

The Utilization of FT-IR for Army Oil Condition Monitoring

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Abstract: This paper discusses the implementation and progress of Fourier transform infrared (FT-IR) spectroscopy in the U.S. Army Oil Analysis Program (AOAP). Improvements in the basic FT-IR method, the addition of new analysis capabilities and the impact FT-IR has made on AOAP are presented—expansion of FT-IR to cover hydraulic fluids (petroleum and phosphate ester fluids), new fuel analysis procedures and new cleaning solvent option. The implementation of FT-IR in the Army enabled the return of previously removed aircraft equipment (ODDS) to the AOAP.

Key Words: Army Oil Analysis Program (AOAP); Condition monitoring; Fourier transform infrared (FT-IR) spectroscopy; oil analysis.

Introduction: In the past, the Army Oil Analysis Program (AOAP) determined the condition of lubricants through qualitative, subjective and antiquated tests. Due to progressive equipment degradation, equipment users and materiel developers determined more precise testing technology was needed, particularly in the area of corrosion detection. This requirement was passed to the Joint Oil Analysis Program Technical Support Center (JOAP-TSC) for evaluation. The JOAP-TSC evaluated FT-IR spectroscopy [1,2,3] as a possible replacement for the old methodology. Test and evaluation studies were conducted [4,5,6,7] and the Army adopted the FT-IR as the appropriate technology to meet advanced physical property test requirements. Since adoption, the Army has procured and fielded FT-IR systems at 12 Army laboratories

worldwide. Partially because of this technology, the U.S. Army Aviation and Missile Command has enrolled all of the aviation fleet in the program. The implementation of FT-IR supports the Chief of Staff of the Army's position to aggressively pursue state-of-the-art diagnostics.

Improvements: Condition monitoring programs require continual review and update to ensure maximum reliability and benefits. In addition, the implementation of any new technology such as FT-IR is bound to require change as it is adapted to the equipment maintenance environment. While much work was done to adapt FT-IR prior to its introduction in the Army, new fuels and lubricants have required modification to several of the search areas and algorithms.

Fuel Dilution: Fuel is perhaps the most difficult parameter to measure due to its similarity to lubricating oils. Engine fuels can consist of a wide variety of straight chain and branched aliphatic compounds, aromatic compounds and other substituted compounds blended to produce a desired set of physical properties. As the composition and viscosity of a liquid fuel can vary greatly, any single analytical method to detect fuel will suffer from serious limitations. In addition, the conditions in an engine will cause the overall composition of the fuel to change because of both partial combustion and distillation of lighter components. FT-IR determines fuel contamination by measuring the absorbance bands of specific components in the fuel. The fuels studied in this program are diesel and jet fuels (JP4, JP5 and JP8).

Jet fuels are similar to diesel fuels and all consist of different compounds, additives and reformates. A marker band typical in fuel contaminated oil samples was found at 810 cm^{-1} . This absorbance band is typical for out-of-plane bending of two adjacent hydrogens in a para-substituted aromatic ring. For condition monitoring, the exact identification of specific compounds is not relevant. As the fuel marker is a narrow, specific band, restricted baselines are used. Baseline points are taken as the minima between $835\text{ to }825\text{ cm}^{-1}$ (left) and between $805\text{ to }795\text{ cm}^{-1}$ (right). The area is measured over the range of $815\text{ to }805\text{ cm}^{-1}$.

Experience has shown (and reported elsewhere) that some diesel and jet fuels are formulated with little or no aromatic content. These fuels lack the marker band (810 cm^{-1}) discussed above. To overcome the sometimes poor reliability of fuel measurement, a new approach was developed. Instead of a single measurement point, several fuel peak areas are integrated into a single measurement (Figure 1).

The specific areas of interest were determined by gas chromatograph infrared (GC-IR) analysis of several fuel types. The GC separated the fuel into its separate components e.g., 1,2,3 trimethylbenzene, ethylbenzene, indane, isopropylbenzene, etc. The individual infrared responses of the major fuel constituents were compared to infrared responses in contaminated and uncontaminated Army oils. This study suggested a series of specific areas depending on the lubricant type. By choosing multiple measurement points, it is hoped that the normal variance in fuel constituents will not adversely affect the reliability of fuel measurement. Please note, the chemical constituents of lubricants impact the fuel

areas chosen and different areas are integrated for petroleum and ester oils.

