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Information on the Aromatic Structure of Internal Diesel Injector Deposits From Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

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Abstract

The nature of internal diesel injector deposits (IDID) continues to be of importance to the industry, with field problems such as injector sticking, loss of power, increased emissions and fuel consumption being found. The deposits have their origins in the changes in emission regulations that have seen increasingly severe conditions experienced by fuels because of high temperatures and high pressures of modern common rail systems and the introduction of low sulphur fuels. Furthermore, the effect of these deposits is amplified by the tight engineering tolerances of the moving parts of such systems. The nature and thus understanding of such deposits is necessary to both minimising their formation and the development of effective diesel deposit control additives (DCA).

The focused ion beam technique coupled with time of flight secondary ion mass spectrometry (ToF-SIMS) has the ability to provide information on diesel engine injector deposits as a function of depth for both organic and inorganic constituents. Our previous work with this novel technique is unique in that it has shown layering effects in deposits which may be due to the residual fuel either evaporating and leaving residues or being unable to keep insoluble residues in solution during the injection process. As part of our on-going work to understand the nature of field deposits, the aromatic compounds present have been investigated. To help interpret the results for the aromatic structures present, spectra of a model polycyclic aromatic hydrocarbon (PAH), coronene (C₂₄H₁₂), and coal tar pitch (CTP) have been used as a basis to determine the ring structure of internal diesel; deposits. This work confirms the presence of aromatic ring structures of greater than six rings in composition in injector needle carbonaceous deposits.

Introduction

The current industry interest in internal diesel injector deposits (IDID) shows no sign of decline. In fact, CRC (Central Research Council Diesel Performance Group-Deposit Panel Bench/Rig/Investigation sub panel), CEN (Committee European de Normalisation TC19/WG24 Injector Deposit Task Force, engine test, and CEC (Coordinating European Council TDFG-110) in Europe have sub committees and panels investigating the production and characterization of these deposits. This interest continues because injector malfunction is manifested in:

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

These effects continue to be found throughout the world.

Internal injector deposits, a perhaps tendentious subsection of deposit problems in modern common rail diesel systems, has its origins in the same sources, [figure 1](#) as others such as filter deposits.

The reports of deposits continue to grow and their origins summarised in [figure 1](#) more complex. These origins have been discussed in the literature on several occasions. The production of carbonaceous deposits from the degradation of fuel by injector temperature and pressure increases in recent years in conjunction with the ability of newly introduced ULSD to solubilise deposit forming material was discussed first in 2009 [1]. Recently studies of corrosion in the infrastructure of the fuel supply chain, have also found acetic acid in fuels [2, 3]. 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.



Figure 1. Possible Sources of Deposits

The IDIDS, which have been investigated, have led to the following categorization of deposits being put forward:

1. Carbonaceous: Black in colour carbon based.
2. Metal soaps: White in colour sodium carboxylate based.
3. Amide based: Brown coloured, polymeric.
4. Lacquer based visualised on some injectors difficult to reproduce; may be a carbonaceous precursor?
5. "Sticky" Deposit: often seen in conjunction with aged fuels.

Our work [4] has shown IDIDS to be more complex in constitution with common links between filter and injector deposits and are not of a single origin [4].

In this paper, the focus is on the carbonaceous type of deposits on the injector needle found in many field failures. Previous work [5, 6, and 7] has examined the injector tip and the fuel filter. The distribution of aromatic species in the fuel injector tip sample were extremely complex when compared to the earlier

fuel filter sample investigated, and it was concluded that the aromatic compounds on the tip of the injector were of relatively small ring size and heavily alkyl substituted with no substituted PAH being observed. Whereas the fuel filter residues showed intermediates that have been postulated in the transformation from fuel to carbonaceous deposit by a hydrogen abstraction mechanism. The tip residues may be an indication of the rapid degradation of the fuel brought about by the high temperatures and pressures it experienced in the high pressure fuel system. Further TPO (Temperature Programmed Oxidation) studies showed the deposits formed on the injector tip were amorphous in nature whilst the deposits formed on injector needles were more structured. This work will further describe the aromatic structure of the needle deposit.

Methodology

The needle was of European origin, from the field, failure was attributed to stuck injectors. The injector had been operated on current specification EN590 fuel. Removing the needle from its housing proved difficult, and required some force. The deposit was found at the top of the needle and along the shaft.



Figure 2. Injector Needle

Initial SEM (Scanning Electron Microscopy) and EDAX (Energy Dispersive X-ray analysis) showed the presence of chlorine, iron, sulphur, sodium, calcium and potassium. Previous work [4] showed the presence of aromatic archipelago structures on the injector needle. In this work an ion beam technique is used to understand the nature of these aromatic species in more detail.

