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Separation and Characterization of Reactive and Non-Reactive Sulfur in Petroleum and Its Fractions

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⑤ Supporting Information

ABSTRACT: We present an efficient, easy-to-use chromatographic method to separate reactive and nonreactive sulfur compounds in crude oil for subsequent quantitative analysis and molecular characterization. Sulfur compounds in petroleum samples are separated by ligand exchange chromatography (LEC) on a silver-modified strong-cation exchange (SCX) solid-phase extraction (SPE) cartridge. LEC separation takes advantage of the bonding affinity of different sulfur types with silver-cations. The elution of a particular sulfur type (reactive or nonreactive) depends on the "strength" of the solvent used. One solvent mixture elutes nonreactive sulfur compounds (thiophenics and diaryl sulfides) into the first fraction. A second solvent mixture elutes reactive S-compounds (sulfides and disulfides) into the second fraction. A third reactive sulfur class (thiols) irreversibly reacts with the impregnated silver-ion to form silver thiolates that are insoluble in the solvent mixtures employed. The distribution of reactive and nonreactive sulfur in a sample can be determined by measurement of sulfur content in separated fractions. The isolated fractions are also well-suited for molecular characterization by a variety of techniques including gas-chromatography-based methods (e.g., GC or GC × GC-SCD, GC-MS) and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), both of which are demonstrated herein.

■ INTRODUCTION

Sulfur content in a crude oil is one of the major factors affecting its price and refinery suitability. Governmental regulations associated with environmental, health, and safety concerns mandated a drastic decrease of sulfur level in finished fuels.[1−3] A recent cut of sulfur content for gasoline in the U.S.A. by 90% (from 300 to 30 ppm) required about $10 billion in capital investments to upgrade refineries. The proposed cut for gasoline from 30 to 10 ppm (only 3 times decrease) is estimated to cost another $10 billion.[4] Sulfur compounds in petroleum exist in a variety of chemical structures and are generally described by chemical class (mercaptans, disulfides, sulfides, thiophenes, etc.). Knowledge of the structure and properties of sulfur species in petroleum is necessary to improve our understanding of the mechanisms and kinetics of conversion processes to facilitate the development of superior hydrodesulfurization catalysts, optimize processing conditions, and minimize/predict corrosion of pipelines and refinery equipment.[5]

Typically, aromatic sulfur (i.e., thiophenics) is the most prevalent form of organosulfur compounds in petroleum. Although thiophenic sulfur is noncorrosive, it requires hydrodesulfurization treatment at more severe conditions (therefore "non-reactive") to meet regulations for transportation fuels. A common petroleum "rule of thumb" assumes that 2/3 of the total S is thiophenic.[6,7] Deviations from this approximation abound, and thus, it is not adequate for refinery operations, especially with rapidly changing crude oil slates. Conversely, the three other classes (sulfides, disulfides, and mercaptans) are readily hydro-convertible, but corrosive in refinery pipestill operations and are termed "reactive" or

"corrosive". The reactive sulfur compounds attack refinery equipment at elevated temperatures (240−380 °C), and engineering predictions of sulfur corrosion have been based on a variety of H_2S evolution tests with or without metals present.[8−15] Alternatively, corrosion predictions were also based on five wet chemical analyses,[16] and reviews of sulfidic corrosion highlight the need for simple analytical technique for the quantitative and qualitative determination of sulfur classes.[17−20]

Sulfur analyses generally report total sulfur and do not differentiate between S-types, although both reactive and nonreactive sulfur classes play different, important roles in refinery operations. No convenient method for measurement of the distribution of S in its reactive and nonreactive classes exists. Reactive and nonreactive S-classes overlap in adsorption chromatography (silica or alumina).[21−23] Reactive S-classes can be estimated from total S fractions obtained by deconvolution of XPS spectra.[24] Mercaptans and disulfides can be determined by standard potentiometric titration methods.[25−28] Sulfides have been separated by multistep oxidation, reduction, and chromatographic procedures.[29,30] Nonreactive thiophenic S-compounds have been separated from aromatic hydrocarbons on both Pd^{2+} and Ag^+ impregnated silica with different solvent systems.[31−36] Multiring thiophenics, mainly dibenzthiophenes and higher benzologs, have been separated first into aromatics by adsorption chromatography and then fractionated by aromatic ring number by LEC.[37−40] Qualitative molecular

speciation of S-compounds has been reported by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) without prior separation.[21,41−46] However, ionization efficiency of different organic classes is not uniform, and multistep separations and derivatization schemes have been used to distinguish between reactive and nonreactive S types.[40,45,47−54] Other quantitative techniques for characterizing some reactive S-classes have been reported. NMR[55] and GC/MS[56] methods have been used to characterize individual reactive or nonreactive S-classes after derivatization of S-compounds. Two dimensional (comprehensive) gas chromatography with sulfur chemiluminescence detection (GCxGC-SCD) has been also used to quantify the distribution of molecular species in heavy oils.[57,58] Although these methods allow some measure of quantitative characterization of classes within S types, none provides a simple S-type separation based on readily available materials.

Silver has been long recognized as a useful cation for ligand exchange separations, especially in the form of $AgNO_3$ impregnated silica gel.[59] For example, a LEC method based on Ag+-SCX was used for separation of lipids and fatty acid methyl esters by their unsaturation.[60] We recently demonstrated that interaction of organo-sulfur compounds with silver-cation in solution forms stable, charged complexes that are extremely beneficial for mass spectrometry analysis. In that work, nonpolar sulfur compounds, which are typically not ionized by conventional electrospray (ESI), were efficiently ionized by silver cationization (+) ESI FT-ICR mass spectrometry. Thus, tedious and time-consuming derivatization was now unnecessary.[43]

Here we present a method to separate, quantify, and speciate reactive and nonreactive S-types in crude oil and petroleum fractions by LEC separation with subsequent quantitation by X-ray fluorescence and/or ICP MS and speciation by GCxGC-SCD and/or FT-ICR MS. The method utilizes a commercially available solid phase extraction (SPE) cartridge packed with strong cation exchange (SCX) sorbent that was modified to its Ag+ form (Ag+-SCX) in-house.

■ EXPERIMENTAL SECTION

Samples and Reagents. Model sulfur compounds (tetrahydrothiophene, dibutyl sulfide, ethyl phenyl sulfide, dibenzyl sulfide, benzyl phenyl sulfide, 1-dodecanethiol, 1-hexadecanethiol, 1-octadecanethiol, dihexyl disulfide, dibenzyl disulfide, diphenyl sulfide, 1-benzothiophene, 2,3-dibromobenzo[*b*]thiophene, dibenzothiophene, 1,2-benzodiphenylene sulfide) were purchased from Sigma-Aldrich (St. Louis, Mo). Solvents (dichloromethane (DCM), acetone (ACE), toluene (TOL), acetonitrile (ACN), and methanol (MeOH)) were JT Baker HPLC grade procured from VWR International (Suwanee, GA). High-purity silver triflate (AgOTf) and silver nitrate ($AgNO_3$) were purchased from Acros Organics (Geel, Belgium). Solid-phase extraction (SPE) cartridges filled with 1 g propyl sulfonic acid silica in a 6 mL tube (Bond Elute PRS, part no. 12256010) were purchased from Agilent Technologies (Santa Clara, CA). Ten refinery samples (Table 1) including a crude oil and distillates with known boiling range and total nitrogen (ppm) and sulfur (%) content were obtained for method evaluation.

