

Identifying important differences in mass spectra generated by secondary ion mass spectrometry (TOF-SIMS) in a tribochemical study

Elize Smit^{1*}, Werner Jordaan², Stefan de Goede³, Egmont R. Rohwer¹

¹ Department of Chemistry, University of Pretoria, Lynnwood Road, Pretoria, South Africa

² Materials Characterization, National Metrology Institute of South Africa, Meiring Naude Road, Pretoria, South Africa

³ Sasol Technology, Fuels Research, Sasol, Klasie Havenga Street, Sasolburg, South Africa

Abstract

In order to better understand the lubricating properties of diesel fuel, species that were present on tribological surfaces were investigated using secondary ion time-of-flight mass spectrometry (TOF-SIMS). Traditionally, only certain species that are expected to be present at the interface are investigated and their presence or absence is used to make conclusions regarding the mechanism of lubrication. In this work an alternative and complementary approach to data analysis and interpretation is proposed, previously demonstrated for TOF-SIMS and based on multivariate analysis methods, where the mass spectral data are investigated more comprehensively. The main objective was to interpret variation within and between different areas of a tested surface and ultimately to contribute to the understanding of the tribochemical reactions that occur at the interface. The validity of this approach was confirmed when the palmitate ion (which would normally be targeted) was shown to contribute significantly (together with other ions) to chemical differences between scratched and unscratched areas of the surface.

Keywords

Petrochemical Industry ; Statistical Analysis; Diesel Engines; SIMS; Bench Wear Tests

1. Introduction

Lubricity is the ability of a substance to prevent wear in a system where two surfaces are in close contact. This physical property is important in diesel since certain parts of a diesel fuel injection system rely on the fuel for lubrication [1]. Surfactants or surfactant-like compounds, containing a polar and non-polar group, are often added to diesel in small amounts to improve the lubricity performance of the fuel [2]. Literature suggests that the polar region adsorbs onto the surface whilst the long hydrocarbon chain protrudes away from the surface [3,4]. This monolayer acts as a barrier between the interacting surfaces. When metal surfaces are in close contact with one another, high temperatures are generated and nascent metal may be exposed due to removal of the oxide layer during the wear process [5]. This may cause substances in the fuel to interact or react with the surface and the field of science concerned with investigating this is known as tribochemistry [6].

Sensitive surface analysis techniques play an important role in studying these reactions and interactions. Several techniques have been used to investigate tribological surfaces including grazing angle Fourier Transform Infrared (FTIR) spectroscopy [4,7], X-ray photoelectron spectroscopy (XPS) [4,8], time-of-flight secondary ion mass spectrometry (TOF-SIMS) [7,9] and atomic force microscopy (AFM) [10].

The interpretation of TOF-SIMS data obtained during tribological studies has mostly consisted of determining the presence or absence of specific peaks that are expected to be present, i.e. targeting specific species [7,9]. This is understandable due to the complex nature of the data obtained from this highly sensitive technique. The recent advances in time-of-flight technology, which enable the accurate determination of ion masses with high resolution, allow for the possibility of analysing data more comprehensively. Multivariate techniques such as principal component analysis have been used for many years to aid in the interpretation of complex mass spectra

* To whom correspondence should be addressed. E-mail: Elize.Smit@tuks.co.za

obtained from TOF-SIMS analyses [11-13] and to our knowledge this has not yet been applied to mass spectral data obtained from tribological surfaces.

In this work an alternative and complementary approach (based on multivariate techniques) was used to interpret TOF-SIMS data from tribological surfaces in order to identify species that were adsorbed and/or formed at the interface during the wear process. This is done in an attempt to better understand the tribochemical reactions that take place at the interface.

2. Experimental procedure

Two model fuels were used with hexadecane (anhydrous, $\geq 99\%$, Sigma Aldrich) as base fluid. Palmitic acid ($\geq 98\%$, Merck) and oleic acid ($\geq 90\%$, Aldrich) were used respectively as lubricity additives at concentrations of 2000 mg/l. The lubricities of these model fuels were measured with a high frequency reciprocating rig (HFRR, PCS Instruments, London, England) according to ISO 12156-1. The metal sphere and disc used during the tribological test were made from AISI E-52100 stainless steel. Note that the wear scar on the upper specimen is typically measured to evaluate lubricity, but for practical purposes the wear track on the disc was analysed using TOF-SIMS. The relationship between the wear scar on the ball and wear track on the disc has been discussed in literature [14]. Prior to surface analysis, discs were washed with hexane to remove the bulk fuel, followed by rinsing with ethanol to remove any physisorbed species. Note that the bulk of the debris (formed by the scratching process) was not washed away by these solvents as shown in Figure 1 below. To avoid contamination the discs were stored in an aluminium container until surface analysis was carried out. Care was taken not to disturb the surface.

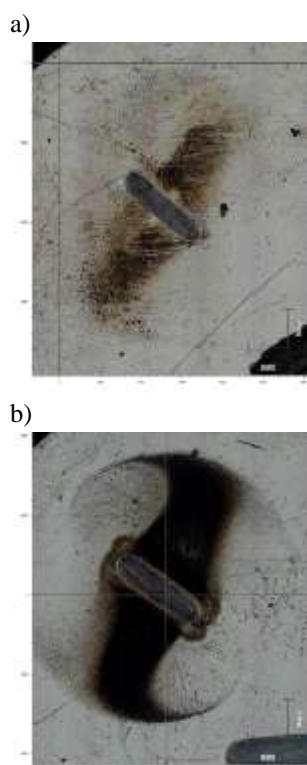


Figure 1. The wear tracks obtained from HFRR tests using model fuels containing palmitic acid (a) and oleic acid (b) as lubricity additives.

An ionTOF TOF.SIMS 5 time-of-flight secondary ion mass spectrometer was used to probe different areas on each disc. The primary ion (Bi^{1+}) beam was rastered over an area of approximately 300 x 300 microns using a pulsed beam current of 1 pA, 25 kV acceleration voltage and 1 ns pulse width. The secondary ions were extracted at 2 kV into the flight tube of the analyser. Inspection of raw data confirmed that none of the mass

spectral peaks were saturated. Mass to charge ratios between 1 and 400 amu were recorded, although only values between 50 and 400 amu were used for principal component analysis. Resolution ($m/\Delta m$) was calculated using the full width at half maximum (FWHM) criterion, and was found to be above 8000 at mass 52 (positive ion spectra). A more conservative measure of resolution which is identical to the 10 % valley definition of resolution, with Δm from width at 5 % peak height, was calculated to be above 4000 at mass 52 (positive ion spectra) [15]. All the spectra were calibrated using the same set of low-mass ion peaks and were exported in ASCII format after successive binning of three channels along the x-axis (this reduced the exported file size by a factor of three).

Three areas of interest were identified; the wear track itself, the area surrounding the wear track where debris was present as well as the unscratched area of the disc. Three spots were analysed for each of these areas (see Figure 2) in positive and negative ion mode. The aim was to find chemical differences between and within these areas which may give an indication of the type of chemical reactions that took place during the tribological test.

