



Battling Fuel-Washing: Detection of Accutrace S10 in Commercial Diesel Samples

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Key Words: Petroleum, Diesel, Fuel Marker, Benchtop GC-TOFMS, Fuel Washing

1. Introduction

Government-subsidized farm fuels are often dyed to distinguish them from consumer diesels. "Fuel-washing", where dye is removed from fuel that is subsequently resold at a higher price, has been a major concern for many tax, regulatory, and law enforcement agencies. Accutrace S10, a new fuel marker developed for use in the UK, is more difficult to remove and can be detected at low concentrations to prevent dilution and illegal reselling of fuel. According to the UK agency HMRC (Her Majesty's Revenue and Customs), advanced fuel marker analyzers should be able to quantitate the fuel marker in diesels that have been diluted by up to a factor of 100, a requirement easily met by the Pegasus[®] BT in less than 15 minutes without additional sample preparation.

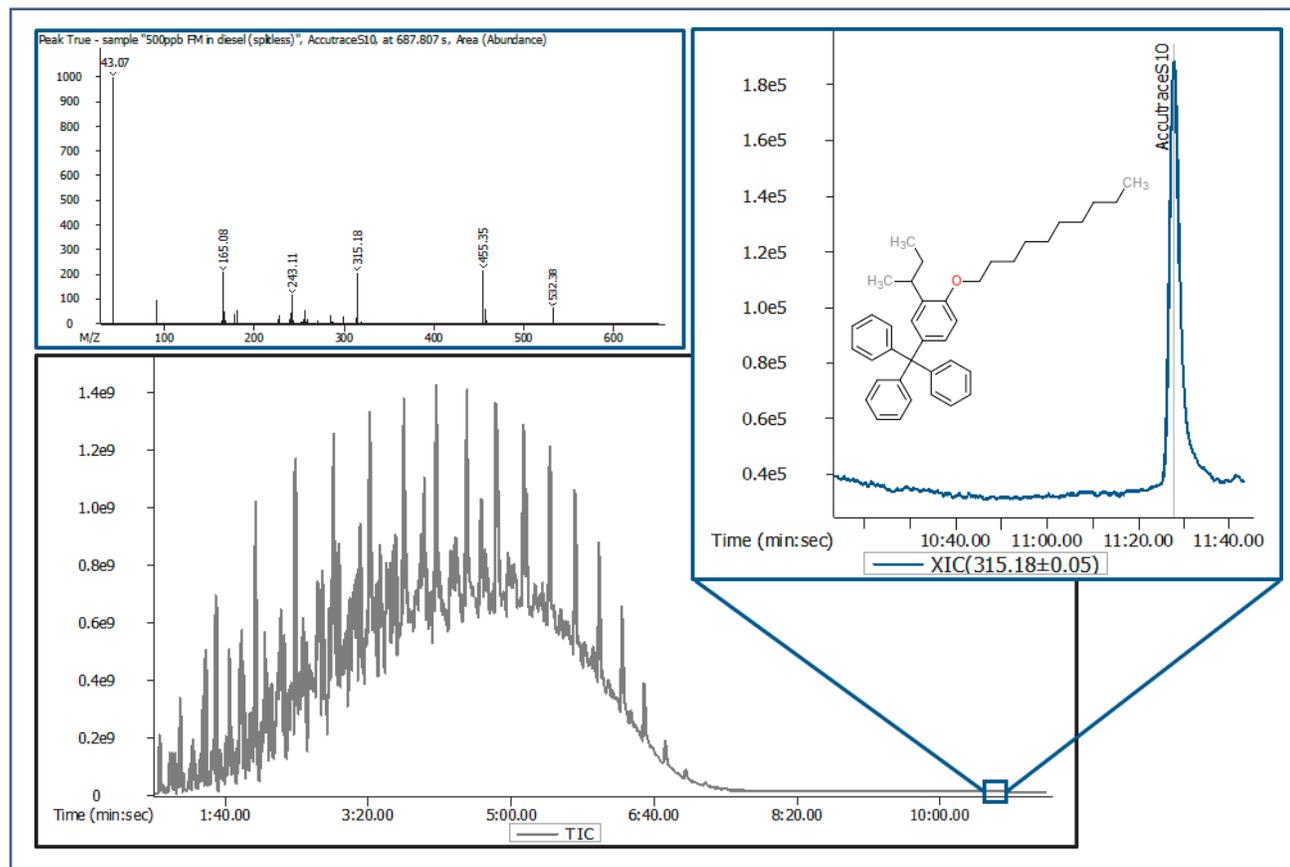


Figure 1. The full TIC chromatogram of a spiked commercial diesel sample is shown along with a deconvoluted Peak True spectrum for the fuel marker compound. The zoomed inset shows a characteristic mass trace of the fuel marker, Accutrace S10, at a concentration of 500 ppb, the required detection limit for a roadside analyzer.

2. Experimental

