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## Insights into Deposit Formation in High Pressure Diesel Fuel Injection Equipment

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### ABSTRACT

The need to meet the US 2007 emissions legislation has necessitated a change in Diesel engine technology, particularly to the fuel injection equipment (FIE). At the same time as these engine technology changes, legislation has dictated a reduction in fuel sulphur levels and there has also been increased use of fatty acid methyl esters (FAME) or biodiesel as a fuel blending component. The combination of changes to the engine and the fuel has apparently led to a sharp rise in the number of reports of field problems resulting from deposits within the FIE. The problem is usually manifested as a significant loss of power or the engine failing to start. These symptoms are often due to deposits to be found within the fuel injectors or to severe fouling of the fuel filter. The characteristics of the deposits found within different parts of the fuel system can be noticeably different. A variety of analytical techniques have been investigated to gain knowledge of the characteristics of these different forms of deposit. Work has also been performed to characterise some of the fuels that may be causing the deposits.

This paper concentrates on the characterisation of deposits found specifically in the fuel injectors. Deposits found within different parts of the injector have been analysed using, Gas Chromatography with Mass Spectrometry detection (GC/MS), Fourier Transform Infra-red analysis (FTIR), Inductively Coupled Plasma spectroscopy (ICP), Nuclear Magnetic Resonance spectroscopy (NMR) and elemental analysis. Fuel samples that have been associated with the deposit formation have also been analysed. The techniques

discussed are high resolution mass spectrometry, and ICP. The results are also placed in context with previously published work on both filter and injector deposits.

### INTRODUCTION

Due to legislative changes in the US there have recently been step changes in both engine technology and fuel specifications. To comply with US 2007 emissions certification limits diesel engine manufacturers have striven to improve the combustion process within the engine. This has called for better mixing of the fuel and air to reduce the amount of combustion that takes place in fuel rich regimes. Generally, this can be achieved by improving fuel atomisation and penetration into the cylinder from the fuel injectors [1, 2]. Reduction in fuel injector hole size, and an increased fuel pressure at the point of injection, has been fundamental in this progression [3, 4]. It has been suggested that these engineering improvements and the resultant high pressures and temperatures, contribute to the observed fouling problem by accelerating the ageing of the fuel. There has also been widespread use of aftertreatment devices, the performance of which can be adversely affected by fuel sulphur [5, 6]. A coincident change was therefore made to reduce the permitted fuel sulphur levels to no more than 15 mg/kg. Due to the requirement to meet renewable fuels mandates the inclusion of fatty acid methyl esters (FAME) or biodiesel also became common.

Coincident with these changes to engines and fuels there was also an apparent increase in the incidence of reported operational problems due to deposit build-up within the fuel



injection equipment (FIE). The inclusion of biodiesel into the fuel has shown an increased propensity to cause fouling of the fuel injection system, both in the fuel injectors [7] and the fuel filters [8]. However, problems have been reported for both Ultra Low Sulphur Diesel (ULSD) and fuels containing biodiesel. Bio-components may therefore be a contributory factor in deposit formation process; however, they are clearly not the sole cause. Some of the many other possible causes of deposit formation are shown in Figure 1.

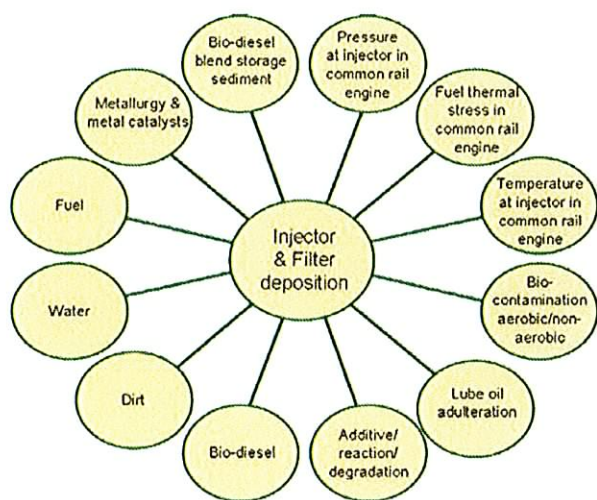


Figure 1. Possible causes of fuel system deposits.

Most of the causes shown in Figure 1 have been seen in recently collected field samples; either as a single cause or in combination. Previous work [9] has reviewed some of the possible fuel degradation mechanisms that could lead to deposit formation. However, matching hypothesised mechanisms with the reality of what is being seen in the field relies on accurate characterisation of the deposits and the fuels that are leading to these deposits. Previous publications have reported on work to characterise the deposits on fuel filters [10, 11] and fuel injectors [12]. This paper builds on this earlier work to further characterise fuel injector deposits and also to characterise the fuels that are causing these deposits in conjunction with fuels that have no apparent propensity to form deposits.

## EXPERIMENTAL PROCEDURES

In order to further understand the nature of the chemical species present in fuel systems additional analytical techniques have been employed that go beyond the mass spectrometry techniques presented in earlier work [10]. To identify and quantify the metals present in the fuels and deposits the Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP) technique was used. The following paragraphs give a brief outline of the techniques and equipment used for this work.

## INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY

This is a multi element analytical method which has considerably fewer matrix effects than atomic absorption spectroscopy but with comparable detection limits. The instrument used was a Varian Vista Pro CCD simultaneous OES (radial type); the methodologies used were according to ASTM method D7111 and after ashing by ISO method 11885.

## GAS CHROMATOGRAPHY - MASS SPECTROMETRY (GC-MS)

The instrument used for the GC-MS was a Thermoquest Trace MS with a Phenomenex Zebron ZBwax, the column was of 30m × 0.25mm and 0.25 urn film. This instrument was used to initially analyse the composition of the sample from which it was then possible to identify areas of interest for further analysis. The operating conditions for the instrument are listed below:

Initial temperature: 40°C; Initial time: 4 minutes; Temperature ramp: 5°C/minute; Final temperature: 240°C; Final time: 16 minutes; Injector temperature: 220°C; Injection volume: 1µL; Injection mode: Splitless; Ionisation type: 70 eV electron ionisation (EI); Mass range: 20-520 Da; Scan speed: 2 scans per second.

## LOW RESOLUTION ELECTROSPRAY MASS SPECTROMETRY (LR-ESI-MS)

The instrument used for this work was a Waters ZMD single Quadrupole M/S. This provided for a more detailed analysis of the sample and a wider mass range to be investigated; enabling ions to be targeted for subsequent identification by accurate mass analysis. Analysis was by Infusion ESI MS, the instrument parameters were an infusion rate of 5µL/minute of a solution of 1mg/mL of ULSD in methanol.

## HIGH RESOLUTION ELECTROSPRAY MASS SPECTROMETRY (HR-ESI-MS)

The instrument used for this work was a Bruker Apex III Fourier transform ion cyclotron resonance mass spectrometer.

Analysis was by Infusion ESI MS, the instrument parameters were an infusion rate of 5µL/minute of a solution of 1mg/mL of ULSD in methanol; the instrument was externally calibrated.



