Supporting Information: Response of Different Types of Sulfur Compounds to Oxidative Desulfurization

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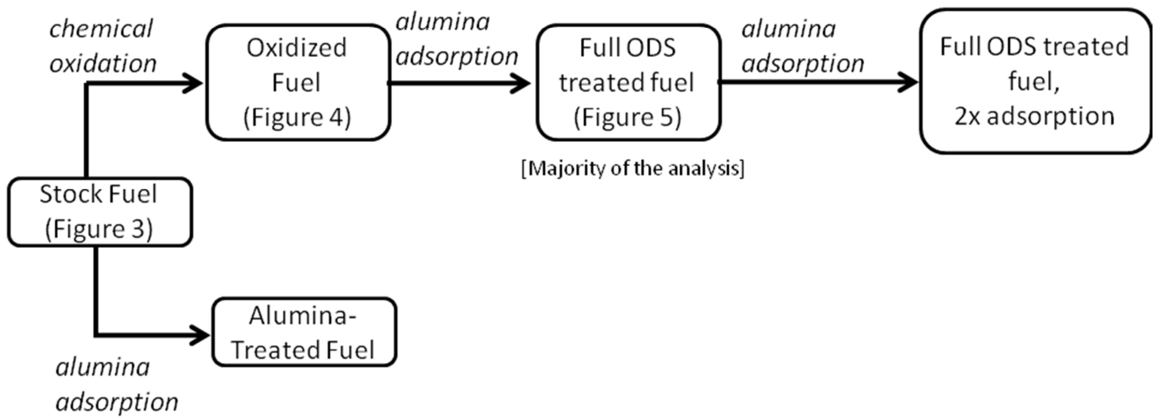
Treatment of Samples. Figure S-1 is a schematic of the treatment procedures that were used for the jet fuel samples. In brief, samples were analyzed following alumina treatment alone (which showed little effect); following oxidation (which showed conversion of sulfur compounds to more polar and less volatile compounds identified as sulfones in Figure 4 of the main manuscript); following the combined oxidation + adsorption treatment (i.e., the full ODS treatment, which showed removal of the sulfones formed by oxidation – and as shown in Figure 5 of the manuscript); and following oxidation and two alumina adsorption treatments.



GC×GC-SCD Analysis of Jet Fuel #3773. In the main manuscript, we show GC×GC-SCD chromatograms for the analysis of fuel sample 4177. We focus on 4177 as its chromatogram contained a more substantial unresolved complex mixture (UCM) than did 3773. Here, we provide the corresponding chromatograms for 3773 – as shown in Figure S-2a (stock), S-2b (oxidized), and S-2c (full ODS treatment). As anticipated in the main body of the manuscript, the sulfur content of 3773 is dominated by benzothiophenes compounds. Following oxidation, Figure 2b shows near quantitative conversion of the native sulfur compounds to less volatile and more polar compounds for sample 3773. We identify the new compounds in the oxidized 3773 sample as sulfones. Figure 2c shows that after oxidation and alumina treatment, the sulfur content of the 3773 sample consists primarily of benzothiophenes compounds in their native, non-oxidized states.

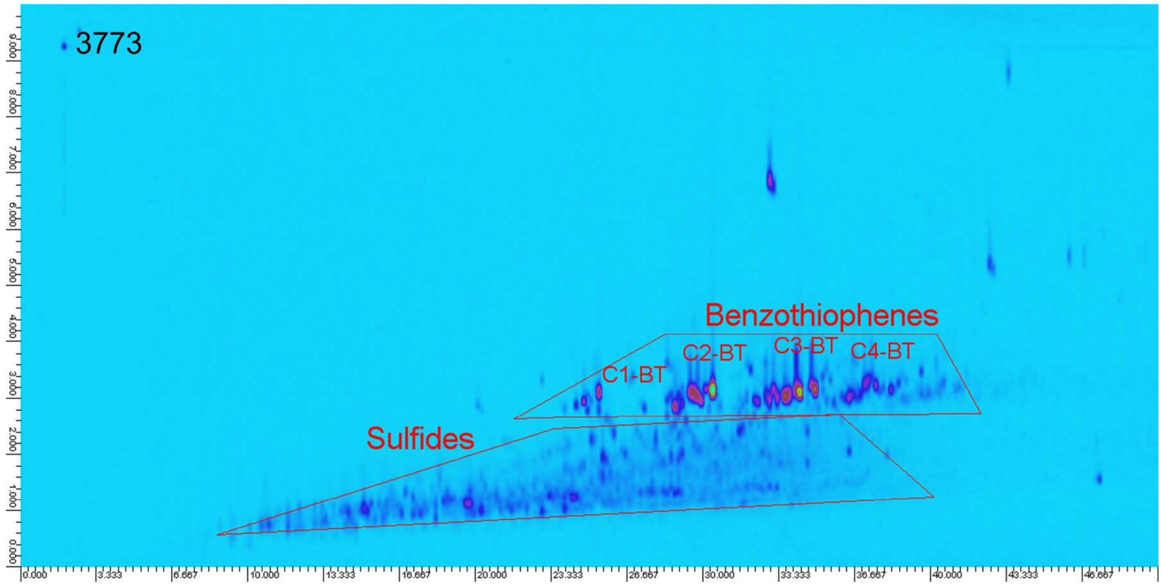


Figure S-2a. GC×GC-SCD chromatogram of stock sample 3773, showing the breakdown between benzothiophenes (dominant) and SDT (minority).

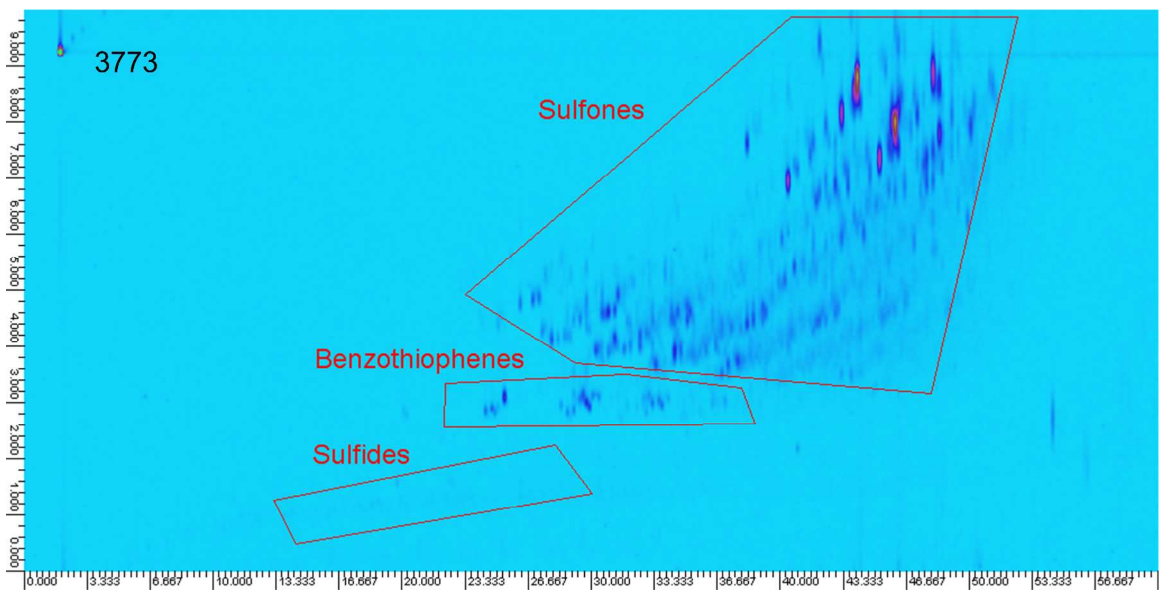


Figure S-2b. GC×GC-SCD chromatogram of oxidized sample 3773, showing that the SDT compounds were nearly quantitatively converted to sulfones and only benzothiophenes remain in their native form.

