

Super-resolution in FT-ICR MS by non-Fourier Transform genetic evolution signal processing

Marc HAEGELIN

Miniaturization for Synthesis, Analysis & Proteomics, USR 3290

EU FT-ICR Prague 2021



Recall plan

1 What is an evolutionary algorithm ?

2 Sinus_it

3 Results

Evolutionary algorithms (EAs)

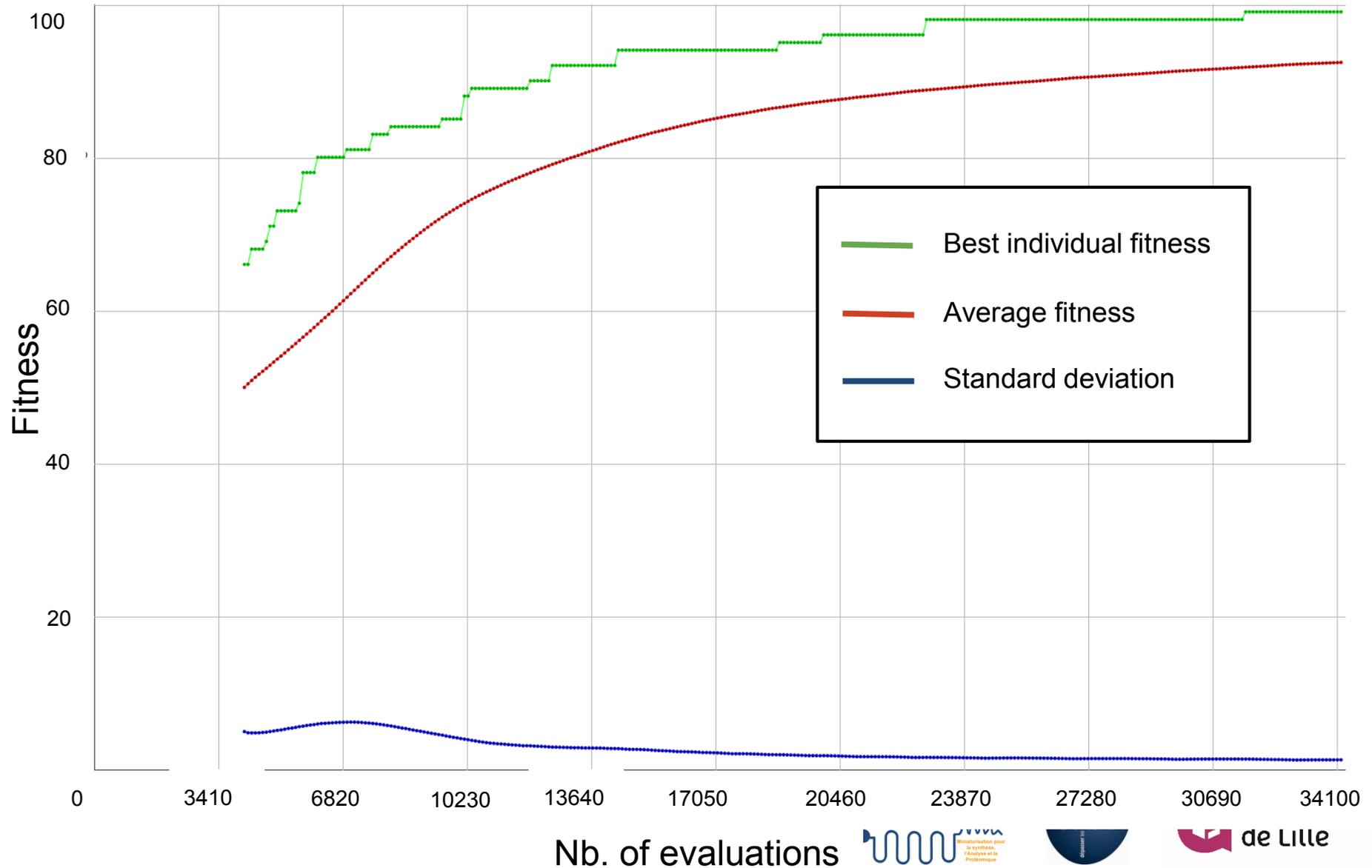
- Bio-inspired algorithms that simulate evolution by natural selection in order to solve optimization problems or find innovative solutions
- We create a virtual population of individuals that are candidate solutions to the problem we want to solve
- Used in artificial creation, travel salesman problem, signal processing



Evolutionary algorithm (example : onemax)

- An individual is a combination of N bits : ...1001011100010110...
- A mutation corresponds to the modification of a bit (0 switches to 1 or the inverse)
- The crossover function consists in cutting the individual into two and exchange the first/second part of each individual
 - ...10010111 00010110... become ...10010111 11011010...
 - ...00110010 11011010... ...00110010 00010110...
- Evaluation function is to count the number of 1's
- Stopping criteria : the maximal value was found (only 1's).

Plotting onemax results (N=100 bits / $\approx 10^{30}$ combinations !)



Recall plan

1 What is an evolutionary algorithm ?

2 Sinus_it

3 Results

Implementation

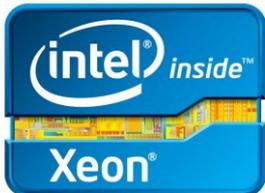
- Sinus_it is an evolutionary algorithm implemented with EASENA from CSTB, Strasbourg University
- The program is in C++/CUDA in order to have high control over the hardware and to benefit from the speed of the C++ language.