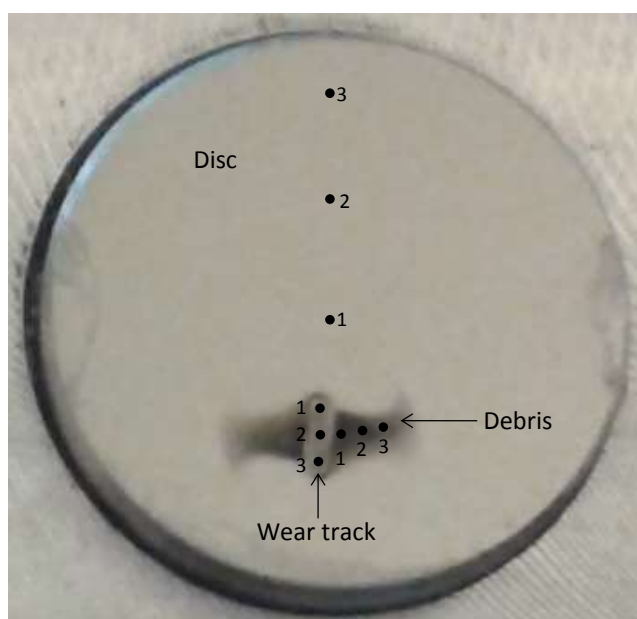


Figure 2. HFRF disc indicating spots that were analysed with TOF-SIMS. The wear track itself, the area surrounding the wear track where debris was present as well as the unscratched area of the disc were analysed. Three spots were analysed for each of these areas.

3. Data analysis

The mass spectra, obtained for each of the spots analysed for the discs produced with the different fuels, were very complex. Two approaches (targeted and untargeted) were used to aid in interpreting the data. In the targeted approach, specific ions (which were expected to be present at the interface) were selected and investigated. Since only a small part of each mass spectrum was considered in the targeted approach, there exists a possibility that more information may still be hidden in the data. Therefore an alternative approach to interpret the data was followed, based on techniques used to identify characteristic peaks in complex mass spectra often obtained from biological samples, such as proteins [11]. In this part of the work, the aim was to identify mass spectral peaks that may be responsible for differences in the mass spectra obtained for different spots. In the following sections a data set will refer to all positive or negative mass spectra collected from different areas of a specific disc.

Several factors contribute to the complexity of TOF-SIMS spectra. This includes the high energy of the primary ions causing ionisation of both organic and inorganic species, as well as extensive fragmentation of molecular species or atomic clusters. The high resolution is another factor that contributes to spectral complexity as more

than one peak can be detected per nominal mass. The high sensitivity of the technique also contributes as secondary ions of trace substances are also detected.

The following data pre-processing steps were performed in order to prepare the data for statistical analysis: Firstly a set of candidate peaks was selected (process described below), followed by normalisation and intensity scaling. The data was then mean-centered prior to principal component analysis (PCA). It is important to note that the order in which these steps are performed are important and may influence the outcome of the PCA. The assumptions made during data pre-processing, together with various ways of performing peak selection, normalisation and scaling has been discussed in literature [13]. For some applications it may be useful to bin data into 1 amu bins (during peak selection) when the user is aware of specific species that may be important. For tribological surfaces however, the accurate mass information is vital and should not be discarded, since it can be used to distinguish between metal-containing and organic species, e.g. m/z 55.9349 (Fe^+) and m/z 56.0626 (C_4H_8^+).

The raw data was collected in the form of a continuous profile. This data was imported into MassLynxTM 4.1 mass spectrometry software (Waters Inc., Milford, Massachusetts, USA) which was used to integrate mass spectral peaks and obtain data where the intensity of each peak is represented by its height. The MarkerLynxTM platform (an application within the MassLynxTM software) was then used to align the mass spectra in each data set, which is a vital step for further chemometric analysis. The software produced a table containing candidate peaks, that were present in at least two of the samples (spots analysed) in the data set and with a count threshold of 10, together with their relative intensities for each sample. It is assumed that peaks that are only present in one of the nine mass spectra will not contribute to the chemical differences between the mass spectra (since three spectra were acquired per area).

The intensities were normalised in such a way that the total ion count for each mass spectrum was the same. This removes variances in peak intensity due to external factors, e.g. surface roughness [13]. Elemental compositions were tentatively assigned to the candidate peaks, based on their accurate masses and known isotopic masses of elements. The predicted atomic composition of each ion was limited to the following number range of atoms: 0 – 50 C; 0 – 100 H; 0 – 10 O; 0 – 10 Si, 0 – 10 Cr; 0 – 10 Mn; 0 – 10 Fe; 0 – 1 Bi. For an elemental composition to be tentatively assigned, the mass difference (between monoisotopic mass of predicted elemental composition and the measured mass) had to be within 5 mDa. The mass spectra (average spectrum of three spots analysed for each of the three areas of the surface) in Figure 3 show that similar peaks were observed for different areas of the surface with only their relative intensities differing. Similar results were obtained for both the oleic acid and palmitic acid samples for both positive and negative ion spectra (i.e. for each data set). The peaks at m/z 73.0531, 147.0703, 207.0237 and 281.0419 may represent fragments of polydimethylsiloxane (PDMS), which is a common surface contaminant.