**Table 1. ICP Metals Analysis ULSD Fuels**

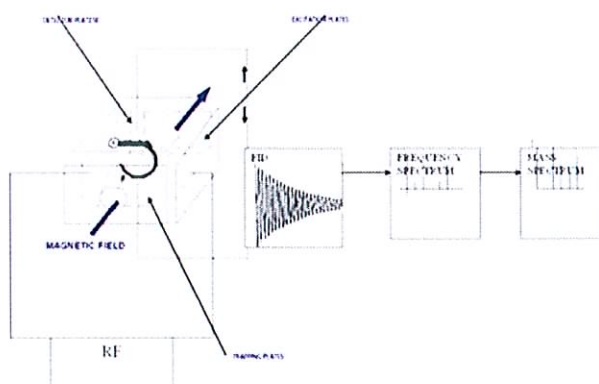
Fuel	Ca mg/kg	Fe mg/kg	Mg mg/kg	Si mg/kg	Na mg/kg	Zn mg/kg	Coking
1	2.5	0.3	0.3	0.5	1	<0.1	No
2	1.7	0.1	0.3	0.3	0.7	<0.1	Yes
3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	Yes
4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	No
5	1.8	0.2	0.3	0.1	1	0.2	Yes

Metals tested for and found to be <0.1 mg/kg were Ba, Cd, Cr, Cu, Ni, Pb, Li, Mn, Mo, Ni, V, and Ti

### FTICRMS: FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY

This technique involves the generation of sample ions by an external ion source. These are then injected into a cell in a spatially uniform magnetic field, in which the cyclotron motion of ions having different mass to charge ratios are excited by pulse or radio frequency electric field applied perpendicular to a magnetic field. The individual excited cyclotron motion of the ions is then detected by receiver plates yielding a complex frequency versus time spectrum or FID. Application of Fourier Transformation to the observed FID yields a frequency domain FT-ICR signal, which on the basis of the inverse proportionality between frequency and the mass/charge ratio, can be converted into a mass spectrum. The advantages of this technique are:

It is a very high mass resolution technique in that masses can be determined with very high accuracy and precision. Mass resolution beyond 1,000,000 is routinely achievable affording resolution of nominally isobaric species and elemental formulae of these compounds to be identified.



**Figure 2. A FTICRMS Schematic**

### RESULTS

A series of samples of fuel injectors were obtained from the field, having been removed from the engine after the operator had reported operational problems. Fuel samples were also collected from the field in order to determine if there was a correlation between the composition of the fuel and the deposits to be found on the injectors. Fuel samples were also collected from the field where no reported fuel system fouling problems had been associated with these fuels. This allowed for a comparison to be made between the characteristics of problem and non-problem fuels. All fuels and injectors were of North American origin. The injectors were from heavy-duty diesel engine in the field or from OEM engines running development testing in test cells. The problems manifest as power loss resulting from needle sticking, and injector failure.

### FUELS

A number of fuels of known provenance have been sourced from the field. Fuels that are known to have deposit problems are referred to as “coking” fuels whilst those that have no record of associated problems are referred to as “non-coking” fuels. Deposits were noted by customers in both internal and external areas. The fuels were analysed by ICP and the various mass spectroscopy techniques noted above.

### Results of ICP

To allow an initial understanding of any metal interaction in the deposit forming process, five fuels were subject to metal analysis by ICP. The results are expressed as mg/kg and are tabulated in [Table 1](#).

The data shows the presence of a number of metals that have been implicated in the deposit forming process. From [Table 1](#) it can be seen that there is no correlation between the concentration of these metals present in the fuel and the fuels propensity to cause deposit problems. With this limited data set it is of course not possible to totally eliminate the possibility that there is some combination of metals that when present will have some synergistic effect on deposit formation. It is interesting to note that fuel 5 has lower or equal concentrations of all the metals, except zinc, when compared to Fuel 1. Fuel 5 has a propensity to form deposits

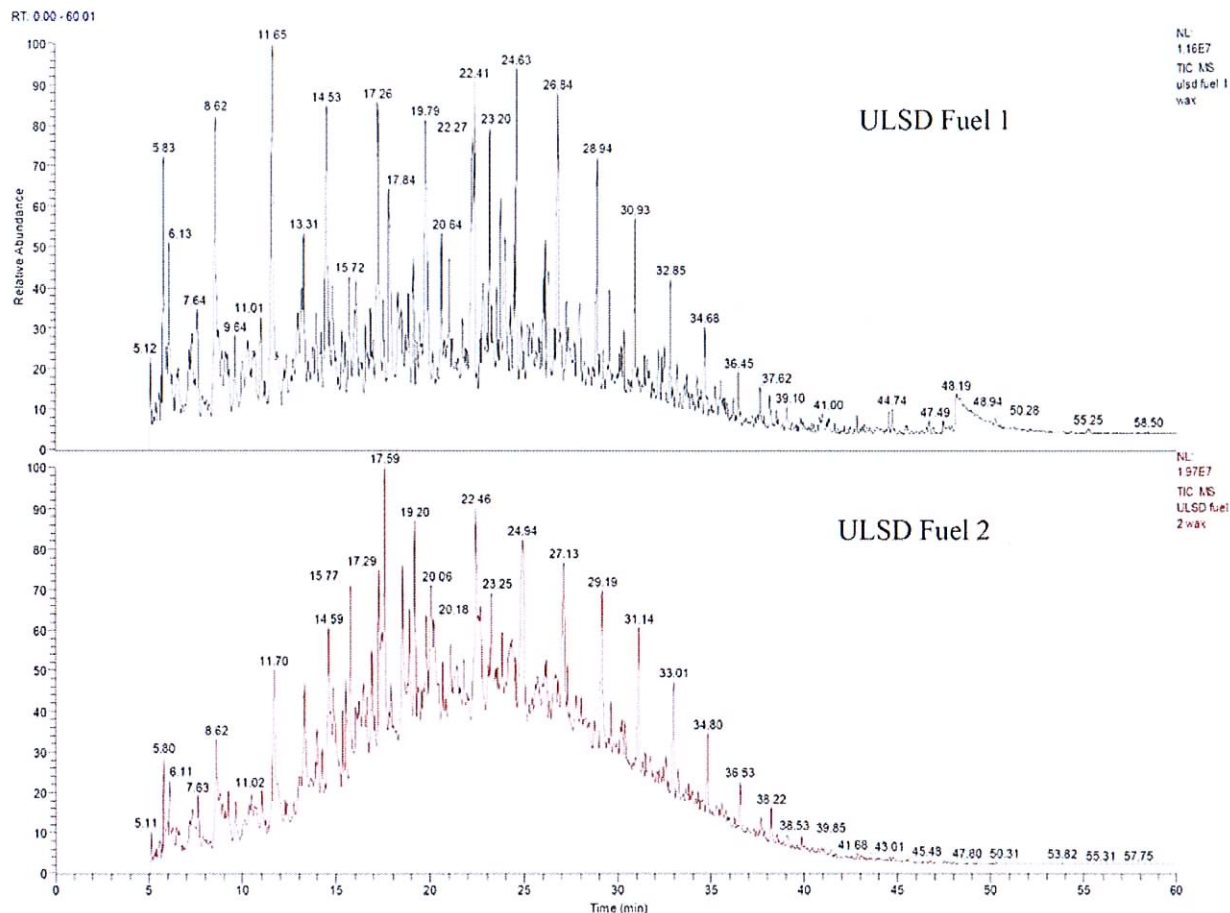


Figure 3. TIC chromatograms of ULSD Fuel 1 and ULSD Fuel 2.

whilst Fuel 1 does not. The presence of zinc at 1.0mg/kg has been associated with an increased propensity to form deposits in the European DW10 test and the literature [13-14]. In the case of sodium which has been associated with sodium carboxylate salt deposits, the spread of results is 1 to <0.1 mg/kg with both the high of 1.0 mg/kg and the low of <0.1mg/kg being associated with “coking fuels”.

### Results of mass spectrometry

Initial results are presented for two fuels. One of the fuels (ULSD Fuel 1) has no record of causing deposits and is thus considered a non-coking fuel and the other fuel (ULSD Fuel 2) has a history of causing deposit problems and is considered a coking fuel. Both of these fuels were analysed by GC-MS, LR-ESI-MS, and HR-ESI-MS.

For all acquired data sets the results are consistent with there being a difference between ULSD Fuel 1 and ULSD Fuel 2. The results of each mass spectrometry technique have been used to try and understand those differences. The following gives a brief summary of the outcome of the three different mass spectrometry techniques:

### Gas chromatography - mass spectrometry (GC-MS)

The comparison of the two Total Ion Current (TIC) chromatograms is presented in Figure 3.

The differences in the two fuels around a retention time of 48 minutes and the degree of unresolved material under the peaks and the characteristic “hump” merited further investigation as part of a long term investigation of coking and non-coking fuels

### Low resolution electrospray mass spectrometry (LR-ESI-MS)

Figure 4 shows the negative ion ESI mass spectra for ULSD Fuel 1 and ULSD Fuel 2.

