

The Application of New Approaches to the Analysis of Deposits from the Jet Fuel Thermal Oxidation Tester (JFTOT)

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ABSTRACT

Studies of diesel system deposits continue to be the subject of interest and publications worldwide. The introduction of high pressure common rail systems resulting in high fuel temperatures in the system with the concomitant use of fuels of varying solubilizing ability (e.g. ULSD and FAME blends) have seen deposits formed at the tip of the injector and on various internal injector components. Though deposit control additives (DCAs) have been successfully deployed to mitigate the deposit formation, work is still required to understand the nature and composition of these deposits.

The study of both tip and internal diesel injector deposits (IDID) has seen the development of a number of bench techniques in an attempt to mimic field injector deposits in the laboratory. One of the most used of these is the Jet Fuel Thermal Oxidation Tester or JFTOT (ASTM D3241). The tester was originally designed to assess the oxidation of jet fuel, based on the principle that low stability fuels produce deposits that form on metal surfaces. Recently it has been modified so that under suitable conditions it may be used to determine the deposit forming potential of diesel fuels. The JFTOT technique has been used by a number of groups to try and understand diesel injector deposits. The ineradicable nature of the material on the JFTOT tube has seen the deposits analyzed by laser scanning microscopy, ellipsometry and recently infra-red microscopy. Other methods have been invasive involving either solvent washing or scraping off the deposit. In this paper other techniques for the analysis of deposits will be described yielding both chemical and metrological characteristics of the deposits. Fourier Transform Infrared Microscopy (FTIRM), and Time-of-Flight Secondary Ion Mass Spectrometry (ToFSIMS) will be used to describe the surface characteristics. Measurements from a Profile meter will be used to estimate deposit surface roughness and data from Scanning Electron Microscopy (SEM) will be employed to describe the morphology. The final techniques described will be Direct Analysis In Real Time Mass Spectrometry (DARTMS) using ambient mass spectrometry, and Fourier Transform Ion Cyclotron Resonance Mass spectrometry (FTICRMS). The advantage of the DART method is that mixtures and objects can be subjected to mass spectrometric analysis with the minimum of pre-treatment and sample preparation. Thus the technique is well suited for analyzing deposits on JFTOT tubes as it requires little sample preparation. A number of studies of materials deposited on JFTOT tubes will be described showing the suitability of these techniques for analyzing and providing the potential characterization of JFTOT deposits. The FTICRMS will be used to assign species in the JFTOT test fuels both pre and post test.

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INTRODUCTION

The build-up of deposits in diesel fuel injectors has been known for many years. In the 1980s, the build-up of deposits on the pintle of a fuel injector was reported by Montange *et al* [1]. The development and introduction of fuel additives to reduce injector fouling subsequently followed [2]. In 1991, Gallant *et al* [3] noted that

deposits caused spray hole plugging and sticking of close fitting parts leading to power loss and increased emissions. Recent deposit problems have come from the promotion of diesel engine technology advances resulting in improved combustion process from finer fuel atomization. A consequence of the improved combustion process is reduced emissions, improved energy efficiency and better

performance. Sophisticated high pressure common rail fuel injection systems have been deployed to deliver improved efficiencies in emission reduction and energy efficiency. This combined with the introduction of legislation driven fuels with different solubilizing abilities such as Ultra Low Sulfur Diesel (ULSD) in the United States have produced a number of field failures manifested as multiple problems such as cold start difficulties, no start, rough idling and increased emissions. The introduction of ULSD worldwide has seen similar issues manifest themselves in other geographic areas, though those using DCA technology have seen less impact. The critical factor is the diesel fuel delivery system which has seen deposits formed throughout its architecture [4] and especially within the injectors. The injectors have very tight clearances between their moving parts thus blocking or fouling internally can cause less efficient fuel delivery, poor mixing with air and sticking parts. The injectors work at high pressure in excess of 3000 bar and high temperature over 100°C. Thus the fuel experiences very high stress in the injector and part of that stressed fuel is returned to the fuel tank which results in carbonaceous deposit formation. The deposits that are attracting the most industry interest at present are the internal injector deposits (IDID). They are layered [5] and have been described as five different types (Figure 1). Some are excursion deposits such as metal salts, resulting from unusual activity such as adulteration, refinery upset, poor quality blending components or supply chain issues such as metal salts; others carbonaceous. The former may be reduced for example by good housekeeping, the latter are inherent to the system. A number of standard engine and rig tests have been used and are being developed to understand the formation of such deposits and to measure the effectiveness of deposit control additives to prevent and remove them. CRC (Central Research Council Diesel Performance Group-Deposit Panel Bench/Rig/Investigation sub panel), CEN (Comite European de Normalisation TC19/WG24 Injector Deposit Task Force) and CEC (Co-ordinating European Council TDFG-110) in Europe have sub-committees and panels investigating the process.