The focused ion beam technique coupled with time of flight mass spectrometry (ToF-SIMS) has the ability to provide information on diesel engine injector deposits as a function of depth for both organic and inorganic constituents. Our previous work with this novel technique is unique in that it has shown layering effects in deposits, which may be due to the residual fuel either evaporating and leaving residues or being unable to keep insoluble residues in solution during the injection process

[4]. To help interpret the results of the aromatic structures found, spectra of a model polycyclic aromatic hydrocarbon (PAH), coronene ($C_{24}H_{12}$), and coal tar pitch have been used here as the basis to determine the ring size distribution of the internal injector deposits.

ToF-SIMS

The technique has been described in detail in an earlier paper by the authors [4]. 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 surface can be gradually eroded away by a separate sputter ion beam. A plot of the intensity of a given mass signal as a function of time is a reflection of the variation of its abundance and concentration with depth below the surface. The technique has 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.

Spectra of coronene and a coal tar pitch as reference aromatic materials and depth profiling of the contaminant region of an injector 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 $300 \times 300 \mu m$ where only the central $100 \times 100 \mu m$ area was analysed with the Bi_3^+ ion beam.

For depth profiling of the injector deposit, the pulsed Bi_3^+ primary ion beam had a spot size of $< 2 \mu m$ diameter and was rastered in a 128×128 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 sputter crater. Depth profiles were subsequently acquired using 'noninterlaced' 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 repeat areas were undertaken using a $300 \mu m$ crater with the central $100 \mu m$ area analysed.

Results

Coronene and Coal Tar Pitch (CTP)

The spectra obtained from negative mode ionisation for coronene and coal tar pitch are given in [figure 3](#). For coronene, the extensive fragmentation gives rise to a series of even numbered carbon ions (C_nH^-) from C_2 to above C_{10} . Clusters of ions with decreasing intensity then occur with decreasing intensity before ions of increased intensity ($C_{23}H_{11}^-$ and $C_{24}H_{11}^-$) are found close to the molecular mass of coronene after which there is a sharp decline in intensity.

For coal tar pitch, the even numbered low molecular mass ions are evident as for coronene, indicating that these are effective markers for polyaromatic structures. However, at higher molecular mass, the distribution is far more complicated than that for coronene due to coal tar pitch being a complex mixture of PAHs with some alkyl substitution. Further, ions are observed at molecular masses in excess of 250 reflecting the fact that coal tar pitch does contain PAHs with larger ring size than coronene. A similar distribution was found for the IDID deposit [figure 5](#) reflecting that again some PAHs with ring sizes larger than coronene are present.

In positive mode [figure 4](#), fragmentation is somewhat less severe with diagnostic aromatic ions including $C_7H_7^+$ (also C_{10} , C_{12} and C_{20}) being evident and, for coronene, the parent $C_{24}H_{12}$ is detected. The coal tar pitch gives a far more complicated distribution due to the supposition of fragment and parent ions. However, combination reactions are more evident in positive mode and, for coronene, ions from dimeric species (masses around 600 are observed). This makes positive mode somewhat less certain than negative mode for defining the maximum sized aromatic structure in deposits from the highest molecular mass fragments observed.

The repeat C_2H^- , C_4H^- etc. fragment ions are clearly observable in the 5 keV Cs^+ depth profile for the injector deposit and have been used here as PAH markers C_5^- and C_8H^- , [figure 6](#) together with the C_3N^- ion which is diagnostic of nitrogen-containing PAHs. Their intensities are compared with that of iron oxide in [figure 7](#) which shows that nitrogen and normal PAHs are more concentrated closer to the surface relative to FeO. The relative ion intensities close to the surface are presented in [Figure 8](#) to illustrate this trend. These latest result provides further confirmation of the ability of ToF-SIMS to depth profile inorganics relative to PAHs constituting coke in injector deposits.

The distribution of aromatic rings C_3N^- , iron oxide and the markers show the complexity and layering of the deposit. [Figures 8, 9, 10 and 11](#).