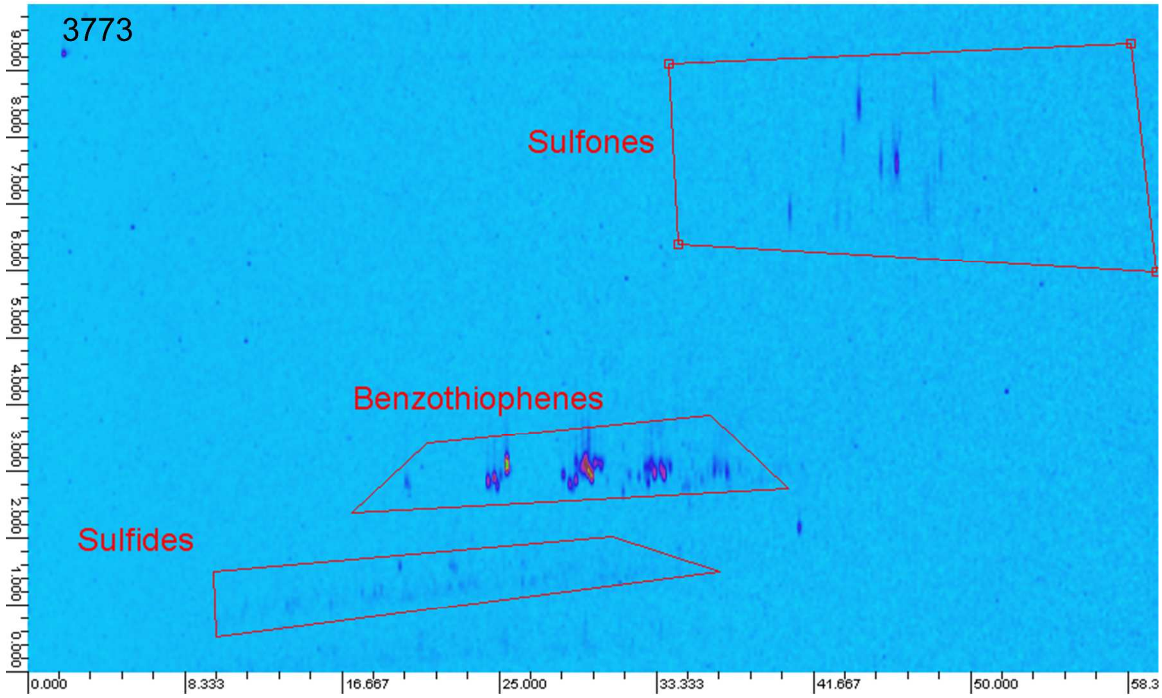


Figure S-2c. GC×GC-SCD chromatogram of the sample 3773 after full ODS treatment (oxidation and adsorption), showing the benzothiophenes are the primary remaining source of sulfur compounds in the fuel.

GC×GC-ToFMS Analysis of Jet Fuels. We performed GC×GC-ToFMS analysis of the stock and treated jet fuels. Figures S-3a and S-3b show the benzothiophenes (BT) before (S3a) and after (S3b) ODS treatment for the 3773 jet fuel samples. In accord with the GC×GC-SCD measurements, the BT peaks have clearly been reduced substantially. Figure S3c shows new peaks, which we attribute to benzothiophenes-sulfones (BT-S), have appeared in the ODS treated jet fuel. Figures S-4a and S-4b provide similar data to Figures S-3a and S-3b, but for the 4177 sample. Figures S-5 and S-6 provide greater detail on the peaks we attribute to C2- and C3- BT-S compounds. Figure S-5a shows 3 peaks (A, B, and C) that would correspond to the primary 3 isomers of C2-BT compounds present in 3773 and apparent in Figure S-3a. Figures S-5b, c, and d show the mass spectra of peaks A, B, and C, showing that in each case that the ions attributable to C2-BT-S compounds (194 and 151) signals present. Figure S-6 is analogous to Figure S-5, with Figure S-6a showing 3 peaks (X, Y, and Z) that would correspond to the 3 primary isomers of C3-BT-S compounds, and Figure S-6b, c, and d showing the mass spectra of each of these peaks that are indeed consistent with C3-BT-S compounds with insignificant amounts of contamination from other ion sources. In a similar way, we attempted to identify oxidized sulfur peaks resulting from non-BT compounds in the stock jet fuel and were unable to locate anything conclusive. The challenge for identifying non-BT compounds is much greater than the BT compounds – even after oxidation – because: 1) the non-BT compounds are present in a far greater number of different types than the BT compounds and 2) seemingly, the mass spectra of the non-BT compounds and non-BT-S compounds are less distinct from the hydrocarbons that dominate jet fuels. Molecular identification of the non-BT compounds present in jet fuel is an important goal, as this information would aid efforts to design specific adsorbents for their removal. Future work in this area might take advantage of the increased polarity of the non-BT-S compounds to separate them from the fuel matrix prior to GC or GC×GC analysis.