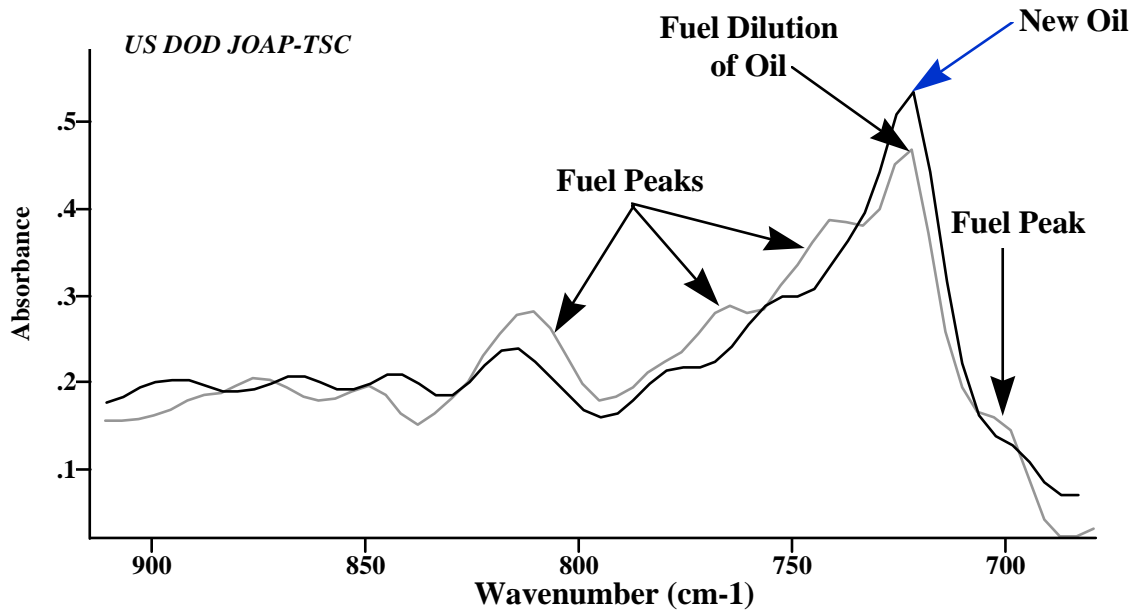


Figure 1: Fuel measurement areas in a Mil-L-2104

It is important to remember that trending lubricant components also indicates fuel contamination, because as fuel contamination increases, the levels and thus infrared response of the lubricant components decrease. A drop in the trend of other lubricant parameters can be used in conjunction with the fuel marker bands to improve the indication of fuel contamination. In addition, the “incorrect fluid” parameter for a polyol ester measures the presence of a petroleum fuel as efficiently as a petroleum oil. The total response of the FT-IR should be evaluated when diagnosing a potential fuel problem.

Base Stock Breakdown in Polyol Ester Oils: Base stock breakdown in polyol ester synthetic lubricants is presently monitored in two regions. First, the region around 3535 cm^{-1} indicates that the breakdown products are mostly composed of weakly hydrogen bonded alcohol or acid groups. Here, base stock degradation is measured over the range 3595 to 3500 cm^{-1} . A single baseline point for this measurement is taken at 3595 cm^{-1} to eliminate any interference from water contamination because as water contamination increases, the baseline shifts accordingly. The second area is in the hydrogen bonded O-H stretch region (symmetric and asymmetric) and is due to the numerous hydrogen bonded by-products formed from the polyol ester lubricant breakdown. The measurement algorithms initially recommended were the same as that for the hydrogen bonded O-H stretch vibrations of liquid water in petroleum based lubricants—over the range of 3500 to 3150 cm^{-1} with a general baseline over the range of 4000 to 2000 cm^{-1} . The area included the ester overtone band at 3460 cm^{-1} and the antioxidant band (s) at approximately 3380 cm^{-1} . Since all polyol esters had these bands, the contribution from

these peaks was essentially uniform and the petroleum 3500 to 3150 cm^{-1} area was used for simplicity.

