

Lithium Cationization for Petroleum Analysis by Positive Ion Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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ABSTRACT: Lithium cationization can significantly extend the compositional range for analysis of petroleum components by positive electrospray ionization [(+) ESI], by accessing species that lack a basic nitrogen atom and, hence, are not seen by conventional (+) ESI that relies on protonation as the primary ionization mechanism. Here, various solvent compositions and lithium salts enabled us to optimize ionization by formation of lithium adducts ($[M + Li]^+$), and the results are compared to production of $[M + H]^+$ by conventional (+) ESI with formic acid. Lithium cationization (+) ESI Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) of Athabasca bitumen heavy vacuum gas oil (475–500 °C) and North and South American crude oils demonstrates considerable improvement over protonation for production of ions from compounds belonging to S_xO_y ($SO, SO_2, SO_3, SO_4, S_2O, S_2O_2$, etc.) heteroatom classes. Those compounds exhibit much higher affinity for lithium cation than for proton and yield abundant $[M + Li]^+$ ions. Li^+ cationization thus opens a pathway for detection and characterization of S_xO_y class compounds that preferentially concentrate at the interface in oil/water emulsions.

■ INTRODUCTION

The polar constituents of crude oil (containing N, O, and S heteroatoms) generate severe negative industrial (corrosion, emulsion and deposit formation, catalyst poisoning, etc.) and environmental (pollution of soil and water because of an oil spill, emission of NO_x and SO_x to the atmosphere, etc.) impacts and have become the subject of detailed compositional characterization by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS).^{1–4} Knowledge of the structure and chemistry of these compounds is critical for design and development of new production and processing technologies as well as evaluation of environmental consequences of oil leakage and spills.

ESI FT-ICR MS can eliminate tedious and time-consuming fractionation and sample preparation and yields molecular weight, type [rings plus double bonds to carbon = double bond equivalents (DBE)],⁵ and heteroatom and carbon number distributions in complex organic mixtures. Prior work demonstrates that the nonpareil mass accuracy [root-mean-square (rms) mass error less than 500 ppb] and ultrahigh mass resolving power ($m/\Delta m_{50\%} > 500\,000$ up to 1000 Da, in which $\Delta m_{50\%}$ is the mass spectral peak full width at half-maximum peak height) of ESI FT-ICR MS allow for the rapid identification of up to tens of thousands of different elemental compositions ($C_xH_yN_zO_wS_t$) of polar components of petroleum crude oil and its derivatives.³ The success of the first ESI FT-ICR MS analyses of crude oil^{6–8} led to the rapid expansion of electrospray ionization (ESI) to other petroleum-derived materials, coal,^{9–11} and environmental applications.^{12–16}

Conventional ESI typically generates $[M + H]^+$ or $[M - H]^-$ ions at atmospheric pressure via protonation or deprotonation and, thus, enables rapid characterization of acidic and basic components in petroleum mixtures.^{1,4,8,17,18} However, only the most basic (typically pyridinic nitrogen) or acidic (typically carboxylic) functionalities are protonated (typically by formic acid) or deprotonated (typically by ammonium hydroxide) by conventional ESI. Compound classes that are insufficiently basic (e.g., sulfoxides and non-basic N heterocycles) or acidic (e.g., phenols) are either not ionized at all or ionized only to a small extent.¹⁹

The addition of alkali metal cations has been observed for a wide range of organic and biologically important molecules (e.g., peptides, proteins, and carbohydrates).^{20–22} Here, we offer a simple, solution-based alternative to conventional positive-ion electrospray to access a wider range of chemical functionalities through Li^+ cationization and demonstrate its applicability to petroleum when coupled to ultrahigh-resolution FT-ICR mass analysis.

