

A Novel Technique for Investigating the Characteristics and History of Deposits Formed Within High Pressure Fuel Injection Equipment

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ABSTRACT

The recent developments in diesel fuel injection equipment coupled with the moves in the US to using ULSD and biodiesel blends has seen an increase in the number of reports from both engine manufacturers and fleet operators regarding fuel system deposit formation issues. These deposits not only form on and within the fuel injectors but they also form elsewhere in the fuel system, due to fuel recirculation. These will eventually accumulate in the fuel filters. Historically, diesel fuel system deposits have been attributed to contamination of the fuel or the degradation of the fuel with age. Such age related degradation has been attributed to oxidation of the fuel via well documented pathways, although the initiation of this process is still poorly understood. Papers at recent SAE meetings in Florence, San Antonio, Rio de Janeiro, San Diego and Kyoto have addressed many of these causes.

However, in recent cases the deposits internal to the fuel injector have become prevalent and characterisation of the deposits on the injector needle has become an industry priority. The deposits are different from those traditionally encountered, with inorganic and carbon components being found. This paper will describe for the first time the application of Time-of-Flight Secondary Ion Mass spectrometry (ToF-SIMS), for the analysis of these deposits. This technique involves: surface spectroscopy; static SIMS, the application of very low primary ion dose densities yielding quasi nondestructive surface analysis. Combined with surface imaging which involves the rastering of a finely focussed ion beam over the surface yielding mass resolved secondary ion images; chemical maps, and depth profiling. Every pixel of a ToF-SIMS map represents a full mass spectrum. The technique also allows dynamic SIMS; and 3D Rendering. Where the application of high primary ion dose densities to the sample yields, successive removal of top surface layers and from the resultant mass spectra elemental in-depth distribution. Thus for the first time both the surface and the inner layers of a deposit may be characterised in three dimensions.

This paper also discusses the insights that such analysis can bring to the constitution, origin, and build-up history of these deposits and could provide a basis for the development of strategies to minimise such deposit formation.

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INTRODUCTION

The three major factors in the formation of both filter and injector deposits are the injector engineering, the fuel and legislation which drives development of the first two. The claim in Diesel's original patent that any type of fuel in any aggregation is suitable for use in a diesel engine[1], has been challenged over the years, with the increase in the variety of fuels; e.g. vegetable oils[2], inducing issues such as injector

fouling, and PM emission increase [3]. The concomitant change in injector technology associated with the introduction of common rail fuel injection systems has seen the development of fuel injection systems capable of pressures of 300MPa, with a reduction in nozzle hole diameter and associated significant increase in operating temperature. Nozzles of 100µm have been developed [4]; to create better fuel spray atomisation and improve emissions. This engineering is producing tighter tolerances, and hence

an intolerance to deposit generators. The pinnacle of these deposit reports coincided with legislation driven introduction of Ultra Low Sulphur Diesel (ULSD) in the USA in 2006. The introduction of more stringent emissions regulations and the increase in injector temperatures and pressures saw an increase in US field reports around 2008-9 with filter deposits and injector deposits manifesting themselves as rough idling and running, poor drivability, and no cold start performance issues [5]. The resultant proactive industry investigation has seen a number of studies to determine the cause, and origins of these deposits. The possible causes summarised in [figure 1](#) continue to grow and become more complex.

