

# Method Optimization for Comprehensive Characterization of Petroleum with High Resolution Time-of-Flight Mass Spectrometry Platforms

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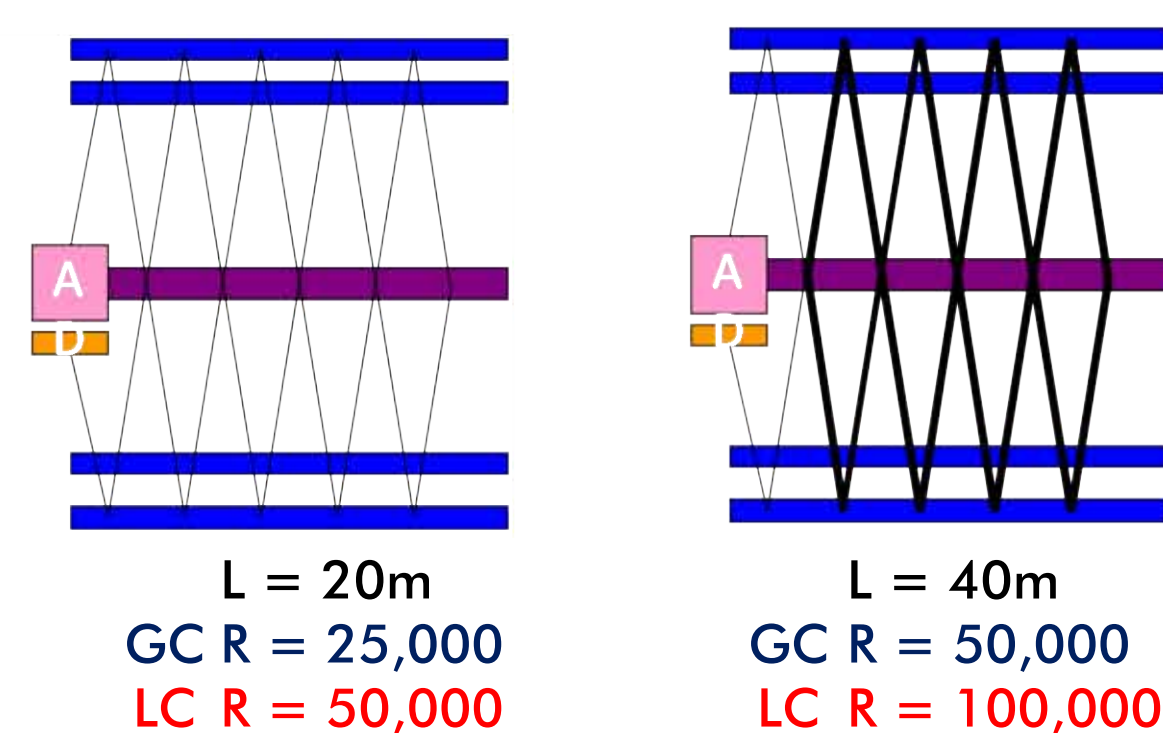
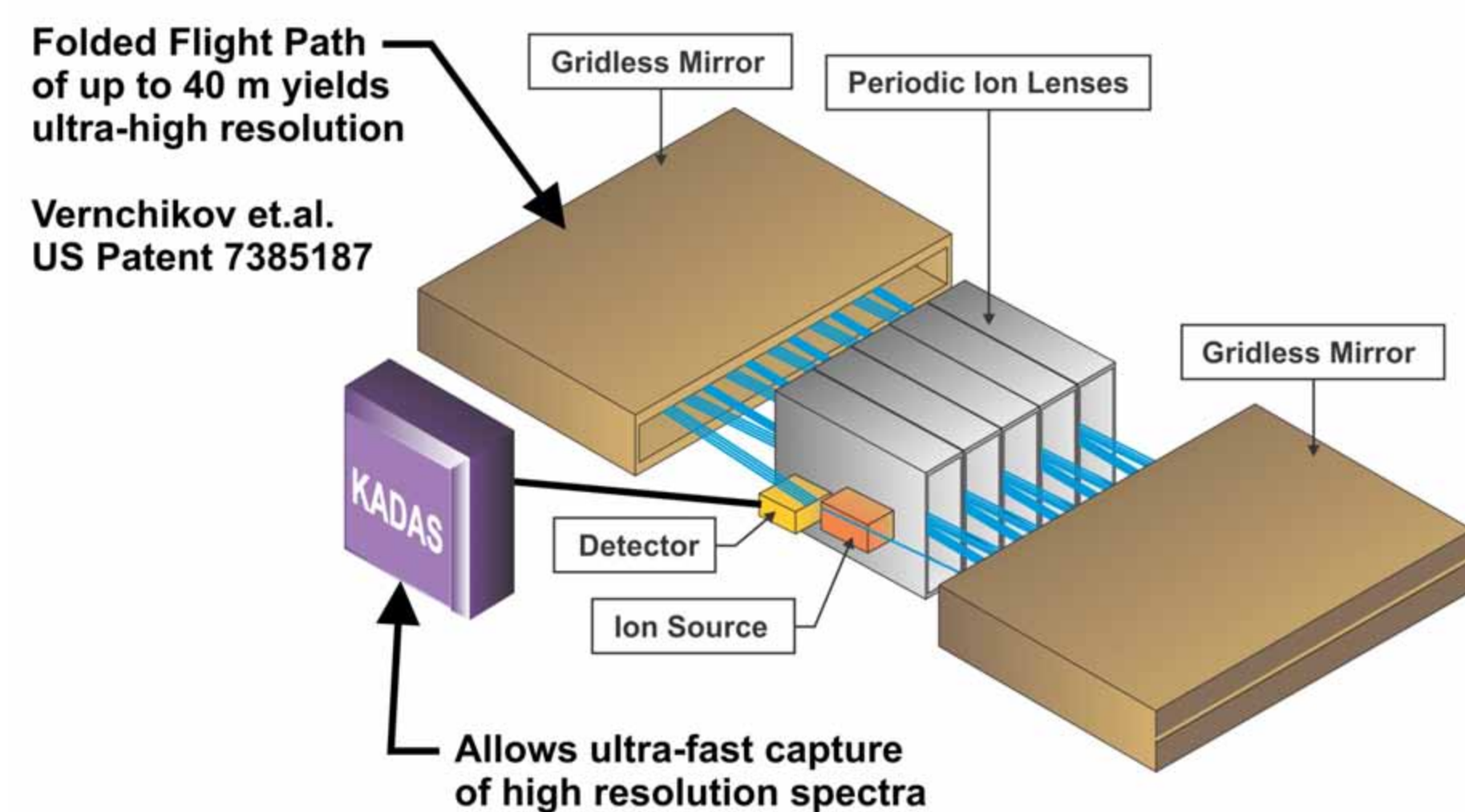
## Background

