Crude Oil Analysis

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Characterization of Supercomplex Crude Oil Mixtures: What Is Really in There?

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Dedicated to Professor Michael Linscheid on the occasion of his 60th birthday

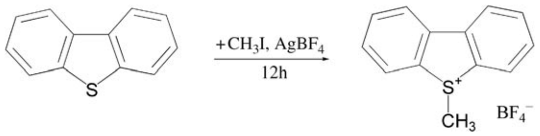
The issue of how to provide society with a reliable yet affordable and environmentally not too damaging supply of energy is one of the basic problems facing mankind today. Until sustainable energy sources have been developed on a scale that can satisfy the demand, fossil fuels will continue to play a decisive role.

The increased consumption of crude oil and its sharply rising price have led to the realization that nontraditional sources of fuel, such as oil sands and shale oils, as well as the higher-boiling fractions of crude oil that so far have been used mainly as maritime transportation fuels possess realistic economic potential as raw materials for the production of fuel.[1] Fractions like vacuum gas oils (VGOs) and vacuum residues (VRs) are disadvantageous in that they contain a high abundance of heteroatoms, for example, sulfur that causes acid rain[2] on combustion. To counter this, many countries, including the USA and members of the EU, have stringent legislative limits on the sulfur concentration in transportation fuels.[2,3] The predominant method for the removal of sulfur is hydrodesulfurization (HDS),[4] a catalytic process that is operated at high hydrogen pressure and at elevated temperature. HDS of VGO is less efficient than that of lighter distillates[5] which may be because of the presence of polycyclic aromatic sulfur heterocycles (PASHs) with a variety of aromatic rings, substituted at different positions with a plethora of alkyl chains.

It is clear that a speciation of these PASHs is of great importance for the optimization of the catalytic process. Sulfur in crude oil is routinely analyzed as total sulfur, determined for every crude oil and individual fraction, but the information obtained here is insufficient to optimize the catalytic process owing to the absence of any structural information.

Although research in this field started more than half a century ago, gaining structural information on PASHs remains a challenge.[6] Two-dimensional gas chromatography (GC × GC) presents an unsurpassed resolution for samples of sufficient volatility.[7] Recently, the use of GC × GC for crude oil analysis was reported.[8] However, PASHs in higher boiling ranges, of interest here, must be studied by other methods because of the low volatility of high-molecular-weight PASHs.[9] Both the number of possible parent systems as well as the number of isomers of the alkyl side chains grow enormously with an increase in the number of carbon atoms. For instance, decane ($C_{10}H_{22}$) has 75 isomers, but triacontane ($C_{30}H_{62}$) is estimated to possess over four billion. The compounds studied here contain roughly 20–50 carbon atoms. It is unrealistic to expect individual compounds to be analyzable in such supercomplex mixtures; therefore, the goal is to gain statistical information that allows a classification of the compounds. The method of choice will be liquid chromatography–mass spectrometry. A chromatographic simplification of the sample in combination with ultrahigh-resolution mass spectrometry (Fourier transform ion cyclotron resonance mass spectrometry, FT-ICR MS) gives indispensable data that lead to the elemental composition of the sample components.[10]

As PASHs are nonpolar, they cannot be ionized by electrospray ionization (ESI). We typically derivatize the PASHs, which are pre-isolated from the matrix utilizing a palladium(II)-containing column, by methylating the sulfur atom (Scheme 1).[9] These thiophenium salts are introduced into the mass spectrometer through the ESI inlet. In this way, a range of heavy PASH-containing fossil materials have been studied.[9,11]



Scheme 1. Derivatization of a PASH by methylation.[9a]

ESI and atmospheric pressure photoionization (APPI) of the methylated PASHs were recently compared for the PASHs of a vacuum bottom residue, without pre-isolation on palladium(II), and it was concluded that the methylation procedure was suitable only for light distillate fractions. Compounds having higher double-bond equivalents (DBEs) were found to be insufficiently methylated and therefore, detected only by APPI. This opens up the fundamental question: how true to the sample composition is the mass

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spectral representation? How strongly does this representation depend on the ionization method? Do different ionization methods show different degrees of discrimination of or selectivity towards certain components? Such questions affect the fundamentals of the use of MS for crude oil analysis.

To investigate these basic questions using the energy-relevant PASH compounds as a probe, we here report results from electrospray ionization (ESI), matrix-assisted laser desorption/ionization (MALDI), atmospheric pressure chemical ionization (APCI), atmospheric pressure photo ionization (APPI), and atmospheric pressure laser ionization (APLI)[12] and investigate two different derivatization procedures for the PASHs, namely, methylation and phenylation (Scheme 1 and Scheme 2).

