

Robust, Sensitive, and Reliable ACCUTRACE™ Plus Fuel Marker Analysis by Two-Dimensional GC/MS Using Hydrogen as the Carrier Gas

Authors

Luca Godina and
Remko van Loon
Agilent Technologies, Inc.

Abstract

Fuel marking is an authentication method used by governments to ensure that the national fuel supply comes from a legal source and complies with the regional standards. It is necessary to have a solid method to deter illegally traded fuel. At the same time, laboratories are reducing their helium dependence due to its high cost and they desire methods that use alternative carrier gases without sacrificing chromatographic performance.

This application note demonstrates the analysis of a newly introduced fuel marker in diesel fuel by two-dimensional GC/MS with the use of hydrogen as the carrier gas. A capillary flow technology (CFT) Deans switch is used to provide a robust and sensitive analytical solution for the detection and quantitative analysis of the fuel marker. It allows analysis down to low mg/L levels by direct injection of diesel fuel, to comply with all regional regulations.

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 fuel. In different countries, fuel designated for agricultural use in farm vehicles and machinery, for example, as well as fuel oil for heating purposes, attracts a lower tax duty rate than fuel designated for use in road vehicles. Lower-tax fuels are "marked" with different combinations of colored dyes to identify them clearly. It is a criminal offence to use different fuels than the ones allowed for specific vehicles.¹

The European Commission has established a common fiscal marker for gas oils and kerosene. Its commercial name is ACCUTRACE™ Plus, developed by a worldwide leading chemical company, and it contains butoxybenzene as the preferred marker. The European Commission also states that every member shall set a marking level of this new marker to be at least 9.5 mg of butoxybenzene per liter, and not more than 14.25 mg of butoxybenzene per liter of energy product.²

Experimental

Chemical and reagents

- Butoxybenzene (CAS registration number 1126-79-0) and all solvents were purchased from VWR, Germany. Unmarked diesel was purchased directly from a local petrol station.
- All standards were prepared and diluted in *m*-xylene.
- All the analyses were carried out using hydrogen as the carrier gas.
- A six-point calibration curve was prepared from pure butoxybenzene at the following concentrations: 0.05, 0.1, 0.2, 0.5, 1.0, and 10 mg/L.

Instruments and method

An Agilent 8890 GC system, including:

- Split/splitless inlet
- Flame ionization detector
- Pneumatic switching device (PSD)
- Deans switch
- Agilent J&W DB-17ht GC column, 15 m × 250 μm, 0.15 μm
- Agilent J&W DB-WAXetr GC column, 30 m × 250 μm, 0.5 μm

An Agilent 5977B GC/MSD, including:

- Extractor source
- Extractor lens, 9 mm
- SIM mode for *m/z* 94 and 150, with a 100-millisecond dwell time

All the method parameters are available in Table 1.

Table 1. GC/MS method.

Agilent 8890 GC system			
Oven	°C/min	Hold (°C)	Hold (min)
	10	100	1
	30	165	0.5
		240	0.5
Inlet (Split/Splitless)			
Liner	p/n 5190-2295		
Temperature	250 °C		
Mode	Split		
Split Ratio	70:1		
Column 1			
Column	Agilent J&W DB-17ht, 15 m × 250 μm, 0.15 μm (p/n 122-1811)		
Mode	Ramped flow		
Column 1 Flow Settings	Rate	Flow	Hold Time
	100 mL/min	1 mL/min –2 mL/min	4 min End of the run
Column 2			
Column	Agilent J&W DB-WAXetr, 30 m × 250 μm, 0.5 μm (p/n 122-7333)		
Mode	Constant pressure		
Pressure	9.7 psi		
Column 3			
Retention Gap	0.48 m, 100 μm, 0 μm		
Mode	Constant pressure		
Pressure	9.7 psi		
Deans Switch			
Time (min)	Setpoint		
3.68	On		
3.78	Off		
Agilent 5977B GC/MSD			
Acquisition Mode	SIM		
Gain Factor	1		
SIM Ions			
<i>m/z</i>	Dwell Time		
94	100		
150	100		

Deans switch setup

The use of the CFT Deans switch is critical to providing the robust analytical performance required for this fuel marker analysis. The Deans switch provides a two-dimensional GC method (often referred to as "heart cutting"). It 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 and is transferred to a second column, with different polarity, and is analyzed by 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 a post-run backflush to remove any remaining high boilers from the primary column. The four stages of the Deans switch operation are shown in Figures 1 to 4.

