Detection and quantitation of ACCUTRACE™ S10, a new fiscal marker used in low duty fuels using a novel ultra-high performance supercritical fluid chromatography – mass spectrometry approach

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ABSTRACT: A new ultra-high performance supercritical fluid chromatography – mass spectrometry (UHPSFC-MS) method has been developed using electrospray ionisation (ESI) to detect and quantify a new fiscal fuel marker, ACCUTRACE™ S10 that was introduced into fuel in the UK and Ireland from April 1st 2015. S10 is synthesised by the Dow Chemical Company and is used as a replacement for UV-visible fuel markers, such as quinizarin, Euromarker and Solvent Red 24. It is UV invisible, is doped at a low level (2.5 ppm) and was designed for detection using modern gas chromatography – mass spectrometry (GC-MS) instrumentation. All currently proposed methods for the determination of ACCUTRACE™ S10 fuel marker in diesel fuel [automotive diesel oil, current specifications EN 590 and U.S. ASTM D975] use gas chromatography-mass spectrometry (GC-MS), and 2-dimensional GC-MS (2-D GC-MS) is necessary to detect the marker at tank dilutions. However the lower limit of detection (LLOD) and lower limit of quantification (LLOQ) for S10 are severely compromised using legacy GC-MS instrumentation and measurement at tank dilutions is not feasible. ACCUTRACE™ S10 exhibited unusual ionisation characteristics when analysed by atmospheric pressure ionisation techniques, the ionisation is modelled and discussed and the strong ionisation response utilised to develop a new approach to detection and quantitation of the new fuel maker. The novel UHPSFC-MS method utilises this phenomenon, allows injection of undiluted fuels and affords detection and quantitation at doping and tank dilution levels.

INTRODUCTION

Markers are added to fuels to identify low duty fuels and deter their use in applications intended for higher-taxed fuels. Examples of low duty fuels include off-road diesels for agricultural, mining, construction and marine environments, and kerosene used for heating[1-4]. In the United Kingdom (UK) these diesel fuels are charged by Her Majesty's Revenue and Customs (HMRC) with an excise duty of 11.14 ppl (pence per litre) instead of the full rate of 57.95 ppl[5].

Until recently, low duty fuel contained markers such as Solvent Red 24 and quinizarin (both fiscal markers in the UK), giving the fuel a visible colour allowing for easy identification[6]. The detection and determination of these coloured dyes is undertaken using the UV-vis test method IP 298[7-8].

Unfortunately, these visible dyes can easily be removed from low duty marked diesel fuels. Fraudsters have developed chemical and physical methods to strip these markers from diesel allowing for its illegal use/sale for applications intended for higher taxed fuels. In the UK this has resulted in a loss of around £1.1 billion p.a. in tax revenue and with potential damage to fuel systems[9-10]. Worldwide the loss of taxable revenue through illegal fuel laundering is over $100 billion p.a.[11-12].

A new fuel marker, ACCUTRACE™ S10, has been developed by the Dow Chemical Company. It is "significantly more effective than the current markers, and highly resistant to known laundering techniques"[5] and "it can still be detected in fuel lines and tanks for up to four or five fuel cycles."[10]. ACCUTRACE™ S10, 3-sec-butyl-4-decyloxyphenylmethanetriyl tribenzene, is shown in Figure 1. It is designed to be compatible with other dyes in use, such as Euromarker and was introduced in the UK on 1st April 2015 at a typical dosage of 2.5 mg/L (2.5 ppm) in diesel fuel[9, 13]. Together with a low ppm treat rate it is cost effective and contains "no known ozone-depleting additives"[10].