5. LAQUER BASED: Visualised on some injectors may be a carbonaceous precursor.



6. CARBOXYLATE SALTS: White in colour, often sodium or calcium based

Figure 1. (cont.) Types of IDID deposits.

The cost of these tests has pushed those in the field to look for a mimic bench test which will be easier to use and provide data at a lower cost. The JFTOT test is one such laboratory bench test. The Jet Fuel Thermal Oxidation Tester (JFTOT) is used to test the thermal oxidation stability of aviation fuel according to ASTM D-3241. It has been used by number of workers [5,8] to investigate IDID formation. When used with diesel, the test fuel is passed over a heated metal test piece and can be thought to simulate fuel passing through a diesel injector. At the end of test, the metal test piece is rated visually or by ellipsometry for the degree of deposit formation. The deposits have been characterized by invasive techniques in the main such as scraping or solvent washing which can remove the deposits history. Analyzing these deposits *in situ* will allow for the retention of that history and herein we will describe proof of concept data using several techniques.

Recent work to characterize these deposits by infra-red microscopy and ellipsometry [7, 9] has shown that there is information to be learnt by analyzing the tube deposits *in situ*. In this paper we will also describe the deployment of other analytical techniques such as DART and ToFSIMS, to the analysis of JFTOT tube deposits.

TECHNIQUES

FTIR-Microscopy

Recent work to characterize these deposits by infra-red microscopy [7,9] allows the surface of a deposit to be analyzed for chemical functionality with a spatial resolution approaching 5 microns. Images are generated by the combination of a microscope and an array detector. The image pixels generated each contain an infra-red spectrum. Thus a map of a deposit surface can be generated which shows the distribution of infra- red active species on the surface based on wavelength.

ToFSIMS

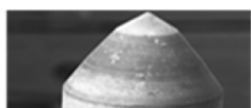
This technique has been described in other papers [4,10,11] but a brief description follows. A pulse of ions bombards the specimen and the energy of these primary ions is transferred to target atoms by atomic collisions. This results in a collision cascade and part of the energy is transported back to the surface enabling surface molecules and atoms to overcome surface binding energy. A cloud of molecules and atoms results some of which are ionized. The mechanism is



1. CARBONACOUS: Carbon based black in colour



2. AMIDES : Brown in colour polymeric



3. INORGANIC SALTS: Off-white in colour e.g. sulphates



4. AGED FUEL DEPOSIT: "Sticky Deposit" possible bio origin.

Figure 1.

“soft” enough to allow large non-volatile molecules with masses of up to 10,000 Daltons, with this part of the cloud showing relatively little fragmentation. The ionized particles of one polarity, atomic and molecular secondary ions, are accelerated into a Time of Flight spectrometer. The principle of the spectrometer is that the “Time of Flight” of an ion is proportional to the square root of its mass. Thus different masses are separated during flight with the lighter ones arriving before the heavier ones. This is despite the ions all leaving the sample at the same time and being subject to the same accelerating voltage. Measuring the flight time for each ion allows the determination of its mass. The time interval between consecutive pulses is critical as the next pulse of primary ions cannot start until the primary pulse secondary ions have left the analyzer. This time interval may be used for other activities such as sputtering or charge neutralization. The start time of all the secondary ions is determined using extremely short pulses having duration of less than one nanosecond. Variations in the technique allows surface analysis, image mapping and depth profiling of a sample.