Commercially available diesel samples were spiked with Accutrace S10 purchased from LGC and analyzed with full mass range acquisition on a new benchtop GC-TOFMS system. ChromaTOF[®] brand software was used to identify the fuel marker in matrix at low ppb concentrations, utilizing peak finding with both deconvolution and Target Analyte Find features.

Table 1. GC-TOFMS (Pegasus BT) Conditions

Gas Chromatograph	Agilent 7890 with Agilent 7693 Liquid Autosampler
Injection	1 μ L injection, Pulsed Splitless @ 250°C
Carrier Gas	He @ 1.4 mL/min, Constant Flow
Column	Rxi-5ms, 15 m x 0.25 mm i.d. x 0.25 μ m coating (Restek, Bellefonte, PA, USA)
Oven Program	50°C (1.5 min), to 320°C @ 34°C/min (4 min)
Transfer Line	250°C
Mass Spectrometer	LECO Pegasus BT
Ion Source Temperature	250°C
Mass Range	35-650 m/z
Acquisition Rate	10 spectra/s

3. Results and Discussion

Samples were initially processed with automated deconvolution to identify the fuel marker in matrix. While no NIST library spectrum for Accutrace S10 exists, the combination of full mass range spectral information and retention time correlation with the neat standard allowed for confident identification of the fuel marker compound.

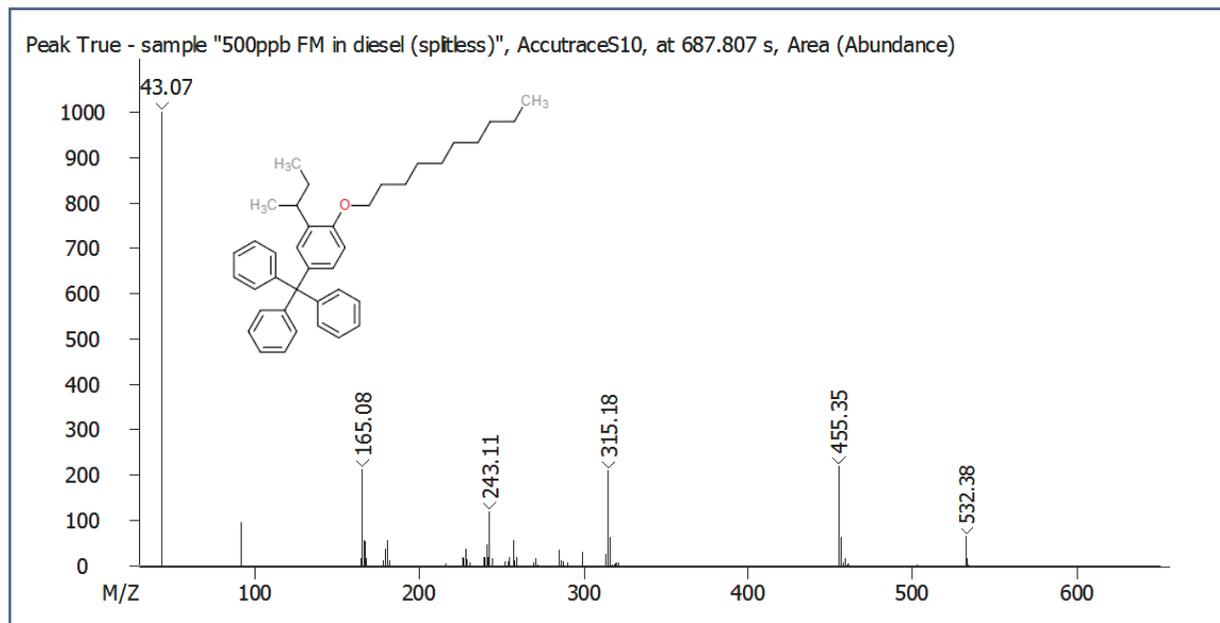


Figure 2. The deconvoluted Peak True mass spectrum of the Accutrace S10 peak is shown above, with major fragments labelled.