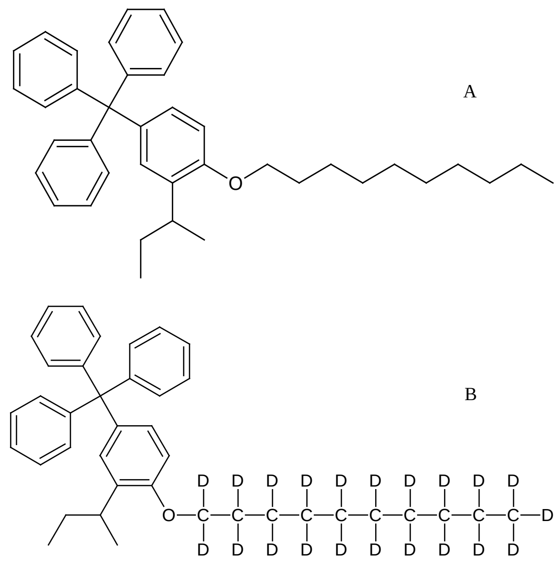

Figure 1. (A) Structure of 3-sec-butyl-4-decyloxyphenylmethanetriyltribenzene, ACCUTRACE™ S10 fuel marker (molecular weight = 532 g/mol) and (B) d-21 isotopically labelled ACCUTRACE™ d21-S10 fuel marker (molecular weight = 553 g/mol)

Since ACCUTRACE™ S10 is not UV active at the wavelength demanded by IP 298 this method is not applicable for its detection, therefore a number of alternative GC-MS methods have been proposed[13-15]. These methods detect and quantify ACCUTRACE™ S10 within a surrogate contaminated diesel sample with the composition in the following ratio; 70% Diesel: 27% Castrol GTX 5w30 Lubricating Oil: 3% Gear Oil 80w90[15]. The Dow Chemical Company[15] method uses a high temperature DB-17HT capillary column (30 m x 0.25 mm i.d., 0.15 µm film thickness) with a final high temperature of 365°C. Further improvements to this method were suggested in conjunction with Agilent using conventional 2-D GC-MS (heart cutting)[13]. The main advantage to using 2-D GC-MS, with a capillary flow technology Deans switch, is that contamination of the ion source is prevented. In this set-up the fuel matrix either side of the S10 fuel marker peak is diverted away to waste or to a flame ionisation detector (FID) and not introduced into the ion source. As a result, a reduction of ion source cleaning and a longer operational period is achieved for the GC-MS giving rise to the optimum signal-to-noise ratio for the ACCUTRACE™ S10 fuel marker. A method using 2-D GC-MS with a DB-1HT pre-column and a DB-17HT column reported a lower limit of detection (LLOD) of <= 1 ppb for ACCUTRACE™ S10 fuel marker in gasoline[15].

The fuel industry *via* ASTM (American Society for Testing and Materials) and the Energy Institute demand that any test method must be transferable across a range of routinely available analytical platforms. To investigate this stipulation, adapted approaches using legacy GC-MS instrumentation were explored and data are presented in the result and discussion section.

To address the industry wide issue of lack of 2D GC-MS capability and the fact that legacy GC-MS instrumentation cannot deliver a solution, an alternative analytical approach using ultra-high performance supercritical fluid chromatography (UHPSFC-MS) method was investigated. In its simplest form UHPSFC can be considered as a surrogate normal phase chromatography technique. Supercritical CO_2 (*sc*CO_2) is the primary mobile phase used and is a supercritical fluid above its critical point of 31.1 °C and 73.8 bar where it has properties intermediate between those of a gas and a liquid[16]. For many reasons *sc*CO_2 is the most commonly used mobile phase; its critical point is easily obtainable, it is readily available, inexpensive, considered green and relatively safe to use[16]. It is also hexane-like as a solvent and so readily amenable to the analysis of refined petrochemical materials, such as AVTUR fuels, gasoline and diesel, where injections of undiluted fuels can be made[16-17]. The renaissance in use of SFC and particularly UHPSFC-MS has been driven somewhat by the introduction of a robust instrumentation by major instrument manufacturers, namely Waters, Agilent and Shimadzu. This means that access to UHPSFC-MS is more commonplace and ease of use has allowed integration into the open access chromatography – mass spectrometry facility at the University of Southampton.

