Supporting Information

Title: Petroleomics via Orbitrap mass spectrometry with resolving power above 1,000,000

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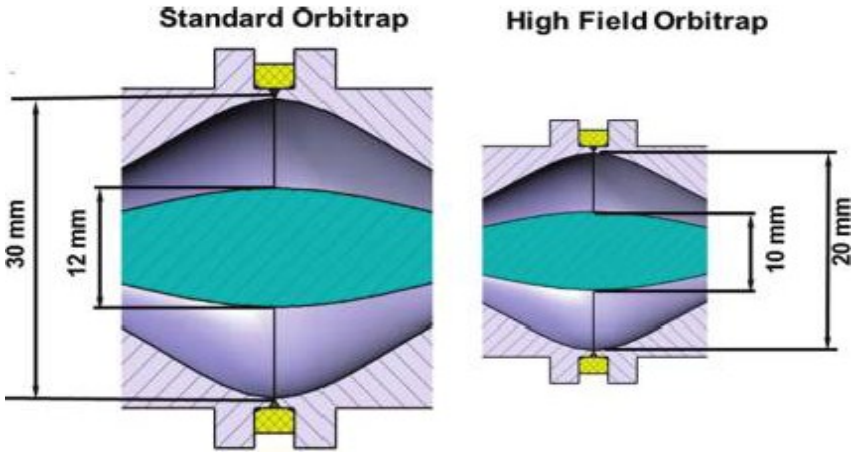

Figure S1: The standard Orbitrap geometry (left) and that of a compact high-field Orbitrap (right) analyzer. The outer electrodes are separated by a quartz ring and used for detection and therefore are maintained at the virtual ground of the preamplifier, whereas the central electrode is used for trapping at a voltage – Ur (Ur > 0 for positive ions). Courtesy of © Thermo Fisher Scientific (Bremen) GmbH.

Table S1: Molecular formula assigned to ions detected and separated by the standard Orbitrap, the 7.2 T FT-ICR and the MegaOrbitrap analyzers in the *m/z* 504.26 – 504.46 range.

Molecular Formula	Theorical Mass	Mass Analyzer	Experimental Mass	Absolute intensity	Error (ppm)	Resolving Power
$C_{38}H_{34}N$	504.26858	Std. Orbitrap	X	X	X	X
		FT-ICR	504.26790	2346.4	-1.342	252,100
		MegaOrbitrap	X	X	X	X
$C_{36}H_{42}NO$	504.32609	Std. Orbitrap	504.32721	4294	2.218	73,900
		FT-ICR	504.32558	4342.7	-1.014	234,700
		MegaOrbitrap	504.32635	15873.7	0.513	665,004
$C_{33}H_{46}NOS$	504.32946	Std. Orbitrap	X	X	X	X
		FT-ICR	X	X	X	X
		MegaOrbitrap	504.32986	2961.1	0.797	630,456
$C_{27}H_{54}NOS_3$	504.33620	Std. Orbitrap	X	X	X	X
		FT-ICR	X	X	X	X
		MegaOrbitrap	504.33557	9152.9	-1.257	621,404
$C_{31}H_{52}OS_2$	504.34541	Std. Orbitrap	504.34509	2205.9	-0.633	75,000
		FT-ICR	504.34489	2260.7	-1.029	248,400
		MegaOrbitrap	X	X	X	X
$C_{37}H_{46}N$	504.36248	Std. Orbitrap	504.36185	33785	-1.243	91,502
		FT-ICR	504.36186	61057.8	-1.223	266,600
		MegaOrbitrap	504.36279	106921.5	0.621	634,604
$C_{34}H_{50}NS$	504.36585	Std. Orbitrap	X	X	X	X
		FT-ICR	504.36503	5488.8	-1.621	273,600
		MegaOrbitrap	504.36603	14255.1	0.361	664,404

