UNVEILING THE MOLECULAR COMPLEXITY OF PRODUCED WATER: FROM PREDICTIVE MODELING TO HPLC-21T FT-ICR MS

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Produced water (PW) is a highly complex byproduct of the petroleum industry that contains environmentally toxic naphthenic acids (NAs) [1]. Characterizing these persistent contaminants requires resolution far beyond standard methods. Here, we detail a progressive analytical framework utilizing high-resolution mass spectrometry to characterize, quantify, and predict NA behavior, aiding both environmental mitigation and operational decisions.

Our foundational research established petroleomic baselines utilizing ESI(-)-Orbitrap and 7T FT-ICR MS. To translate these molecular fingerprints into actionable operational insights, we simulated NA migration from 23 crude oils into artificial seawater. Extracting the simulated PW via dispersive liquid–liquid microextraction (DLLME), we leveraged UHRMS-derived descriptors to construct a random forest (RF) classifier. This model successfully predicted NA migration propensity—quantified by the migrated fraction (MigF) — with predictive metrics (AUC = 1.00; precision = 1.00). The data revealed selective migration of lower-molecular-weight structures up to a double-bond equivalent (DBE) of 12. This predictive tool effectively captures nonlinear NA migration patterns in real samples, enabling proactive operational adjustments before acids accumulate in the PW.

Despite these advances, standard direct infusion (DI) analyses suffer from severe ion suppression, obscuring highly polar, multi-oxygenated environmental markers. To further scrutinize these organic extracts, we implemented an ultra-high-resolution HPLC-21T FT-ICR MS workflow. Chromatographic separation utilized a dimethylaminopropyl-functionalized polymeric stationary phase [2] across a 105-minute gradient, transitioning from pure methanol to a water/diethylamine mixture.

This chromatographic deconvolution completely redefined the sample's molecular profile. Early eluting fractions consisted of low-polarity species, while later fractions systematically shifted toward highly polar, oxygen-rich species. As visually evidenced by comparative Ox class distributions, DI intensity appears artificially flattened (peaking modestly at 13-16% for O4-O6. Conversely, fractionated LC-MS unmasks extreme, localized concentrations: LCMS Peak 5 exhibits a massive intensity spike at the O2 class (~29%), Peak 4 is dominated by species (~25%), and Peak 3 isolates a majority of O4 species (>32%).

Crucially, this HPLC-21T FT-ICR MS approach expands our analytical window continuously through the class into high O/C chemical space. By unlocking previously suppressed multi-oxygenated NAs and polar aromatic compounds, this integrated workflow provides the granular mapping essential for environmental monitoring and supporting advanced water treatment processes.

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