In many modern UHPSFC applications 100% *sc*CO_2 is rarely used due to its weak polarity. Polar organic co-solvents (modifiers) are added to extend the breadth of application areas accessible by UHPSFC by modifying the polarity of the mobile phase. Methanol is the most commonly used co-solvent and its influence can be further enhanced through the use of additives, *e.g.* ammonium acetate. UHPSFC can be easily coupled to a mass spectrometer using an atmospheric pressure ionisation source with a flow splitter. Further a make-up solvent, such as methanol with formic acid, is added to the splitter configuration to enhance performance and aid ionisation. This is particularly crucial if separation is achieved with low levels of modifier *e.g.* below 5% co-solvent.

EXPERIMENTAL

Chemicals. Methanol (LC-MS grade) and dichloromethane (HPLC grade) were purchased from Thermo Fisher Scientific (Loughborough, UK). Food grade carbon dioxide was purchased from BOC Special Gases. Ammonium acetate was purchased from Sigma−Aldrich (Gillingham, UK). ACCUTRACE™ S10 fuel marker and the deuterated internal standard, d21-S10 and a variety of dosed fuel samples were supplied by Innospec Ltd (Ellesmere Port, UK).

S10 Stock Solution. A total of 0.0100 g of ACCUTRACE™ S10 fuel marker was dissolved in dichloromethane (10 g) to give a 1000 mg/kg (1000 ppm) S10 solution. Alternatively 25 µL of 20% ACCUTRACE™ S10 solution (in aromatic solvent) was dissolved in dichloromethane to give a total volume of 5 mL, *i.e*., standard solution of 1000 µL/L (1000 ppm). Either of these solutions was then used as the nominal working solution and further diluted with methanol.

Internal Standard (d21-S10) Solution. A total of 0.00100 g of deuterated internal standard d21-S10 was dissolved in dichloromethane (10 g) to give a 1000 mg/kg (1000 ppm) internal standard solution. This solution was then used as the nominal working solution and further diluted with methanol.

Sample Preparation. A variety of fuels, doped with ACCUTRACE™ S10 fuel marker, were supplied by Innospec Ltd, and these samples were used undiluted and analysed by UHPSFC−MS.

GC−MS. 70 eV electron ionisation mass spectra were recorded using a Trace GC-MS (Thermo Finnigan, Manchester, UK) equipped with an RTX-5 fused silica capillary column (Restek Corporation, Bellefonte, PA, USA), 30 m x 0.25 mm i.d., 0.25 µm film thickness. 1 µL samples were introduced *via* a splitless injector at a temperature of 240°C. The oven temperature program used was 40°C for 5 min, ramped at a rate of 15°C/ min to 240°C, then ramped at a rate of 20°C/min to 320°C and held at the final temperature for 6 min. Helium was used as carrier gas at a constant flow rate of 1.2 mL/min. Mass spectra were acquired between *m/z* 20 – 558 at a scan rate of 2 scans/second. Xcalibur™ software was used for GC−MS data acquisition and processing.

Single ion monitoring (SIM) was used to detect the base peak and molecular ion, SIM: *m/z* 455, 476, 532 and 553 (S10 base peak, d21-S10 base peak, S10 molecular ion, d21-S10 molecular ion respectively). Dwell time: 0.03 s, mass span: 0.5 *m/z* units.

UHPSFC. Separations were performed using an Acquity ultra-high performance convergence chromatograph (UPC^2, Waters, Manchester, U.K.) with a Waters HSS C18 SB packed column, 1.8 µm particle size, 3 × 100 mm. The column was held at 40°C in a column oven and 2.0 µL of each sample was injected. *sc*CO_2 with methanol (25 mM ammonium acetate) co-solvent were used for separation at a flow rate of 1.5 mL/min. The *sc*CO_2 back pressure of the system was set to 150 bar. A gradient elution was performed using the method in Table 1 and a 1 minute isocratic pre-run used for column equilibration.