Ag+-SCX Ligand Exchange Separation. The separation of reactive and nonreactive sulfur is carried out in a two-step procedure on a SPE cartridge with eluent flow rates of 1−2 mL min−1 (Figure 1). The top panel outlines the modification of a stationary phase in the cartridge. The stationary phase is conditioned with 5 mL of ACN, treated with 3 mL of an $AgNO_3$ solution at 30 mg mL−1, and rinsed with 10 mL of ACN to remove unbound Ag+. The SCX-sorbent is assumed to be fully modified to its Ag+-form so that the capacity

Table 1. Characteristics of Refinery Stream Samples

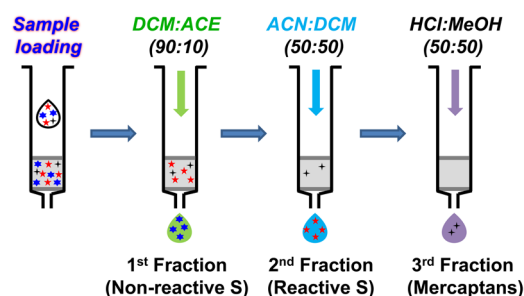| sample	boiling range (°C)	total S, %	total N, ppm
1	112−224	0.33	7
2	145−256	0.51	12
3	178−283	0.74	19
4	217−330	1.23	39
5	263−373	1.91	132
6	313−477	2.56	562
7	328−527	2.71	1010
8	365−583	3.34	1925
9	vacuum resid	5.77	5295
10	whole crude	3.43	2520
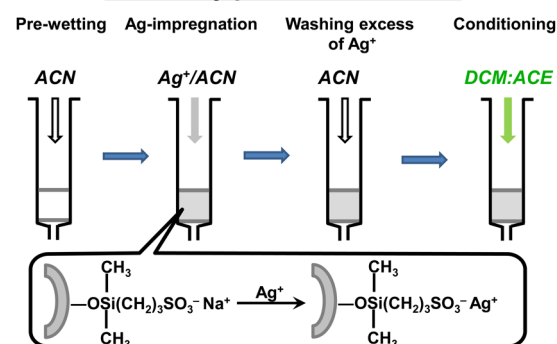
Figure 1. (*Top*) Preparation of Ag-SCX stationary phase: The SCX stationary phase is prewet with ACN, impregnated with $AgNO_3$ solution (ACN), rinsed with ACN, and preconditioned with DCM:ACE. (*Bottom*) Step-wise procedure for separation of S-compounds by S-type: A sample is loaded onto the Ag+-SCX followed by the subsequent elution of the first (nonreactive sulfur) and the second (reactive sulfur) fractions. Mercaptans (thiols) can be recovered by an additional step outlined in the text.

(meq) of Ag+ is equal to the original ion exchange capacity of the stationary phase. The modified SPE cartridges (Ag+-SCX) may be preserved for up to 1 month by refrigeration, covered with aluminum foil.

Figure 1 (bottom) shows the procedure for separation of sulfur classes from petroleum sample by Ag+-SCX SPE. The mass of sample loaded onto the stationary phase is calculated from bulk sulfur measurements so that the total sulfur content does not exceed the ion-exchange capacity of the SPE cartridge (≥2.5 mg of S). Prior to sample loading, the Ag+-SCX cartridge is conditioned with 6 mL of DCM:ACE (90:10). Viscous samples may be diluted in 1 mL of DCM prior to loading. After the sample is loaded, nonreactive sulfur is eluted with 18 mL of DCM:ACE (90:10). Next, two classes of reactive sulfur (sulfides and disulfides) are eluted with 18 mL of ACN:DCM (50:50).

Mercaptans are not eluted in either sulfur fraction. Mercaptans may be recovered by the addition of 6 mL of concentrated HCl:MeOH
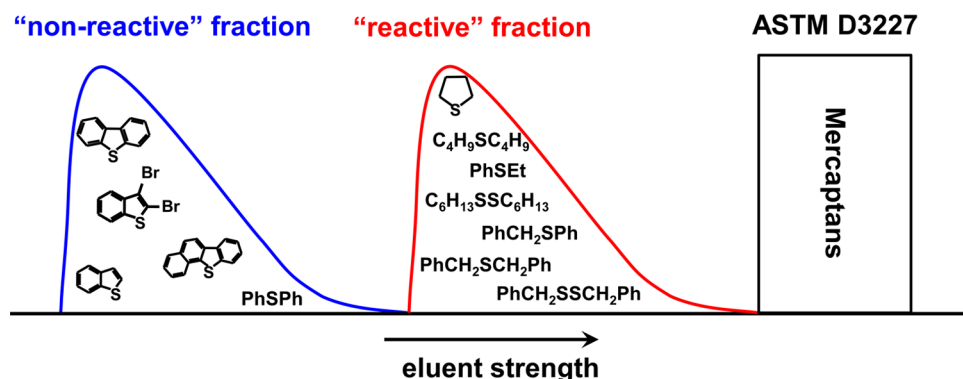
15 model sulfur-compounds
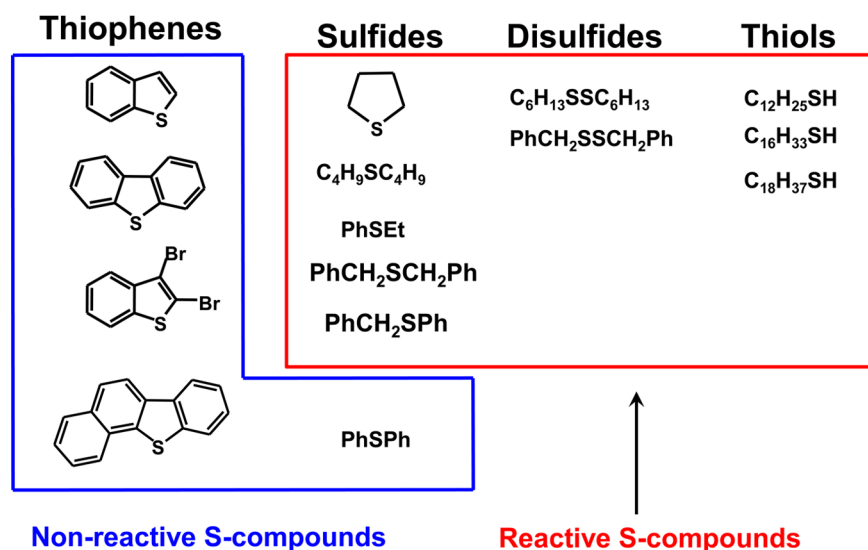
Figure 2. (Top) Structures of S-model compounds and their classification by reactivity. (Bottom) Elution sequence of the model compounds by S-types into two fractions.

(50:50) to the cartridge followed by 12 mL of TOL:MeOH (50:50). These steps are repeated again, and an additional 12 mL of toluene is percolated through the cartridge in the end. The solvent composition of the combined eluates forms a two-phase system. The organic phase (top layer) is isolated and dried with sodium sulfate. The isolated fraction can be directly analyzed by routine analytical methods appropriate for sample boiling range.

GC/MS Analysis. Model compound mixture, distillate samples, and Ag$^+$-SCX separated fractions were analyzed by GC/MS on an Agilent 5973 mass spectrometer equipped with an Agilent 6890 gas chromatograph. A 1 μL sample was injected into the GC inlet (270 °C) with a 1:20 split ratio. Separation was carried out with an Agilent J&W HP-5 fused silica capillary column (30 m long, 0.32 mm ID, and 0.25 μm film thickness) with helium carrier gas at 1.5 mL min^{-1}. The oven temperature was initially held for 3 min at 50 °C and then ramped at 10 °C min^{-1} to a final temperature of 250 °C and held for 10 min. The MS used 70 eV electron impact (EI) ionization, and ion source was held at 200 °C. Positive ion data (m/z range of 30−650)

was collected at an acquisition rate of 1 scan s^{-1}. Total ion current (TIC) was used to reconstruct the chromatographic signal.

