

Jet Fuel Chemical Composition, Weathering, and Identification as a Contaminant at a Remediation Site, Determined by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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We have characterized a jet fuel (JP-8) contaminated site and compared its chemical constituents to a set of unweathered JP-4, JP-5 and JP-8 weathered standards by use of an all-glass heated inlet system (AGHIS) coupled to a home-built 6.0 T Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. From as little as a 1 μ L septum injection of JP-8, JP-5, or JP-4 into the AGHIS, we obtained high-resolution mass spectra containing ~ 400 peaks, $50 \leq m/z \leq 280$, with as many as 4 peaks at the same nominal mass. A molecular formula (elemental composition) could be assigned to each peak, solely on the basis of accurate mass measurement to ± 0.8 ppm. With increased "weathering" (i.e., evaporation), JP-8 exhibited a significantly increased number and relative abundance of higher-mass ($200 \leq m/z \leq 250$) species, in accord with a previously observed increase in gas retention times with increased weathering. By extraction and subsequent FT-ICR mass analysis of JP-8 contaminated soil, we were able to identify and correlate many species to those present in the unweathered/weathered standards, as well as identify a small number of new species attributed to degradation products from prolonged weathering and matrix components arising from species extracted from the soil.

Environmental Importance. The U. S. consumes more than 100 billion gallons of fossil fuel annually.¹ Consequently, hydrocarbon spills represent the largest and most widespread cause of soil and groundwater contamination. A large portion of the contamination is the direct result of leaking underground storage tanks. In 1993, the United States Environmental Protection Agency identified approximately 1.5 million leaking underground storage tank sites in the United States. At approximately 40% of these sites, petroleum hydrocarbons had leaked into the groundwater, thereby increasing the potential for drinking water contamination and off-site hazard migration/liability.² In addition, pipeline ruptures, tanker failures, and various other production and transportation

accidents can produce hydrocarbon-contaminated soil and groundwater. The potential for a large release of hydrocarbon fuels into the environment and the alarming frequency of smaller releases from USTs has prompted greatly increased interest in remediation research and contaminant characterization and its applications to petroleum-contaminated sites.

Analytical Difficulties. The complex nature of the soil matrix coupled with the complexity of the hydrocarbon fuel itself poses a monumental problem for analysis of hydrocarbon-contaminated soil extracts.^{3–10} To date, the failure to unravel the complex mixtures that make up commercial fuels is the direct result of the compositional diversity of the fuels and the failure of modern analytical techniques to resolve adequately their individual components.^{11–16} Chromatographic techniques coupled with mass spectrometry have been the most successful but are still unable to identify all of the individual components that comprise the fuel. Headspace gas chromatographic analyses are used to eliminate many of the soil matrix contributions,^{9,17} but also suffer in the

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identification of the contaminant components due to limited chromatographic resolution.^{18,19}

Apart from limited analytical resolution, other problems arise in almost every aspect of contaminant monitoring. For example, the contaminant(s) may adsorb to soil particles and may slowly leach from the soil.^{20,21} As a result, it is essential to define the composition of the retained contaminant, its degradation products, and leaching behavior, to evaluate remediation of the contaminant site and determine the impact of the contaminant on the surrounding environment. Furthermore, for large terrestrial releases, the primary solvent of the soil itself shifts dramatically from water to that of the contaminant.^{21,22} As the large volume of bulk contaminant migrates downward through the soil, a portion will become attached to the soil as a result of capillary forces.²³ The retained contaminant is known as immobile or "residual saturation". If the volume of the hydrocarbon contaminant is small relative to the soil surface area, the contaminant will be exhausted, and its downward migration will cease. If the volume is large relative to the surface area of the soil, the contaminant can cause soil shrinkage¹ and could penetrate the clay soil layer and enter the groundwater. If the contaminant plume penetrates below the clay soil layer, the nonpolar hydrocarbon contaminants will float on top of the groundwater and advance according to the speed and direction of the groundwater flow. If the plume is not acted on soon after release, most of the hydrocarbons will rise and fall with the groundwater level so as to produce a smearing effect so that the bulk hydrocarbon layer is now exposed to a larger surface area of uncontaminated soil.^{24,25} Such increased exposure results in an increase in the "residual fraction" and increases the volume of soil that will require cleanup, thereby increasing the cost of remediation. Penetration into the clay soil layer also results in a solvent extraction of the polar components of the hydrocarbon contaminant from the bulk fuel to the groundwater.²⁶ Once contaminated, the groundwater requires immediate costly remediation, due to increased contaminant mobility and risk of human exposure.²⁷