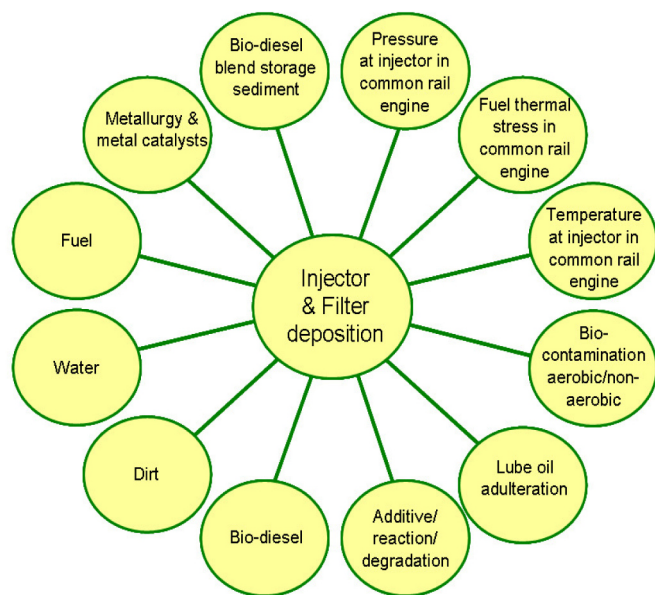


Figure 1. Possible Sources of Deposits

For example a recent study [6] found formic acid, to be formed in aged fuel, and the copper, zinc and lead from the fuel system combining with it to yield significant deposits. Furthermore, the numerous studies of the other major concern facing the industry; corrosion in the infrastructure of the fuel delivery supply chain, have also found e.g. acetic acid in fuels [7]. These are other possible deposit precursors. The possible origins of the acid itself are complex with biodiesel instability, bio contamination, ULSD residuals, ULSD degradation, or fuel cross contamination all being put forward as possibilities. Recent elegant work by Ikemato et al [8] has also shown that zinc in a fuel and a low molecular weight carboxylic acid in the combustion gas of a diesel engine combine to form zinc carboxylates in the nozzle, which may have some part to play in the problems found in the field.

The current industry effort has focused on internal injector needle deposits despite evidence that this is part of a larger issue involving filters, tip deposits and other internal part injector deposits [9]. This also ignores the “poor housekeeping” umbrella: of bio-contamination, lube oil adulteration, dirt, metals in fuels and biodiesel degradation [10]; together with incorrect levels of addivation, or a

combination of all these factors. The oxidation of the fuel component to produce deposit precursors has been reviewed by Cook and Richards [11], and work by Ullmann has shown some materials accelerate fuel ageing [6]. Work by Schwab [12] suggested that mono-acid lubricity improvers played no part in injector deposit formation, despite proposing sodium salts of similar chemistry, from alkenyl succinic acids were one possible cause. Such deposits were produced in a laboratory but required atypical levels of sodium to be present. It was also claimed tests on the thermal stability of problematic fuels showed them to be very stable. Arters [13], reported that they were unable to replicate with heating and mixing experiments of neat fuel additive components, the internal injector deposits found using Fourier Transform Infra-Red Spectroscopy (FTIR), by other investigators. In addition no evidence for high molecular weight polymeric materials, which may be found in laquer type deposits, was found. Barker [9] studied internal injector deposits by a novel hydropyrolysis technique. The data showed that internal injector deposits contained small archipelago structures of small ring size heavily alkyl substituted aromatics. Further studies using Temperature Programmed Oxidation (TPO) [14], showed a degree of crystallinity in the carbon of the internal injector deposits which was not found in the external deposits. This may be thought indicative of rapid degradation of the fuel by the high temperatures and pressures of the fuel system. Later work [15] showed that a fuels propensity to foul is not correlated to when sodium carboxylates were present, or metals such as calcium, sodium or zinc.

The recent effort to understand the deposits described above has led to many theories and numerous laboratory studies and field analysis. These have shown the explanation to be complex and undoubtedly not of single origin, and furthermore that there are common links between the various injector deposits found and filter deposits.

The analytical techniques used to analyse both injector and filter deposits though useful have limitations: For example, FTIR only “detects” those molecules with an infra-red signature which may not be characteristic of all of the constituents of the sample. The SEM/EDAX (scanning Electron Microscopy / Energy Dispersive Analysis by X-ray) technique yields only qualitative elemental analysis. The challenge is therefore to find more techniques to analyse the injector deposits.

The Time of Flight Secondary ion Mass Spectroscopy, (ToF-SIMS) technique has been successfully applied to the structural properties of electronic materials such as Indium arsenide nitride epilayers [16]. In fuels, it has been limited to the analysis of volatile nanoparticles emitted from diesel engines [17]. This paper first outlines the technique and then describes how it has been applied to the characterisation of internal injector deposits. The aim of the ToF-SIMS study was twofold, first to understand the surface of the deposit and secondly, to move through the layers of the deposit to understand its morphology.