Although the negative ion data initially suggested the possibility of carboxylate species, dodecenylsuccinic acid at  $m/z$  281, hexadecenylsuccinic acid at  $m/z$  339 and oleic acid at  $m/z$  283 may be present. The possible ions associated with these species are in both fuels, coking and non-coking, it was the difference in molecular constituents which was of interest

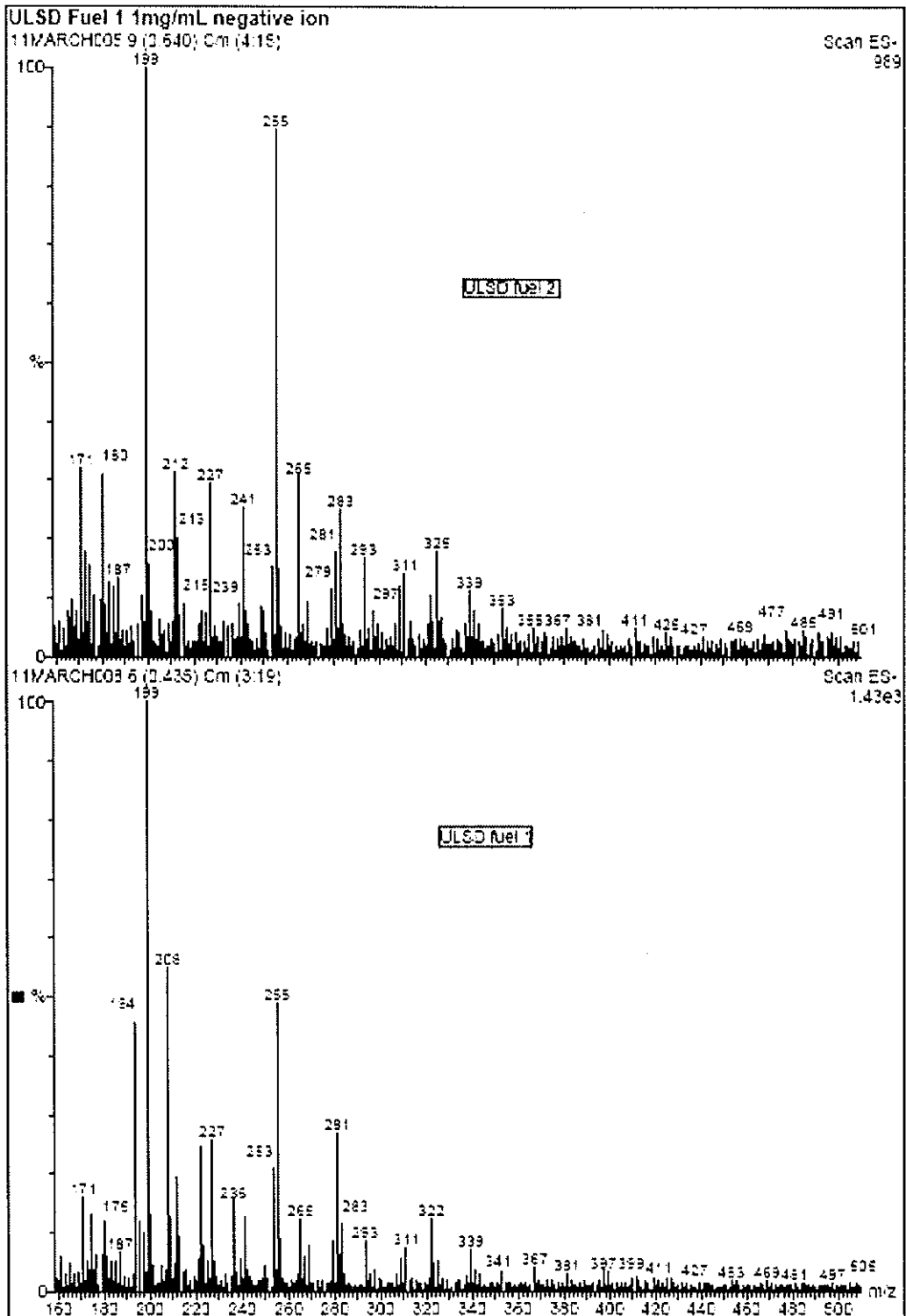


Figure 4. Negative ion ESI mass spectra for ULSD Fuel 1 and ULSD Fuel 2

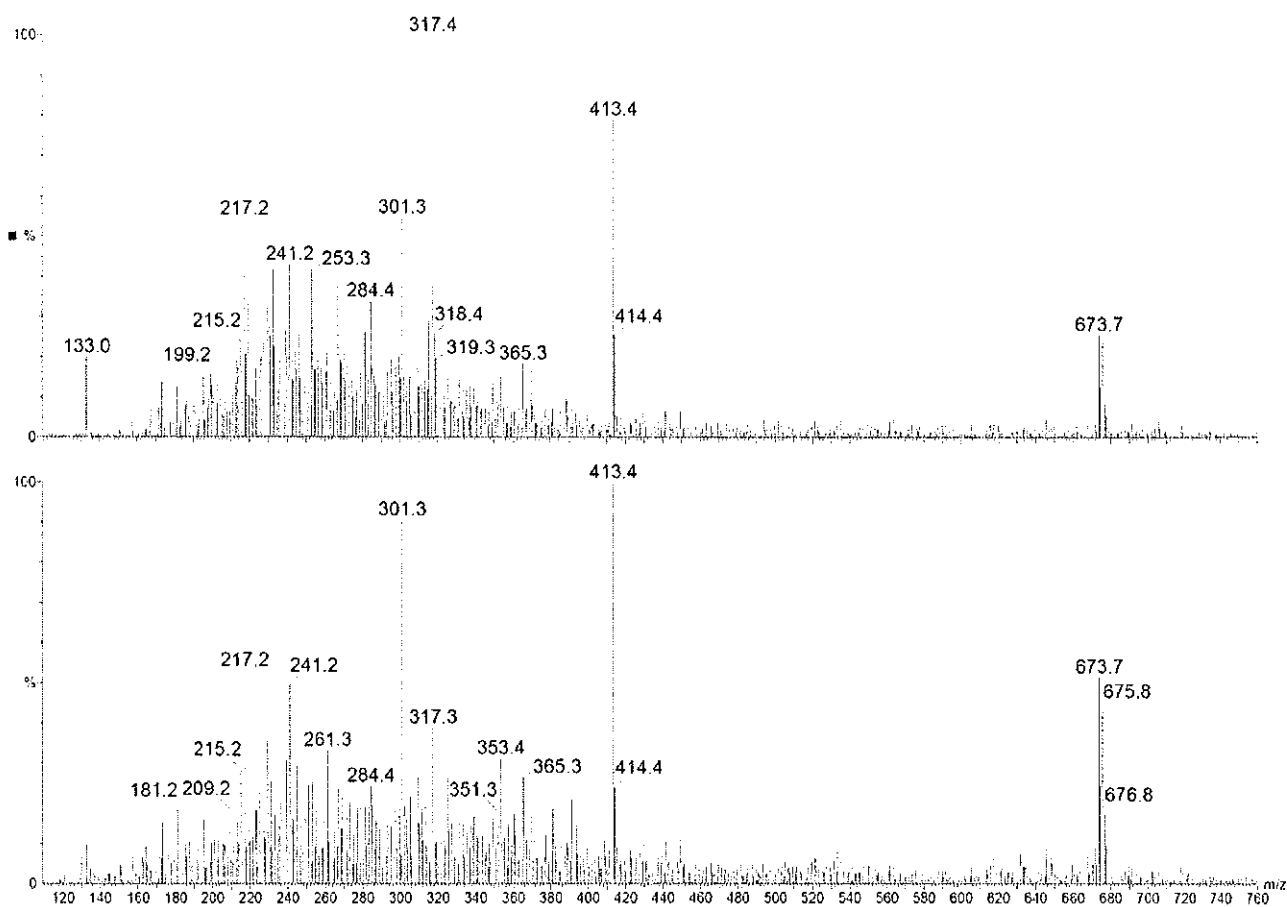


Figure 5. LR-ESI-MS of ULSD Fuel 1 and ULSD Fuel 2

regarding these fuels. The positive ion spectra were investigated and the details of the negative ion spectra will be reported elsewhere.

