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