In the default stage, the primary column effluent (DB-17ht) is diverted to the FID via a restrictor column, as shown in Figure 1. During the heart cut, the Deans switch valve is operated (Figure 2), and the outlet of the primary column is sent to the secondary column (DB-WAXetr). On this column, with another phase, butoxybenzene is further separated from the diesel matrix. After the heart cut time, the Deans switch valve position is changed again, so the primary column effluent is sent to the FID. The advantage of the Agilent Deans switch setup with PSD is that concurrent backflushing of the primary column can be done while the separation of the butoxybenzene is still going on in the secondary column (Figure 4). Concurrent backflushing reduces overall analysis time since there is no waiting for the remaining sample matrix to elute from the primary column.

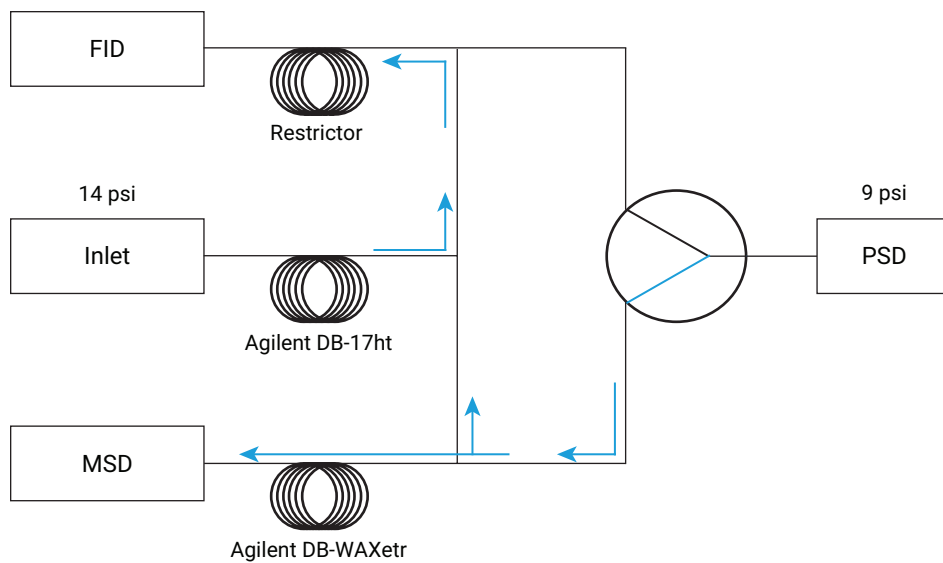


Figure 1. Primary column effluent diverted to the FID.

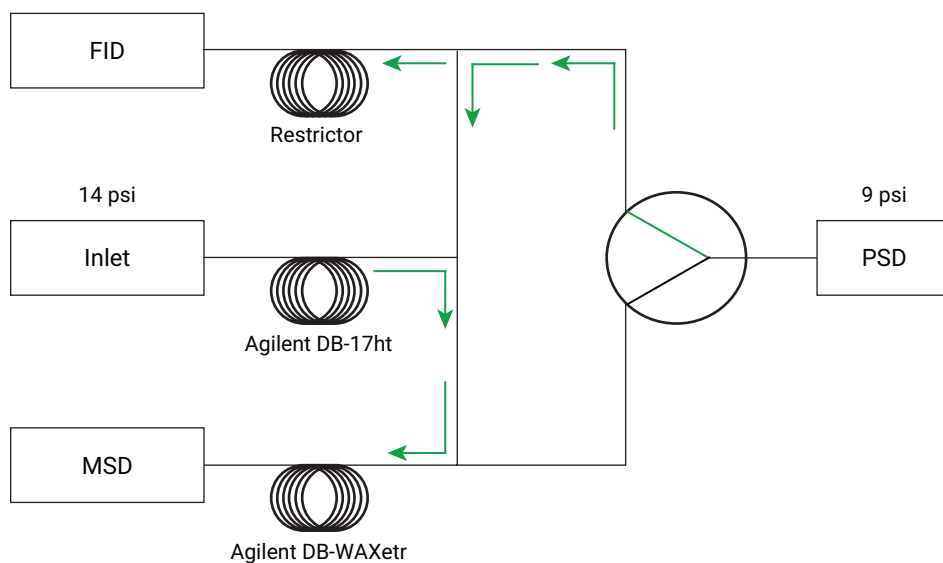


Figure 2. Primary column effluent diverted to the MSD.