■ EXPERIMENTAL SECTION

Samples and Reagents. Previously characterized Athabasca bitumen heavy vacuum gas oil at 475–500 °C, (National Centre for Upgrading Technology, Devon, Alberta, Canada)^{19,23} a North American crude oil, and a South American crude oil^{24,25} were selected as representative crude oil samples. Methanol (MeOH), acetonitrile (AcCN), toluene [all solvents of high-performance liquid chromatog-

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raphy (HPLC) grade], concentrated formic acid (HCOOH), lithium triflate (LiOTf), lithium bromide (LiBr), and lithium chloride (LiCl) in the highest commercially available purity were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO). Each petroleum sample was dissolved in a 1:1 (v/v) solution of toluene/methanol to a final concentration of $250 \mu\text{g/mL}$. LiOTf , LiBr , or LiCl were introduced at various concentrations to study the effect of selective lithium cationization, and the (+) ESI FT-ICR MS results were compared to those for toluene/methanol solutions of the samples containing 1% HCOOH (i.e., protonation is the only mechanism of ionization). Optimal conditions for the generation of ions under ESI by Li^+ cationization were achieved at a LiCl concentration of $500 \mu\text{g/mL}$.

Instrumentation. The samples were analyzed with a custom-built FT-ICR mass spectrometer equipped with a 9.4 T horizontal 220 mm bore diameter superconducting solenoid magnet,²⁶ equipped with a modular ICR data station (Predator) for instrument control, data acquisition, and data analysis.²⁷ ESI was produced from a syringe-pumped (400 nL/min) needle (50 μm inner diameter) under typical ESI conditions (electrospray needle, +2.2 kV; tube lens, +350 V, and heated metal capillary operated at $\sim 10 \text{ W}$).²⁸ Ions were accumulated in an external linear octopole ion trap²⁹ for 1 s and transferred by radio frequency (rf)-only octopoles³⁰ to a 10 cm diameter, 30 cm long ICR cell. ICR time-domain transients were collected from a 7 segment open cylindrical cell with capacitively coupled electrodes based on the Tolmachev configuration.^{31,32} Octopoles were operated at 2.0 MHz and 240 V_{p-p} amplitude. Broadband frequency sweep (chirp) dipolar excitation (70–700 kHz at 50 Hz/ μs sweep rate and 350 V_{p-p} amplitude) was followed by direct-mode image current detection to yield 8 Mword time-domain data. A total of 100 time-domain acquisitions were co-added, Hanning-apodized, and zero-filled once before fast Fourier transform and magnitude calculation.

Mass Calibration and Data Analysis. ICR frequencies were converted to ion masses based on the quadrupolar trapping potential approximation.^{33,34} Each mass spectrum was internally calibrated on the basis of the most abundant homologous series of singly charged ions containing one nitrogen atom ($200 < m/z < 1200$) with a relative abundance greater than six standard deviations of baseline rms noise (6σ). The peak list was exported to a spreadsheet, after conversion to the Kendrick mass scale,³⁵ for easier identification of homologous series. For each elemental composition, $\text{C}_x\text{H}_y\text{N}_z\text{O}_w\text{S}_t$, the heteroatom class ($\text{N}_n\text{O}_o\text{S}_s$), type, and carbon number (C#) were tabulated for generation of heteroatom class relative abundance distributions and isoabundance-contoured DBE versus carbon number images constructed for each heteroatom class.³

RESULTS AND DISCUSSION

Conventional (+) ESI. Conventional electrospray performed in the presence of dilute formic acid protonates basic compounds to form $[\text{M} + \text{H}]^+$ ions. Figure 1 shows heteroatom class distribution plots for the most abundant classes of electrosprayed positive ions from Athabasca bitumen heavy vacuum gas oil (HVGO) at 475–500 °C and North and South American crude oils in the presence of 1% (by volume) formic acid. Each bar represents the summed relative abundances of compounds of the same heteroatom composition but different DBE and carbon number. Figure 1 shows that the most abundant positive ion heteroatom classes in all samples correspond to compounds containing at least one nitrogen atom. The inset isoabundance-contoured DBE versus carbon number plots³ provide an image of the aromaticity and carbon number range for the three most abundant classes. Molecules lacking a basic moiety are not protonated by conventional ESI, thereby limiting its application for crude oil characterization to only the most basic species.