Some of the new polyol ester blends approved for use in the military do not have the antioxidant peaks. The absence of these peaks impacts the overall reading (lower values). The proposed new area is from 3330 to 3150 cm^{-1} with a general baseline over the range of 4000 to 2000 cm^{-1} (Figure 2).

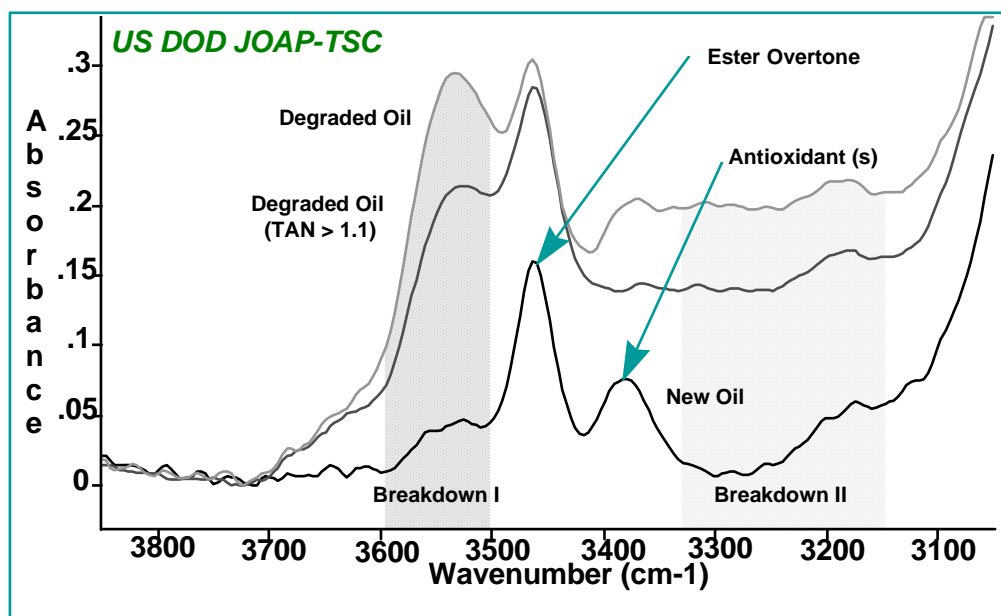


Figure 2: Breakdown in polyol ester lubricants

Solvents: Heptane, a flammable solvent, is used to clean the transmission cell between samples. One Army base suggested a terpene based, non-flammable solvent, Electron, be evaluated for cell cleaning to reduce their waste disposal requirement. Electron is already used in the AOAP for sample stand cleaning in atomic emission spectrometers. Using this solvent doubles the cleaning times for most lubricants and triples it for hydraulic fluids. The base felt the additional time was acceptable for their purposes. Heptane is still used for cleaning at the end of the day to ensure no terpene residue remains. As an added note, polyethylene IR cards are being evaluated as a solventless solution for FT-IR sample introduction [8,9].

New Analysis Capabilities: In early 1995, the first FT-IRs were placed in Army laboratories. The initial methods development focused on Mil-L-2104 and Mil-L-23699, the primary fluids in the Army (84%). Since implementation, the Army has requested methods for hydraulic fluid analysis (petroleum and phosphate ester based). In addition, the Army has recently changed the lubricant used in AH6 main transmission and tail rotor gearboxes to a phosphate ester.

Petroleum Hydraulic Fluids: Fluids with EP or TEP additives inhibit the clear observation of either a hydrogen bonded OH stretch or non-hydrogen bonded OH stretch. Water contamination in these fluids is observed as a baseline rise or offset (Figure 3) but does not show the evidence of Tyndal—particulate or colloidal scattering as seen with insolubles (soot) which show a tilted baseline offset. Also note that soot should not be present in these fluids.