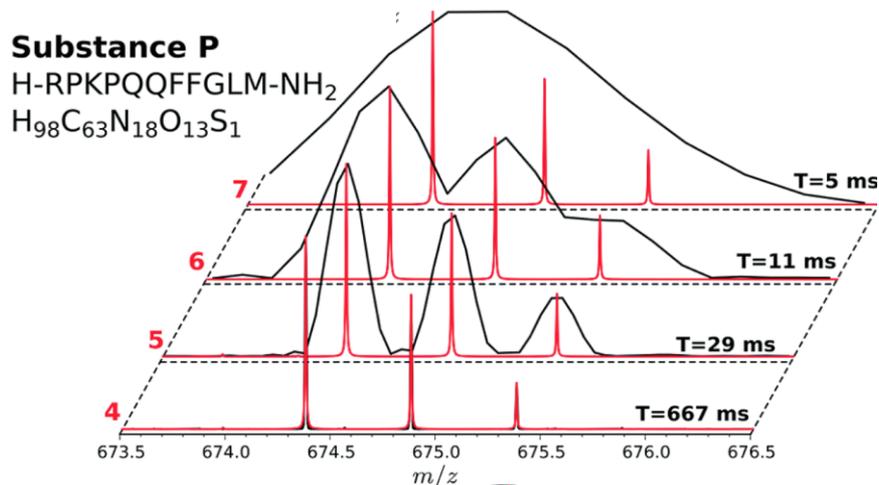
NVIDIA RTX 2080 Ti



- The program was run on a 2 × 16 cores 2.1 Ghz Intel Xeon server with one GPU Nvidia RTX 2080 Ti card

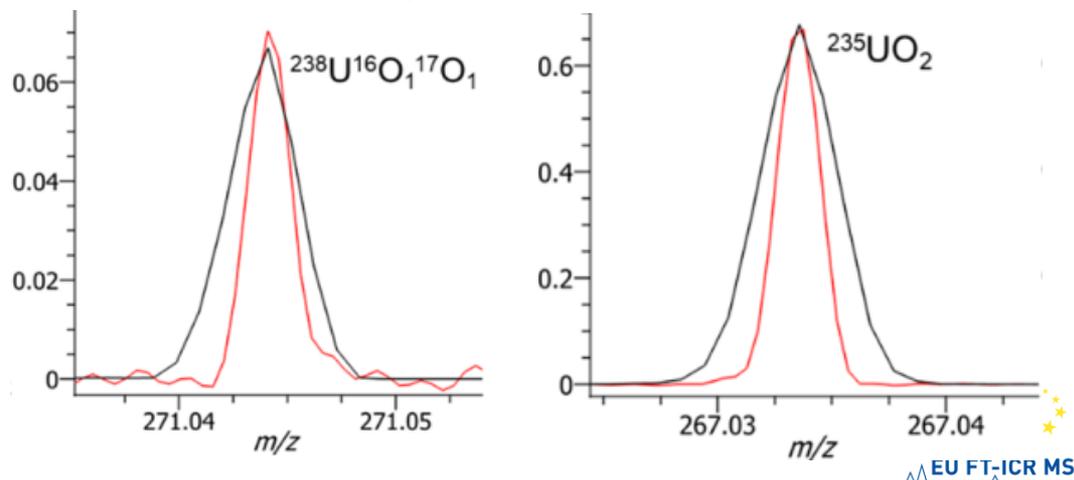


- **Filter diagonalization to achieve super-resolution**



KOZHINOV, Anton N. et TSYBIN, Yury O. Filter diagonalization method-based mass spectrometry for molecular and macromolecular structure analysis. *Analytical chemistry*, 2012, 84, 2850-2856.

- Or having correct **mass isotopic ratios**

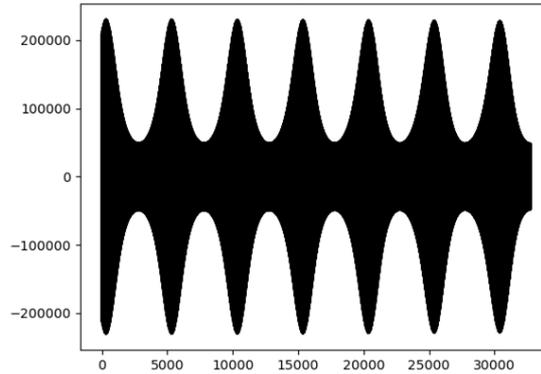


BILLS, Jacob R., NAGORNOV, Konstantin O., KOZHINOV, Anton N., *et al.* Improved Uranium Isotope Ratio Analysis in Liquid Sampling-Atmospheric Pressure Glow Discharge/Orbitrap FTMS Coupling through the Use of an External Data Acquisition System. *Journal of the American Society for Mass Spectrometry*, 2021, 32, 1224-1236.

