

Direct Analysis of the Polar Fraction of Heavy Petroleum Crude Oil using a Finnigan LTQ FT Hybrid Mass Spectrometer

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Key Words

- Finnigan™ LTQ FT™
- Crude Oil Analysis
- FTICR-MS
- High Resolution
- Petrolicomics

Introduction

As world-wide petroleum reserves evolve towards heavier crude oils, effective processing of heavy petroleum become increasingly important. Heavy crude oil is a complex mixture of hydrocarbons, containing multiple aromatic rings including heterocycles of N, S and O and crude acids in its polar fraction.^[1,2] Variation in the oil composition directly affects the downstream processing. The chemical makeup of low and mid boilers has been extensively studied by such techniques as GC/MS and LC/MS,^[3,4] however, the data on heavy fractions is scarce, primarily due to analytical difficulties presented by their complex nature. Not only are traditional vaporization/ionization methods ineffective with heavy crude, but its extraordinary complexity requires ultra-high resolving power and sensitivity, specifically for the analysis of polar components, including nitrogen-containing heterocycles and cyclic acids, as they are found in low concentrations in petroleum samples.

Previous work on characterization of the petroleum polar fraction relied on chromatographic separation to simplify the composition of the analyte.^[5] Recent work by Marshall and co-authors^[1,2] demonstrated the unique utility of high field (9.4 T) ESI-FTICR mass spectrometry for direct analysis of crude oil. Identification of more than 3000 nitrogen containing compounds in a single experiment became possible due to ultra-high resolving power of the FTICR-MS and its high detection limits. Here we used an LTQ FT Hybrid Linear Ion Trap Mass Spectrometer with a 7 T magnet to directly analyze polar compounds in heavy petroleum. Mass accuracy of better than 2 ppm was obtained routinely with external calibration. More than 5,000 ion signals belonging to chemically different elemental compositions have been separated with 200,000 resolving power ($m/\Delta m_{50\%}$ at m/z 400) in both positive and negative electrospray spectra. The robustness of the LTQ FT, combined with unprecedented ease of use, ultra high mass accuracy, high sensitivity, and excellent resolving power make it an ideal instrument for petrochemical analysis.

Materials and Methods

The South American heavy crude oil samples were diluted in toluene:methanol:acetic acid (NH_4OH for negative ion detection) (1:1:0.003, v/v) to 1 mg/mL and directly electrosprayed into the LTQ FT mass spectrometer at 2 $\mu\text{L}/\text{min}$. The electrospray capillary (New Objective Inc., Woburn, MA) was held at 1.7 kV (-1.5 kV for negative mode) versus the inlet of the mass spectrometer, with transfer tube held at 300 °C. The ion optics were tuned to provide an optimal signal for m/z 120–1,000 range. The 10^6 (5×10^4 for negative mode) ion number was used in all experiments. The instrument was calibrated externally using the mixture of caffeine, MRFA and ultramark.

Results and Discussion

Our goal was to demonstrate the utility of the LTQ FT mass spectrometer for direct ESI analysis of polar compounds in heavy petroleum. The unique advantage of this instrument derives from using its high resolving power to separate multiple isobaric species,^[1,2] combined with its ability to measure masses accurately and reproducibly based on external calibration. These features were used to resolve and identify different heteroatomic isobars containing N, N_xO_y , $\text{N}_x\text{O}_y\text{S}_z$, NS, S_nO_m , and O groups in the heavy petroleum fraction.

Positive Ion ESI

Figure 1 shows the positive ESI spectra containing a distribution of singly charged ions distributed from m/z 200 to 750 with an apex at m/z 462. An expanded segment (m/z 425–500) shows ions at every nominal mass with a clear 14.016 amu repeat attributed to $-\text{CH}_2-$ periodicity. Even-mass ions were more abundant than odd-mass ions. Positive electrospray ionization favors the formation of pseudomolecular ions by proton attachment to the neutral molecule. Using the nitrogen rule it becomes obvious that these even-mass ions would have to contain an odd number of nitrogen atoms. In fact, most of the odd-mass ions were the ^{13}C isotopes of the even-mass ions, pointing out that nitrogen-free molecules were not effectively ionized by electrospray.^[1]

The mass accuracy routinely achievable with external calibration on the LTQ FT instrument is better than 2 ppm. Combining this capability with high resolving power (~218,000) allowed unambiguous elemental formula determination of multiple isobaric signals (Figure 2, Table 1). Out of eleven compounds present

in m/z 400.1–400.4 segment shown in Figure 2, nine were positively identified as either N or NO heteroatoms, detailed in Table 1. In light of the previously published results it is likely that the majority of even-mass species contained basic nitrogen.^[1]