The loss of the contaminant by means other than bioremediation, namely, abiotic loss and abiotic transformation, is important

in the risk assessment evaluation of a contaminated site.^{28,29} Abiotic loss can occur by physical removal (washout), sorption, leaching, and stripping. Such losses are undesirable because of transfer of the contaminant from one matrix to another (soil to air, soil to water). However, abiotic loss can help slow progress of the contaminant plume (e.g., by sorption, as noted above) or may itself provide a remediation technique (e.g., vacuum extraction and soil venting). Abiotic transformations, distinct from physical abiotic losses, include reactions such as hydrolysis, photodegradation, and reduction/oxidation reactions that chemically modify or break down the target contaminant.^{30–32} Both processes must be accounted for on a component by component basis, to describe fully the fate of compositionally diverse contaminants as they disperse in the environment and to assess the health risks of the entire site.^{33,34} There have been significant advances in this area of remediation analysis.^{28,31,35–38} However, conclusions based on those analyses are restricted to broad generalized classes of compounds, because it has not been possible to identify specific individual hydrocarbon contaminant components.^{39–44}

FT-ICR MS is a mass spectrometry technique that offers ultrahigh mass resolving power ($(m/\Delta m_{50\%}) > 1\,000\,000$, in which $\Delta m_{50\%}$ is the mass spectral peak full width at half-maximum peak height), high mass accuracy (less than 1 ppm), and rapid analysis,^{45–53} making it attractive for the analysis of complex

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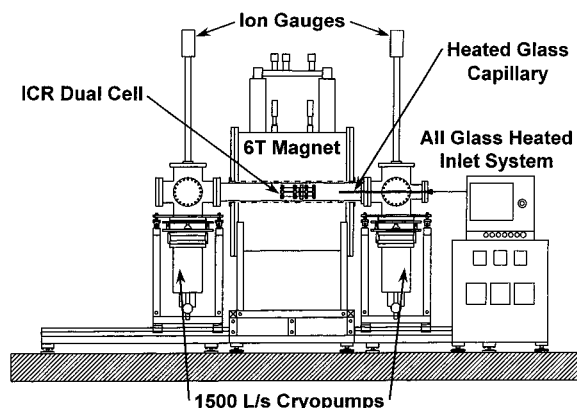


Figure 1. Schematic diagram of the 6.0 T Fourier transform ion cyclotron resonance mass spectrometer coupled to an all-glass heated inlet system (AGHIS) via a heated glass capillary for volatile mixture analysis.

volatile mixtures.⁵⁴ Here we report environmental applications of FT-ICR mass spectrometric analyses for preliminary characterization of a U. S. Air Force jet fuel (JP-8) spill site by use of a home-built 6.0 T FTICR-MS coupled to an All-Glass Heated Inlet System (AGHIS).⁵⁵ We have obtained high-resolution mass spectra of electron-ionized jet fuel samples from as little as a 1- μ L septum injection into the AGHIS. Molecular formulas (elemental compositions) may be assigned from accurate mass measurement alone. On the basis of analysis of unweathered and weathered jet fuel standards, all components may be identified by their individual mass (and molecular formula), monitored as a function of weathering, and then compared with the residual fraction extracted from the JP-8 contaminated soil. The composition of the residual fraction can then be monitored as a function of time to provide a component-by-component evaluation of the remediation effectiveness, thereby directly yielding leaching information useful for risk assessments.