PROFILE METER

An optical microscope with infinite depth imaging, a Zdot optical profiler a true colour CCD camera and dual high brightness IED source allow the mapping of the surface of the deposit and hence its roughness.

DART-MS

is an atmospheric pressure ionization source that can ionize gases, liquids and solids in open air under ambient conditions. The initial ionization step involves Penning ionization. DART grew out of discussions between Laramée and Cody at JEOL USA, Inc. These covered the development of an atmospheric pressure thermal electron source which could replace the radioactive sources commonly used in detectors for chemical weapons agents and explosives [12,13].

The source typically consists of two chambers through which the DART gas flows, as shown in Figure 2. In the first chamber, a corona discharge between a needle electrode and perforated disk electrode produces ions, electrons and excited state atoms known as metastable atoms or molecules. The cold plasma then passes through the second chamber where an electrode is used to remove cations from the gas stream. The gas stream is then passed over a gas heater and onto a final grid electrode that removes oppositely charged species, leaving only neutral gas molecules and metastable species [12].

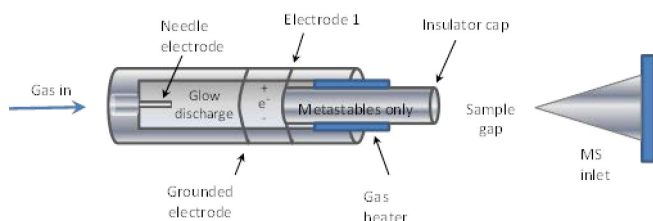


Figure 2. Schematic diagram to show the DART ionization source and MS inlet. Reference adapted from JEOL USA, Inc..

The ability to heat the gas allows for control of both the thermal desorption and pyrolysis of samples. Finally, as the gas exits the insulator cap it is directed towards the sampling orifice of an API interface or may hit the sample surface at an angle suitable for its

reflection into the entrance of the mass spectrometer. The insulator cap ensures that no exposure to high voltages occurs outside of the plasma chamber [13].

Ion formation in DART typically involves gas-phase ionization processes and DART- ionization may generate positive or negative ions which are predominately even-electron species. Several ionization mechanisms are possible in DART depending on the polarity, the reagent gas used, the proton affinity and ionization potential of the analyte as well as the presence of dopants or additives.

The benefits of DART-MS include the speed and simplicity of the technique, with spectra obtained in a few seconds with no or limited sample preparation needed which is very useful for trace analysis. DART-MS does not produce multiply charged states or adduct ions. Instead it only produces $[M + H]^+$ species. The technique is also unaffected by the choice of solvents and chromatographic separation is unnecessary. It can be used to analyze samples which are not amenable to other atmospheric pressure ionization techniques *e.g.* electrospray ionization or atmospheric pressure chemical ionization.

Due to the nature of the technique, analysis can be undertaken in open air under ambient conditions, including the ionization of gases, liquids and solids. Ionization can take place directly on the sample surface.

METHODOLOGY

An Alcor JFTOT III Jet Fuel Thermal Oxidation Tester (JFTOT) was adapted to assess deposit formation in three diesel fuels. A volume of fuel was pumped at a fixed rate of 3 mL/min through an initial filter unit containing a 4 μ m filter paper cut from a diesel fuel filter. The fuel was then passed over a stainless steel test piece heated to 260°C. The total test time was 2.5 hours and at the end of test, the metal test piece was cleaned with analytical grade toluene and acetone and dried. Three rods were produced, 1) ULSD, 2) B20 and 3) a composite of ULSD and B20. The fuel deposit matrix on the rods was studied by the techniques described to provide proof of concept to be demonstrated. The first two were for 150 minutes with B20 rapeseed methyl ester (RME) fuel (20% RME 80% diesel) and ultra-low sulfur diesel (ULSD). The third test was for a total of 450 minutes, three cycles of 150 minutes as before. This was done firstly with B20 fuel, then ULSD and finally B20 again.