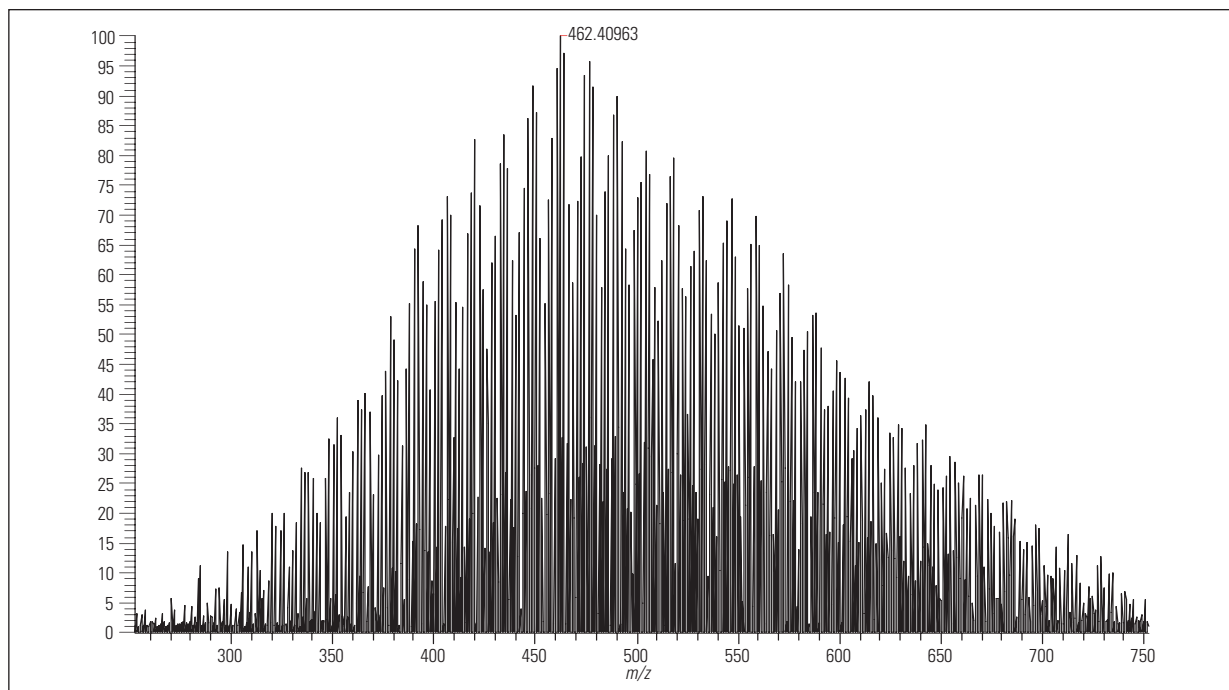


Figure 1a: Positive ion ESI mass spectrum of a heavy crude oil sample acquired at 200,000 ($m/\Delta m_{50\%}$ at m/z 400) resolving power.