EXPERIMENTAL SECTION

All experiments were carried out on a home-built FT-ICR mass spectrometer equipped with a horizontal 15-cm diameter room bore 6 T magnet (Oxford Corp.) and a modular ICR data station (MIDAS).⁵⁶ The mass spectrometer features dual closed perforated cylindrical Penning ion traps⁵⁷ and is evacuated by a pair of 1500 L/s (N_2) cryopumps (CryoTorr 8, CTI Cryogenics, Mansfield, MA). The system, as shown in Figure 1, is coupled to an All-Glass Heated Inlet System (AGHIS) (R. J. Brunfeldt Co.) via a resistively heated glass transfer line (0.5-mm i.d.) containing a drawn glass conductance limit ($\sim 80 \mu\text{m}$ i.d.) as described in more

detail elsewhere.⁵⁸ The sample is volatilized in one of two inlets (septum or ampule) and led to the source cell by a heated glass capillary terminating within 2 in of the dual ICR ion traps. This arrangement restricts the sample vapor to an all-glass path from the septum to the ICR cell and enables analysis of hydrocarbon samples while minimizing fragmentation that would otherwise result from catalytic cracking at a hot metal surface. The AGHIS oven temperature ($\sim 250^\circ\text{C}$) and transfer lines ($\sim 200^\circ\text{C}$) were maintained at elevated temperature to ensure that the sample remains in the gas phase throughout its passage to the mass spectrometer. The source vacuum cross was kept at $\sim 150^\circ\text{C}$ to prevent the sample vapor from condensing onto the chamber walls.

The volatilized sample (1- μ L injection volume) was ionized by a low-energy electron beam (18 eV and 500-ms beam duration) at a source pressure of $\sim 5 \times 10^{-9}$ Torr (measured ~ 1 m above the source cell) before ion transfer to the analyzer trap ($P = 5 \times 10^{-10}$ Torr, again measured ~ 1 m above the analyzer vacuum cross) for excitation and detection. [The electron energy in the present experiments (18 eV) was carefully selected to maximize ion production and trapping efficiency while minimizing fragmentation in a test hydrocarbon mixture of known compounds.] The trapping potential was lowered to 0.4 V for ~ 100 ms prior to broadband frequency-sweep excitation (100 kHz to 1.56 MHz, sweep rate of 1×10^9 Hz/s, $21.3 V_{p-p}$) followed by direct-mode image current detection (2.56 MHz Nyquist bandwidth) to yield 2 Megaword time-domain data. Time-domain data were Hanning apodized, followed by a single zero-fill, followed by FFT and magnitude calculation. The three highest magnitude points for each resolved FT-ICR frequency-domain spectral peak were fitted to a quadratic. Two-parameter frequency-to- m/z conversion⁵⁹ (see below) generated a final m/z spectrum. Accurate mass and peak height are reported as the centroid of that quadratic, to yield a peak list of elemental compositions.

The jet fuel (JP-8) was obtained from Eglin Air Force Base (Fort Walton Beach, FL) and used as an unweathered standard. Unweathered JP-5 and JP-4 standards were obtained from Restek Corp. as neat liquids. Weathered standards were prepared from the unweathered JP-8 standard in the following manner. Aliquots of the unweathered fuel (JP-8) were transferred to glass vials and placed under a gentle stream of dry nitrogen. Weathering is defined by percent weight loss: e.g., 25, 50, 75, 85, and 95% weathered JP-8. CH2M Hill (Gulf Breeze, FL) provided the contaminated soil samples taken from a jet fuel (JP-8) contaminated site at Eglin Air Force Base. The soil sample consisted primarily of sand with little vegetative matter. A portion of the soil sample (20 g) was placed in a pure cellulose extraction thimble and Soxhlet extracted in chloroform (~ 200 mL) for 24 h. The remaining extract was distilled over a hot plate until only ~ 10 mL remained. The liquid was then placed in a SpeedVac for ~ 3 h to remove the excess solvent before removal to a freezer until analysis. Removal of the extraction solvent yielded a small amount ($\sim 5 \mu\text{L}$) of brownish liquid that was injected ($\sim 1 \mu\text{L}$ injection volume) into the AGHIS and analyzed for compositional similarity to unweathered/weathered jet fuel standards.

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The extraction of uncontaminated soil produced no significant (liquid) product, thereby precluding sample introduction by the septum injection method used for contaminated soil extracts. The soil consisted almost entirely of sand, with virtually no extractable organics. We attempted to vaporize the uncontaminated soil sample directly, but observed only a few mass spectral peaks. It appears likely that our present glass inlet allows excessive dilution of the sample by room air. A new inlet and mass spectrometer designed for introduction of low-concentration organics is currently under construction.