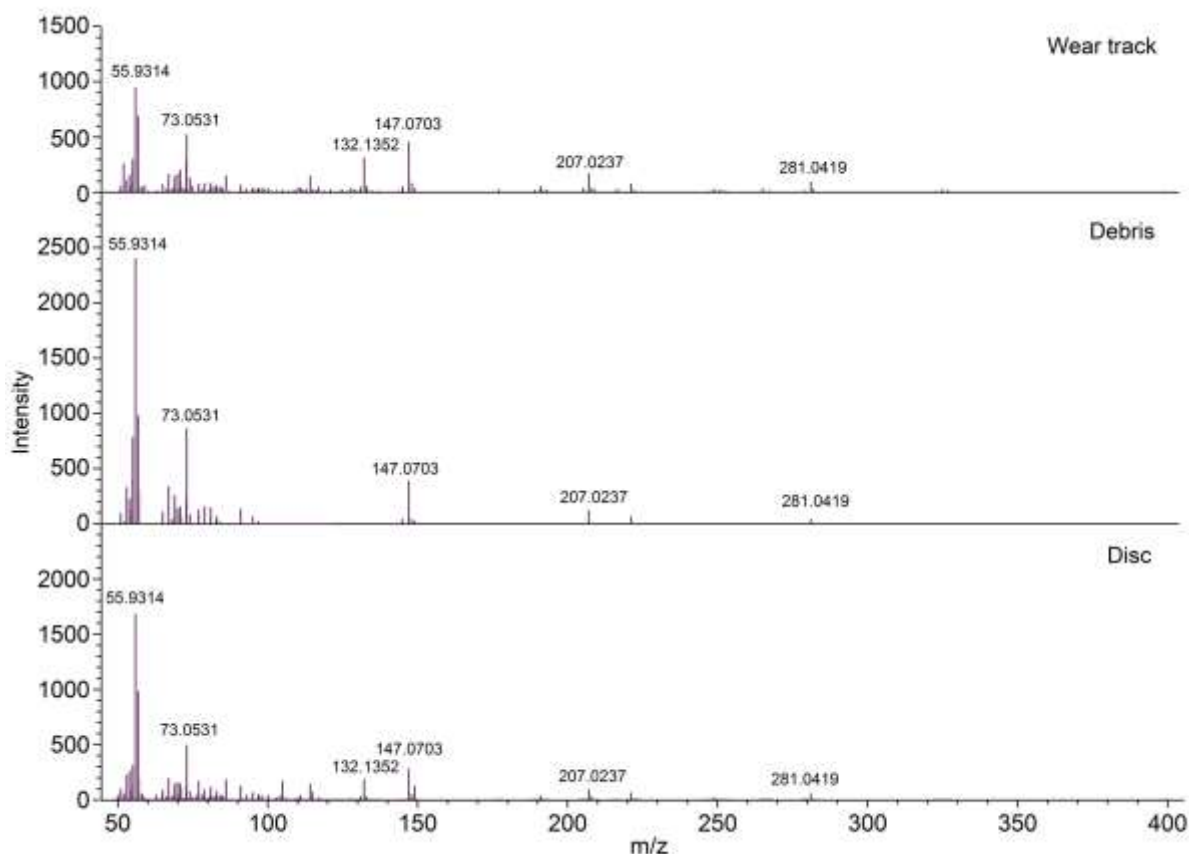


Figure 3. Comparison of (averaged) normalized mass spectra (positive ions) obtained for the different areas of an HFRR disc analyzed with TOF-SIMS. The test fuel was hexadecane with oleic acid as an additive (2000 mg/l).

Furthermore the majority of the lower m/z ions most likely represent fragments of compounds seen at higher mass values. Since different compounds may form similar fragments, important information may be contained at higher m/z values where less fragmentation has occurred and intensities are very low. This is a phenomenon observed for all ionization techniques leading to extensive fragmentation such as electron ionization, where it is known that heavier ions are present in small amounts but generally carry more significant information. In order to amplify the intensities of these heavier ions the square root of the normalised intensities were calculated. This was followed by mean-centering the data (for each mass spectral peak, the mean intensity for all the samples was determined and subtracted from the intensity of that peak for each sample).

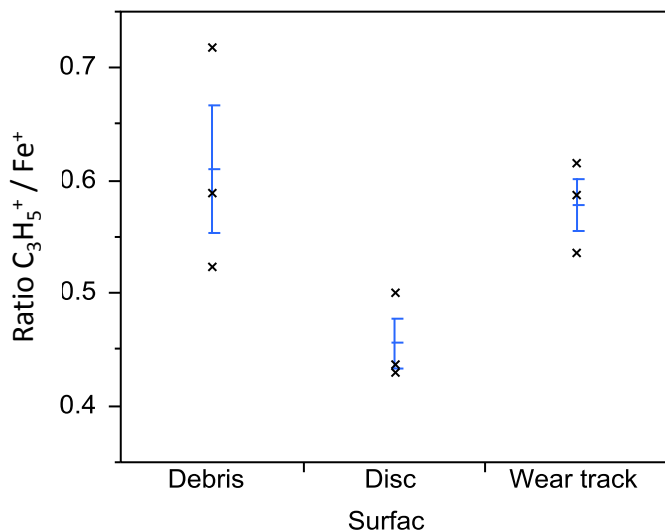
JMP® 10.0.0, a statistical software package from SAS® Institute Inc. (Cary, North Carolina, USA), was used to perform multivariate data analysis in order to decide which of the candidate peaks could be considered to be important. PCA was used to summarise the variation in the dataset into independent linear combinations of peaks. This results in the creation of new axes called principal components. PCA results in the creation of two new matrices, the scores (which describe the relationship of the samples) and the loadings (which show which variables / peaks are responsible for any differences seen in the scores). In this way one can look to see which peaks correspond to any difference seen in the areas analyzed and relate them back to their contributions to tribochemistry.

4. Results and Discussion

In the targeted approach, the raw data was used and specific ions (which were expected to be present at the interface) were selected and investigated. These included metals, metal oxides, ions from the friction modifiers as well as metal-carboxylate ions. In literature some alkyl- and alkylene iron ions have also been detected,

including CH_3Fe^+ , $\text{C}_2\text{H}_5\text{Fe}^+$, $\text{C}_2\text{H}_3\text{Fe}^+$, $\text{C}_3\text{H}_5\text{Fe}^+$, $\text{C}_4\text{H}_7\text{Fe}^+$ [9]. In most cases some or all of these “targeted ions” were found in the data. Literature also indicates that the ratio of the C_3H_5^+ ion intensity relative to the Fe^+ ion intensity gives an indication of the amount of organic species adsorbed onto the surface [7]. This ratio was calculated for both the oleic and palmitic acid samples, as shown in Figure 4. Slight differences in the amount of organic species adsorbed in the different areas can be observed, but further investigation by analysis of variance (ANOVA) showed that there were no statistically significant differences between the different areas of the surface (calculations not included). This indicates that further investigations are necessary to interpret the complex mass spectra even though slight differences can be observed in the normalized data shown in Figure 3.

a) Oleic acid



b) Palmitic acid

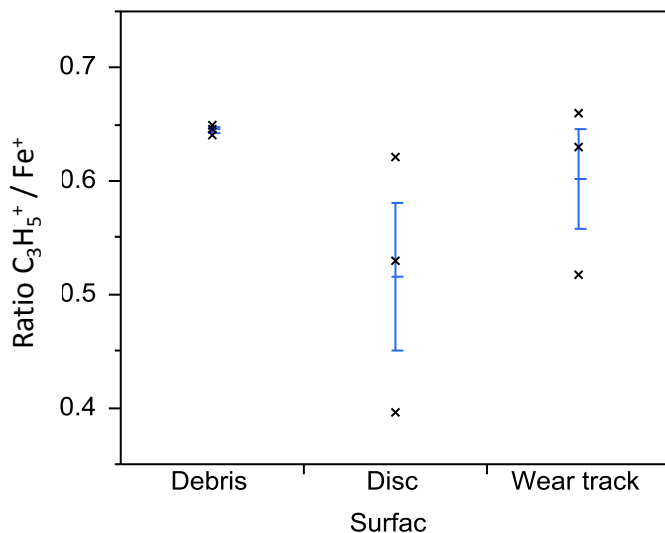


Figure 4. Ratio of C_3H_5^+ relative to Fe^+ for different areas of the surfaces lubricated with oleic acid (a) and palmitic acid (b) respectively.

