

Battling Fuel-Washing: Identification and Quantification of Accutrace S10 in Diesel Samples Using a New Benchtop GC-TOFMS System

Christina N. Kelly, David E. Alonso, Jonathan D. Byer, Lorne M. Fell, Joseph E. Binkley | LECO Corporation, St. Joseph, MI

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 United Kingdom, 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.



LECO Pegasus BT GC-TOFMS

Methods

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

Gas Chromatograph	Agilent 7890 with Agilent 7693 Liquid Autosampler
Injection	1 µL, 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 µm 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

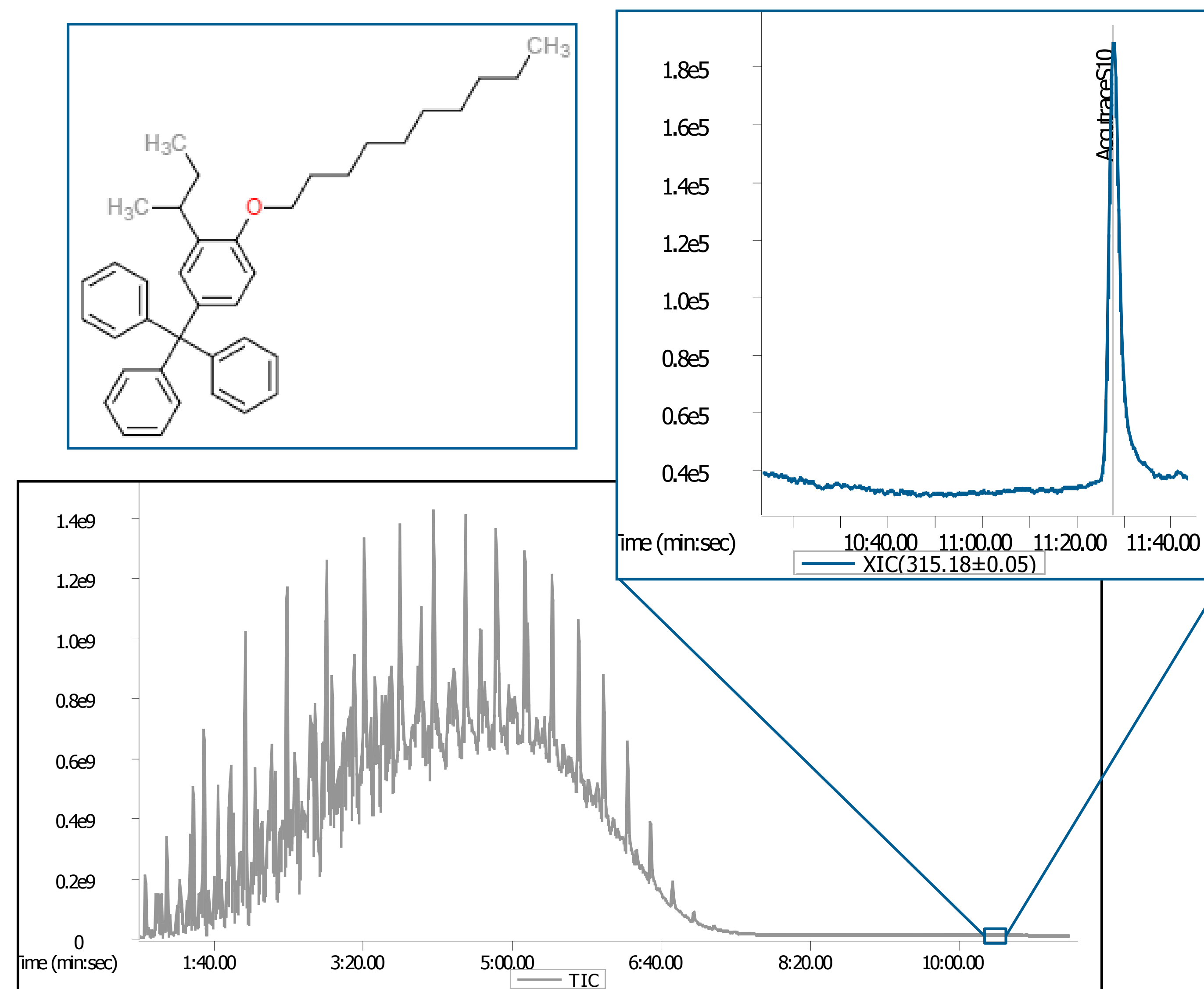


Figure 1: The total ion chromatogram (TIC) of a commercial diesel sample is shown above, along with the structure of the Accutrace S10. The zoomed inset shows the fuel marker peak spiked in at a concentration of 500 ppb.

