CHEMICAL & ENERGY ANALYSIS

FUEL MARKER ANALYSIS IN DIESEL FUEL USING 2D-GC/MS

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Solution Note

Chemical and Energy

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GC/MS Configuration

7693A Auto-Liquid Sampler

7890B Gas Chromatograph with Multimode Inlet, Capillary Flow Deans Switch and Flame Ionization Detector

5977A Single Quadrupole Mass Spectrometer with Extractor Ion Source

Abstract

This Solution Note demonstrates the analysis of a new fuel marker in diesel fuel by 2-Dimensional GC/MS. A Capillary Flow Technology (CFT) Deans Switch is employed to provide a robust and sensitive analytical solution for the detection and quantitative analysis of the fuel marker down to low ppb levels by direct injection of diesel fuel.

Introduction

Tax avoidance can cause Governments to lose enormous sums of money every year. There are many forms of tax avoidance, including avoiding paying tax on commodities such as alcohol, tobacco and fuel. In the United Kingdom, Ireland and many other countries, fuel designated for agricultural use in farm vehicles, farm machinery etc attracts a lower rate of tax duty compared to fuel designated for use in road vehicles. Lower tax fuels are 'marked' with different combinations of coloured dyes to clearly identify them. 'Red Diesel' is the term commonly used to refer to lower tax fuel designated for agricultural use. It is a criminal offence to use 'Red Diesel' in road vehicles. Unfortunately, the lower cost of 'Red Diesel' has attracted the attention of criminals who 'launder' the fuel to remove the coloured dye and then profit from re-sale.

A new fuel marker (further technical details are available on request), proven to be resistant to laundering, has been developed by a leading, World-wide chemical company. Although the dye may be removed by laundering, the marker chemical remains in the fuel and can be detected and quantified by GC/MS. Typically, diesel fuel is marked at the 2.5 mg/L (2.5 ppm) level and this is referred to as 100% marked fuel.

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The diesel fuel is analysed by direct injection into the GC/MS without any sample preparation. The high concentration of diesel fuel can quickly compromise the performance of the GC/MS system due to contamination of the mass spectrometer ion source – an issue compounded by the fact that criminals may also add other components to laundered diesel fuel such as engine oil, lubricating oil or vegetable oils. Contamination of the ion source causes a rapid drop in sensitivity and necessitates frequent ion source cleaning.

A robust GC/MS method, described in this Solution Note, employs a CFT Deans Switch to divert the majority of the diesel fuel to 'waste' (an FID detector) thereby protecting the ion source from contamination and allowing extended operation without the need to clean the ion source. The CFT Deans Switch also facilitates back flush to remove higher boiling components from the primary column after the marker compound has eluted. Back flush shortens analysis cycle time by negating the need for a period of high temperature 'bake-out'. The use of an FID also enables review of the diesel fuel profile and will indicate if additional, higher boiling oils have been added to the diesel fuel.

Analysis Conditions

The analysis method employs a 7693A Auto-liquid sampler, 7890B GC with a Multimode Inlet, CFT Deans Switch, Flame Ionization Detector and a 5977A MSD with extractor ion source. Diesel fuel (1µL) is injected directly into the GC/MS using hot splitless mode. The marker is detected using electron impact ionisation and Selected Ion Monitoring (SIM) mode.

Deans Switch Operation

The use of the CFT Deans Switch is critical to providing robust analytical performance of the GC/MS system for this fuel marker analysis. The Deans Switch provides a 2-Dimensional GC method (often referred to as 'heart-cutting') that diverts the bulk of the Diesel fuel to the FID and only a small portion of the chromatogram (the heart-cut time window) in which the marker chemical elutes is transferred to the MSD. By design, the MS ion source is only exposed to a very small amount of the Diesel fuel with each injection and that is the small amount of matrix that elutes along with the marker compound. After the marker compound has eluted, the system uses post-run back flush to remove any remaining high boilers from the primary column. The 4 stages of Deans Switch operation are shown in Figure 1.