### Introduction

Petroleum is the most complex matrix in nature, constituted by many thousands of compounds. As such, petroleum analysis presents an analytical challenge, and for mass spectrometric analysis we need equipment with high resolving power and high mass accuracy. The matrix complexity and characterization needs demand analytical solutions that will identify individual components (micro-) while also providing differential information on contributions from key functional group contributions (macro-characterization). Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS) is the gold standard for comprehensive analysis of crude oil and petroleomic studies and offers both analytical capabilities mentioned. An alternative to FT-ICR MS is time-of-flight mass spectrometry (TOFMS), which offers continuous full range non-skewed mass spectral information and fast acquisition rates ideal for analyte identification of complex mixtures. TOFMS also offers the significant advantage of being readily interfaced to GC and providing acquisition rates compatible with GC. Advances in the resolution of TOFMS provide an alternative for most routine petroleomic MS studies using ESI, APCI, EI, and CI.

### Objective

In a previous work we compared the performance of an ultra-high resolution time-of-flight mass spectrometer with a Fourier transform ion cyclotron resonance mass spectrometer, showing an alternative for most routine crude oil analysis. In this work, we study the optimization and explore the capability of the analysis for comprehensive petroleomics based in ultra-high resolution time-of-flight mass spectrometry coupled with EI, CI, ESI, and APCI.



## Experimental

### MS Analysis

For ESI (+) and ESI (-) analysis, the crude oil samples were dissolved in 0.1% formic acid, or 0.1% ammonium hydroxide in 1:1 toluene/methanol to a concentration of 0.2 mg·mL<sup>-1</sup>. The sample solution at a flow rate of 10 μL·min<sup>-1</sup> was directly infused into the ESI source of a high resolution mass spectrometer with a multi-reflecting time-of-flight analyzer with resolving power ≥100,000 and mass accuracy of <1 ppm. Data were recorded in full MS mode from m/z 200-700 varying the number of spectra collected and the acquisition rate. Analysis using APCI (+) was performed with crude oil samples diluted in hexane in concentrations of 0.2 mg·mL<sup>-1</sup>, infused at a flow rate of 50 μL·min<sup>-1</sup>. The samples were diluted in toluene and injected into the gas chromatograph's split/splitless inlet with helium carrier gas. The analyses were performed in both EI and CI (CH<sub>4</sub>) modes to aid in structural elucidation. Data was acquired in high resolution mode yielding a nominal resolving power of 25,000 with mass accuracy of <1 ppm. Data were recorded in full MS mode from 50-800 m/z.

