**Paper from 9<sup>th</sup> International Colloquium Fuels Conventional and Future Energy for Automobiles January 15-17 2013. Technische Akademie Esslingen in Stuttgart/Ostfildern.**

# Diesel Deposits

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**Summary**

The diesel engine has traditionally been the choice for heavy duty applications with its reliability, robustness, relative lack of fuel sensitivity and economy being its prime advantages. The fuel efficiency advantage has also spurred a recent growth in light duty applications, especially in the passenger car market. To meet ever stricter emission regulations the fuel injection system of the diesel engine has been engineered to ever tighter tolerances and higher pressure regimes. This has coincided with legislative changes in fuels, and the result has been a greater sensitivity to deposit formation and an upsurge in reported field problems such as adverse effects on drivability, cold start and power loss. As a result there has been significant interest in the causes of the nature of deposits with numerous papers, forums and conference proceedings in this area of study since 2008.
The complex nature of deposits will be described, their possible origins and the application of analytical techniques for the characterisation of the most recent outbreak of injector fouling issues.

## 1. INTRODUCTION

Though deposit formation has been an issue within diesel fuel injection equipment since its inception [1-3], the design of the older fuel injection equipment and the lack of emission regulations meant that they were of limited concern. In the USA in 2008-9, there was an increase in the number of reports from both engine manufacturers and fleet operators regarding the formation of deposits in fuel systems. Since then reports have continued and spread to other parts of the world. Initially deposits were noted on filters, then on the injector nozzles and recently on the internal mechanisms of the injector, and in cases from the field all three. The deposits resulted in :

- Misfiring
- Stalling
- Rough Idling
- Increase in smoke
- Higher emissions
- Lack of power
- Reduced fuel economy
- No cold start performance

The major factors in the formation of both filter and injector deposits are the fuel and injector equipment, with the overarching driver of emissions legislation pushing both. The common rail fuel injection system has seen the development of fuel injection systems capable of pressures of 300 Mpa with concomitant temperatures of 150°C and even higher nozzle tip temperatures. This combined with the multiple injection strategies has required component clearances of less than 1μm [4], nozzle hole diameter reduction to 100μm and hence a resultant intolerance to deposit generators. Indeed a recent laboratory study showed that 100 mg of fine dust in 50 litres of highly contaminated and recirculated but unfiltered test fluid was sufficient to cause damage [5] with the resultant cost of replacement parts and unscheduled downtime. Legislation in the form of emissions regulations is driving diesel engine manufacturers to systems capable of near to zero emissions. In Europe and the US, the trend is towards tougher regulations on road. Euro 5+ and Tier 4 are being implemented, and by 2015 off road will be in place. Other examples such as railway diesel engines will be regulated in 2012-2015. Fuels have not escaped legislation either, with the introduction of ULSD in the US. The desulphurisation and refinery process changes carried out to assist emission reduction resulted in

the loss of lubricity and reduction in the solubilising power of the fuel for deposits or their precursors. [6-10] Unsurprisingly an outbreak of field deposits occurred after the introduction of ULSD in the US .

This resulted in significant industry activity to try and characterise and understand the formation of these deposits [11-22], which is still ongoing. The reports of deposits continues to grow and their origins summarised in figure 1 more complex.

For example a recent study [14] found formic acid in aged fuel. Copper, zinc and lead from the fuel system was found to combine with the formic acid to yield significant deposits. Furthermore, numerous studies of corrosion in the infrastructure of the fuel delivery supply chain, have also found acetic acid in fuels [23,24]. This is another possible deposit precursor. The possible origins of the acid itself are complex, with ethanol, bio contamination, biodiesel instability, bio contamination, ULSD residuals, ULSD degradation and fuel cross contamination all being put forward as possible causes.