GC × GC-SCD Analysis. Two-dimensional gas chromatography with sulfur chemiluminescence detection was conducted with an Agilent 7890 GC (LECO, St. Joseph, MI) and SCD Model 355 (Agilent Technologies, Santa Clara, Ca). Samples were dissolved in dichloromethane at 5 mg/mL and 1 μL was injected at split ratio 1:10. The helium carrier gas (99.9999% purity) flow rate was 1.5 mL/min. The gas chromatograph inlet temperature was 300 °C. The main (first) oven temperature was initially set at 80 °C, held for 0.5 min, then ramped at 1.5 °C/min to 320 °C and held at maximum temperature for 10 min. The secondary oven was offset by +5 °C from the first oven, and followed the same time profile with start temperature, 85 °C (held for 0.5 min), 1.5 °C/min ramp rate, and final temperature, 325 °C held for 10 min. The modulator offset temperature was +10 °C from the first oven, and the modulation period was 8 s with a hot pulse of 1 s. The signal was acquired and processed with ChromaTOF software (v.4.50.8.0) from LECO Corp.
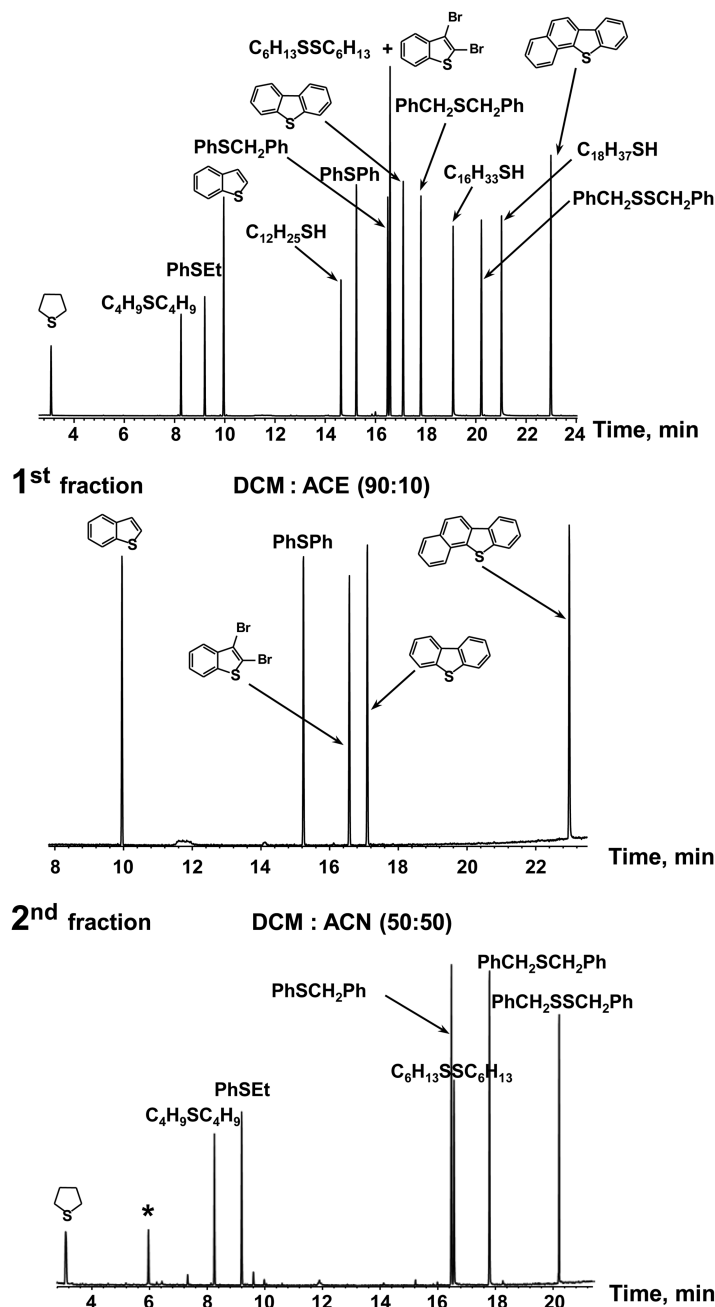
Figure 3. (Top) GC/MS chromatogram (TIC) of the 15 model compound mixture. (Middle) GC/MS chromatogram (TIC) of the first (nonreactive sulfur) fraction. (Bottom) GC/MS chromatogram (TIC) of the second (reactive sulfur) fraction. *- solvent contaminant.

FT-ICR Mass Spectrometry and Data Analysis. High-resolution mass spectra were collected with a custom-built 9.4 T FT-ICR mass spectrometer.[61] Predator ICR data station provided instrument control and data analysis.[62] Positive ions were generated by (+) electrospray (ESI) with silver cationization as described elsewhere.[43] Each unfractionated sample and corresponding reactive and nonreactive fractions were diluted to a final concentration of 500 μg mL^{-1} in a 1:1 (v/v) solution of TOL:MeOH. Silver triflate (AgOTf) was added to the solution at 50 μg mL^{-1}. Analyte solutions were pumped through a fused silica capillary at 0.5 μL min^{-1} through a 100 μm ID fused silica micro-ESI needle (needle, 2.3 kV; tube lens, 350 V; heated metal capillary current, ~ 5.0 A). PetroOrg software was used for peak assignments and data visualization.[63] Heteroatom class distribution plots and iso-abundance images (contoured double bond equivalents (DBE, number of rings plus double bonds to carbon[64]) vs carbon

number) were constructed to reflect heteroatom content, degree of unsaturation, and extent of alkylation within each homologous series.[65]

X-ray Fluorescence Analysis. Sulfur analysis of petroleum samples and separated LEC fractions were performed with a benchtop energy-dispersive XRF instrument Epsilon 3XL (PANalytical, Almelo, The Netherlands) equipped with rhodium anode tubes. The samples were diluted in toluene, and a 10 mL aliquot was placed in a cap with Mylar film. S-standards (CONOSTAN, Champlain, NY) were used for quantitative calibration of the instrument.

ICP-MS Analysis. Sulfur content in LEC fractions was measured by inductively coupled plasma mass spectrometry (ICP-MS) after mineralization within a high-pressure asher (Anton Paar GmbH, Graz, Austria). Samples (0.15 mL) were combined with 2 mL of concentrated nitric acid and 0.3 mL of 30% hydrogen peroxide in a 15 mL quartz tube and digested at 300 °C and 100 bar for 6 h. After

Table 2. Mass and %S in Eluted Ag$^+$-SCX Fractions of High Boiling Samples

sample	total S, %	% mass non-reactive	%S non-reactive	% mass reactive	%S reactive
5	1.91	92 ± 2	47 ± 3	7 ± 1	46 ± 3
6	2.56	91 ± 2	56 ± 5	9 ± 2	39 ± 3
7	2.71	90 ± 2	56 ± 4	8 ± 1	37 ± 3
8	3.34	89 ± 3	58 ± 5	12 ± 2	36 ± 2
9	5.77	56 ± 4	40 ± 4	23 ± 1	27 ± 3

cooling to room temperature, the digested solutions were diluted 40-fold with deionized water. ICP-MS analysis was performed with Element II mass spectrometer (Thermo Electron, Bremen, Germany) by detection of two sulfur isotopes (^{32}S and ^{34}S). Sulfur (500 ppm) in crude oil standard (CONOSTAN, Champlain, NY) was used for quantitative calibration of ICP-MS. To mimic matrix effects, the sulfur standard was diluted in the solvents used for elution fractions and digested with a high pressure asher in the same manner as the sulfur fractions. The instrument was operated at medium resolution (5000, 10% valley method) to enable separation of isobaric peaks (primarily ^{32}S vs 2^{16}O). Digested sample solutions were introduced to the ICP-MS at 150 μL min^{-1} by self-aspiration.