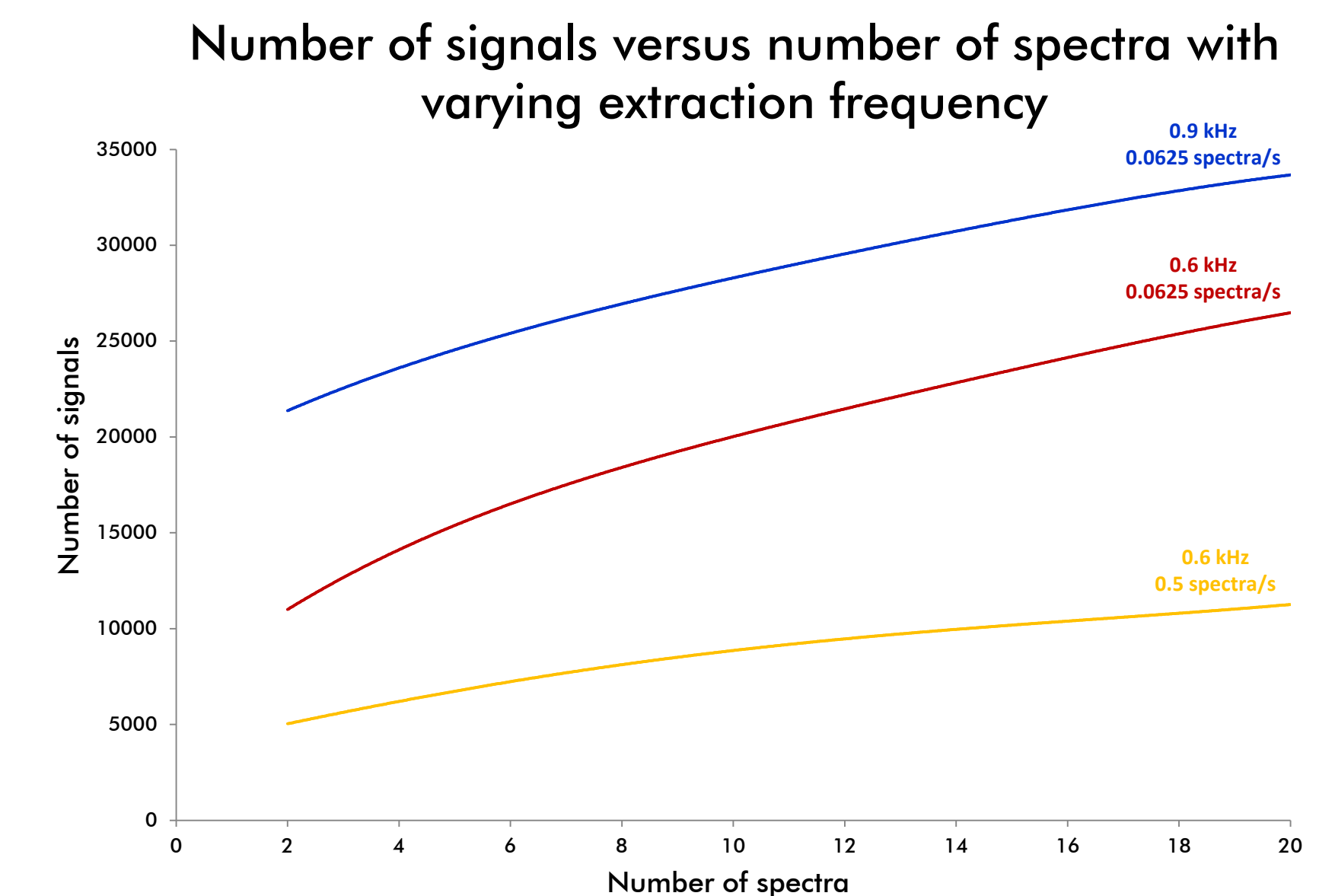
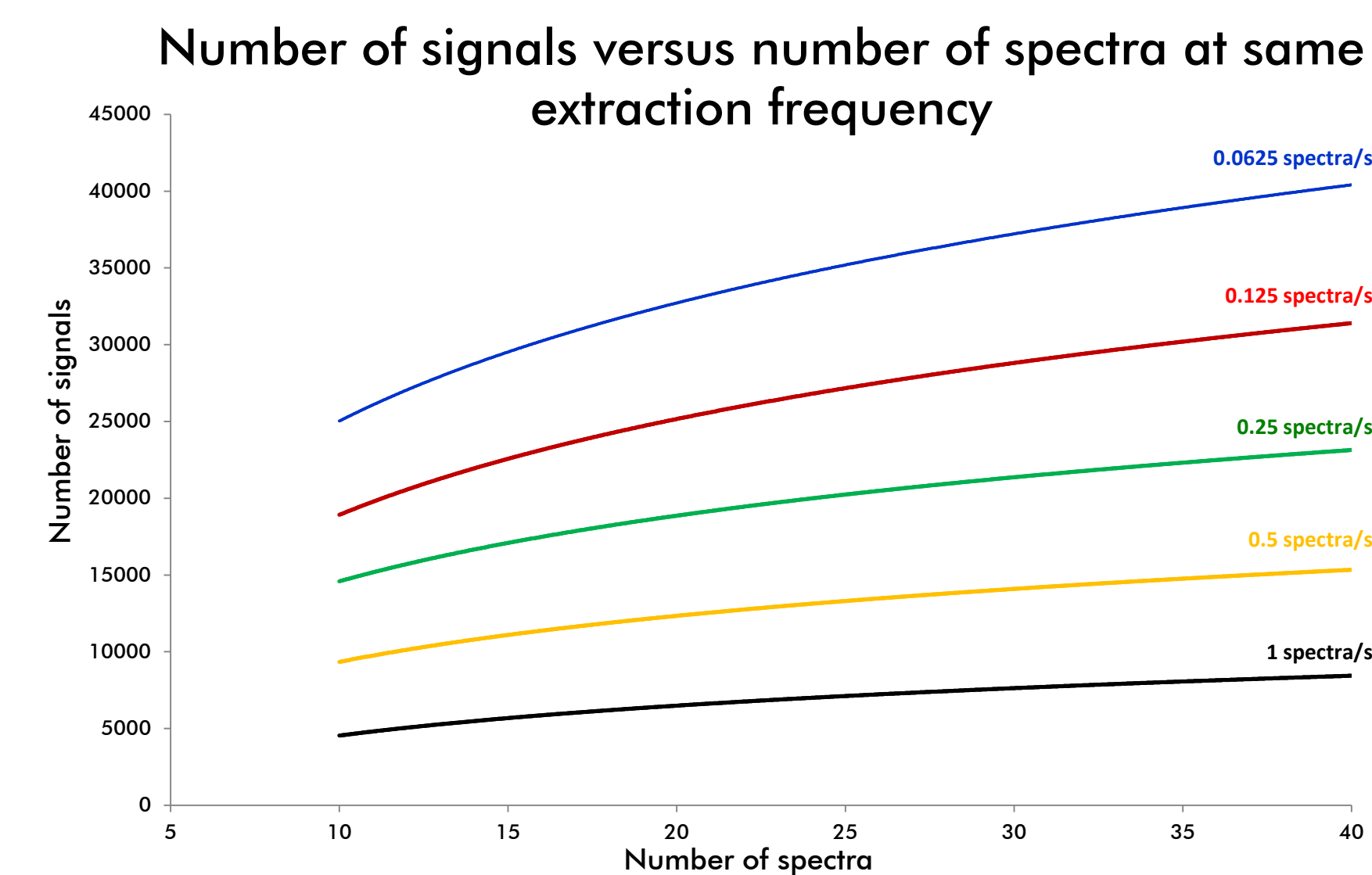
### Data Analysis