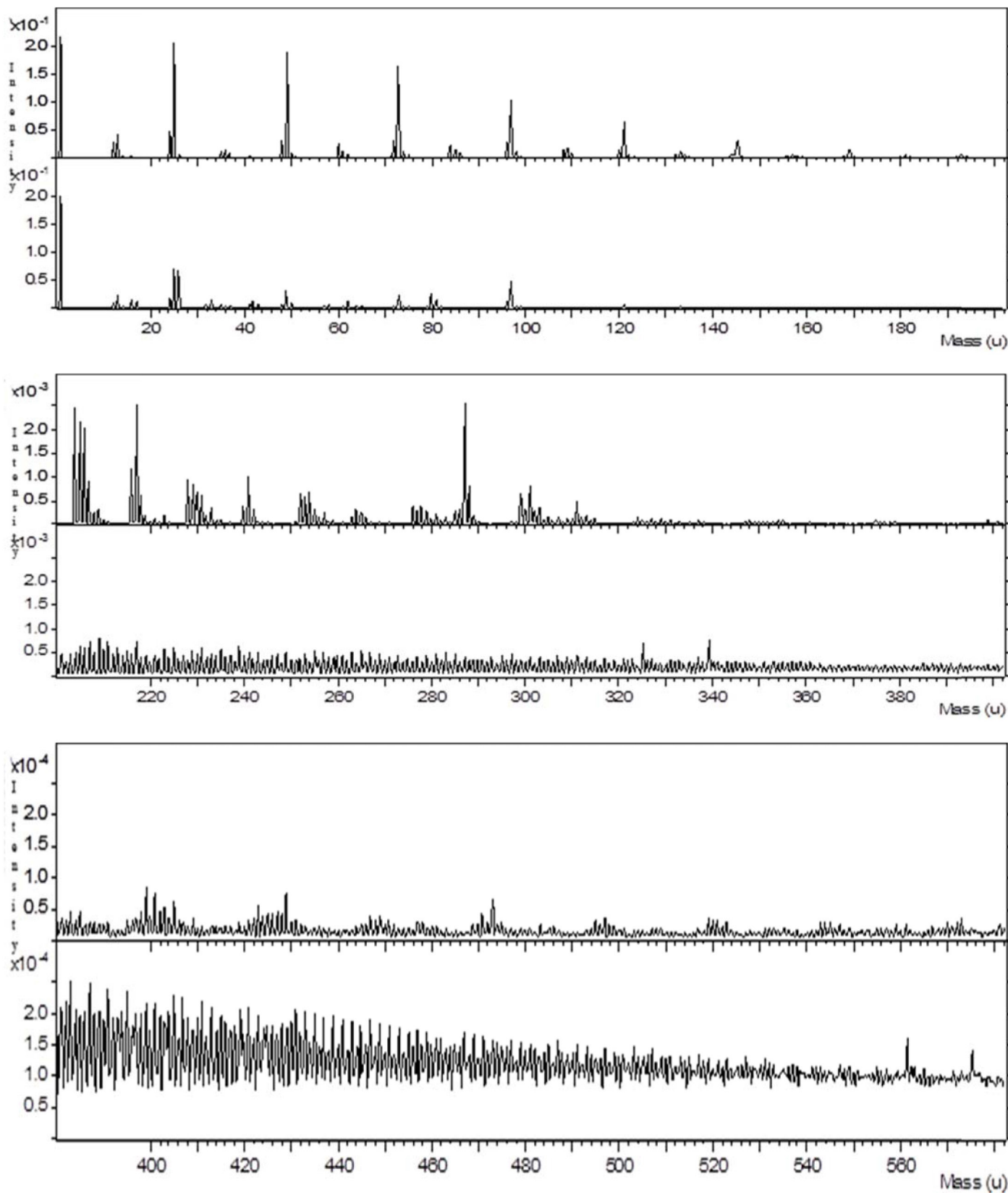


Figure 3. Negative Ion Mode Analysis of Coronene (top) and Coal Tar Pitch (bottom) over three mass ranges