Workflow

TRANSIENT

Spec 32k, Exp transient (blue)

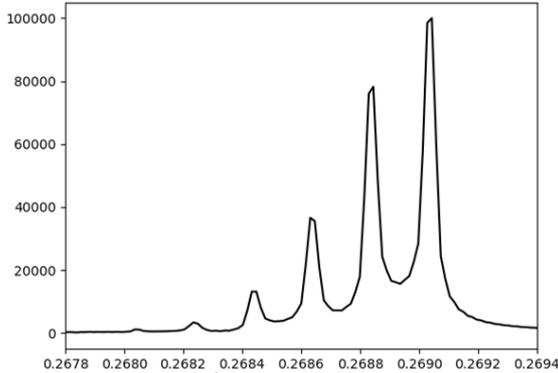


1) Fourier transform

2) Butterworth filter

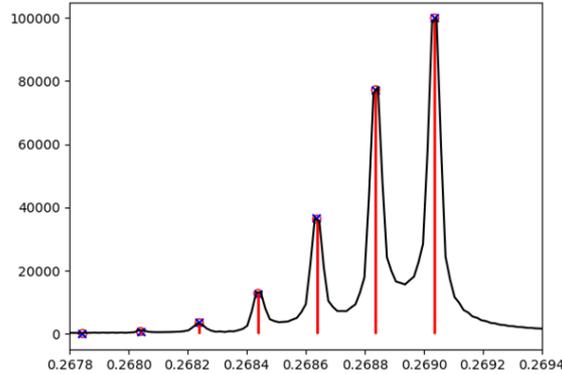
3) Butterworth filter

Spec 32k, FFT_apod (black), sinus_it (red), target (blue)



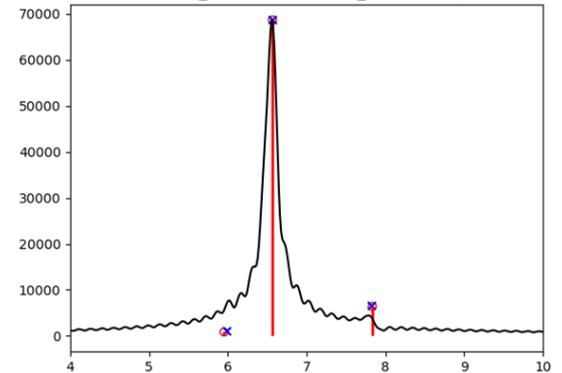
Classical
FFT

Spec 32k, FFT_apod (black), sinus_it (red), target (blue)



Sinus_it
coarse isotopic

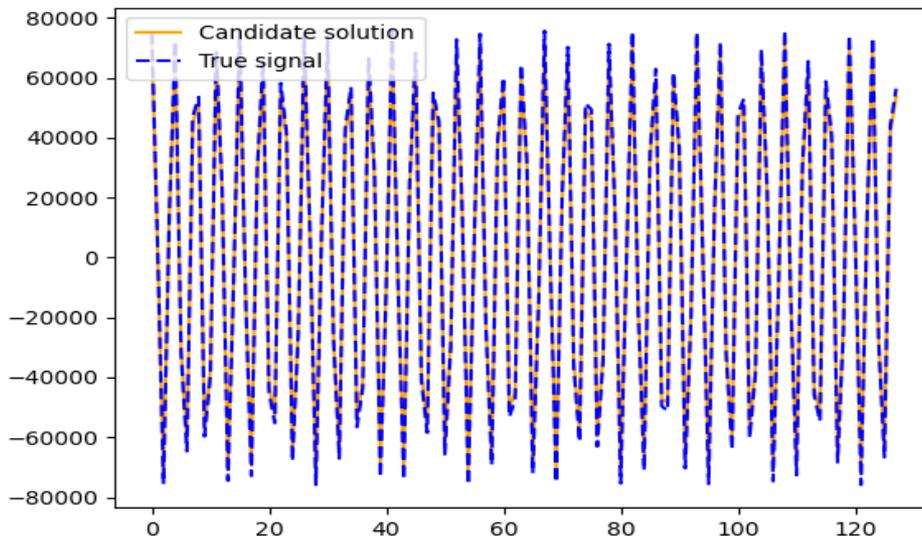
Spec 16M, FFT_apod (black), sinus_it (red), target (blue)



Sinus_it fine isotopic

Signal fitting

- Sinus_it tries to approach/fit the decaying sinusoidal signal
 - e.g. With an individual
 - $\text{sine1} = 6578.95 * \sin(2*\pi*0.2688379 + 1.40878)$
 - $\text{sine2} = 68232.5 * \sin(2*\pi*0.2688365 + 1.41167)$
 - $\text{sine3} = 1142.58 * \sin(2*\pi*0.2608350 + 1.41348)$
 - The real signal is
 - $\text{sine1} = 6575.94 * \sin(2*\pi*0.2688378 + 1.40905)$
 - $\text{sine2} = 68139.09 * \sin(2*\pi*0.2688365 + 1.41165)$
 - $\text{sine3} = 1150.13 * \sin(2*\pi*0.2688359 + 1.41284)$



Comparison of the real signal (blue dash) and the candidate solution (orange line)