The exported m/z lists with respective intensities were processed in PetroOrg software (Omics, LLC, Tallahassee, FL) for class distribution and Carbon Number versus DBE plots. The raw data was calibrated using tables of theoretical homologous series for the most abundant class observed in each sample. DBE (C<sub>c</sub>H<sub>h</sub>N<sub>n</sub>O<sub>o</sub>S<sub>s</sub>) = c - h/2 + n/2 + 1.

## Results

Preliminary results show that gas chromatography coupled with high resolution time-of-flight mass spectrometry with electron and chemical ionization can be useful for petroleomic studies, with evaluation of carbon number and DBE plots (PetroOrg) serving the same role, and being comparable to those from ESI-MS. The hydrocarbons and aromatics are the most abundant class, and heteroatomic class in abundance greater than 1% can be analyzed. Besides saturated and aromatic hydrocarbons, sulfur compounds which do not ionize with electrospray can be identified with chemical ionization as thiophenes, benzo- and dibenzothiophenes. Chemical ionization provides additional information of class composition, showing the relative distribution of hydrocarbons and (N, O, S)- heterocyclic compounds. Members of homologous series are better distinguished and compared using CI in conjunction with EI. The robust mass accuracy (<1 ppm) and high resolving power provide information not previously and directly available. Acquisition rates of eight to ten spectra/second are sufficient for the GC-HRT MS analysis of crude oil. For direct infusion with ESI- and APCI-HRT MS, the acquisition rate of one spectrum/second is sufficient for the characterization of the most abundant classes of heteroatomic components. Slow acquisition rates (0.0625 spectra/second) with 20 summed spectra allow for the characterization of all heteroatomic class in abundance greater than 1% with better accuracy than higher acquisition rates. Peak area values provide a more robust measure than peak height, and facilitates more signal assignments. Mass accuracies of better than 1 ppm were typically observed, and system resolution was 100,000 or higher. Atmospheric pressure chemical ionization can be effectively used for petroleomic studies to provide information which is complementary to that from ESI. The hydrocarbons and aromatics are the most abundant class, and heteroatomic class in abundance greater than 1% can be analyzed. Besides saturated and aromatic hydrocarbons, sulfur compounds which do not ionize with electrospray can be identified with atmospheric pressure chemical ionization. The mass accuracy and resolution are pivotal to the identification and quantification of the low abundance sulfur-containing components.