In the untargeted approach candidate peaks were selected and the variation within the different data sets was summarised using PCA. During PCA the largest variation is summarised by the first principal component (PC), whilst the following principal components summarise the remainder of the variation. In our results the first principal component describes the largest variation within the sample set (in this case between different areas of

the surface, i.e. the wear track, disc and debris), whilst the second principal component describes the spread within a sample area (in this case within a specific area of the surface, e.g. wear track). The ellipses shown in the figures below represent 95 % confidence intervals.

For the oleic acid (positive ions) dataset the score plot (Figure 5a) indicates that PC 1 and 2 summarise the variation between the different areas of the surface. PC 1 summarises the variance between the debris and wear track. The loadings on PC 1 (Figure 5b and Table 1) indicate that Cr^+ ions are relatively more intense inside the wear track whilst Fe^+ ions are relatively more intense in the debris around the wear track. This suggests that the iron atoms / clusters are removed from the surface during the wear process due to mechanical interaction or chemical reactions whilst an underlying Cr-rich layer is exposed in the wear track. It is also interesting to note that the debris contains mostly organic species whilst the wear track contains organic, inorganic and organometallic species. This may be an indication that the organic species act as a (renewable) sacrificial layer which protects the surface against wear [16]. PC 2 summarises the variance between the disc and the other areas of the surface (wear track and debris). The loadings on PC 2 (Figure 5c and Table 1) indicate that a variety of ions contribute to these differences. The loadings of the C_4H_7^+ and $\text{C}_3\text{H}_3\text{O}^+$ peaks indicate that these ions are more intense in the debris and wear track compared to the disc and therefore may represent fragments of a tribofilm. It is interesting to note that the chemical differences between the wear track and debris were more prominent than the differences between the scratched areas (wear track and debris) and the unscratched area of the surface.

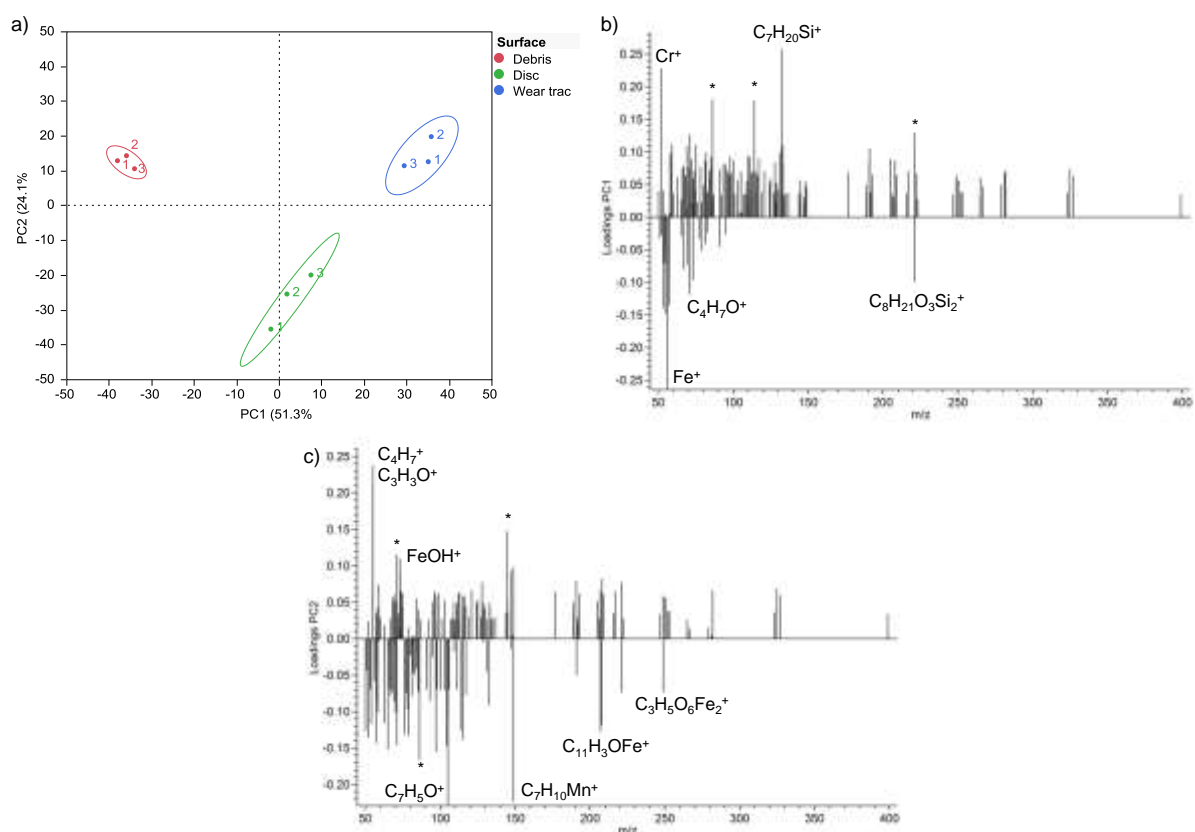


Figure 5. Results obtained from principal component analysis of mass spectra (positive ions) for the HFRR disc lubricated with oleic acid (2000 mg/ml). The numbers in the score plot (a) represent the position of the spot analysed using TOF-SIMS and corresponds to the numbers in Figure 2. The loadings plots for PC1 (b) and PC2 (c) are also shown.

Table 1. Summary of mass spectral peaks that contribute significantly to the differences between the mass spectra (positive ions) obtained from a HFRR disc lubricated with oleic acid (2000 mg/ml).

PC	Positive loadings	Negative loadings
1 (51.3 %)	132.1352: $C_7H_{20}Si^+$, 51.9382: Cr^+ , 86.0944 ^a , 114.1271 ^a , 221.0911 ^a , 71.0645 ^a , 59.0327: $C_2H_7Si^+$, 75.0247: $C_6H_3^+$, 133.0132: $C_3H_{13}SiFe^+$, 68.9388: $CHFe^+$	55.9314: Fe^+ , 55.0541: $C_4H_7^+$, 53.0381: $C_4H_5^+$, 57.0702: $C_4H_9^+$, 71.0488: $C_4H_7O^+$, 71.0870: $C_5H_{11}^+$, 221.1029: $C_8H_{21}O_3Si_2^+$, 73.0531 ^a , 57.0332: $C_3H_5O^+$, 67.0539: $C_5H_7^+$
2 (24.1 %)	55.0541: $C_4H_7^+$, 55.0178: $C_3H_3O^+$, 144.8604 ^a , 71.0645 ^a , 72.9343: $HOFe^+$, 149.0646: $C_4H_{17}Si_3^+$, 147.0703: $C_5H_{15}OSi_2^+$, 73.0531 ^a , 208.0244: $C_4H_{16}O_2Si_4^+$, 190.8345: $CH_3OCr_2Fe^+$	105.031: $C_7H_5O^+$, 149.0157: $C_7H_{10}Mn^+$, 86.0944 ^a , 97.0994: $C_7H_{13}^+$, 64.927 ^a , 104.0217: $C_7H_4O^+$, 71.087: $C_5H_{11}^+$, 56.9623: HSi_2^+ , 115.053: $C_9H_7^+$, 52.0298: $C_4H_4^+$

^a Peaks for which elemental compositions could not be assigned.