$C_{34}H_{50}NO_2$	504.38361	Std. Orbitrap	504.38235	5622.7	-2.491	86,602
		FT-ICR	504.38284	2683	-1.519	220,900
		MegaOrbitrap	504.38394	21729.2	0.662	668,904
$C_{35}H_{54}NO$	504.41999	Std. Orbitrap	504.41995	4192.1	-0.083	77,400
		FT-ICR	504.41939	3695.9	-1.193	229,100
		MegaOrbitrap	504.42035	13535.1	0.710	692,604
$C_{31}H_{56}N_2O_3$	504.42855	Std. Orbitrap	X	X	X	X
		FT-ICR	X	X	X	X
		MegaOrbitrap	504.42947	10397.3	1.834	654,904
$C_{30}H_{64}OS_2$	504.43931	Std. Orbitrap	X	X	X	X
		FT-ICR	504.43856	1063.5	-1.486	284,300
		MegaOrbitrap	504.43976	7245.1	0.893	670,604
$C_{32}H_{60}N_2S$	504.44717	Std. Orbitrap	X	X	X	X
		FT-ICR	504.44688	12948.9	-0.579	251,500
		MegaOrbitrap	504.44775	28837.3	1.146	665,604
$C_{36}H_{58}N$	504.45637	Std. Orbitrap	504.45572	172385.9	-1.303	96,506
		FT-ICR	504.45573	199385.4	-1.283	268,401
		MegaOrbitrap	504.45670	479846.7	0.640	695,501

X= Not detected in this condition

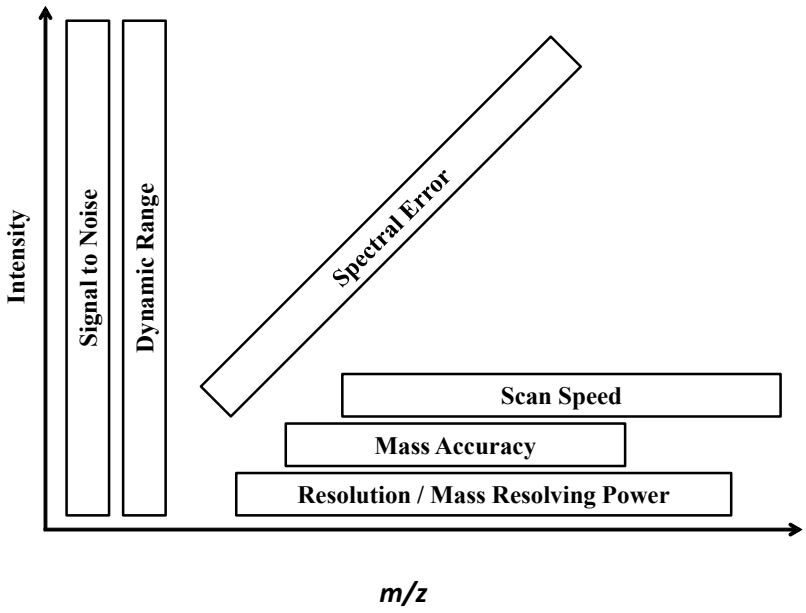

Figure S2: Major figures of merit used in mass spectrometry and their correlation with *m/z* values and peak intensity.