## HRT MS Direct Analysis of Crude Oil Sample Optimization



### Best Acquisition Condition for Crude Oil

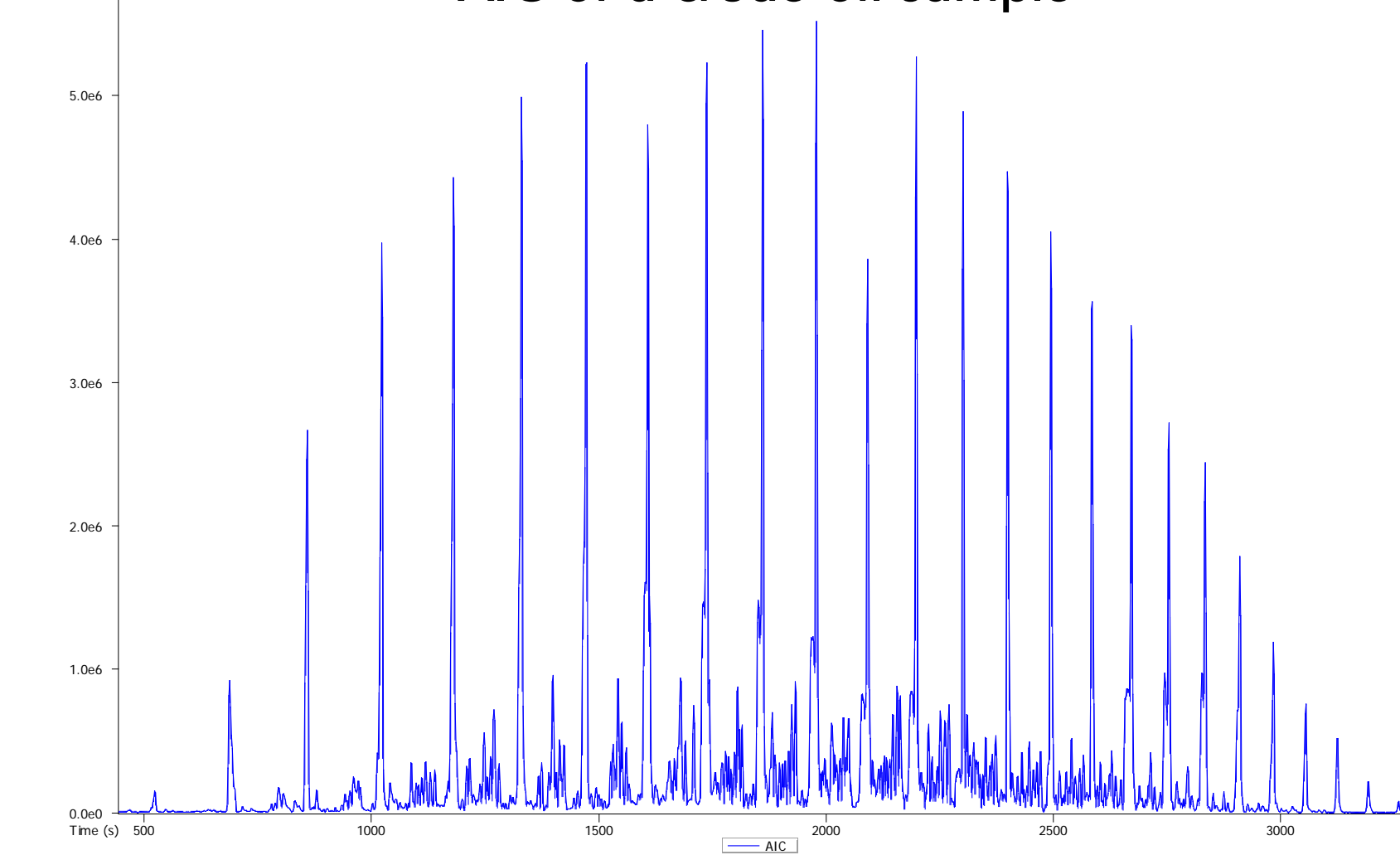
Class N RMS					
# Spectra	Spectra/s	Error (ppm)	Identified m/z	# Classes	Time (s)
20	0.0625	0.65	2251	20	320