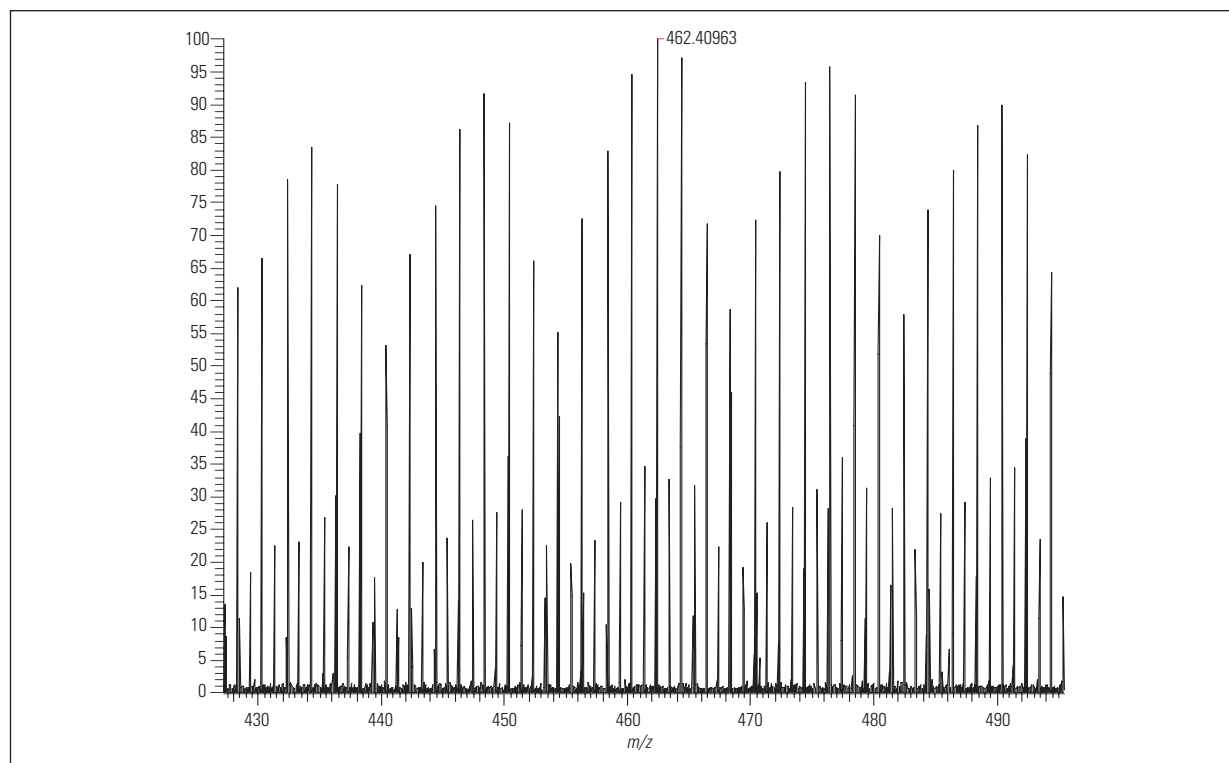


Figure 1b: An expanded segment of the full range spectrum, showing the ion signals at every nominal mass with clear 14.016 amu repeat. Even-mass ions are more abundant than odd-mass ions.

Advantages of High Resolving Power

The complexity of crude oil ESI spectra increases with molecular weight. From Figures 2 and 3 it is obvious that the number of chemically distinct signals is greater at m/z 828 than at m/z 400 in a window of the same width. However, FTICR mass resolving power is inversely pro-

portional to m/z . Thus, while at m/z 400 the effective resolving power is on average 218,000 (Figure 2), it becomes only 100,000 at m/z 828 (Figure 3, top), making it more difficult to resolve the greater number of overlapping isobars at higher mass and to measure their mass accurately. By increasing resolving power to $\sim 400,000$ at