Time	CO_2	Modifier
0.00	98	2
3.15	95	5
4.00	60	40
5.00	98	2
6.00	98	2

Table 1. UHPSFC gradient

Electrospray Ionisation – Mass Spectrometry (ESI-MS). Positive ion ESI mass spectra were recorded using a single quadrupole mass spectrometer (SQD2) and ESCi multi-mode ionisation source (Waters, Manchester, UK) with the following conditions: capillary voltage 3.5 kV; cone voltage 20 V; extractor 3.0 V; source temperature 150°C; desolvation temperature 350°C; desolvation gas flow 650 L/h (nitrogen) and acquisition and data processing achieved using MassLynx™ version 4.1. Mass spectra were acquired between *m/z* 80 – 1000 at a scan rate of 5 scans/second (scan time 0.20 s). An internal solvent manager (ISM) (Waters, Manchester, UK) was used to introduce the make-up solvent, methanol (50 µM ammonium acetate) at a flow rate of 0.5 mL/min.

SIM was used to detect the ammoniated S10 $[M + NH_4]^+$ and ammoniated d21-S10 $[M + NH_4]^+$, nominal *m/z* 550 and *m/z* 571 respectively. All parameters were the same as the full scan method and a dwell time of 0.010 s was used.

Calibration Solution Preparation.

ACCUTRACE™ S10 fuel marker and d21-S10 Internal standard calibration standards were prepared containing nominally 1, 5, 10, 25, 100, 250, 500, 1000, 2500 and 5000 ppb (v/v) of ACCUTRACE™ S10 fuel marker and 500 ppb d21-S10 internal standard, both using volumetric dilution of the working solutions (1000 ppm w/v) in methanol for analysis by UHPSFC-MS. The higher calibration points are on the edge and outside the linear range of the calibration curve and so dilution of the solutions is required.

Molecular Modelling. The three-dimensional structures, electrostatic potential maps and geometry optimisations were performed using Spartan’14 v1.1.8 (Wavefunction Inc., Irvine, CA, USA)[18]. The full geometry optimisation (calculation of equilibrium geometry at ground state) was undertaken using Becke’s three-parameter[19] Lee-Yang-Parr[20] hybrid density functional theory method with 6-31G** basis set[21] (B3LYP 6-31G**). The structures were optimised *in vacuo*. The surface maps were generated using the same level of theory as used for the optimised molecules.

RESULTS AND DISCUSSION

ACCUTRACE™ S10 was designed specifically for detection by GC-MS with electron ionisation the favoured ionisation technique but this new marker is not detectable using IP 298. Under EI conditions an intense molecular ion is observed at nominal *m/z* 532 (~45%) and a base peak is formed by loss of a phenyl group at nominal *m/z* 455, see Figure 2. The relatively high *m/z* of these distinctive ions improves the detection and quantitation of this compound.

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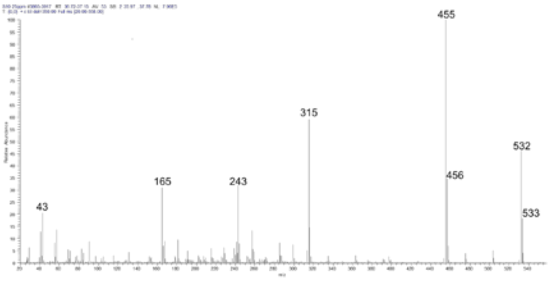

Figure 2. 70 eV EI-MS of ACCUTRACE™ S10

A GC-MS single ion monitoring (SIM) method was implemented using a more commonly available RTX-5 column (30 m x 0.25 mm i.d., 0.25 µm film thickness) and used with a simple legacy GC-MS instrument, namely a Trace GC 2000 with auto-sampler and single quadrupole mass spectrometer. Quantitative detection of ACCUTRACE™ S10 at the 2.5 ppm level could only be achieved immediately following cleaning of the ion source volume, (see Figure 3) and at tank dilutions the marker could not be detected. Replicate detection of ACCUTRACE™ S10 at the doping level could not be achieved without onerous and daily cleaning of the ion source volume. The results of these experiments confirm the necessity for the 2-D GC and MS approach. Unfortunately this specialist and sophisticated instrumentation and/or specialist operator is not routinely available in analytical laboratories across the fuel industry.