RESULTS AND DISCUSSION

Separation Validation. The separation of sulfur-containing species by reactivity was developed, optimized, and validated (by GC/MS analysis) with a mixture of model compounds that represent four main sulfur compound classes (thiols, sulfides, disulfides, and thiophenes). Figure 2 shows the structure of these compounds, classification by reactivity and elution order by a sulfur type. In general, thiols (1-dodecanethiol, 1-hexadecanethiol, and 1-octadecanethiol), sulfides (tetrahydro-thiophene, dibutyl sulfide, ethyl phenyl sulfide, dibenzyl sulfide, and benzyl phenyl sulfide), and disulfides (dihexyl disulfide, dibenzyl disulfide) are considered as reactive sulfur species, whereas nonreactive compounds have sulfur incorporated as a part of aromatic system (1-benzothiophene, 2,3-dibromobenzo-[b]thiophene, dibenzothiophene, and 1,2-benzodiphenylene) where S atom is sp^2-hybridized and diaryl sulfide (diphenyl sulfide). In the case of diaryl sulfides, the sulfur atom is attached directly to aromatic ring (and an electron pair of S atom is partially conjugated with the aromatic system) to form two strong bonds with sp^2-hybridized carbon atoms. As a result, diaryl sulfides are more thermally stable relative to a dialkyl- or alkyl aryl sulfides.[66]

The Ag$^+$-SCX separation of sulfur model compounds into S types was confirmed by GC/MS analysis (Figure 3). The top chromatogram shows the model compounds identified by their mass spectrum before separation. LEC on Ag$^+$–SCX takes advantage of differences in molecular orbital configurations of sulfur electrons with the vacant d-orbitals of the Ag$^+$. Nonreactive S-compounds (diaryl sulfides and thiophenes) that bond weakly to Ag$^+$–SCX elute with a mixture of DCM and ACE in a first fraction (Figure 3, middle). Two reactive S-types (sulfides, disulfides) are recovered from the Ag$^+$-SCX in the second fraction by ligand exchange with the ACN in DCM (Figure 3, bottom). The complexing ability of ACN allows reactive S types to be eluted without the backflush used in other Ag$^+$-SCX separations.[67] The third class of reactive S (mercaptans) reacts with Ag$^+$ to form insoluble salts (silver mercaptides) that are not eluted by solvents. Mercaptans are a typically small fraction of the total S and contribute mainly to reactive S in lower boiling fraction, where they are routinely determined by standard potentiometric titration with Ag$^+$ (e.g., ASTM D3227).[67,68] We evaluated a potential recovery of thiols

captured as silver thiolates on Ag$^+$-SCX sorbent with the procedure described in the Experimental Section. High-boiling-point mercaptan (1-octadecanethiol) was used as a test compound to estimate the yield gravimetrically after solvent evaporation. The procedure for isolation of the third fraction (Figure 1, bottom) was done in triplicate and provided the recovery for 1-octadecanethiol at 93 ± 3% (Figure 1S). Although mercaptans can be isolated by the Ag$^+$-SCX procedure for characterization, titration still is a preferred method for the determination of the mercaptan contribution to reactive S.

Alternative Stationary Phases. Although the method described here utilize commercially available strong cation exchange SPE cartridges, the separation method was also applied with equal success using SPE and HPLC columns packed in-house. Both alkyl or aromatic sulfonic acid silicas (available from a variety of sources in the form of prepacked SPE cartridges and HPLC columns) or polymer-based substrate analogues (e.g., polystyrene-sulfonic acid) were tested. However, the amount of Ag$^+$ required to fully modify sorbent depends on its weight and ion-exchange capacity. Thus, Ag loading must be calculated separately for each SCX substrate. Similarly, a calculation is required to determine the maximum allowable sulfur load to avoid column overload. Moreover, the composition of solvents and their volume to elute nonreactive and reactive fractions can vary from those presented here, and elution schemes need to be adjusted on the basis of sorbent nature and weight.

Distribution of Reactive and Nonreactive S in Refinery Samples. The Ag$^+$-SCX method was applied to 10 petroleum samples representing a full range of refinery streams (Table 1). The total sulfur (%) and nitrogen (ppm) content varies from a sample to sample with the lowest values for low boiling fraction (sample 1) and the highest for vacuum resid (sample 9). The samples were separated into nonreactive and reactive S-fractions by elution through Ag$^+$-modified SCX cartridges as described in the Experimental Section.

To evaluate the influence of a real petroleum matrix on separation of S-types, we conducted control experiments in which we spiked the model compound mixture into two samples (samples 1 and 9) of different boiling point range, and widely different sulfur (17-fold difference) and nitrogen content (750-fold difference). The GC/MS analyses of these two samples, spiked with the model compound mixture, show that N-content has little effect on the S-type separation (Figure 2S). As expected, model sulfur compounds are detected in the GC analysis of high boiling fractions but few of the petroleum components elute from GC column under conditions used due to boiling point limitations. To demonstrate recovery for Ag$^+$-SCX separations, we determined %S (by XRF) and measured the weight after solvent evaporation for the two eluted fractions. Volatility of low boiling samples limits accurate mass measurement. Therefore, recoveries were determined in triplicate for only the higher boiling fractions (sample 5−9)

that might be expected to have few mercaptans. High mass (95−100%) and sulfur (93−95%) recoveries were obtained for the gas oil samples (5−8) (Table 2). However, lower mass (∼80%) and sulfur (∼70%) recoveries were obtained for vacuum resid (9), typical of chromatographic methods applied to vacuum resids and asphaltene bearing fractions.

To demonstrate the feasibility of the LEC separation for the range of refinery samples including volatile distillates, a more sensitive ICP-MS analysis was applied after mineralization of organic fractions (Table 1S). The distribution of reactive and nonreactive S types can be determined either by analysis of both elution fractions or by difference. For the latter, the distribution of sulfur types in a sample is determined from its total %S and the %S in the first fraction with reactive S (sulfides, disulfides, mercaptans) calculated by the difference. ICP-MS analysis provides great sensitivity for sulfur analysis (on ppb level) with an average standard deviation of ±3%. The results for sulfur distribution are consistent with literature and show that the contribution of reactive S is larger in the low boiling fractions where mercaptans are often one of the major contributors to total S.[69,70]

Characterization of Reactive and Non-Reactive Sulfur.
The LEC separation facilitates molecular-level characterization of sulfur classes that may otherwise overlap. Figure 4 shows GCxGC-SCD chromatograms for VGO (sample 6) and its two fractions. Although GCxGC-SCD gives good resolution of thiophenic ring distributions, it does not separate mercaptans, sulfides, and disulfides from monothiophenes efficiently.[57,58,67−70] Further, because the second dimension is based on aromaticity, mixed sulfides (alkyl-aryl sulfides) are distributed away from the alkyl sulfides. Thus, without LEC separation, GCxGC-SCD cannot effectively resolve sulfur compounds into reactive and nonreactive S-types. For sample 6, the position of reactive sulfides in the second dimension in Figure 4 (bottom) suggests an abundance of phenyl or monoaromatic sulfides. In addition, the application of GC-based techniques for characterization and quantitation of petroleum and its fractions has to be done with a caution because of the boiling point limitation for some petroleum compounds. For example, it was reported that 40% of components of even a light crude oil are not amenable for GC-based methods.[71] Oversight can be even more dramatic for heavy crude oils and high boiling fractions (e.g., VGO, vacuum resid).