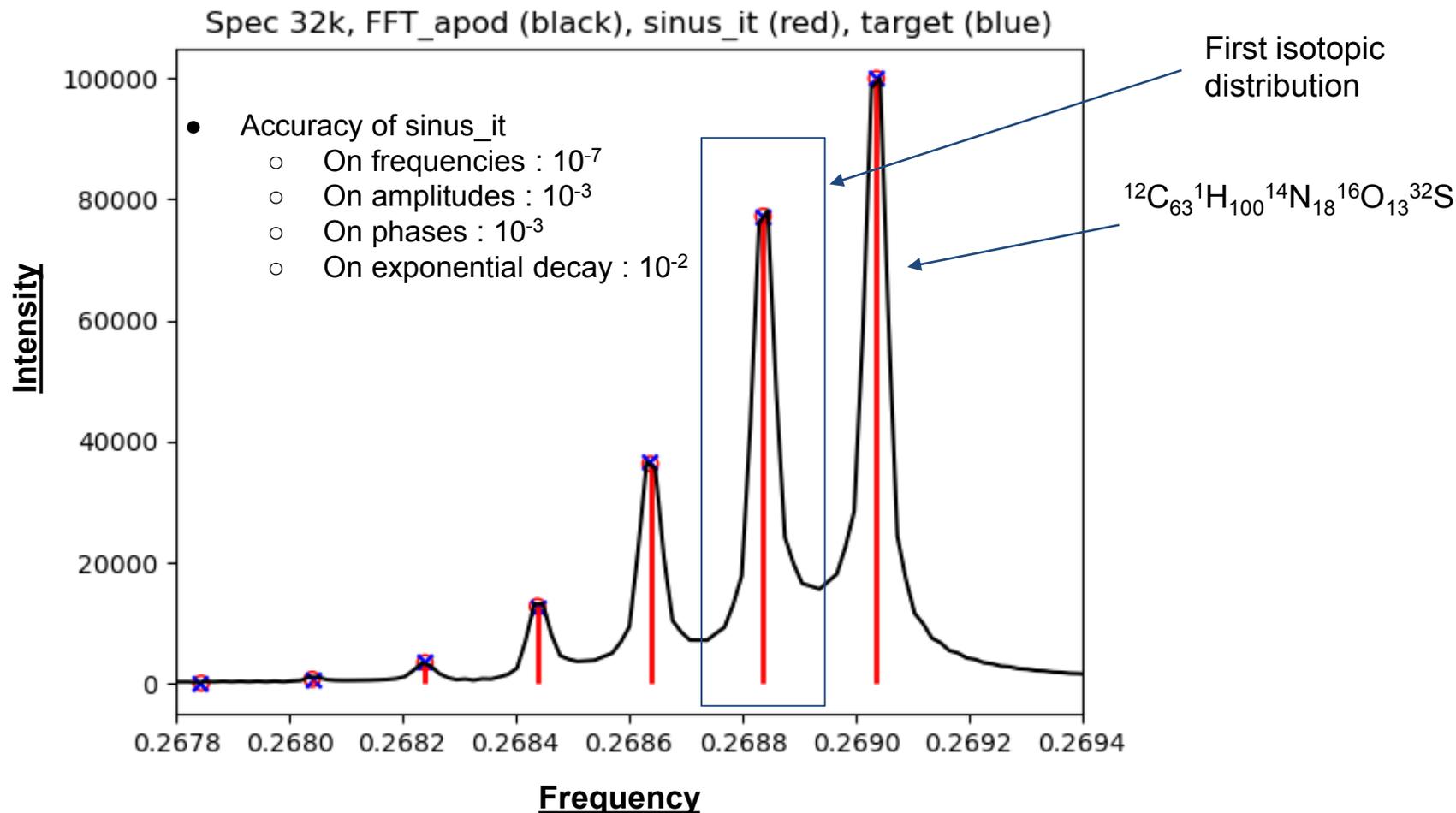
Recall plan

1 What is an evolutionary algorithm ?

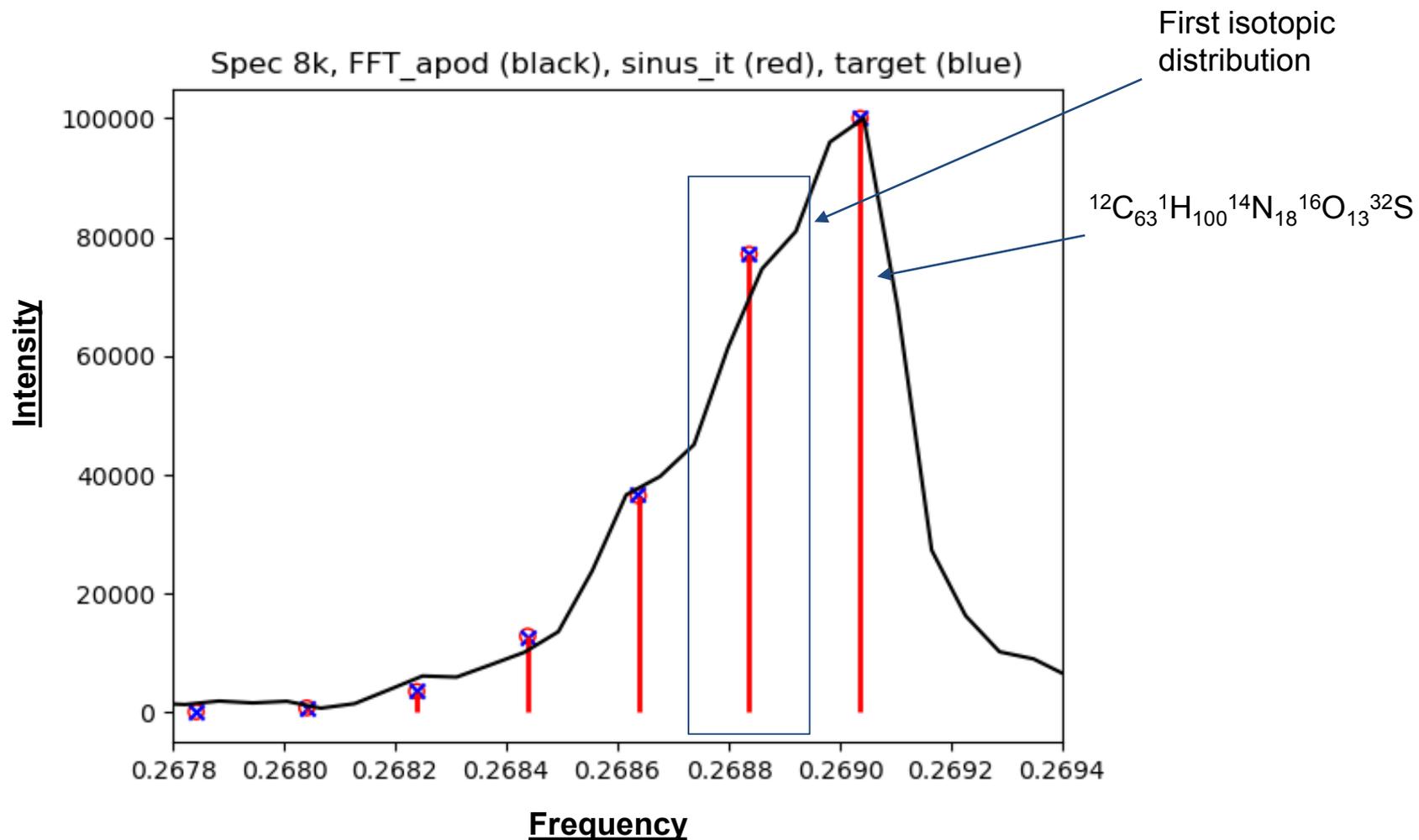
2 Sinus_it

3 Results