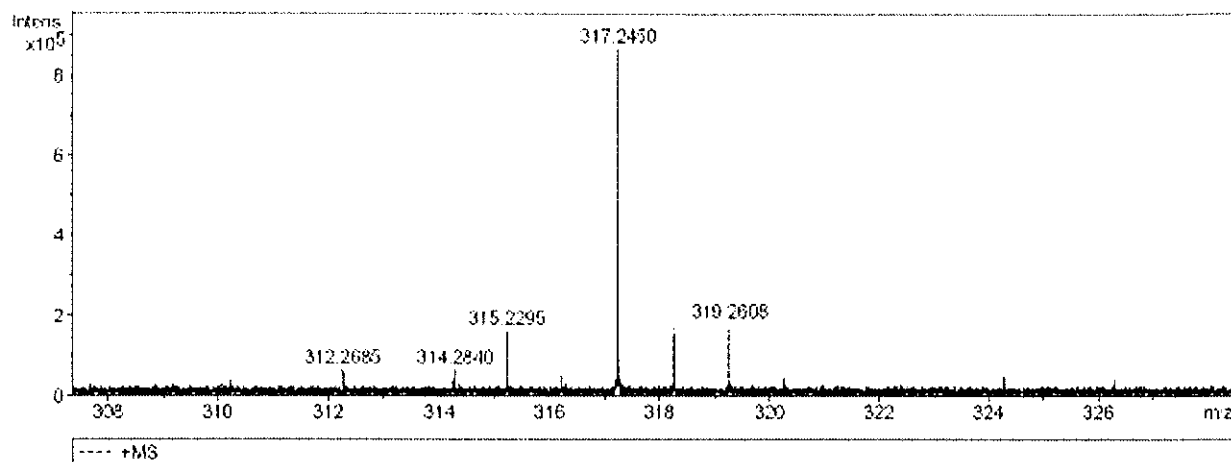
The data contains ions at  $m/z$  301 and  $m/z$  413 which are due to phthalate background contamination and may be dismissed from the investigation. The data show differences in the two fuels, for example in the abundance of  $m/z$  317 in ULSD Fuel 1 and presence in both fuels of species at  $m/z$  673. These two ions were thought to be of sufficient interest to be studied further. Firstly, in the case of  $m/z$  673 it was a distinct example of high molecular weight material in the fuels. Secondly, both ions may contain sodium which has been implicated in fouling [15]. To investigate these interesting ions further the FT-ICR MS technique was used, this technique has been used to great effect by Marshall and co workers [16,17,18,19,20,21] to characterize fuel systems.

High resolution electrospray mass spectrometry (HR-ESI-MS)

Only data for ULSD Fuel 1 will be described in detail and the focus is on the major ions that are different between this fuel and the analysis of ULSD Fuel 2; i.e. ions at  $m/z$  315,  $m/z$  317 and  $m/z$  319, together with the high molecular weight species at  $m/z$  673 and  $m/z$  675 that are found in both fuels. This data is shown in Figures 6, 7, 8, 9, and 10.

The high resolution electrospray MS measurements, undertaken using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry, provide an accurate mass measurement that correlates to a number of possible elemental formulae. Other factors, related known likely composition of species present, related MS criteria and orthogonal analytical data may lead to unequivocal identification of one elemental formula. One caveat is that since there is no chromatographic separation involved in making this measurement, the formulae produced may be related to isomeric species present.

For the species at  $m/z$  317 the most likely assignment of molecular formula is  $C_{19}H_{34}O_2Na$  and this hypothesis is consistent with the presence of species of relative molecular



Sum Formula	Sigma	m/z	Err (ppm)	Mean Err (ppm)	Err (mDa)	rdb	N Rule	e <sup>-</sup>
C 19 H 32 Na 1 O 2	0.742	315.2225	-0.26	-24.18	-0.03	3.50	ck	even
C 17 H 27 N 6	0.743	315.2292	-1.14	-27.88	-0.32	7.50	ck	even

Figure 6. Accurate Mass Report m/z 315 ULSD Fuel 1

mass m/z 294 in the GC-MS data for ULSD Fuel 1. This ion at m/z 294 was identified by a reconstructed ion chromatogram (synonym extracted ion chromatogram). This is a chromatogram created by plotting the intensity of the signal observed at a chosen m/z value or set of values in a series of mass spectra recorded as a function of retention time, as shown in [figure 11](#).

For the upper trace (ULSD Fuel 1) shows four major RICs for m/z 294, i.e. 29.72, 33.62, 35.32 and 39.41 min. In comparison these signals are less obvious in the lower trace (ULSD Fuel 2), suggesting that these species are present at lower levels, present below the detection limit of the system or absent. Note there is an electrical noise spike at 32.95 min in the lower trace.

The high molecular weight material at m/z 673 that is present in both fuels has a likely assignment of the molecular formula C<sub>40</sub>H<sub>74</sub>O<sub>6</sub>Na. The most likely candidate being a long chain carboxylate salt. It is difficult to comment on the origin of these molecules.

The spectra for ULSD Fuel 1 show the presence of a C<sub>19</sub> acid species that have been identified in a previous paper [[11](#)]. Interestingly this is a non-deposit forming fuel. The deposit forming fuel ULSD Fuel 2 does not contain the C<sub>19</sub> acid species but does contain the high molecular weight material with ions at m/z 673 that are also seen in ULSD Fuel 1. This and the lack of ions associated with carboxylate sodium salts of dimer, dodecylsuccinic and hexadecenyl succinic acids shows it is not necessary for the presence of sodium

carboxylates in a fuel for fouling to occur. Further, it is not a case of concentration being a factor since the sodium levels shown in [Table 1](#) are similar for ULSD Fuel 1 and ULSD Fuel 2. The high molecular weight material at m/z 673 may be sodium stearyl palmityl tartrate; stearyl palmityl tartrate is used as an emulsifier.

This is as far as the in depth interrogation of two fuels has progressed but the results are interesting and work continues both on these and other fuels.

## INJECTORS

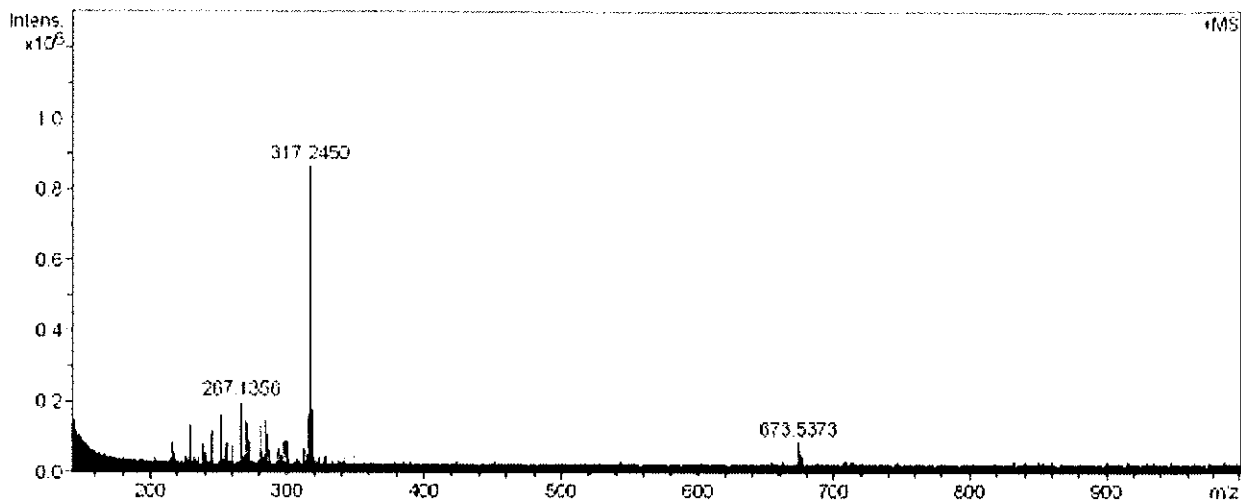
The current interest in fuel, filter and diesel injector issues has yielded a number of samples from the field which have been subject to variety of analyses. The preliminary work on two examples is described below. On receipt the injector is broken down into its individual components as shown in [figure 12](#).