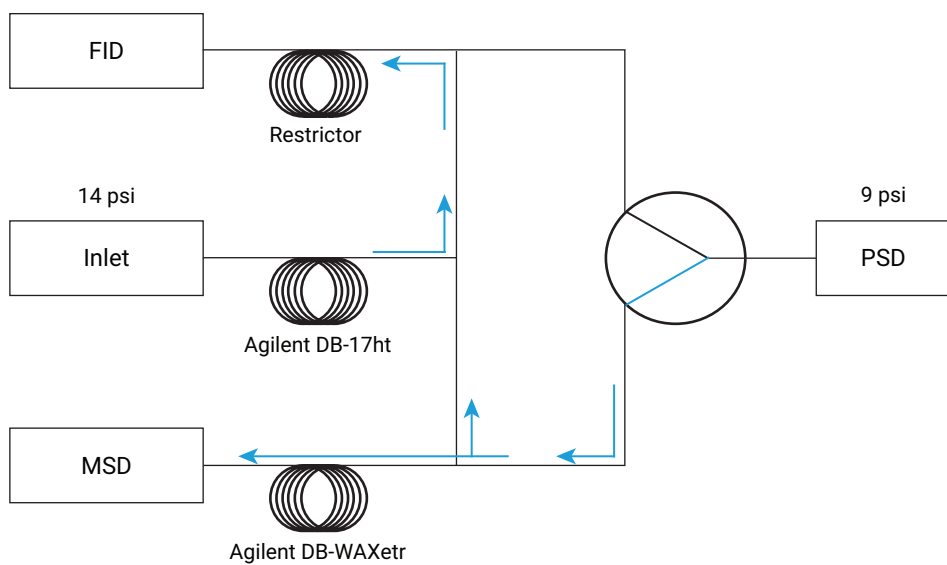


Figure 3. Primary column effluent diverted back to the FID.

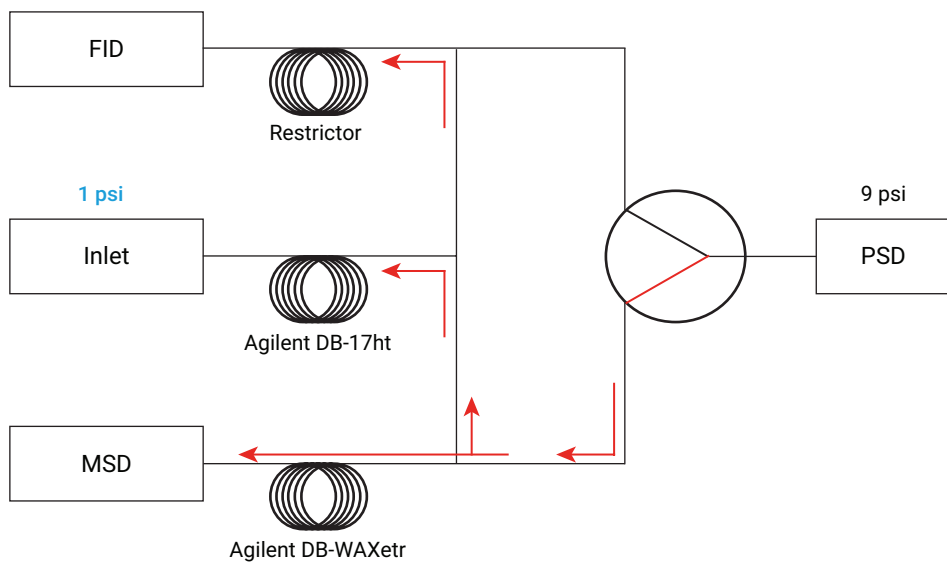


Figure 4. Concurrent backflush. Inlet pressure is dropped to 1 psi, and the heavier boilers are pushed backward into the inlet and out through the split vent line.