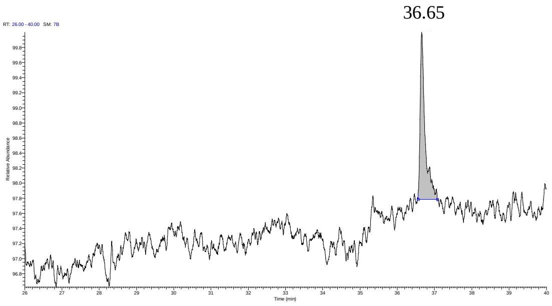

Figure 3. 70 eV EI GC-MS SIM (*m/z* 455) of ACCUTRACE™ S10 at 2.5 ppm (S/N = 15)

When the ACCUTRACE™ S10 is spiked into a fuel, the nature and complexity of the matrix requires long GC acquisition times, of the order of 45 minutes, with the fuel marker eluting at the retention time of 36.5 minutes. For legacy GC-MS systems, such as the Trace MS, detection of the ACCUTRACE™ S10 at the 2.5 ppm doping level is only achievable with a pristine ion source volume. The sensitivity and performance of the instrument decreases rapidly with repeat fuel injections demanding an ion source volume change within six analyses. Further the limit of quantitation for this legacy instrumentation is around 2 ppm. These limitations can be overcome through use of more modern, state of the art GC-MS systems but to deliver the robust and routine analytical procedure requires either the use of 2-D GC or a Deans switch. The latter approach allows the majority of the sample to be diverted to waste with only the ACCUTRACE™ S10 and its internal standard introduced to the ion source of the mass spectrometer.

UHPSFC-MS was considered as an alternative approach to GC-MS for the analysis of ACCUTRACE™ S10. The hexane-like properties of $scCO_2$ have previously been used advantageously for the analysis of biodiesel in aviation turbine fuel where the undiluted fuel was injected directly into the UHPSFC solvent stream[16]. The structure of ACCUTRACE™ S10, see Figure 1 (A), suggests that even though the molecule was designed for use with electron ionisation, it should also be an ideal candidate for atmospheric pressure photoionisation (APPI) due to its aromaticity. Further the design of the UHPSFC (Waters UPC^2) readily affords a route for introduction of an APPI dopant by replacing the make-up flow solvent (usually methanol with formic acid) with 100% toluene. When a 2.5 ppm standard solution of ACCUTRACE™ S10 was injected on to the UHPSFC column a very intense signal was observed in the total ion current chromatogram (TICC) though surprisingly this was for the sodiated molecule and not the radical cation as would be expected for dopant-assisted APPI. The production of the cationised molecule suggested that photoionisation was not taking place, and the ion formed by an ion evaporation process, therefore positive ion electrospray ionisation was investigated since this technique can readily produce cationised molecules as well as protonated molecules, see Figure 4.

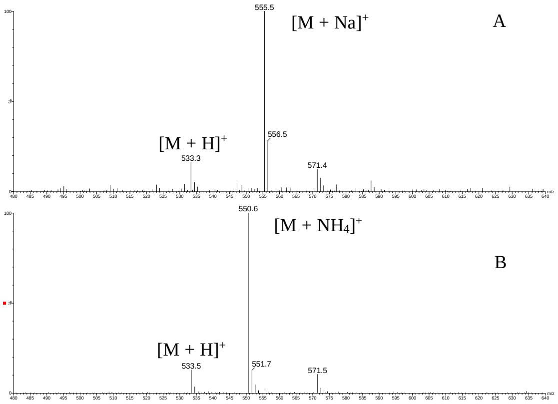

Figure 4. (A) Positive ion APPI-MS and (B) ESI-MS of ACCUTRACE™ S10

The chromatography conditions were subsequently developed and optimised, requiring 25 mM ammonium acetate additive in the methanol co-solvent. 50 µM ammonium acetate in methanol was used as the make-up flow solvent, thus promoting formation of the ammoniated molecule. Ionisation of this molecule by electrospray ionisation was still unexpected, since the fuel like structural motifs of ACCUTRACE™ S10 are not polar. For a 2 µL injection of a 2.5 ppm standard solution of ACCUTRACE™ S10 analysed using a selected ion monitoring (SIM) method a retention time of 2.43 minutes was reported. The extracted ion current chromatogram (EICC) for the ammoniated molecule *m/z* 550 gives a signal-to-noise of 766.