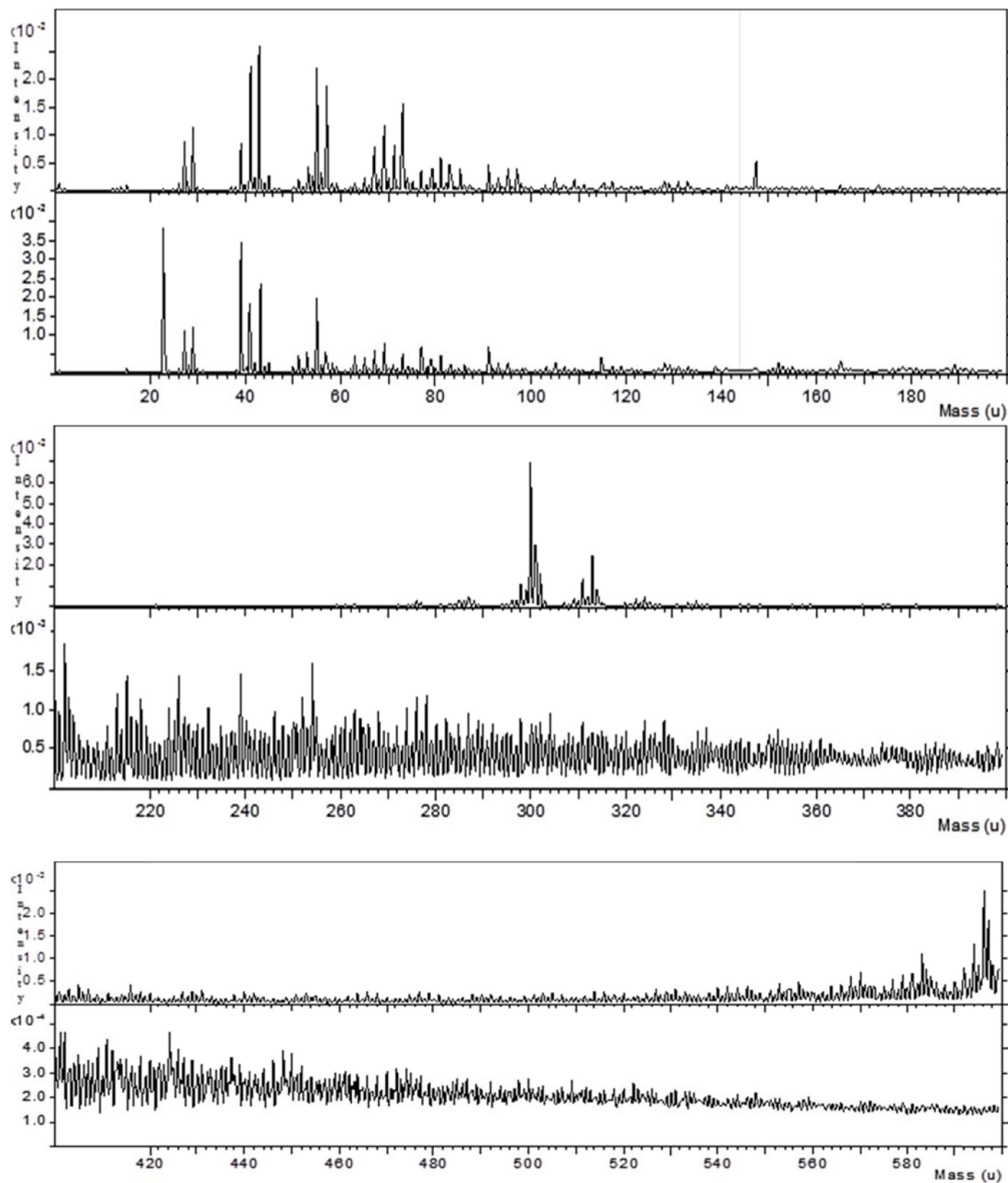


Figure 4. Positive Ion Mode Analysis for Coronene (top) Coal tar Pitch (bottom) over three mass ranges