To reduce the amount of matrix that is diverted to the MSD, it is important to select the narrowest possible heart cut window. This ensures not only the best resolution of the compound of interest on the second column but also keeps the MSD source protected from such a high level of possible contamination. A chromatogram showing the selection of the cut window is visible in Figure 5.

Optionally, as soon as butoxybenzene is on the second column, it is possible to activate a concurrent backflush, by dropping the pressure on the inlet. This feature reduces the amount of matrix reaching the detectors and helps shorten the total run time.

Calibration

The calibration was carried out at six different concentrations between 0.05 and 10 mg/L to show that the trace-level detection capabilities of the system are also suitable for quantifying the marker even when blended with unmarked fuel (Figure 6).

The method shows a linear regression of 0.99998, with accuracies always below 10% for all the calibration points, as shown in Table 2.

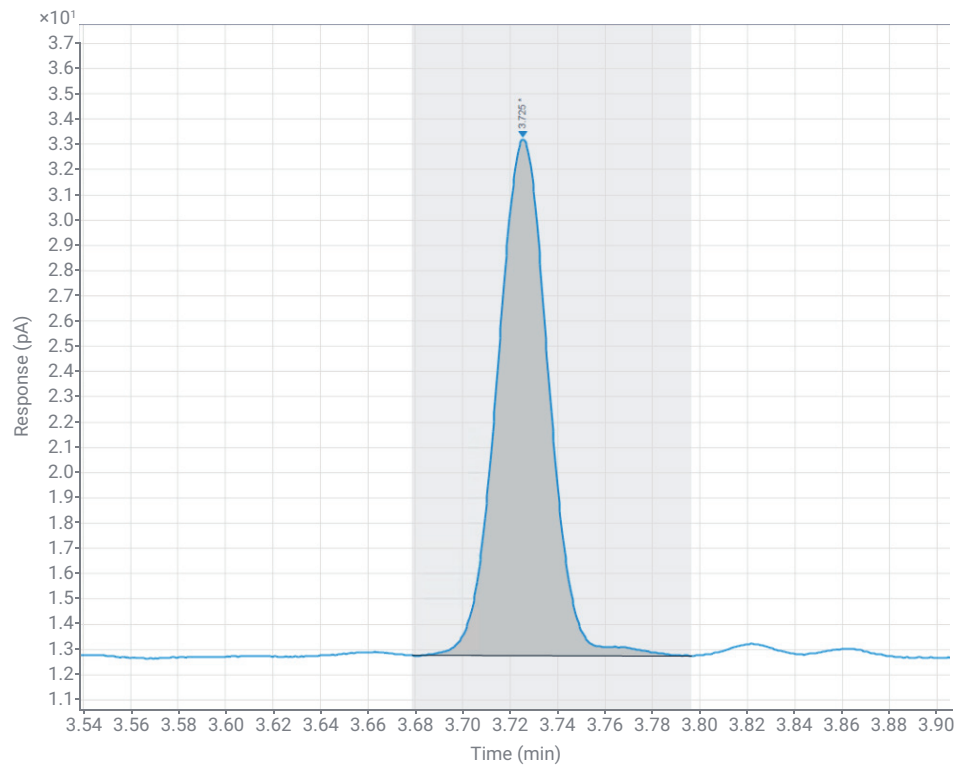


Figure 5. The heart cut window is set based on injection with the Deans switch in the off position. From this chromatogram, the window is set to be between minutes 3.68 and 3.76.