FT-ICR mass spectrometry in a combination with soft ionization methods (e.g., ESI) provides a complementary method for characterization of complex mixtures of organic compounds including petroleum samples. In this case, compounds are ionized, and formed ions are separated according to their mass (to be more precise by mass-to charge ratio, m/z). Utilization of various ionization methods and polarity (positive or negative ions) gives an opportunity to be specific to certain classes of compounds. For example, silver cationization (+) ESI FT-ICR mass spectrometry demonstrated to be an efficient method for detection of nonpolar sulfur compounds that are not ionized efficiently by protonation or deprotonation under conventional ESI. The sulfur compounds are detected as a doublet for each elemental composition: [M+^{107}Ag]$^+$ and [M+^{109}Ag]$^+$ ions; and the peaks relative abundance corresponds to natural silver isotope distribution (^{107}Ag-51.84% and ^{109}Ag-48.16%). Thus, the presence of silver isotopes enables distinctive isotopic peak pattern that, in turn, provides additional conformation for assignment of elemental
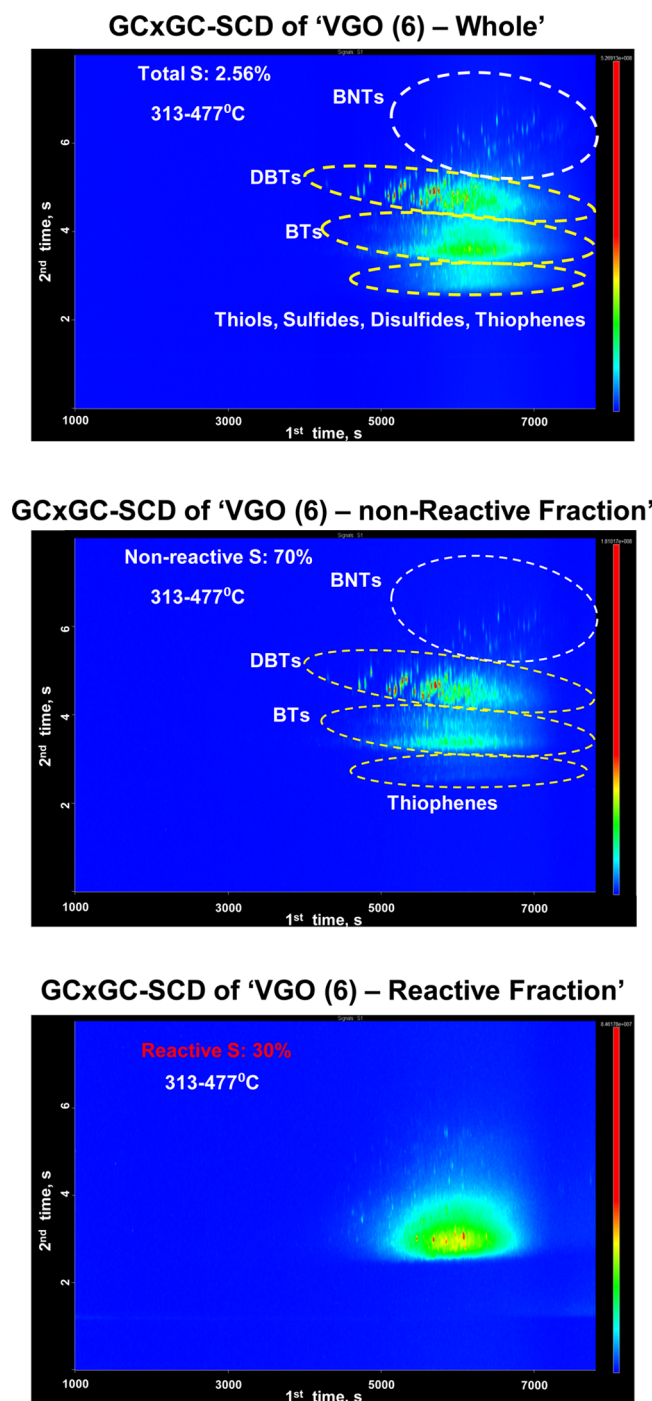

Figure 4. (Top) GCxGC-SCD chromatogram of VGO (sample 6). (Middle) GCxGC-SCD chromatogram of a of the first (nonreactive sulfur) fraction from the VGO. (Bottom) GCxGC-SCD chromatogram of the second (reactive sulfur) fraction from the VGO.

composition.[43] FT-ICR mass spectrometry provides broadband ultrahigh-mass resolving power ($m/\Delta m_{50\%}$ > 500 000) enabling the resolution of the SH$_4$ vs C$_3$ mass split (common in petroleum samples) up to m/z 1000. Broadband FT-ICR mass spectra for a vacuum gas oil (VGO, sample 6) and its reactive and nonreactive S fractions are complex, and the spectra contain several thousand peaks corresponding to different elemental compositions (Figure 3S). The total number of peaks in the spectra of the two fractions is greater than in the whole sample. Ag$^+$ combined with (+) ESI

efficiently ionizes both aromatic hydrocarbons[72,73] and thiophenics,[43] and thus, the first fraction contains characteristic peaks for both classes of compounds. The relative abundance of heteroatom classes derived from Ag^{+}-cationization (+) ESI FT-ICR mass spectra show differences between the whole oil and its fractions (Figure 5). Hydrocarbons (aromatics) are the most
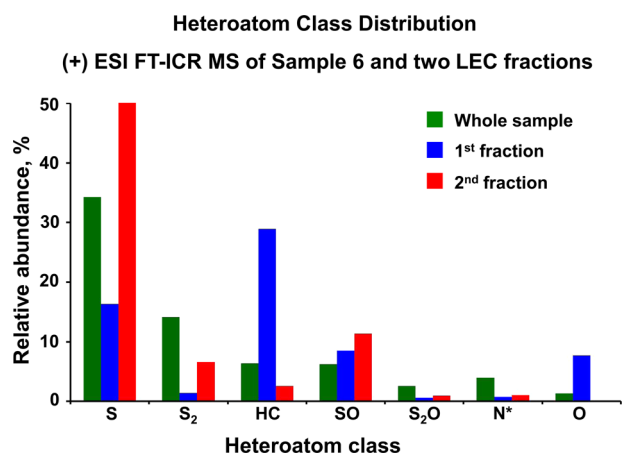

Figure 5. Heteroatom class distribution plot for vacuum gas oil and its two LEC fractions. Classes are detected as $[M + Ag]^+$ except for the nitrogen containing compounds (N-class), which are detected as $[M + H]^+$ ions.

abundant class in the first fraction because they are ionized as well as the thiophenic sulfur by Ag^{+} cationization. It is worth noting that ionization efficiency of S-compounds varies and depends on availability of lone pairs of electrons at the S atom, which, in turn, depends on sulfur type. However, because sulfur compounds in LEC fractions (reactive and nonreactive fractions) are separated on the basis of S-type, we expect that compounds inside each fraction have lower variations in ionization efficiency.

Each heteroatom class can be graphically presented as iso-abundance plots of DBE versus carbon number where the relative abundance of ions within the class is represented as contours on a color scale. Iso-abundance plots characterize the three most abundant classes (hydrocarbon (HC), S, and S_2) in the VGO and its Ag^{+}-SCX fractions (Figure 6). The structures that shown are consistent with elemental formulas and are only for illustrative purpose.

The HC class for the whole vacuum gas oil extends from DBE ∼ 2−12 with a carbon number distribution from ∼17−30. In the first fraction, the hydrocarbons narrow to DBE ∼ 4−12, over same carbon number range consistent with thiophenes and benzologs. In the second fraction, the HC class has a lower DBE (∼2−8) and carbon number (∼17−27). In contrast to naphthenes that elute from Ag^{+} substrates before aromatics, olefins form strong ligand bonds with Ag^{+}.[59] Thus, olefins and cyclo-olefins are the most likely species being detected in the HC class in the "reactive sulfur" fraction from this sample.

The S_1 class for the whole VGO extends from DBE ∼ 1−10 with a carbon number distribution from ∼17−27. The S_1 species in the first fraction (nonreactive S) range from DBE ∼ 3−10 (maximum at DBE of 6) with C number of 17−27 are consistent with thiophenic structures. Specifically, DBE of 3 corresponds to alkyl-substituted thiophenes and DBE of 6 corresponds to benzothiophenes. The second (reactive) S fraction has lower DBE ranging from 1 to 7 (max at DBE 2)
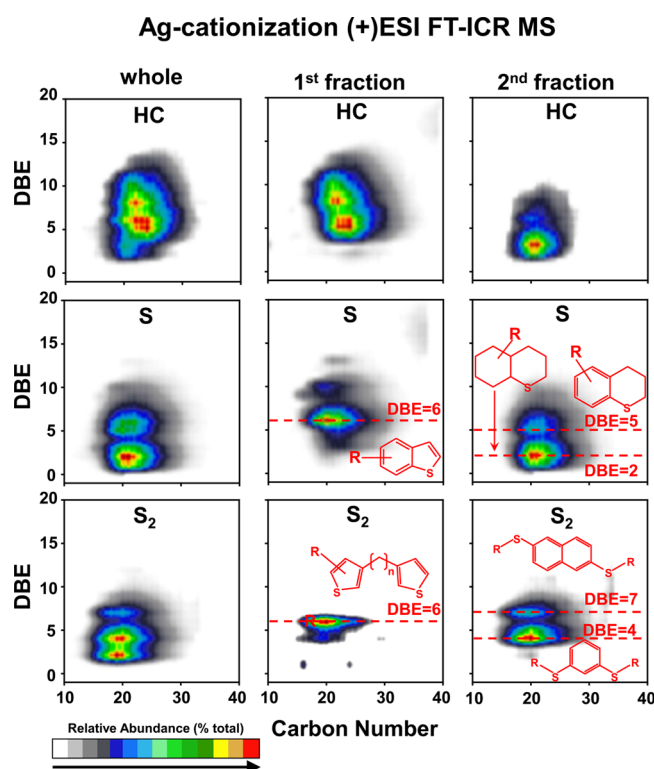