### ICP analysis

To understand the metal composition profile of deposits on the injectors, injector parts from a failed injector were subject to solvent extraction using tetrahydrofuran, (60mL). The resulting extract solutions were evaporated down to dryness and then subjected to ICP analysis.

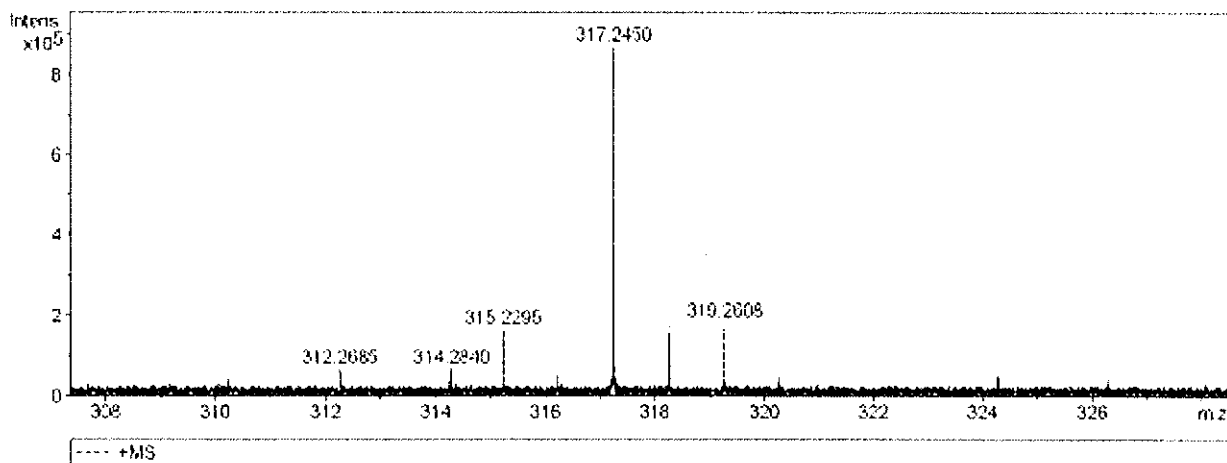
The results, expressed as mg/kg, are presented in [Table 2](#).





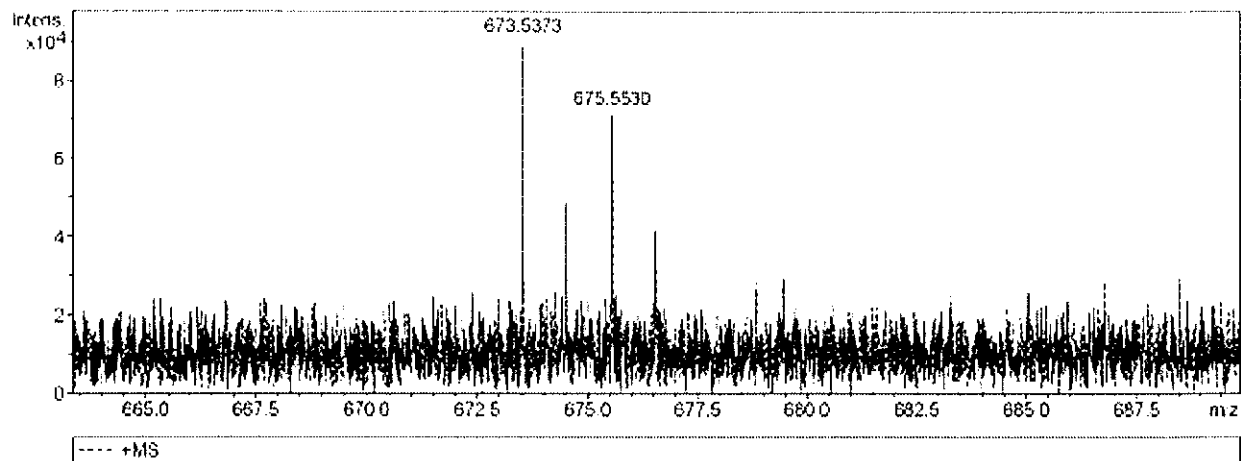
Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e <sup>-</sup>
C 17 H 29 N 8	0.109	317.2448	-0.43	-5.59	-0.14	8.50	ck	even
C 19 H 34 Na 1 O 2	0.107	317.2451	0.45	-3.94	0.14	2.50	ck	even
C 16 H 33 N 2 O 4	0.108	317.2435	-4.65	-9.50	-1.48	1.50	ck	even

Figure 7. Accurate Mass Report m/z 317 ULSD Fuel 1



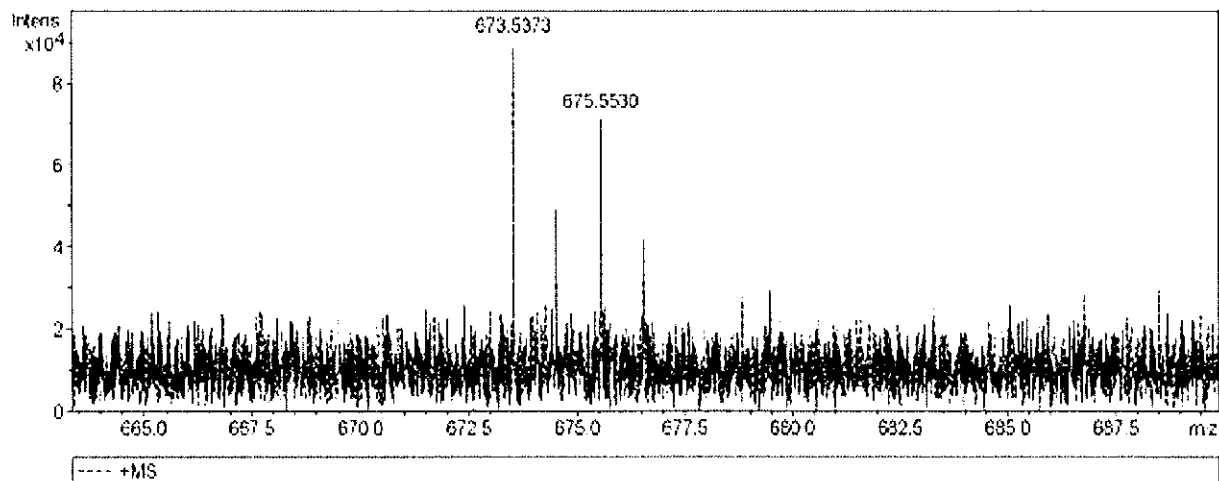
Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e <sup>-</sup>
C 19 H 38 Na 1 O 2	0.122	319.2603	-0.27	-0.27	-0.09	1.50	ck	even
C 17 H 31 N 6	0.122	319.2625	-1.15	-1.15	-0.37	5.50	ck	even

Figure 8. Accurate Mass Report m/z 319 ULSD Fuel 1



Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdB	N Rule	e <sup>-</sup>
C 40 H 74 Na 1 O 6	0.410	673.5378	0.69	-5.88	0.46	3.50	ok	even
C 15 H 86 Na 1 O 24	0.378	673.5401	4.20	-3.04	2.83	-27.50	ok	even
C 22 H 82 Na 1 O 19	0.386	673.5343	-4.52	-12.11	-3.05	-18.50	ok	even

Figure 9. Accurate Mass Report m/z 673 ULSD Fuel 1



Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdB	N Rule	e <sup>-</sup>
C 40 H 76 Na 1 O 6	0.229	675.5534	0.64	0.64	0.43	2.50	ok	even
C 15 H 88 Na 1 O 24	0.097	675.5568	4.14	4.14	2.80	-28.50	ok	even
C 22 H 84 Na 1 O 19	0.132	675.5499	-4.56	-4.56	-3.08	-19.50	ok	even