Recent industry effort has focused on internal injector deposits. These deposits show a lack of propinquity and have been categorised as follows:

        **Carbonaceou**s: Black in colour carbon based.
        **Metal soap**s: White in colour sodium carboxylate based.
        **Amide base**d: Brown coloured, polymeric.
        **Lacquer based:** Visualised on some injectors difficult to reproduce; may be a carbonaceous precursor?
        **"Sticky" Deposit:** often seen in conjunction with aged fuels.
        Not all of these have been reproduced under laboratory conditions. Field samples are more complex [25] and appear to vary in frequency and type, depending on location.
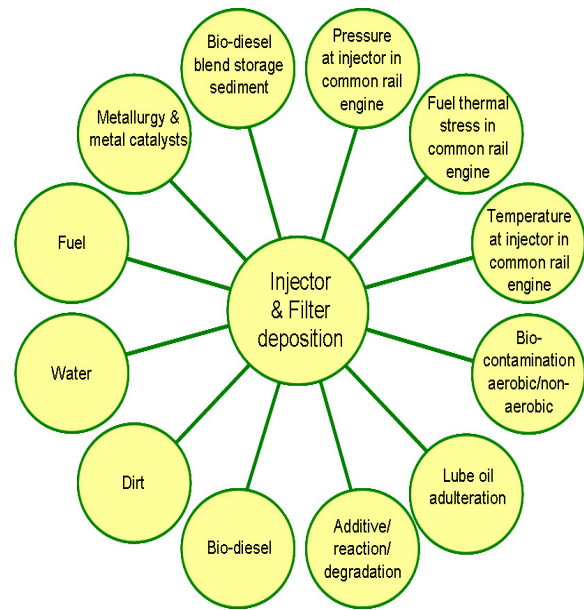


**Figure 1 Possible Sources of Deposits**

## 2.      PREVIOUS WORK

The current industry focus is on internal injector needle deposits. The effort to understand these deposits has led to many theories and laboratory studies and field analyses. The results of these studies have shown the explanation to be complex, having common links between filter and injector deposits and not to be of a single origin [1].

Cook and Richards [8] for example surveyed the possible causes of deposit formation in fuel systems caused by the oxidation of the fuel components to produce fuel deposits. The ability of Ultra Low Sulphur Diesel (ULSD) to solubilise such deposits was also questioned. Schwab et al [17] concluded that the application of monoacid lubricity improvers showed no performance issues relating to injector deposit formation. The same paper found that so called "problematic" fuels were found to be very stable. Furthermore, one other cause of deposit formation put forward was due to insoluble alkenyl succinic acid sodium salts Ullmann [18] et al however found interactions between a monoacid lubricity improver and detergent additives. In both cases the laboratory production of both deposits required atypical levels of reactants to be present. Quigley[16] reported the inability to replicate these effects in the laboratory, when heating and mixing neat fuel additives. Others [20] have found, using the Temperature Programmed Oxidation technique (TPO), that internal injector the carbonaceous deposits have a degree of crystallinity not found in external injector deposits. Further investigation using the hydropyrolysis technique [1] showed these deposits to consist of archipelago structures of heavily alkylated aromatics of

small ring size. This would be consistent with the degradation caused by the temperatures and pressures experienced by the fuel in the injector. Recent work [4,10] has also pointed to sodium chloride as a carboxylate salt precursor, which is unlikely [26]. The presence of trace amounts of sodium hydroxide is a more obvious alternative. Another recently described potential cause [4,10] is the production of deposits from low molecular weight polyisobutylenesuccinimide (PIBSI) detergents. The authors noted that normal molecular weight distributed PIBSIs do not produce deposits.

Recent work from Spain [11] using Infrared spectroscopy (IR) and Gas chromatography mass spectrometry (GC/MS), has implicated the salts of C12 succinic, C16 palmitic, and C18 steric/oleic acids with sodium as internal injector deposits. Their origin is believed to be from pipeline corrosion inhibitors. The paper exonerated PIBSI from being a source of deposits. It was also noted that a number of criteria had to be in place such as concentration, boundary conditions, time and availability of reactants for deposit formation to occur. Arondel et al [12] implicated Dodecyl succinic acid (DDSA), and Hexadecyl succinic acid from corrosion inhibitors as possible sodium carboxylate based internal injector deposits.