An Iranian light VGO fraction was used for all experiments. The sample preparation is described in the experimental section (see the Supporting Information). The polycyclic aromatic compound (PAC) fraction was isolated through chromatography on silica/alumina. The use of a a chromatographic palladium(II) phase,[13] which allows the separation of the PASHs in the PAC fraction from the hydrocarbons, oxygen heterocycles, and nonaromatic sulfur-containing species, is essential for the sample preparation.

The FT-ICR mass spectra of the VGO using the five ionization techniques are shown in Figure 1. It is clear that the spectra are quite different depending on the ionization method. More details are obtained when only a small section is viewed (Figure 2). Here, two different mass ranges are displayed. The top two spectra show ESI and MALDI data obtained from the methylated samples (Figure 2a). With APCI, APPI, and APLI (Figure 2b), the derivatized samples gave results that agree with those obtained from the nonderivatized sample. Since for these methods a heated nebulizer with temperatures up to 350 °C was used, the thermal removal of the *S*-methyl group from the methylated components is likely under these experimental conditions . For verification, we compared a methylated standard with a nonmethylated standard (benzonaphthothiophene), which confirms this observation (for details see the Supporting Information). The spectra show the same components as mostly radical cations with APPI and APLI as those detected with ESI or MALDI, but with masses which are 15 mass units lower because of loss of the CH_3 group, while APCI gives $[M-CH_3+H]^+$ ions.

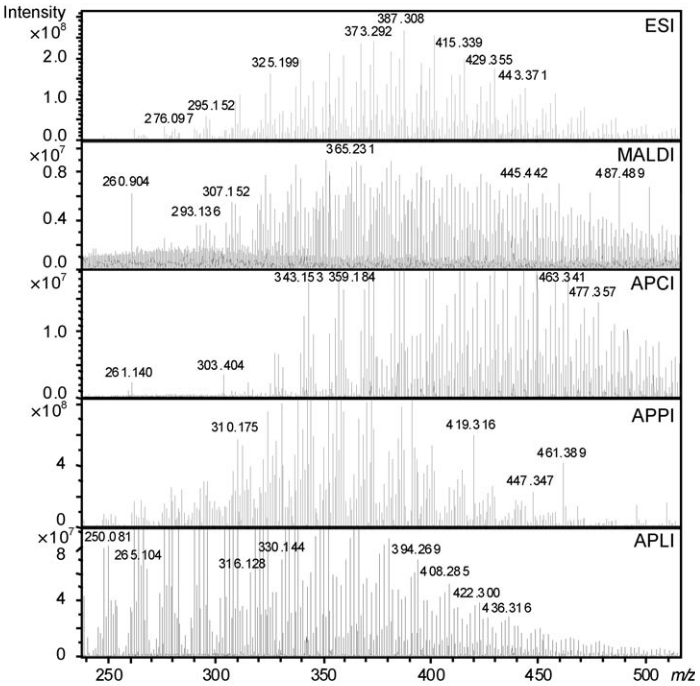
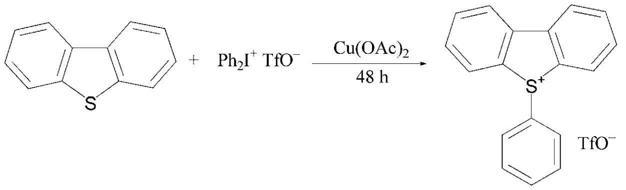


Figure 1. Comparison of mass spectra obtained for the PASH fraction from an Iranian light VGO after methylation using ESI, MALDI, APCI, APPI, and APLI. In this overview it can be seen that intensities of different signals vary. Additional signals are due to impurities and resonance frequencies from the mass spectrometer.



Scheme 2. Derivatization of a PASH by phenylation.

The weakest signals were detected with MALDI, but the spectrum otherwise resembles that obtained with ESI, although the intensity maximum lies at somewhat lower masses. Both techniques show practically only S_1 and rarely S_2 and O_1S_1 compounds. APCI shows mainly quasi-molecular ions and displays much higher intensity for high-molecular-weight compounds and weak or no signals for the low-molecular-weight compounds that are detected with the other techniques.

