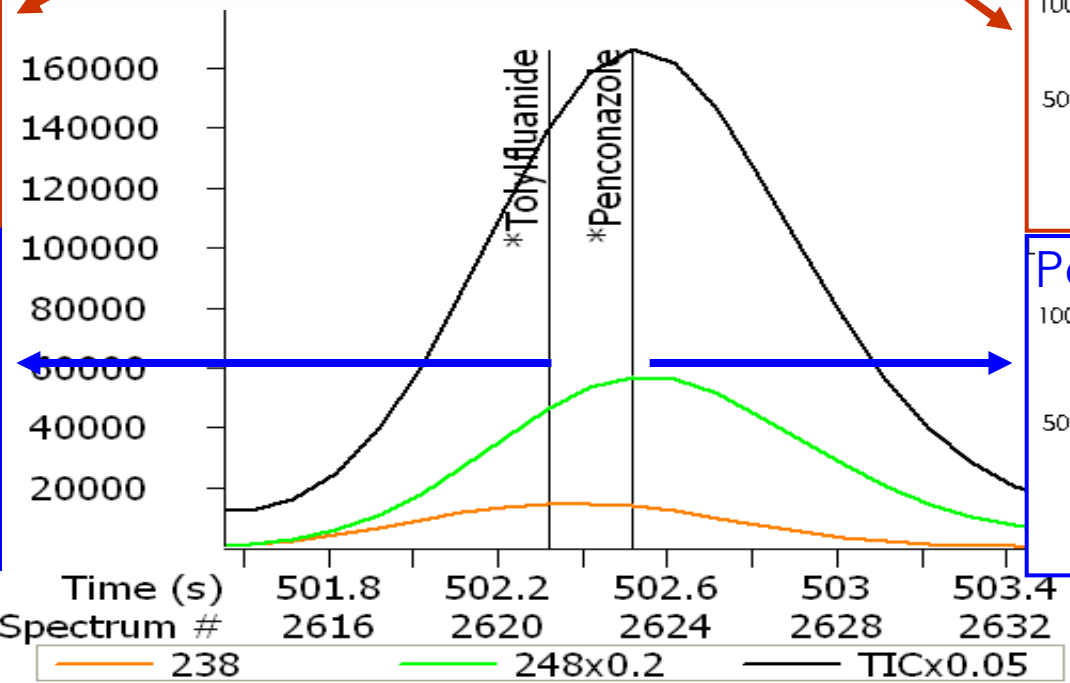








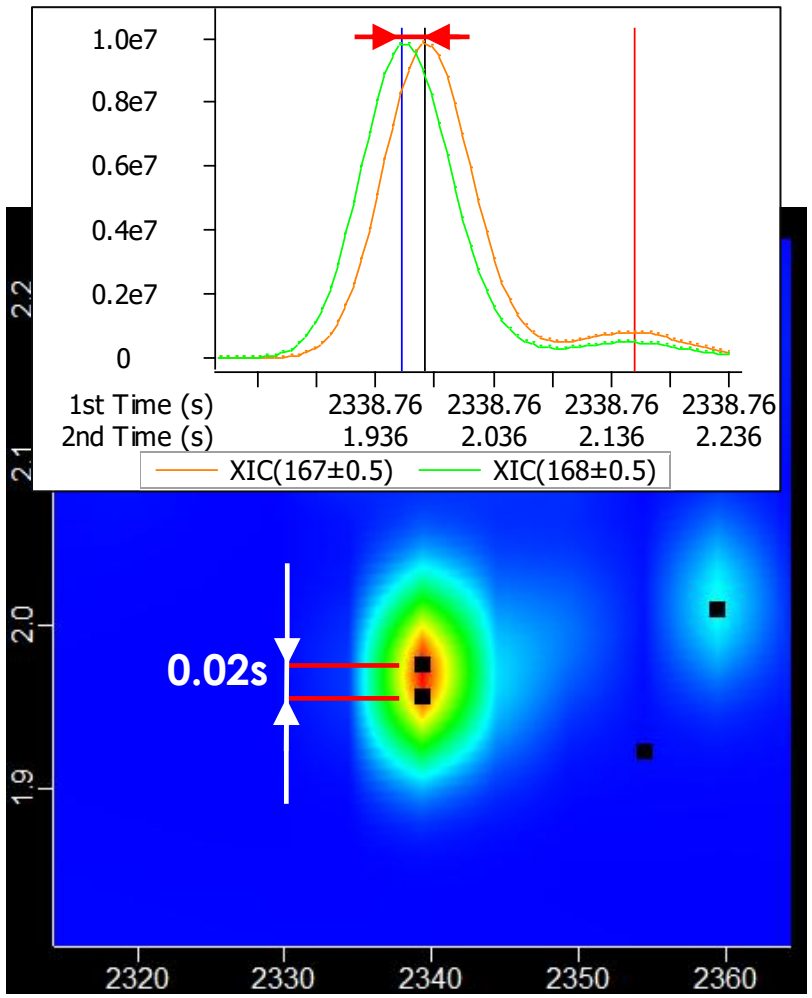




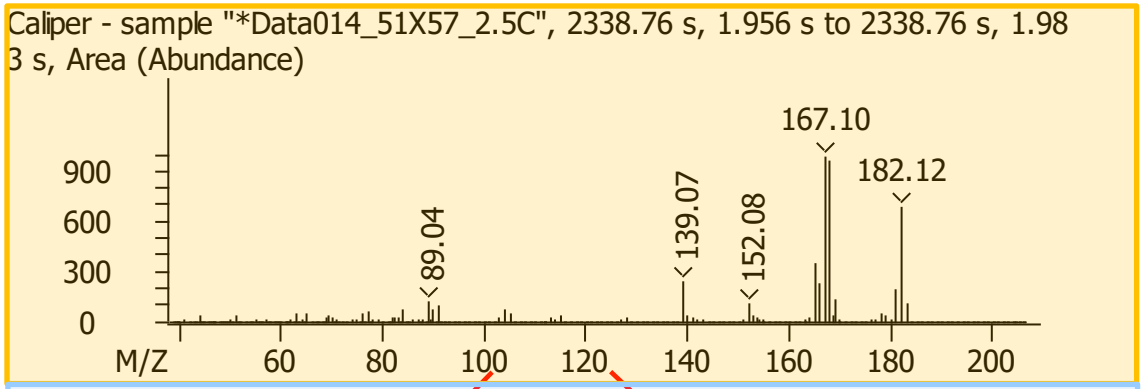
Advanced SW algorithms – Peak Find & TSD® Deconvolution