Signal to Noise *

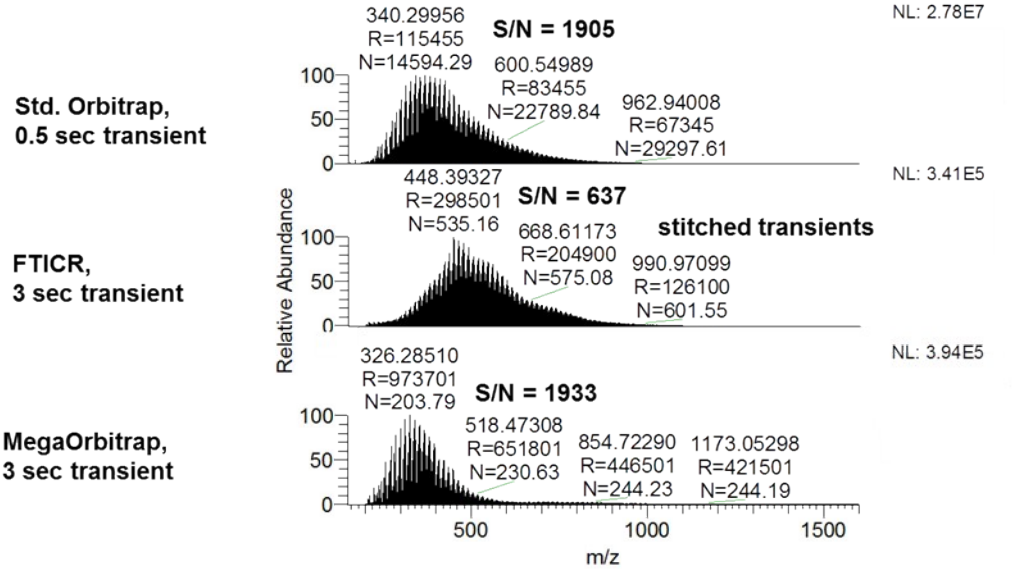

Figure S3*: Signal-to-Noise ratio obtained from the analysis of a typical crude oil sample in Standard Orbitrap, FT-ICR, and MegaOrbitrap.

Dynamic Range

Std. Orbitrap

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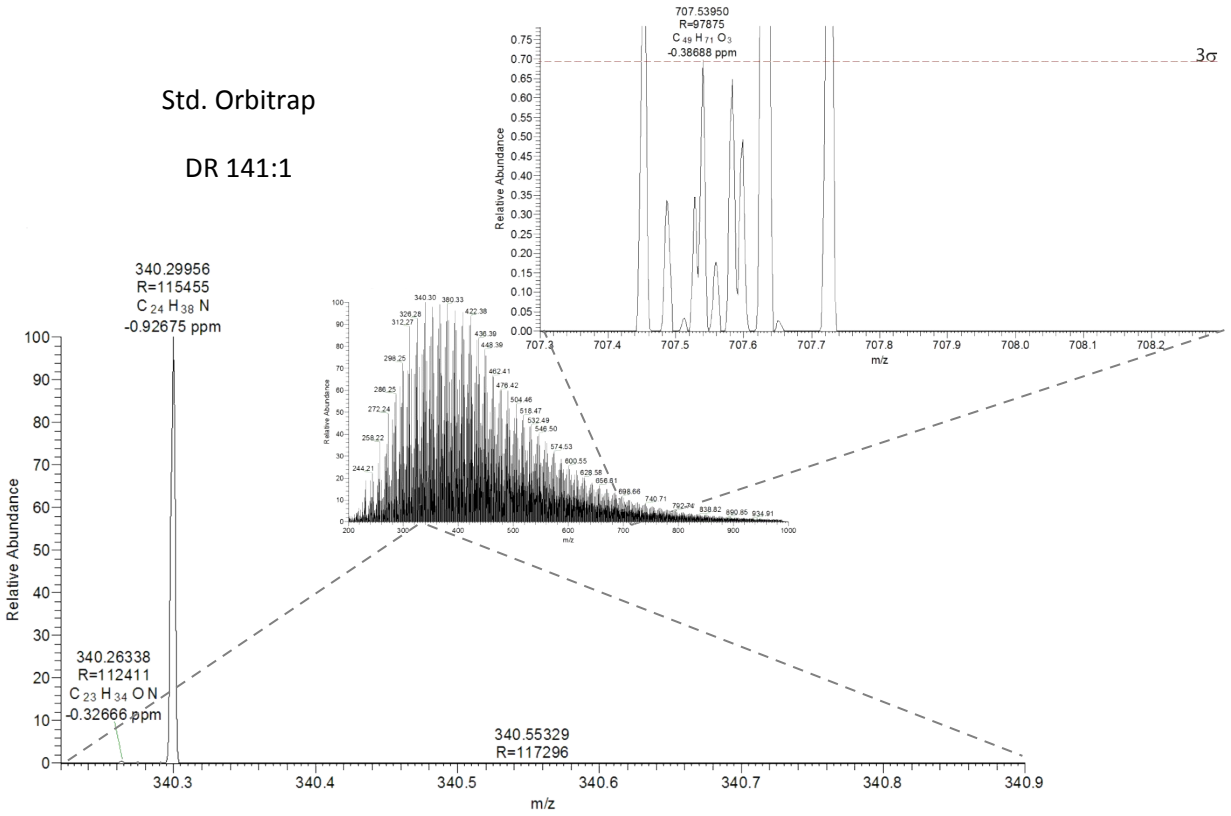