Each high-resolution mass-to-charge ratio spectrum was processed to obtain molecular formulas for all peaks. The analysis resulted in the resolution and assignment of 300–500 peaks in each mass spectrum in the range $50 \leq m/z \leq 280$. Molecular formulas were assigned by use of the Molecular Formula Calculator in the MIDAS FTMS analysis software with the possible molecular formulas limited to isotopic contributions from ^{12}C , ^{13}C , ^1H , ^{14}N , ^{16}O , ^{32}S , and ^{34}S . Heavy isotope contributions were limited to two heavy isotopes to restrict the number of possible molecular formulas and because very low abundance species (arising from other isotopes) cannot be reliably distinguished from noise. Error tolerance was set to ~ 3 times the standard deviation of the error in assignment of the internal mass calibrants (~ 2 ppm). External frequency-to-mass calibration based on (separate) detection of a set of 10 standard hydrocarbon compounds sufficed to identify highly saturated (highest mass defect at each nominal mass) components of the jet fuel. Unequivocal identification of saturated species bracketing the entire mass range of interest then provided a reference set for (more accurate) internal mass calibration. The internal calibration was further confirmed by use of the resulting jet fuel internal calibration coefficients to predict the m/z s of the external calibration peaks in the 10-component mixture.

The standards were each run twice and yielded very similar spectra. A stability evaluation of the current inlet has been performed in three separate experiments by two different researchers on two different instruments,^{49,54,58} twice with standard hydrocarbon mixtures^{49,58} and once with a raw diesel fuel,⁵⁴ all with similar results. At high inlet temperature ($>150^\circ\text{C}$) and an injection volume ranging from 0.5 to 2 μL , the inlet was stable for over 3 h.

RESULTS AND DISCUSSION

Unweathered JP-4, JP-5, and JP-8/Weathered JP-8 Jet Fuels. A 1- μL aliquot of the unweathered jet fuel injected into the septum inlet of the AGHIS provided a stable source pressure of $\sim 5 \times 10^{-9}$ Torr for 1 h. The spectrum consisted of ~ 300 peaks (Figures 2 and 3) in the range $50 \leq m/z \leq 220$, with as many as 3 peaks at each individual nominal mass and a mass resolving power ($m/\Delta m_{1/2}$) of $\sim 120\,000$. A zoom mass inset of the unweathered JP-8 (Figure 2, top) illustrates the chemical complexity of the mass spectrum, showing resolution of three chemically distinct peaks at the same nominal mass. After a single mass calibration over the mass range of interest ($50 \leq m/z \leq 220$), molecular formulas were assigned by the Molecular Formula Calculator in the MIDAS FTMS Analysis software with an average error of ~ 0.5 ppm. At that level, determination of elemental composition from mass is unequivocal. The elemental compositions of all the species in the mass spectrum provide a chemical “fingerprint” of the unweathered JP-8. Deviations from that “fingerprint” then serve to identify

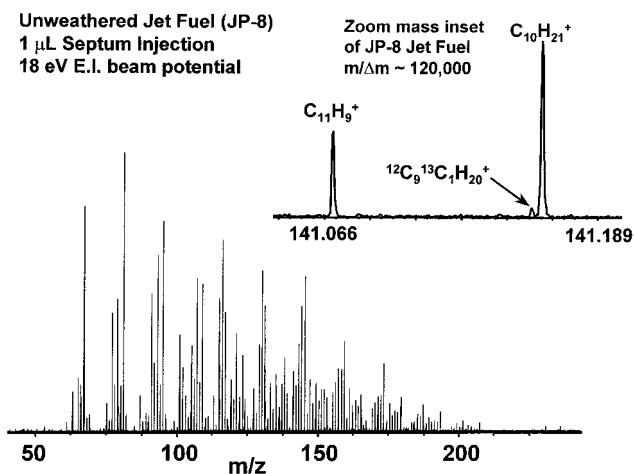


Figure 2. Full-range mass spectrum of the unweathered jet fuel (JP-8) sample resulting from a 1- μL septum injection into the AGHIS (bottom). The voltage of the electron beam used to ionize the vaporized JP-8 sample is held to 18 eV to maximize the abundance of molecular radical cations while reducing the degree of fragmentation. A zoom mass inset of the unweathered JP-8 mass spectrum (top) illustrates the complexity of the mass spectrum. Notice the baseline resolution of three components present at the same nominal mass at a mass resolving power ($m/\Delta m_{50\%}$) of $\sim 120\,000$, in which $\Delta m_{50\%}$ is the mass spectral peak full width at half-maximum peak height.