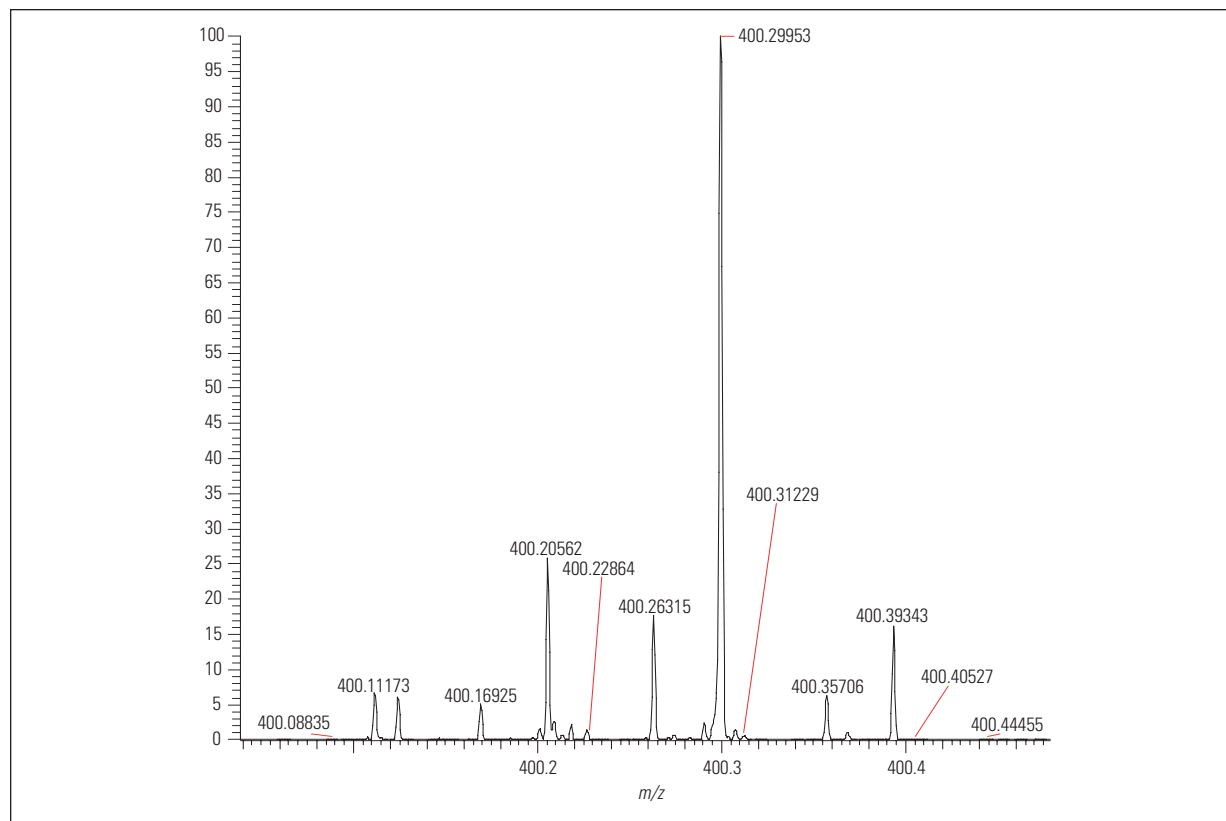


Figure 2: Narrow segment spectrum acquired by selective ion monitoring of mass m/z 400 ± 2 . Ultra-high resolving power ($\sim 218,000$) and high mass accuracy allow direct assignment of nine chemically distinct species at a single nominal mass with 0.9 ppm RMS error (Table 1).

m/z	Relative Intensity	Elemental Composition (Pos. Ion)	Theoretical Mass	Error (ppm)
400.11173	6.85	C ₃₁ H ₁₄ N	400.11208	-0.9
400.12434	6.28	NO ID		
400.16925	5.27	C ₂₉ H ₂₂ N O	400.16959	-0.9
400.20562	25.51	C ₃₀ H ₂₆ N	400.20598	-0.9
400.21836	2.33	NO ID		
400.22683	1.45	C ₂₇ H ₃₀ O ₂ N	400.22711	-0.7
400.26315	17.99	C ₂₈ H ₃₄ NO	400.26349	-0.9
400.29053	2.43	C ₂₉ (13) C ₂ H ₃₆ N	400.29094	-1.1
400.29953	100	C ₂₉ H ₃₈ N	400.29988	-0.9
400.35706	5.52	C ₂₇ H ₄₆ ON	400.35739	-0.8
400.39343	14.90	C ₂₈ H ₅₀ N	400.39378	-0.9

Table 1: Possible elemental compositions of ions from Figure 2

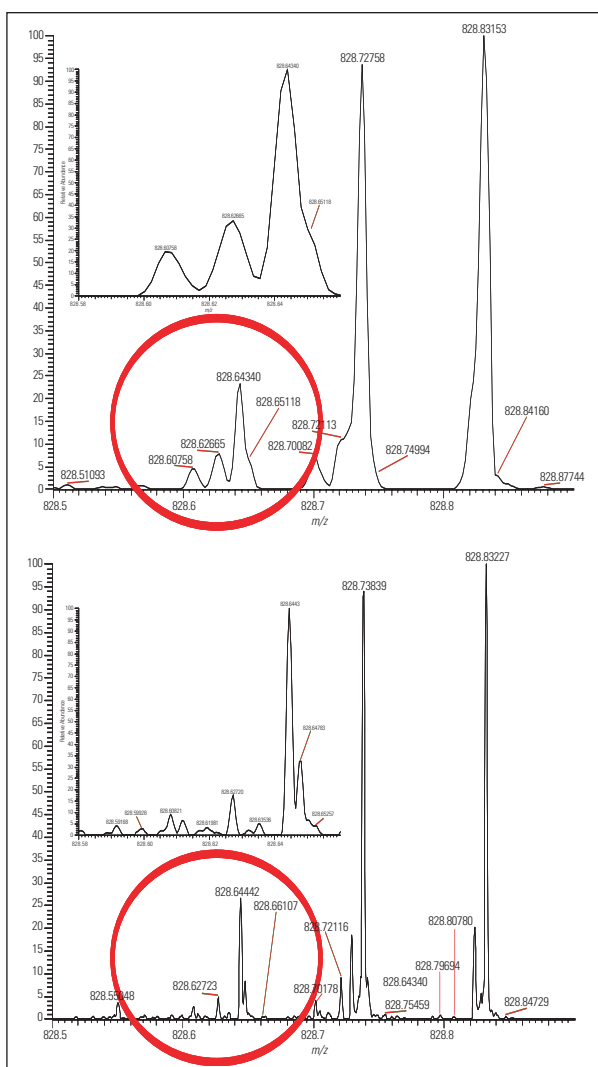


Figure 3 (Top): Narrow segment spectrum acquired by selective monitoring of mass m/z 828 ± 2 at 200,000 resolving power. Actual resolving power at this mass is only 100,000. (Bottom): the same spectrum with experimental resolving power of 400,000 (Table 2). The peak assignments are in Table 2.

