The qualitative and quantitative analysis of lubricant oil additives by direct analysis in real time-mass spectrometry

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ABSTRACT

The application of direct analysis in real time combined with mass spectrometry (DART-MS) to the qualitative analysis of lubricant and oil additives, and the quantitative analysis of a lubricant antioxidant additive is reported. The additives were analysed alone and in the presence of a base oil, from filter paper, glass and steel surfaces, showing the potential of the DART-MS technique for the direct, rapid analysis of lubricant oil additives. The quantitative capabilities of the technique were evaluated for the antioxidant in an oil matrix at concentrations in the range 0.1–8 mg/mL in oil (1–80 μg antioxidant on spot), using a structural analogue of the antioxidant as an internal standard. The linearity ($R^2 = 0.997$), precision (% RSD = 2.6%) and LOD (0.04 mg/mL in oil) of the method demonstrates that DART-MS is capable of the rapid determination of additives in oil without pre-extraction.

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1. Introduction

Lubricating oils contain complex mixtures of chemical additives dissolved in a base oil that function to improve the performance characteristics of the formulation. These chemical additives have different properties, such as antioxidants, corrosion inhibitors and friction modifiers, which determine the chemical and physical nature of the product. Advances in engine development to improve performance have resulted in complex tribological environments in which optimisation of the lubricant formulation is essential. The analysis of lubricant additives provides information regarding the age and degradation state of the product.

A range of techniques have been applied to the analysis of oil additives including scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), thermogravametric analysis and mass spectrometry (MS) [1–5]. The use of mass spectrometry can generate highly detailed information regarding the chemical composition of lubricants and enable quantification of additives. Mass spectrometry is typically hyphenated with chromatographic techniques, such as supercritical fluid chromatography [6,7], gas chromatography [8] and liquid chromatography [9] to separate the additives from each other and the base oil matrix. However, these techniques are often time consuming and may require sample preparation, such as derivatization, prior to analysis [10,11]. Additionally, removal of the sample from within the tribological system is necessary, which results in the loss of information that would be generated by the analysis of additives directly from surfaces.

Ambient ionization enables the direct analysis of samples by mass spectrometry with minimal, or no, sample preparation. Unlike other mass spectrometry ionization methods that require the sample to be present in either a liquid or gaseous state, ambient ionization allows native state sample interrogation. Ambient ionization techniques including atmospheric solids analysis probe (ASAP) [12] and desorption electrospray ionization (DESI) have been applied to the analysis of lubricants and lubricant additives [13], as has direct analysis by matrix assisted laser desorption ionization (MALDI) [14,15].

Direct analysis in real time (DART) is an ambient ionization method that uses a heated flow of metastable nitrogen or helium gas to desorb and ionize target analytes directly from surfaces [16]. An electrical discharge from a needle electrode is used to create a plasma of nitrogen or helium that contains metastable species. This is directed towards a sample deposited on a surface where ionization of target compounds occurs primarily through Penning ionization to yield gas phase analyte ions. Desorption of target analytes from the surface in DART is facilitated through both thermal desorption, as a result of the heated gas flow, and by energy transfer from the metastable atoms and molecules to the surface. As a result of the ionization and desorption process in DART, the volatility of

the target analyte will therefore affect the ionization potential and sensitivity of the technique.

DART has been used to desorb molecules from a wide range of surfaces [17,18], for target analyte determination in forensic, food and environmental samples [19–22], and for the analysis of petroleum fractions and self-assembled monolayers [23–25]. The application of DART, hyphenated with high performance thin layer chromatography, to the qualitative determination of lubricant additives has been demonstrated [26]. However, the application of DART to the qualitative and quantitative analysis of lubricant additives directly from surfaces with no sample preparation has not been previously studied. We report here the DART-MS analysis of commercially available lubricant oil additives present on range of surface materials, both with and without an oil matrix. The quantitative capabilities of the technique have been evaluated for the determination of an antioxidant additive in oil.

2. Materials and methods

2.1. Reagents and chemicals

Cyclohexane, methanol, water (all HPLC grade) and concentrated sulphuric acid were purchased from Fisher Scientific (Loughborough, UK). Toluene and tetrahydrofuran (THF) were purchased from Sigma Aldrich (Gillingham, UK). The antioxidant additive octyl (4-hydroxy-3,5-di-*tert*-butylphenyl)propionate (**1**) and a lubricating base oil (group one treated base oil) were supplied by BP (Pangbourne, UK) for the analysis. Ethylene glycol monopentyl ether was purchased from Sigma Aldrich (Gillingham, UK) and 3,5-di-*tert*-butyl-4-hydroxyphenylpropionic acid was purchased from Alfa Aesar (Heysham, UK) for the synthesis of 2-(pentyloxy)ethyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate (**2**). A series of structurally related quaternary amine corrosion inhibitor additives; benzyldimethyldodecylammonium chloride (**3**), benzyldimethyltetradecylammonium chloride (**4**) and benzyldimethylhexadecylammonium chloride (**5**) were purchased from Sigma Aldrich (Gillingham, UK) and were 99%, 97% and cationic detergent grade respectively. The additive (*Z*)-Octa-9-decenamide (**6**, ≥99.9% purity) was also purchased from Sigma Aldrich (Gillingham, UK). The structures of the oil additives are shown in Fig. 1. Filter paper (Whatman 541), glass and steel (cold rolled, Grade 1008–1010, polished) surfaces were selected for analysis.