In a recent paper [25] the application of Time of Flight secondary ion mass spectroscopy (ToF –SIMS) was used to characterise US origin field internal injector deposits. For the first time the complexity and layering of the deposit was reported, (Figure 2). The previous way in which deposits were
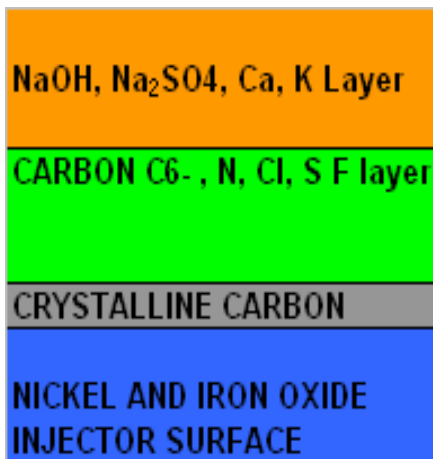


Figure 2 Schematic of US injector deposit Constitution

Ascribed to one source: metal carboxylate salt; "soap type", carbonaceous; or lacquer-amide was shown to be a simplification, and that reality was much more complex. In this paper the latest findings using this technique will be described for a field sourced European injector, where the internal deposit on the needle

was put forward as the reason for failure. The injector had been operated on current specification EN590 fuel.

## 3. LATEST WORK



**Figure 3 Injector needle**

The needle was removed from its housing with difficulty and was clearly stuck. The deposit is clearly visible both at the top of the needle and down the shaft of the needle (figure 3). Preliminary analysis was carried out using Scanning Electron Microscopy (SEM), (figures 4 and 5) and Energy Dispersive X-ray analysis (EDAX):
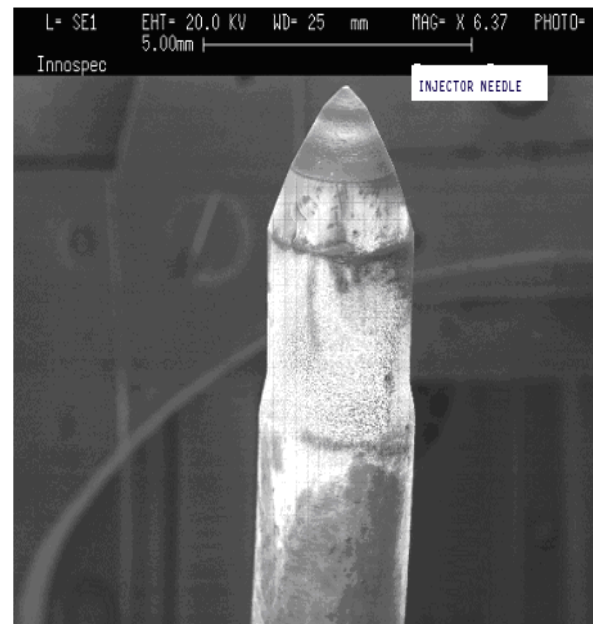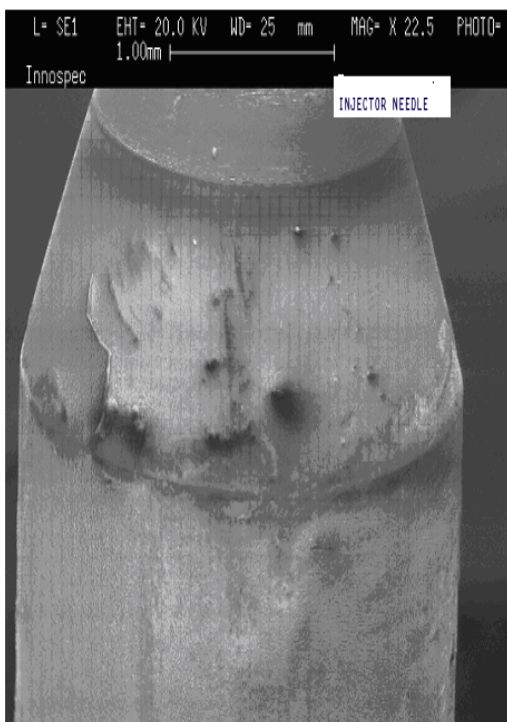


**Figure 4 SEM of needle tip**

**Figure 5 SEM of needle barrel**

EDAX indicated the presence of chlorine, iron , sulphur, sodium, calcium and potassium.