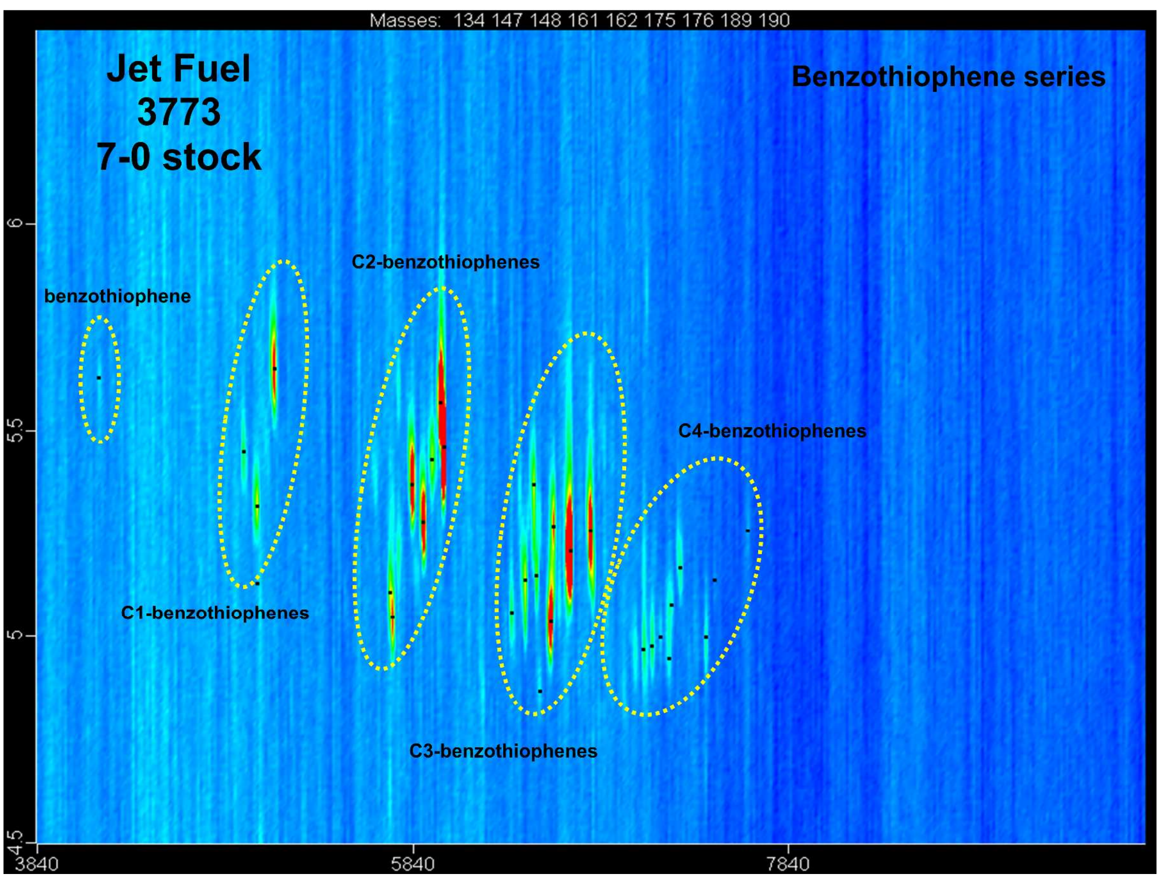


Figure S-1a. Jet fuel (3773 POSF) prior to any treatment. Ion count for benzothiophenes shown, 134, 147, 148, 161, 162, 175, 176, 189, 190.

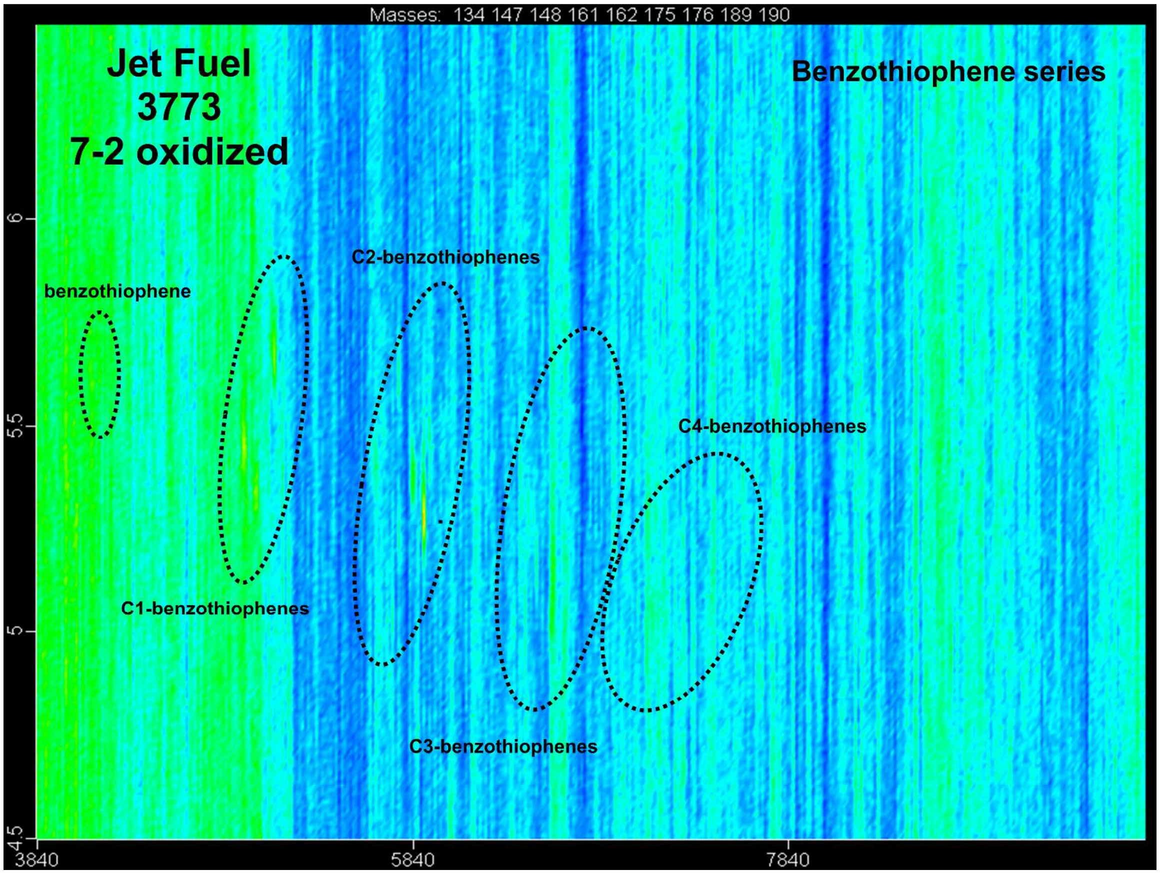


Figure S-1b. Jet fuel (3773 POSF) following ODS treatment. Ion count for benzothiophenes shown, 134, 147, 148, 161, 162, 175, 176, 189, 190.