2.2. Synthesis of 2-(pentyloxy)ethyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (2)

2-(pentyloxy)ethyl3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate (**2**), a related compound to **1**, was synthesised *via* a Fischer esterification reaction as described previously [15]. Ethylene glycol monopentyl ether (150 μL) and 3,5-di-*tert*-butyl-4-hydroxyphenylpropionic acid (71.4 mg) were mixed in a HPLC vial and concentrated H_2SO_4 (~1 μL) was added as a catalyst. A pierced lid was fixed onto the vial to enable water to escape from the reaction mixture as steam, and the sample vortexed. The reaction vial was then heated to 100 °C for 6 hours.

2.3. Sample preparation

2.3.1. Qualitative studies

Optimisation of the DART source and the investigation into the effect of surface material and helium gas temperature on analyte response was evaluated using aliquots (10 μL) of ~2 mg/mL solutions of **1–5**, deposited onto the filter paper, glass or steel surface to give ~20 μg additive on spot. For the qualitative analysis of **1**, a mixture of **1** (10 mg/mL) and **2** (nominal concentration of 13.4 mg/mL) was prepared and then diluted five-fold in either cyclohexane or the

base oil to give final concentrations of 2 mg/mL **1** and 2.7 mg/mL **2**. Stock solutions of **3–5** were prepared in 1:1 methanol:water so that the additives were present at 1.8 mg/mL (**3**), 2 mg/mL (**4**) and 2.1 mg/mL (**5**) in solution. The base oil was spiked with **3–5** by preparing stock solutions of the additives in 1:1 methanol:toluene, so that the additives were present at 180 mg/mL (**3**), 200 mg/mL (**4**) and 210 mg/mL (**5**), before 10 μL of each solution was spiked into 930 μL base oil to give additive concentrations of 1.8–2 mg/mL in oil. Compound **6** was dissolved in THF (1 mg/mL) before deposition onto the steel surface and left to air dry. The sample of **6** on the steel surface was subsequently exposed to several solvent washes using cyclohexane, methanol and toluene in which the surface was washed with the solvent before excess solvent was removed using a Kimwipe. Sample analysis by DART-MS was carried out after each wash.

2.3.2. Quantitative studies

Stock solutions of **1** were prepared by dissolving known weights (0.5–40 mg) in 1 mL cyclohexane and spiking in 10 μL of a solution of **2** in cyclohexane to give a concentration of 6.7 mg/mL **2**. An aliquot of each standard solution containing **1** and **2** (100 μL) was added to the base oil (400 μL), so that the additive was present in the oil at concentrations in the range 0.1–8 mg/mL. The spiked oil (10 μL) was spotted onto a filter paper surface to give deposited amounts of additive in the range of 1–80 μg of **1** per spot.

2.4. DART-MS instrumentation and parameters

A commercially available DART source (DART-SVP, IonSense, MA, USA) was used for the analysis. The DART source was positioned 2.3 cm away from the mass spectrometer inlet and at an angle of 45° to the inlet, to enable interrogation of surfaces. The sample surface was positioned under the DART source, so that it was located ~1 mm below the mass spectrometer inlet and 5 mm below the tip of the DART source. A gas temperature (helium) of 200 °C was found to be the optimum temperature for desorption and ionization of **1**. The helium gas temperature was varied in the range of 50–300 °C for the analysis of **3–5** and maintained at 300 °C for the analysis of **6**. The grid voltage was set to 350 V in both positive and negative ion modes. There is no independent gas flow control on the model DAT-SVP ion source. The DART source was hyphenated with an Orbitrap Q Exactive Plus mass spectrometer (Thermo, MA, USA), operated in both negative ion (**1** and **2**) and positive ion (**3–6**) modes. The mass spectrometer instrumental parameters were: capillary temperature 250 °C, scan range *m/z* 133–1000, resolution 140,000 and ACG target 1e6. For all experiments, data were acquired for 1.5-2.5 min before inserting the sample into the DART source. For the quantitative study of **1**, six replicates of each concentration of **1** in oil were analysed. Data were acquired for 2 min for each sample and the intensities of the deprotonated molecules of **1** and **2** used to calculate their relative response.

3. Results and discussion

3.1. Qualitative analysis of additives by DART-MS

The application of DART-MS to the direct analysis of a commercially available lubricant antioxidant additive (**1**), corrosion inhibitors (**3–5**) and a friction modifier additive (**6**), deposited on a range of different surfaces alone and in an oil matrix, has been studied. The effects of surface material, matrix and DART gas temperature on the desorption profiles and molecular ion responses of the target analytes were evaluated. The DART source was positioned 2.3 cm away from the mass spectrometer inlet at
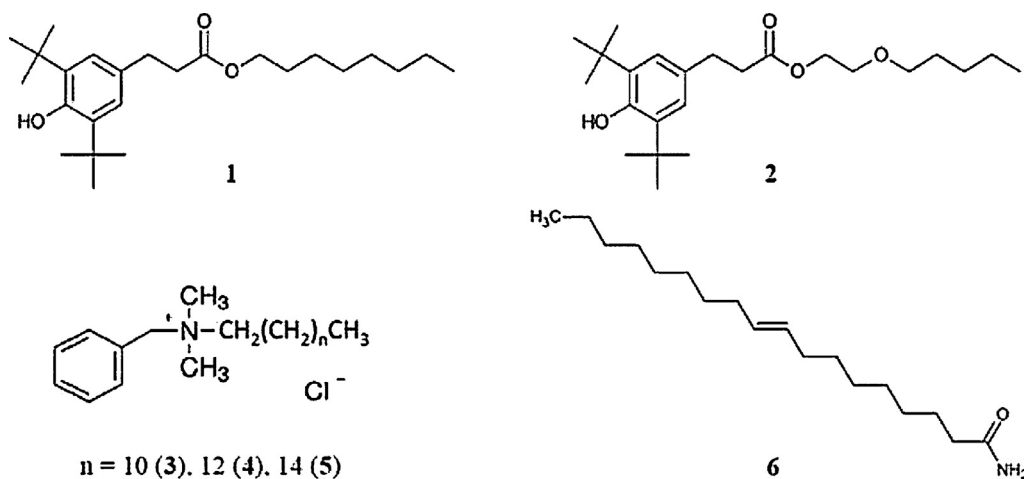
Fig. 1. Structures of lubricant oil additives **1–6**.