EXPERIMENTAL

FTIR Microscopy

The infra-red maps were acquired using a Nicolet iN10MX microscope in reflective mode and cooled detector. Spectral resolution was 4 cm^{-1}

Profilometry

Roughness data was collected with a Zeta 20 3D Optical Profiler and analysed with Zeta 3D software. The sample areas analyzed were 100 x 800 μ m with a 50x optical lens. The roughness measurements stated are an average of three line analysis taken for each sample area. The error bars are one standard deviation.

SEM

Scanning Electron Microscopy (SEM) analysis of the JFTOT tubes was carried out using a JEOL 6490LV SEM. The accelerating voltages used were between 10-20 kV. For the scattered electron mode the spot size was 3.0.

ToFSIMS

The technique was undertaken using a ToF SIMS IV Iontof GMBH. Surface Spectroscopy (static SIMS): The application of very low ion dose densities, allows quasi nondestructive surface analysis. Principle Component Analysis (PCA)[14] was then used to analyze the data. The PCA technique emphasizes variation and brings out strong patterns in a dataset. PCA is a simple non-parametric method of extracting relevant information from large data sets. It can be used to reduce complex data sets to a lower dimension thus revealing a simplified structure which underlies a complex data set. In the case of ToFSIMS. A mass list is made from each spectrum and joined together produce a combined list of masses. These are then applied to each spectrum. Using Matlab PCA tool box programme Eigenvalues were produced which give an indication to which principal component number (PCN) would yield useful data. For positive data it was to PCN 10 and negative data it was PCN 6, with PCN 1 will giving the biggest difference in ion intensity. For negative data hydrogen ions were removed to allow smaller difference to be easily identified. The PCNs 1 & 2 shows the biggest variations and hence shows the biggest difference between samples.

Dart

Positive ion DART mass spectra were acquired using a DARTSVP™ ion source (IonSense, Saugus, MA, USA) interfaced to an LCQ ion trap-MS (Finnigan MAT, USA). The JFTOT fuel samples were dipped onto the closed end of the Dipit- capillary tubes™ (IonSense) and positioned on a rack between the DART ion source and detector inlet (Figure 3).

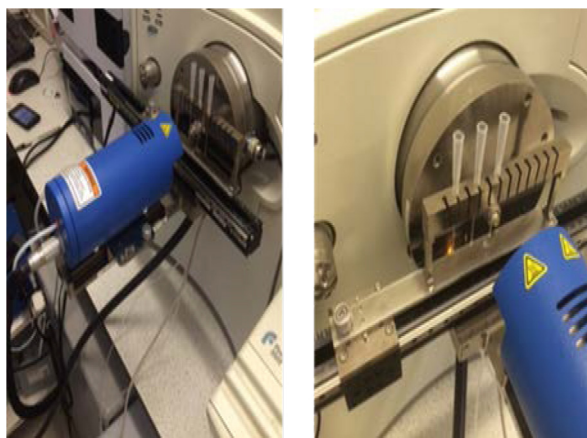


Figure 3. DART for Fuels Configuration.

The rack was placed on a linear rail system which provided automated delivery of the sample to the correct sampling position. The rack was perpendicular to the ionizing gas stream and allowed reproducibility, automation and optimal positioning of the sample. The rack was

transported along the rail system at 0.2 mm per second while acquiring the data. An external standard of caffeine was used and placed on a Dipit- tube to calibrate the position of the JFTOT tube.

The JFTOT rods had to be sampled directly from the metal surface of the rod. The angle of the DART gun had to be positioned and optimized for effective ionization of the sample surface of the rod shown in (Figure 4). The rod was secured into place onto a metal holder typically used to hold capsules. The external calibration standard (caffeine) was placed on either side of the JFTOT rod in areas free from deposits. The metal holder was placed on the linear rail system and transported along the system at 0.2 mm per second. Data analysis was performed by Xcalibur software (Version 2.0).

