

Autophaser: An Algorithm for Automated Generation of Absorption Mode Spectra for FT-ICR MS – Supporting Information

Comparison of Phase Correction Success – Autophaser and the method of Xian *et al.*¹

Using the phase correction curves presented in Figure 1 of the manuscript, the spectrum of a ruthenium bound insulin spectrum was phase corrected and displayed in absorption mode. In Figure S1 below is a zoomed portion of that spectrum showing that the phase correction function generated by the Autophaser algorithm has successfully corrected for the phase shift whereas the method described by Xian *et al.* has not, in this case. As is described in the manuscript, we have ascribed this to a change in the oscillation frequency of the ions after excitation.

Experimental Parameters for the ruthenium Bound Insulin Spectrum

~0.5 μ M insulin (purchased from Sigma Aldrich) in 50:50 methanol and water (generated using a Millipore Direct Q UV system) with 0.1% formic acid. The ruthenium complex was synthesized using the method of Habtemariam *et al.*² The spectrum was recorded using positive mode electrospray on a 12T Bruker Daltonik Solarix FT-ICR MS.

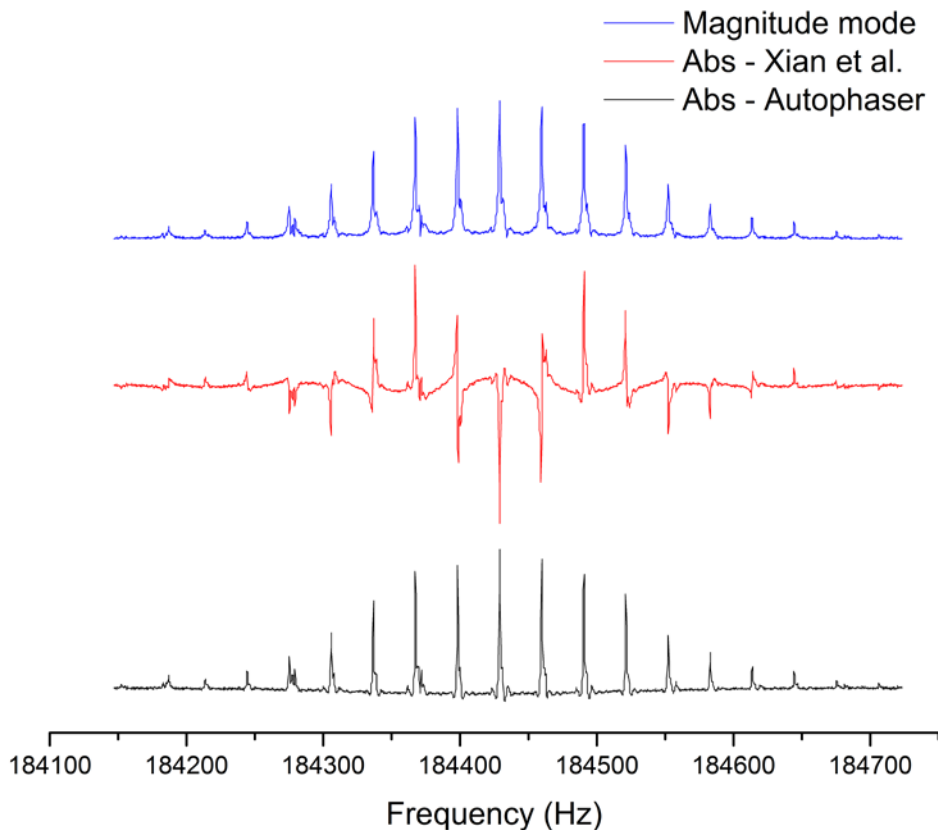


Figure S1 – Comparison of the quality of phase correction achieved using the method of Xian et al. and the Autophaser algorithm.