an approximate angle of 45° to enable the direct analysis of surfaces. The samples were mounted on a platform located within the DART source to reduce variation in ion response that could result from changes in sample positioning and to enable rapid sample throughput.

3.2. Antioxidant additive

The successful desorption and ionization of the antioxidant additive **1** deposited on filter paper, glass and steel surfaces using DART-MS in the negative ion mode with a helium gas temperature of 200 °C is shown in Fig. 2. For each analysis, a 2 min blank of the surface away from the sample spot was acquired before the introduction of the sample into the DART source. The desorption profile of the deprotonated molecular ion of **1** ([M−H]⁻, m/z 389) was monitored for ~18 min before the sample was removed. The desorption profile of the [M−H]⁻ ion of **1** was influenced by the target surface material. Analysed from the filter paper and glass surfaces, a response for the [M−H]⁻ ion of **1** was observed immediately after the sample was placed under the heated flow of metastable helium gas (Fig. 2a and c), which reached a maximum response within a few seconds. Continued interrogation of the surface resulted in an initial rapid fall in intensity for the filter paper surface followed by a steady depletion of the sample over the 18 min investigated. The glass surface showed a similar drop in intensity, but the initial rate of fall was slower. The desorption profile of the [M−H]⁻ ion of **1** deposited on the steel surface and analysed by DART-MS shows a different profile to the filter paper and glass surfaces, Fig. 2e. The initial increase in response for [M−H]⁻ of **1** is more gradual, with the maximum peak intensity observed approximately 1.5 min after sample introduction into the DART source. The depletion of the sample from the steel surface resulted in the response for the [M−H]⁻ ion falling to 10% maximum intensity within 10 min of the first signs of sample depletion. The difference in desorption profile may be a consequence of the thermal conductivity of the metal surface. Exposure of the steel surface to the heated gas flow of the DART source causes an increase in surface temperature. However, conductivity of heat away from the sample spot on the steel surface may result in a lower rate of heating and reduced thermal desorption of **1** from the surface in the early part of the analysis. Removal of the sample from the DART source resulted in the response of [M−H]⁻ of **1** returning to baseline levels within a few seconds for all surface materials.

The DART-MS response for the antioxidant in the presence of the synthetic analogue **2** was investigated by depositing a mixture of **1** and **2** onto filter paper and steel surfaces in cyclohexane,

air drying and monitoring the desorption profiles for the [M−H]⁻ ions. An example of the depletion profiles the of [M−H]⁻ ions of **1** and **2** deposited onto filter paper and analysed by DART-MS is shown in Fig. S1 (Supplementary material). The [M−H]⁻ ions for **1** and **2** showed the same depletion profiles as a result of the two compounds being chemically and structurally related and therefore having similar ionization efficiencies and volatilities.

The mixture of **1** and **2** was spiked into a base lubricating oil to investigate the potential of DART-MS for the direct analysis of lubricating oil additives without extraction of the additives from the oil matrix. Typically additive analysis is carried out using methanol or SPE extraction procedures, before analysis by ESI or LC–MS, but this requires sample preparation steps that can be time consuming. DART offers the ability to rapidly analyse a sample deposited on a surface with no sample preparation, increasing sample throughput. Compounds **1** and **2** were both successfully desorbed and ionized by DART-MS in the negative ion mode when deposited on filter paper and steel surfaces in oil as shown in Fig. 3(a) and (b). However, the presence of the oil did affect the desorption profiles of the two analytes compared to desorption in the absence of the oil. The oil matrix reduced the depletion rate of **1** and **2** from the surface and the analyte response was observed over a prolonged period of time. In addition, a small delay in the initial response for the additive was noted after the sample was placed into the DART source in the presence of oil (Fig. 3), compared to the profile without the oil matrix (Fig. S1a). The resulting mass spectrum (Fig. 3c), shows the deprotonated molecules for **1** and **2** as the most intense ions, with very little chemical background resulting from the oil matrix because of preferential desorption and ionization of the target compounds in the base oil during the DART analysis. This can be advantageous in reducing the complexity of the spectrum observed and improve selectivity for the target analytes when applying the DART technique to the direct analysis of additives present in a complex oil matrix.