ToF-SIMS:
The technique: has been described previously, [25]. Briefly it involves using a primary ion beam to produce a secondary cloud of ions from a target surface. These ions are then extracted into a time of flight mass spectrometer and analysed. The technique exhibits several advantages including the parallel detection of different chemical species, their mapping over the surface analysed, all of which can be simultaneously performed whilst eroding the surface with a 'sputter' ion beam.

Depth profiling of the contaminant region of the sample was performed using a ToF-SIMS IV (IONTOF GmbH, Münster, Germany) time-of-flight secondary ion mass spectrometer. The instrument was equipped with a 5 keV $Cs^+$ ion source and a 25 keV cluster $Bi_3^+$ ion source, employed for sputtering and analysis respectively. Both ion sources were set at incident angles of 45°. In order to avoid any problems arising from an overlap of the analysed area with regions that had not received a constant $Cs^+$ ion dose, the $Cs^+$ sputter area was set to a $300 \times 300$ μm where only the central $100 \times 100$ μm area was analysed with the $Bi_3^+$ ion beam.

The pulsed $Bi_3^+$ primary ion beam had a spot size of < 2 μm diameter and was rastered in a $128 \times 128$ pixel array. Owing to the insulating nature of the sample, charge compensation using a low energy (20 eV) electron flood gun was applied. The sputtering and analysis ion beams were aligned before measurements so that the spectral analysis area was at the centre of the sput-

ter crater. Depth profiles were subsequently acquired using 'non-interlaced' mode with periods of 100 and 6.9 s of sputtering and analysis respectively, with an intermediate 'pause' period of 0.5 s. The sample was analysed twice using a 300 micron crater and a second time as a repeat using a smaller crater of 100 microns. The decrease in crater size increases the speed of the profiling which is apparent in the x-axis of the two graphs.

The depth profile images of the predominant ions present are shown below. To some extent they mirror the EDAX data in that iron, chlorine in addition to nitrogen containing carbon species and a CH- species are found. Though the layering found is similar to that of the US injector deposit, the constitution is not as complex.
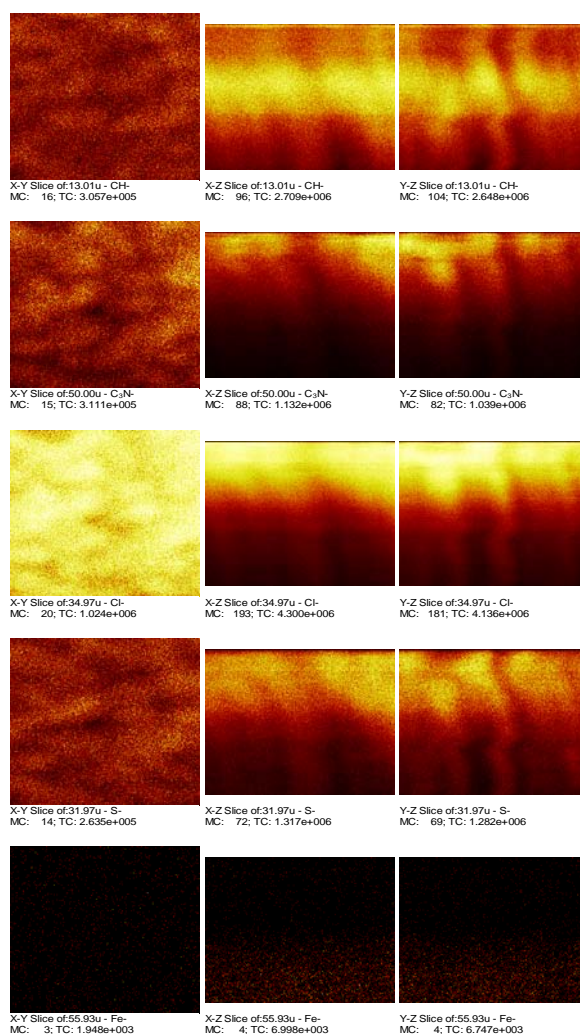