Excellent spectral deconvolution for closely (0.02s) coeluted peaks

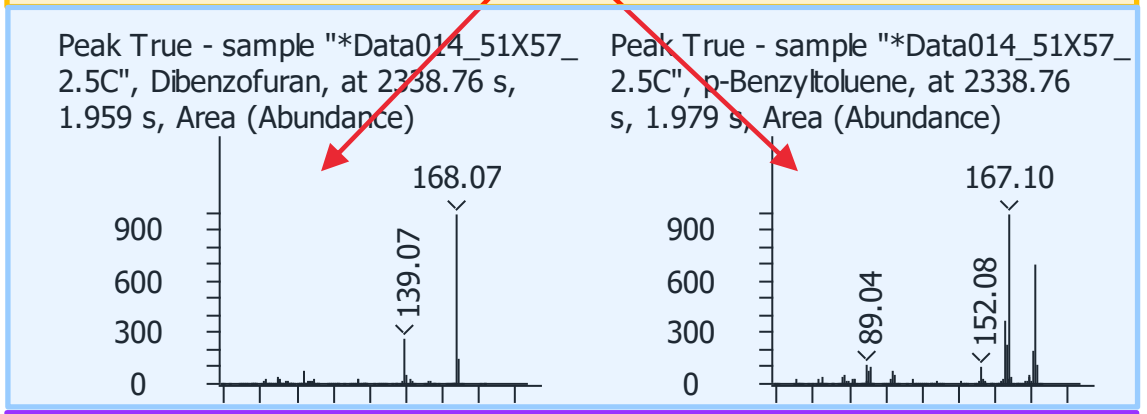
RT peak apexes difference 0.02s



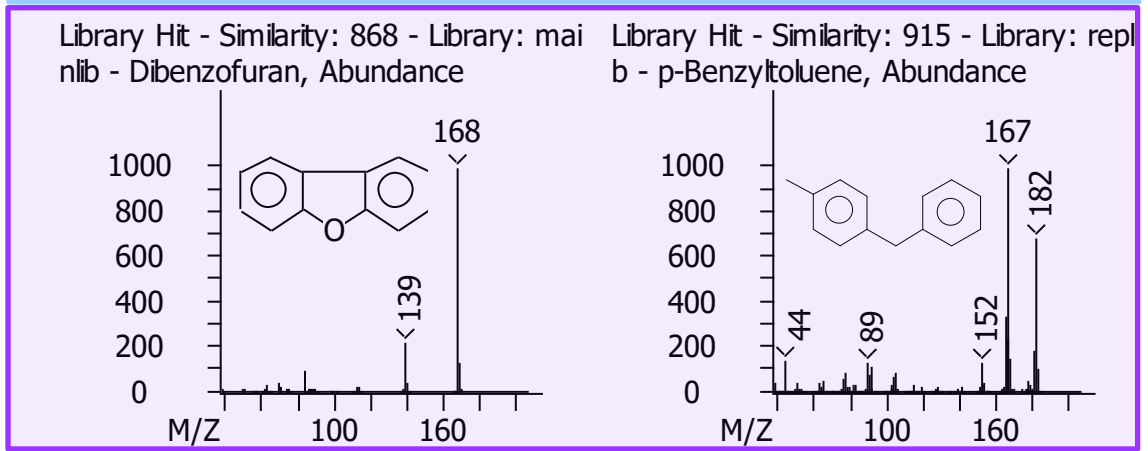
Undeconvoluted



Deconvoluted

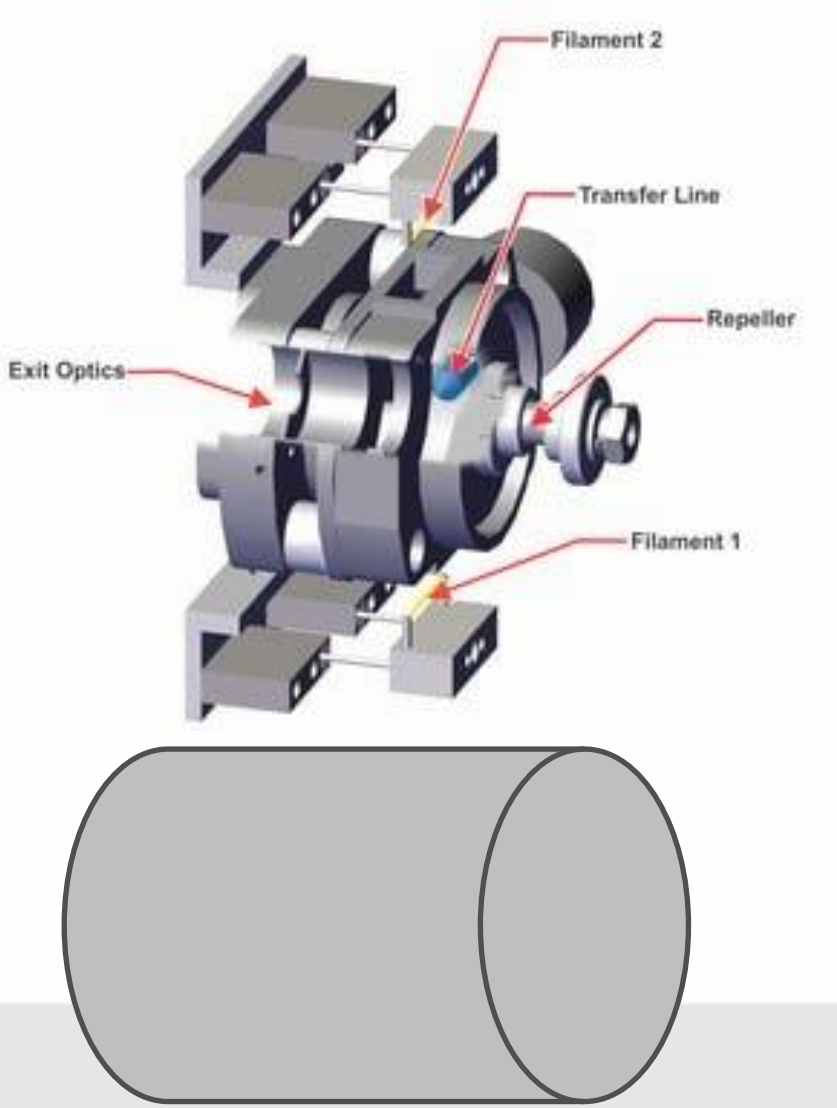


Library hit



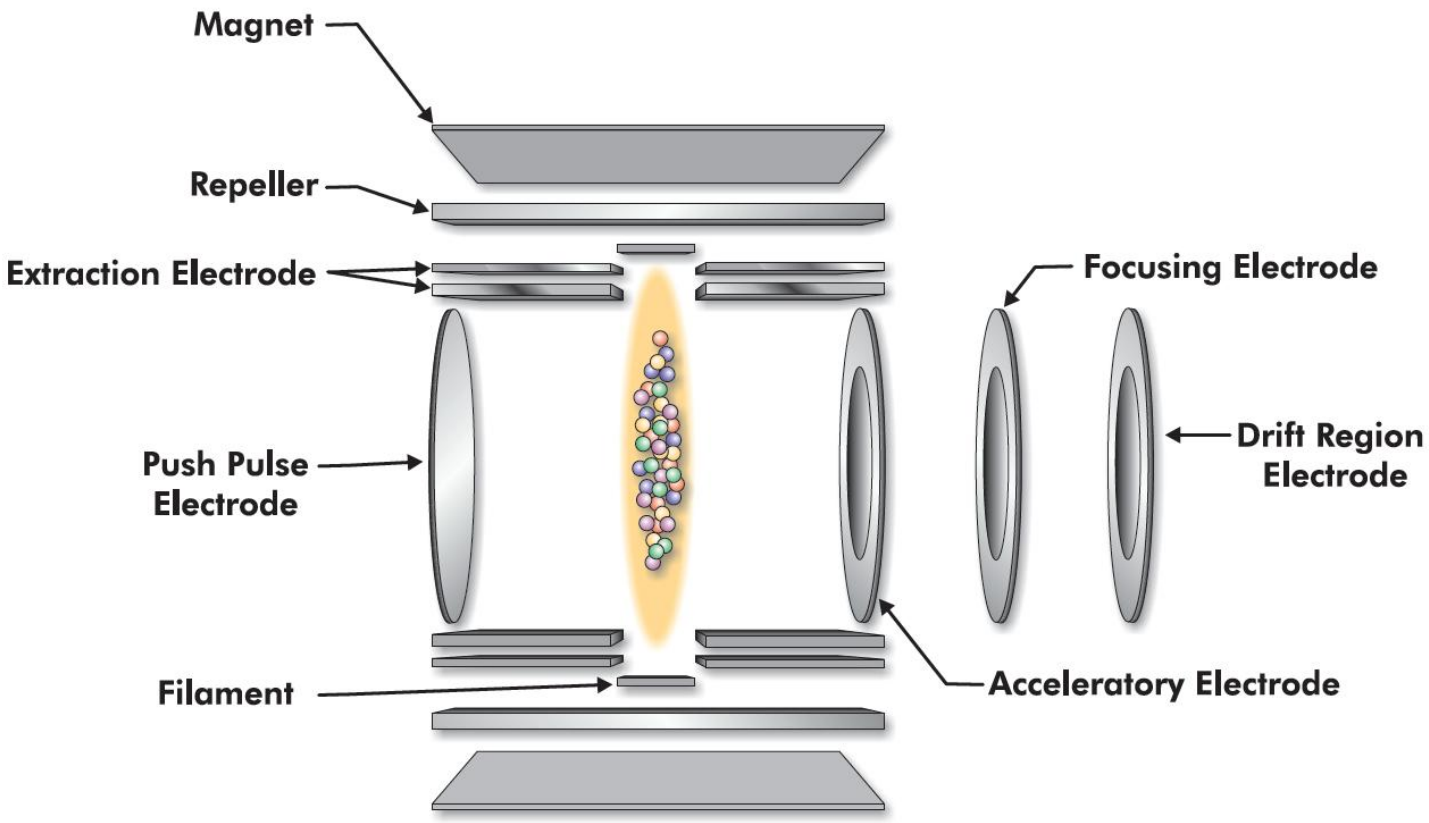
Ion sources

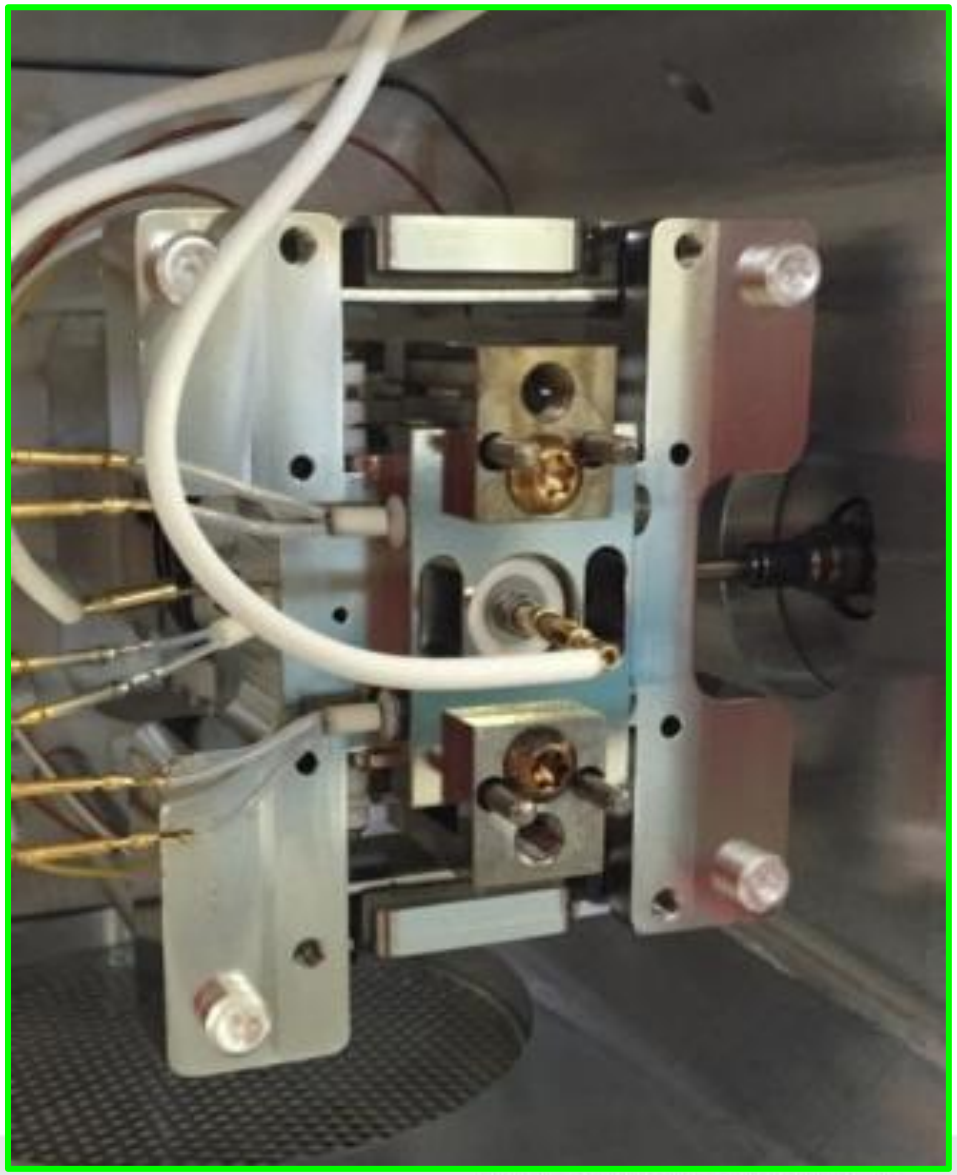
Pegasus BTX - StayClean® Ion Source for EI