To explore the unexpected electrospray ionisation of this molecule, molecular modelling of the ACCUTRACE™ S10 molecule was undertaken in an attempt to determine the likely site for ionisation, see Figure 5.

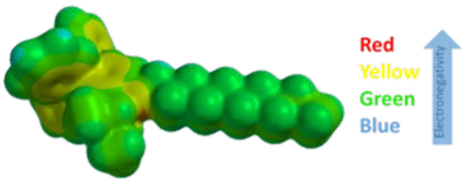

Figure 5. Molecular model of ACCUTRACE™ S10 electronegativity map.

There are no obvious basic sites for ionisation in the molecule to give the intense positive ion electrospray ionisation response. The only heteroatom in the molecule is the decyl ether oxygen atom. The electron density map shows the greatest electronegativity at the ether oxygen atom though this is not accessible due to the shape of the molecule. The ionisation event appears to be related to attraction of the cation to the highly electronegative regions of the aromatic rings. The initial experiments showed the electrospray ionisation affinity for sodium ions, but when UHPSFC-MS was used ammonium ions are present in the co-solvent and so added to the make-up flow solvent to drive ionisation to the ammoniated molecule.

The Dow Chemical Company produced an isotopically labelled version of ACCUTRACE™ S10 for use in quantitative measurements. For this molecule every hydrogen atom of the decyl ether chain is replaced with a deuterium atom to give the d21- S10 compound, see Figure 1.

A stable isotope label is used as an internal standard for quantitative analysis because this compound should have near identical chemical properties to that of the analyte, for example it should have the same extraction efficiency from the matrix, chromatographically it should co-elute with the analyte and so experience the same ionisation conditions and signal suppression issues as the analyte if they occur. Figure 6 A and B show that the ACCUTRACE™ S10 and the ACCUTRACE™ d21-S10 are chromatographically separated by GC-MS and UHPSFC-MS respectively, with the isotopically labelled isomer eluting first in both cases. The degree of chromatographic separation must be due to the high number of incorporated deuterium atoms, where three or five deuterium atoms would be the norm for an isotopically labelled internal standard. The excessive deuteration compromises the use of the d21-S10 as a stable isotope labelled standard and so it should be treated as an analogue internal standard for ACCUTRACE™ S10 quantitation purposes.

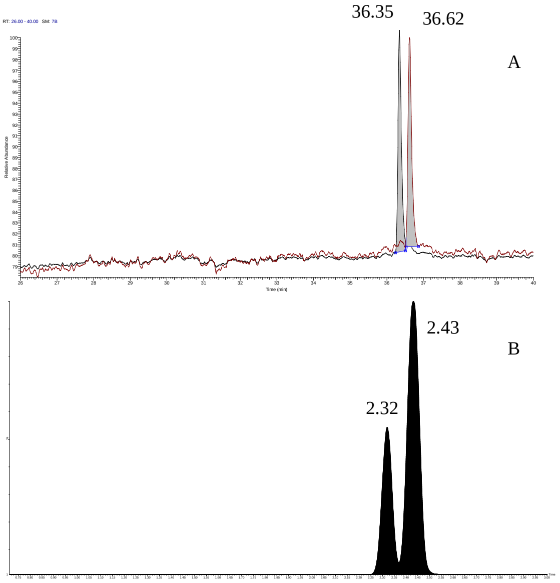

Figure 6. SIM chromatograms of molecular species for (A) GC-MS and (B) UHPSFC-MS showing chromatographic separation of ACCUTRACE™ d21-S10 and ACCUTRACE™ S10 respectively (labelled S10 eluting earliest in both cases)

All of the calibration standards were prepared in methanol (solvent used to allow direct comparison with infusion ESI-MS, dichloromethane solutions showed no change in chromatography or detection limits, data not shown) and were analysed using the optimised UHPSFC-MS method using the SIM methods for ACCUTRACE™ S10 (*m/z* 550). The ACCUTRACE™ d21-S10 was used as an internal standard at 500 ppb with the SIM method (*m/z* 571). Lower limit of quantification (LLOQ) of 5 ppb (S/N 21:1) was used for ACCUTRACE™ S10 in methanol with a calibration curve showing an R^2 value of 0.9972 as shown in Figure 7.