For the palmitic acid (positive ions) dataset the score plot (Figure 6a) indicates that the first PC summarises the chemical differences between the unscratched area of the disc and the other areas of the HFRR disc (the debris and wear track). A smaller amount of the total variance is explained by the first two principal components compared to the oleic acid (positive ions) dataset. This indicates that the chemical differences between the different areas of the surface are more prominent for the oleic acid dataset. The loadings on PC 1 (Figure 6b and Table 2) indicate that Cr^+ ions are relatively more intense inside the wear track and relatively less intense in the unscratched areas of the disc. The peak representing the $C_7H_5O^+$ ion is relatively more intense in the unscratched area of the disc, which is similar to what was observed for the oleic acid (positive ion) dataset. PC 2 summarises the variance between the wear track and the debris together with some variance within different areas of the disc. From the loadings on PC 2 (Figure 6b and Table 2) it can be observed that the wear track (together with some areas of the disc) contain larger amounts of organometallic species whilst alkyl-iron ions and alkyl fragment ions are more prominent in the debris (negative loadings on PC 2).

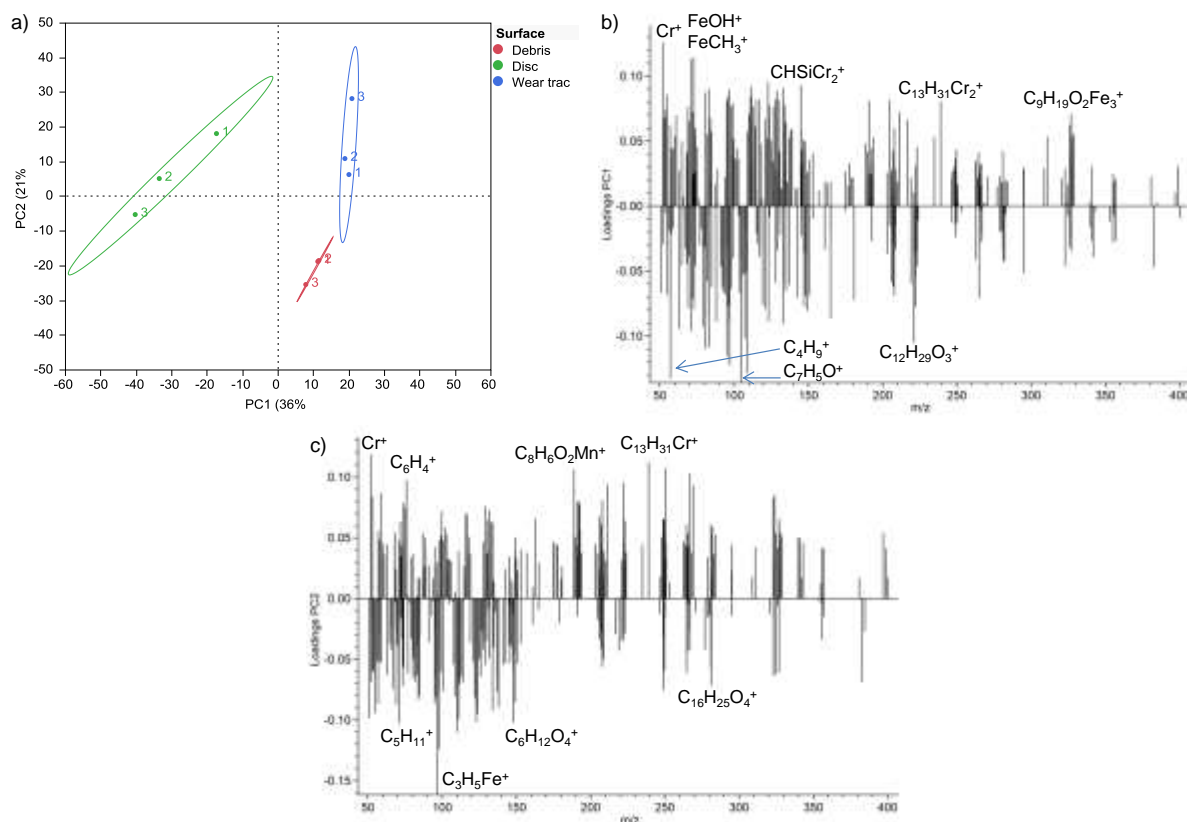


Figure 6. Results obtained from principal component analysis of mass spectra (positive ions) for the HFRR disc lubricated with palmitic acid (2000 mg/ml). The numbers in the score plot (a) represent the position of the spot analysed using TOF-SIMS and corresponds to the numbers in Figure 2. The loadings plots for PC1 (b) and PC2 (c) are also shown.

Table 2. Summary of mass spectral peaks that contribute significantly to the differences between the mass spectra (positive ions) obtained from a HFRR disc lubricated with palmitic acid (2000 mg/ml).

PC	Positive loadings	Negative loadings
1 (36 %)	51.9384: Cr ⁺ , 72.9346: HOFe ⁺ , 70.9552: CH ₃ Fe ⁺ , 122.9414: H ₃ O ₄ Fe ⁺ , 144.861: CHSiCr ₂ ⁺ , 111.8658: Fe ₂ ⁺ , 133.0114: C ₇ H ₅ OSi ⁺ , 82.9542: C ₂ H ₃ Fe ⁺ , 96.9251: HOSiCr ⁺ , 128.8701: HOFe ₂ ⁺	105.0314: C ₇ H ₅ O ⁺ , 57.0699: C ₄ H ₉ ⁺ , 109.1029: C ₈ H ₁₃ ⁺ , 97.1005: C ₇ H ₁₃ ⁺ , 95.085: C ₇ H ₁₁ ⁺ , 80.9454: CHOCr ⁺ , 83.0861: C ₆ H ₁₁ ⁺ , 221.2125: C ₁₂ H ₂₉ O ₃ ⁺ , 107.0856: C ₈ H ₁₁ ⁺ , 71.0871: C ₅ H ₁₁ ⁺
2 (21 %)	51.9384: Cr ⁺ , 239.1823: C ₁₃ H ₃₁ Cr ⁺ , 250.7497: HSi ₃ Mn ₂ Fe ⁺ , 188.9738: C ₈ H ₆ O ₂ Mn ⁺ , 266.9926: C ₁₂ H ₁₅ CrFe ⁺ , 76.0271: C ₆ H ₄ ⁺ , 222.0967: C ₇ H ₂₂ O ₂ Si ₃ ⁺ , 211.1534: C ₉ H ₂₃ O ₅ ⁺ , 268.9845: C ₂₀ HSi ⁺ , 58.9934: CH ₃ OSi ⁺	96.9693: C ₃ H ₅ Fe ⁺ , 97.9779: C ₃ H ₆ Fe ⁺ , 109.9785: C ₄ H ₆ Fe ⁺ , 71.0871: C ₅ H ₁₁ ⁺ , 148.0726: C ₆ H ₁₂ O ₄ ⁺ , 122.9894: C ₅ H ₇ Fe ⁺ , 110.9865: C ₄ H ₇ Fe ⁺ , 51.022: C ₄ H ₃ ⁺ , 123.9982: C ₅ H ₄ O ₂ Si ⁺ , 55.054: C ₄ H ₇ ⁺