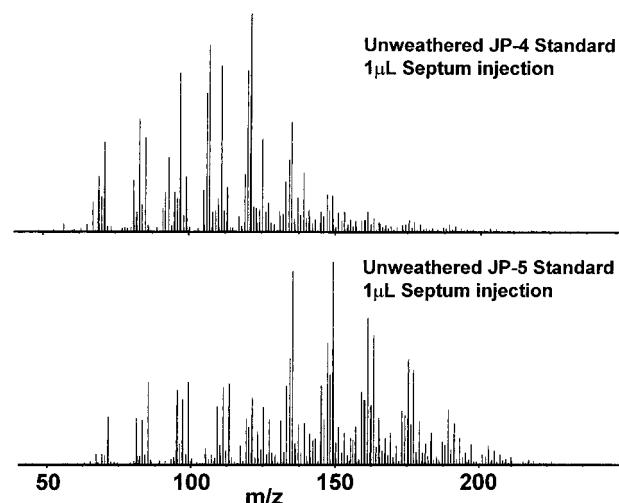


Figure 3. Full-range FT-ICR mass spectrum of unweathered JP-4 (top) and JP-5 (bottom) jet fuels resulting from separate 1- μL septum injections into the AGHIS. Elemental compositions of all the peaks present in each of the mass spectra could be assigned (as well as that of unweathered JP-8 shown in Figure 2), with an average mass error of ~ 0.5 ppm and thereby serve to characterize the soil contaminant fuel by the chemical composition of its constituents.

JP-8 in contaminated soil, as well as to differentiate JP-8 from other fuels and other soil constituents.

As described above, 1- μL aliquots from each of 25, 50, 75, 85, and 95% weathered JP-8 samples were also analyzed and molecular formulas assigned for all peaks in the mass spectrum. A slight shift in relative abundances toward higher m/z was evident in proceeding from unweathered to 25 and 50% weathered, becoming more pronounced at 75, 85, and 95% weathered, as shown (for unweathered and 95% weathered JP-8) in Figure 4, left (broadband mass spectrum) and Figure 4, right (zoom mass insets, $200 \leq m/z \leq 250$). A similar shift (without resolution of individual

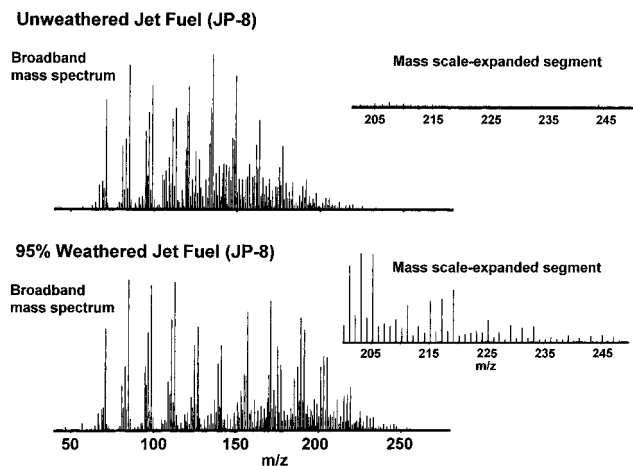


Figure 4. Full-range FT-ICR mass spectrum of an unweathered jet fuel sample (JP-8) (top left) and 95% weathered JP-8 sample (bottom left) resulting from separate 1- μ L septum injections into the AGHIS. Note the substantial increase in the number and relative abundances of higher mass components after weathering. Mass scale-expanded segments ($200 \leq m/z \leq 250$) for both unweathered and 95% weathered JP-8 show the drastic increase in the number and relative abundance of high-mass components as a result of weathering. The spectra have been vertically scaled to the same baseline noise level.