Lithium Cation Affinity. The cationization of a neutral molecule by a metal cation offers a potential route for ESI of less basic petroleum compounds. Adducts of organic

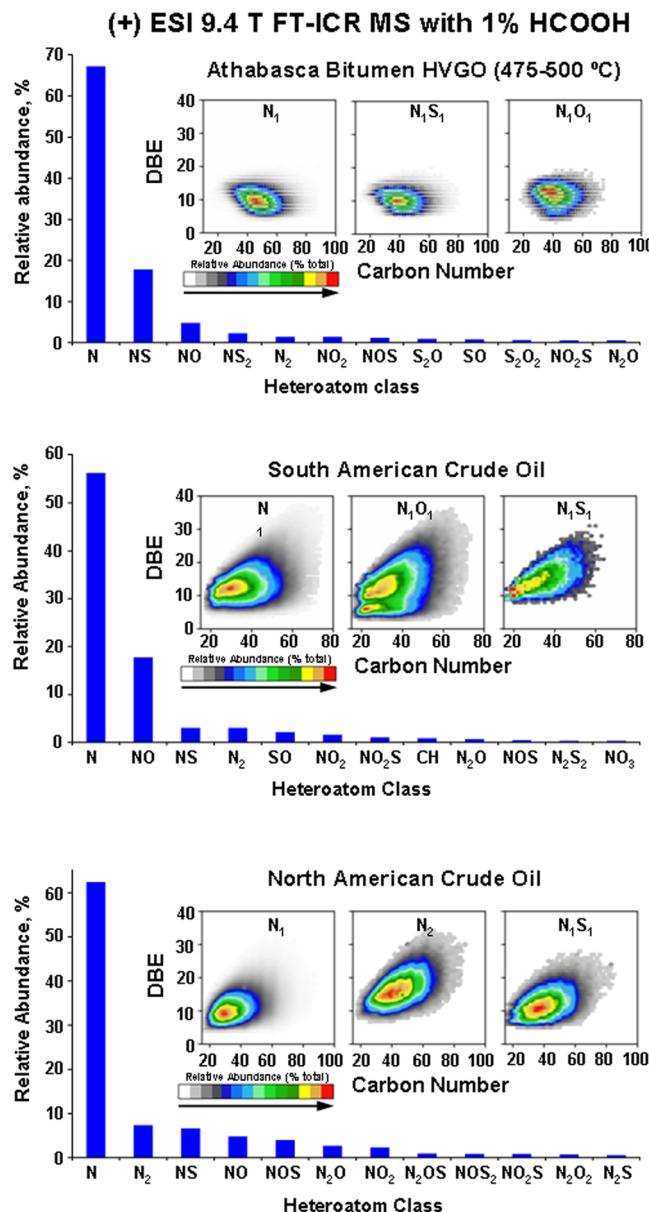


Figure 1. Heteroatom class distributions from (+) ESI 9.4 T FT-ICR MS with 1% HCOOH as a modifier: (top) Athabasca bitumen HVGO (475–500 °C), (middle) South American crude oil, and (bottom) North American crude oil. The insets are isoabundance-contoured plots of DBE versus carbon number plots for the most abundant heteroatom classes.

compounds, polymers, and biomolecules (peptides, proteins, carbohydrates, etc.) with alkali metals are often observed in mass spectrometry, according to the affinity of the molecules to a given metal cation.^{20–22} In general, interaction of an alkali metal with a neutral molecule depends upon the metal ionic radius and the nature of the attached molecule. Steric factors are also extremely important in metal-neutral binding, as evidenced by the strong complexation of alkali metals with crown ethers (“host–guest” effect) in both gas phase³⁶ and solution.³⁷

Mass spectrometry is widely used to measure the affinity of metal cation binding to neutral molecules in the gas phase.^{20,38} The gas-phase experiments give an opportunity to study the intrinsic behavior of the chemical compound without effects of

solvent, counterions, and intermolecular interactions. A comparison of gas- and solution-phase data enables evaluation of their role in reactivity and selection of optimal conditions for a process. For some gas-phase processes, direct analogy with condensed-phase reactions has been observed.³⁹