Phase correction by the method of Xian et al. was achieved using the information stored in the “ExciteSweep” and “apexAcquisition.method” files, generated from the Bruker Solarix Control software:

Excitation frequency range - 1250097.2 Hz – to 61417.47 Hz (Note sweep direction)

Excitation Frequency sweep - 20 μ s each at 1903 steps within the frequency range. The excitation sweep is not a smooth curve, but is a series of steps (recorded frequency step varies between 624.97 and 624.96 Hz throughout the sweep). (the time of the last step must be added to the recorded delay time. (Hence, the sweep rate = -196337934.1 rad.s⁻²)

Delay time (recorded) – 3500 μ s (excluding the final 20 μ s of the excitation ramp. Hence, total delay time = 3520 μ s)

Gradients of the phase correction curves (calculated for frequencies in Hz):

Coefficients	Xian et al. (eq 5)	eq 28 (ignoring frequency change effect)	Autophaser
a (quadratic term)	2.01073816E-7	1.00536908E-7	1.005337006E-7
b (linear term)	0.00976737	0.00976737	0.009661245

Comparison of Phase Correction – Autophaser and the method of Qi *et al.*³

An APPI oil spectrum (described previously³) was phase corrected using the method of Qi *et al.* and the Autophaser algorithm. Figures S2 and S3 show the resulting spectra, which illustrate the similarity of the results by both methods. Note - the Autophaser algorithm uses the baseline correction method described in the manuscript, whereas the method of Qi *et al.* does not.

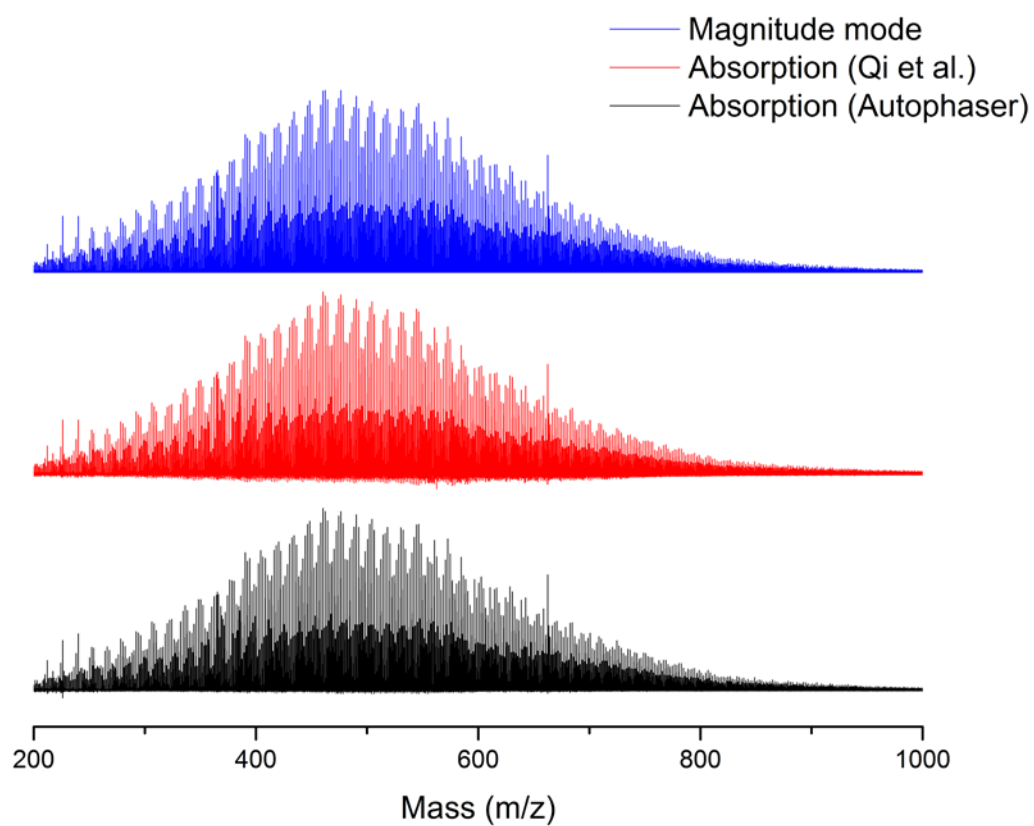


Figure S2 – Complete mass spectra of a crude oil sample in magnitude mode and in absorption mode generated using the method of Qi *et al.* and using the Autophaser algorithm.