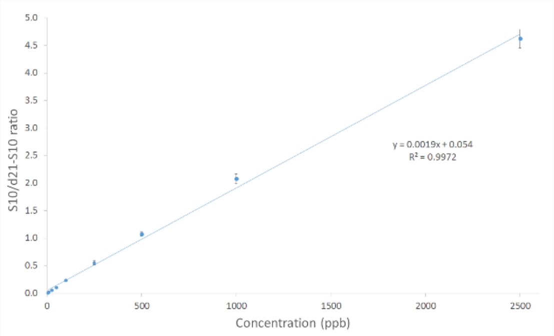

Figure 7. Calibration curve for ACCUTRACE™ S10 (number of replicate measurements = 5)

Table 2 shows the experimental and measured ratios for ACCUTRACE™ S10 and d21-S10 highlighting that this simple ratio can be used to easily determine the concentration of the level of fuel marker.

Concentration ACCUTRACE™ S10 fuel marker (ppb)	Ratio of S10/d21-S10 (Concentration of d21-S10 = 500 ppb)		Error
	Calculated	Measured	s.d.
5	0.01	0.011	0.001
10	0.02	0.021	0.002
25	0.05	0.055	0.001
50	0.1	0.104	0.004
100	0.2	0.231	0.016
250	0.5	0.552	0.037
500	1	1.077	0.041
1000	2	2.078	0.089
2500	5	4.624	0.171

Table 2. Ratio of ACCUTRACE™ S10 to d21-S10 internal standard.

For the 1 and 2.5 ppm measurements dilution of the sample before addition of the internal standard would improve the precision of measurement.

The LLOD and LLOQ achieved using this UHPSFC-MS can be further improved though the use of selected reaction monitoring (SRM) where the transitions from the precursor ions to the trityl ion (*m/z* 243) product ion for both ACCUTRACE™ S10 and the ACCUTRACE™ d21-S10 are used (data not shown) though this required the use of a triple quadrupole MS.

Marked fuel is doped at 2.5 ppm (100% marked fuel) and any analytical method must be able to detect the marker at tank dilutions to the level of 25 ppb (1%). The UHPSFC-MS method used here has LLOD and LLOQ levels lower than that of a 1% marked fuel. The preferential ionisation properties of electrospray ionisation is also an added advantage to the analysis of ACCUTRACE™ S10 in doped fuels since the base fuels are not ionised by electrospray ionisation due to the lack of suitable functional groups and so are invisible in the UHPSFC-MS chromatograms.

To test the validity of this new method, six different fuel stocks, reported to have been doped at the point of origin with 2.5 ppm with ACCUTRACE™ S10 were analysed and returned an average concentration of 2.67 ± 0.4 ppm. The accuracy and precision of the original doping process is unknown.

CONCLUSIONS

The new UHPSFC-MS method has proven to be a quick, robust and quantitative assay for the determination of ACCUTRACE™ S10 fuel marker. The method has an analysis time of 8 minutes and is approximately 5 times faster than the recommended GC-MS method.

UHPSFC-MS is compatible with injections of neat fuel (containing S10) with the addition of the internal standard, and is sufficient to detect and quantify S10 with little or no source cleaning issues that are observed with the use of simple GC-MS instrumentation.

The unexpected and favourable ionisation of the ACCUTRACE™ S10 fuel marker under positive ion electrospray ionisation conditions also means that it is easier to detect in doped fuels at tank dilution levels as the fuel components remain invisible under these ionisation conditions.

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Notes
The authors declare no competing financial interest.

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