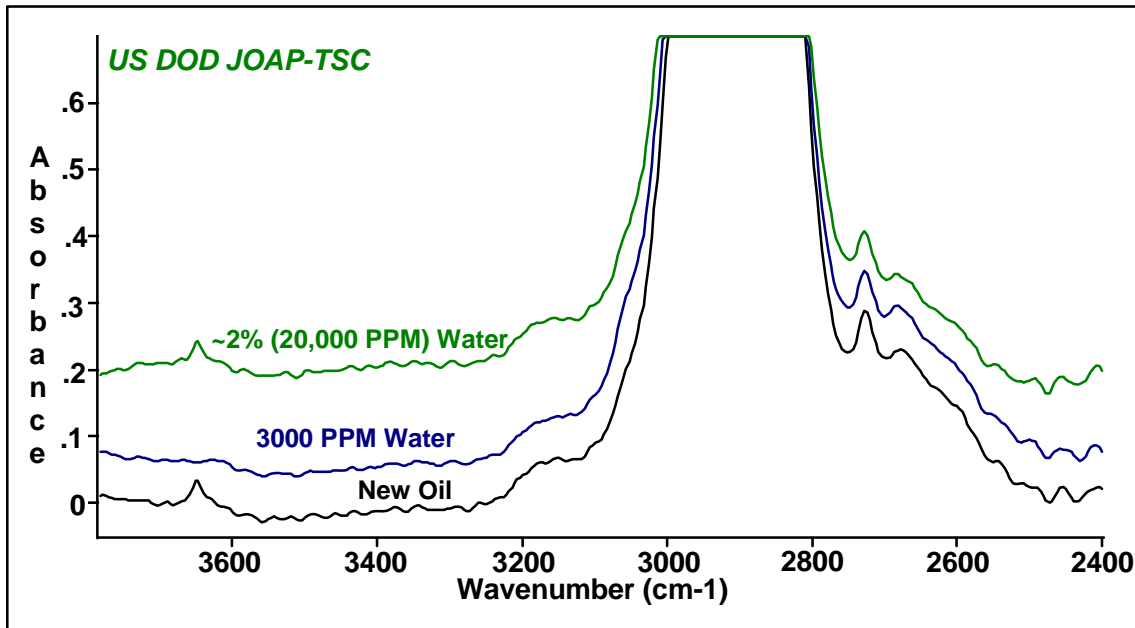


Figure 3: Water in EP fluids

During equipment operation, the organic compounds of all lubricants are exposed to high temperatures and stresses in the presence of oxygen and/or water, resulting in the formation of partially oxidized compounds. These acidic by-products can be oxidation, nitration or sulfate compounds. The FT-IR individually measures these by-products.

Oxidation By-Products: FT-IR determines the level of oxidation by-products by a general response in the carbonyl region. In this region, infrared energy is absorbed due to the C=O stretch from ketones, esters, carboxylic acids, carbonates, aldehydes, anhydrides, and amides, to name a few. Monitoring this region is thus a direct measurement of the oxidation. The infrared area is measured over the range of 1800 to 1670 cm^{-1} with two minima taken as the baseline correction. The left baseline (high wavenumber side) is taken as the minimum over the region of 2200 to 2000 cm^{-1} and a right baseline (low wavenumber side) over the region of 600 to 550 cm^{-1} . Very few compounds found in new and used petroleum lubricants have significant absorbance in these baseline areas (Figure 3). This baseline definition corrects for any offset and tilt due to soot and particulates. The same area is used for petroleum lubricants and hydraulic fluids. The petroleum hydraulic fluids tend to have sharper, tighter bands than the petroleum lubricants—this is may be due to lower concentration of additives in the

hydraulic fluids.

Sulfate By-Products: Sulfur compounds are found in some crudes and as additives in some fuels (antioxidants and biocides for storage) and petroleum oils (EP additive). These compounds increase the production of varnishes and sludges and generally degrade fluid performance. Sulfates are measured over the region of 1180 to 1120 cm^{-1} using the general 2000 to 600 cm^{-1} baseline. Over this measurement region, the most probable absorption group will be either from an SO_2 symmetric stretch or the SO_3 stretch from a $\text{C-SO}_3\text{-H}_3\text{O}^+$. Various levels of oxidation and sulfate by-products are shown in Figure 4.