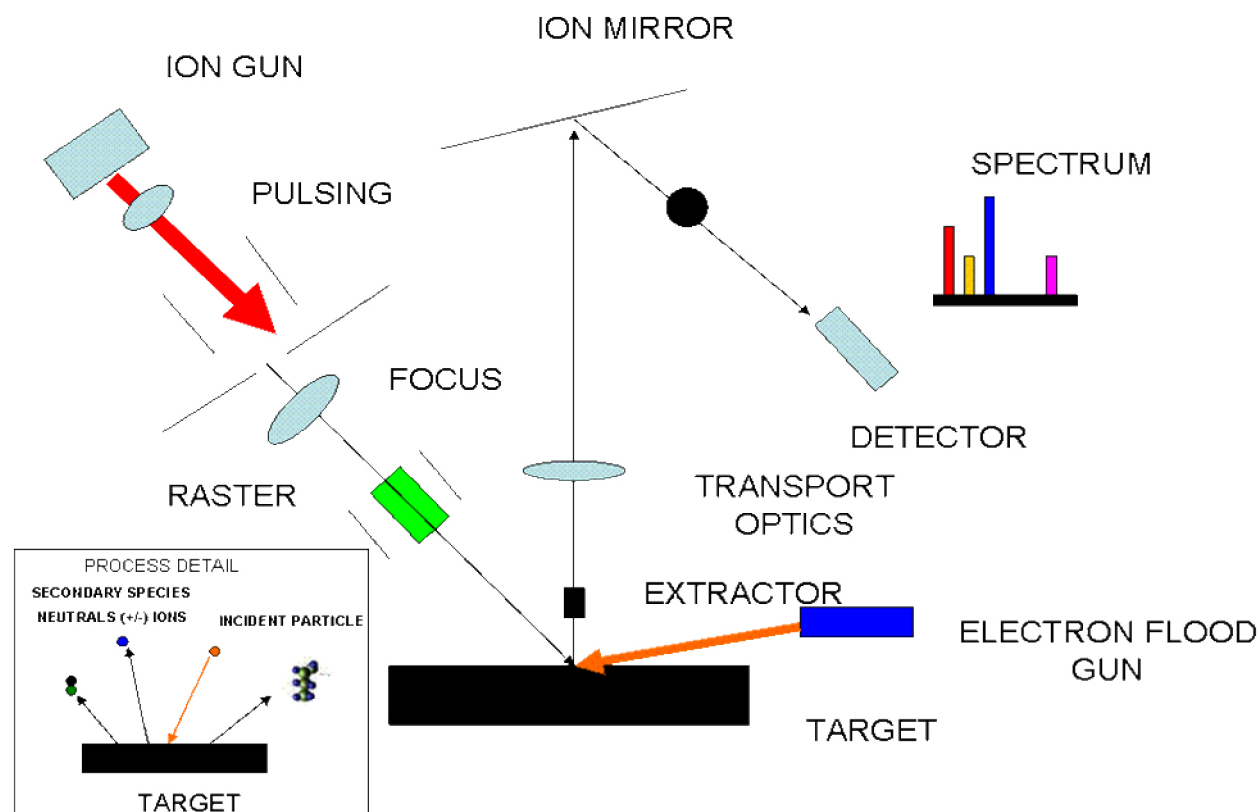


Figure 2. ToF-SIMS Schematic

THE TECHNIQUE

A simplified schematic of the technique is shown in [figure 2](#). A pulse of ions bombards the specimen and the energy of these primary ions is transferred to target atoms by atomic collisions. This sets up a collision cascade and some of the energy is transported back to the surface enabling surface atoms and molecules to overcome surface binding energy. This yields a cloud of molecules and atoms some of which are ionised. The mechanism is “soft” enough to allow large non-volatile molecules with masses of up to 10,000 Daltons to escape without much fragmentation. The ionized particles of one polarity, atomic and molecular secondary ions, are accelerated into a Time of Flight spectrometer, which is essentially a long tube with ion detection and counting systems. 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 analyser. This time interval may be used for other activities such as sputtering or charge neutralisation. The start time of all the secondary ions is

determined using extremely short pulses having a duration of less than one nanosecond.

Ion images may also be produced by scanning the primary ion source over the sample and measuring the ion activity relative to position. The associated SEM image is better than 60nm resolution and the ion image better than 100nm.

The configuration of the ToF analyser is vertical to allow the secondary ions to travel up to an ion mirror, then down to the detection system to allow easy compensation of the energy spread of species resulting from sputtering.

The detector consists of a channel plate, scintillator, photomultiplier and fast electronic counter.

The technique allows for variations which are useful when analysing and depth profiling materials. In more detail they are:

1. Surface Spectroscopy (static SIMS): The application of very low ion dose densities, allows quasi non destructive surface analysis. ([Figure 3](#)).
2. Surface Imaging: The rastering of a finely focussed beam over the sample surface yielding mass resolved secondary ion images which can be regarded as chemical maps. ([Figure 4](#)).
3. Depth Profiling (dynamic SIMS) & 3D rendering the application of high primary ion dose densities allows