Lithium cation, because of its small size, has high charge density and is therefore highly solvated in solution. Among all alkali metal cations, Li⁺ typically exhibits the highest gas-phase affinity to various organic compounds. Lithium cation affinity (LCA) is defined as the negative of standard enthalpy change ($-\Delta H^\circ$) upon binding. LCA has been determined for many compounds, including gases (He, Ne, Ar, Kr, Xe, H₂, CO, and NH₃), solvents (CH₃OH, CH₃CN, acetone, etc.), and various organic molecules.^{20,38,40,41} Gas-phase LCA offers a qualitative estimate of metal cation affinity for organic molecules under electrospray conditions. Table 1 lists LCA values for

Table 1. Gas-Phase LCA of Neutral Molecules, in kJ/mol at 0 K

compound	LCA (kJ/mol)	compound	LCA (kJ/mol)
CH ₃ OH	155.0	<i>o</i> -dimethyl phthalate	197.0
C ₂ H ₅ OH	164.0	<i>m</i> -dimethyl phthalate	157.1
<i>i</i> -C ₃ H ₇ OH	173.0	<i>p</i> -dimethyl phthalate	152.0
<i>t</i> -C ₄ H ₉ OH	178.0	methylbenzoate	154.6
CH ₃ CN	180.0	phenol	178.0
(CH ₃) ₂ SO	225.0	benzene	161.0
PhS(O)CH ₃	229.7	toluene	183.0
Ph ₂ SO	233.8	naphthalene	187.2
(CH ₃) ₂ SO ₂	203.1	dimethyl ether	165.0
PhS(O ₂)CH ₃	212.7	pyridine	181.0
Ph ₂ SO ₂	217.9	<i>o</i> -methylpyridine	194.0
CH ₃ SCH ₃	138.0	acetone	188.3
C ₆ H ₅ OCH ₃	184.4	aniline	191.5

compounds with functional groups and structural fragments similar to those of petroleum constituents. As for protonation, the LCA magnitude is increased by the presence of two or more functional groups positioned such that the Li⁺ cation may be chelated. The LCA values for *ortho*-, *meta*-, and *para*-dimethyl phthalates presented in Table 1 demonstrate the chelating effect (possible only for the *ortho* isomer) on the stability of the corresponding Li complexes.⁴² Taft et al. showed that the complexation through chelation is more pronounced for Li⁺ than for H⁺.^{40,43} The lithium cation is better able to accommodate the double interaction than the proton, because of the longer (Li⁺–basic center) distances and the more flexible nature of the electrostatic bonding with Li⁺.⁴²

As seen from Table 1, a wide range of compounds exhibits positive LCA in the gas phase and, hence, can potentially form adducts with Li⁺ during ESI. The efficiency of cationization under ESI conditions is determined by (a) solvation of Li⁺ in solution and (b) difference in Li⁺ affinity between petroleum compounds and the solvent. For example, substitution of MeOH by AcCN in the solvent mixture used to dissolve petroleum leads to a decrease in the number of [M + Li]⁺ analyte ions in (+) ESI FT-ICR mass spectra, because of the higher LCA for AcCN (180 kJ/mol) than for MeOH (155 kJ/mol). Note that the gas-phase LCA for toluene (the second component of the solvent system) is 183.0 kJ/mol (i.e., higher than for MeOH and AcCN). However, in solution, the Li⁺ cation is more highly solvated by polar molecules (MeOH or

AcCN), and thus, [AcCN + Li]⁺ persists (rather than [toluene + Li]⁺) during the electrospray process.