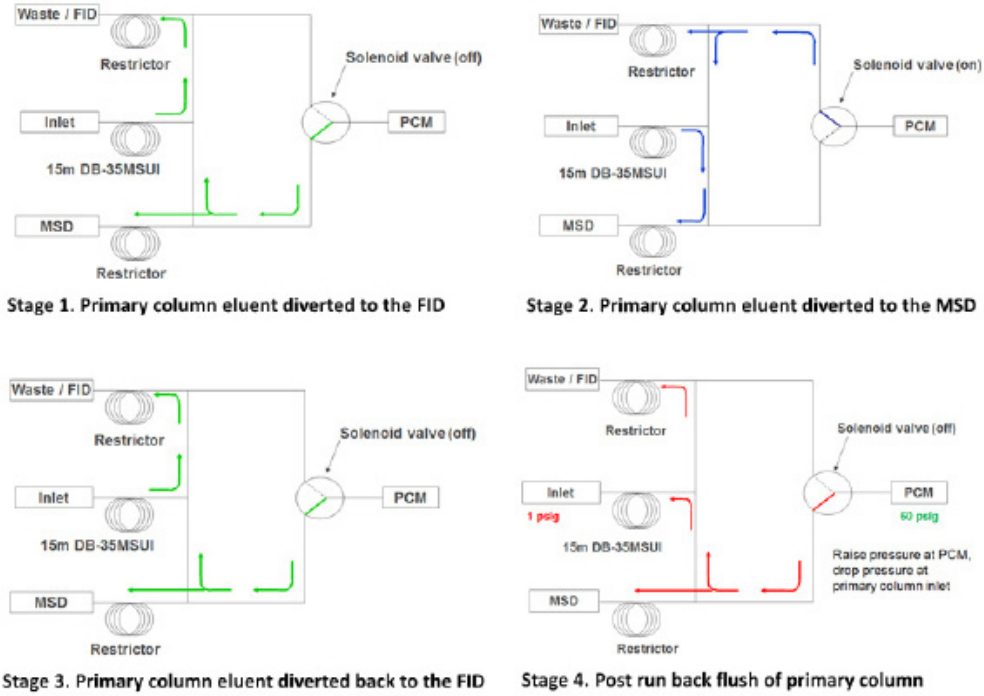

Figure 1. The four stages of Deans Switch operation to perform heart-cut and post-run back flush (Carrier gas flow path is designated by the coloured arrows).

In order to reduce the amount of Diesel fuel matrix transferred to the MSD it is important to employ as a short heart-cut window as possible. A diagram showing the switching of the Deans Switch during and after the analysis is shown in Figure 2.

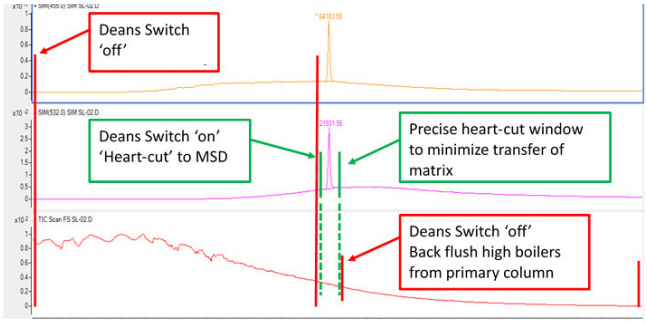

Figure 2. Deans Switch operation showing timing of heart-cut and post-run back flush

The FID and SIM EIC chromatograms (m/z 455 and m/z 532) for the diesel fuel calibration standard spiked at 50 ppb (2%) are shown in Figure 4. The inset shows the SIM EICs in more detail.

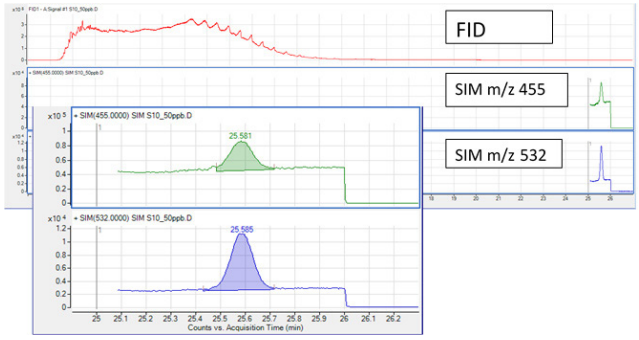

Figure 4. FID and SIM chromatograms for a 1µL hot splitless injection of Diesel fuel marked at 50 ppb (2%)

Results

The GC/MS was calibrated by adding the marker chemical to blank (un-marked) Diesel fuel across a concentration range of 25 ppb to 2.5 ppm (equivalent to 1% -100% concentration in marked fuel). A five point calibration was performed using 1uL hot splitless injections and SIM mode. A linear response was obtained over the range of interest with an R^2 value of 0.99995. The external standard calibration curve is shown in Figure 3.