APLI is a laser-based ionization method operating at 248 nm and is highly selective towards aromatic compounds. It was connected to our FT-ICR MS through a home-built ion source that is not yet commercially available.[14] APLI primarily leads to radical cations which means that signals are detected at even numbers, in contrast to the odd number of quasi-molecular ions $[M+H]^+$. APLI is selective towards aromatic compounds in general but not to derivatized sulfur species. The broadest range of signals is found for APPI which shows the largest number of signals although both radical cations and quasi-molecular ions are detected from the same component, thus making the spectrum more complex.

The results shown in Figure 1 and Figure 2 make it clear that each ionization technique leads to a different mass spectrum. Especially APPI and APLI ionization allows a deeper look into the VGO, with APPI giving more signals and allowing the classification of different species. While APCI gives data about S_1, S_1O_1, and some minor O_1 compounds, APPI and APLI allow the detection of a broader range of compounds, including those with more than one oxygen and sulfur atom. An overview of the different compounds

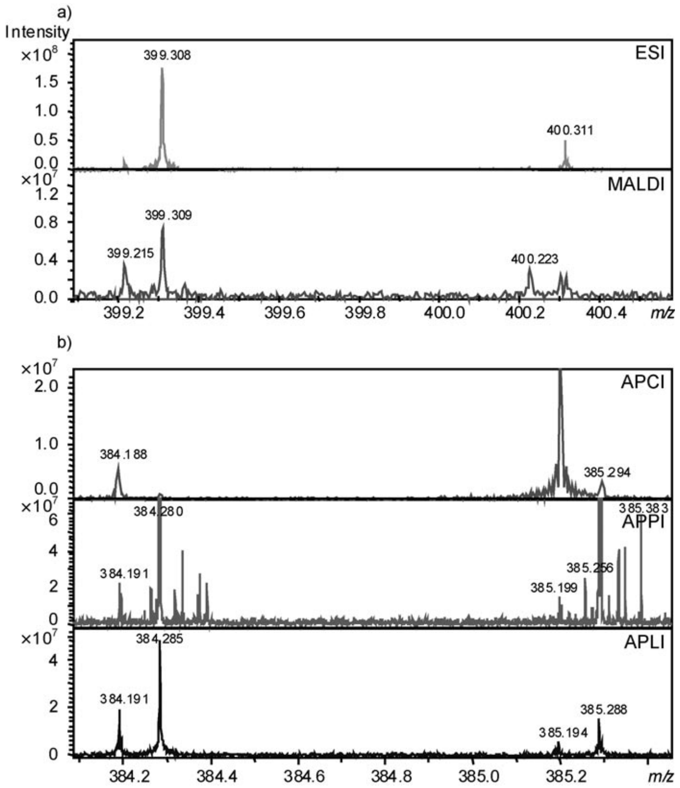


Figure 2. a) Comparison of mass spectra (*m*/*z* 399–400) of the PASH fraction from an Iranian light VGO after methylation generated by ESI and MALDI. (Here methylation stays intact). b) Since it appears that the thermal nebulization used for APLI, APPI, and APCI leads to the removal of the derivatization group, this was considered and a lower mass range (*m*/*z* 384–385) was used to display the same compounds lacking the methyl groups.

detected with each method is shown in Figure 3, where the intensities of all signals that were assigned to a class are compared. APPI shows the broadest range of components, while ESI with derivatization is highly selective towards S_1 compounds.

It was recently stated[15] that the methylation discriminates PASHs of higher DBE (> 10). Therefore we compared this derivatization reaction, necessary when ESI is used, with another derivatization procedure and with another ionization method for the same sample. The second derivatization is a phenylation of the sulfur atom (see Scheme 2). This reaction involves a completely different mechanism than the methylation.

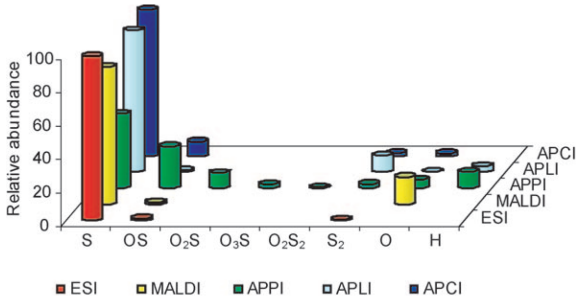


Figure 3. Comparison of results from different ionization methods. Note that relative and not absolute abundances are shown; the summary of all abundances from one method is 100%.