**Figure 6 Ion Image slices for Injector needle (Total X-Y area ( is $100 \times 100$ μm$^2$)**

Three of the most prolific ions were used to depth .
profile the deposit through to the injector surface
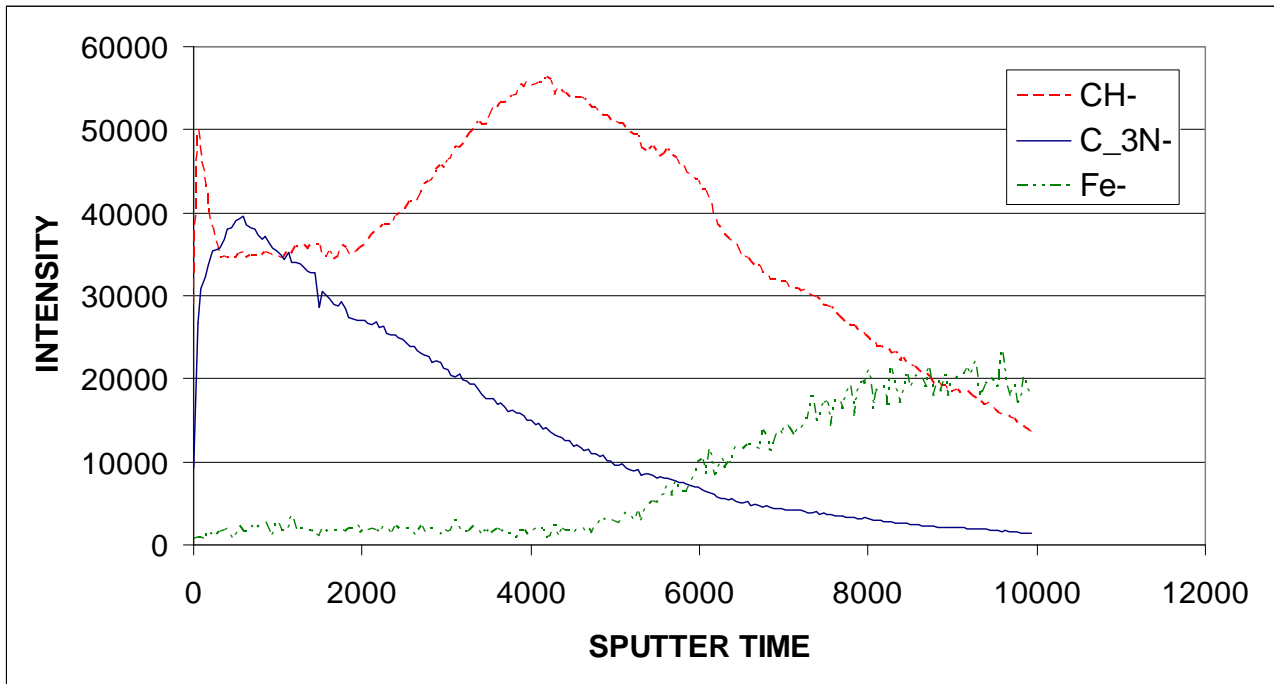
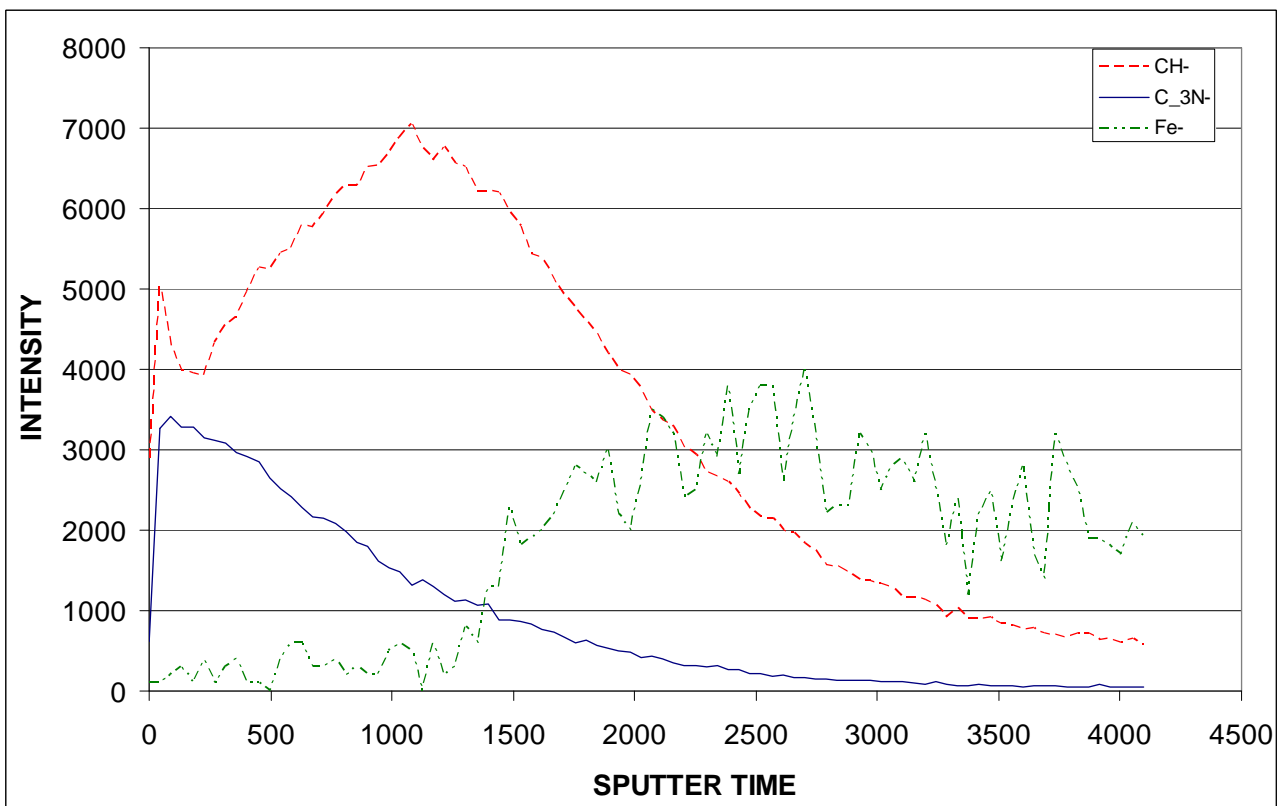