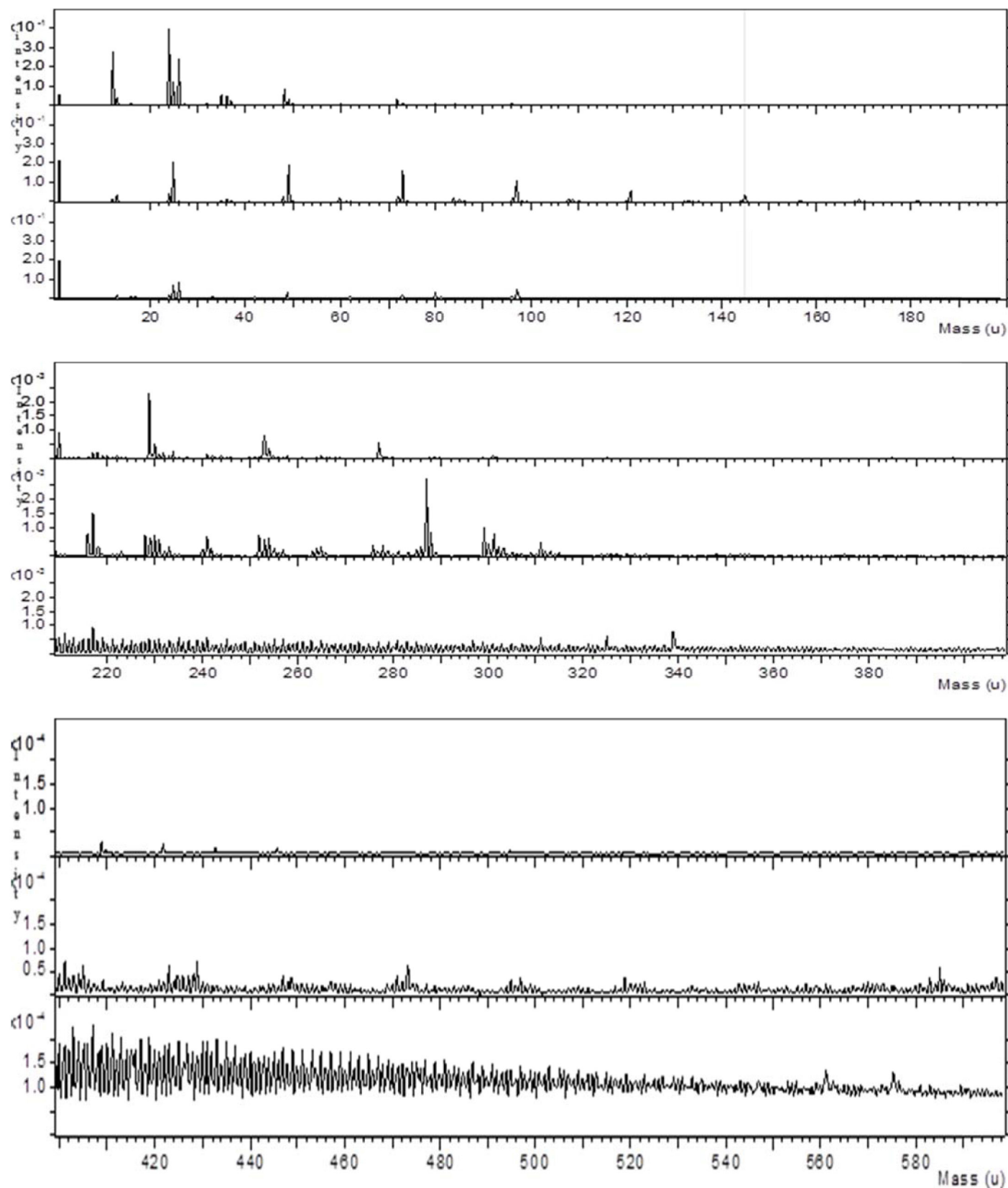
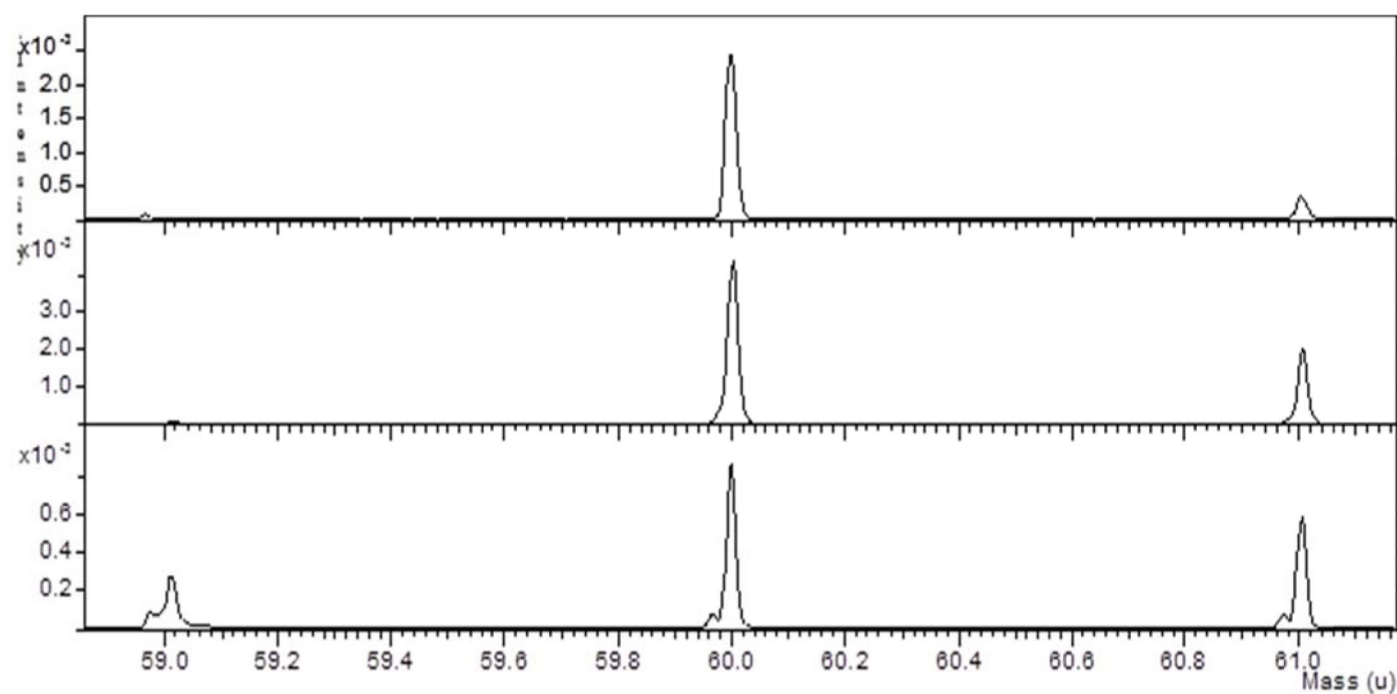