m/z	Elemental Composition (pos. ion)	Theoretical Mass	Error (ppm)	Resolving Power
828.55040	C62 H70 N	828.55028	0.2	369325
828.57116	C59 H74 O2 N	828.57141	-0.3	213919
828.60820	C60 H78 ON	828.60779	0.5	296133
828.61176	C57 H82 ONS	828.61116	0.8	259394
828.62720	C59 (C13) H79 N2	828.62713	0.3	373929
828.64420	C61 H82 N	828.64418	0.3	386577
828.64783	C58 H86 NS	828.64755	0.3	400252
828.66104	NO ID			303801
828.70177	C59 H90 NO	828.70169	0.1	384812
828.70481	C56 H94 ONS	828.70506	-0.3	420560
828.72118	NO ID			358007
828.72939	C50 H102 O3 N S2	828.72956	-0.2	412194
828.73840	C60 H94 N1	828.73808	0.4	416827
828.82328	NO ID			
828.83227	C59 H106 N	828.83198	0.4	402329

Table 2: Possible elemental compositions of ions shown in Figure 3 (bottom)

m/z 828 (Figure 3, bottom), however, it is possible to separate most of the otherwise unresolved isobars. The proposed elemental assignments indicate that in addition to N and NO containing heterocycles, there are also $N_xO_yS_z$, and NS containing compounds, which were not present at mass 400. Overall, twelve out of fifteen distinct chemical components were identified in the m/z 828.55–828.85 window (Table 2).

Negative Ion ESI

The negative ESI spectrum contained singly charged ion species distributed from m/z 200 to 1,000 (Figure 4) with an apex at m/z 552. The expanded segment m/z 515–555 shows ions at every nominal mass with a clear 14.016 amu repeat. As in the case with positive ions, even-mass ions were more abundant than odd-mass ions. Negative electrospray ionization favors the formation of pseudomolecular ions by proton detachment from the neutral molecule. Out of twelve compounds present in the m/z 456.14–456.43 segment, the nine most abundant were positively identified as either N or NO heteroatoms (Figure 5, Table 3). At the same time detailed analysis of the m/z 363.10–363.40 segment revealed at least fifteen components (Figure 6, Table 4). These would have to contain either an even number of nitrogen atoms or none at all. The eleven most abundant ions were positively identified in this spectra with $C_{25}H_{31}O_2$, a dicyclic diaromatic acid being a major component.^[2] Another dicyclic acid had an elemental composition of $C_{24}H_{43}O_2$. We also found O_3S , O_4S , and O_3S_2 species, similar to what was previously reported for an enriched acidic oil fraction.^[2] Thus the odd-mass cluster was mainly composed of crude acids, while the even-mass cluster was composed of nitrogen-containing heterocycles.