Coarse isotopic graph (Substance P simulated / 7 peaks)

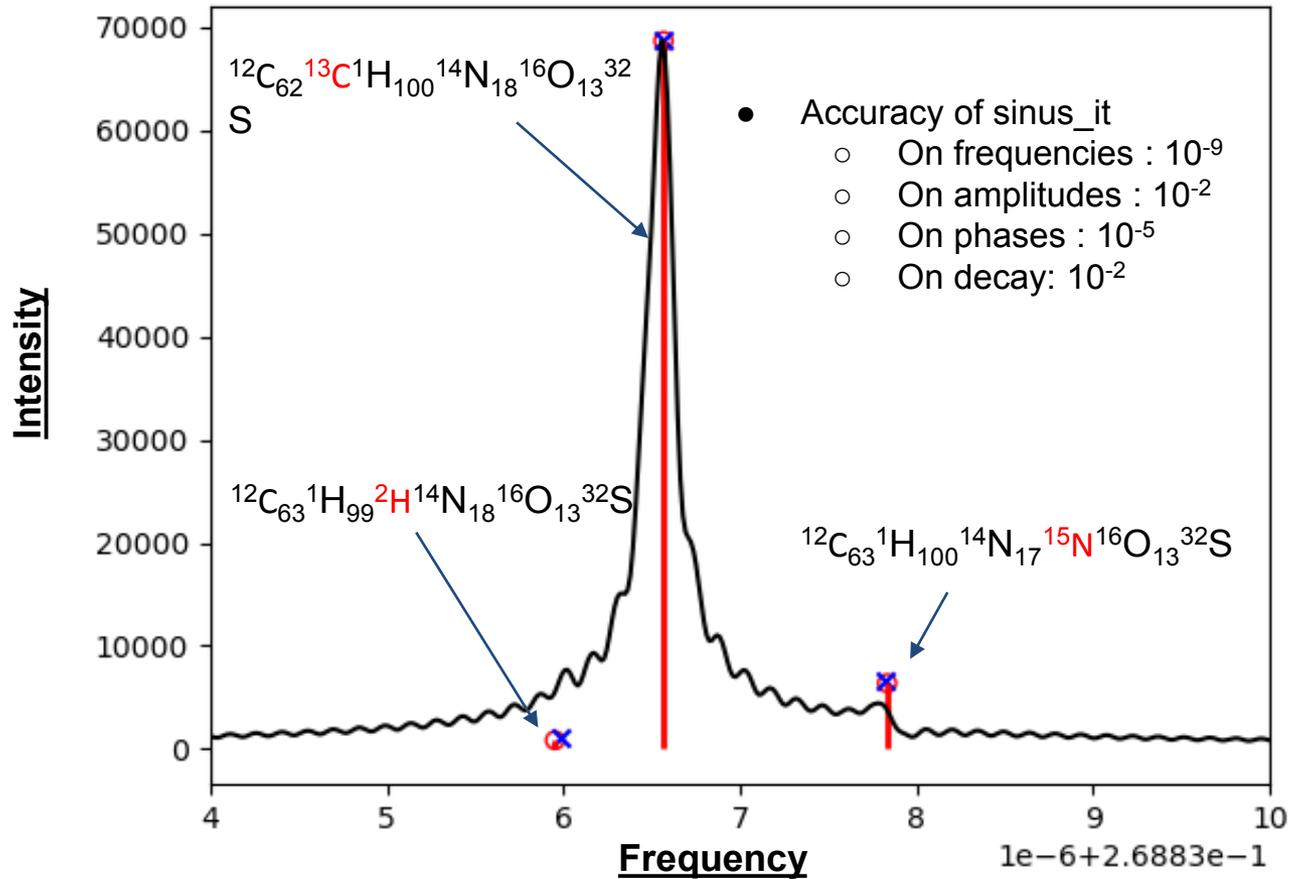


Coarse isotopic graph (Substance P simulated / 7 peaks)