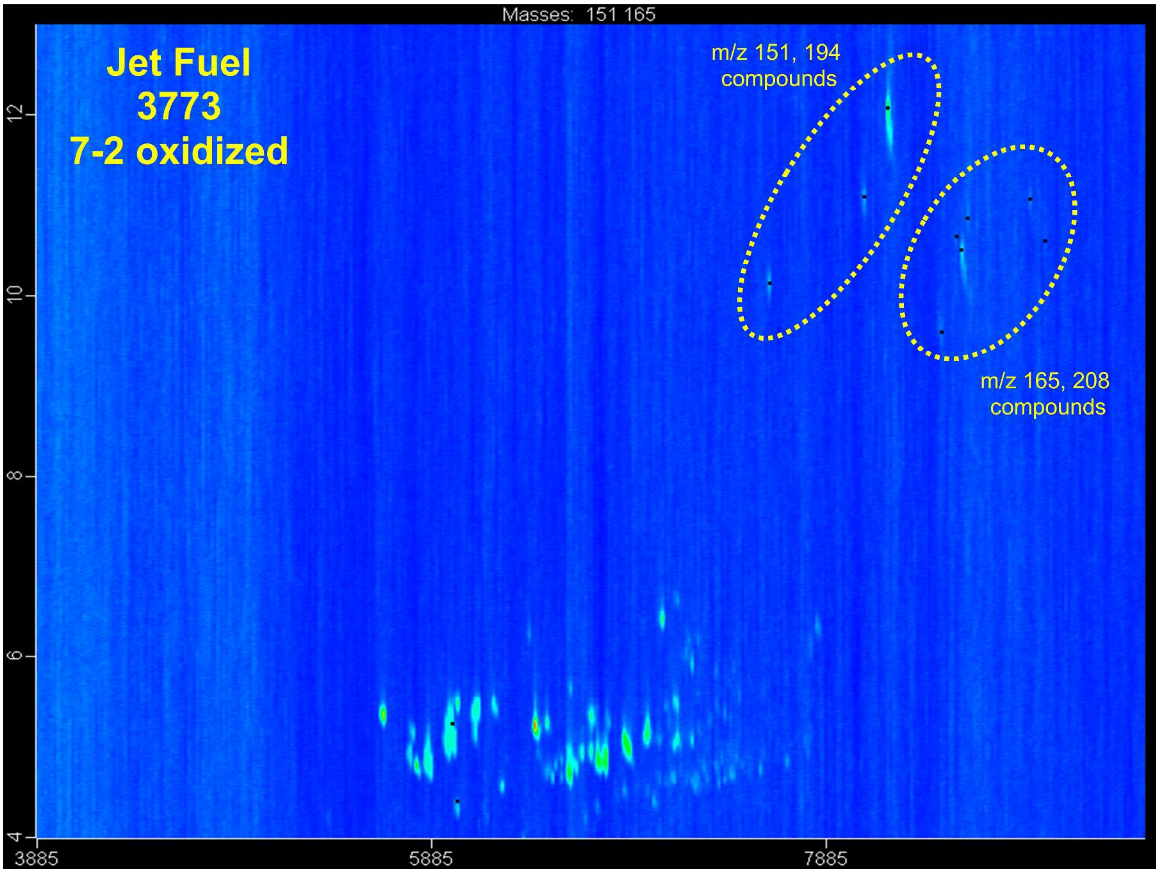


Figure S-1c. Jet fuel (3773 POSF) following ODS treatment. Ion count for benzothiophenes-sulfones shown, 151 and 165.

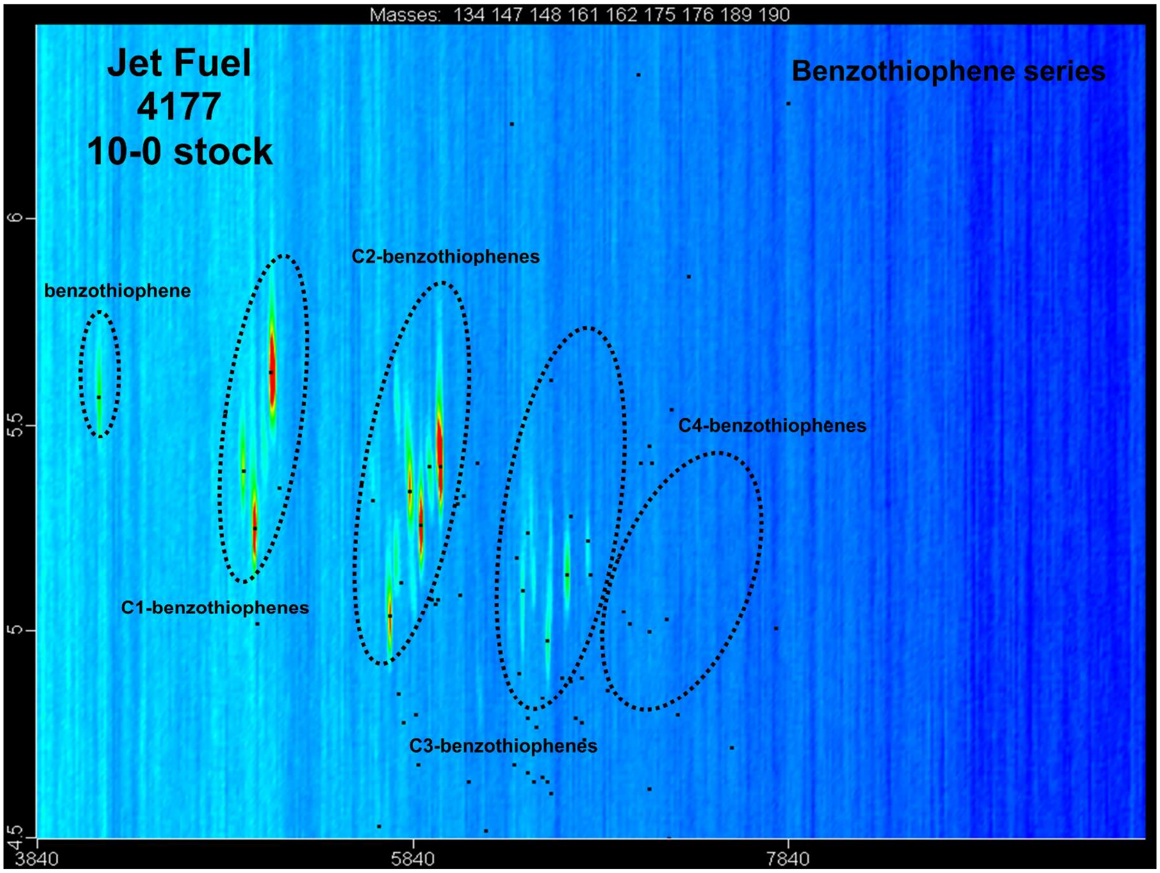


Figure S-2a. Jet fuel (4177 POSF) prior to any treatment. Ion count for benzothiophenes shown, 134, 147, 148, 161, 162, 175, 176, 189, 190.