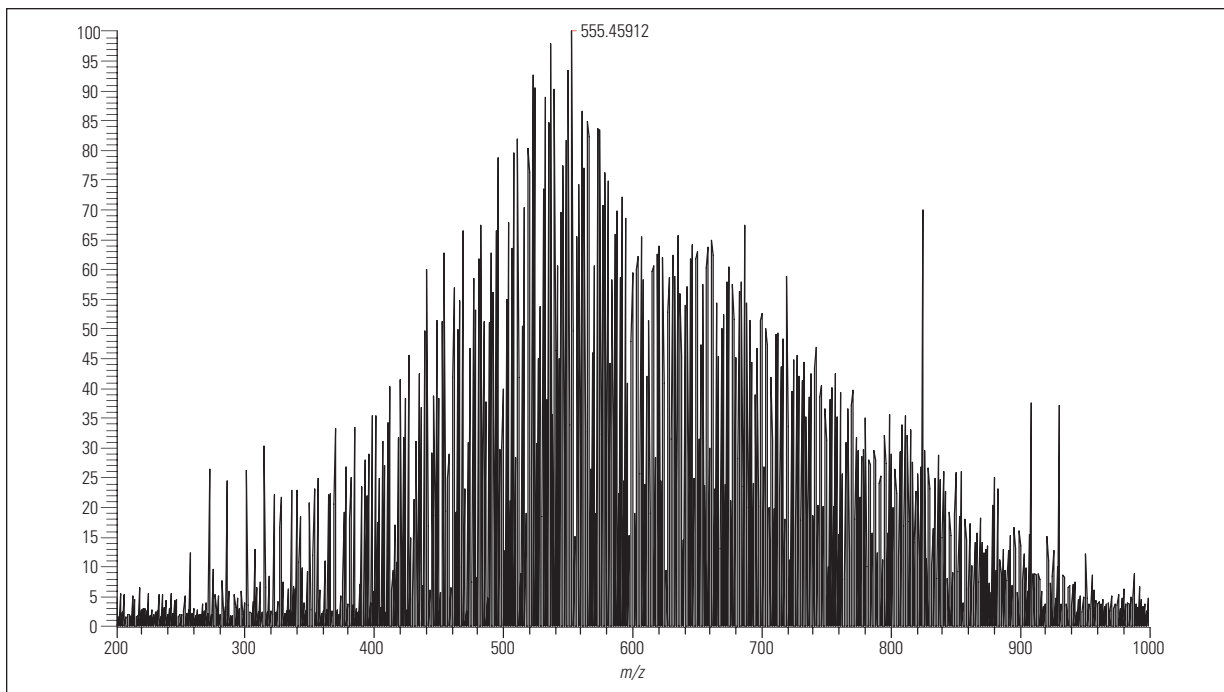


Figure 4a: Negative ion ESI mass spectrum of a heavy crude oil sample acquired at 200,000 resolving power.

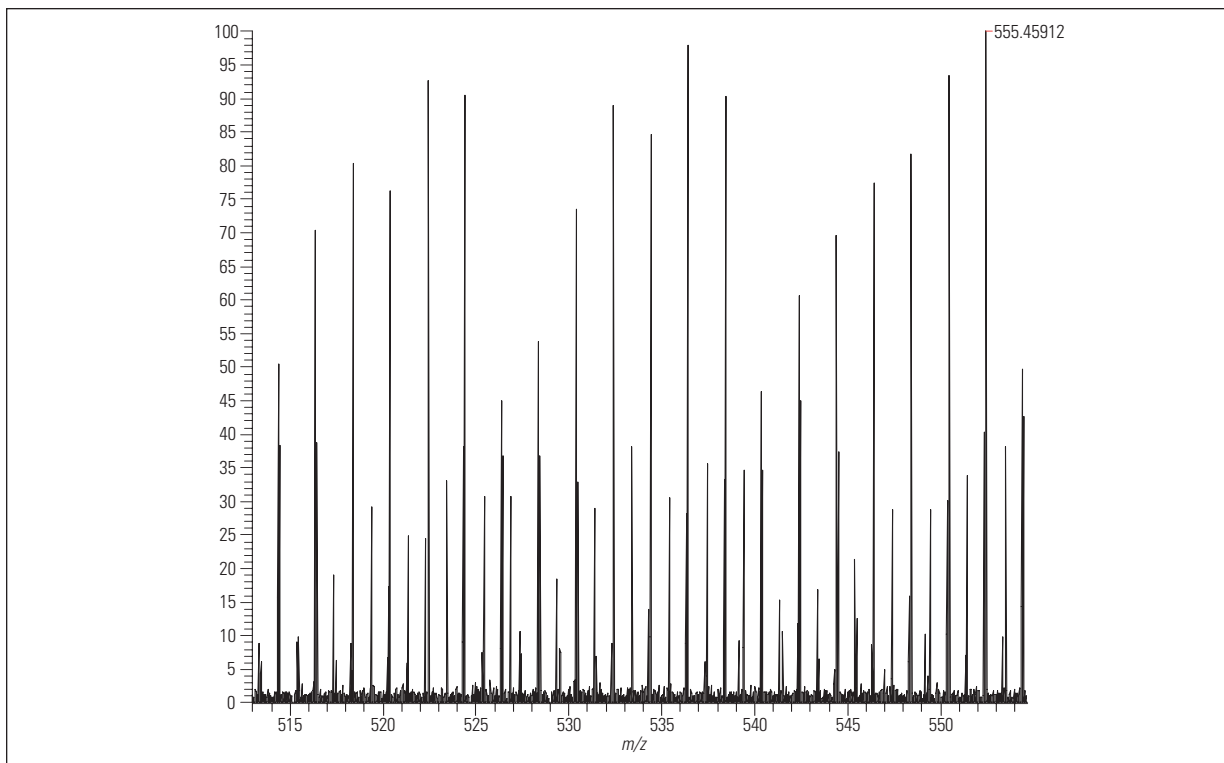


Figure 4b: An expanded segment of the full range spectrum, showing the ion signals at every nominal mass with clear 14.016 repeat.