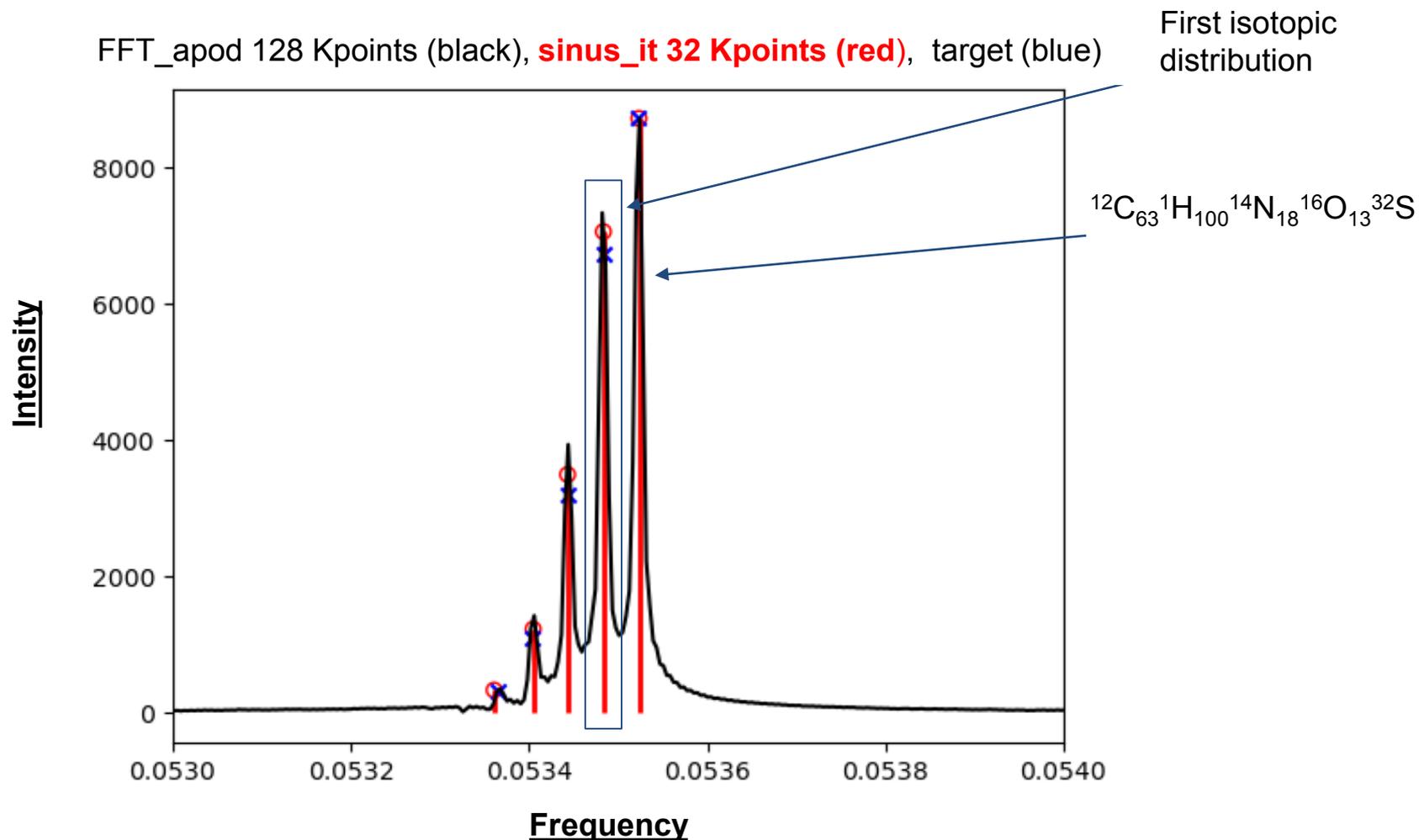


Fine isotopic graph (Substance P simulated / 1st isotope)

FFT_apod 16 Mpoints (black), **sinus_it 1 Mpoints (red)**, target (blue)