Figure 10. Accurate Mass Report m/z 675 ULSD Fuel 1

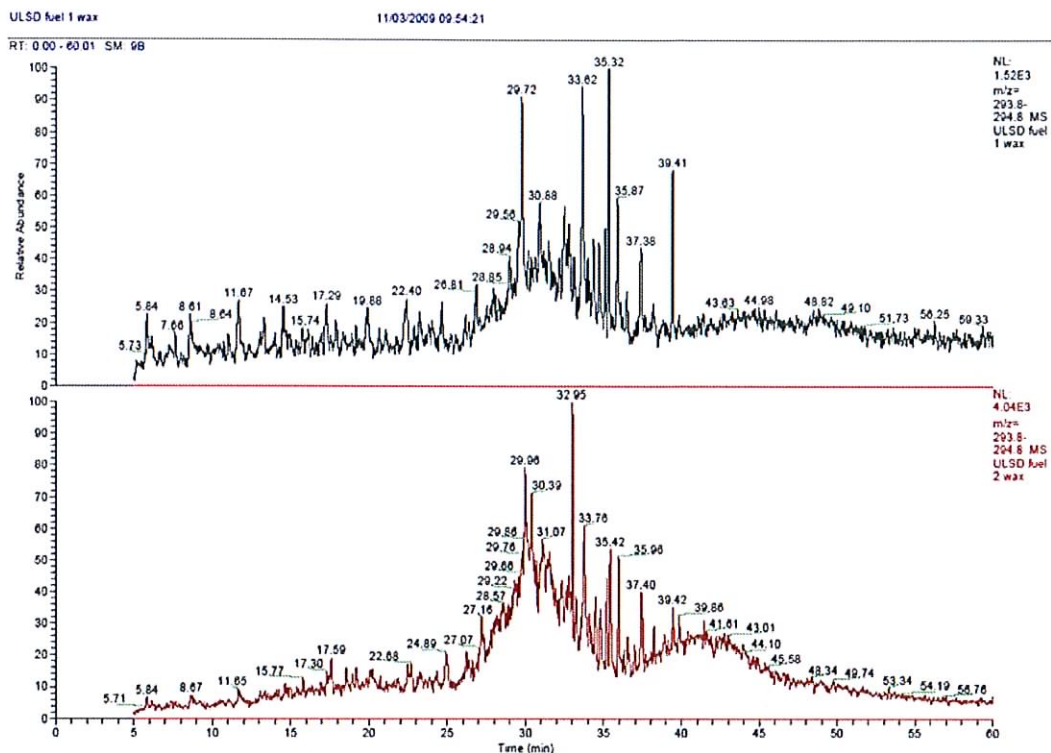


Figure 11. Reconstructed ion Current chromatograms (RICs) for  $m/z$  294 for ULSD Fuel 1 (upper trace) and ULSD Fuel 2 (lower trace).

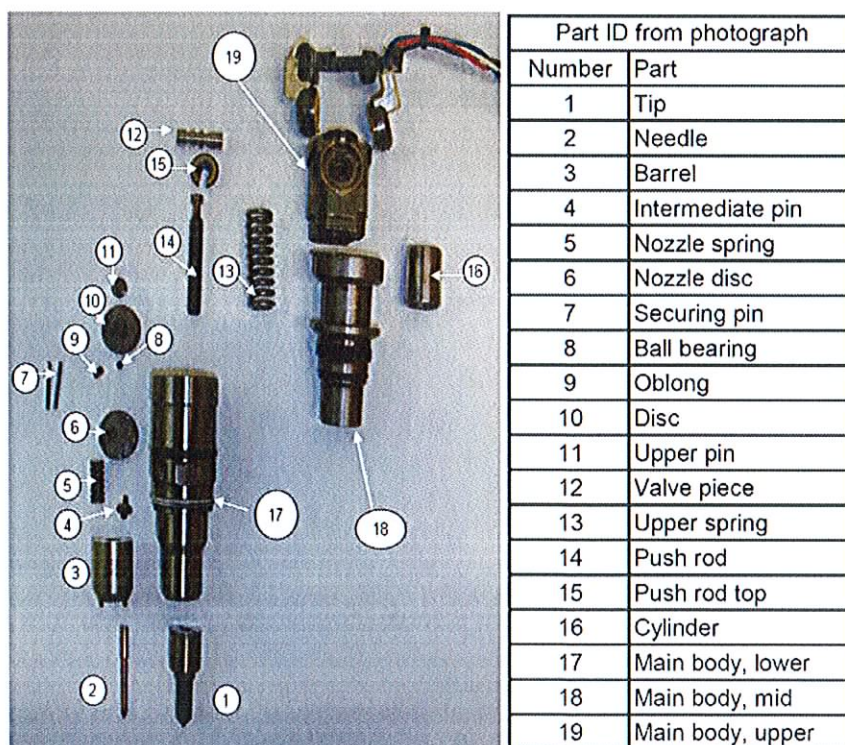


Figure 12. Diagram showing fuel injector components



**Table 2. ICP Metals Analysis Injectors**

Sample	Injector A				Injector B
	Blank THF	Tip	Needle	Pin	Tip
Extract grns	N/A	0.24709	0.00010	0.00050	N/A
Metals					
Al	2.8	0.2	<0.1	<0.1	179
Ba	0.5	3.4	0.2	0.5	86
B	<0.1	<0.1	<0.1	<0.1	46
Cd	<0.1	<0.1	<0.1	<0.1	<20
Ca	0.6	1.5	1.2	1.2	5440
Cr	<0.1	0.5	<0.1	<0.1	115
Cu	<0.1	<0.1	0.1	<0.1	503
Fe	0.5	16.3	0.6	0.4	447
Pb	<0.1	<0.1	<0.1	<0.1	20
Mg	<0.1	0.2	0.2	0.2	399
Mn	<0.1	1	<0.1	<0.1	<20
Mo	<0.1	<0.1	<0.1	<0.1	<20
Ni	<0.1	<0.1	<0.1	<0.1	<20
P	<0.1	<0.1	0.1	<0.1	593
Si	0.1	<0.1	<0.1	0.1	4500
Ag	<0.1	<0.1	<0.1	<0.1	<20
Na	0.4	1.3	1.4	1.7	1820
Sr	0.2	3.6	0.4	<0.1	<20
V	<0.1	<0.1	<0.1	<0.1	<20
Ti	<0.1	0.1	<0.1	<0.1	n/r
Zn	<0.1	2.2	<0.1	<0.1	613

The black and brown deposits found on two examples of failed North American injectors were investigated. The data for injector A; [Table 2](#); shows the variation in deposit level across the injector components, and similar low levels of sodium and calcium in the deposition on each part. It is noteworthy that the major deposition is at the tip of injector A with the needle and pin showing a lower level. In some cases injectors were found to be fouled to such an extent that solid lumps of deposit came away from the body of the injector without the need to resort to extraction, as was the case with injector B. Data on this type of injector is also shown in [Table 2](#).

At first glance the high sodium levels might suggest a sodium carboxylate issue and although this cannot be completely ruled out, a more likely scenario considering the calcium,

phosphorus and zinc levels is lubricating oil contamination. The high levels of metal found for injector B are indicative of the significant amount of deposit formed, and although the high values may suggest dirt or engine wear the deposit is nevertheless a field failure and it should be noted the lower levels detected on injector A is also associated with a failure.

Since sufficient sample was available further tests were carried out the deposit from injector B.

#### Infra-red analysis

The infra-red analysis of the deposit from injector B does not match a sodium carboxylate; the expected bands at  $\sim 1565\text{cm}^{-1}$  and  $\sim 1439\text{cm}^{-1}$  being absent.

In conclusion, although the presence of sodium carboxylate salts has been implicated in injector fouling, their presence in fuels does not necessarily cause fouling. Furthermore, when injector deposits are found which are rich in sodium, it does not follow that the source is a sodium carboxylate.

#### NMR analysis

A sample of the tip deposit from injector B was partially dissolved in Deuterated chloroform ( $\text{CDCl}_3$ ) and subject to proton NMR spectroscopy.

The NMR result shows the soluble material to be aliphatic, with  $\text{CH}_3$  and  $\text{CH}_2$  signals present. Compared to the aliphatic NMR region of ULSD fuels there is slightly more complication indicating degradation. There is no indication of functional groups or aromatic content.

