Supplementary Material

Increasing molecular coverage in the analysis of fossil oils by coupling gas chromatography prior to atmospheric pressure laser ionization FT-ICR MS

Paolo Benigni[†], J. Daniel DeBord[†], Christopher J. Thompson[‡], Piero Gardinali[⊥,†], and Francisco Fernandez-Lima[†,§,*]

[†]*Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199, USA.*

[‡]*Bruker Daltonics, Inc., Billerica, Massachusetts 01821, USA*

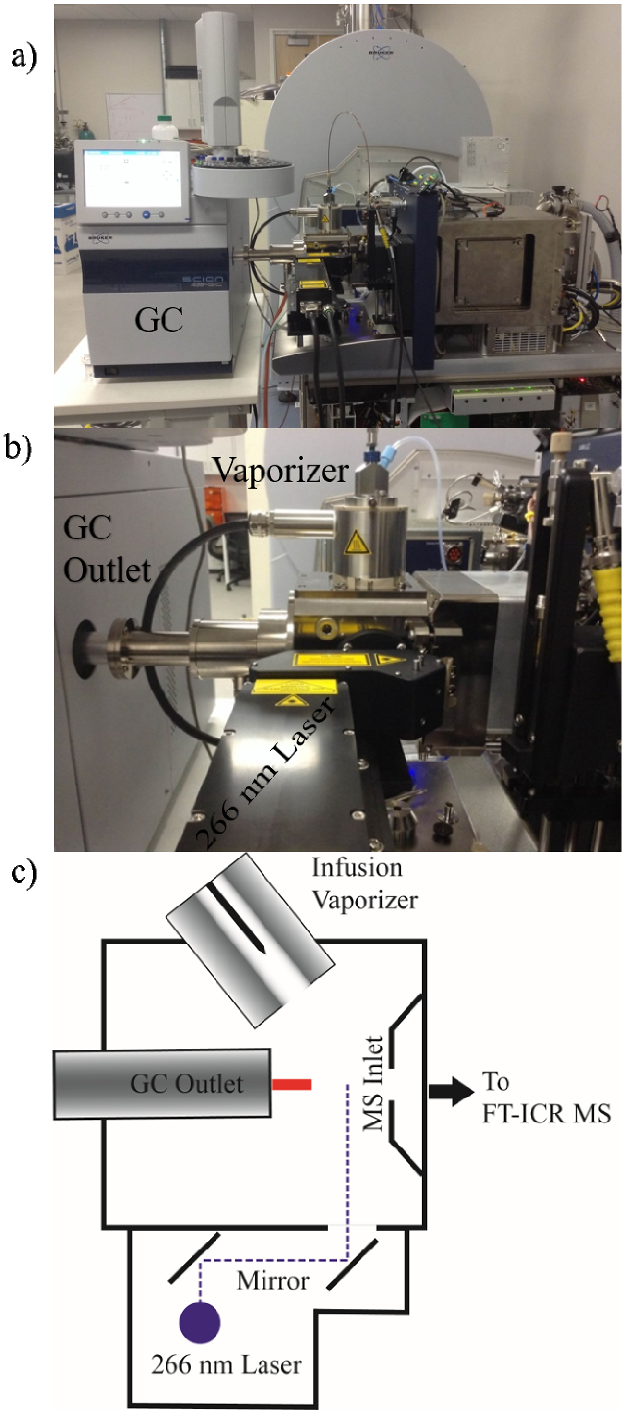
[⊥] *Southeast Environmental Research Center (SERC), Florida International University, Miami, FL 33199, USA*

[§]*Biomolecular Sciences Institute, Florida International University, Miami, FL 33199, USA*