For the oleic acid (negative ions) dataset the score plot (Figure 7a) indicates that PC 1 and 2 summarises the variation between the different areas of the surface. From the score and loadings plots one can deduce that the C₇H₅O₂⁻ ion plays an important role in the chemical differences between the different areas of the disc (positive loading in PC 1 and negative loading in PC 2). From the loadings on PC 1 (Figure 7b and Table 3) the C₂H₂O₂⁻, C₂H₃O₂⁻, C₃H₃O₂⁻ and FeO₂H⁻ ions seem to contribute to the chemical differences within the debris. These species may represent fragments of the oleic acid molecule as well as the iron oxide layer that were removed from the surface during the wear process. This was confirmed by closer inspection of the loadings on PC 3 (details not shown). Inspection of mass spectral data revealed that these peaks become less intense as one moves away from the wear track. This may be a function of the thickness of the debris, which also decreases as one moves away from the wear track (see Figure 1).

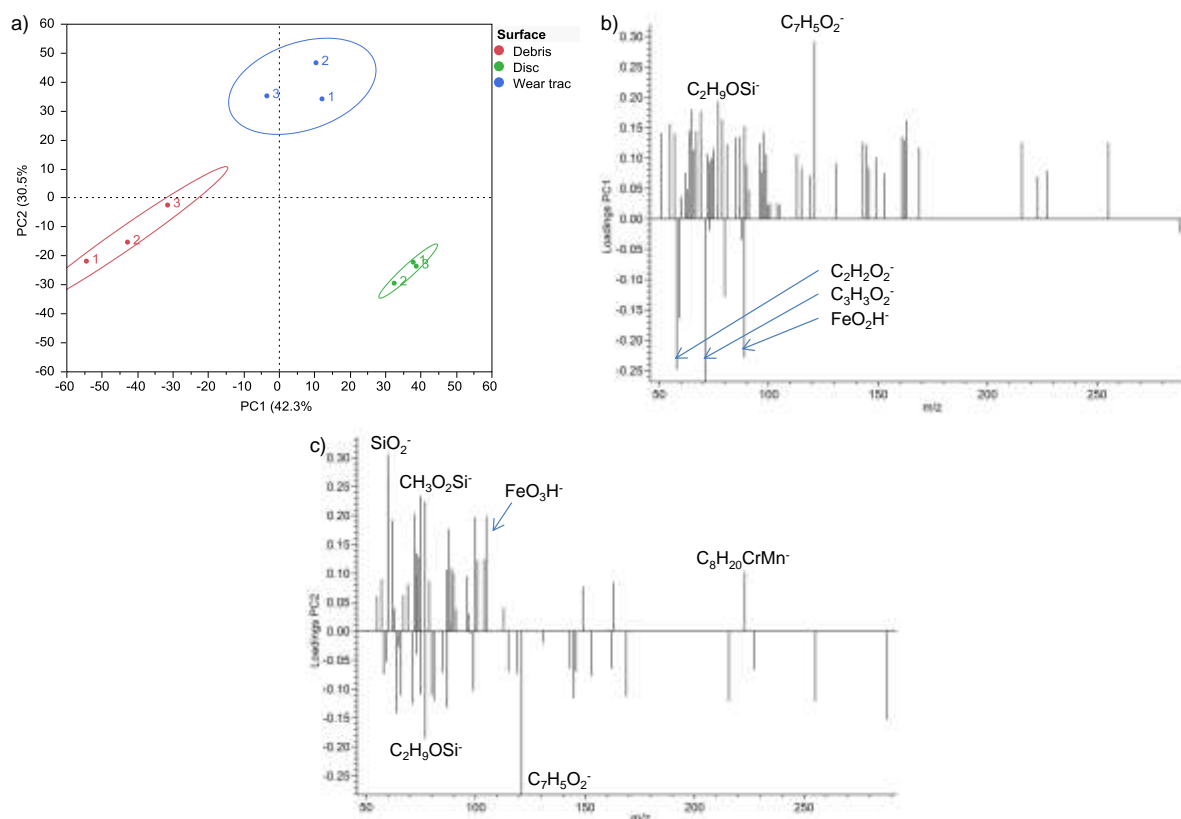


Figure 7. Results obtained from principal component analysis of mass spectra (negative ions) for the HFRR disc lubricated with oleic acid (2000 mg/ml). The numbers in the score plot (a) represent the position of the spot analysed using TOF-SIMS and corresponds to the numbers in Figure 2. The loadings plots for PC1 (b) and PC2 (c) are also shown.

Table 3. Summary of mass spectral peaks that contribute significantly to the differences between the mass spectra (negative ions) obtained from a HFRR disc lubricated with oleic acid (2000 mg/ml).

PC	Positive loadings	Negative loadings
1 (42.3 %)	121.0246: C ₇ H ₅ O ₂ ⁻ , 77.0411: C ₂ H ₉ OSi ⁻ , 65.0029: C ₄ HO ⁻ , 68.9982: C ₃ HO ₂ ⁻ , 78.959 ^a , 163.0663 ^a , 55.0195: C ₃ H ₃ O ⁻ , 89.0459: C ₃ H ₉ OSi ⁻ , 63.9617 ^a , 67.0192: C ₄ H ₃ O ⁻	71.014: C ₃ H ₃ O ₂ ⁻ , 58.0057: C ₂ H ₂ O ₂ ⁻ , 88.9326: HO ₂ Fe ⁻ , 59.014: C ₂ H ₃ O ₂ ⁻
2 (30.5 %)	59.9667: O ₂ Si ⁻ , 59.9846: CO ₃ ⁻ , 74.9908: CH ₃ O ₂ Si ⁻ , 76.9695: HO ₃ Si ⁻ , 71.9289: OFe ⁻ , 99.9266: OSi ₃ ⁻ , 104.9271: HO ₃ Fe ⁻ , 61.9879 ^a , 87.9243: O ₂ Fe ⁻ , 73.0108: C ₂ H ₅ OSi ⁻	121.0246: C ₇ H ₅ O ₂ ⁻ , 77.0411: C ₂ H ₉ OSi ⁻ , 287.7255: CH ₄ CrMn ₄ ⁻ , 63.9617 ^a , 87.0102: C ₂ H ₇ Si ₂ ⁻ , 71.014: C ₃ H ₃ O ₂ ⁻ , 215.7915: O ₃ Fe ₃ ⁻ , 255.2333: C ₁₆ H ₃₁ O ₂ ⁻ , 80.9648: C ₂ HSi ₂ ⁻ , 144.8687: HO ₂ Fe ₂ ⁻

^a Peaks for which elemental compositions could not be assigned.