FT-ICR

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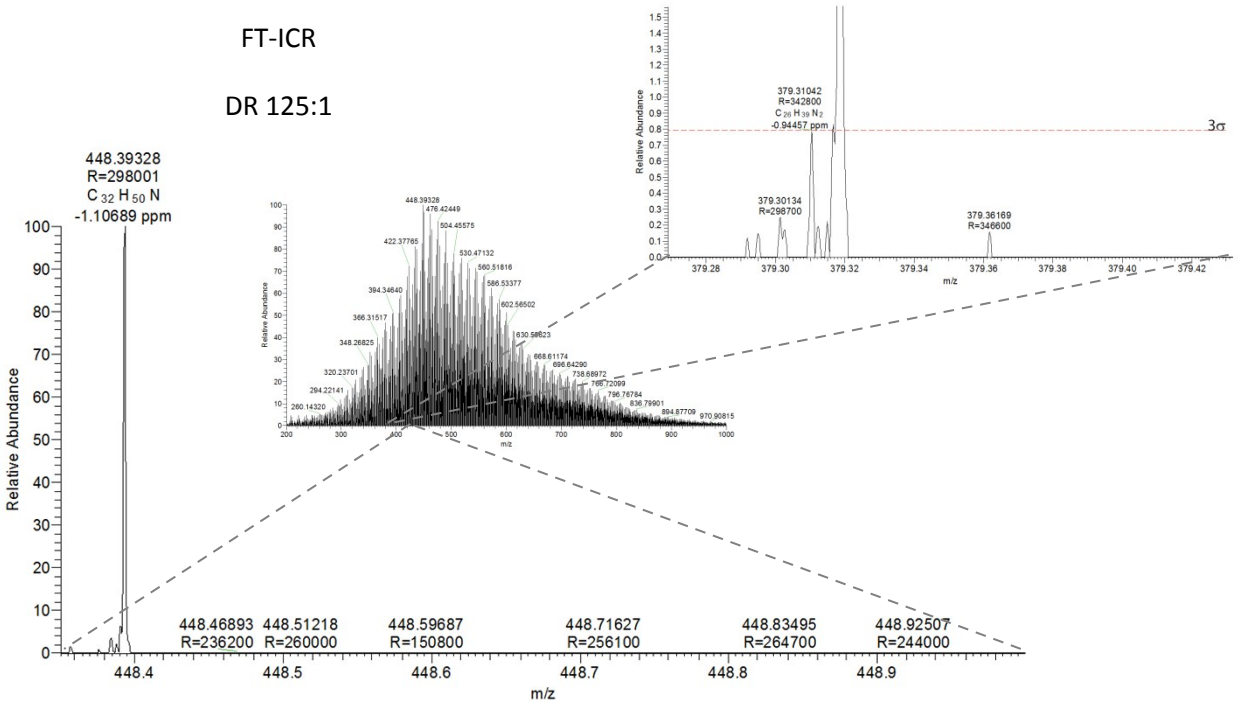