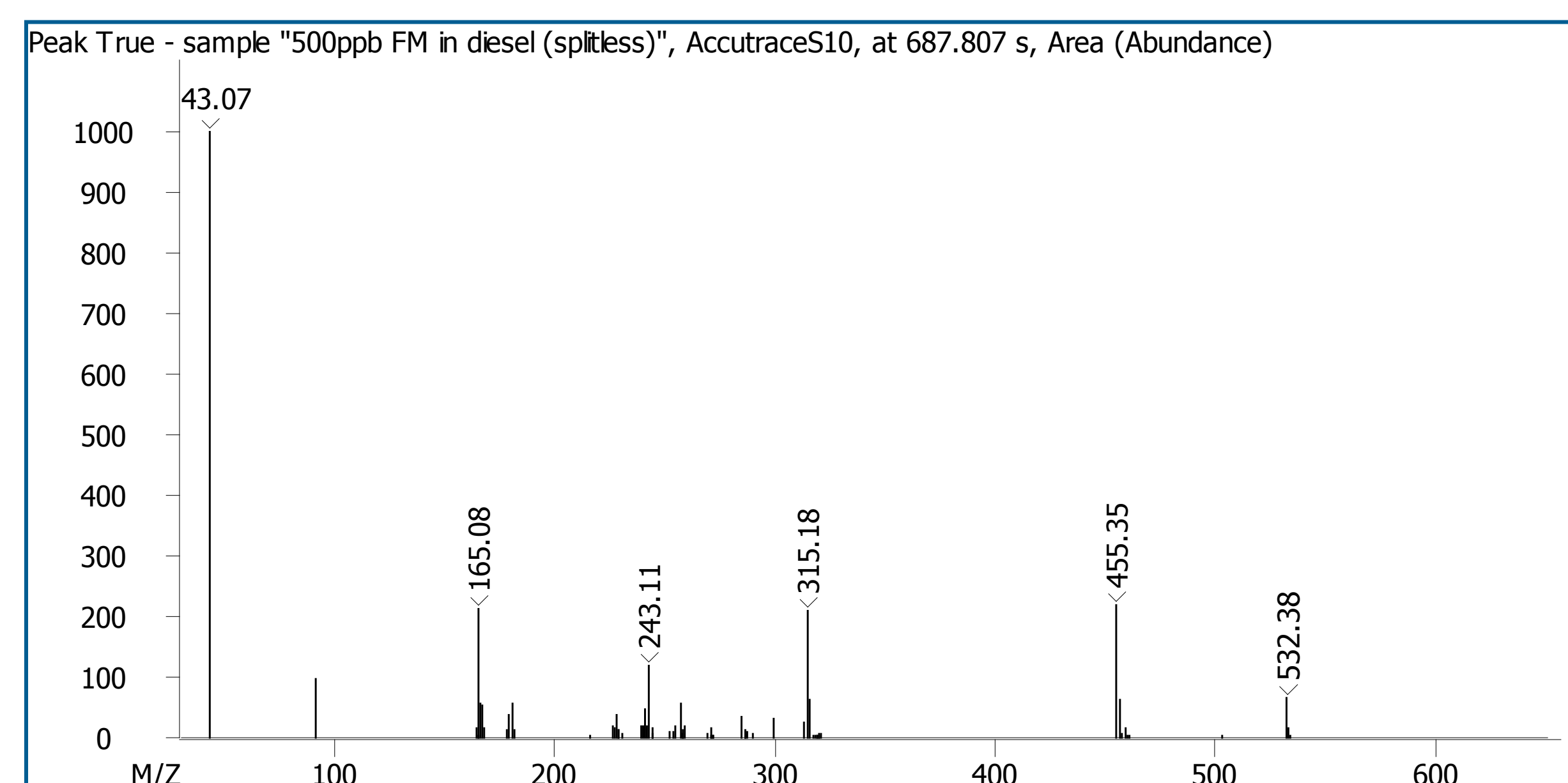


Figure 2: The deconvoluted Peak True spectra for the fuel marker, Accutrace S10, is shown above.

Results

Samples were initially processed with Automated Peak Find with NonTarget Deconvolution to identify the fuel marker peak 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.