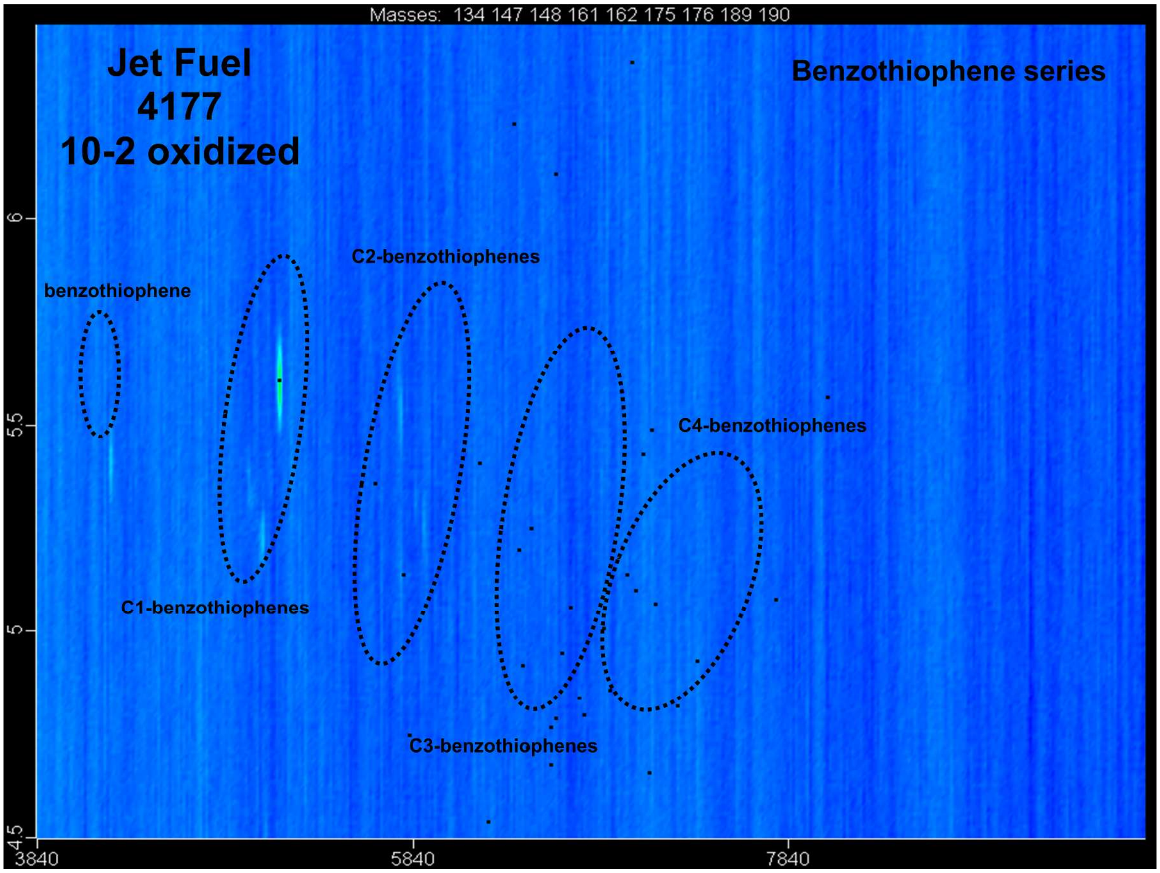


Figure S-2b. Jet fuel (4177 POSF) after ODS treatment. Ion count for benzothiophenes shown, 134, 147, 148, 161, 162, 175, 176, 189, 190.

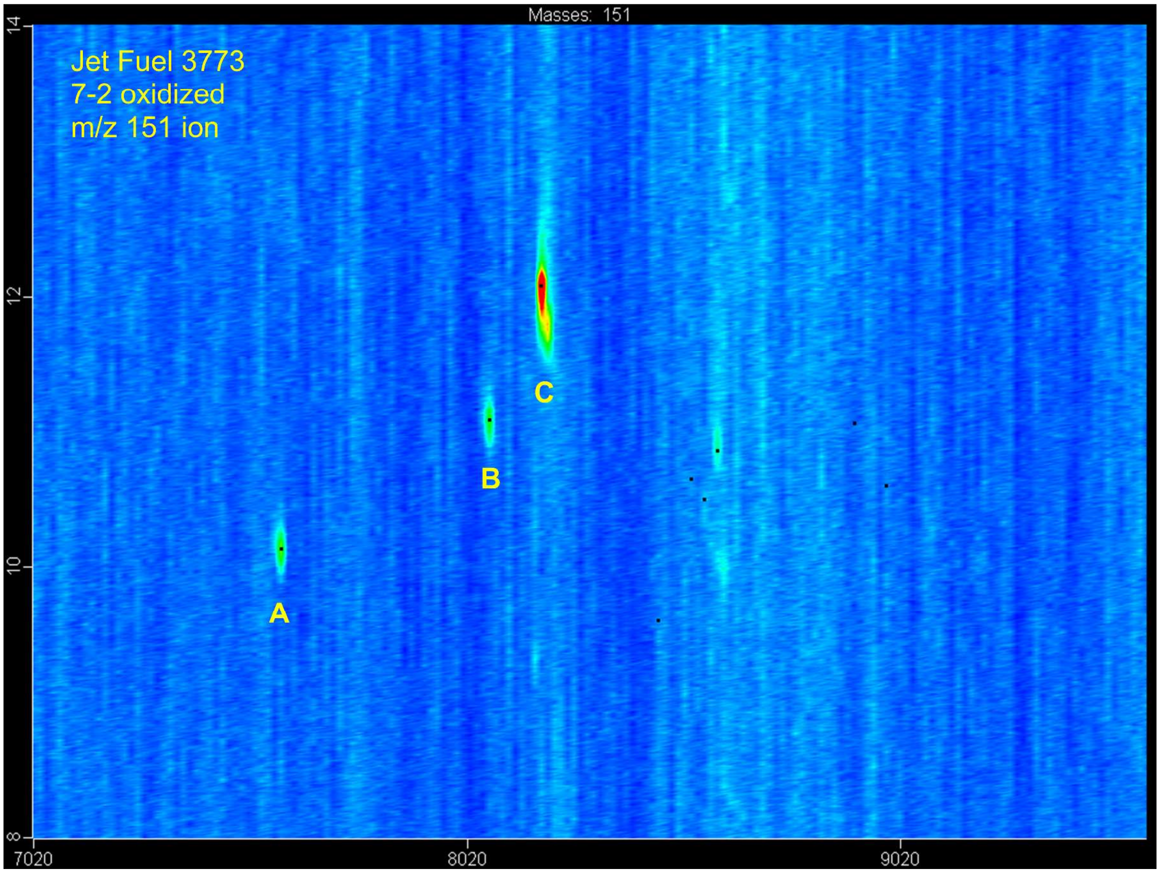


Figure S-3a. Jet fuel (3773 POSF) after ODS treatment, focusing on the region of m/z 151 elution. Peaks A, B, and C are attributed to C2-benzothiophene-sulfones.