- **Open style** design with strong vacuum pump – no residuals remains → **no deposit** inside
- **Very robust**, no need of cleaning
- **Proven technology** in previous model series for more than two decades
- **Consistent results**

StayClean™ Ion Source – open design

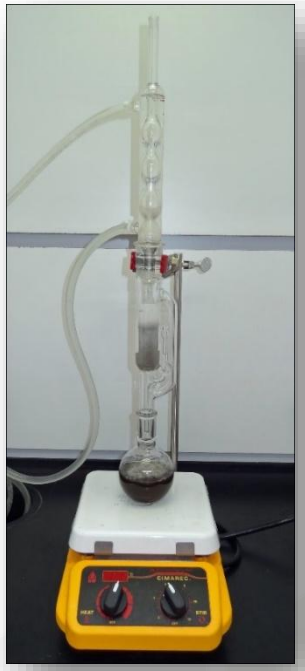




The Pegasus BTX : StayClean™ Ion Source











Raw Sludge Sample

Soxhlet Extraction

Neat Sludge Extract

Sludge Extract Diluted 100:1

3000 injections no change in



Part II - Sensitivity



The New Pegasus BTX

Key Product Specifications:

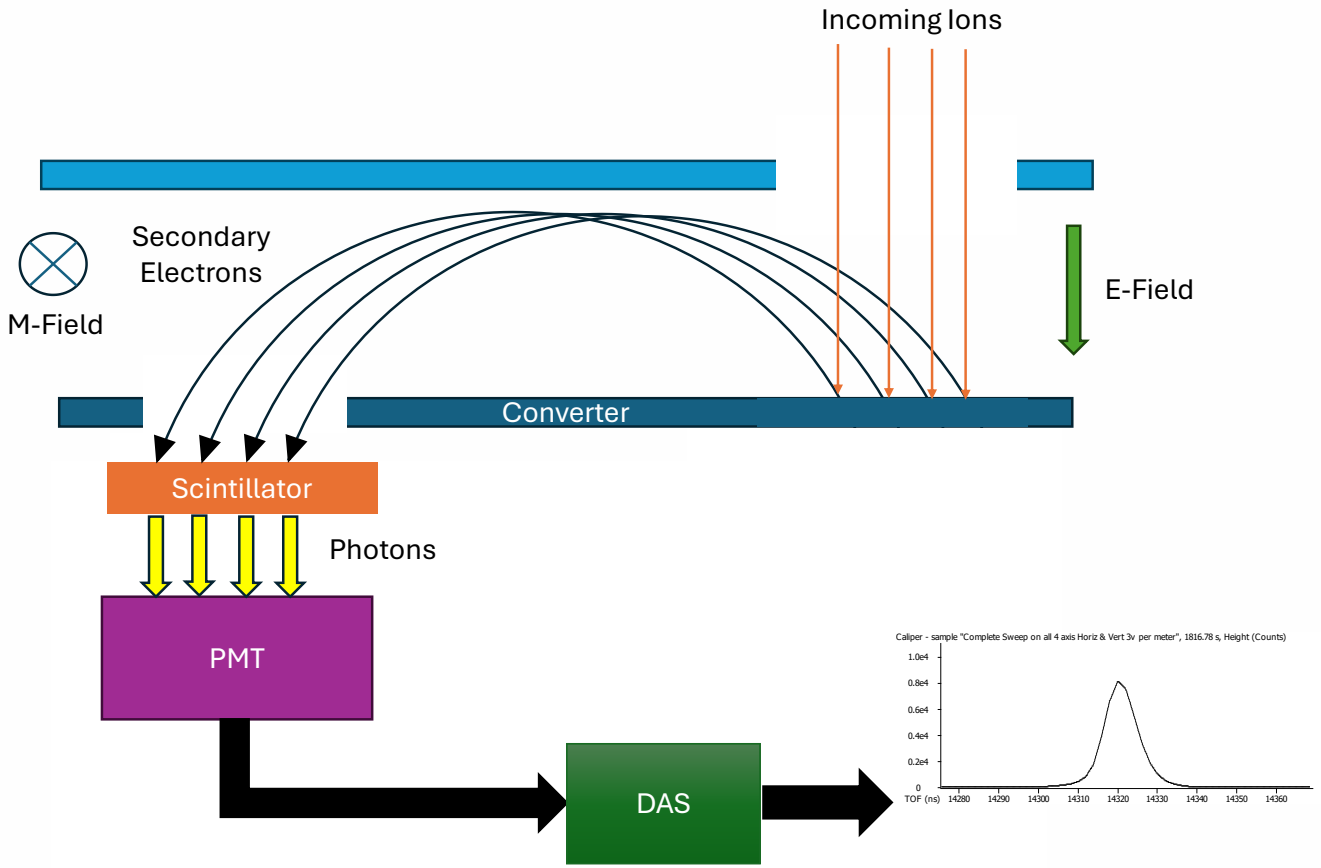
Detector:	Scintillator – Photomultiplier Tube with extended lifetime
Mass Analyzer:	Time-of-Flight Mass Analyzer with Dual Stage single Reflectron
Mass Range:	10 – 1500 m/z
Mass Resolution:	> 1,100 at m/z 219
Spectral Acquisition Rate:	1-500 spectra/second – up to 35,000 transients/second
Detection Limit:	10fg OFN with Quant S/N > 10 (Helium carrier gas)
	10fg OFN with Quant S/N > 10 (Hydrogen carrier gas)
IDL:	< 4fg OFN injected, < 1g OFN injected in GCxGC
Precision:	< 5% RSD 100fg OFN
Linear Dynamic Range:	5 orders of magnitude

IDL with GCxGC (thermal modulation) >1fg OFN



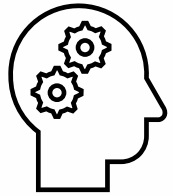
The New Pegasus BTX

New Detector Technology at a Glimpse:





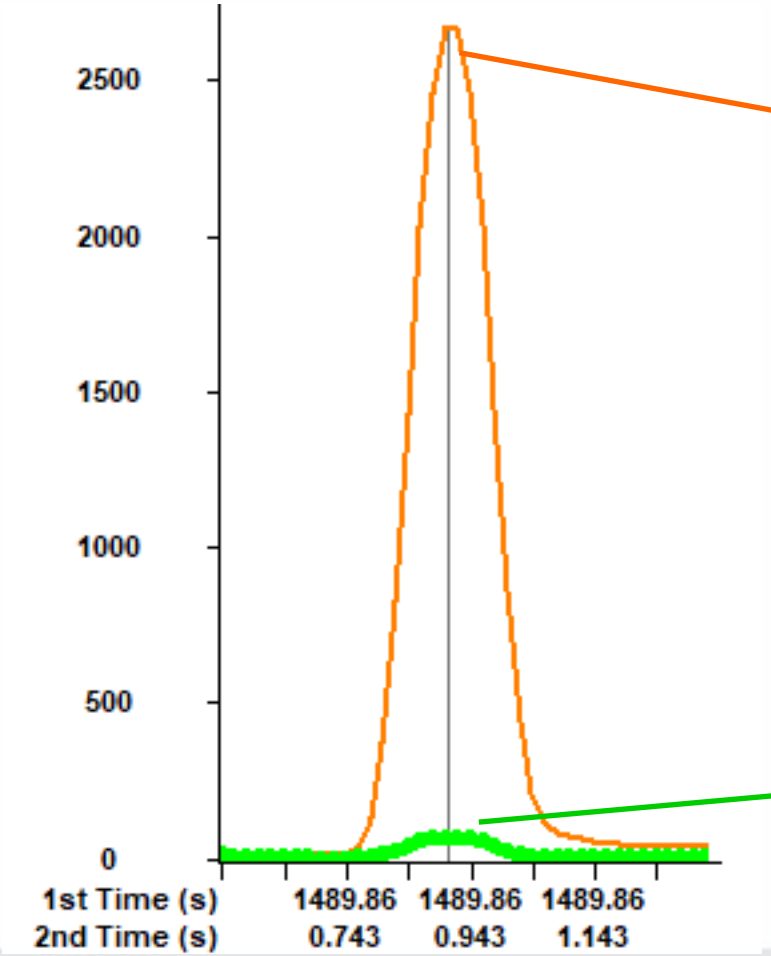
Part III - Straightforward identification