### Repeatability

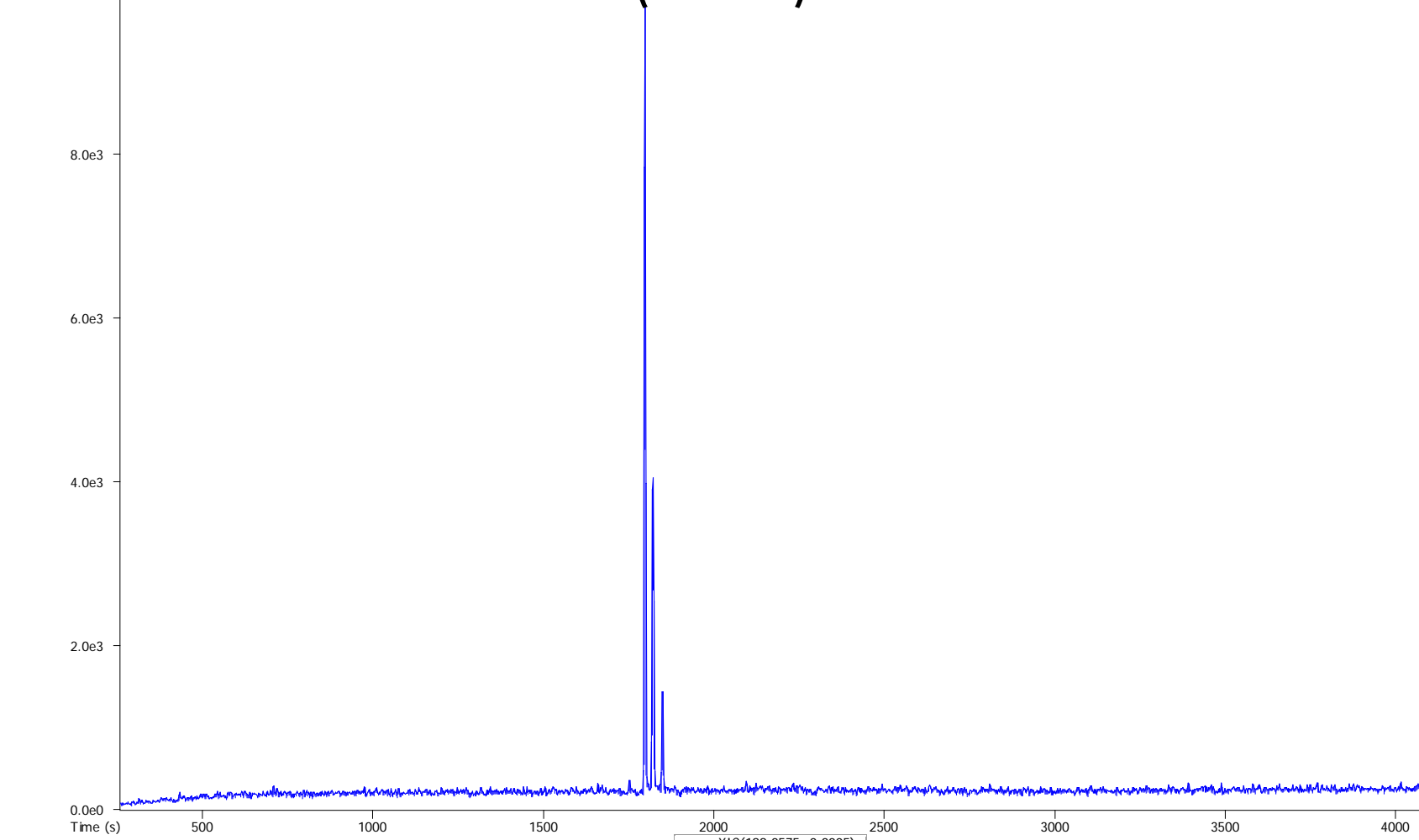
Analysis	Class N		Average m/z	Average Carbon #	Average DBE #	Average Measured m/z *	Error* (ppm)
	RMS Error (ppm)	Identified m/z					
1	0.66	2505	415.9083	29.91	10.91	406.34675	+0.20
2	0.63	2251	415.2115	29.86	10.93	406.34678	+0.13
3	0.65	2490	414.3675	29.79	10.89	406.34679	+0.11
4	0.63	1924	413.2184	29.71	10.86	406.34685	-0.03
5	0.65	2299	414.4425	29.80	10.88	406.34677	+0.16