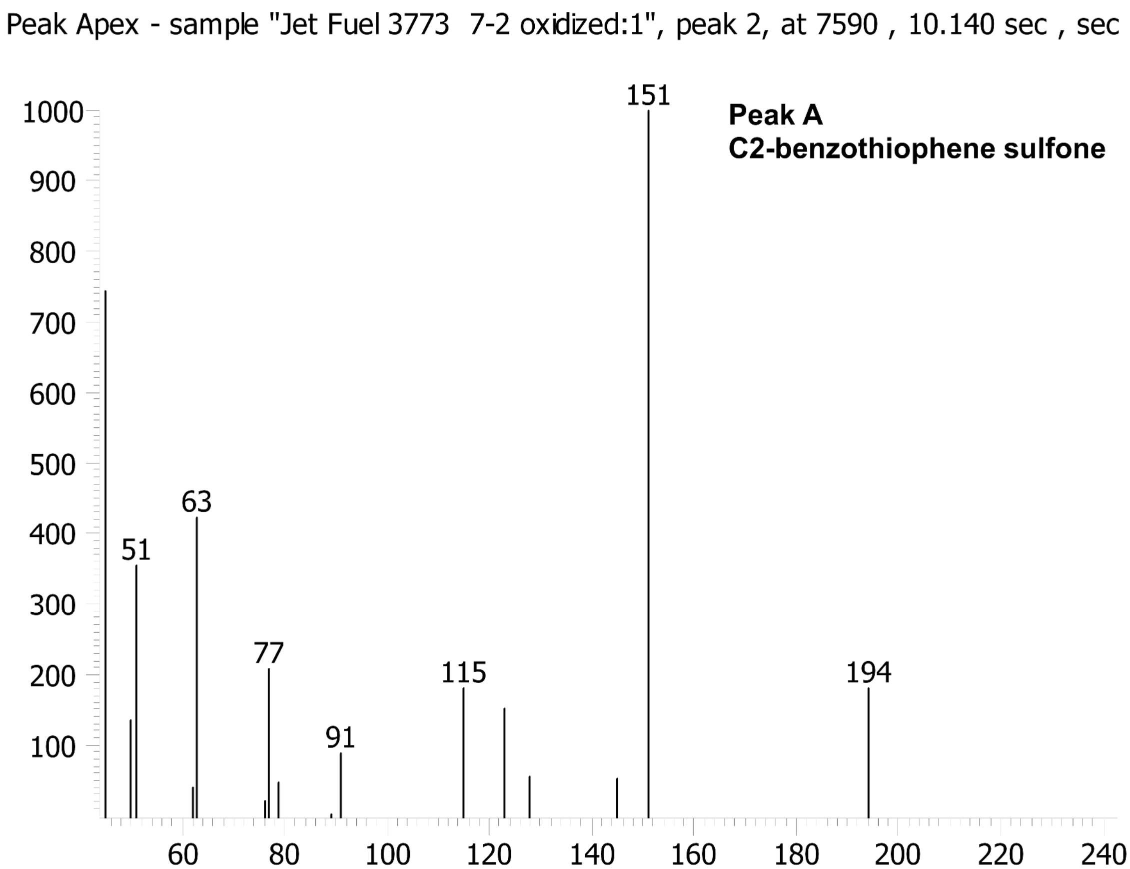


Figure S-3b. Mass spectrum of Peak A from Figure S-3a. Jet fuel (3773 POSF) after ODS treatment.

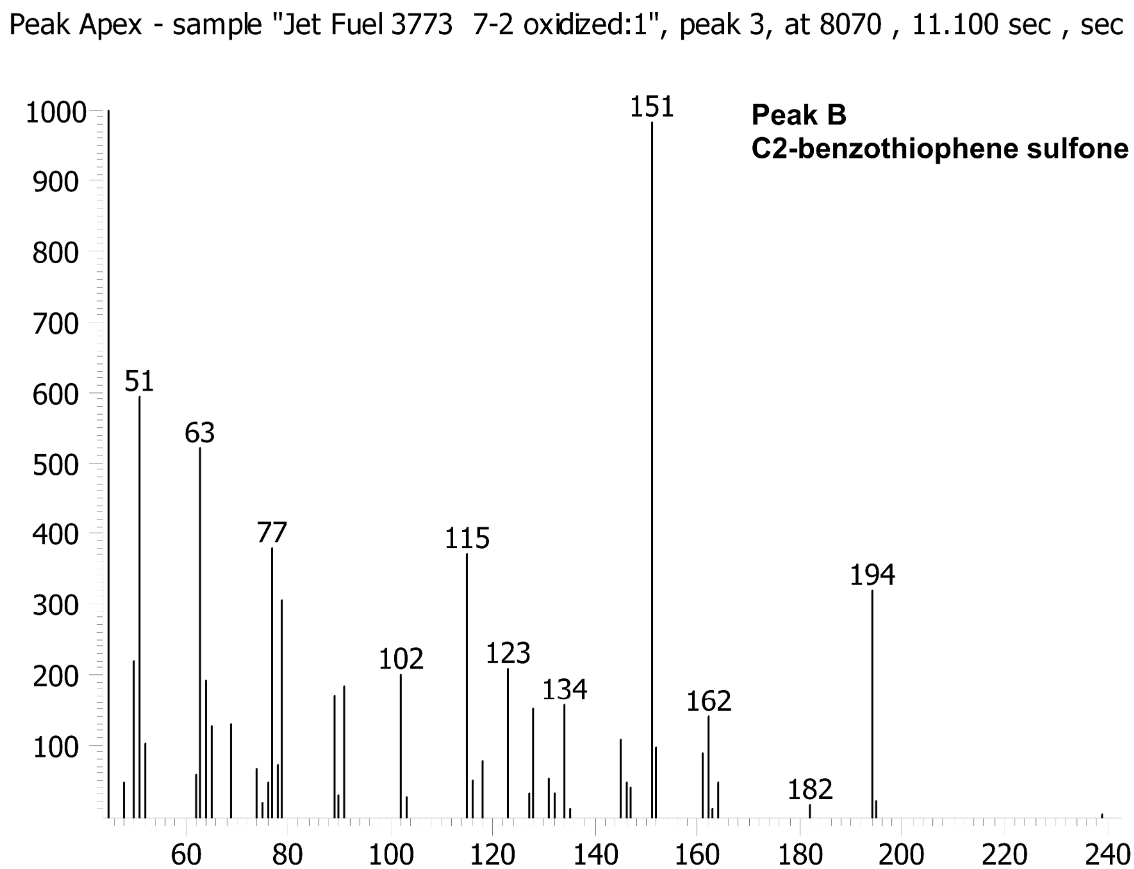


Figure S-3c. Mass spectrum of Peak B from Figure S-3a. Jet fuel (3773 POSF) after ODS treatment.

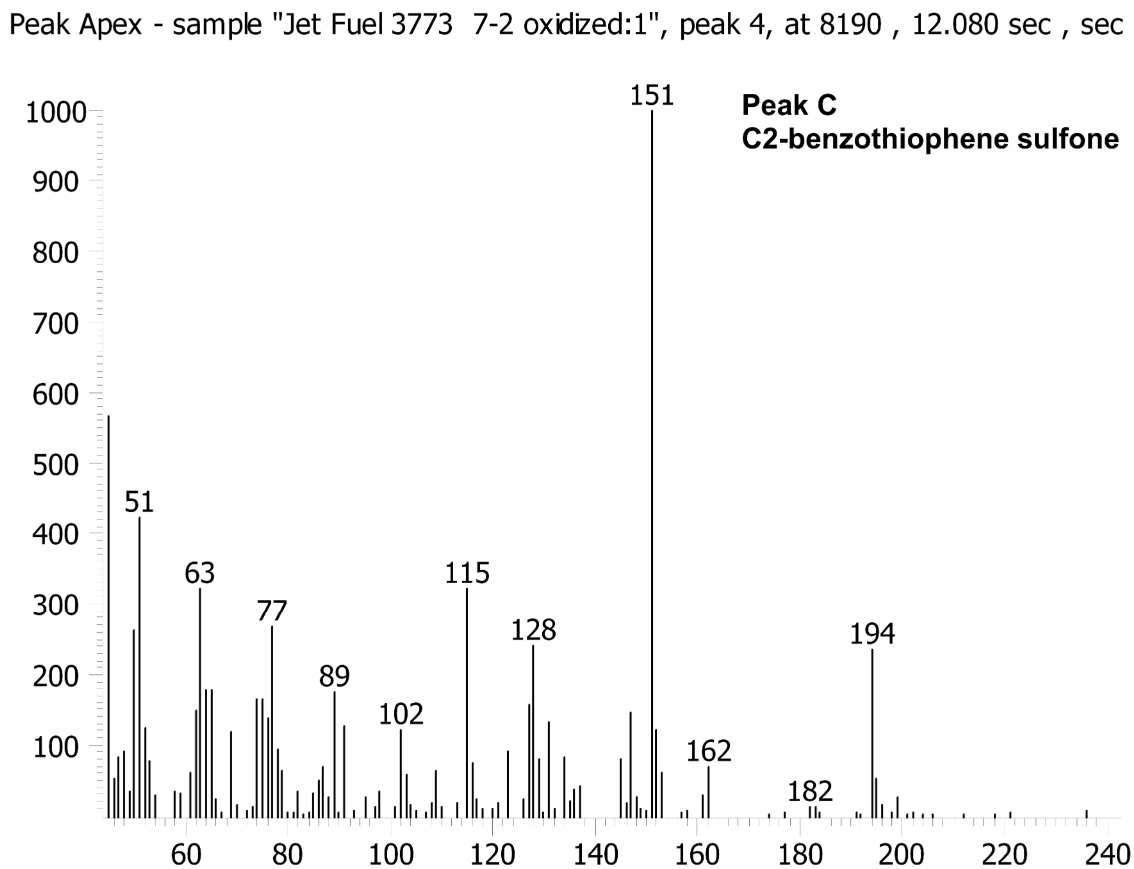


Figure S-3d. Mass spectrum of Peak C from Figure S-3a. Jet fuel (3773 POSF) after ODS treatment.