For the palmitic acid (negative ions) dataset the score plot (Figure 8a) indicates that the first PC summarises the variance (chemical differences) between the unscratched area of the disc and the other areas of the HFRR disc (wear track and debris). From the loadings on PC 1 (Figure 8b and Table 4) it can be deduced that the palmitate ion (C₁₆H₃₁O₂⁻) was present in larger amounts in the debris and wear track compared to the unscratched area of the disc. The palmitate ion [M-H]⁻ together with the peak representing a palmitate ion containing one ¹³C isotope contribute significantly to chemical differences between the different areas of the surface. The ability to identify ¹³C isotopes illustrates the importance of high resolution mass measurement when working with complex mass spectra. A peak tentatively assigned as the C₇H₅O₂⁻ ion was found to be more prominent in unscratched areas of the disc, similar to observations made for the oleic acid (negative ions) data set. The second PC explains the variation between the debris compared to the wear track and disc. The loadings on PC 2 (Figure 8c and Table 4) suggest that a more intense peak was observed for the palmitate ion in the debris together with other carboxylate anion peaks. These carboxylate anion fragments were larger than those observed in the oleic acid (negative ion) dataset.

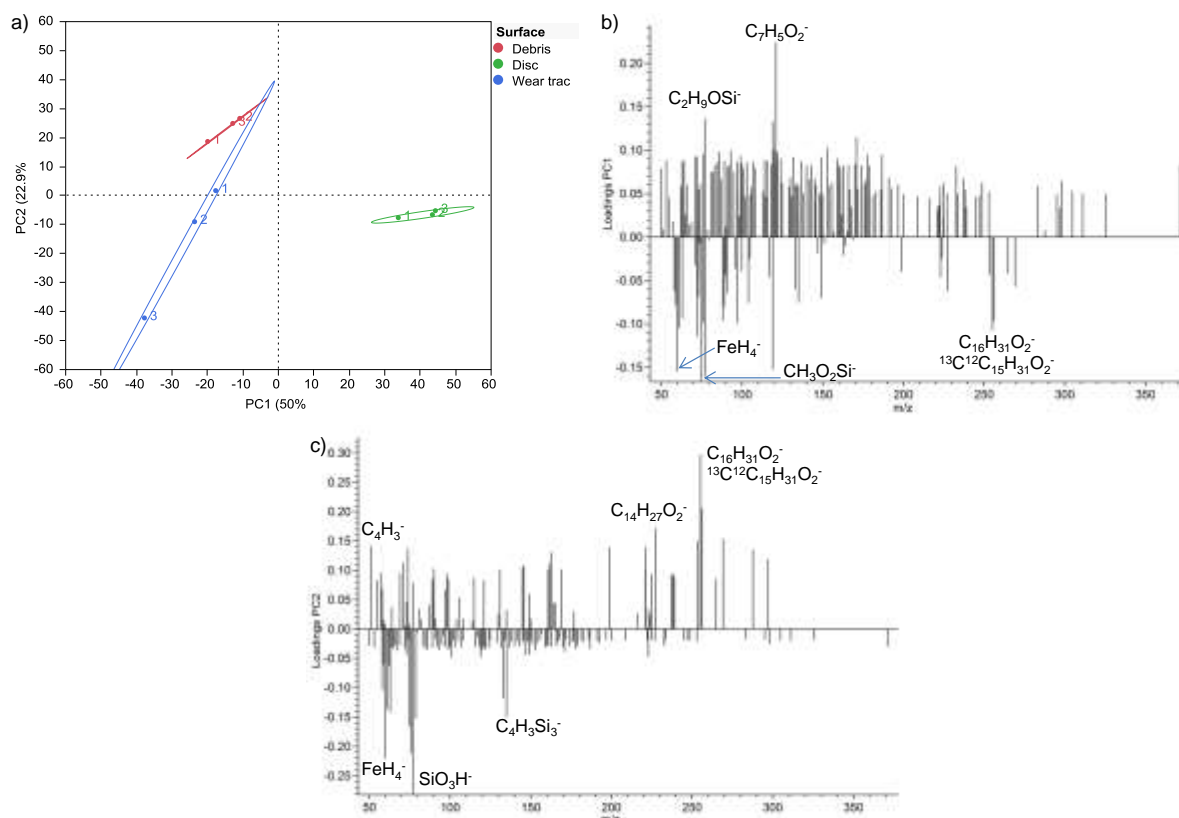


Figure 8. Results obtained from principal component analysis of mass spectra (negative ions) for the HFRR disc lubricated with palmitic acid (2000 mg/ml). The numbers in the score plot (a) represent the position of the spot

analysed using TOF-SIMS and corresponds to the numbers in Figure 2. The loadings plots for PC1 (b) and PC2 (c) are also shown.

Table 4. Summary of mass spectral peaks that contribute significantly to the differences between the mass spectra (negative ions) obtained from a HFRR disc lubricated with palmitic acid (2000 mg/ml).

PC	Positive loadings	Negative loadings
1 (50 %)	121.0241: C ₇ H ₅ O ₂ ⁻ , 77.0408: C ₂ H ₉ OSi ⁻ , 118.9459: H ₃ O ₂ Si ₃ ⁻ , 170.8873: CH ₃ OSiMn ₂ ⁻ , 152.9038: C ₂ H ₂ OSi ₂ Mn ⁻ , 119.9423: C ₄ HOMn ⁻ , 93.0349: C ₆ H ₅ O ⁻ , 86.0056: C ₂ H ₆ Si ₂ ⁻ , 121.9285: CH ₆ Cr ₂ ⁻ , 76.0323: C ₆ H ₄ ⁻	74.9907: CH ₃ O ₂ Si ⁻ , 76.9697: HO ₃ Si ⁻ , 59.9665: H ₄ Fe ⁻ , 118.9559: H ₈ Si ₂ Mn ⁻ , 71.9287: OFe ⁻ , 255.2343: C ₁₆ H ₃₁ O ₂ ⁻ , 60.9745: HO ₂ Si ⁻ , 96.9605: CH ₅ SiCr ⁻ , 75.9612: H ₄ OFe ⁻ , 256.2377: ¹² C ₁₅ ¹³ CH ₃₁ O ₂ ⁻
2 (22.9 %)	255.2343: C ₁₆ H ₃₁ O ₂ ⁻ , 256.2377: ¹² C ₁₅ ¹³ CH ₃₁ O ₂ ⁻ , 227.2028: C ₁₄ H ₂₇ O ₂ ⁻ , 269.2143: C ₁₅ H ₃₃ Si ₂ ⁻ , 253.2189: C ₁₆ H ₂₉ O ₂ ⁻ , 51.024: C ₄ H ₃ ⁻ , 199.1714: C ₁₂ H ₂₃ O ₂ ⁻ , 221.0529: C ₄ H ₁₃ O ₁₀ ⁻ , 73.9466: H ₂ OFe ⁻ , 287.7242: CH ₄ CrMn ₄ ⁻	76.9697: HO ₃ Si ⁻ , 59.9665: H ₄ Fe ⁻ , 75.9612: H ₄ OFe ⁻ , 74.9907: CH ₃ O ₂ Si ⁻ , 78.9591: C ₂ H ₃ Cr ⁻ , 134.9552: C ₄ H ₃ Si ₃ ⁻ , 62.9663 ^a , 60.9745: HO ₂ Si ⁻ , 75.991: C ₅ O ⁻ , 132.9754: C ₅ H ₅ OCr ⁻

^a Peaks for which elemental compositions could not be assigned.