#### GC-MS: Mass spectrometry

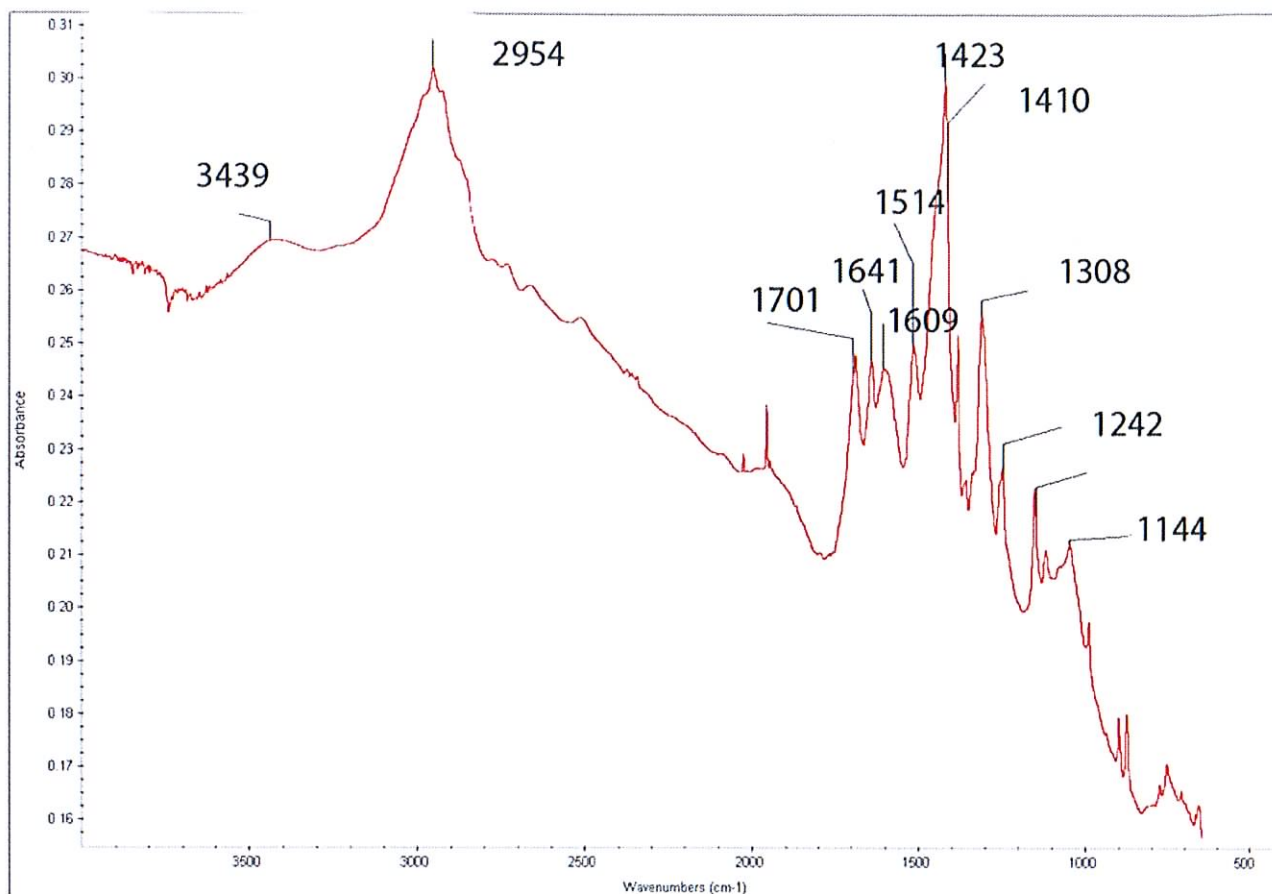
Each component of injector B was diesel "wet" on receipt and was subject to a hexane wash. This wash was then subject to GC/MS protocols to determine the presence of acidic species which may be associated with the presence of sodium.

The data is consistent with diesel fuel that does not contain any biodiesel. There is also no evidence for the presence of organic acids within this sample.

#### Elemental analysis

The deposits from the tip of Injector B were subject to elemental analysis. The results were as follows as percent mass/mass: C = 55.9 %, H = 3.1%. This gives an H/C ratio of 0.66.

The H/C ratio indicates a coke type deposit nearer to amorphous carbon than distillate fuel.



**Figure 13. Infra-red spectrum of tip deposit injector B**

### Temperature programmed oxidation

The tip of Injector B was also subjected to Temperature Programmed Oxidation (TPO). The TPO experiments were performed using a Leco® RC612 Carbon/Hydrogen/Moisture Determinator. The technique is described more completely in [reference \[12\]](#). A starting temperature of 270°C was used. This was increased to 900°C at a rate of 100°C per minute. The oxygen feed rate was 0.75 litres per minute.

The peak at 605°C is indicative of amorphous carbon material [\[12\]](#). The slight shoulder at around 470°C is indicative of a more hydrogen rich material whilst the absence of much emission at temperatures above 700°C indicates the absence of graphitic material seen in other fouled injector deposits [\[12\]](#).

In summary the injector tip residue is carbonaceous and contains calcium and sodium.

Although the presence of sodium carboxylate salts has been implicated in injector fouling, the data from ULSD Fuel 1 and ULSD Fuel 2 shows their presence in fuels does not

necessarily cause fouling. Furthermore, when injector deposits are found which are rich in sodium; injector B, it does not follow that the source is a sodium carboxylate.

### **CONCLUSIONS**

The recent changes to both fuel; ULSD, biofuel; and the injector technology in the US has coincided with a significant increase in reports regarding fuel system deposit formation. In order to formulate possible solutions a great deal of time and effort is being expended in trying to identify the compositional nature of these deposits and the mechanisms leading to their formation. As part of a long term programme to understand the deposit formation phenomena a variety of analytical techniques have been applied to both the fuels causing deposit formation and the deposits themselves. For comparison purposes analysis was also undertaken on fuels that do not cause fouling problems. The work presented here does not provide a definitive answer to the problem, although it does confirm that there is no one simple answer.

Regarding the metal concentrations in the fuels analysed it was found that:

