Chromatographic Enrichment and Subsequent Separation of Nickel and Vanadyl Porphyrins from Natural Seeps and Molecular Characterization by Positive Electrospray Ionization FT-ICR Mass Spectrometry

Putman, J.C.; Rowland, S.M. (NHMFL, FSU, Chemistry); Corilo, Y.E. (NHMFL, Chemistry); McKenna, A.M. (NHMFL, Chemistry)

Results and Discussion

We report a novel chromatographic method to enrich and separate nickel and vanadyl porphyrins from a natural seep sample, and combine molecular level characterization by positive-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Vanadyl and nickel porphyrin model compound elution from primary secondary amine (PSA) stationary phase combined with UV-vis spectroscopy confirms enrichment and subsequent fractionation of nickel and vanadyl porphyrins into polarity-based sub-fractions. A more than 100-fold increase in signal-to-noise ratio for nickel porphyrins enables unequivocal elemental composition assignment confirmed by isotopic fine structure for all isotopes >1% relative abundance, and the first mass spectral identification of ^{61}Ni porphyrin isotopologues derived from natural seeps. Oxygen-containing vanadyl porphyrins and sulfur-containing vanadyl porphyrins are isolated in the same fraction simultaneously from the same sample. We provide the first chromatographic evidence of carboxylic acid functionalities peripheral from the porphyrin core.

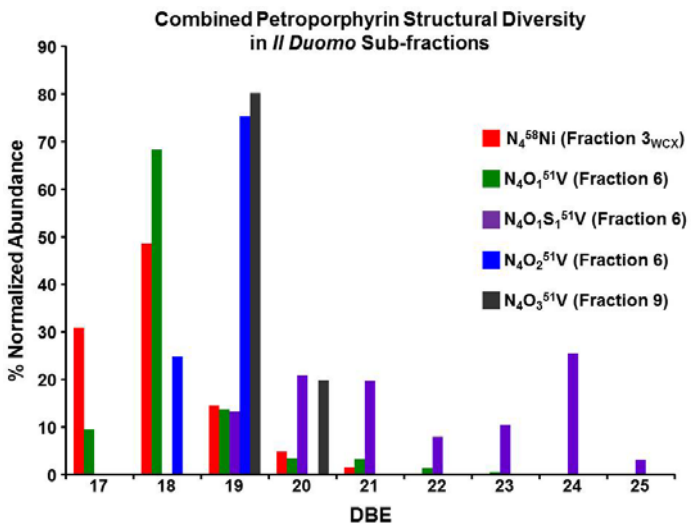

Figure 1. Normalized DBE (double bond equivalents) distribution for $N_4{}^{58}Ni$, $N_4O_1{}^{51}V$, $N_4O_1S_1{}^{51}V$, $N_4O_2{}^{51}V$, and $N_4O_3{}^{51}V$ porphyrin classes identified after chromatographic fractionation. The percent relative abundance for each class was normalized to 100% total abundance for each class. The addition of one oxygen atom ($N_4O_2{}^{51}V$) corresponds to DBE values of 18 and 19, which indicates preferential incorporation of ketone/aldehyde functionalities to etio and DPEP core structures. The observed increase in DBE and coelution of $N_4O_3{}^{51}V$ porphyrins with naphthenic acids provides mass spectral and chromatographic evidence of carboxylic acid-functionalized vanadyl porphyrins, and $C_cH_hN_4VO_2$ porphyrins were detected in fraction 6.

Acknowledgements

This work was supported by NSF Division of Materials Research through DMR-1157490, BP/The Gulf of Mexico Research Initiative to the Deep-C Consortium, and the State of Florida.

References

[1] Putman, J.C., *et al*., Anal. Chem., **86**, 10708-10715 (2014)