## CI (+) GC-HRT MS Analysis of Crude Oil Sample

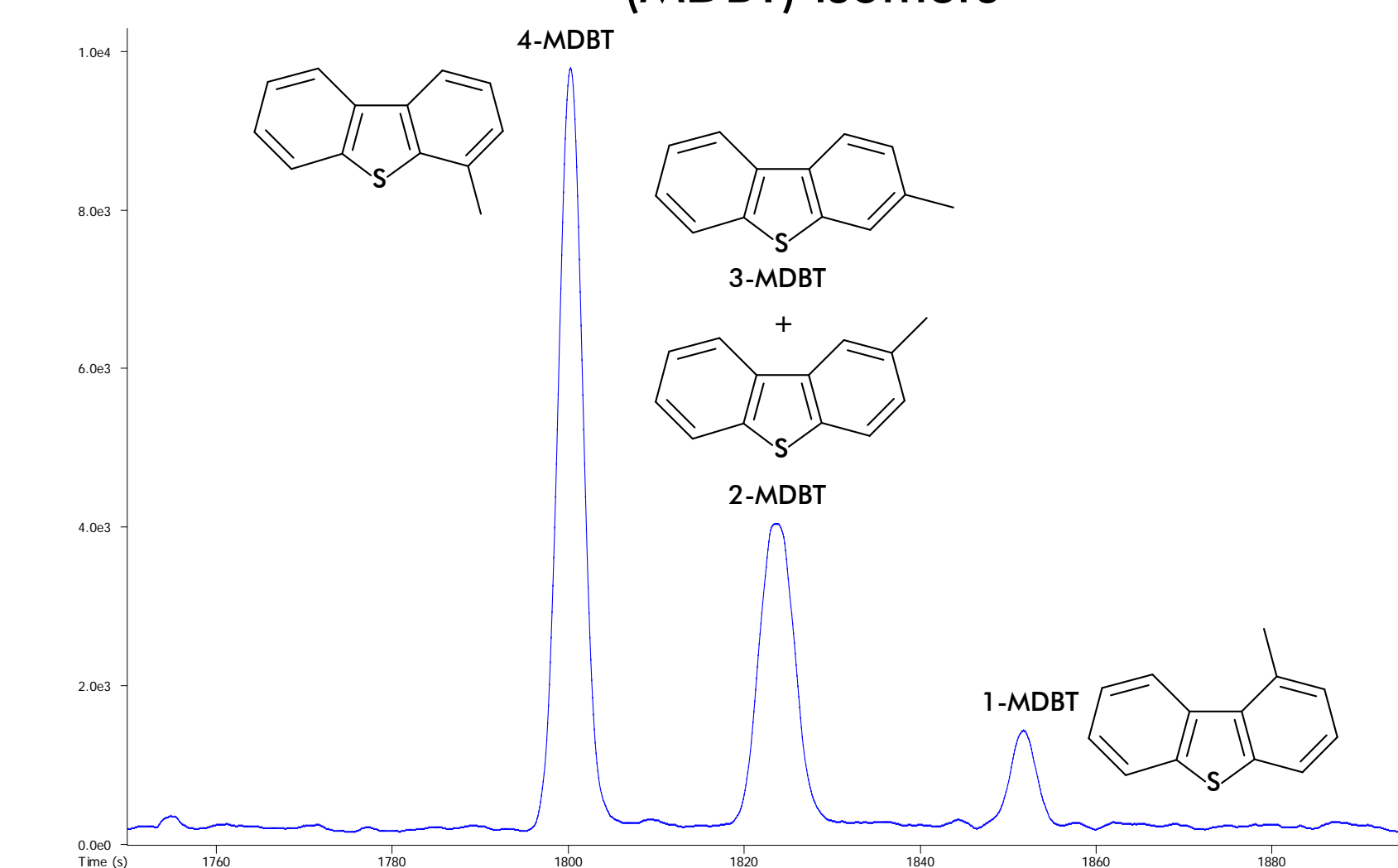
### AIC of a crude oil sample



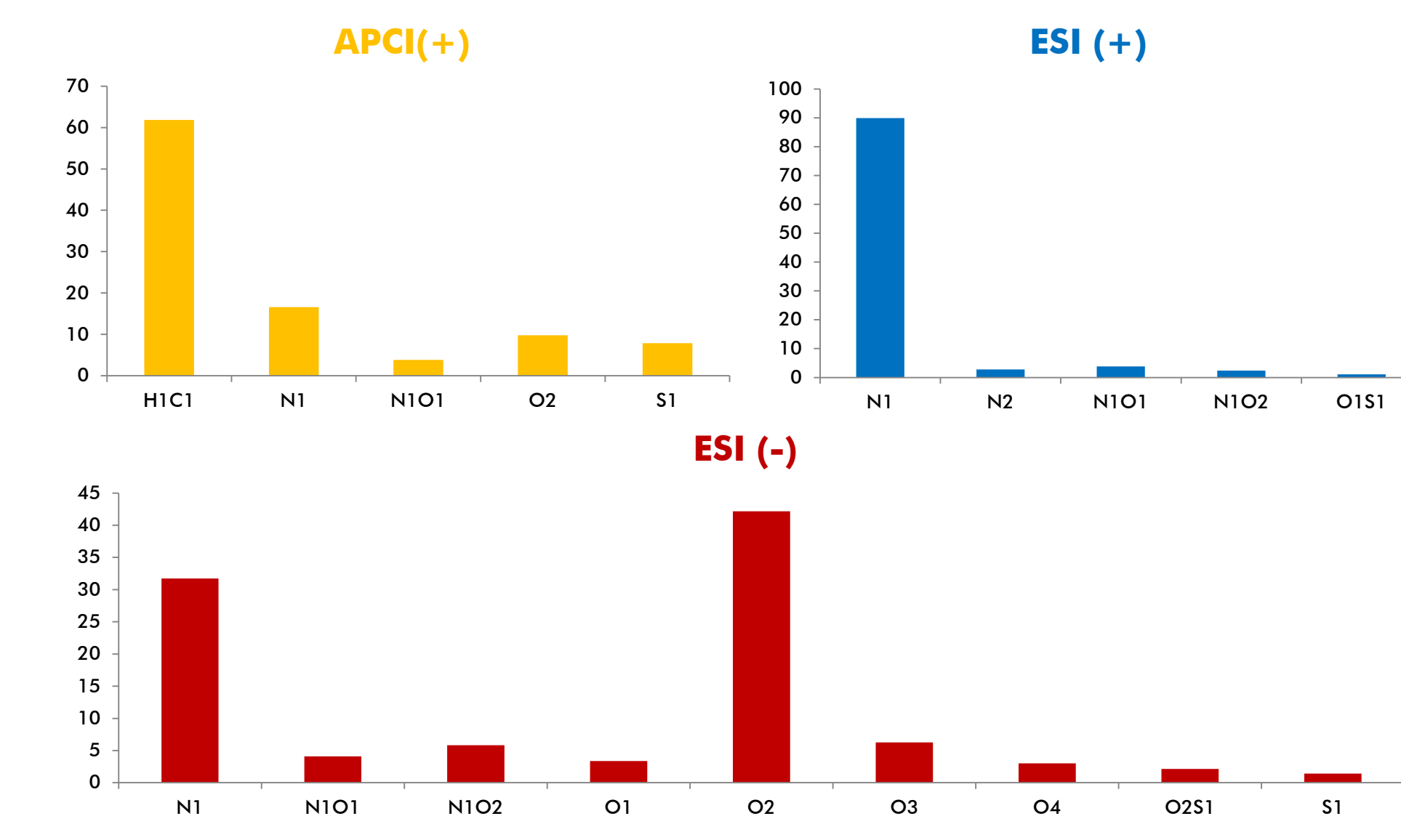
### XIC of m/z 199.0575 for methylidibenzothiophene (MDBT) isomers