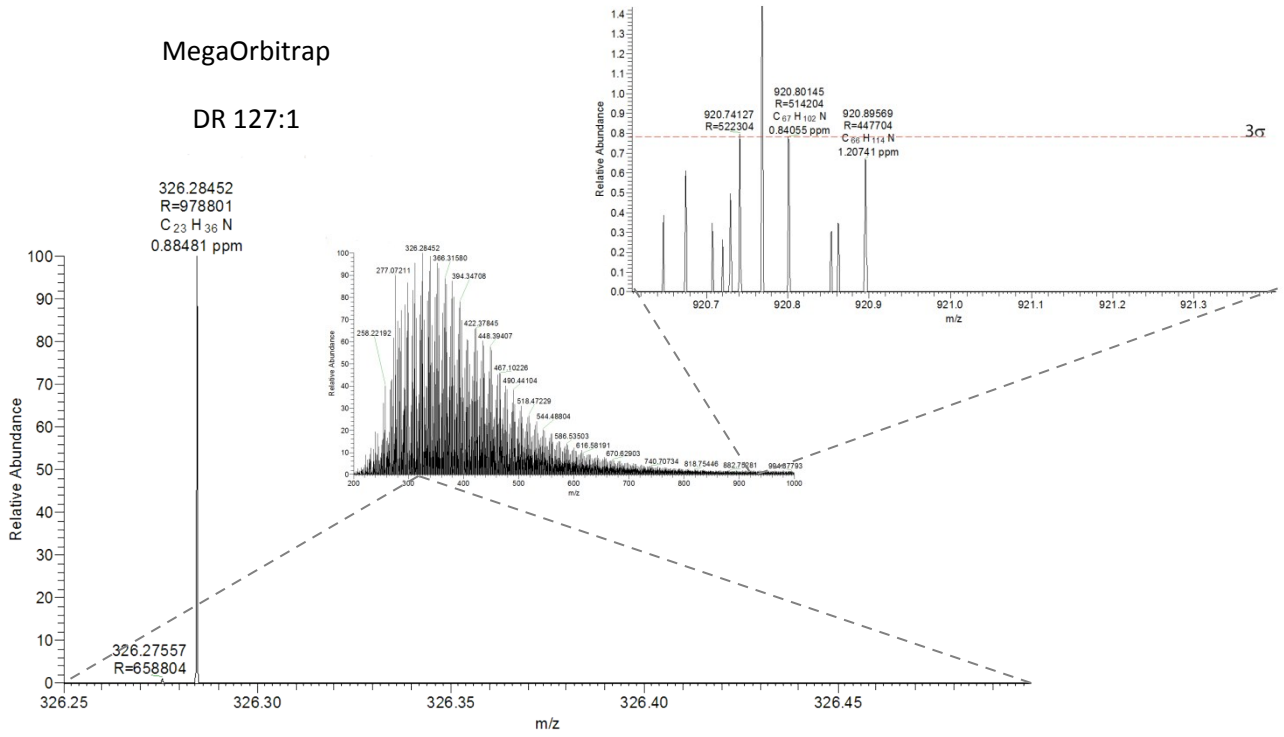

Figure S4*: Calculated Dynamic Range in the analysis of a typical crude oil sample in Standard Orbitrap, FT-ICR and MegaOrbitrap.