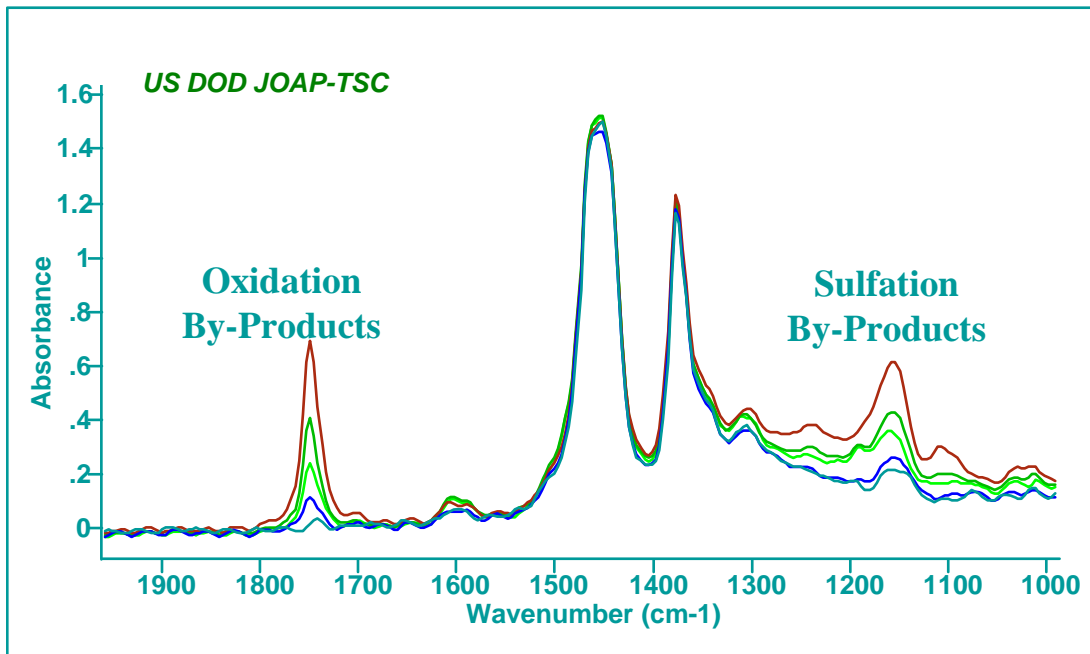


Figure 4: Oxidation and sulfate by-products

Nitration By-Products: In addition to oxidation and sulfation, nitration by-products can also develop when organic compounds are exposed to high temperatures and pressures in the presence of nitrogen and oxygen. While nitration by-products have been observed in petroleum lubricants, they have not been observed to date, in hydraulic fluids.

Phosphate Ester Hydraulic Fluids: These fluids also contain EP or TEP additives which inhibit the clear observation of either a hydrogen bonded OH stretch or non-hydrogen bonded OH stretch. Water contamination in these fluids is also observed as a baseline offset, however, excessive water may be seen in the traditional hydrogen bonded OH stretch region. As for other failure modes, there have been insufficient samples for proper characterization and methods definition.

Other Fluid Systems: The JOAP-TSC also has developed preliminary methods to detect fault mechanisms in other machinery fluid systems such as coolants (silicate esters (coolanol), phosphate ester lubricants, refrigeration lubricants and their respective refrigerants etc. More samples with some fault progression are required for completion of the methods.

Closing: The downsizing of today's military forces, reduced budgets and reduced equipment usage dictates that only state-of-the-art technology be employed for equipment condition monitoring. The use of FT-IR by AOAP increases the overall maintenance posture, improves operational readiness, enhances safety and saves valuable resources—a quantum jump for the Army. And most importantly, it supports the needs of the soldier-in-the-field.

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