Figure 5. Negative Ion Mode Analysis of Coronene (top) and Coal Tar Pitch (middle) and IDID over three mass ranges

C_5H^-



C_8H^- (centre most peak)

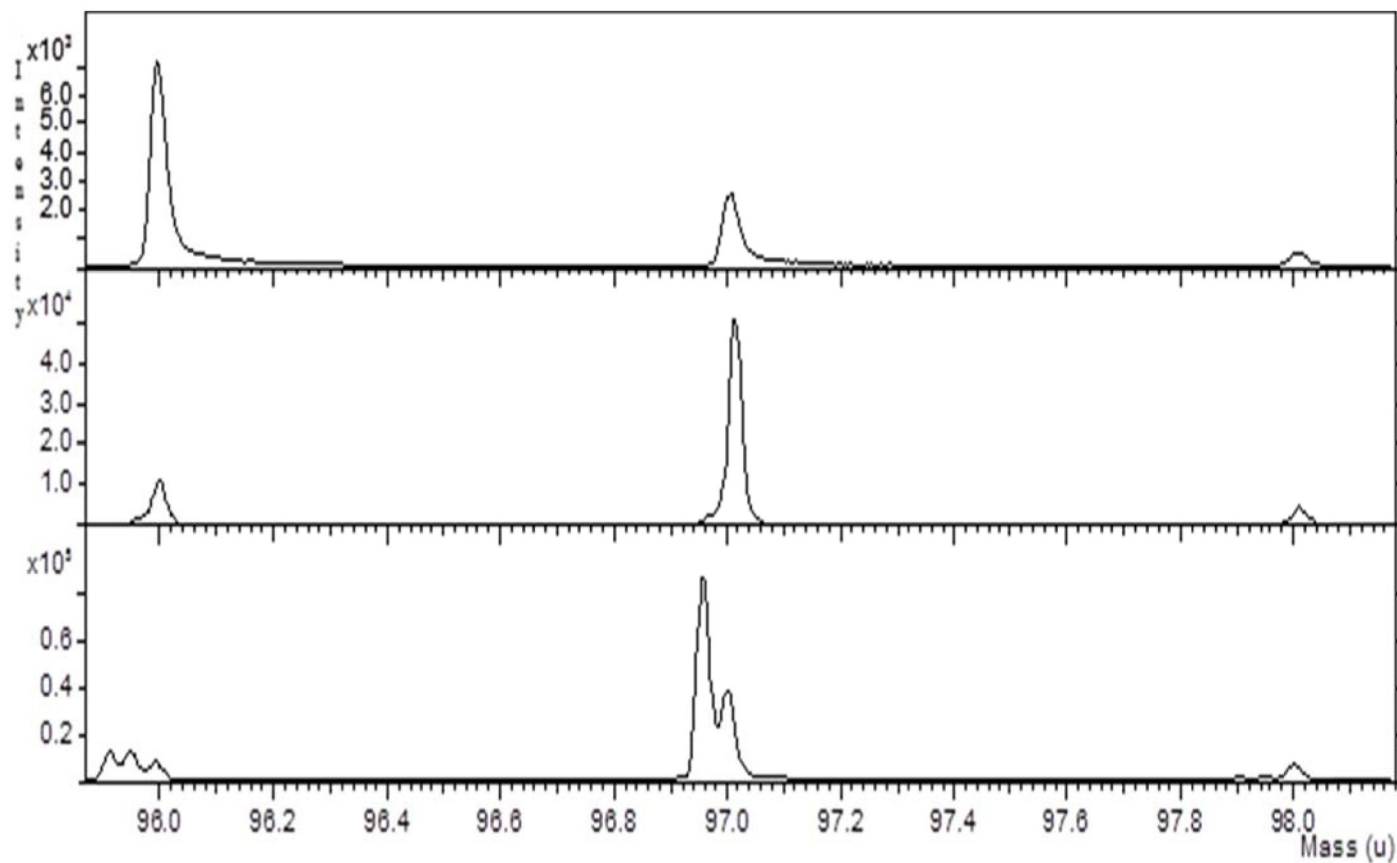


Figure 6. C_5H^- and C_8H^- Marker ions for Coronene (top), Coal Tar Pitch (middle) and IDID (bottom).