3.3. Corrosion inhibitors

The corrosion inhibitors, **3–5**, were deposited individually and as a mixture on filter paper, glass and steel surfaces for analysis by DART-MS (Fig. 4). The corrosion inhibitor quaternary ammonium ions for **3-5** were observed using DART as weak peaks at m/z 304, 332, and 360 for **3**, **4** and **5** respectively (Fig. 4 inset), confirmed by accurate mass measurement, showing their successful thermal desorption from the surface. The intact cations were only observed at helium gas temperatures ≥200 °C for glass (Fig. 4) and ≥300 °C for steel surfaces (data not shown). The thermal desorp-
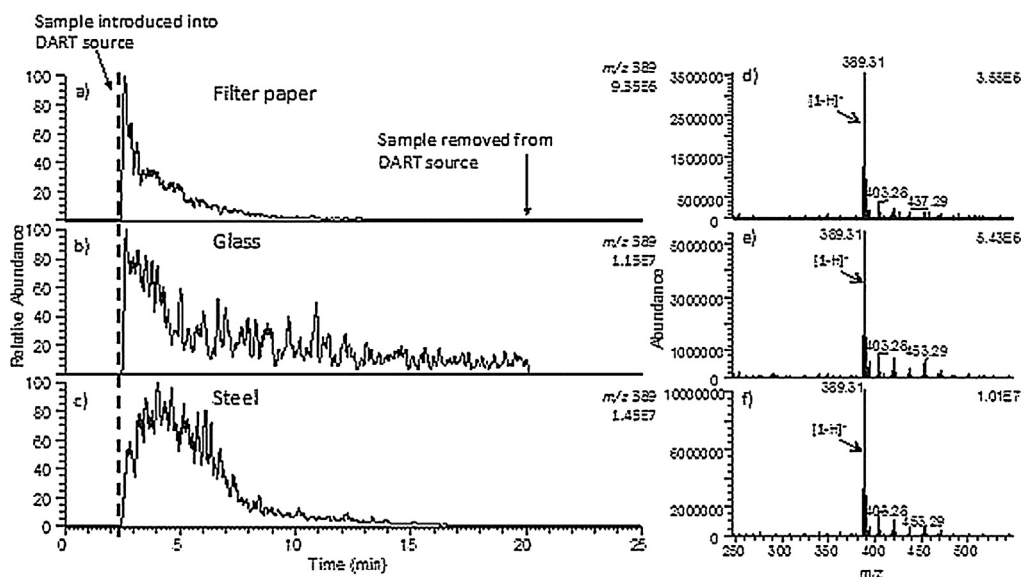
Fig. 2. Desorption profiles for the [M−H]⁻ ion (*m/z* 389) of the additive **1** deposited on (a) filter paper, (b) glass and (c) steel surfaces and analysed by DART-MS. The corresponding mass spectra are shown for (d) filter paper, (e) glass and (f) steel surfaces.
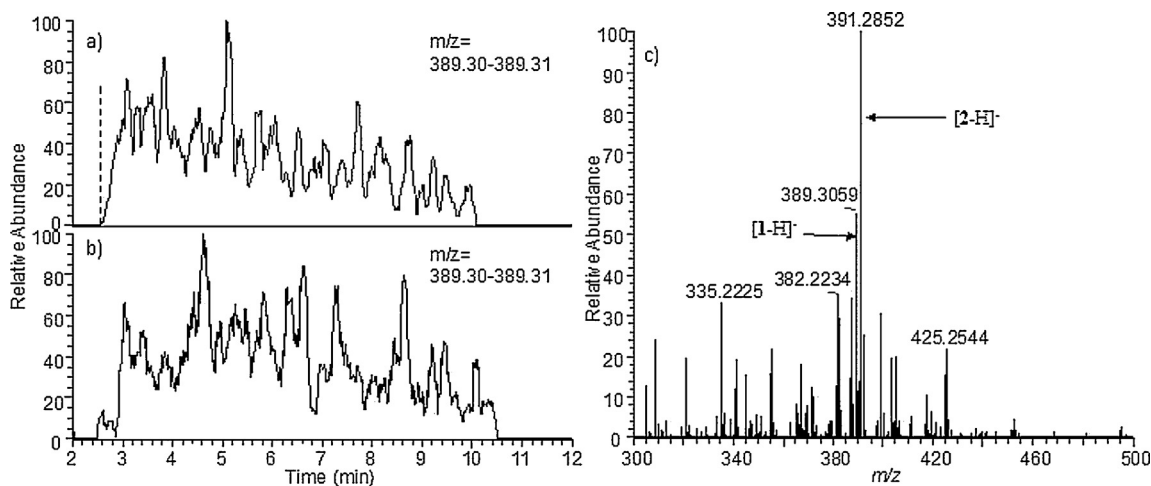

Fig. 3. DART-MS analysis (negative ion) of **1** and **2** in a lubricating base oil showing the selected ion responses for the [M−H]⁻ ion of antioxidant **1** (*m/z* 389), deposited on (a) filter paper and (b) a steel surface and (c) the resulting mass spectrum.

tion and subsequent mass analysis of intact quaternary amines is often difficult due to their low volatility, but detection of quaternary ammonium salts by thermal desorption alone has been previously reported [27]. At helium gas temperatures below 200 °C, desorption of the quaternary ammonium cations was not achieved by DART. However, strong responses at *m/z* 214, *m/z* 242 and *m/z* 270 for samples of **3**, **4** and **5** respectively were observed during the DART-MS analysis from all surface materials investigated (Fig. 5). The observed ions correspond to the free protonated alkylamines for **3** ([$CH_3(CH_3)_{11}N(CH_3)_2$+H]⁺), **4** ([$CH_3(CH_2)_{13}N(CH_3)_2$ + H]⁺) and **5** ([$CH_3(CH_2)_{15}N(CH_3)_2$+H]⁺) respectively, resulting from the common loss of the benzyl group ($C_6H_5CH_2$). The presence of the free amine unreacted synthetic precursors could make a small contribution to the intensity of these protonated amines. However, the origin of these ions is most likely to be as a result of thermal degradation of the quaternary amine followed by gas phase protonation during the DART ionization process. Thermal breakdown of quaternary amines resulting in the loss of R groups attached to the nitrogen is well documented [27–29]. An ion at *m/z* 136 assigned to [$C_6H_5CH_2N(CH_3)_2$+H]⁺ was observed in the mass spectra of **3**–**5** as a