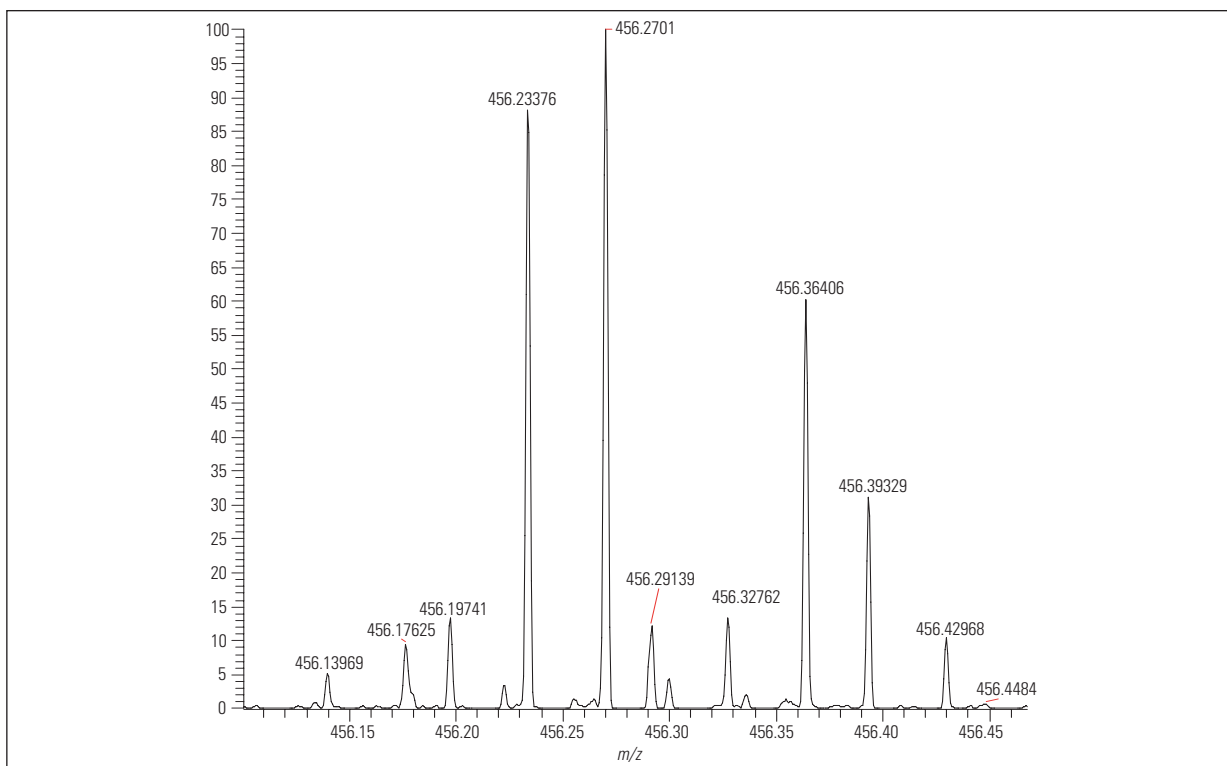


Figure 5: Narrow segment spectrum acquired by selective monitoring of mass m/z 457 ± 2 . Ultra-high resolving power ($\sim 190,000$) and mass accuracy allows direct assignment of nine chemically distinct species at a single nominal mass with 1.1 ppm RMS error (Table 3).

m/z	Relative Intensity	Elemental Composition (Neg. Ion)	Theoretical Mass	Error (ppm)
456.13969	5.78	C ₃₄ H ₁₈ N O	456.13939	0.7
456.17625	9.58	C ₃₅ H ₂₂ N	456.17577	1.0
456.19741	14.28	C ₃₂ H ₂₆ N O ₂	456.19690	1.1
456.22246	4	NO ID		
456.23376	90.44	C ₃₃ H ₃₀ N O	456.23329	1.0
456.25503	1.7	C ₃₀ H ₃₄ N O ₃	456.25442	1.3
456.27016	100	C ₃₄ H ₃₄ N	456.26967	1.1
456.29139	12.61	C ₃₁ H ₃₈ N O ₂	456.29080	1.3
456.32762	13.75	C ₃₂ H ₄₂ N O	456.32719	1.0
456.36406	60.22	C ₃₃ H ₄₆ N	456.36357	1.1
456.39329	31.68	NO ID		
456.42968	10.64	NO ID		