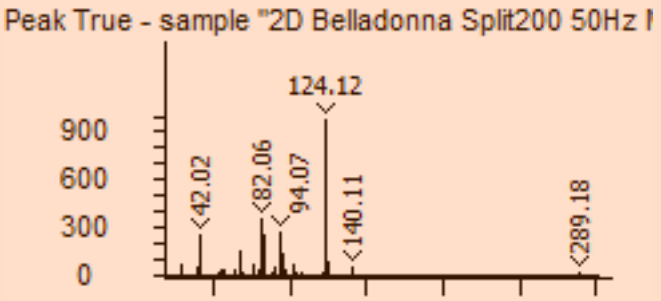


- **Thanks to:**
  - Excellent **Spectral Quality** (TOF) fully comparable with NIST
  - **Peak Find & Deconvolution Algorithms**
  - **High sensitivity**
  - **Additional benefits through HR** – HR data & sub-1ppm mass accuracy

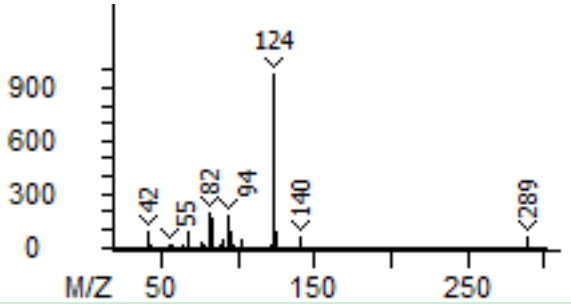
Spectral Quality

Belladonna berry extract - atropine





Split 1:200,
Similarity 962
Mass accuracy: 51 ppm



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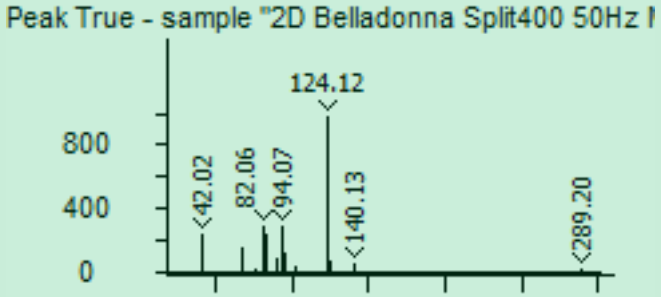


Split 1:400,
Similarity 862
Mass accuracy: 102 ppm

Urine & plasma samples

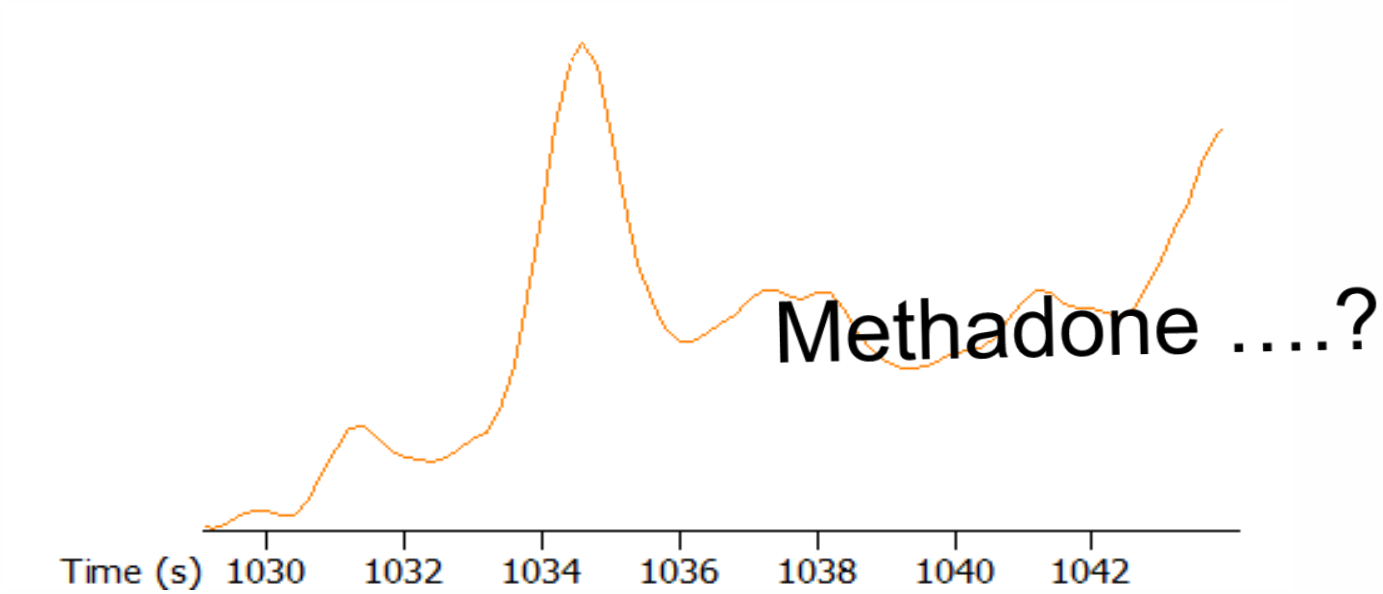
Urine and blood plasma are extremely complex matrices

Misidentification can occur due to matrix interference

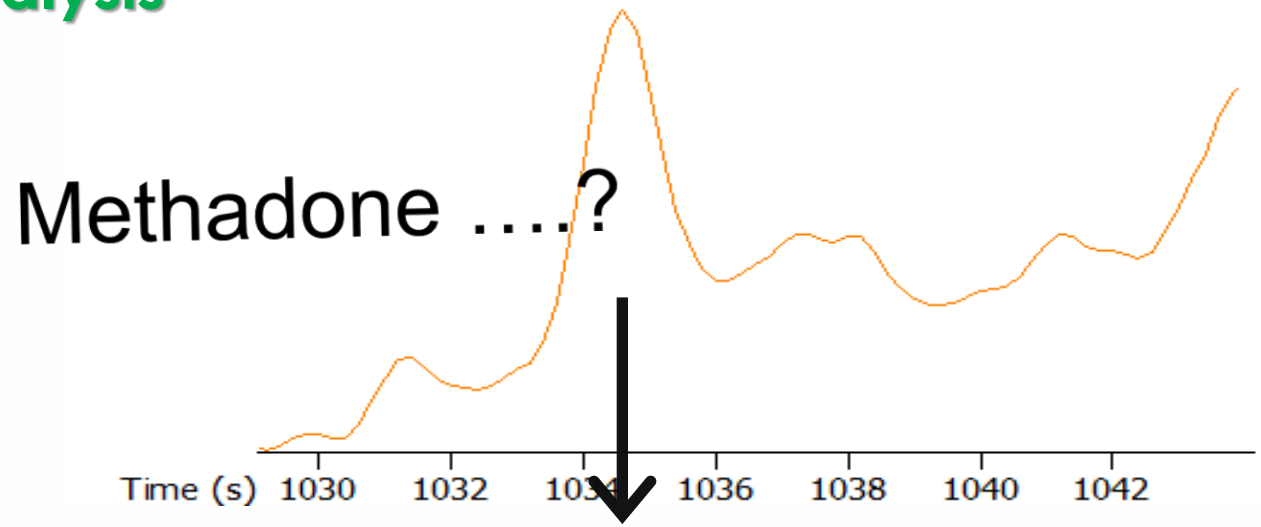
Story behind:

Using a quadrupole MS methadone was detected and identified in blood sample

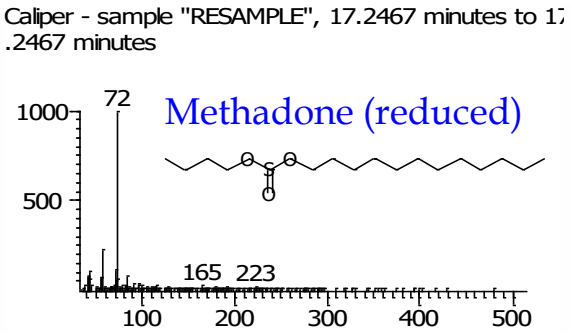
Is that really methadone? .... Verification by GC-TOF MS analysis