Selection of Reagent for Li⁺ Cationization. LiOTf, LiBr, and LiCl were used to study the ionization of petroleum compounds through the formation of [M + Li]⁺ ions. Although efficient [M + Li]⁺ formation was observed for LiOTf, LiBr, and LiCl, highly abundant cluster ions can appear over a wide *m/z* range and hamper the detection of petroleum compounds. The propensity for formation of cluster ions increases with anion size (Cl[−] < Br[−] < TfO[−]) and correlates directly with the lithium salt concentration. LiCl exhibits the least tendency for cluster formation at 500 µg/mL. Lithium fluoride could not be used as a reagent for Li⁺ cationization because of its very low solubility in the electrospray solvent system.

Li⁺ Cationization of N-Containing, O_x, or HC Classes. Figure 2 shows isoabundance-contoured plots of DBE versus

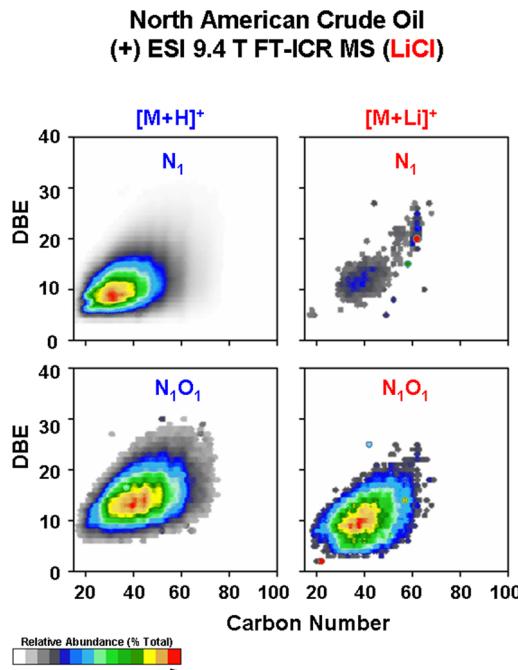


Figure 2. Isoabundance-contoured DBE versus carbon number plots of N₁ and N₁O₁ heteroatom classes detected as [M + H]⁺ and [M + Li]⁺ ions for North American crude oil with LiCl.

carbon number for N₁ and N₁O₁ heteroatom classes from North American crude oil with LiCl as a modifier. Both types of ions ([M + H]⁺ and [M + Li]⁺) are detected, although protonation is more prevalent for compounds containing a basic nitrogen atom. For example, for pyridine, the proton affinity is 930 kJ/mol, whereas the lithium cation affinity is 181.0 kJ/mol. Moreover, members of the N₁O₁ class detected as [M + Li]⁺ ions exhibit higher signal response than lithium-cationized N₁ species, which can be explained by ionization of N₁O₁ species through complexation of Li⁺ with an O atom. Thus, the N₁O₁ species detected as [M + Li]⁺ ions can contain either neutral (pyrrolic) and basic (pyridinic) nitrogen atoms.

The (+) ESI FT-ICR MS relative abundances of the O_x classes (O₁, O₂, and O₃) with Li⁺ cationization are low, although some compounds (e.g., ethers, ketones, esters, etc.) have high LCA and can potentially be ionized as [M + Li]⁺. For example, LCA for acetone (188.3 kJ/mol) exceeds the LCA values for both electrospray solvents: MeOH (155 kJ/mol) and

toluene (183 kJ/mol). Alcohols, phenol, ethers, and esters can also potentially be ionized by Li^+ cationization because their LCA values (shown in Table 1) are higher than those for MeOH and the charged moiety in Li^+ complexes is more likely to be highly solvated by polar molecules such as methanol. Nevertheless, some of O_x classes (e.g., O_2 class and carboxylic acids) are conventionally detected by negative ESI; thus, (+) ESI, even with lithium cationization, cannot compete with (-) ESI detection for some of these chemical functionalities.

Li^+ adducts were observed for the hydrocarbon (HC) class, consistent with the aromatic hydrocarbon LCAs in Table 1. The interaction of the Li^+ cation with the aromatic core occurs through π -complex formation.^{44,45} The presence of alkyl groups in an aromatic ring can increase the binding energy of Li^+ to aromatic molecules because of the “scorpion effect”.⁴⁶ However, the $[\text{M} + \text{Li}]^+$ ion abundance for the hydrocarbon class was even lower than that for the corresponding $[\text{M} + \text{H}]^+$ ions with 1% formic acid as a modifier.