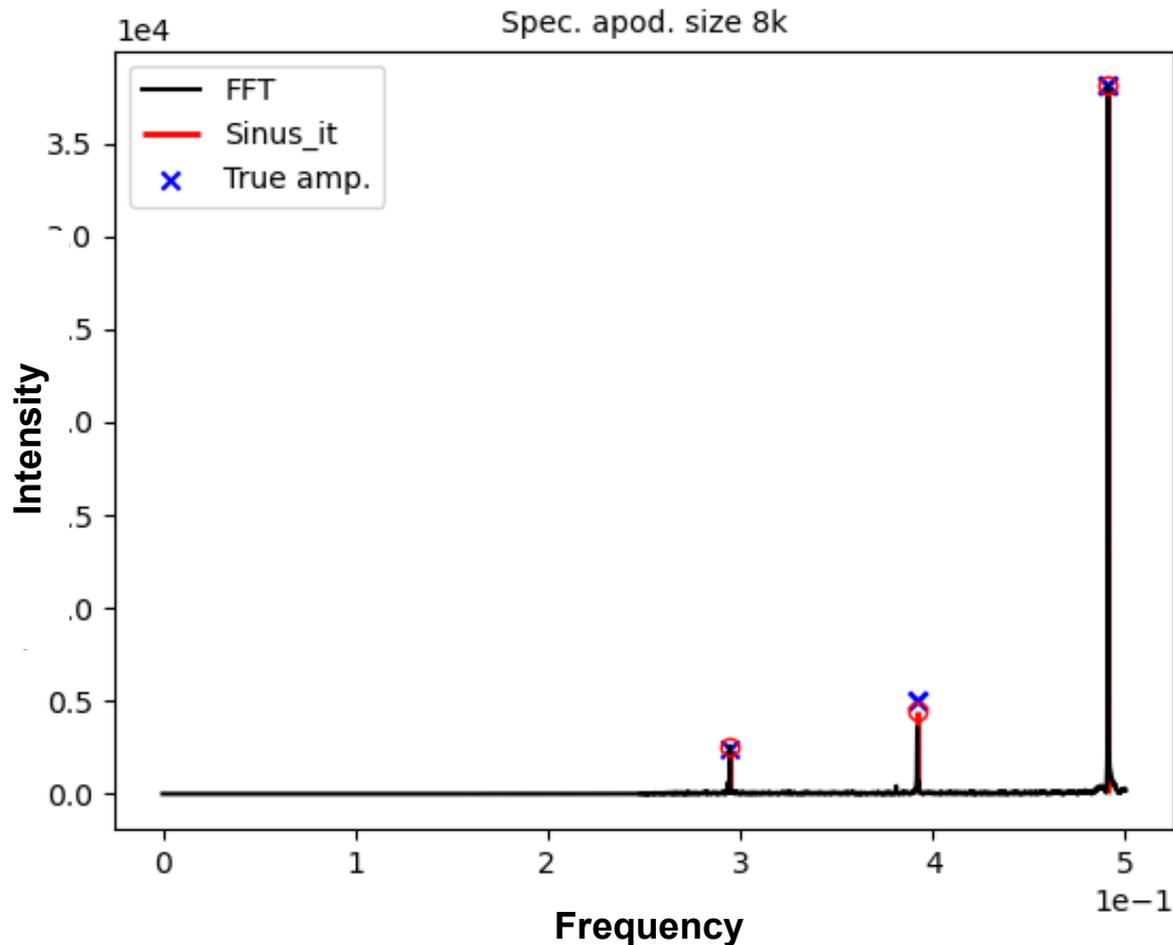


Coarse isotopic distribution (Substance P real signal / 5 peaks)



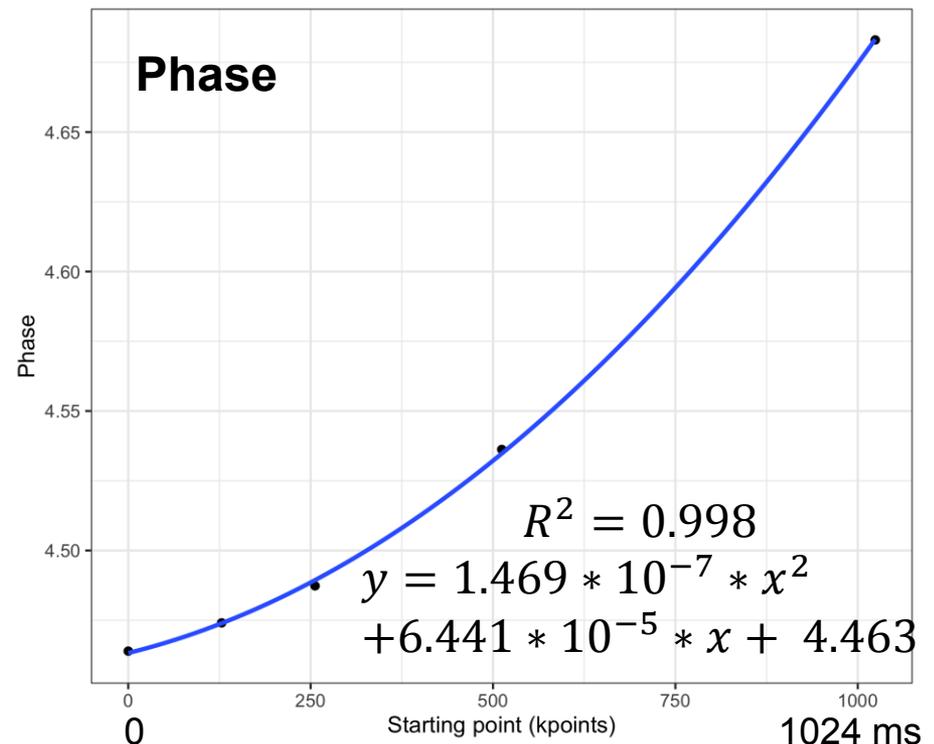
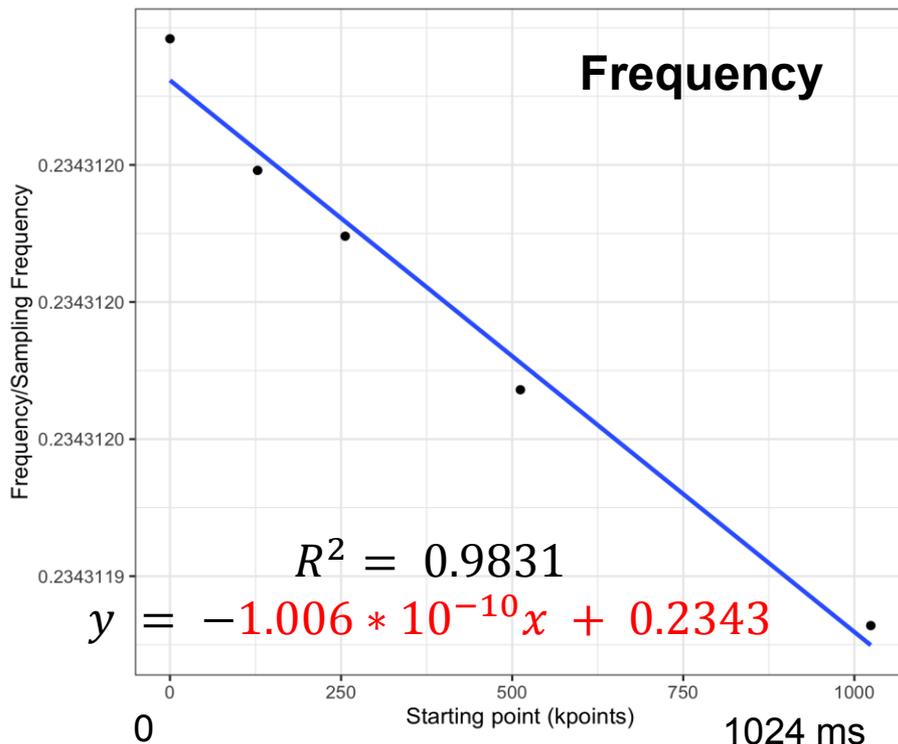
Coarse isotopic distribution (**Gluthation real signal narrow band**)