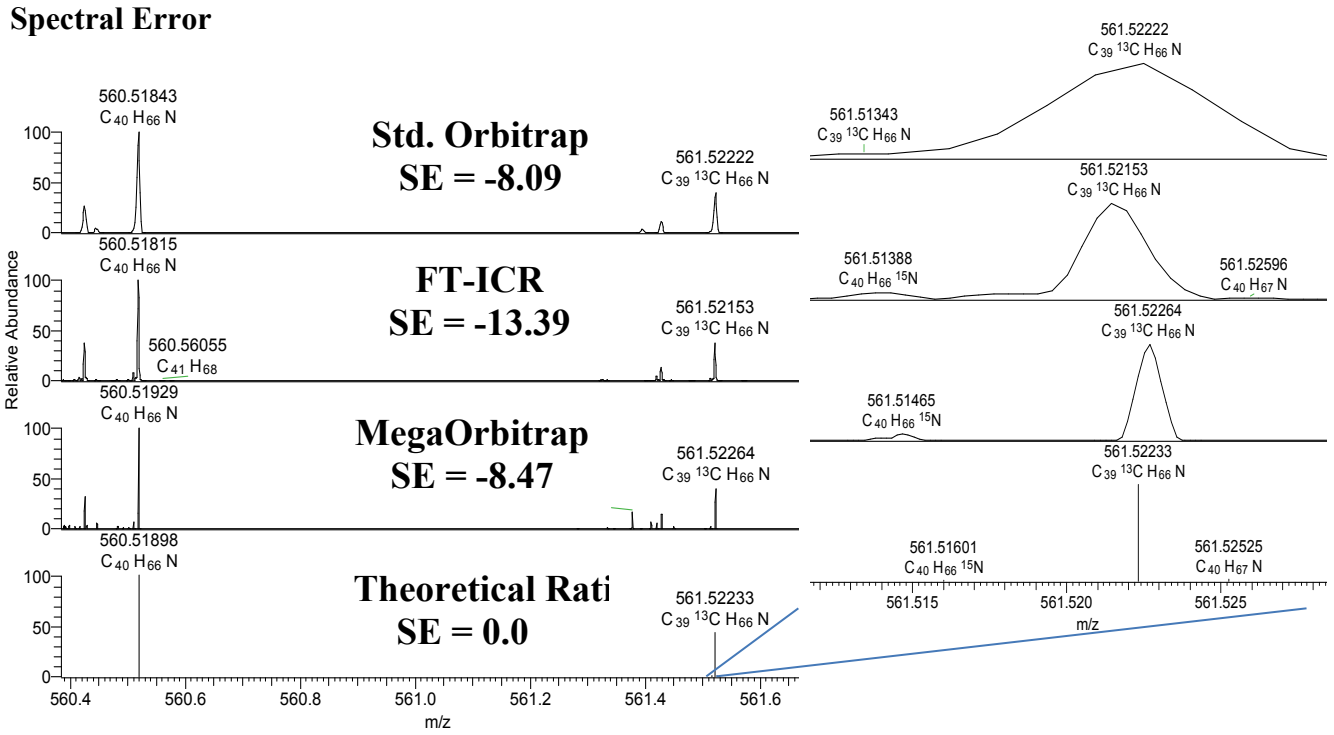

Figure S5*: Spectral Error (SE) for $C_{40}H_{66}N$ and its isotope $C_{39}{}^{13}CH_{66}N$ obtained from the analysis of a typical crude oil sample by Standard Orbitrap, FT-ICR, and MegaOrbitrap.

Table S2*: Mean spectral error (SE) for all molecular formula assigned obtained from the analysis of a typical crude oil sample by using the Standard Orbitrap, FT-ICR, and MegaOrbitrap. The total number of molecular formulas and attributed isotopologues is also shown.

Mass Analyzer	**Mean spectral error (SE) (%)**			Molecular formula (attributed isotopologues)
	M+1	**M+2**	**Total**	
Standard Orbitrap	12 ± 10	29 ± 8	13 ± 10	537 (512)
FT-ICR	14 ± 10	18 ± 10	15 ± 10	2376 (1661)
MegaOrbitrap	14 ± 11	16 ± 11	15 ± 11	1754 (1320)