Li⁺ Cationization of S_xO_y Classes. In contrast, Li^+ cationization significantly enhances the (+) ESI FT-ICR MS abundances of the S_xO_y classes, whose abundances are low or zero with 1% formic acid. Figure 3 shows (+) ESI FT-ICR MS heteroatom class distributions for S_xO_y species with LiCl or HCOOH as modifiers. The low efficiency for protonation of these species is explained by the absence of a basic moiety (e.g., a pyridinic nitrogen atom for “basic” N-containing classes). In contrast, S_xO_y compounds have high LCA values (e.g., higher than for the solvents): e.g., sulfoxides [$(\text{CH}_3)_2\text{SO}$, 225.0 kJ/mol; PhS(O)CH_3 , 229.7 kJ/mol; and Ph_2SO , 233.8 kJ/mol] and sulfones [$(\text{CH}_3)_2\text{SO}_2$, 203.1 kJ/mol; $\text{PhS(O}_2\text{)CH}_3$, 212.7 kJ/mol; and Ph_2SO_2 , 217.9 kJ/mol]. Moreover, Li^+ cationization of these compounds in the gas phase occurs through complexation of the lithium cation with an oxygen atom.⁴⁷ The interaction of Li^+ with neutral S_xO_y in solution most likely also takes place through complexation with an oxygen atom and, thus, does not require significant geometry change during electrospray. In contrast, for example, the complexation of some benzene derivatives (aniline, phenol, anisole, etc.) in solution proceeds through coordination of Li^+ with functional groups, whereas the high gas-phase LCA values correspond to interaction of Li^+ with aromatic π electrons to form π complexes.^{48–50} Such considerable structural changes during complexation of the latter compounds proceeding from solution phase to gas phase render ionization even less favorable.

Figure 4 shows isoabundance-contoured plots of DBE versus carbon number for S_1O_1 , S_1O_2 , S_1O_3 , S_1O_4 , and S_2O_2 heteroatom classes from South American crude oil with LiCl or HCOOH as a modifier. Lithium cationization efficiently ionizes the S_xO_y classes over a wider DBE and carbon number range. S_1O_1 class compounds in the (+) ESI FT-ICR mass spectrum of the crude oil with LiCl as a modifier range from DBE = 1–20 and 15–70 carbons. That class spans narrower ranges of DBE (2–18) and carbon number (15–42) with formic acid as a modifier. S_1O_2 , S_1O_3 , S_1O_4 , and S_2O_2 classes show much greater ionization enhancement by lithium cationization than by protonation. The increase in the number of heteroatoms for the S_xO_y classes ($\text{S}_1\text{O}_2 < \text{S}_1\text{O}_3 < \text{S}_1\text{O}_4$) shifts the distribution to higher carbon numbers. Moreover, the S_2O_2 class also shifts to higher DBE values.

During the contact of crude oil and water, the S_xO_y compounds concentrate mainly in the emulsion interface (the intermediate layer between oil and water phases).^{51–54} These