Calibration Curve

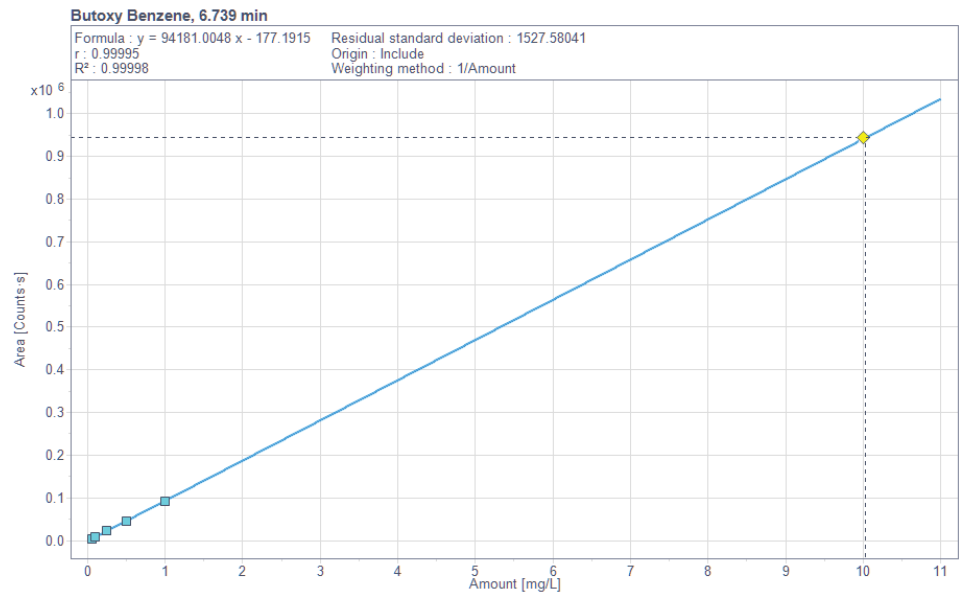


Figure 6. Calibration curve for butoxybenzene.

The method had also been tested for reproducibility in matrix analysis by injecting spiked diesel with an unknown amount of butoxybenzene 20 times (Figure 7). With an average concentration of 0.141 mg/L, the RSD (%) was calculated at 1.07%.

Table 2. Calibration accuracy for butoxybenzene.

Name	RT (min)	Area	S/N	Amount (mg/L)	Calibrated Amount (mg/L)	Accuracy (%)
Butoxybenzene	6.739	4,856.52	28.1	0.053	0.05	6.89
Butoxybenzene	6.739	8,985.51	50	0.097	0.1	-2.71
Butoxybenzene	6.739	22,939.91	110.4	0.245	0.25	-1.82
Butoxybenzene	6.739	45,799.53	331.1	0.488	0.5	-2.37
Butoxybenzene	6.740	92,623.87	677.9	0.985	1	-1.47
Butoxybenzene	6.739	944,485.47	6,425.9	10.03	10	0.3