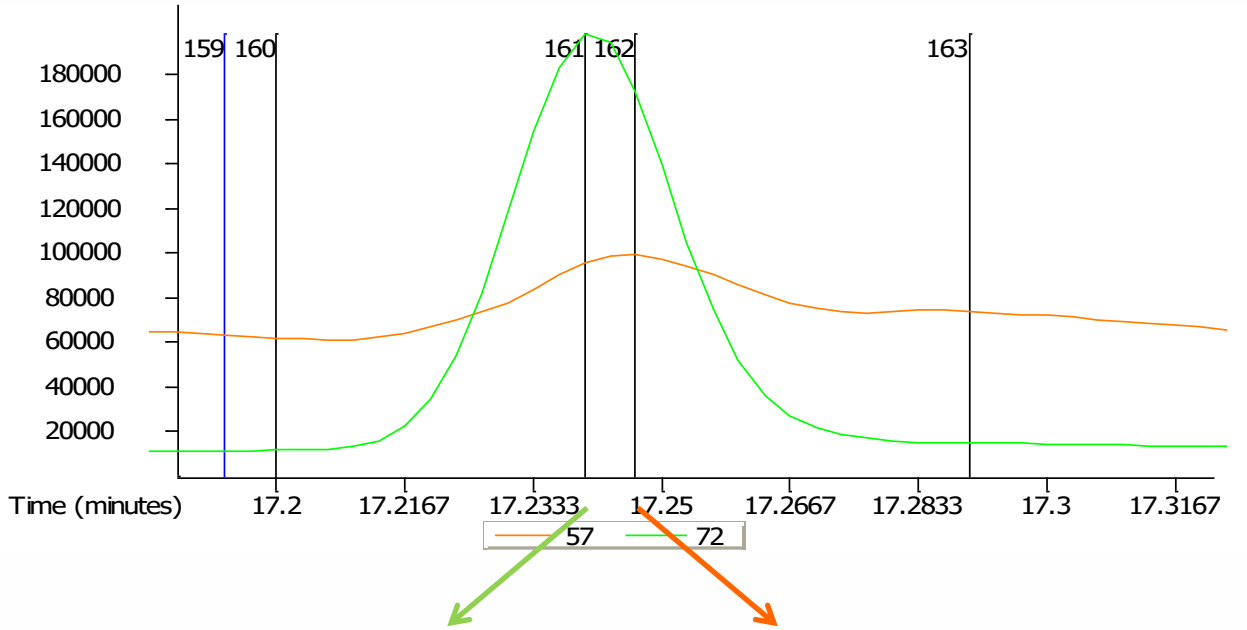
GC-TOF MS analysis



Nondeconvoluted spectrum

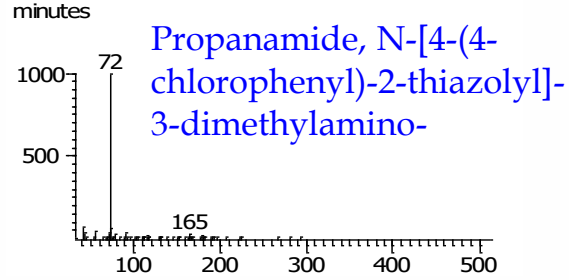


- **The spectrum taken in RT of methadone corresponds to methadone**



Deconvoluted spectrum

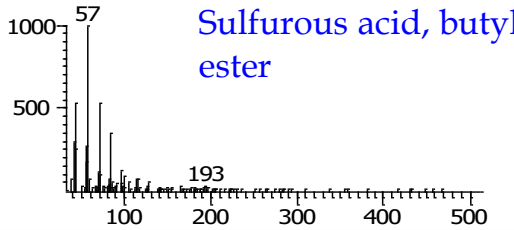
Peak True - sample "RESAMPLE", peak 161, at 17.2
minutes



Propanamide, N-[4-(4-chlorophenyl)-2-thiazolyl]-3-dimethylamino-

Deconvoluted spectrum

Peak True - sample "RESAMPLE", peak 162, at 17.2
67 minutes



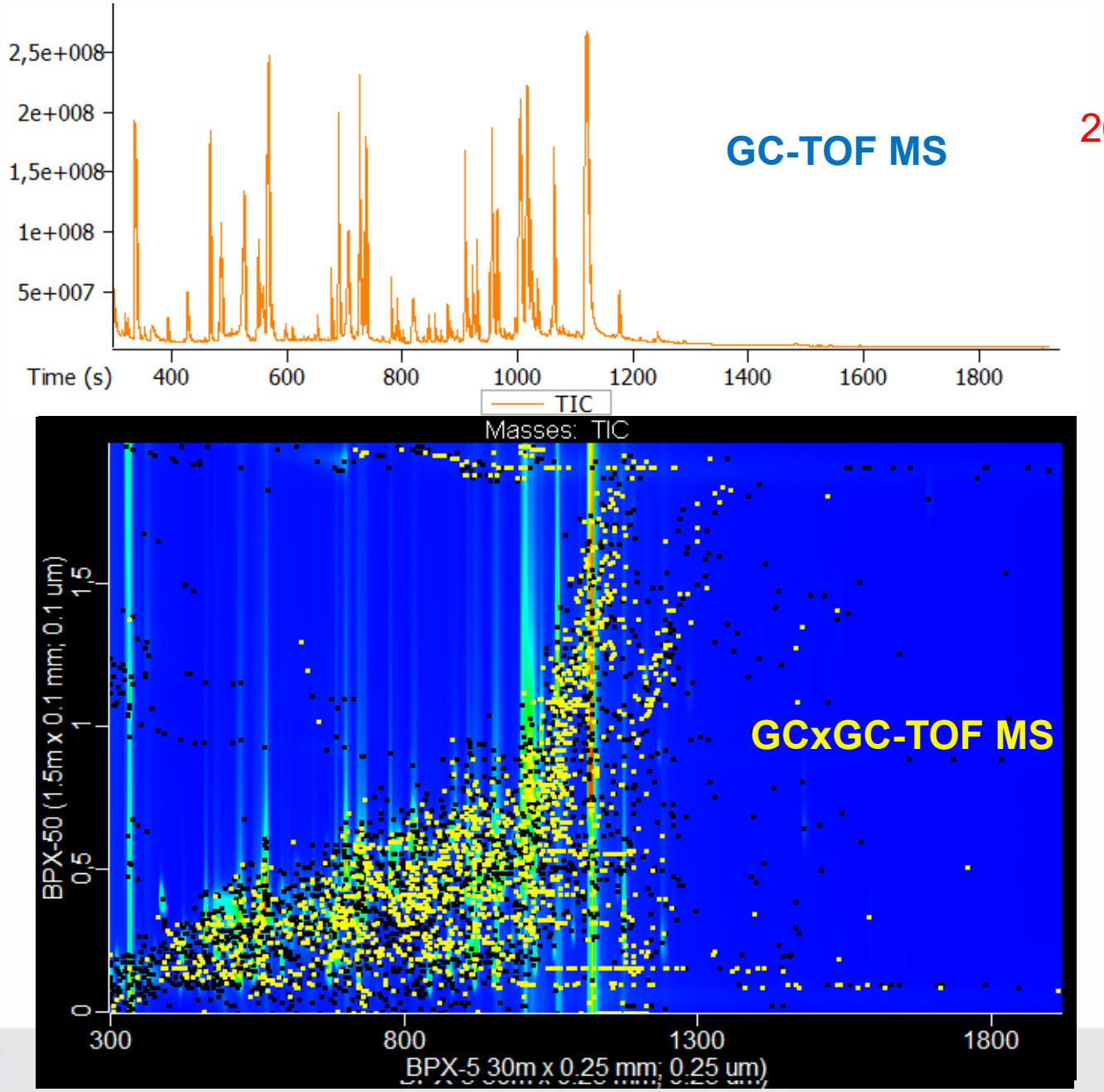
Sulfurous acid, butyl dodecyl ester

HOWEVER

- Using an automated peak find and deconvolution alghoritm, it showed-up that the peak is in fact a coelution of two peaks of matrix components .... NO REAL METHADONE PEAK

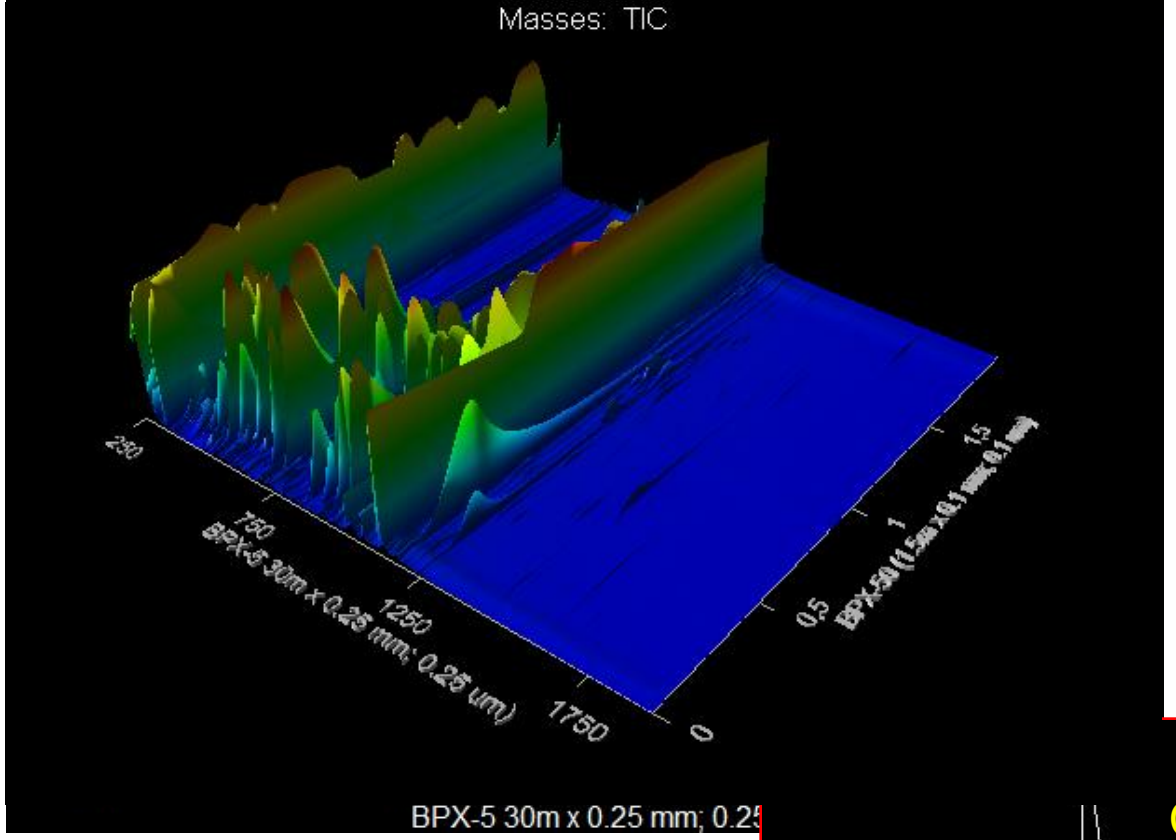
Getting more by GCxGC-TOF MS thanks to enhanced chromatographic separation