common thermal decomposition product of the quaternary amine species. Ions were also observed at *m/z* 290, 318 and 346 in the mass spectra of **3**–**5** (Fig. 4, insert), 14u lower than the expected mass for the M⁺ ions, the mass difference assigned to CH_2 by accurate mass measurement. These ions correspond to the loss of a methyl group followed by a subsequent protonation to generate [**3**-CH_3+H]⁺, [**4**-CH_3+H]⁺ and [**5**-CH_3+H]⁺ species. Similar fragmentation has been observed using techniques such as direct exposure chemical ionization and field desorption for the analysis of quaternary ammonium salts [29]. The combination of these characteristic ions in the mass spectra of the quaternary amine corrosion inhibitors can be used diagnostically to identify the groups attached to the quaternary nitrogen and the length of the alkyl chain present even when the molecular ions is not observed.

The desorption profiles for the intact cation for **5** and thermal fragment ions associated with the loss of the alkyl, benzyl and methyl groups from glass are shown in Fig. S2. The ions show a similar desorption profile to that observed from the DART-MS analysis of the antioxidant additive **1** (Fig. 2b). An initial increase in response is observed for the intact cation and thermal fragment ions
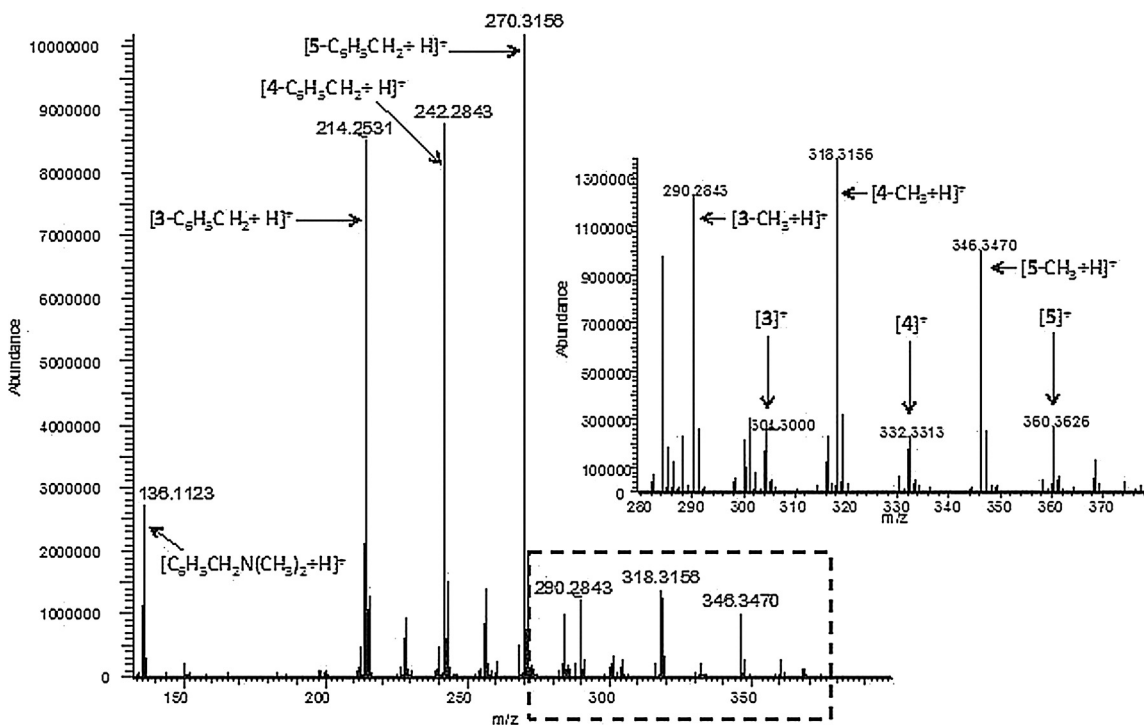
Fig. 4. DART-MS mass spectrum (positive ion) of the corrosion inhibitor additives **3–5** deposited on a glass surface and analysed using a helium temperature of 200C, with mass range expanded in the region *m/z* 280–380 (inset).
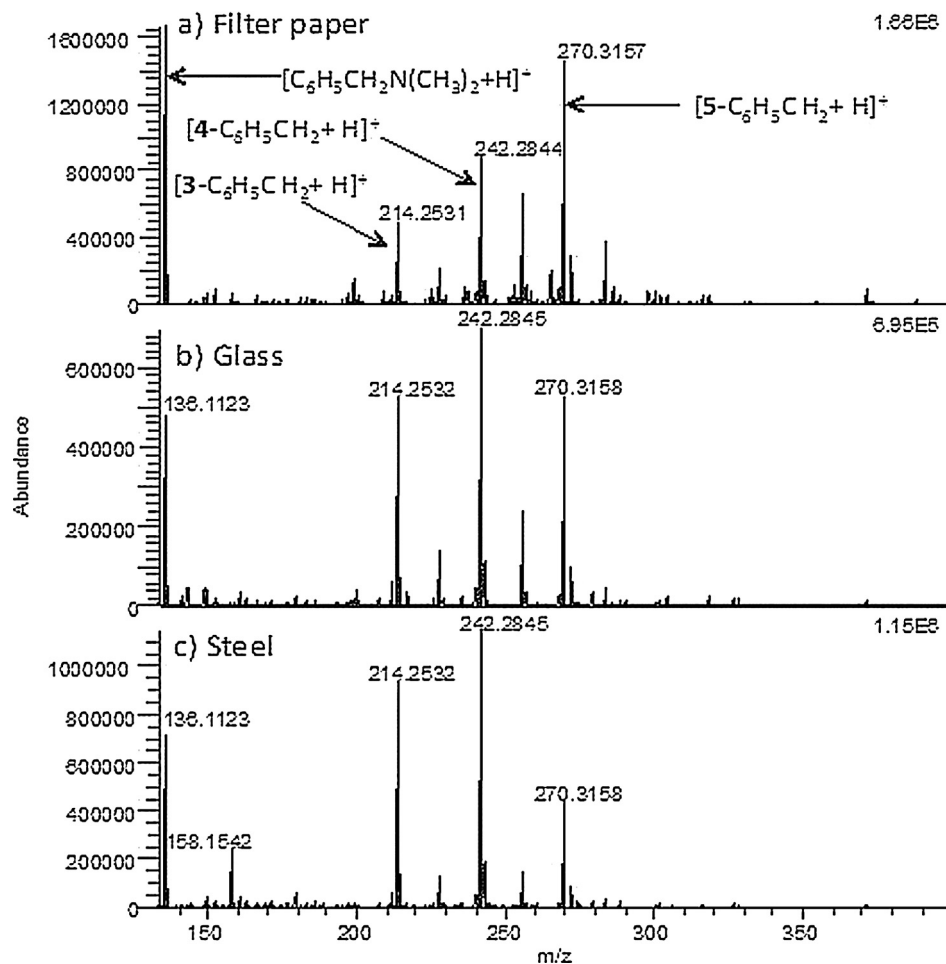

