Unprecedented Ultrahigh Resolution FT-ICR Mass Spectrometry and Parts-Per-Billion Mass Accuracy Enable Direct Characterization of Nickel and Vanadyl Porphyrins in Petroleum from Natural Seeps

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Results and Discussion

The most abundant and problematic metal compounds in crude oil exist as organic complexes of vanadium and nickel in porphyrin structures derived from biological molecules (chlorophyll and heme), the first petroleum biomarkers discovered by Alfred Treibs in the early 1930s.[1] Detailed characterization of the type and structure of porphyrins is critical for development of petroleum upgrading processes, but also link crude oil to source rock conditions. Because petroporphyrins concentrate in heavy oils, direct characterization challenges routine analytical techniques due to the increased complexity associated with heavy crudes. Atmospheric pressure photoionization (APPI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) provides ultrahigh resolving power ($m/\Delta m_{50\%}$ > 1,000,000 at *m/z* 500) and sub-ppm mass error (<50 ppb) required to identify nickel porphyrin isotopes for unambiguous elemental composition assignment. We also report the first simultaneous identification and categorization of both vanadyl and nickel porphyrins in the same sample, without prior sample fractionation. More than 85,000 mass spectral peaks are resolved and identified in a single mass spectrum, and represent the most extensive molecular deconvolution of an organic mixture characterized to date.

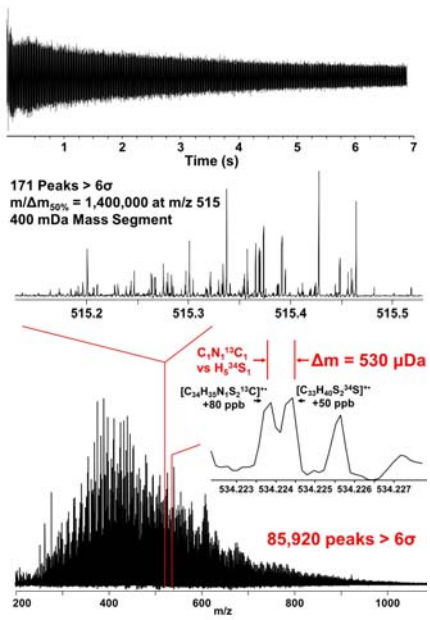

Figure 1. Broadband positive-ion APPI FT-ICR mass spectrum for an *Il Duomo* asphalt volcano sample. The achieved resolving power $m/\Delta m_{50\%}$ = 1,400,000 at *m/z* 515 enables resolution of 85,920 mass spectral peaks, each with magnitude greater than 6σ of baseline rms noise (*m/z* 200-1100) with a mass distribution centered at *m/z* 400. The mass scale-expanded segment at *m/z* 515 shows ~171 peaks. The theoretical resolving power required to separate two equally abundant species that differ in mass by ~548 μDa at 9.4 tesla is 890,000. The presently achieved resolving power ($m/\Delta m_{50\%}$ = 1,400,000 at *m/z* 515) enables separation of species that differ in mass by $C_1N_1{}^{13}C_1$ versus $H_5{}^{34}S_1$, both of nominal mass 39 Da, and differing in mass by 530 μDa—i.e., less than the mass of an electron (548 μDa). To the best of our knowledge, this mass spectrum represents the most peaks resolved and identified in a single spectrum of any kind, and represents the highest broadband resolving power for any petroleum mass spectrum, and emphasizes the need for ultrahigh resolving power achievable only by FT-ICR MS sufficient to separate isobaric overlaps prevalent in complex seep samples.

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References [1] McKenna, A.M. *et al*., Energy Fuels., **28**, 2454-2464 (2014)