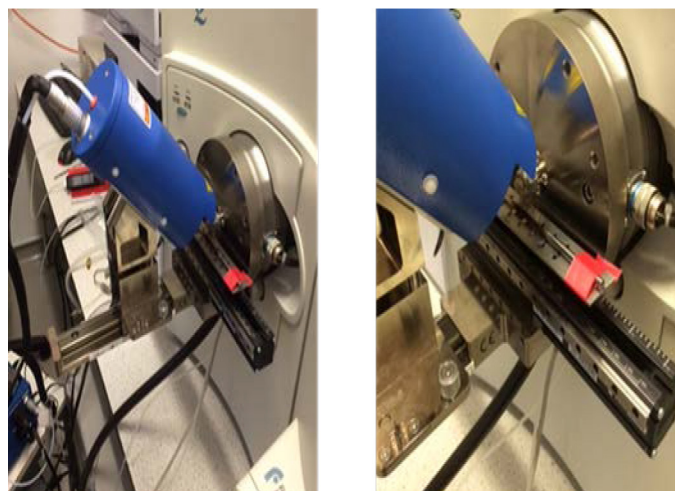


Figure 4. DART for JFTOT Tubes Configuration.

DART-MS was also interfaced to the Waters Synapt G2-MS for accurate mass measurements. DART-MS experimental details are shown above. Synapt G2-MS conditions were as follows: mass spectra were obtained over m/z 50- 800. Background spectra of siloxanes were used as a m/z calibration with their accurate masses calculated. Collision Induced Dissociation (CID) was evaluated in the range of 0-20 V for tandem-MS experiments. Data analysis was performed using Masslynx software (Version 4.1).

Fourier Transform- Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS),

This was conducted using a 4.7 Tesla (T) Solarix mass spectrometer (Bruker Daltonics). The samples were introduced using an ESI source and experiments were undertaken by direct infusion using a 100 μ L Hamilton syringe and syringe pump with the sample solution in methanol. The instrument was calibrated using at a concentration 1 μ g/mL per component calibration solution in methanol. The ESI source parameters plate offset 500 V. Source Voltage 4000 kV, drying gas flow rate 4.0 L/min, drying gas temperature 180 °C with a nebuliser pressure of 1.2 bar. Instrument control and data acquisition were performed using Compass Solarix control (Bruker Daltonics) and data was processed using Compass Data Analysis. Positive ion ESI-MS were acquired between m/z 150-1500.

RESULTS

FTIR-Microscopy

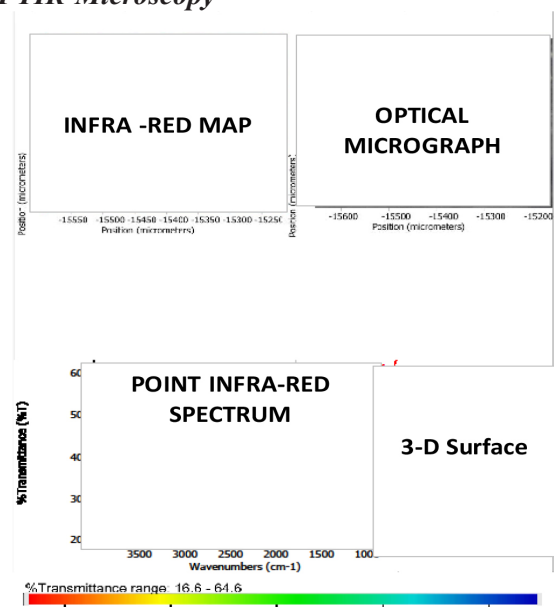


Figure 5. Key to Figures 6, 7 and 8.