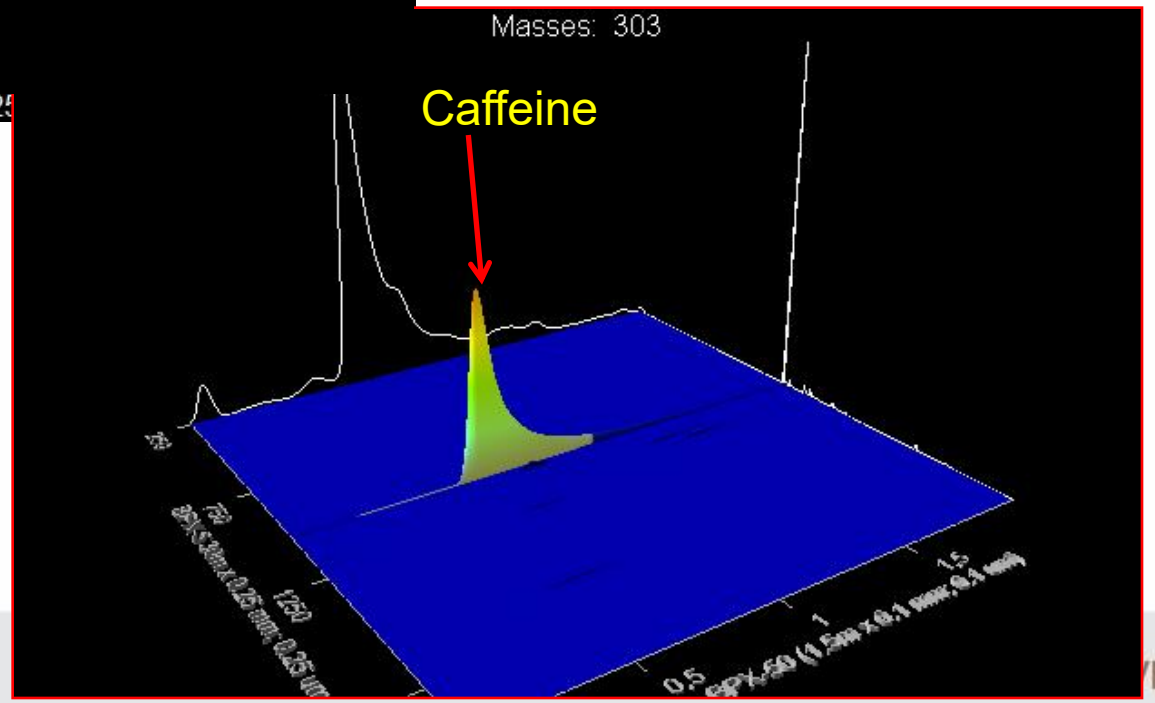
Detection of target and untargeted compounds in blood

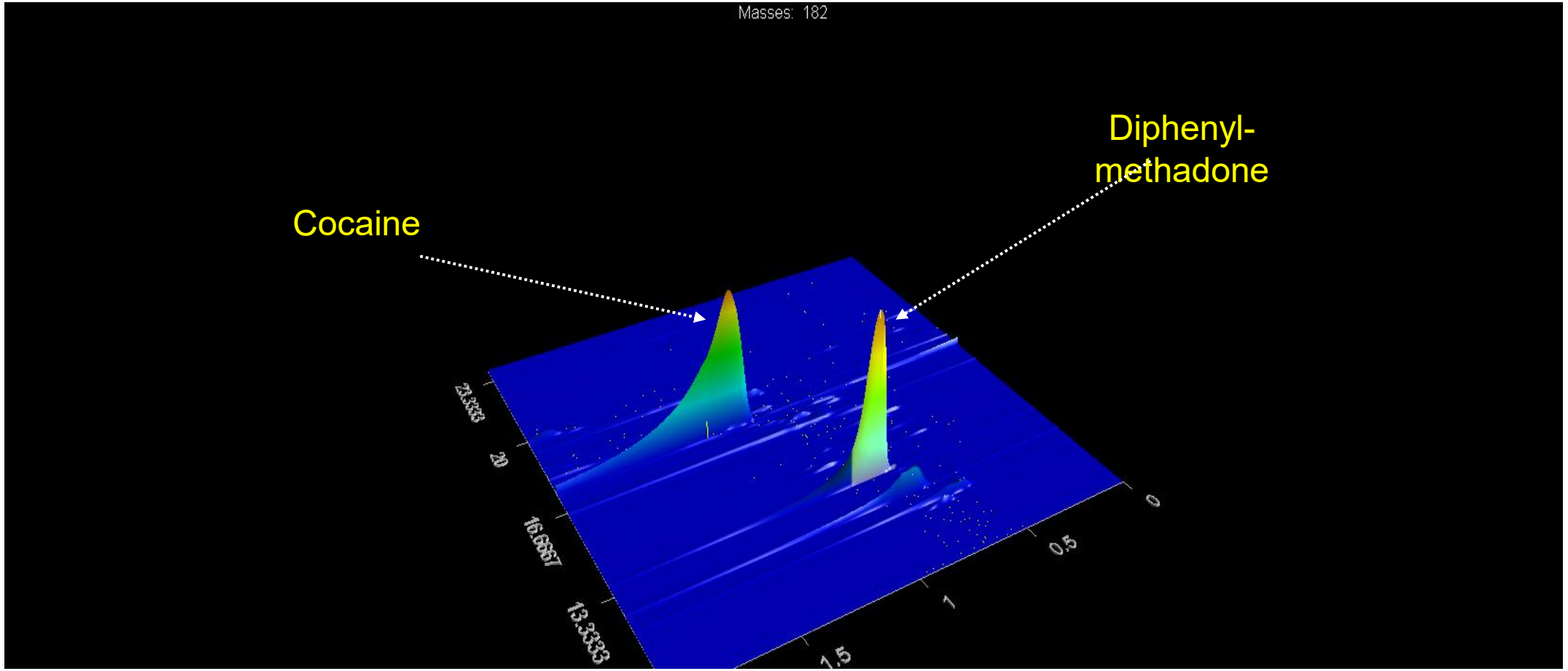


261 componds identified
@ S/N>20

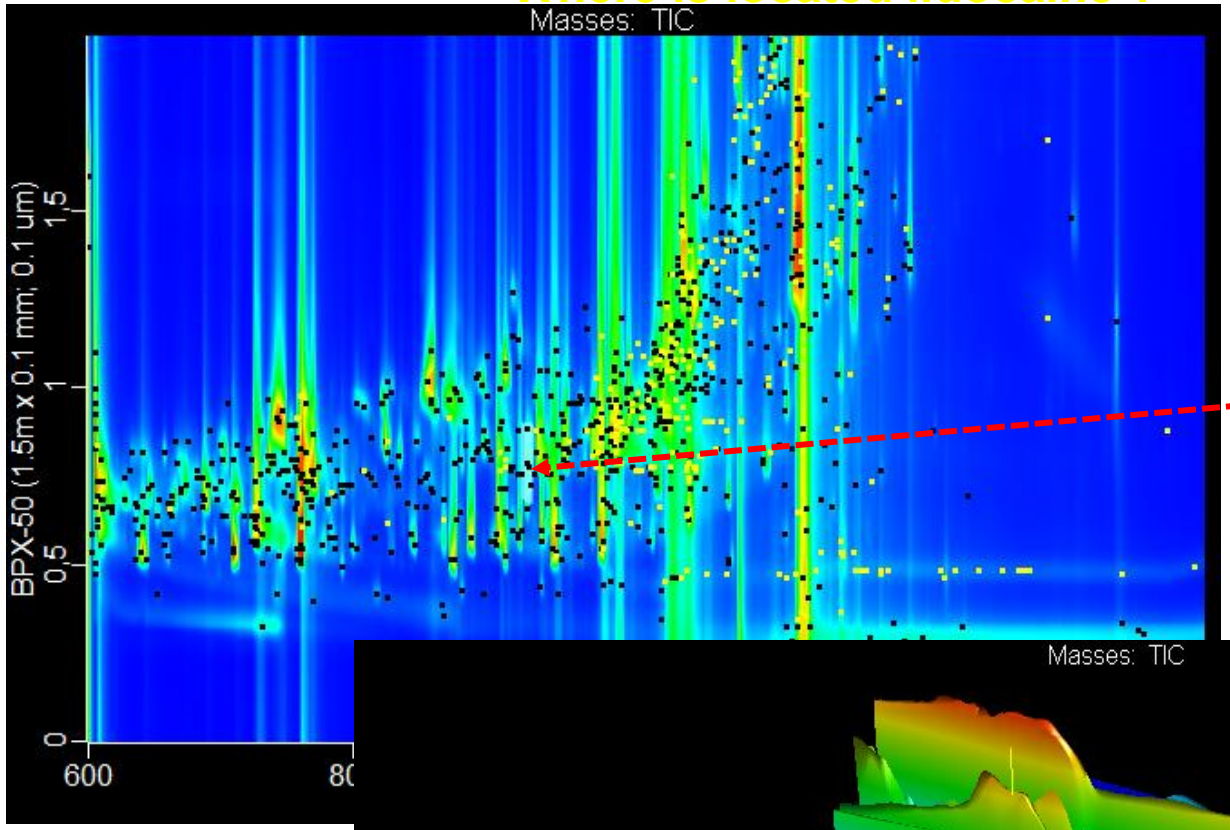
721 componds @
S/N>1000


Masses: TIC
250
750
1250
1750
0
0.5
1
1.5
BPX-5 30m x 0.25 mm; 0.25 um)