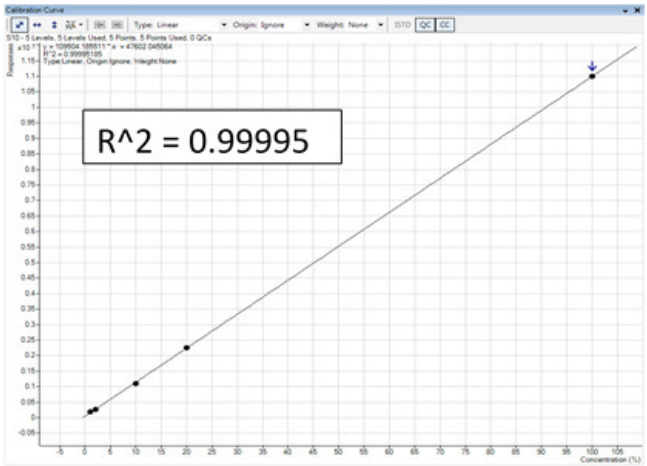

Figure 3. Calibration curve for quantitative SIM ion (m/z 455)

Another important aspect of this application is that there should be no carry-over between samples. An injection of Diesel fuel spiked at 2.5 ppm (100%) was made, immediately followed by a blank (un-marked) Diesel fuel sample. The resultant SIM EIC chromatograms are shown in Figure 5 and these demonstrate that no carry-over is occurring even after a diesel fuel marked at 100% is injected.

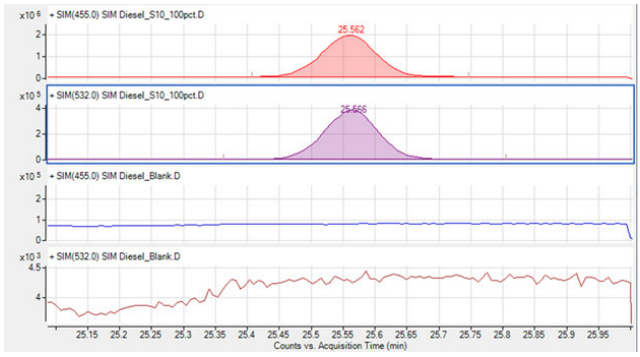

Figure 5. SIM EICs for a 2.5 ppm (100%) marked diesel fuel (upper 2 chromatograms), immediately followed by an injection of un-marked diesel fuel (lower 2 chromatograms).

Quantitative repeatability was calculated by performing a sequence of 12 replicate injections of Diesel fuel marked at a concentration of 50 ppb (2%). The retention time, peak area and quantitative results are shown in Table 1. The quantitative repeatability was less than 10%.

Inj#	Name	RT	Peak Area	Calc. Conc. (%)
1	S10 2% Marked	25.579	277873	1.93
2	S10 2% Marked	25.572	276455	1.92
3	S10 2% Marked	25.572	273542	1.89
4	S10 2% Marked	25.559	278537	1.94
5	S10 2% Marked	25.555	272510	1.88
6	S10 2% Marked	25.554	272845	1.88
7	S10 2% Marked	25.556	335886	2.46
8	S10 2% Marked	25.537	298019	2.11
9	S10 2% Marked	25.553	304592	2.18
10	S10 2% Marked	25.530	290717	2.05
11	S10 2% Marked	25.515	312534	2.25
12	S10 2% Marked	25.538	286367	2.01
	Mean	**25.552**	**289990**	**2.04**
	Std Devn	**0.019**	**19627**	**0.18**
	%RSD	**0.074**	**6.77**	**8.81**

Table 1. Repeatability data for a sequence of 12 injections of diesel fuel marked at 50 ppb (2%)

Summary

The detection and quantitative analysis of a new fuel marker in diesel fuel poses many challenges to the analyst. Not least of these challenges is the rapid deterioration in sensitivity caused by the contamination of the GC/MS ion source due to the large amount of diesel fuel injected on to the column with each analysis.

The 7890B / 5977 Extractor GC/MS system employing a capillary flow technology Deans Switch for heart-cutting and capillary column back flush, provides robust, sensitive and accurate analysis of the fuel marker across the range of interest (25 ppb – 2.5ppm) in diesel fuel.

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