Target Analyte Find was then used to pick out the fuel marker peak and quantitate on m/z 315 more quickly and selectively 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.

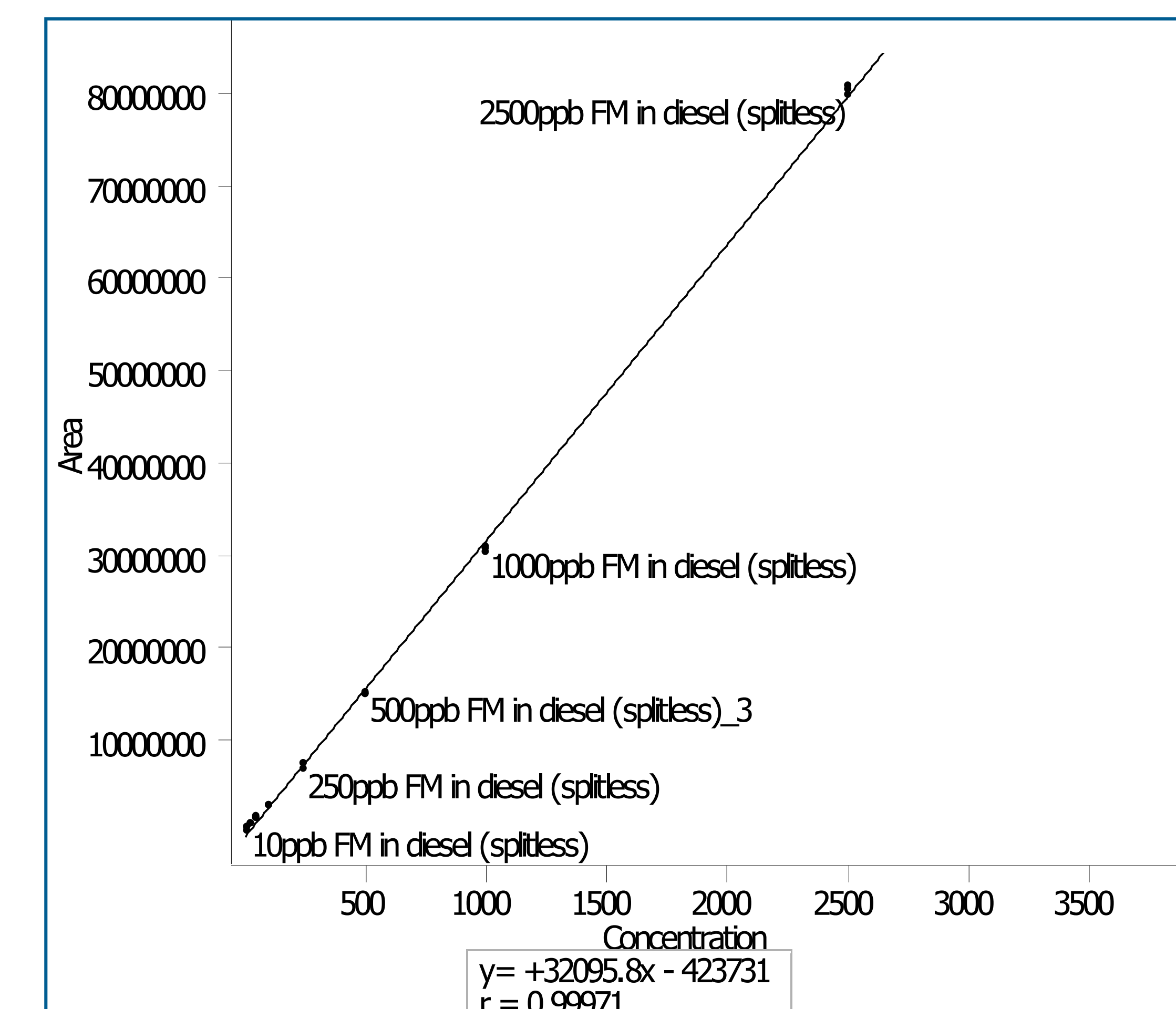


Figure 3: A linear calibration curve was generated for the fuel marker spiked in diesel from 10 ppb to 2500 ppb with an R value greater than 0.999 for accurate quantitation.

Conclusions

Without the need for any additional separation methods or sample preparation such as heart-cutting or further distillation, spiked diesel samples were analyzed in less-than-15-minute runs that allowed 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. This quick analysis that is both simple and quantitative is an excellent addition to the arsenal in the war against fuel-washing.