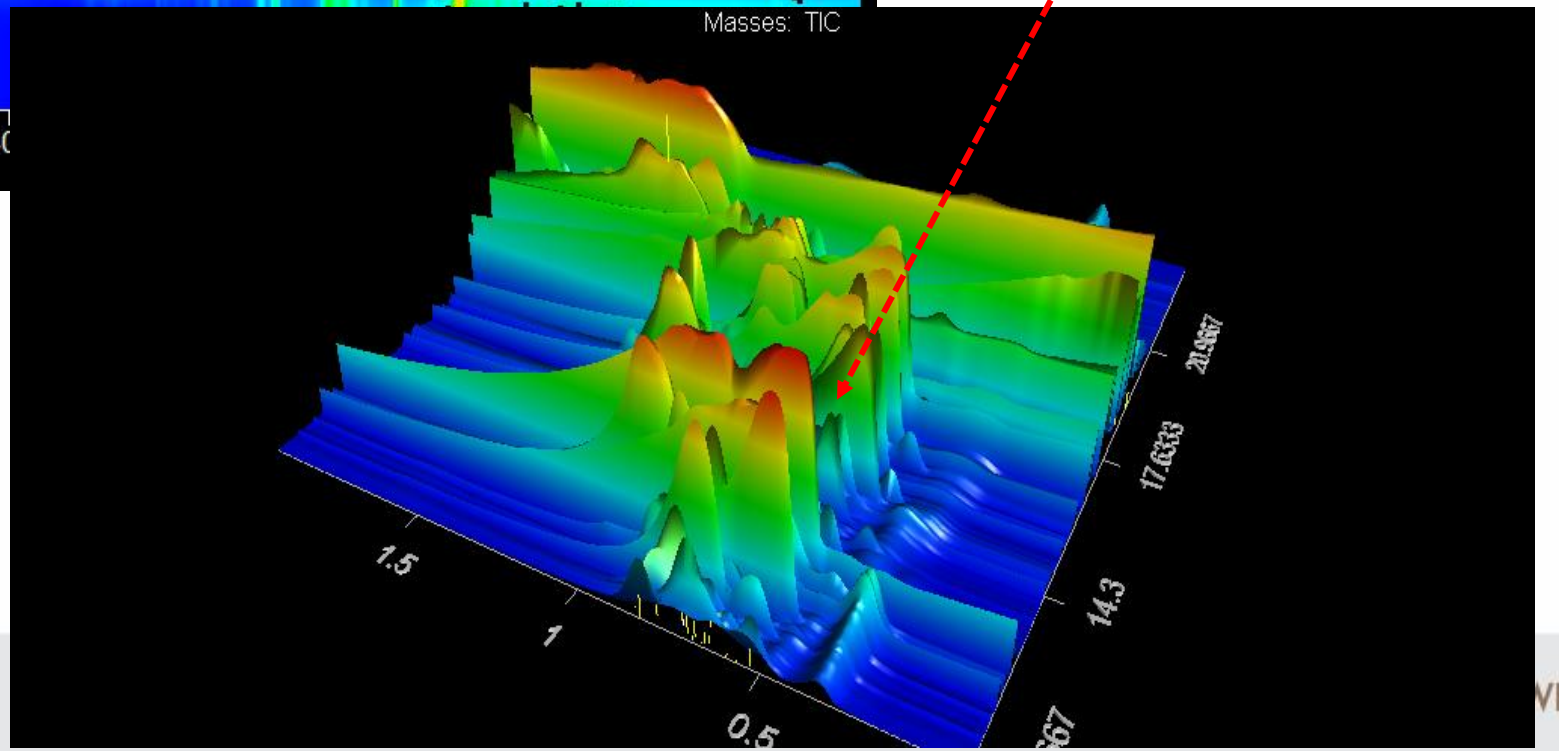

Masses: 303
Caffeine
0.5
1
1.5


Masses: 182
Cocaine
Diphenyl-
methadone
23.333
20
16.6667
13.3333
1.5
1
0.5
0

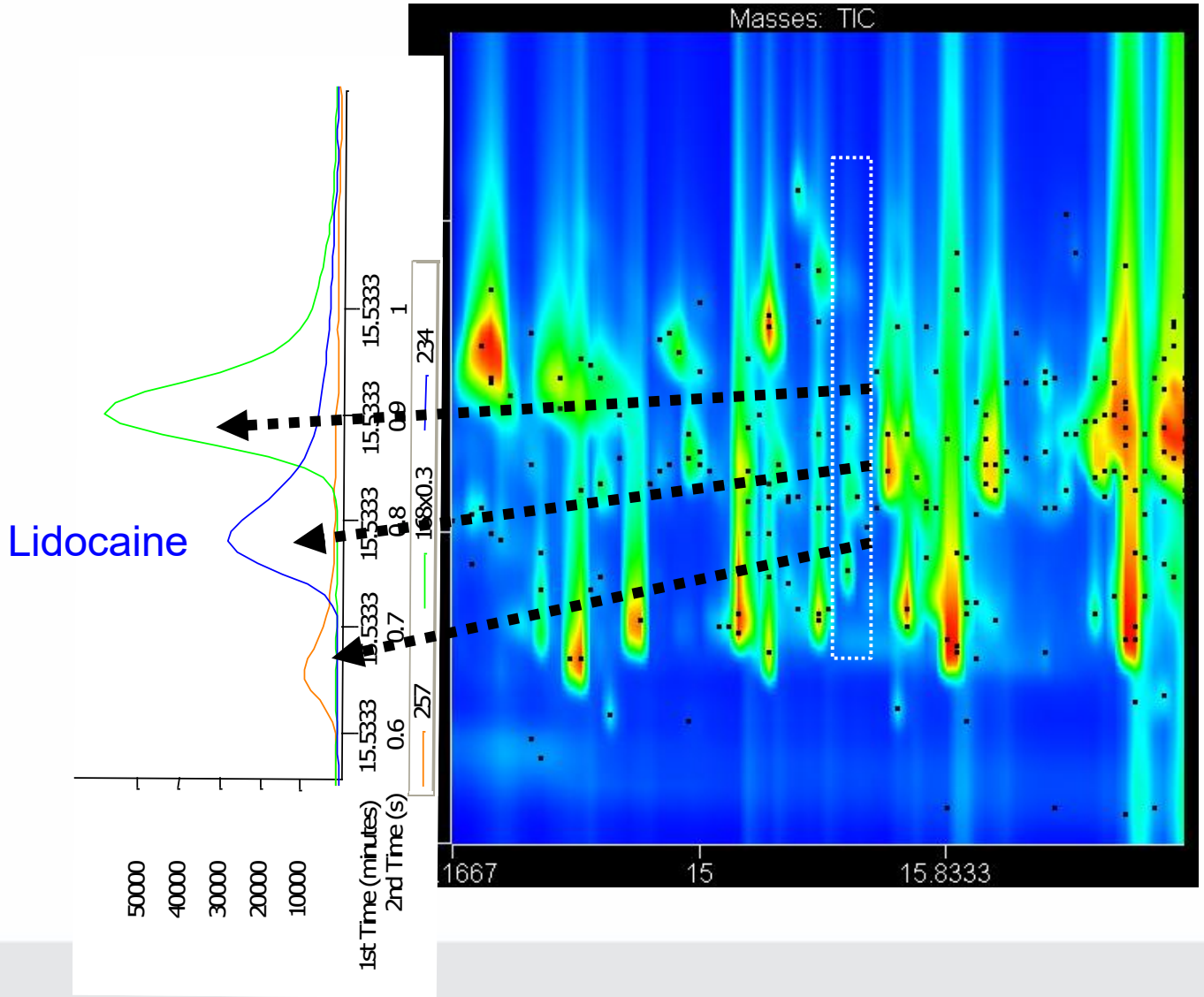
Where is located lidocaine ?