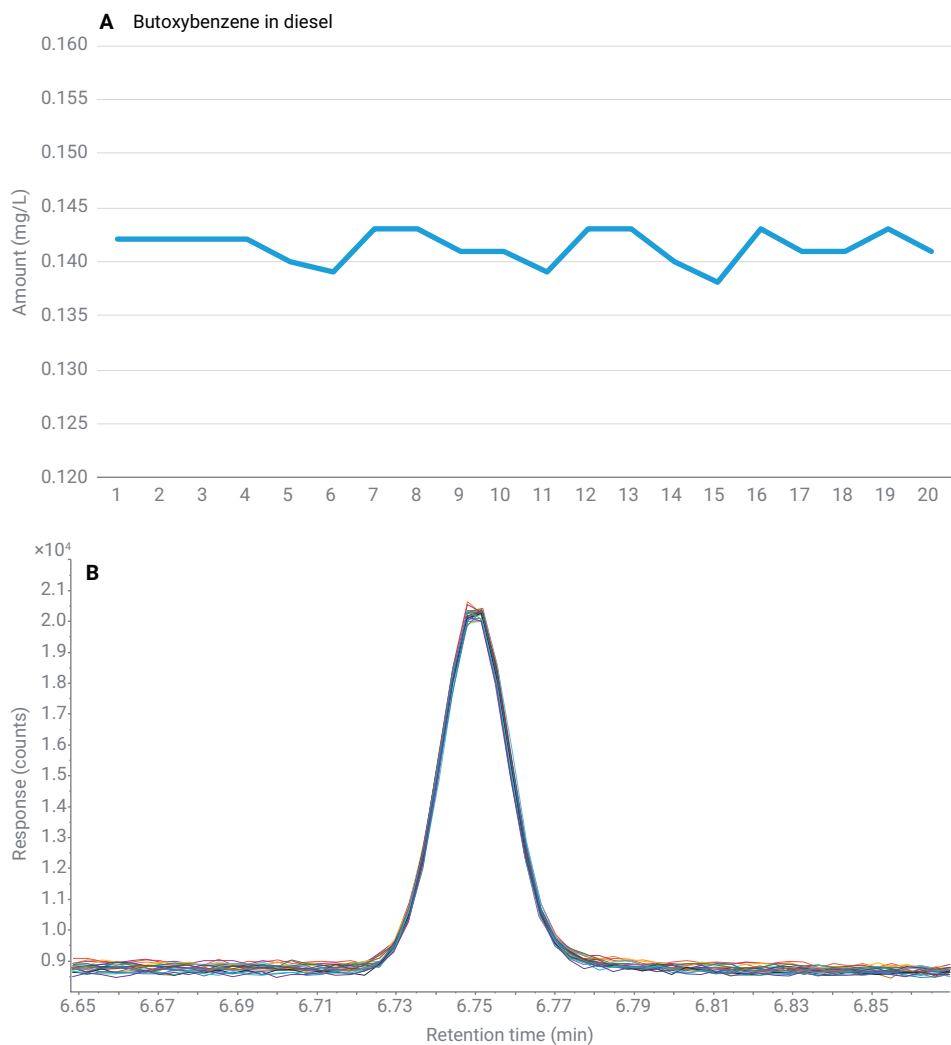


Figure 7. (A) Butoxybenzene reproducibility over 20 replicates. (B) Overlay of 20 replicates of butoxybenzene in diesel.

At the lowest calibration level of 0.05 mg/L, the peak-to-peak signal-to-noise ratio (S/N), with the noise region assigned for 0.4 minutes after the end of the peak, was 28:1 as shown in Figure 8. This indicates a method limit of detection well below the necessary measurement range.

The high precision of the Deans switch device allows for the narrowest possible heart cut from the matrix, to divert the smallest possible amount of matrix to the second column and to the MSD. As shown in Figure 9, the width of the heart cut is 0.1 minutes, and straight after the cut, the backflush can start. Figure 9 also shows the effect and clear benefit of the backflush: no matrix is visible in the FID chromatogram because all of it is flushed through the inlet split vent line.

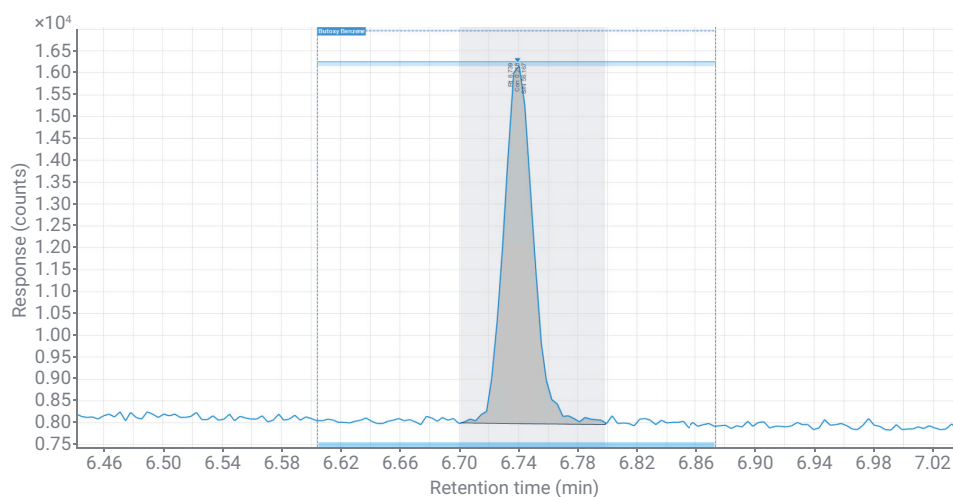


Figure 8. 0.05 mg/L butoxybenzene in xylene produces a S/N of 28:1.