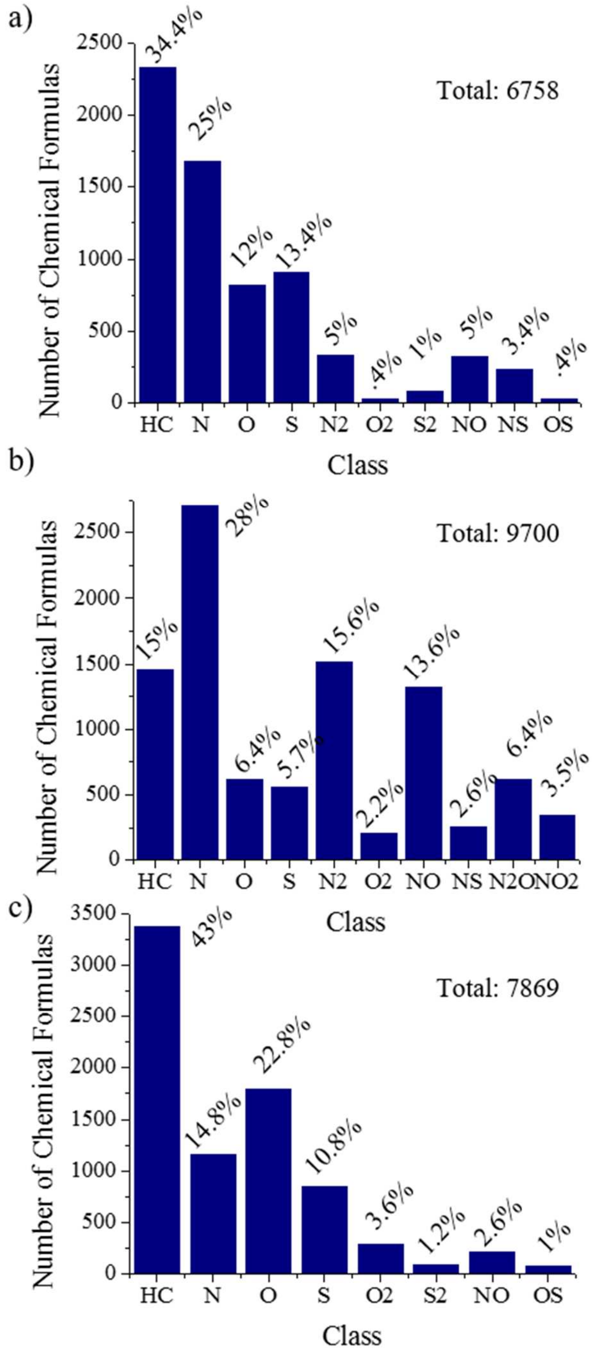
**corresponding author*

ABSTRACT: Thousands of chemically distinct compounds are encountered in fossil oil samples that require rapid screening and accurate identification. In the present paper, we show for the first time the advantages of gas chromatography (GC) separation in combination with atmospheric pressure laser ionization (APLI) and ultra-high resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) for the screening of poly-aromatic hydrocarbons (PAH) in fossil oils. In particular, reference standards of organics in shale oil, petroleum crude oil and heavy sweet crude oil were characterized by GC-APLI-FT-ICR MS and APLI-FT-ICR MS. Results showed that while APLI increases the ionization efficiency of PAHs when compared to other ionization sources, the complexity of the fossil oils reduces the probability of ionizing lower concentration compounds during direct infusion. When gas chromatography precedes APLI-FT-ICR MS, an increase (>2 fold) in the ionization efficiency and in the signal-to-noise of lower concentration fractions is observed, giving better molecular coverage in the *m/z* 100 – 450 range. That is, the use of GC prior to APLI-FT-ICR MS resulted in higher molecular coverage, higher sensitivity and the ability to separate and characterize molecular isomers while keeping the ultrahigh resolution and mass accuracy of the FT-ICR MS separation.

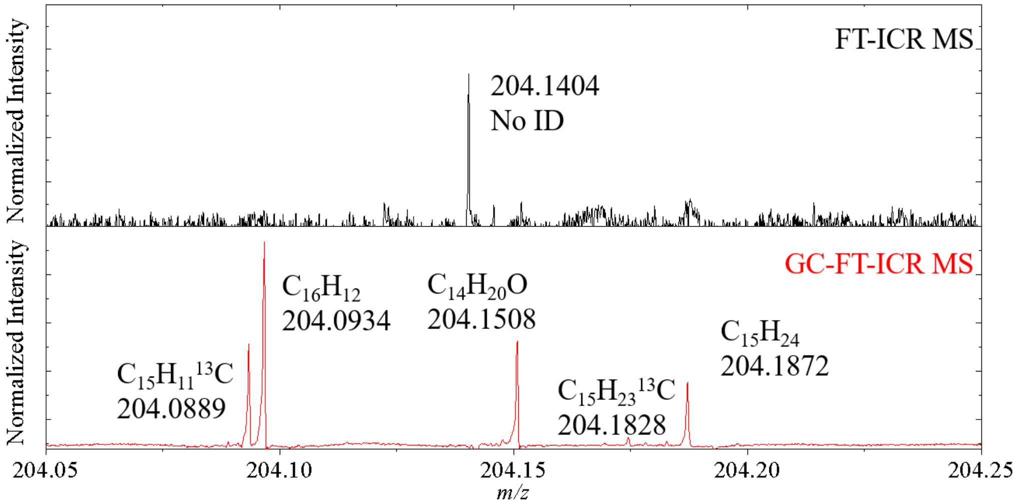
S1. Images of the a) instrumental set up, b) close up of the GC-FT-ICR MS interface, and c) schematic of the interface.