Figure 6. Iso-abundance-contoured DBE vs carbon number plots for HC, S_1, and S_2 classes, derived from silver cationization followed by positive-ion ESI FT-ICR MS for a whole sample of vacuum gas oil (left column), the first (nonreactive S) fraction (middle column), and the second (reactive S) fraction (right column).

with a similar 18−27 C no. range. The node at DBE 2 corresponds to a sulfide in a two-ring naphthene structure and that at DBE 5 (Δ+3 DBE) corresponds to a parallel family of molecules where one ring has been aromatized, with the S remaining in a saturated ring structure. The elemental composition from the MS data is insufficient to identify molecular structure (i.e., the S could be in the ring) within a side chain or an aryl-alkyl sulfide. In the limited number of studies where molecular structure has been determined, sulfur has been consistently found within a ring (i.e., a thiane or thiolane).[74,75]

The relative abundance of S_2 class is smaller than for the S_1 class in the vacuum gas oil and its Ag^{+}-SCX fractions. Although the carbon numbers for the sample and fractions span the same carbon number (∼15−27), the oil and fractions differ in DBE. S_2 in the VGO spans DBE ∼ 2−8, but it appears to be trimodal with nodes at DBE 2, 4, and 6. Because the first fraction should only contain molecules with both S in thiophenic rings, the band around DBE 6 suggests two thiophenic rings in a molecule. (Other classes would not elute in the nonreactive S fraction.) In the second fraction, at least one of the S is reactive but not a mercaptan. The isoabundance plot shows S_2 molecules that span DBE 4−7 with nodes at DBE 4 and 7. The node at DBE 4 may correspond to a number of possible reactive sulfur structures because only a single sulfidic sulfur is required for retention in Ag^{+}-SCX fractionation. Structures could include molecules with an aromatic coupled to two sulfidic groups (shown in Figure 6), a disulfide containing an aromatic ring, a thiophene with sulfide in a side chain, or a 4-ring naphthene incorporating two sulfur atoms. The reactive S_2-class at DBE 7 has potential for similar structural complexity,

although the 3 DBE step suggests an increase in aromaticity. The node at DBE 2 in the whole oil is absent in both the solvent-isolated Ag$^+$-SCX fractions. This suggests that one of the sulfur atoms in the S$_2$ molecules at DBE 2 is present as a mercaptan, which prevents its solvent elution. The other S could be either reactive or nonreactive. It must be emphasized that structures in Figure 6 are included only to illustrate differences among the S-classes and do not represent any observed or preferred structure. For example, although thiophenics include S in a 5-membered ring, sulfidic sulfur can occur in either 5- or 6-membered rings. Without the Ag$^+$-SCX separation, the assignment of S to reactive or nonreactive structures would not be possible.

Figure 4S shows DBE versus carbon number plots for S$_1$ class for a crude oil (sample 10) and two separated fractions. The distribution of S-compounds in the nonreactive fraction is broad along the DBE (3−18) and carbon number (14−45). DBE patterns are consistent with thiophenic sulfur (DBE 3) and benzologs with the maximum band at DBE 6 corresponding to alkylated benzothiophenes. Sulfur in reactive fraction is characterized by a maximum at DBE 2 corresponding to cyclic sulfides. The second DBE band at 5−6 is consistent with sulfides containing one benzene and one (DBE 5) or two (DBE 6) saturated rings.

SUMMARY

A simple, convenient SPE method based on LEC with Ag$^+$-SCX has been developed to separate organosulfur compounds in petroleum into nonreactive (thiophenics) and reactive (sulfides and disulfides) and mercaptan classes. Once a sample is loaded onto the Ag$^+$-modified sorbent, nonreactive S compounds are eluted with a mixture of DCM:ACE (90:10), reactive sulfur compounds are eluted with DCM:ACN(50:50), and mercaptans recovered by toluene extraction after acid hydrolysis of silver mercaptides. The isolated fractions can be analyzed by quantitative methods to determine the S distribution throughout the fractions and/or characterized by qualitative techniques for molecular speciation of S classes. Ag$^+$ on other strong cation exchangers works equally well. This method creates opportunities for improving the understanding the role of sulfur classes in the refinery corrosion and processing.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energy-fuels.5b00780.

> Data on recovery of thiols into the third fraction; influence of real petroleum matrix on S-separation; broadband (+) ESI FT-ICR mass spectra for VGO (sample 6) and two LEC fractions; DBE vs carbon number plots for S$_1$ class for a crude oil (Sample10) and two LEC fractions fractions; relative distribution of reactive and nonreactive sulfur in samples (PDF)

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Notes
The authors declare no competing financial interest.

REFERENCES

(1) Wang, D.; Qian, E. W.; Amano, H.; Okata, K.; Ishihara, A.; Kabe, T. Oxidative desulfurization of fuel oil. Part I. Oxidation of dibenzothiophenes using tert-butyl hydroperoxide. *Appl. Catal., A* **2003**, *253* (1), 91−99.

(2) Babich, I. V.; Moulijn, J. A. Science and technology of novel processes for deep desulfurization of oil refinery streams: a review. *Fuel* **2003**, *82* (6), 607−631.

(3) Song, C. An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel. *Catal. Today* **2003**, *86* (1−4), 211−263.

(4) Tamm, D. C.; Milburn, K. P.; Thomas, R. X. *Potential Supply and Cost Impacts of Lower Sulfur, Lower RVP Gasoline*; Prepared for the American Petroleum Institute; Baker and O'Brien, Inc: Dallas, TX, July 2011; p 96.

(5) Breysse, M.; Djega-Mariadassou, G.; Pessayre, S.; Geantet, C.; Vrinat, M.; Perot, G.; Lemaire, M. Deep desulfurization: reactions, catalysts and technological challenges. *Catal. Today* **2003**, *84* (3−4), 129−138.

(6) Lyapina, N. K. Present Stage of the Problem, Studying the Petroleum Sulfur-Organic Compounds. *Usp. Khimii.* **1982**, *51* (2), 332−354.

(7) Ho, T. Y.; Rogers, M. A.; Drushel, H. V.; Koons, C. B. Evolution of Sulfur-Compounds in Crude Oils. *AAPG Bull.* **1974**, *58* (11), 2338−2348.

(8) Cataldi, H. A.; Askevold, R. J.; Harnsberger, A. E. Estimating the Corrosivity of Crude Oils. *Petroleum Refiner* **1953**, *32* (7), 146−150.

(9) Coleman, H. J.; Thompson, C. J.; Rall, H. T.; Smith, H. M. Thermal Stability of High-Sulfur Crude Oils. *Ind. Eng. Chem.* **1953**, *45* (12), 2706−2710.

(10) Dettman, H. D.; Li, N.; Wickramasinghe, D.; Luo, J. The influence of naphthenic acid and sulphur compound structure on global crude corrosivity under vacuum distillation conditions. Presented at *NACE Northern Area Western Conference*, Calgary, Alberta, Canada, February 15−18, 2010.

(11) Drushel, H. V. Sulfur Compound Type Distribution in Petroleum Using an In-Line Reactor or Pyrolysis Combined with Gas Chromatography and a Microcoulometric Sulfur Ddetector. *Anal. Chem.* **1969**, *41* (4), 569−576.

(12) Jin, P.; Nesic, S.; Wolf, H. A. Analysis of corrosion scales formed on steel at high temperatures in hydrocarbons containing model naphthenic acids and sulfur compounds. *Surf. Interface Anal.* **2015**, *47* (4), 454−465.

(13) Pavelko, G. F. Correlation between thermochemical and antiscuff characteristics of organosulfur compounds. *J. Frict. Wear.* **2012**, *33* (6), 443−452.

(14) Piehl, R. L. Correlation of Corrosion In a Crude Distillation Unit With Chemistry of the Crudes. *Corrosion* **1960**, *16* (6), 305t−307t.

(15) Yang, B.; Tian, S. B.; Zhao, S. L. A study of thermal decomposition of alkanethiols in pressure reactor. *Fuel Process. Technol.* **2006**, *87* (8), 673−678.