Table 3: Possible elemental composition of ions shown in Figure 5

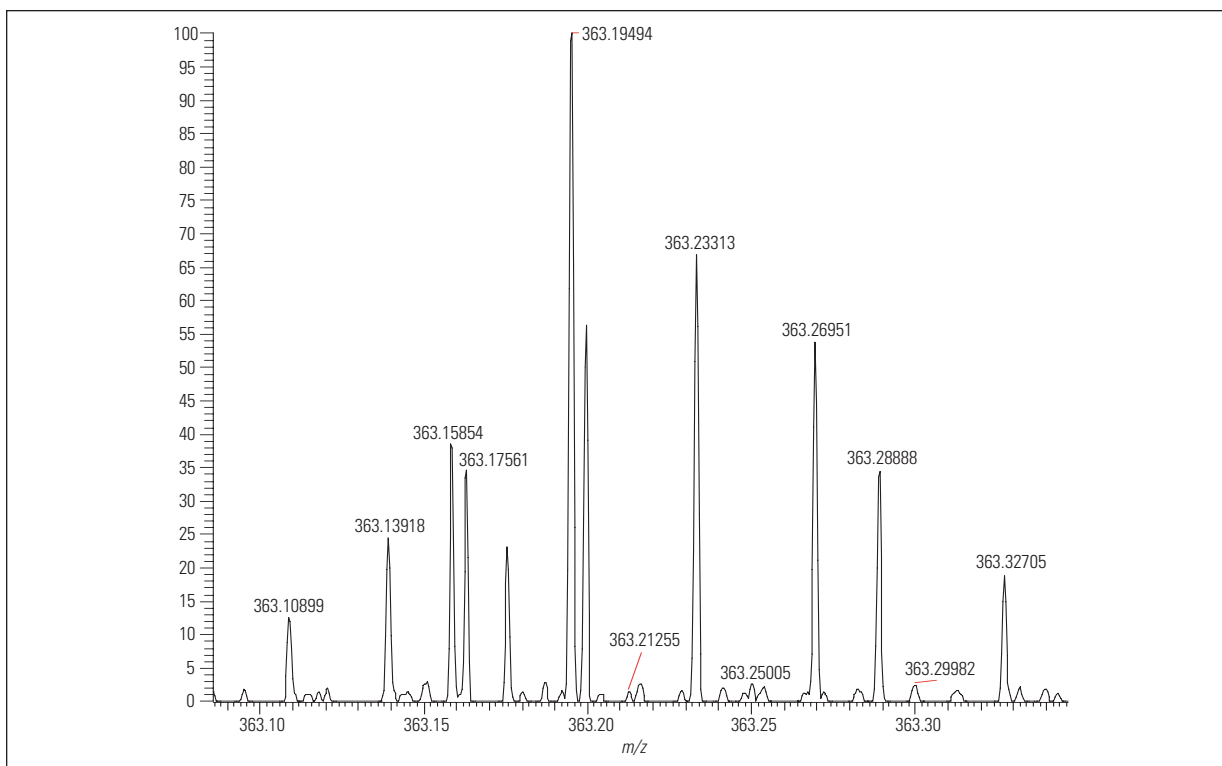


Figure 6: Narrow segment spectra acquired by selective monitoring of mass m/z 363 \pm 2. Ultra-high resolving power (\sim 230,000) and mass accuracy allows direct assignment of eleven chemically distinct species at a single nominal mass with 0.8 ppm RMS error (Table 4).

m/z	Relative Intensity	Elemental Composition (Neg. Ion)	Theoretical Mass	Error (ppm)
363.10899	12.68	C19 H23 O3 S2	363.10941	-1.2
363.13918	23.70	C26 H19 O2	363.13905	0.4
363.15854	39.11	C25 C13 H20 ON	363.15842	0.3
363.16298	34.83	C20 H27 O4 S	363.16356	-1.6
363.17561	22.55	C27 H23 O	363.17544	0.5
363.19494	100	C26 C13 H24 N	363.19481	0.4
363.19942	54.91	C21 H31 O3 S	363.19990	-1.4
363.23313	64.67	C25 H31 O2	363.23296	0.5
363.26951	55.14	C26 H35 O	363.26934	0.5
363.28888	35.01	C25 C13 H36 N	363.28873	0.5
363.32705	18.22	C24 H43 O2	363.32652	0.4

Table 4: Possible elemental compositions of ions shown in Figure 6

Conclusions

We demonstrated that the Finnigan LTQ FT mass spectrometer can be effectively used as a robust system for routine analysis of polar compounds in heavy petroleum. The combination of ultra-high resolving power and excellent mass accuracy allowed the determination of many overlapping isobaric species. In all, more than 5,000 chemically different components were estimated to be present in high resolution ESI spectra of crude oil.

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