(+) ESI 9.4 T FT-ICR MS with HCOOH or LiCl

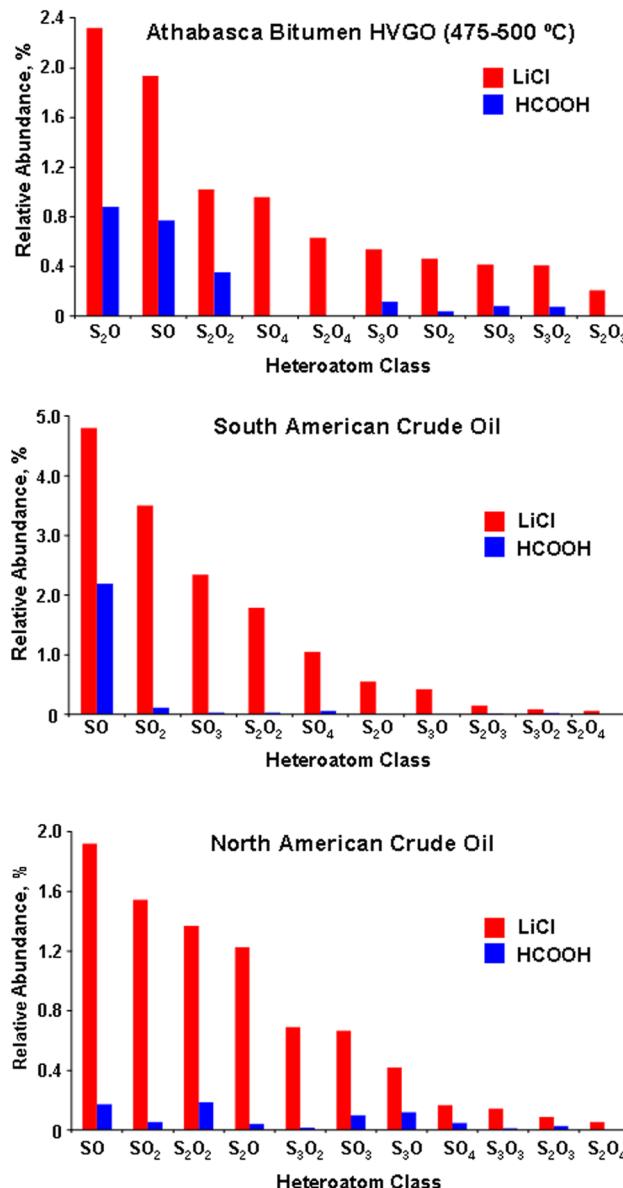


Figure 3. S_xO_y heteroatom class distributions from (+) ESI 9.4 T FT-ICR MS with LiCl or HCOOH as a modifier: (top) Athabasca bitumen HVGO (475–500 °C), (middle) South American crude oil, and (bottom) North American crude oil.

compounds are natural surfactants and partly soluble in water. Crude oil is typically produced with a significant watercut (percentage of water in crude oil by volume). Moreover, crude oil production can require up to several barrels of water per barrel of oil (as for extraction of oil from oil sands or desalting). Oil/water emulsions can also form accidentally because of oil leaks and spills and can lead to severe contamination of soil as well as surface and groundwater. Thus, the development of techniques suitable for efficient ionization and detection of compounds of S_xO_y classes is imperative for industrial and environmental applications.

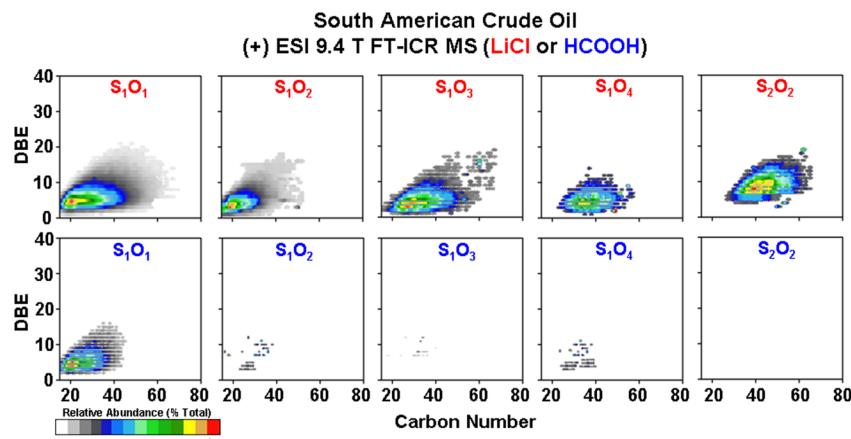


Figure 4. Isoabundance-contoured plots of DBE versus carbon number for the S_xO_y heteroatom classes for South American crude oil with LiCl (upper row) and HCOOH (lower row).

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The authors declare no competing financial interest.

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