Fig. 5. DART-MS analysis (positive ion) of corrosion inhibitor additives **3–5** deposited as a mixture on (a) filter paper, (b) glass and (c) steel surfaces using He gas temperatures <200 °C.
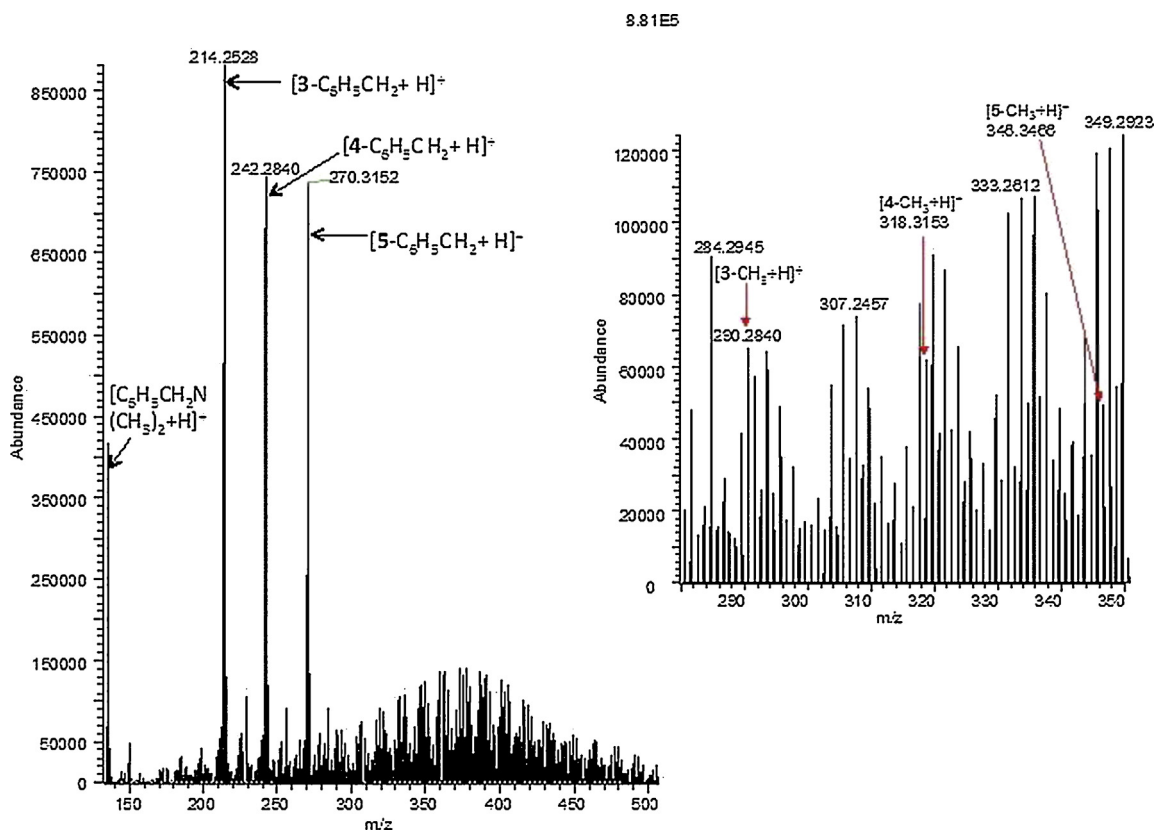
Fig. 6. DART-MS analysis (positive ion) of corrosion inhibitors **3–5** present in lubricating oil deposited onto a steel surface and (inset) expanded in the range *m/z* 280–350.

after sample introduction into the DART source at 1.5 min, which is followed by a steady fall in intensity as the sample is depleted from the surface. The free benzylamine ([$C_6H_5CH_2N(CH3)_2$+H]$^+$; (*m/z* 136) and alkylamine ([$CH_3(CH_2)_{15}N(CH_3)_2$+H]$^+$; *m/z* 270) ions show comparable profiles (Fig. S2a and b). However, a slight delay in initial response is observed for the [**5**-CH$_3$+H]$^+$ and [**5**]$^+$ ions, which is attributed to a reduced initial rate of thermal desorption (Fig. S2c and d). This is likely to be a surface temperature effect.

