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Positive Ion Electrospray Ionization Suppression in Petroleum and Complex Mixtures

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Results and Discussion

Since the emergence of high resolving power crude oil mass spectrometry two decades ago, hundreds of publications and presentations have detailed petroleum complex mixtures by electrospray ionization (ESI) mass spectrometry (MS). None of these works have reported or detailed ion suppression (also referred to as ionization biasing or matrix effects) which is a well-known feature of ESI. Here, we show the extreme consequences of ionization biasing within a narrow, 1 order of magnitude concentration range for crude oil mixture direct infusion experiments in positive ion (+) ESI. An oil spill contaminant, a crude oil, and an equimolar model compound mixture were electrosprayed at various analyte and acid modifier concentrations for 9.4 T Fourier transform ion cyclotron resonance (FT-ICR) and time-of-flight (TOF) MS analysis. A 3-fold increase in the number of elemental compositions is achieved by optimization of analyte and acid concentration. At high analyte concentration, oxygen heteroatom class (i.e., CcHhOx species, denoted henceforth simply as Ox) abundance is attenuated and practically nullified (see Figure 1). The suppression can be understood from (+) ESI TOF mass analysis of a prepared equimolar model compound mixture, particularly those with ketone functional groups. We recommend operating at mass/volume petroleum residue concentration below 0.1 mg/mL in 1:1 (v:v) toluene/methanol with formic acid at 2.5% (v:v)...

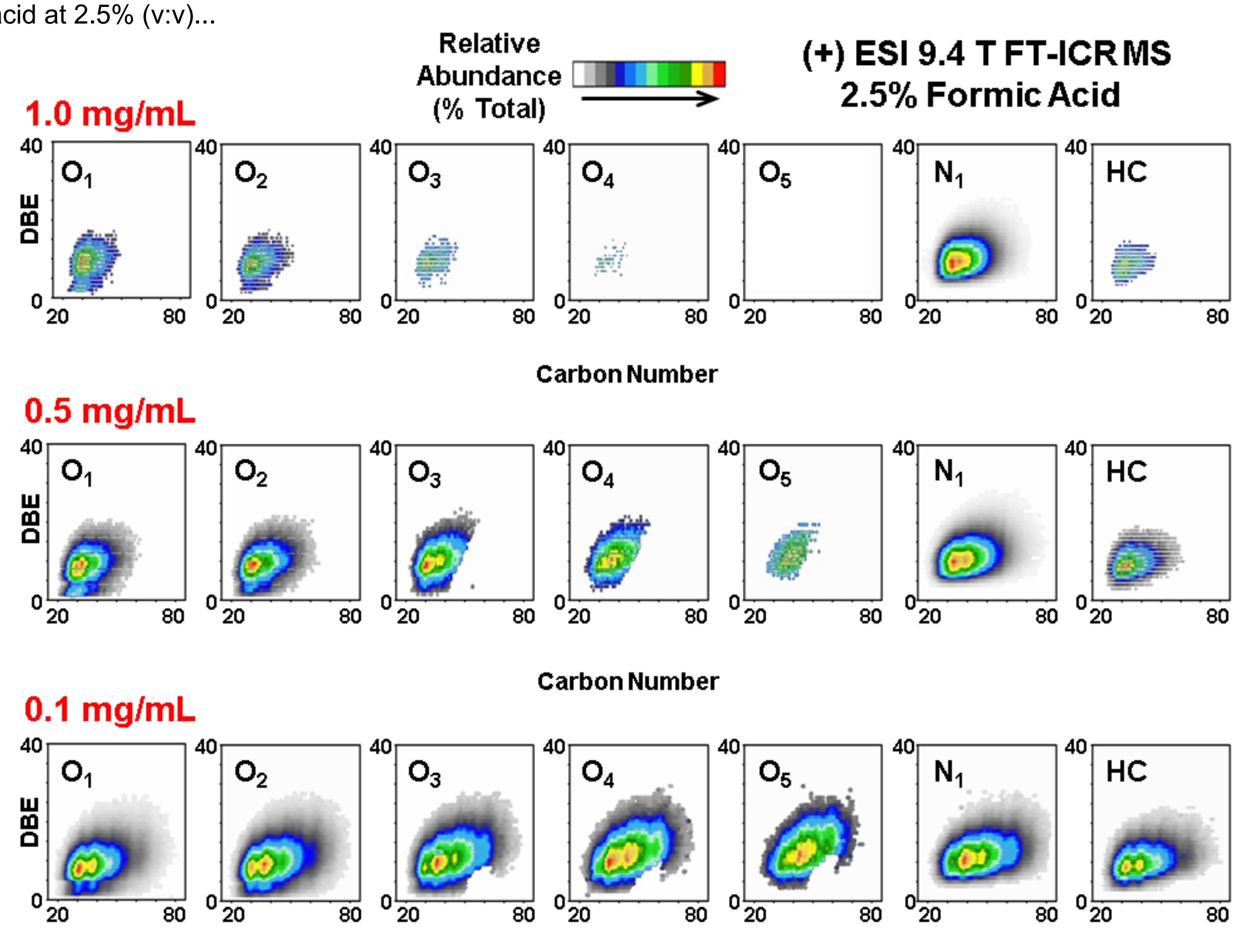

Fig. 1. O_1, O_2, O_3, O_4, O_5, N_1, and hydrocarbon heteroatom class isoabundance-contoured double bond equivalents (DBE) vs. carbon number plots for an oil spill contaminant at 2.5% percent formic acid concentration and analyte concentration 1.0 mg/mL (top), 0.5 mg/mL (middle), and 0.1 mg/mL (bottom)..

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References

[1] Ruddy, B. M.; *et al.*, Energy & Fuels **32**, 2901-2907 (2018).