Note that peaks representing PDMS were shown to contribute to the chemical differences between the different surfaces for all the data sets. These include ions with m/z 59, 73, 133, 147, 207, 221 and 281 in the positive ion spectra and ions with m/z 73, 75, 77 and 89 in the negative ion spectra. The contribution of suspected surface contaminants should be interpreted with care.

5. Conclusions

In this work an untargeted approach was used to identify mass spectral peaks that may contribute to chemical differences observed on a HFRR disc using TOF-SIMS. As shown in other application areas [12], PCA proved to be an invaluable tool to aid in the interpretation of complex TOF-SIMS data obtained from tribological surfaces. An important aspect of this technique is the fact that it is unbiased, and therefore the risk of inadvertently overlooking important information within the data is reduced. The importance of high resolution mass spectrometry in tribochemical applications has also been highlighted. The ability to predict elemental compositions for mass spectral peaks aided in the interpretation of results.

In summary, the positive ion spectra showed that the wear track contains relatively more intense Cr⁺ peaks for both oleic and palmitic acid additives. The debris contained several peaks that were tentatively assigned as alkyl ions (C₄H₇⁺, C₄H₉⁺, C₅H₁₁⁺, C₇H₁₃⁺) for both additives. Some alkyl-iron ions (CH₃Fe⁺, C₃H₅Fe⁺, C₄H₆Fe⁺, C₅H₇Fe⁺) were also present in relatively higher amounts in the debris of the palmitic acid sample, whilst relatively higher amounts of Fe⁺ were found in the debris of the oleic acid sample. For both additives, the C₇H₅O⁺ ion was observed in the unscratched area of the disc. This ion may be related to the C₇H₅O₂⁻ ion found in the negative ion spectra. Other peaks representing carboxylate anions were also found in the debris for both additives, but smaller fragments were observed for the oleic acid sample. For the palmitic acid sample, the palmitate ion (together with its ¹³C isotope containing analog) was found to be present in relatively higher amounts in the wear track and debris compared to the unscratched area of the disc. Based on these results, it is suggested that this approach be used as a complementary method for analysing and interpreting the complex mass spectra obtained from tribological surfaces through TOF-SIMS analyses.

Measureable chemical differences were found for surfaces lubricated by chemically similar additives (oleic and palmitic acid) with almost identical lubricating abilities (wear scar diameters). A method has been established for future tribological studies that can also be used to link lubricity to chemical surface species. It is recommended that replicate data be acquired, e.g. analysing multiple spots in different areas of two or more discs for each data set.

Acknowledgements

The authors would like to thank Jacques Langenhoven for performing the HFRR tests as well as Caryn Beets for guidance and discussions regarding the MassLynx and MarkerLynx software. The financial assistance of Sasol (Sasol Technology, Fuels Research) and the National Research Foundation (DAAD-NRF) towards this research

is hereby acknowledged. Opinions expressed and conclusions arrived at, are those of the authors and are not necessarily to be attributed to the DAAD-NRF.

References

- [1] Margaroni, D.: Fuel lubricity. *Ind. Lubr. Tribol.* 50, 108-118 (1998).
- [2] Wei, D., Spikes, H.A.: The lubricity of diesel fuels. *Wear* 111, 217-235 (1986).
- [3] Fox, M.F.: A model for diesel fuel additive lubricity. *Tribol. Interface Eng. Ser.* 48, 585-591 (2005).
- [4] Sahoo, R.R., Biswas, S.K.: Frictional response of fatty acids on steel. *J. Colloid Interface Sci.* 333, 707-718 (2009).
- [5] Wood, R.J.K., Harvey, T.J., Morris, S., Powrie, H.E.G.: Electrostatic monitoring of boundary and mixed lubrication. *Tribol. Ser.* 40, 83-92 (2002).
- [6] Hsu, S.M., Zhang, J., Yin, Z.: The nature and origin of tribochemistry. *Tribol. Lett.* 13, 131-139 (2002).
- [7] Murase, A., Ohmori, T.: ToF-SIMS analysis of model compounds of friction modifier adsorbed onto friction surfaces of ferrous materials. *Surf. Interface Anal.* 31, 191-199 (2001).
- [8] Kolm, R., Gebeshuber, I.C., Kenesey, E., Ecker, A., Pauschitz, A., Werner, W.S.M., Störi, H.: Tribochemistry of mono molecular additive films on metal surfaces, investigated by XPS and HFRR. *Tribol. Interface Eng. Ser.* 48, 269-282 (2005).
- [9] Crockett, R.M., Derendinger, M.P., Hug, P.L., Roos, S.: Wear and electrical resistance on diesel lubricated surfaces undergoing reciprocating sliding. *Tribol. Lett.* 16, 187-194 (2004).
- [10] Bhushan, B.: Nanotribology and nanomechanics. *Wear* 259, 1507-1531 (2005).
- [11] Wagner, M.S., Castner, D.G.: Characterization of Adsorbed Protein Films by Time-of-Flight Secondary Ion Mass Spectrometry with Principal Component Analysis. *Langmuir* 17, 4649-4660 (2001).
- [12] Graham, D.J., Wagner, M.S., Castner, D.G.: Information from complexity: Challenges of TOF-SIMS data interpretation. *Appl. Surf. Sci.* 252, 6860-6868 (2006).
- [13] Wagner, M.S., Graham, D.J., Ratner, B.D., Castner, D.G.: Maximizing information obtained from secondary ion mass spectra of organic thin films using multivariate analysis. *Surf. Sci.* 570, 78-97 (2004).
- [14] Knothe, G.: Evaluation of ball and disc wear scar data in the HFRR lubricity test. *Lubr. Sci.* 20, 35-45 (2008).
- [15] Leslie, A.D., Volmer, D.A.: Dealing with the masses: a tutorial on accurate masses, mass uncertainties, and mass defects. *Spectroscopy* 22, 32 (2007).
- [16] Hsu, S.M.: Boundary lubrication: current understanding. *Tribol. Lett.* 3, 1-11 (1997).