The additive mixture was spiked into the base oil and deposited on the steel surface before analysis by DART-MS using a helium temperature of 300 °C. The presence of the oil matrix caused an elevated background which prevented the M$^+$ ions from being distinguished from the chemical noise. Weak responses were observed for the [M-CH$_3$+H]$^+$ fragment ions for compounds **3–5** (Fig. 6 inset) within the chemical background. However, the base peaks in the mass spectrum correspond to the protonated alkylamines that act as diagnostic fragments for the quaternary amine compounds. The ions are dominant in the mass spectrum and are not obscured by the oil matrix enabling the direct identification of corrosion inhibitor additives deposited on a steel surface and in the presence of an oil matrix by DART-MS using these thermal fragments.

3.4. Friction modifier

Compound **6,** (Z)-Octa-9-decenamide, is a surface-active friction modifier used in a range of commercially available lubricant oil additives. The (Z)-Octa-9-decenamide creates a layer on the surface that reduces friction at the boundary of two moving counterparts to minimise wear. The application of DART-MS to the direct analysis of **6** deposited onto steel resulted in a strong response for the protonated molecule at *m/z* 282 (Fig. 7a) showing the successful desorption and ionization of the additive from the steel surface.
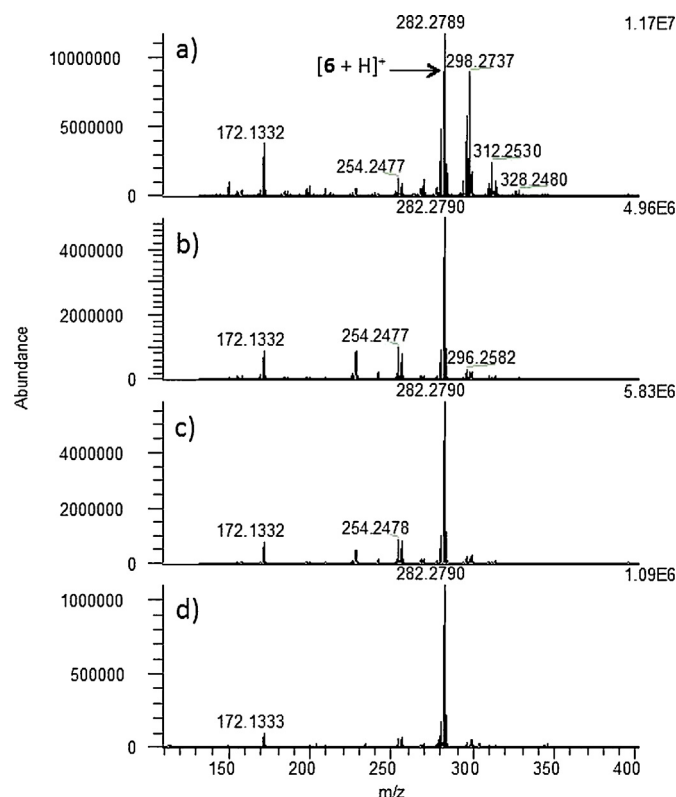

Fig. 7. DART-MS analysis (positive ion) of **6** deposited onto a steel surface. The surface was first analysed by DART-MS (a) before being subjected to sequential solvent washes using (b) cyclohexane, (c) MeOH and (d) toluene with DART-MS analysis carried out after each solvent wash.
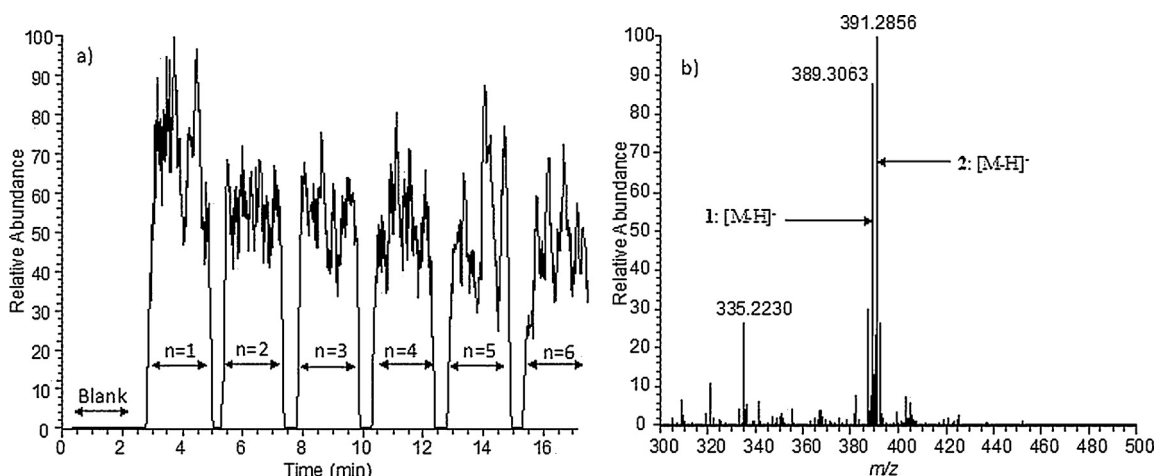
Fig. 8. (a) Selected ion responses for the [M−H]⁻ ion of **1** present in a lubricating oil, deposited on filter paper (10 μg on spot) and analysed by DART-MS, showing a blank filter paper and six replicate samples. (b) The resulting mass spectrum showing ions associated with the deprotonated molecules of **1** and internal standard **2**.