Target Analyte Find was then used to quickly and selectively pick out the fuel marker peak and quantitate on m/z 315.18 to build a quantitation method. Using this data processing method, the fuel marker was detected with S/N greater than 10 at levels as low as 10 ppb in matrix, which is 2.5 times more sensitive than the minimum detection requirement of 25 ppb set by the HRMC for an advanced analyzer. The linear dynamic range encompasses the full range of 100% subsidized fuel at 2500 ppb to even lower than the 1% dilution of subsidized fuel at 10 ppb, as shown in the calibration curve below (Figure 3).

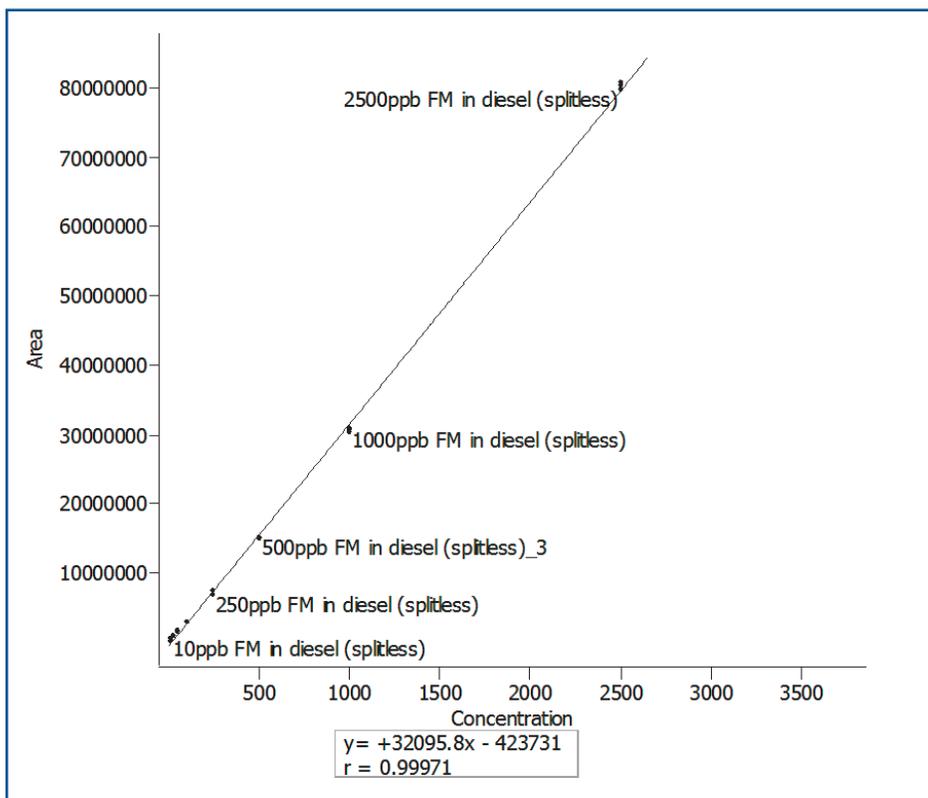


Figure 3. The excellent quantitative ability of the Pegasus BT is demonstrated in this linear calibration curve for the fuel marker, Accutrace S10. Concentrations ranged from 10ppb up to 2500ppb, with each concentration represented in triplicate.

4. Conclusion

Without the need for any additional separation methods or sample preparation such as heart-cutting or further distillation, spiked diesel samples were analyzed in runs of less than 15 minutes, allowing for quantitation in the concentration range of 2500 ppb to 10 ppb, corresponding to ranges of 100% subsidized fuel to less than 1% subsidized fuel and exceeding the HRMC targeted quantitation range on the Pegasus BT. This quick analysis that is both simple and quantitative is an excellent addition to the arsenal in the war against fuel-washing.



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