The results for such comparisons are best displayed in a Kendrick plot. These Kendrick plots[16] (for a detailed description see the Supporting Information) show the DBE value (as calculated from the molecular composition) versus the nominal mass and exhibit a series of dots, representing homologous series of compounds of the same DBE by using the mass defect as a tool. The results from the methylation experiment are displayed in Figure 4, while the data from the phenylation are shown in Figure S2 in the Supporting Information. The two data sets were obtained after subtracting the mass of the derivatization group. The comparison between methylation and phenylation shows that the data are almost the same both with respect to the range of DBEs (3–13) and the mass range with some differences in intensity. In both cases a strong presence of DBE 6 (benzothiophenes), 9 (dibenzothiophenes), and 10 (naphthenodibenzothiophenes) is indicated. Additional possible structures are shown in Table S1 in the Supporting Information. A comparison with APPI is presented in Figure 5. The APPI data do not show any DBE values below 5 (ESI: 3) but a slightly higher aromaticity (DBE 14 vs. 13 for ESI). This early comparison, therefore, does not seem to reveal any major discrimination through the methylation procedure.

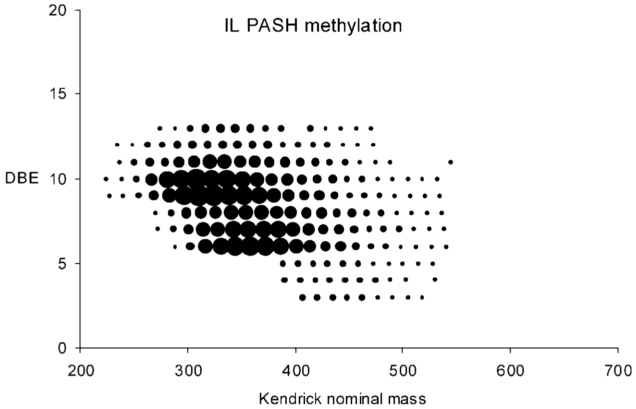


Figure 4. Kendrick plot of PASHs (obtained from an LC separation using a palladium(II)-containing stationary phase) containing one sulfur atom, which were taken from an Iranian light VGO after methylation; the mass spectra were generated with ESI.

These results can only begin to indicate the role that modern methods in analytical chemistry can play in energy research. With the procedure used here it is possible to characterize the types and classes of compounds present in crude oil fractions with a high selectivity for sulfur-containing polyaromatic heterocycles. The combination of chromatographic sample preparation, which gives additional information about the sample content,[11] and detection with high-resolution mass spectrometry allows a detailed characterization with respect to aromaticity using the Kendrick mass defect in combination with DBE values. Although the higher the DBE value is, the more possible structures can be

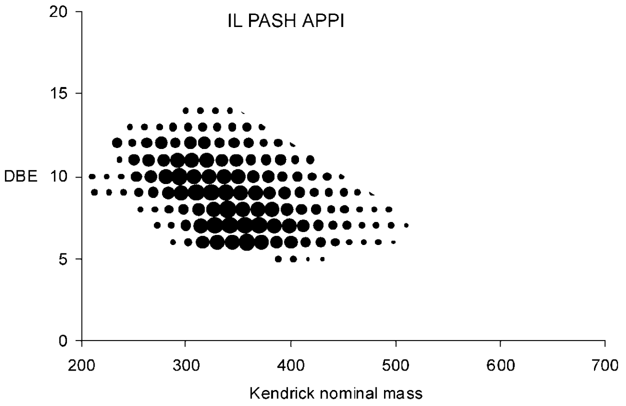


Figure 5. Kendrick plot of PASHs (obtained from an LC separation using a palladium(II)-containing stationary phase) containing one sulfur atom, taken from an Iranian light VGO; the mass spectra were generated by APPI.

imagined, this method can aid in a structure-dependent optimization of the catalytic desulfurization process based on analytical data.

Using different ionization methods is like watching the same sample through different windows, because each method favors certain compounds or discriminates against others. A detection using APPI and APLI allows a more thorough overview of the crude oil sample because more and different species are ionized, while the window is smaller with APCI. MALDI gives the same results as ESI, only with different intensities. When ESI and MALDI are used, only derivatized samples can be investigated, and the window of observation is smaller but very selective towards sulfur-containing species. Mass spectrometry thus supports a thorough characterization of the very complex matrix crude oil, but as shown here it provides different data sets depending on the ionization technique.

In summary, there is not one method that allows a crude oil sample to be truly described, but it is possible to analyze and characterize at least parts of these supercomplex mixtures using this approach. Nice examples are the sulfur species that can be analyzed in crude oil with a high degree of selectivity.

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Keywords: crude oil analysis · hydrocarbons · ionization methods · liquid chromatography · mass spectrometry

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