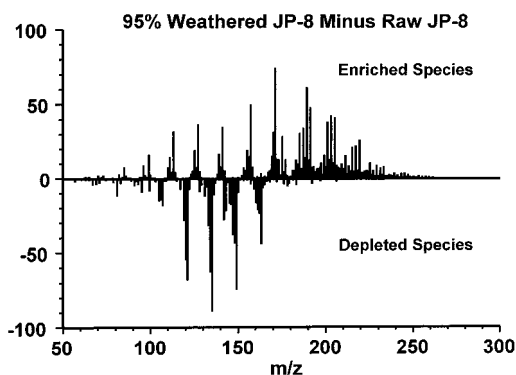


Figure 5. Difference mass spectrum of JP-8 jet fuel (95% weathered minus unweathered). Weathering clearly results in partial or complete removal of low-mass species (negative peaks) to leave high-mass species at higher relative abundance (positive peaks).

components) is also observed in gas chromatographic analyses of other commercial transportation fuels, and is attributed to the preferential vaporization of low boiling point components of the fuel. The FT-ICR mass spectral shift to higher m/z on weathering is reasonable, because the boiling point for most species present in the fuels varies inversely with molecular weight.

Another way to visualize the effect of weathering is from a difference spectrum between 95% weathered and unweathered JP-8 (Figure 5). However, it is not desirable to perform a simple subtraction, in case the two spectra are not perfectly aligned (e.g., due to a different total number of trapped ions in the two spectra). Therefore, before taking a difference, the computer first searches for each analyte peak within an experimentally determined mass window (i.e., wide enough to find one peak, but not so wide as to find a(n) adjacent peak(s)). The computer then determines the relative abundance for each species (in this case, peak height) and subtracts the component abundances in the reference spectrum (in this case, unweathered JP-8) from those in the

20g Soil Extract from JP-8 Jet Fuel
Contaminated Military Site
18 eV Electron Ionization

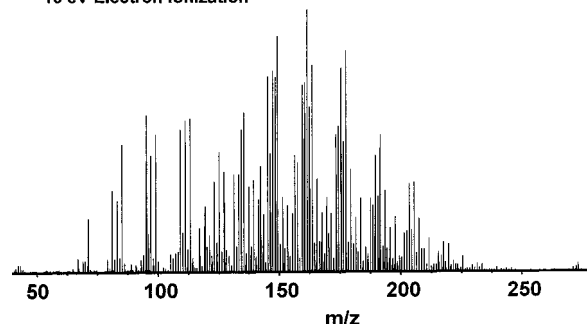


Figure 6. Full-range FT-ICR mass spectrum of a Soxhlet extracted JP-8 contaminated soil sample (20 g) resulting from a 1- μ L septum injection into the AGHIS. Note the good match to the highly (95%) weathered JP-8 standard. Additional peaks resulting from soil matrix components have been identified as well.

analyte spectrum (95% weathered JP-8). Analyte peaks that have no match in the reference spectrum appear as positive peaks and may be identified separately. (To test for a match between analyte and reference, one could assign a score based on the mean squared magnitudes in the above-computed difference spectrum; the lower the score, the better the match.) Positive peaks in the difference spectrum indicate compounds present in the analyte but found at lower abundance in (or absent from) the reference, and the converse for negative peaks in the difference spectrum. Figure 5 clearly shows that extensive (95%) weathering results in decreased relative abundance of low m/z species (negative peaks in the difference spectrum) and increased relative abundance of higher m/z species (positive peaks in the difference spectrum).

JP-8 Contaminated Soil Analysis. After Soxhlet extraction of a contaminated soil sample, and evaporation of the extraction solvent, a 1- μ L aliquot of the remaining liquid was injected into the septum inlet of the AGHIS resulting in a stable source pressure of $\sim 5 \times 10^{-9}$ Torr for a period of 1 h. The spectrum consisted of ~ 400 peaks in the range $50 \leq m/z \leq 280$ (Figure 6), with as many as 4 peaks at a given nominal mass. More oxidized species were present in the mass spectrum (Figure 7) along with several peaks not present in the weathered JP-8 standards. Elemental compositions were assigned based on the basis of accurate mass measurement alone, with an average mass error of ~ 0.5 ppm, an example of which is shown in Figure 7. Although we can determine the elemental compositions of the various species, more complete identification would require MS/MS and/or chromatographic separation prior to mass analysis. In this preliminary investigation, we simply want to show that hundreds of chemical components may be identified and their elemental compositions determined.