(16) *High Temperature Crude Oil Corrosivity Studies*; API Publication 943; American Petroleum Institute: Washington, DC, 1974.

(17) *Overview of Sulfidic Corrosion In Petroleum Refining*; NACE International Publication; NACE: Dallas, TX, 2004; p 34103.

(18) *Guideline for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries. API Recommended Practice 939-C*; American Petroleum Institute: Washington, DC, 2008.

(19) Rebak, R. B. Sulfidic corrosion in refineries - a review. *Corros. Rev.* **2011**, *29* (3−4), 123−133.

(20) Robbins, W. K. Challenges in the analytical characterization of nonthiophenic and thiophenic sulfur compounds in petroleum. *Abstr. Pap. Am. Chem. Soc.* **2000**, *219*, U252−U252.

(21) Rodgers, R. P.; White, F. M.; Hendrickson, C. L.; Marshall, A. G.; Andersen, K. V. Resolution, elemental composition, and simultaneous monitoring by Fourier transform ion cyclotron resonance mass spectrometry of organosulfur species before and after diesel fuel processing. *Anal. Chem.* **1998**, *70* (22), 4743−4750.

(22) Snyder, L. R. Applications of Linear Elution Adsorption Chromatography to Separation and Analysis of Petroleum 0.1. Compound Class Separations over Alumina and Silica. *Anal. Chem.* **1961**, *33* (11), 1527−1534.

(23) Snyder, L. R. Applications of Linear Elution Adsorption Chromatography to Separation and Analysis of Petroleum 0.3. Routine Determination of Certain Sulfur Types. *Anal. Chem.* **1961**, *33* (11), 1538−1543.

(24) Kelemen, S. R.; George, G. N.; Gorbaty, M. L. Direct Determination and Quantification of Organic Sulfur Forms by X-Ray Photoelectron-Spectroscopy (Xps) and Sulfur K-Edge Absorption-Spectroscopy. *Fuel Process. Technol.* **1990**, *24*, 425−429.

(25) *Standard Test Method for Mercaptan Sulfur in Gasoline, Kerosine, Aviation Turbine, and Distillate Fuels (Potentiometric Titration Method)*; Report No. ASTM D 3227-13; ASTM International: West Conshohocken, PA, 2013.

(26) Hubbard, R. L.; Haines, W. E.; Ball, J. S. Quantitative Determination of Organic Disulfides. *Anal. Chem.* **1958**, *30* (1), 91−93.

(27) Karchmer, J. H. Determining Sulfur Compounds in Petroleum Naphtha - the Humble Scheme. *Anal. Chem.* **1958**, *30* (1), 80−85.

(28) Karchmer, J. H.; Walker, M. T. Determining Disulfides in Petroleum Naphtha - Modification of the Acetic Acid-Zinc Reflux Method. *Anal. Chem.* **1958**, *30* (1), 85−90.

(29) Drushel, H. V.; Miller, J. F. Spectrophotometric Determination of Aliphatic Sulfides in Crude Petroleum Oils and Their Chromatographic Fractions. *Anal. Chem.* **1955**, *27* (4), 495−501.

(30) Somogyvari, A.; Zanzotto, L.; Sieben, D.; Auger, J. The Aliphatic Sulfide Sulfur-Content of Some Western Canadian Crudes, Their Distillates and Residues. *Fuel* **1988**, *67* (9), 1269−1272.

(31) Andersson, J. T. Retention Properties of a Palladium-Chloride Silica Sorbent for the Liquid-Chromatographic Separation of Polycyclic Aromatic Sulfur Heterocycles. *Anal. Chem.* **1987**, *59* (17), 2207−2209.

(32) Joyce, W. F.; Uden, P. C. Isolation of Thiophenic Compounds by Argentation Liquid-Chromatography. *Anal. Chem.* **1983**, *55* (3), 540−543.

(33) Nishioka, M. Aromatic Sulfur-Compounds Other Than Condensed Thiophenes in Fossil-Fuels - Enrichment and Identification. *Energy Fuels* **1988**, *2* (2), 214−219.

(34) Nishioka, M.; Campbell, R. M.; Lee, M. L.; Castle, R. N. Isolation of Sulfur Heterocycles from Petroleum-Derived and Coal-Derived Materials by Ligand-Exchange Chromatography. *Fuel* **1986**, *65* (2), 270−273.

(35) Nishioka, M.; Whiting, D. G.; Campbell, R. M.; Lee, M. L. Supercritical Fluid Fractionation and Detailed Characterization of the Sulfur Heterocycles in a Catalytically Cracked Petroleum Vacuum Residue. *Anal. Chem.* **1986**, *58* (11), 2251−2255.

(36) Sripada, K.; Andersson, J. T. Liquid chromatographic properties of aromatic sulfur heterocycles on a Pd(II)-containing stationary phase for petroleum analysis. *Anal. Bioanal. Chem.* **2005**, *382* (3), 735−741.

(37) Ghaloum, N.; Michael, G.; Khan, Z. Separation of sulphur compounds from vacuum gas oil distillates by ligand exchange chromatography. *J. Liq. Chromatogr. Relat. Technol.* **2002**, *25* (9), 1409−1420.

(38) Hegazi, A. H.; Andersson, J. T. Characterization of Polycyclic Aromatic Sulfur Heterocycles for Source Identification. *Oil Spill Environmental Forensics: Fingerprinting and Source Identification* **2007**, 147−168.

(39) Nocun, M.; Andersson, J. T. Argentation chromatography for the separation of polycyclic aromatic compounds according to ring number. *J. Chromatogr. A* **2012**, *1219*, 47−53.

(40) Panda, S. K.; Al-Hajji, A. A.; Muller, H.; Koseoglu, O. R. Ligand exchange chromatography: a vital dimension for the reliable characterization of heterocycles in crude oils and refined products. *Anal. Bioanal. Chem.* **2011**, *400* (5), 1231−1239.

(41) Al-Hajji, A. A.; Muller, H.; Koseoglu, O. R. Characterization of nitrogen and sulfur compounds in hydrocracking feedstocks by Fourier transform ion cyclotron mass spectrometry. *Oil Gas Sci. Technol.* **2008**, *63* (1), 115−128.

(42) Guan, S. H.; Marshall, A. G.; Scheppele, S. E. Resolution and chemical formula identification of aromatic hydrocarbons and aromatic compounds containing sulfur, nitrogen, or oxygen in petroleum distillates and refinery streams. *Anal. Chem.* **1996**, *68* (1), 46−71.

(43) Lobodin, V. V.; Juyal, P.; McKenna, A. M.; Rodgers, R. P.; Marshall, A. G. Silver Cationization for Rapid Speciation of Sulfur-Containing Species in Crude Oils by Positive Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* **2014**, *28* (1), 447−452.

(44) Marshall, A. G.; Rodgers, R. P. Petroleomics: Chemistry of the underworld. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105* (47), 18090−18095.

(45) Purcell, J. M.; Juyal, P.; Kim, D. G.; Rodgers, R. P.; Hendrickson, C. L.; Marshall, A. G. Sulfur speciation in petroleum: Atmospheric pressure photoionization or chemical derivatization and electrospray ionization fourier transform ion cyclotron resonance mass spectrometry. *Energy Fuels* **2007**, *21* (5), 2869−2874.

(46) Schrader, W.; Panda, S. K.; Brockmann, K. J.; Benter, T. Characterization of non-polar aromatic hydrocarbons in crude oil using atmospheric pressure laser ionization and Fourier transform ion cyclotron resonance mass spectrometry (APLI FT-ICR MS). *Analyst* **2008**, *133* (7), 867−869.

(47) Liu, P.; Shi, Q.; Pan, N.; Zhang, Y. H.; Chung, K. H.; Zhao, S. Q.; Xu, C. M. Distribution of Sulfides and Thiophenic Compounds in VGO Subfractions: Characterized by Positive-Ion Electrospray Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* **2011**, *25* (7), 3014−3020.

(48) Liu, P.; Shi, Q. A.; Chung, K. H.; Zhang, Y. H.; Pan, N.; Zhao, S. Q.; Xu, C. M. Molecular Characterization of Sulfur Compounds in Venezuela Crude Oil and Its SARA Fractions by Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* **2010**, *24*, 5089−5096.