Scan Speed

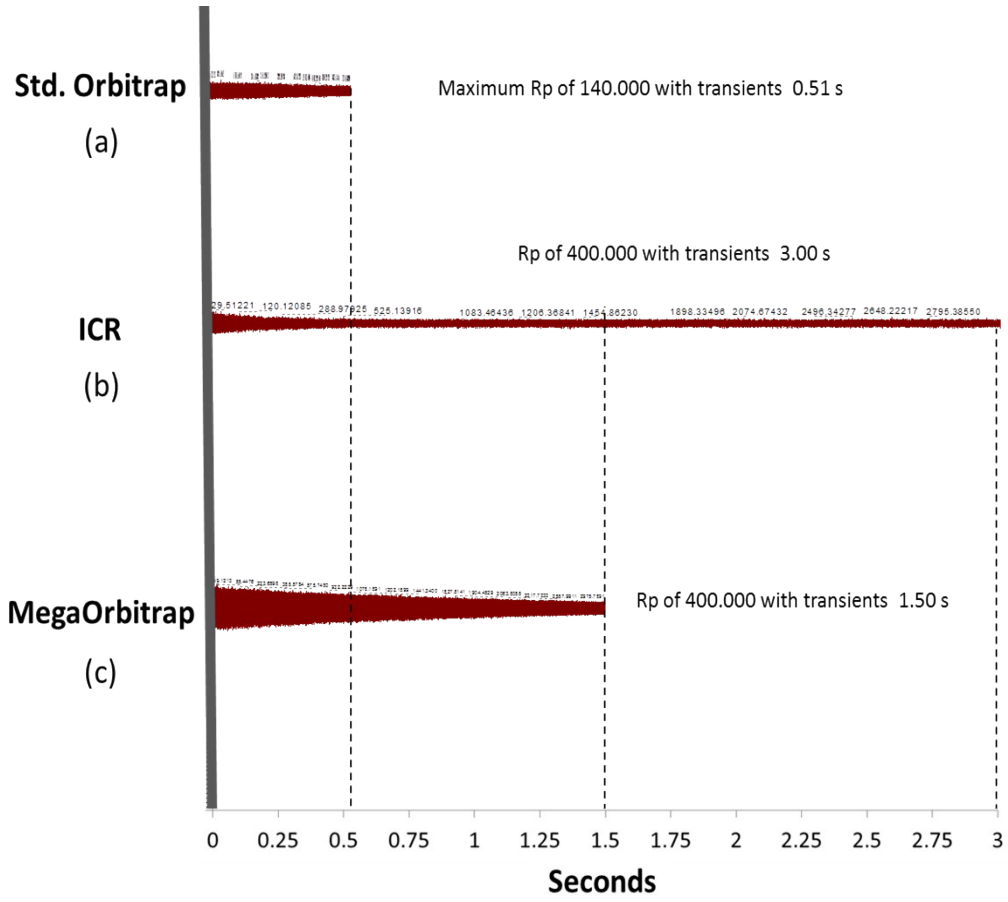

Figure S6*: Transients obtained for each equipment organized in the same time scale in seconds. They refer to (a) Standard Orbitrap (b) FT-ICR and (c) MegaOrbitrap

Mass Accuracy

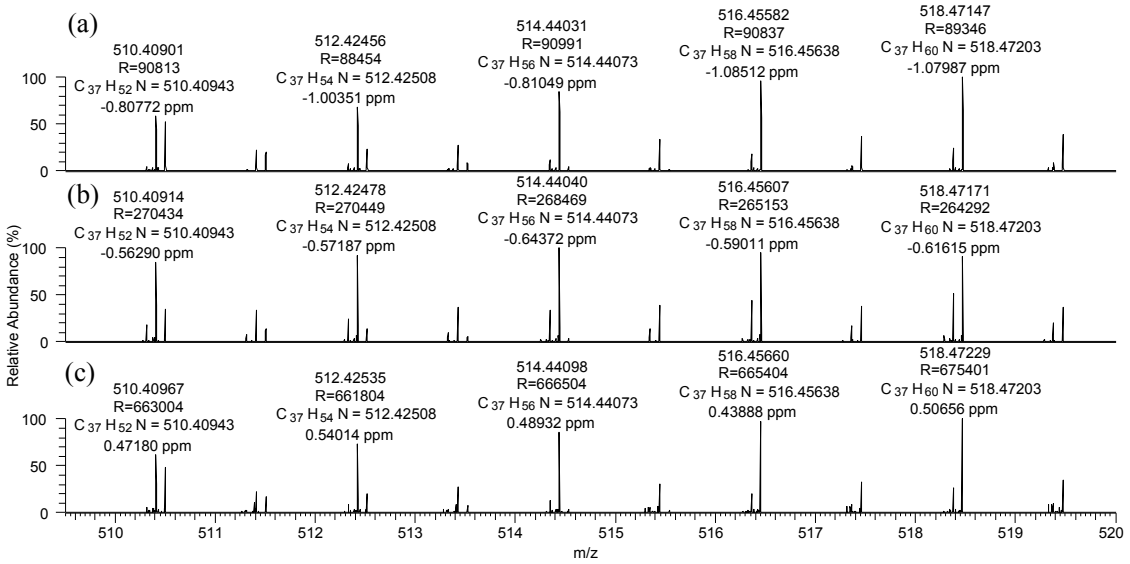

Figure S7*: Spectra in the same mass range showing the differences in mass accuracy and resolution between the equipments studied: (a) Standard Orbitrap (b) FT-ICR and (c) MegaOrbitrap

Table S3*: Minimum resolving power required for resolve compounds differing by C_3 and SH_4 at different *m/z*

m/z	Minimum Resolving Power
200	117647
400	235294
600	352941
800	470588