**Figure 7  Depth profile Fe, C3N and CH**



**Figure 8 depth profile of Fe, C3N and CH ions**

Two craters were formed to show consistency. The depth profiles (figures 7 and 8), show as the sputter time increases and the depth of penetration through the deposit to the injector surface, the following: The intensity of the C3N- ion s are high at the surface of the deposit and then fall away in concentration as the injector surface approaches. The CH- ions start at lower intensity near the surface of the deposit, and become higher toward the surface of the injector. The Fe ions show a low intensity of concentration at the surface of the deposit but nearer the injector surface they increase. In summary they show the surface of the deposit to be a nitrogen based organic species, the majority of the secondary layer is CH- in origin with particles of iron based ions distributed throughout the CH- layer. It is however the profile of these ions in the deposit (figure 9) which is revelationary showing the layers present but also that the iron is present as discrete particles in the CH- layer.



-C3N- LAYER- ER-

CH - LAYER BLUE
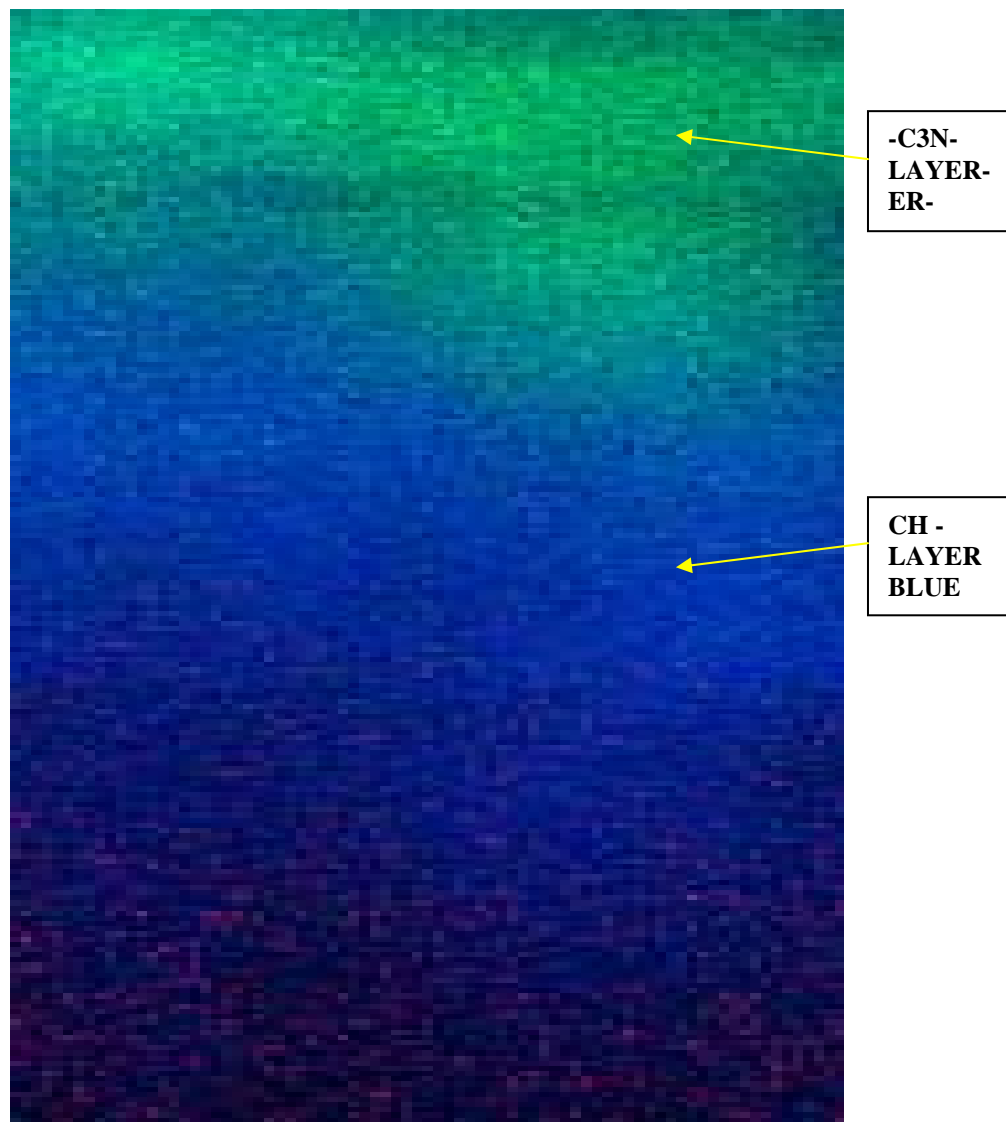
*The dots are iron ions dispersed throughout the CH- layer.*

**Figure 9 Y-Z View of Depth Profile**

## 4 CONCLUSIONS

The ToF -SIMS technique has again shown that injector deposits from the field are not simple. Instead they have been shown to be formed in layers which may be formed by the residual fuel either evaporating and leaving a residue or being unable to keep an insoluble residue in solution during the injection process. The European injector deposit is simpler in constitution than the US injector deposit described previously [25]. Both however are built up of multiple layers and both contain a nitrogen species layer. An interesting finding is that the iron based compound is dispersed as particles throughout the CH- layer, and not contained as a discrete layer. This may be indicative of the iron particle origins: A suspension of the iron in the fuel as discrete particles, possibly from corrosion, or as the result of wear during part of the injector cycle.

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