The steel surface was then washed sequentially using cyclohexane, methanol and toluene with analysis by DART-MS carried out after each wash. The resulting mass spectra are shown in Fig. 7. A slight fall in the intensity of the [M+H]⁺ ion for **6** is observed following the wash stages, but other ions such as m/z 298 and 254, are preferentially removed from the surface, indicating a higher surface activity for **6** on the steel surface. These data show that DART is suitable for the direct desorption and ionization of active friction modifier oil additives present on steel and may also provide information on the surface activity following exposure of the sample to different solvents.

3.5. Quantitative determination of an antioxidant in lubricating oil by DART-MS

The quantitative determination of the antioxidant additive **1** in lubricating base oil was evaluated in the presence of **2** as an internal standard. The determination of **1** in the presence of the structural analogue **2** has been reported previously using DESI-MS [15]. The antioxidant additive **1** was spiked into the base oil at concentrations in the range 0.1–8 mg/mL and the samples were deposited onto filter paper for analysis by DART-MS. Each acquisition consisted of the analysis of a blank region of the surface (2 min) followed by analysis of the area containing **1** and **2** in oil (n = 6, each replicate analysed for 2 min). The relative intensities of the [M-H]⁻ ions for **1** and **2** acquired for the sample during the 2 min analysis were used to calculate their relative responses. Fig. 8 illustrates an example of the analysis.

Good linearity was observed for the DART-MS analysis of **1** in oil, $R^2 > 0.997$, for the relative responses of **1** and **2**. The addition of **2**, an analogue of **1**, as an internal standard helped to minimise variation in relative ion responses that can arise from fluctuation in overall ion current that results from the DART-MS analysis of the surface (Fig. 8a). The chemical and structural similarities between **1** and **2**, with the difference in the two molecules being the substitution of oxygen for CH_2 in the hydrocarbon chain, makes **2** a suitable internal standard for the determination of **1**, as shown by the closely matching desorption profiles for the two species (Fig. S1). The precision of the technique was assessed by conducting replicate analyses to determine the% relative standard deviation (%RSD). The %RSD for the relative response of **1** and **2** was 2.6%. The limit of detection (LOD) was calculated as the blank response for **1** plus three standard deviations of the blank using the absolute selected ion response of **1**. For the DART-MS analysis of **1** in oil the

LOD was calculated to be 0.04 μg **1** on spot, which is equivalent to 0.04 mg/mL of antioxidant in oil.

The quantitative determination of **1** in oil using **2** as an internal standard has been previously reported using the DESI ionization technique combined with a Q-TOF mass spectrometer [15]. Caution should be exercised in comparing the DESI and DART data, which were acquired on different mass spectrometer platforms. However, the two methods both showed good linearity ($R^2 > 0.99$) and precision when using **2** as an internal standard. The %RSD for DESI-MS was 6.4%, which are typical for ambient ionization methods [30,31], but slightly higher than the DART-MS analysis with a%RSD of 2.6%. This demonstrates that DART-MS is applicable to the quantification of additives directly from a filter paper surface at concentrations below the levels (typically 0.1–5%) expected in commercial formulations, with potential for application to other surfaces.

4. Conclusions

The application of DART-MS to the qualitative analysis of commercially available lubricant and oil additives, including an antioxidant (**1**), corrosion inhibitors (**3–5**) and a friction modifier (**6**) has been investigated. The successful desorption and ionization of all additives has been demonstrated from a range of surface materials, including filter paper, glass and steel, both in the presence and absence of a lubricant base oil matrix. The target surface material has been shown to change the desorption profile for the [M−H]⁻ ion of **1**, as a result of differences in the thermal desorption temperature profile of the analyte from the surface. The influence of helium gas temperature on the desorption and thermal fragmentation of the quaternary amine corrosion inhibitors (**3–5**) yields intact quaternary ammonium ions and thermal fragments. The thermal fragmentation of the quaternary ammonium salts produces diagnostic ions that can be used to identify the quaternary amine species even when the molecular ions are not observed. This has been demonstrated for the DART-MS analysis of the corrosion inhibitor additives present in an oil matrix and deposited on steel. [M+H]⁺ ions were observed in the DART spectrum of the friction modifier **6** deposited onto a steel surface. Subsequent washing of the surface with methanol and toluene, in which **6** is soluble, resulted in only a small reduction in ion intensity, indicating the high surface activity of **6** on steel.

An analogue of **1**, was synthesised and used as an internal standard in the quantitative assessment of DART-MS. The matching desorption profiles for **1** and **2** from filter paper (Fig. S1) indicted

that the two compounds behave in a similar physical and chemical manner within the DART source, making **2** a suitable internal standard for the quantitative analysis of **1**. The application of DART-MS to quantify **1** in lubricating oil deposited on filter paper has been demonstrated with good linearity and precision ($R^2 > 0.99$ and 2.6% RSD). The LOD for the technique was calculated to be 0.04 μg of **1** on the surface, which corresponds to 0.04 mg/mL additive in oil. Comparison of DART with previously reported data for the determination of antioxidant **1** using DESI, shows that both ambient ionization techniques are able to quantify the additive at levels below those typically found in commercial formulations with good linearity and precision.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ijms.2016.05.011.

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