Sinus_it with dynamic number of sine



Glutathione (broad band) frequency, phase vs time

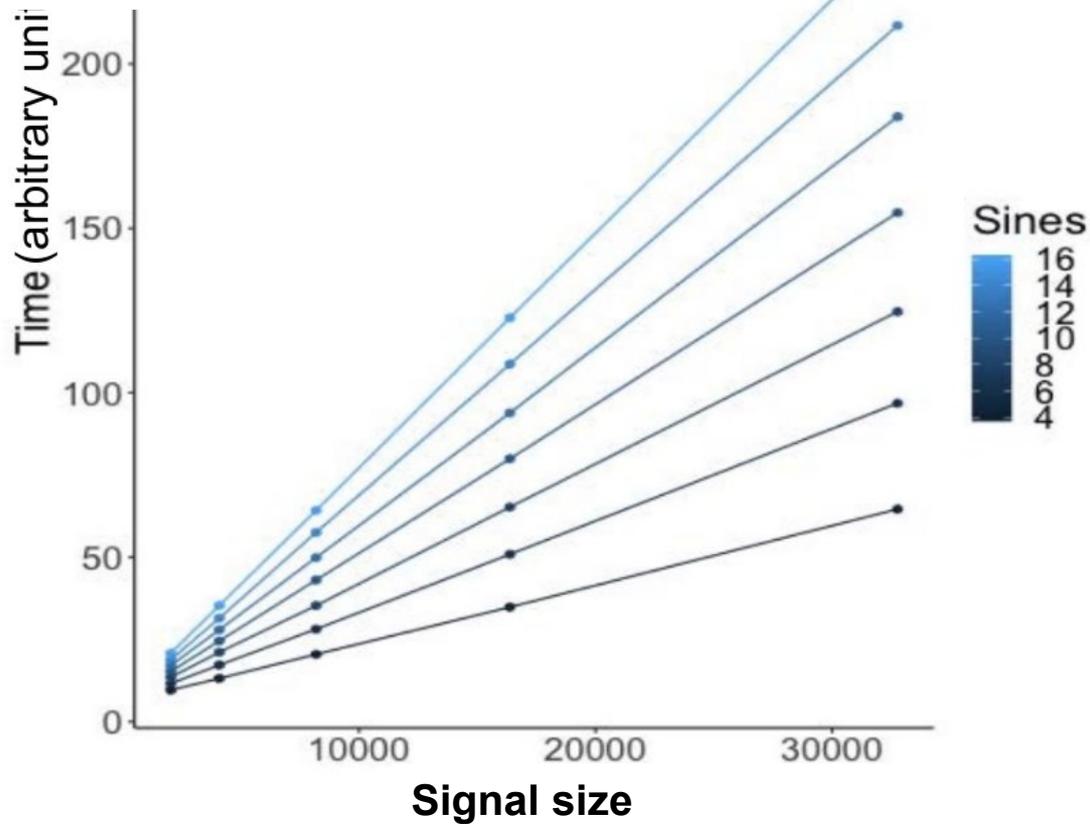
- Glutathione (broad band, sampling frequency 1 MHz), monoisotopic peak
- 32k transients sliced on 16M transient at different time (kpoints = 1.024 ms)



- Phases and frequencies **varie along the transient** and are correlated

Speed and complexity

Sinus_it execution time
Arbitrary units



Sinus_it execution time
proportional to:

- **Sine**
- **Generations**
- Coarse isotopic: **~2-3 hours**
- Fine isotopic: **~4 hours**

Conclusion

- FFT has many drawbacks
 - limited resolving power,
 - Shannon-Nyquist limit,
 - damping, apodization ...
- Sinus_it is a genetic algorithm that achieves harmonic inversion of exponentially damped sine without these drawbacks and is close to the theoretical maximum resolution (super-resolution).

CANDÈS, Emmanuel J. et FERNANDEZ-GRANDA, Carlos. Super-resolution from noisy data. *Journal of Fourier Analysis and Applications*, 2013, 19, 1229-1254.
- Sinus_it can find the right amplitude for quantification, or the decay constant as well as the correct phase.

Acknowledgements

MSAP (Lille)

Dr. Christian ROLANDO
Dr. Fabrice BRAY
Stéphanie FLAMANT
Ziad MAHMOUD
Marie YAMMINE
Caterina BORDIN



ICube (Strasbourg & Baku)

Pr. Pierre COLLET
Dr. Ulviya ABDULKARIMOVA