ULSD Non-Additised

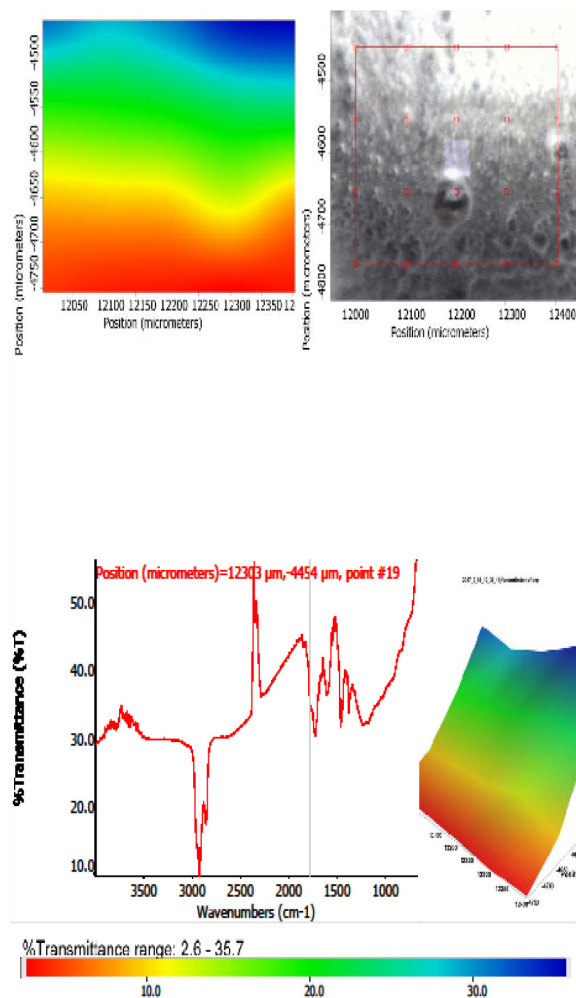


Figure 6. Infra-red micrograph of JFTOT ULSD Fuel Deposit.

Analysis of the FTIR spectrum (Figure 6) shows peaks at 1775, 1748, 1610, 1643 and 1382 cm^{-1} . The first two bands have been attributed to carboxylic acid and aldehyde formation respectively [15]. Similar peaks have been observed in ULSD subject to the Rancimat EN15751 test. The peaks have been attributable to aged fuels but they are also known to originate from fuels taken past their break point. The Infra-red map shows the deposit to contain different amounts of chemical species at different points.

B20

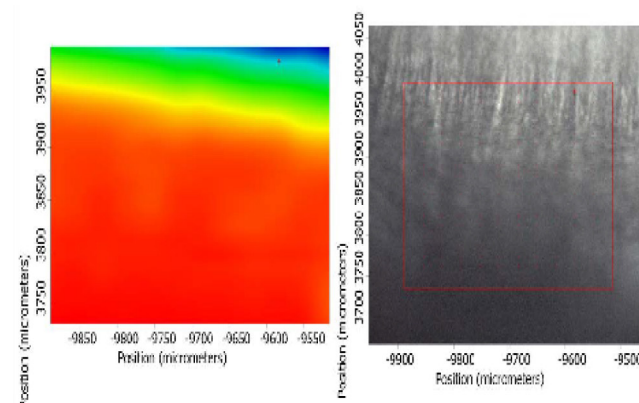


Figure 7. Infra-red Micrograph of Deposit from B20 fuel.

Analysis of the B20 spectrum (Figure 7) shows a strong band at 1762 cm^{-1} attributable to acid species, and further bands at 1376 and 1208 cm^{-1} . Again the infra-red map indicates variation in the chemical species across the deposit. The ULSD B20 layer sample (Figure 8) shows peaks at 1775, 1728, 1604, 1463 and 1383 cm^{-1} . This is part of an ongoing body of work investigating the layer nature of deposits that have been reported on a number of parts of common rail diesel injectors. (4,11,16-18.). These studies have shown that deposits in the field are multilayer and consist of both inorganic and organic molecules. The mixed layer sample analyzed here does show the