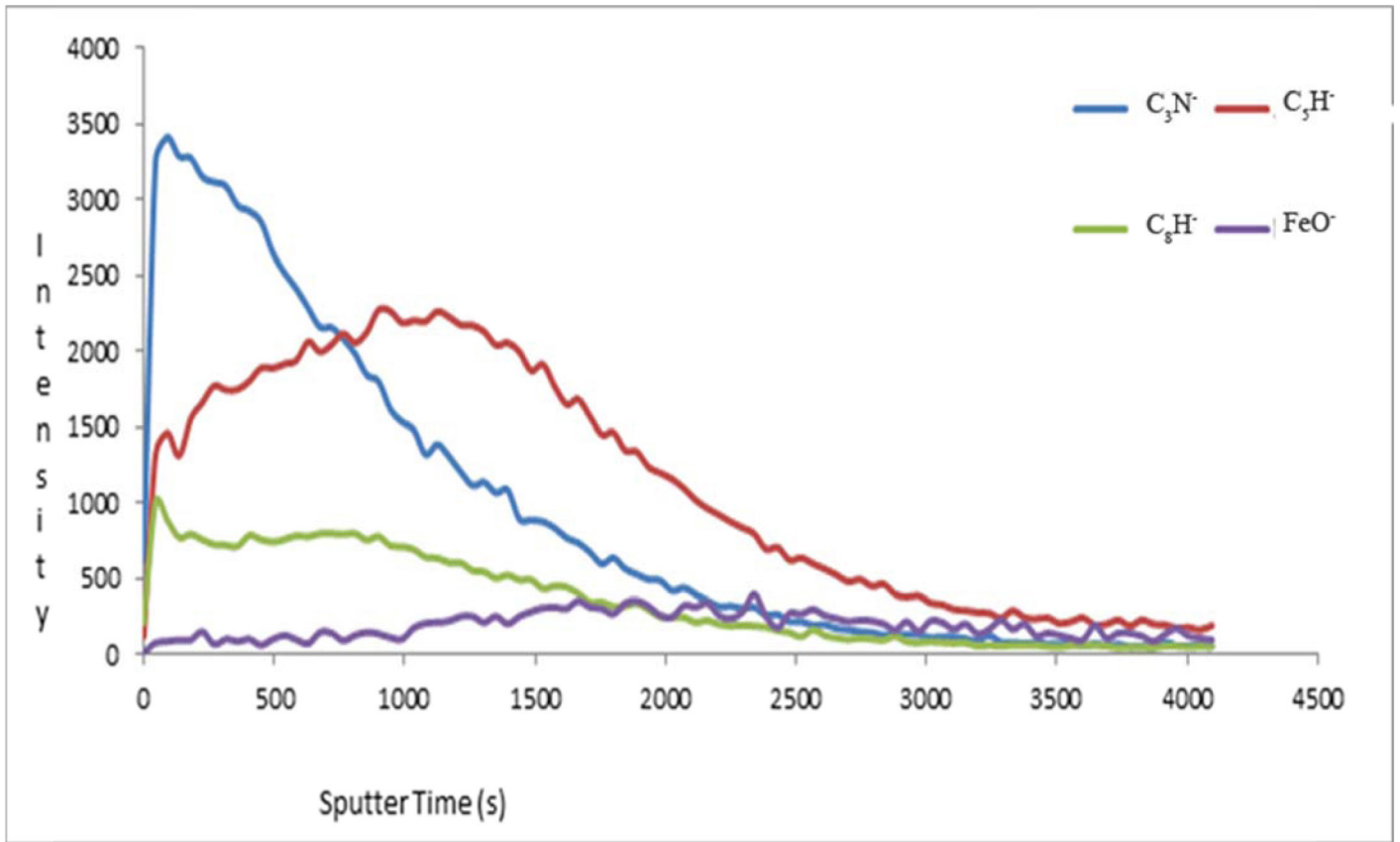


Figure 7. PAH fragment and Fe ions plotted as a function of depth from spluttering.