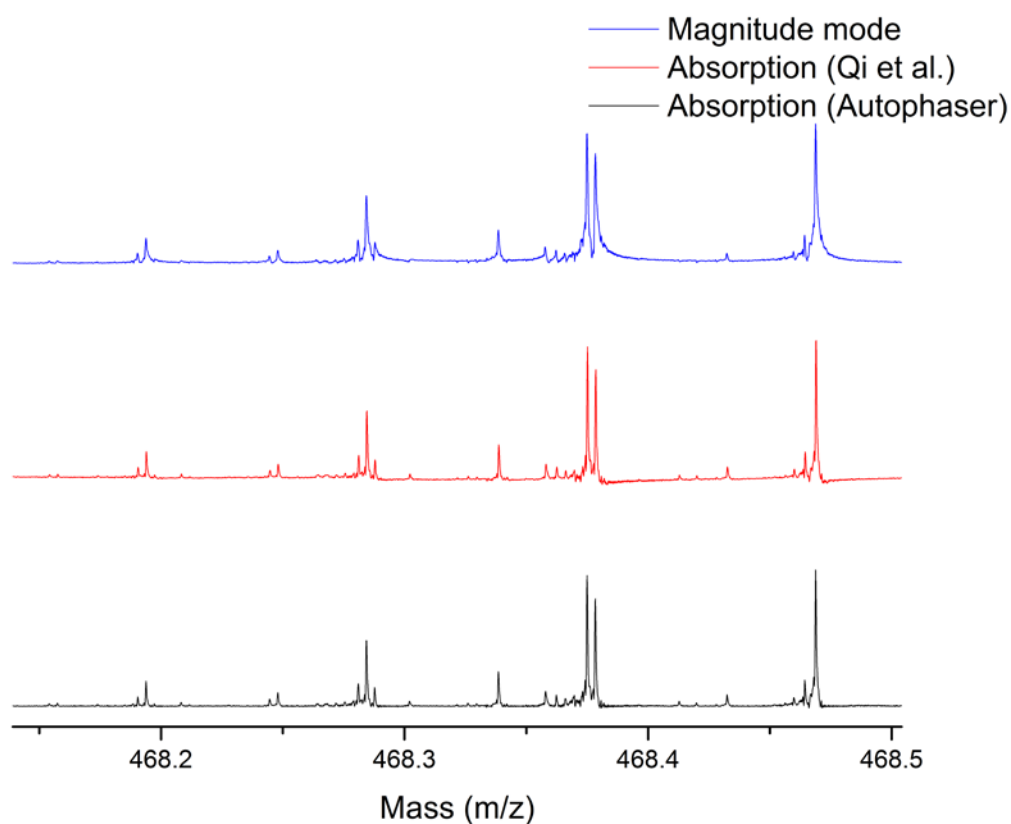


Figure S3 – Portions of mass spectra of a crude oil sample in magnitude mode and in absorption mode generated using the method of Qi *et al.* and using the Autophaser algorithm.

References

- (1) Xian, F.; Hendrickson, C. L.; Blakney, G. T.; Beu, S. C.; Marshall, A. G. *Anal. Chem.* **2010**, *82*, 8807-8812.
- (2) Habtemariam, A.; Melchart, M.; Fernández, R.; Parsons, S.; Oswald, I. D. H.; Parkin, A.; Fabbiani, F. P. A.; Davidson, J. E.; Dawson, A.; Aird, R. E.; Jodrell, D. I.; Sadler, P. J. *J. Med. Chem.* **2006**, *49*, 6858-6868.

(3) Qi, Y.; Thompson, C.; Van Orden, S.; O'Connor, P. *J. Am. Soc. Mass. Spectrom.* **2011**, 22, 138-147.