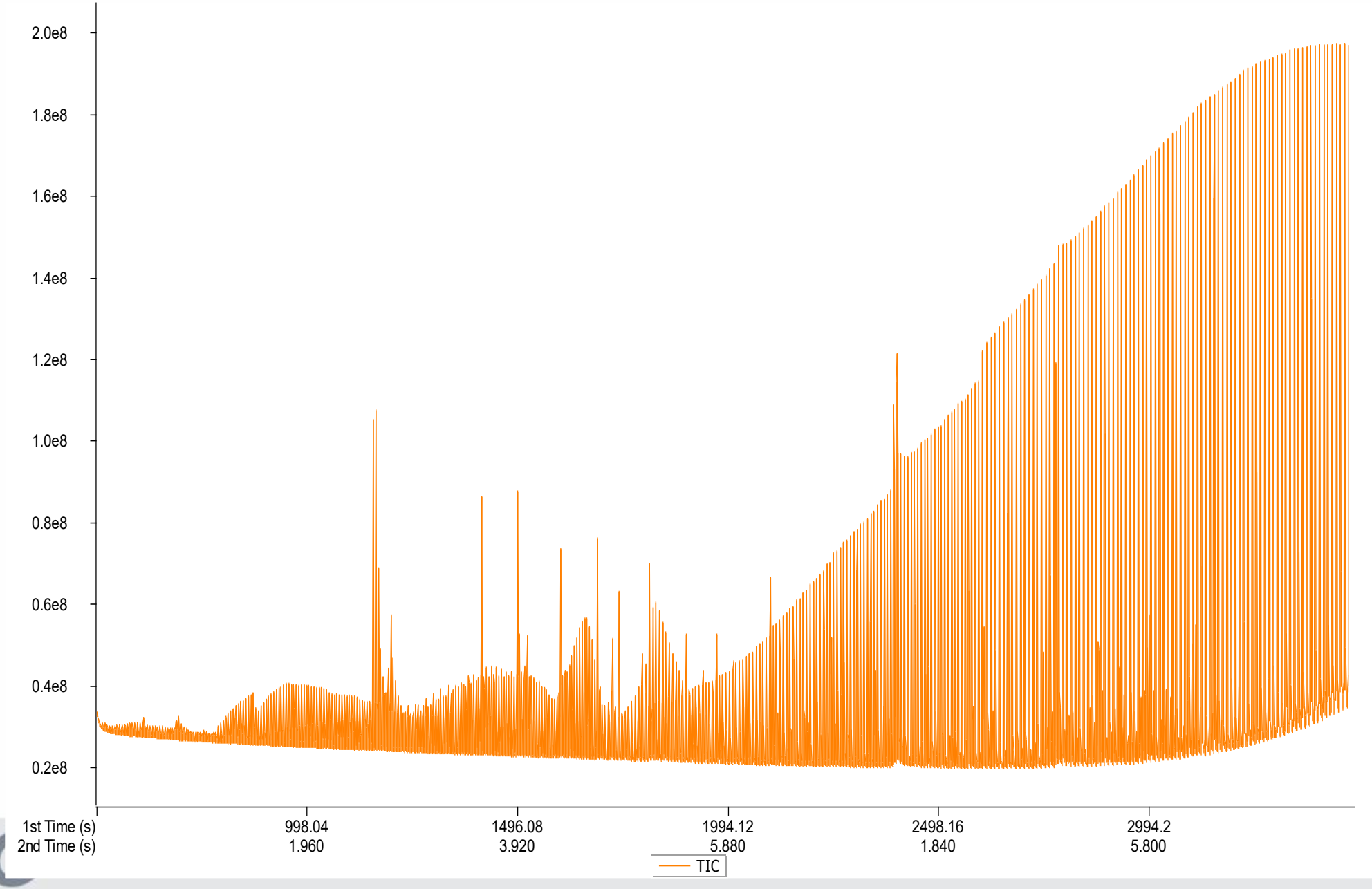
Lidocaine in TIC



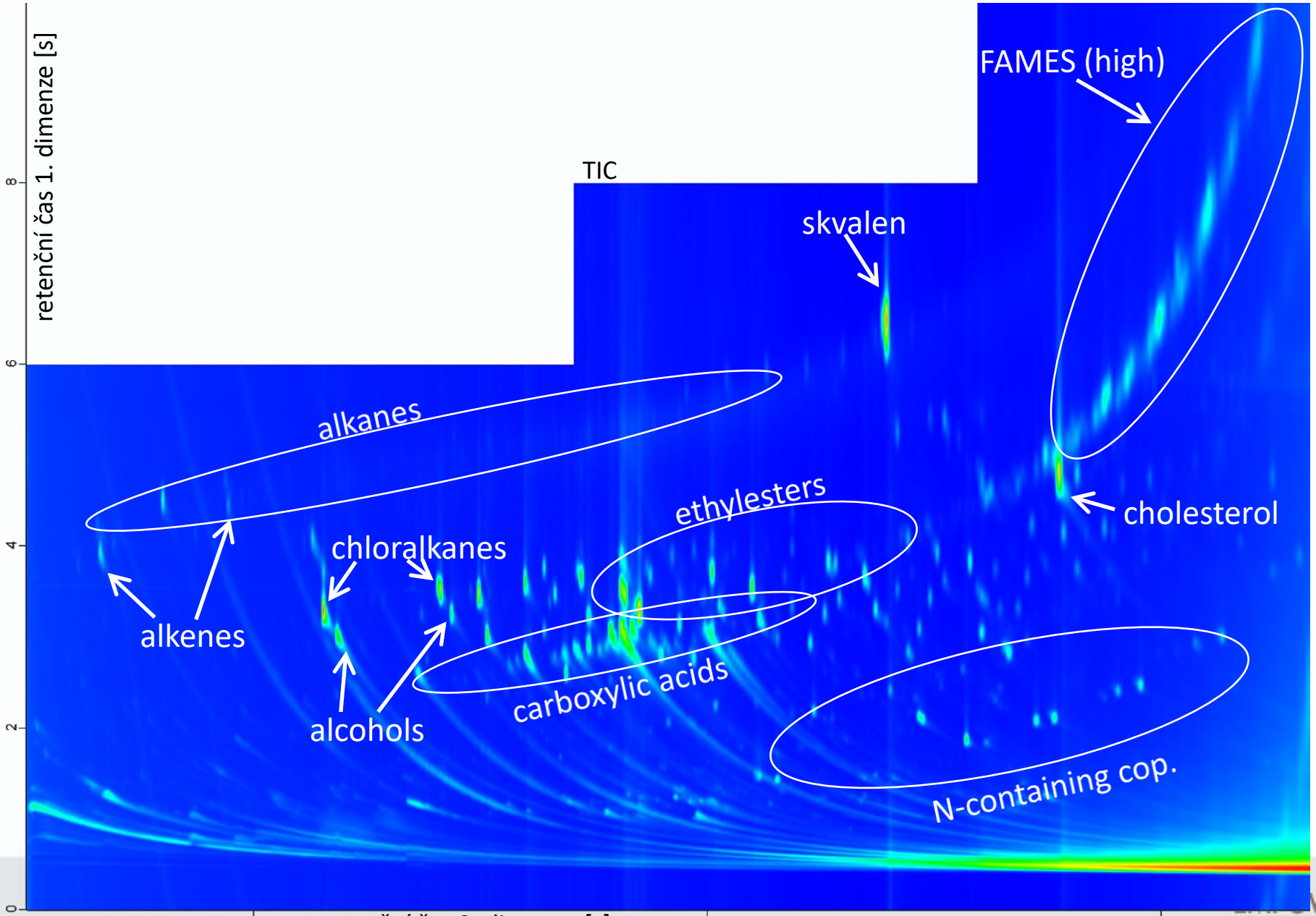
Lidocaine with potentially co-eluted 3 compounds in 1D



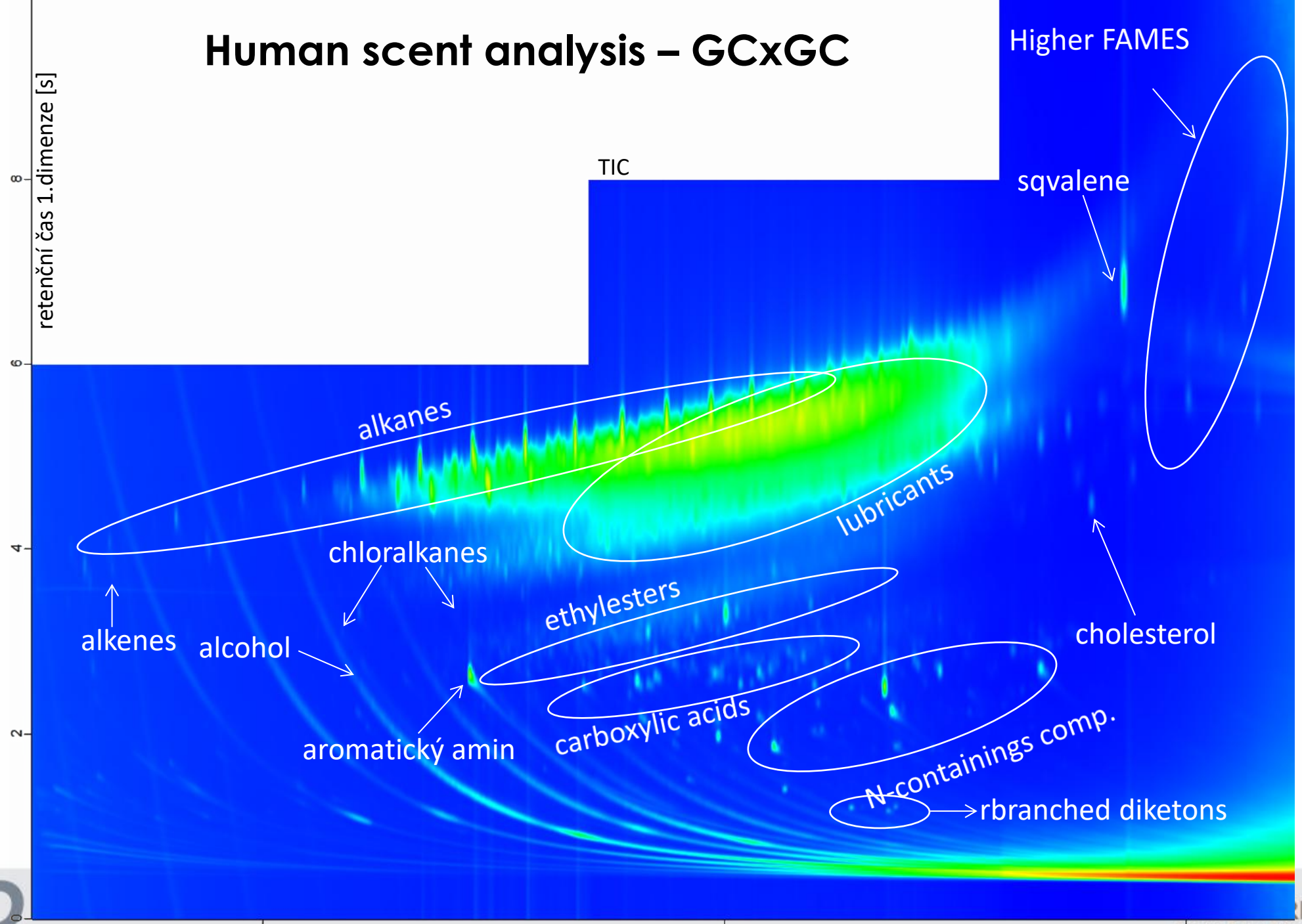
Human scent analysis – 1D



Human scent analysis – GCxGC



Human scent analysis – GCxGC



Conclusion

- **Keep in mind that TOF MS exists and it is**
  - a powerful detector for you GC system
  - best in robustness
  - Super sensitive ~ Tripplequad MS
  - Is easy to operate and handle (both HW & SW)