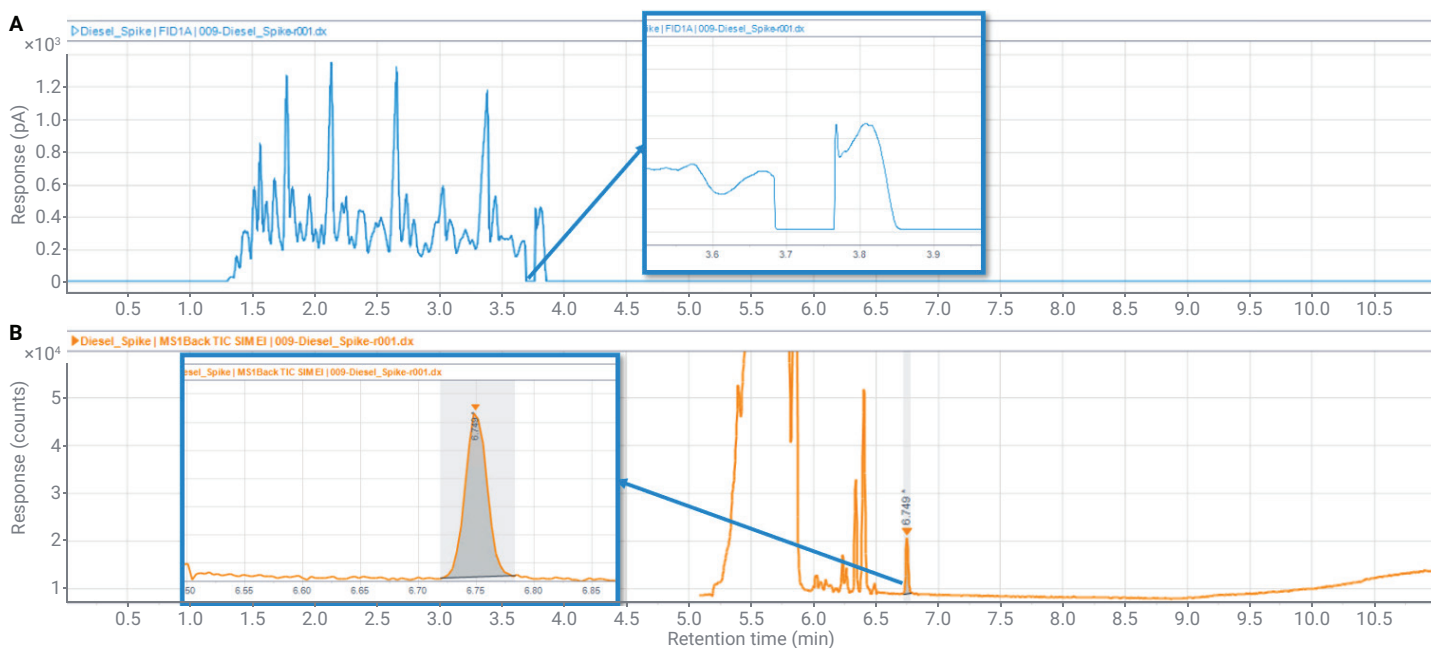


Figure 9. Heart cut window and backflush (A) of a real diesel sample spiked with butoxybenzene (B).

Conclusion

This setup allows the analysis of a newly developed fuel marker at both the specified regulatory amount (mg/L level) and when blended with unmarked fuel at low $\mu\text{g/L}$ levels. The Agilent 8890 GC system equipped with a Deans switch CFT device proves to be a robust solution for the analysis of butoxybenzene marker in diesel fuel. The results obtained with the Agilent 5977 GC/MSD with extractor ion source and hydrogen as the carrier gas satisfy the sensitivity and reproducibility requirements for this analysis, and this will help laboratories that are facing helium supply shortages. With the help of a backflush system, the run time stays well below 15 minutes. In addition, the narrow heart-cut reduces the amount of sample matrix diverted to the MS detector, which helps decrease the frequency of source maintenance.

References

1. Sandy, C. Fuel Marker Analysis in Diesel Fuel Using 2D-GC/MS, *Agilent Technologies solution note*, publication number 5991-6219EN, **2015**.
2. Establishing a Common Fiscal Marker for Gas Oils and Kerosene (notified under document C(2022) 74), *Official Journal of the European Union* L 31/52 COMMISSION IMPLEMENTING DECISION (EU) 2022/197 of 17 January **2022**.

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