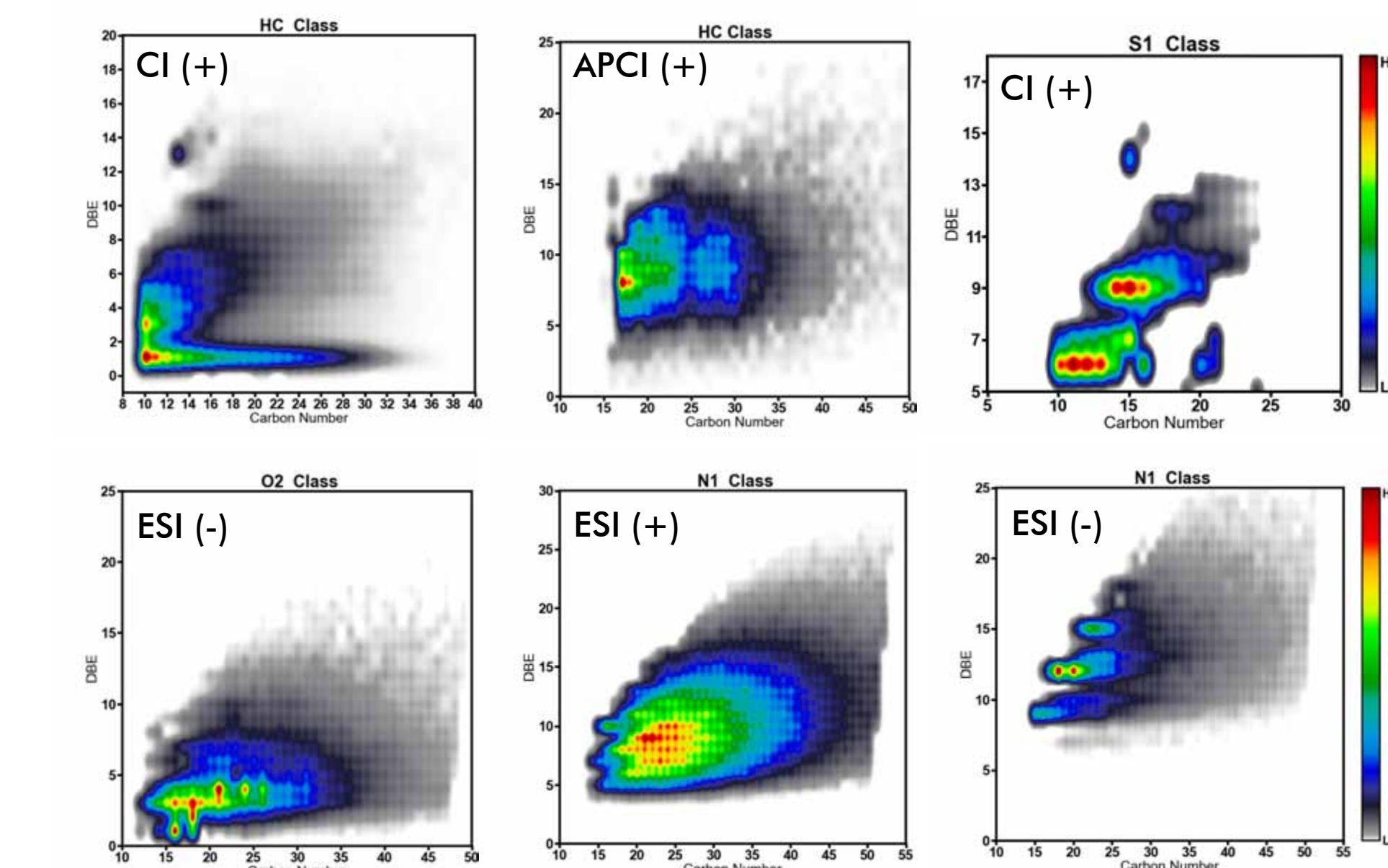
### XIC of m/z 199.0575 for methylidibenzothiophene (MDBT) isomers



## Class Distribution



## DBE vs. Carbon Number Plots



## Conclusions

GC-HRT MS reflects the analysis of ESI-HRT MS and APCI-HRT MS. Sulfur heterocyclic compounds can be easily identified by EI, CI, and APCI. Volatile hydrocarbons and aromatics compounds can be identified by EI and CI. APCI is useful in the characterization of less volatile and more heavy aromatic compounds, and ESI shows the composition of more polar compounds. These results show the utility of high resolution time-of-flight mass spectrometry with high mass accuracy for comprehensive petroleomic studies. GC-HRT MS is especially useful for adding structural information in the analysis of complex samples like crude oil.