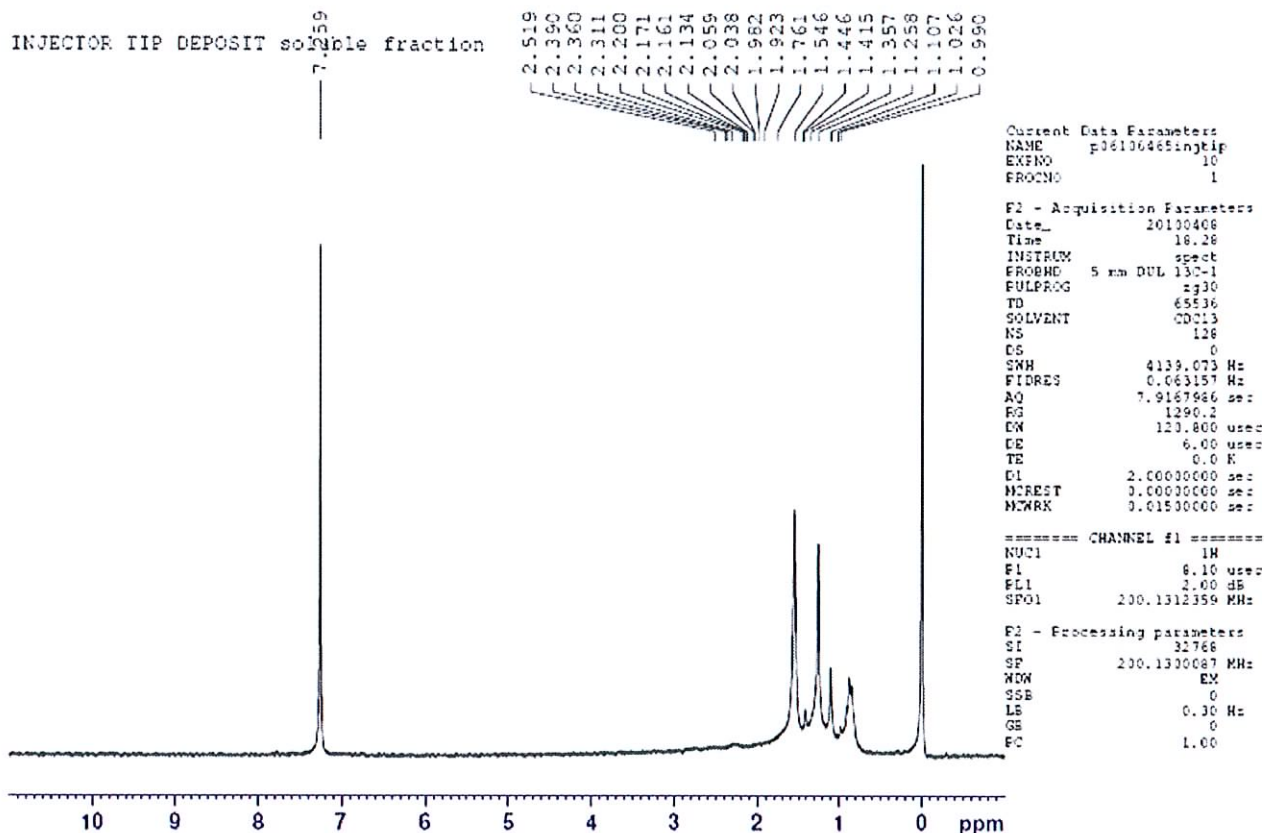


Figure 14. NMR trace of deposits from Injector B

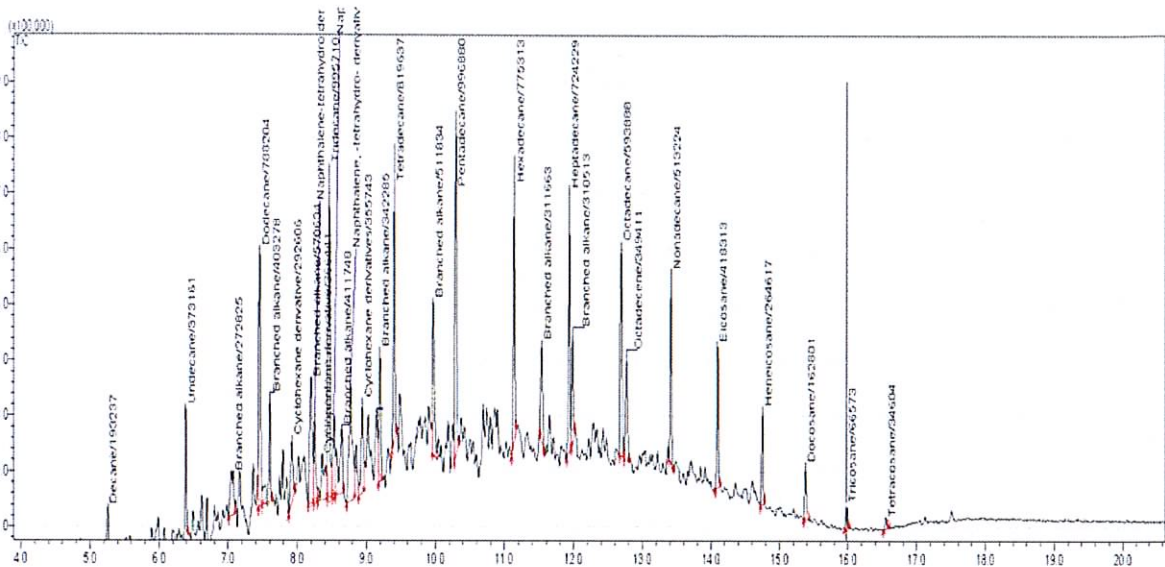
- Only one of the fuels contained a measurable amount of zinc, this fuel was known to have a propensity to form deposits. This is in agreement with earlier work and the fact that in the European Direct Injection, Common Rail Diesel Engine Nozzle Coking Test the test fuel is deliberately adulterated with zinc to promote deposit formation. However, zinc could not be detected in other fuels that are known to promote deposit formation. It is thus concluded that zinc is not the sole cause of deposit forming tendency and other mechanisms must be considered.
- Sodium was also found to be below the detection levels in some of the fuels analysed. In the samples where sodium was found it was only at levels of approximately one part per million. Again there was no correlation between the presence of sodium and the propensity of the fuel to form deposits. It is thus concluded that the presence of sodium is not the sole cause of deposit forming tendency and other mechanisms must be considered.
- For two of the fuels analysed there was no detectable level of metals present; one of these fuels had a propensity to form deposits. The fuel with the highest total metal concentration and with the highest concentration of any of the metals except zinc did not have a propensity to form deposits. It is thus

concluded that the presence of a measurable amount of metal is not a prerequisite for deposit formation.

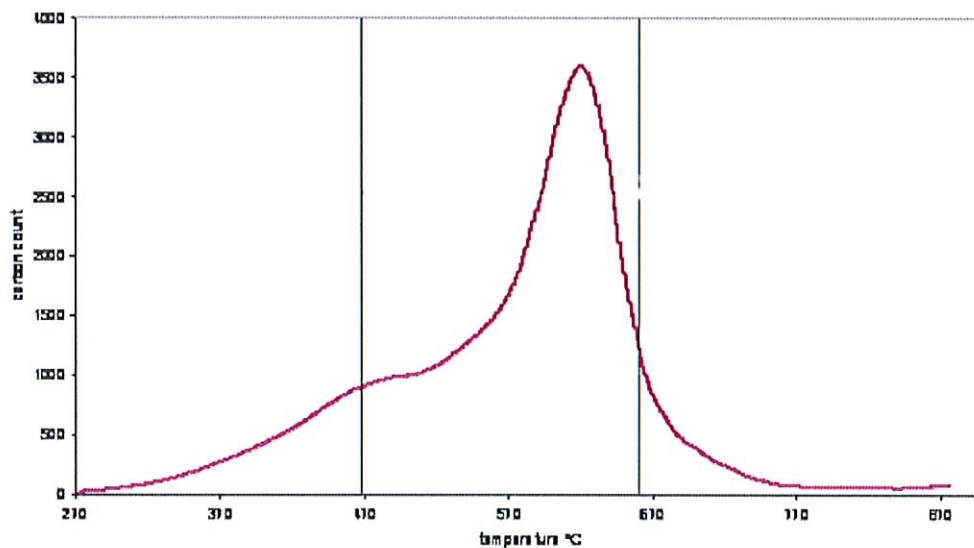
The Mass Spectrometry analysis of the fuels is currently limited to a fuel with a known propensity to form deposits and a fuel with no known deposit forming tendency. However, this limited analysis has shown:

- An ion associated with a C<sub>19</sub> carboxylic salt was identified as being more abundant in the fuel without the deposit forming tendency.
- Both the deposit forming fuel and the non-deposit forming fuel were found to contain a high molecular weight carboxylic acid salt. The conclusion from this limited data is that the presence of carboxylic acid salt does not necessarily result in a propensity to form deposits. However, the levels of such species may be a determining factor and further work would be required to address this issue.
- None of the fuels tested contained any marker for presence of biodiesel. Although poor quality, low oxidation stability biodiesel may promote deposit formation it is clearly not to blame for all instances of deposit formation.





**Figure 15. GC/MS TIC chromatogram of “wash” deposits from Injector B tip**



**Figure 16. TPO of deposit from Injector B**

Analysis of two injectors with brown, black deposits that had caused performance issues in the field showed the following:

- The deposits on the more lightly fouled injector needle and tip contained low levels of sodium.
- The more heavily fouled injector deposits contained substantial amounts of sodium but that it was not present as a carboxylate. The high thermal stability of the carbonaceous deposits indicated a high degree of crystallinity within their structure.

It is thus concluded that proposed routes to generating a fuel with a deposit forming tendency, including the addition of zinc, the presence of sodium carboxylate and the presence of biodiesel, may be valid in some circumstances. However, to blame any one of these causes and develop methods and controls around any of these routes in isolation will not bring about an end to the current problems.

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