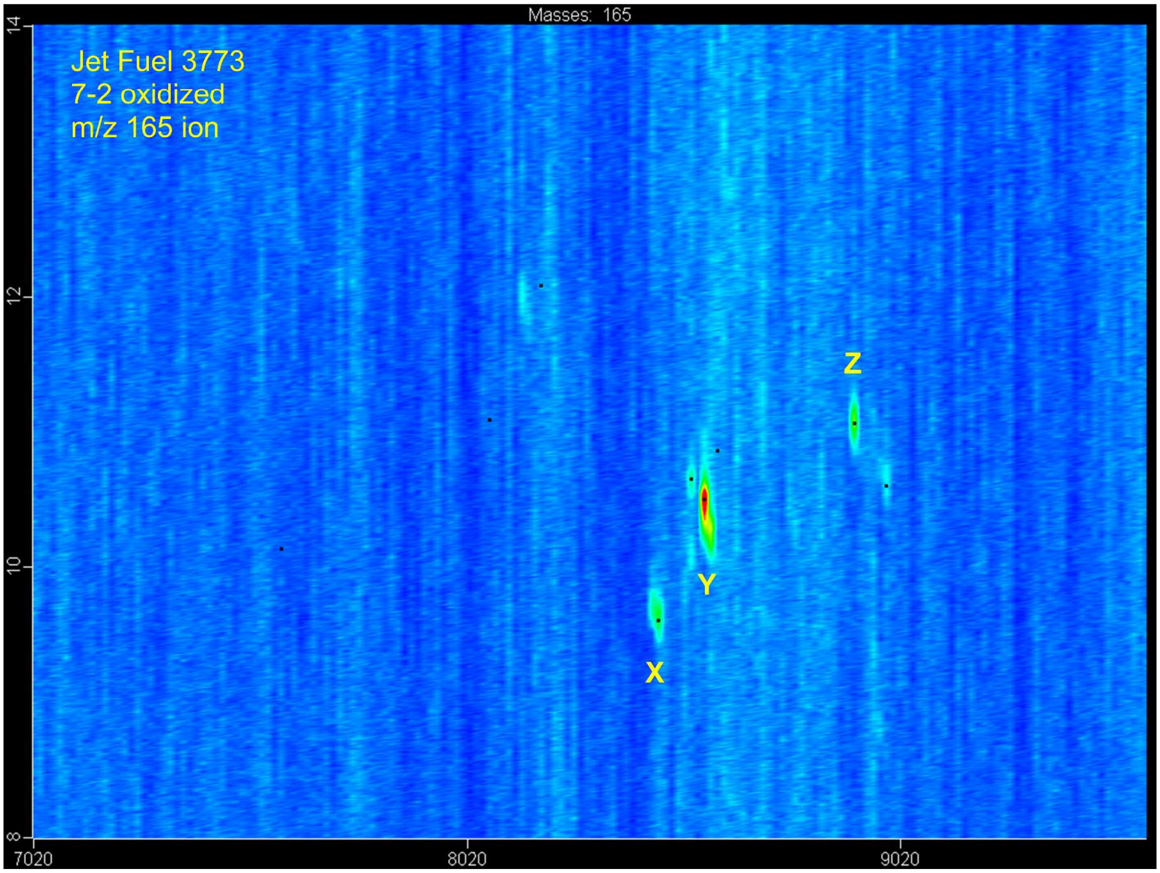


Figure S-4a. Jet fuel (3773 POSF) after ODS treatment, focusing on the region of m/z 151 elution. Peaks X, Y, and Z are attributed to C3-benzothiophene-sulfones.

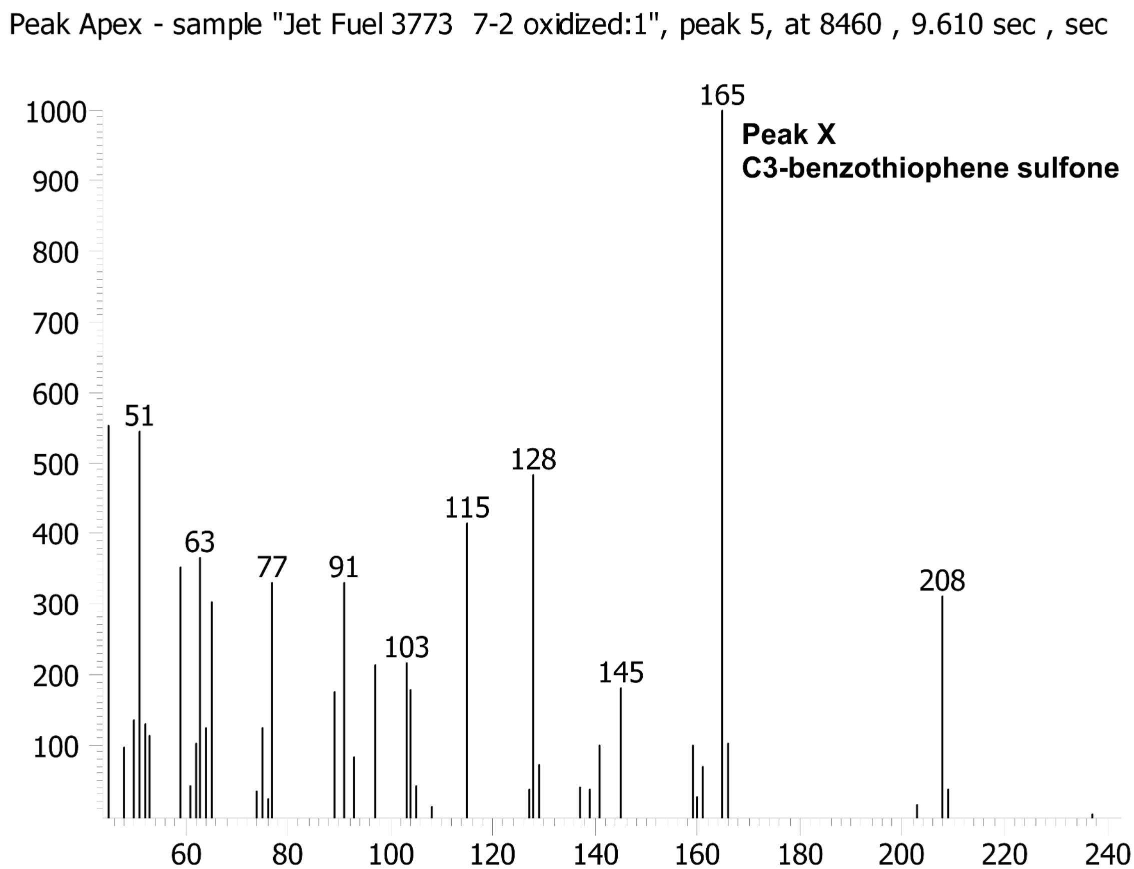


Figure S-4b. Mass spectrum of Peak X from Figure S-4a. Jet fuel (3773 POSF) after ODS treatment.