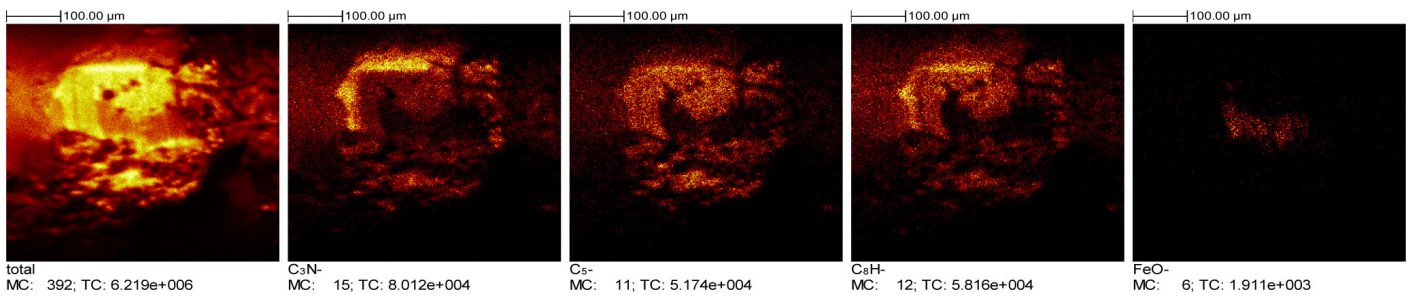


Figure 8. Total and relative ion intensities of the PAH marker and FeO^- ions close to the deposit surface.

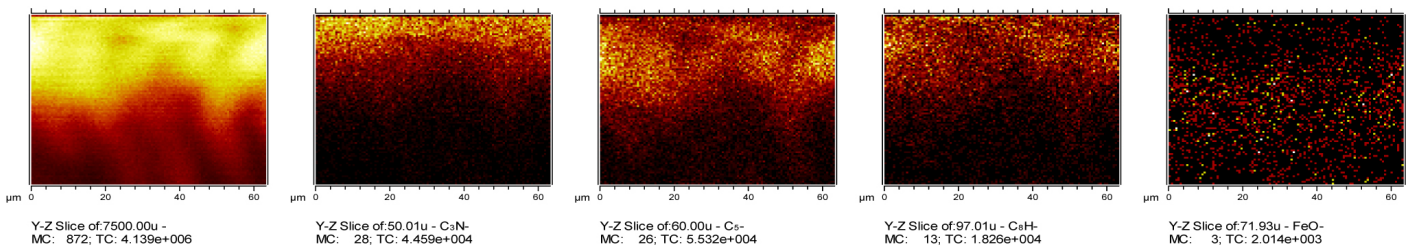
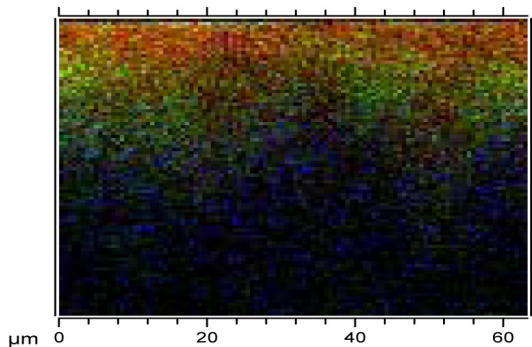
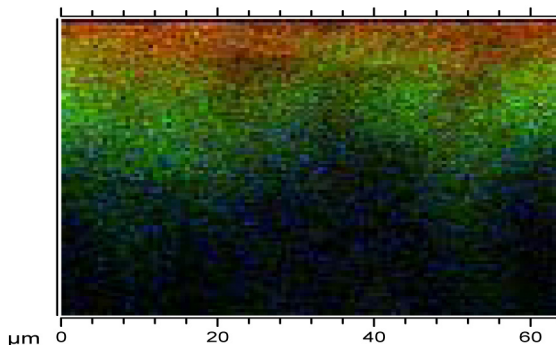


Figure 9. X-Y view Injector Needle Total and Relative Ion Intensities.



Overlay of Y-Z Slice of:50.01u - C₃N⁻, Y-Z Slice of:97.01u - C₈H⁻, Y-Z Slice of:71.93u - FeO⁻

Figure 10. RGB overlay of R = C₃N⁻, G = C₈H⁻ and B = FeO⁻.



Overlay of Y-Z Slice of:50.01u - C₃N⁻, Y-Z Slice of:60.00u - C₅⁻, Y-Z Slice of:71.93u FeO⁻

Figure 11. RGB overlay of R = C₃N⁻, G = C₅H⁻ and B =FeO⁻

Conclusions

ToF-SIMS can show variations in internal diesel engine injector deposits as a function of depth with the latest results indicating that PAHs constituting carbonaceous deposit are more concentrated closer to the surface in relation to iron oxide. Further, based on the distribution of fragment ions obtained for coronene and coal tar pitch as reference materials, fragment ions obtained from a deposit indicates that the ring size distribution extends beyond 6 rings.

This data supports the previous work showing the presence of aromatic rings in the carbonaceous material found on internal injectors. This gives further support to archipelago like aromatic ring build up in diesel injector and filter systems. The data is further evidence towards highly structured ring systems being found in carbonaceous internal injector deposits.

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