(49) Liu, P.; Xu, C. M.; Shi, Q. A.; Pan, N.; Zhang, Y. H.; Zhao, S. Q.; Chung, K. H. Characterization of Sulfide Compounds in Petroleum: Selective Oxidation Followed by Positive-Ion Electrospray Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Anal. Chem.* **2010**, *82* (15), 6601−6606.

(50) Shi, Q. A.; Pan, N.; Liu, P.; Chung, K. H.; Zhao, S. Q.; Zhang, Y. H.; Xu, C. M. Characterization of Sulfur Compounds in Oilsands Bitumen by Methylation Followed by Positive-Ion Electrospray Ionization and Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* **2010**, *24*, 3014−3019.

(51) Wang, M.; Zhao, S. Q.; Chung, K. H.; Xu, C. M.; Shi, Q. Approach for Selective Separation of Thiophenic and Sulfidic Sulfur Compounds from Petroleum by Methylation/Demethylation. *Anal. Chem.* **2015**, *87* (2), 1083−1088.

(52) Muller, H.; Andersson, J. T.; Schrader, W. Characterization of High-Molecular-Weight Sulfur-Containing Aromatics in Vacuum Residues Using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Anal. Chem.* **2005**, *77* (8), 2536−2543.

(53) Muller, H.; Adam, F. M.; Panda, S. K.; Al-Jawad, H. H.; Al-Hajji, A. A. Evaluation of Quantitative Sulfur Speciation in Gas Oils by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry:

Validation by Comprehensive Two-Dimensional Gas Chromatography. *J. Am. Soc. Mass Spectrom.* **2012**, *23* (5), 806−815.

(54) Japes, A.; Penassa, M.; Andersson, J. T. Analysis of Recalcitrant Hexahydrodibenzothiophenes in Petroleum Products Using a Simple Fractionation Process. *Energy Fuels* **2009**, *23*, 2143−2148.

(55) Payzant, J. D.; Mojelsky, T. W.; Strausz, O. P. Improved Methods for the Selective Isolation of the Sulfide and Thiophenic Classes of Compounds from Petroleum. *Energy Fuels* **1989**, *3* (4), 449−454.

(56) Thomson, J. S.; Green, J. B.; McWilliams, T. B. Determination of sulfides and thiols in petroleum distillates using solid-phase extraction and derivatization with pentafluorobenzoyl chloride. *Energy Fuels* **1997**, *11* (4), 909−914.

(57) de Peinder, P.; Visser, T.; Wagemans, R.; Blomberg, J.; Chaabani, H.; Soulimani, F.; Weckhuysen, B. M. Sulfur Speciation of Crude Oils by Partial Least Squares Regression Modeling of Their Infrared Spectra. *Energy Fuels* **2010**, *24*, 557−562.

(58) Dijkmans, T.; Van Geem, K. M.; Djokic, M. R.; Marin, G. B. Combined Comprehensive Two-Dimensional Gas Chromatography Analysis of Polyaromatic Hydrocarbons /Polyaromatic Sulfur-Containing Hydrocarbons (PAH/PASH) in Complex Matrices. *Ind. Eng. Chem. Res.* **2014**, *53*, 15436−15446.

(59) Williams, C. M.; Mander, L. N. Chromatography with silver nitrate. *Tetrahedron* **2001**, *57* (3), 425−447.

(60) Christie, W. W. Silver Ion Chromatography Using Solid-Phase Extraction Columns Packed with a Bonded-Sulfonic Acid Phase. *J. Lipid Res.* **1989**, *30* (9), 1471−1473.

(61) Senko, M. W.; Hendrickson, C. L.; Pasa-Tolic, L.; Marto, J. A.; White, F. M.; Guan, S.; Marshall, A. G. Electrospray ionization Fourier transform ion cyclotron resonance at 9.4 T. *Rapid Commun. Mass Spectrom.* **1996**, *10* (14), 1824−1828.

(62) Blakney, G. T.; Hendrickson, C. L.; Marshall, A. G. Predator data station: A fast data acquisition system for advanced FT-ICR MS experiments. *Int. J. Mass Spectrom.* **2011**, *306* (2−3), 246−252.

(63) Corilo, Y. E. *PetroOrg Software*; Florida State University; *All rights reserved.* http://www.petroorg.com.

(64) McLafferty, F. W.; Tureek, F. *Interpretation of Mass Spectra*, 4th ed.; University Science Books: Sausalito, CA, 1993; p 371.

(65) Rodgers, R. P.; Marshall, A. G. Petroleomics: Advanced Characterization of Petroleum-Derived Materials by Fourier Transform ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS). In *Asphaltenes, Heavy oils, and Petroleomics*; Mullins, O. C., Sheu, E. Y., Hammani, A., Marshall, A. G., Eds.; Springer: New York, 2007; pp 63−89.

(66) Voronkov, M. G.; Deryagina, E. N. Thermal transformations of organic compounds of divalent sulfur. *Usp. Khimii.* **2000**, *69* (1), 90−104.

(67) Hegazi, A. A. H.; Andersson, J. T. Limitations to GC-MS determination of sulfur-containing polycyclic aromatic compounds in geochemical, petroleum, and environmental investigations. *Energy Fuels* **2007**, *21* (6), 3375−3384.

(68) Hua, R. X.; Wang, J. H.; Kong, H. W.; Liu, J.; Lu, X.; Xu, G. W. Analysis of sulfur-containing compounds in crude oils by comprehensive two-dimensional gas chromatography with sulfur chemiluminescence detection. *J. Sep. Sci.* **2004**, *27* (9), 691−698.

(69) Machado, M. E.; Bregles, L. P.; de Menezes, E. W.; Caramao, E. B.; Benvenutti, E. V.; Zini, C. A. Comparison between prefractionation and fractionation process of heavy gas oil for determination of sulfur compounds using comprehensive two-dimensional gas chromatography. *J. Chromatogr. A* **2013**, *1274*, 165−172.

(70) Mahe, L.; Dutriez, T.; Courtiade, M.; Thiebaut, D.; Dulot, H.; Bertoncini, F. Global approach for the selection of high temperature comprehensive two-dimensional gas chromatography experimental conditions and quantitative analysis in regards to sulfur-containing compounds in heavy petroleum cuts. *J. Chromatogr. A* **2011**, *1218* (3), 534−544.

(71) Reddy, C. M.; Arey, J. S.; Seewald, J. S.; Sylva, S. P.; Lemkau, K. L.; Nelson, R. K.; Carmichael, C. A.; McIntyre, C. P.; Fenwick, J.; Ventura, G. T.; Van Mooy, B. A. S.; Camilli, R. Composition and fate of gas and oil released to the water column during the Deepwater Horizon oil spill. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109* (50), 20229−20234.

(72) Laali, K. K.; Hupertz, S.; Temu, A. G.; Galembeck, S. E. Electrospray mass spectrometric and DFT study of substituent effects in Ag+ complexation to polycyclic aromatic hydrocarbons (PAHs). *Org. Biomol. Chem.* **2005**, *3* (12), 2319−2326.

(73) Takino, M.; Daishima, S.; Yamaguchi, K.; Nakahara, T. Determination of polycyclic aromatic hydrocarbons by liquid chromatography-electrospray ionization mass spectrometry using silver nitrate as a post-column reagent. *J. Chromatogr. A* **2001**, *928* (1), 53−61.

(74) Gug, S.; Schaeffer, P.; Adam, P.; Klein, S.; Motsch, E.; Albrecht, P. Identification of a sulfide derivative with a bicyclic hydrocarbon skeleton related to squalene. Part I: synthesis of a dithiane triterpenoid. *Org. Geochem.* **2009**, *40* (8), 876−884.

(75) Payzant, J. D.; Mcintyre, D. D.; Mojelsky, T. W.; Torres, M.; Montgomery, D. S.; Strausz, O. P. The Identification of Homologous Series of Thiolanes and Thianes Possessing a Linear Carbon Framework from Petroleums and Their Interconversion under Simulated Geological Conditions. *Org. Geochem.* **1989**, *14* (4), 461−473.