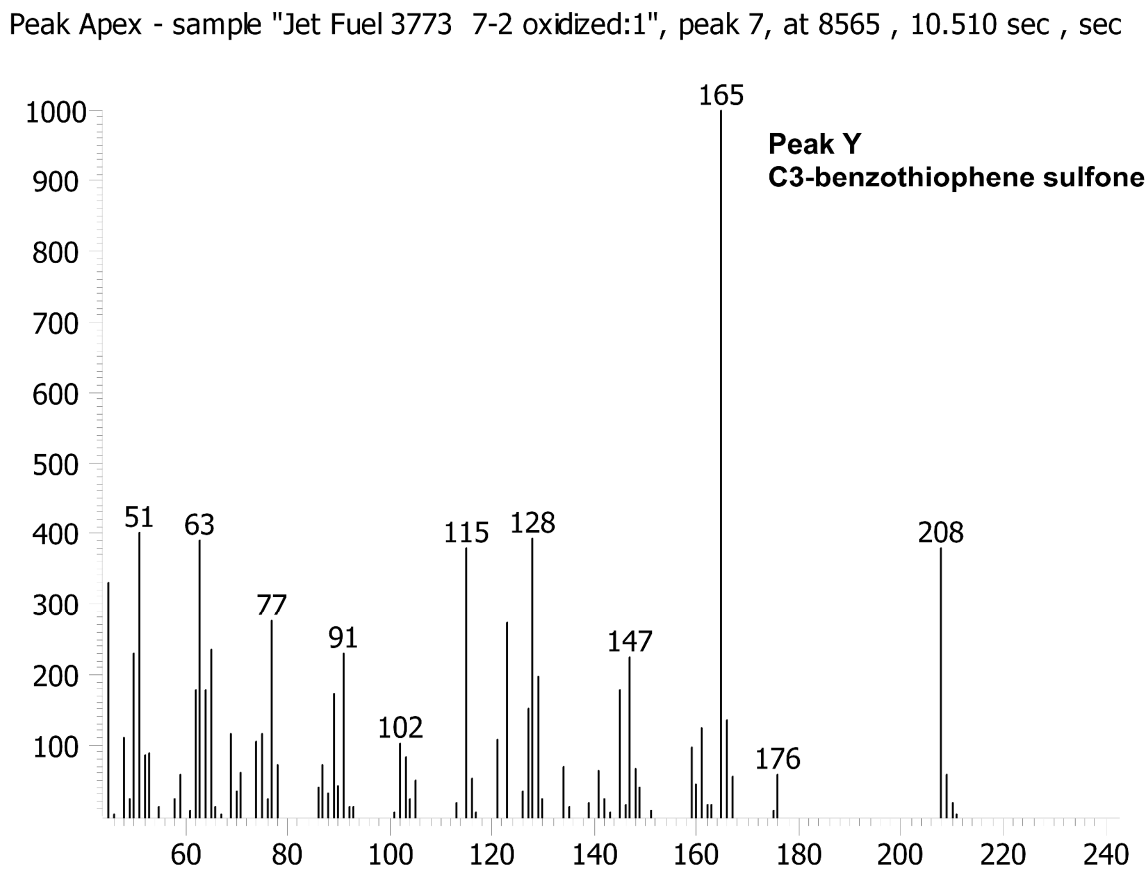


Figure S-4c. Mass spectrum of Peak Y from Figure S-4a. Jet fuel (3773 POSF) after ODS treatment.

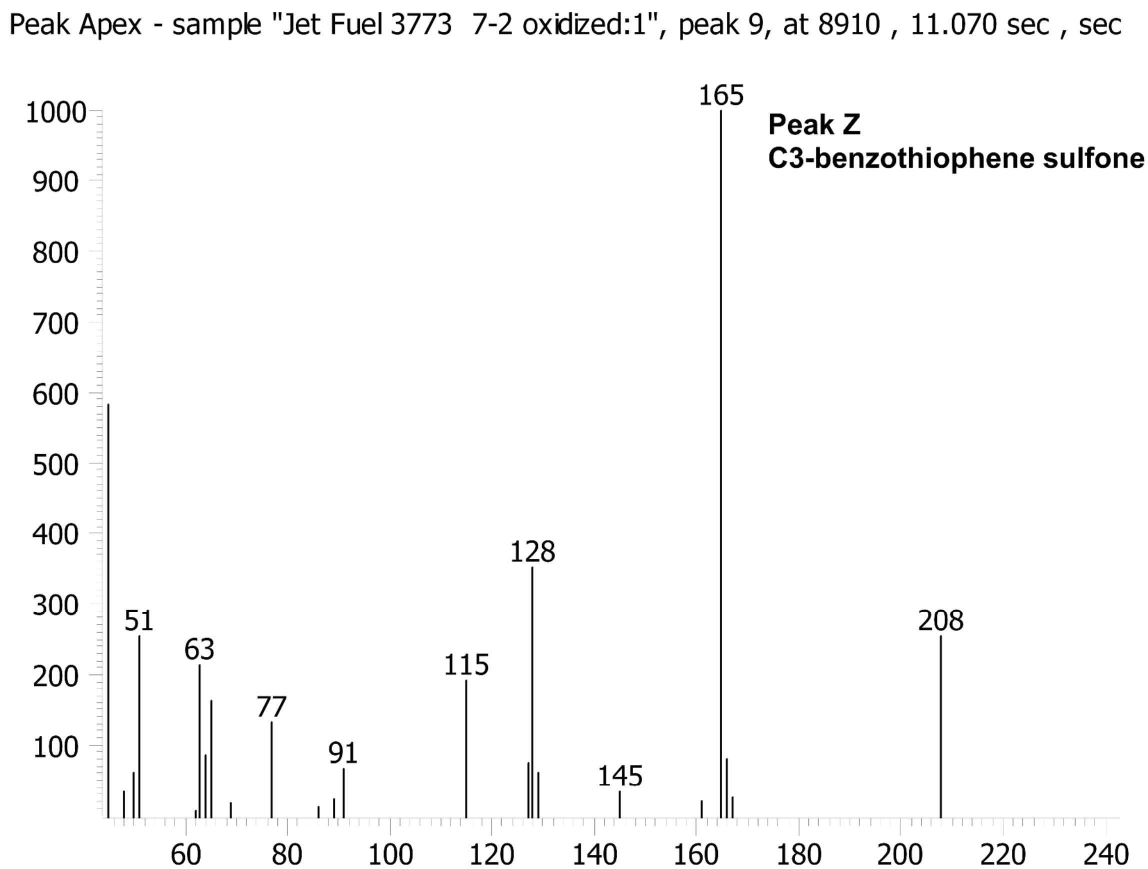


Figure S-4d. Mass spectrum of Peak Z from Figure S-4a. Jet fuel (3773 POSF) after ODS treatment.