Elemental compositions from JP-4, JP-5, and JP-8 jet fuels were compared with the species in the soil extract in an effort to identify the jet fuel contaminant. Characteristic peaks unique to each of the three jet fuels were searched in the soil extract mass spectral peak list and resulted in the positive identification of the contaminant as JP-8. Specifically, comparison of the (unweathered) JP-8 and JP-4 standards led to the identification of 72 unique elemental compositions present in JP-8 but not in JP-4. We found 56 of those 72 species in the (hundreds of) unique elemental compositions from the soil extract mass spectrum. A similar comparison between unweathered JP-8 and JP-5 standards identified 53

Zoom Mass Inset of Soil Extract

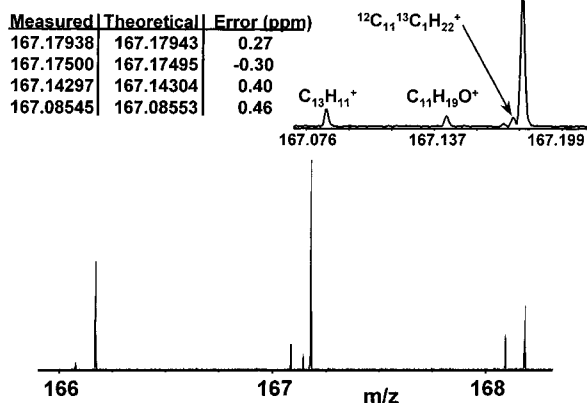


Figure 7. Mass scale-expanded segment showing the chemical complexity of the contaminated soil extract (bottom). Elemental compositions of each of the four species resolved at m/z 167 (top) were determined by mass measurement, to within an average mass error of ~ 350 ppb, at a mass resolving power, $m/\Delta m_{50\%}$, of $\sim 80\,000$.

elemental compositions present in JP-8 but not in JP-5. We identified 34 of those 53 in the soil extract. In both searches, more than 60% of the elemental compositions unique (among JP-4, JP-5, and JP-8) to JP-8 peaks were identified in the soil extract. The soil extract therefore clearly contains JP-8.

The observed effect of weathering on the JP-8 standard is a decrease in the relative abundances of low m/z species, with correspondingly higher relative abundances of species of $m/z > 120$, corresponding to a carbon number of ~ 8 . Those higher mass components have boiling points well above that of chloroform and are therefore unlikely to evaporate during extraction. On the basis of the (approximate) relative abundances of high-mass components in the soil extract relative to the weathered standard, we estimate that the JP-8 in the soil extract is 75% weathered. A better estimate will require experiments to determine the effect of solvent extraction on fuel composition, as well as analysis of weathering of fuels in standard soil samples.

Because the number of different elemental compositions in each of these fuels is so high, and because dozens of compositions

are unique to each fuel, we feel safe in predicting that it will be feasible to identify a particular fuel by simple extraction and EI FT-ICR MS alone. Although weathering of such a fuel in the laboratory changes the relative abundances of the components, most of the original components are still present and therefore available for identification. Finally, even if some components of the fuel react chemically in actual soil, the present results show that there are still plenty of unchanged elemental compositions to provide for unambiguous identification of the fuel from the soil extract.

In conclusion, from a simple Soxhlet extraction, FT-ICR mass spectral analysis of a contaminated soil sample clearly identifies its jet fuel contaminant as JP-8 and provides a molecular inventory of the contaminant and extractable soil components. These assignments provide a unique compositional fingerprint which, when monitored as a function of weathering or applied remediation techniques, could be used to assess changes in the fuel on a component-by-component basis. In this way, one can characterize the leachable and residual fractions for improved understanding of the potential fate and risk associated with a contamination site. Finally, future monitoring of a JP-8 contaminated site after remediation has been initiated will provide a detailed chemical pattern of the effectiveness of the chosen remediation scheme.

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