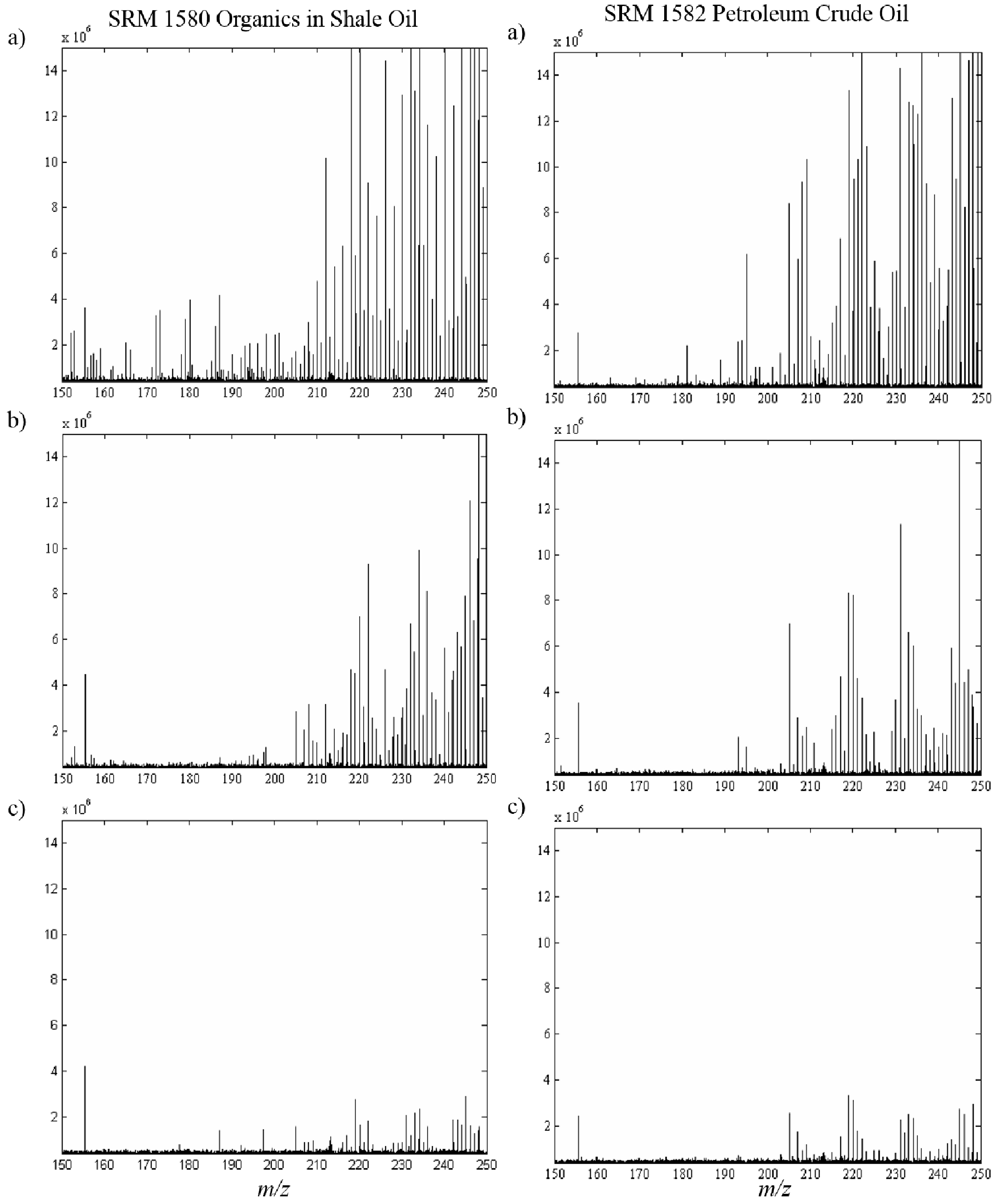
S2. Combined number of IDs per class for a) Petroleum Crude Oil, b) Organics in Shale, c) Heavy Sweet Crude Oil using GC-APLI-FT-ICR MS and APLI-FT-ICR MS



S3. Comparison of *m/z* 204 for the heavy sweet crude oil sample analysed by direct infusion (top, black) and by GC (bottom, red)



S4-S5 Matrix suppression experiments for Organics in Shale and Petroleum Crude Oil at a) 1:5, b) 1:10, and c) 1:100 dilution



Supplementary Table 1. Assignments and error in assignment for m/z 178 and 256 in the Organics in Shale oil GC-APLI-FT-ICR MS analysis found in figure 4.

m/z		Formula	Error (ppm)
178	A	$C_{10}H_{12}NS$	0.4
	B	$C_{14}H_{10}$	-0.21
	C	$C_{11}H_{16}NO$	0.03
	D	$C_{12}H_{20}N$	0.12
256	A	$C_{14}H_{14}N_3O_2$	0.00
	B	$C_{16}H_{18}NS$	-0.78
	C	$C_{13}H_{14}N_5O$	0.16
	D	$C_{20}H_{16}$	0.2
	E	$C_{17}H_{20}S$	-0.03
	F	$C_{17}H_{20}O_2$	0.27
	G	$C_{16}H_{21}NO^{13}C$	-0.25
	H	$C_{17}H_{20}NO$	0.0
	I	$C_{18}H_{24}O$	0.14
	J	$C_{17}H_{25}N^{13}C$	-0.16
	K	$C_{18}H_{26}N$	0.06
	L	$C_{19}H_{28}$	0.24