Analysis of EU Fiscal Fuel Markers

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Abstract

Fuel laundering is the illegal process of removing chemical markers or dyes from government-subsidized fuel to sell as more expensive and higher-taxed fuel. In some nations, subsidized fuel is used for agricultural purposes and residential heating as well as other specific uses. Some methods for removing the chemical markers and dyes include chemical treatment, filtration, and distillation. The illegal laundering of fuel has many negative consequences for the surrounding community, such as the government missing out on the tax revenue needed to maintain critical public services; the improper disposal of chemical waste leading to the contamination of the environment; exposing humans and animals to health risks; and the creation of negative economic aftereffects with market distortion.

Countermeasures developed to combat this problem involve the development of a more sophisticated fuel marker that is harder to remove and easier to detect. This application note provides a one-dimensional GC-MS analytical method for the identification and quantitation of a commercial fiscal marker and its preferred marker compound.

Related Products

- *Rxi-5ms column, 30 m, 0.25 mm, 0.25 µm (cat. # 13423).*
- *Topaz Precision 4.0 mm ID single taper inlet liner with wool (cat. # 23305).*
- *2 mL Autosampler Vials (cat.# 21142) and Caps (cat.# 24488)*

Introduction

Fuel laundering describes an effort to remove fiscal markers from fuel, making it difficult and ineffective for most testing methods. This adulterated fuel, which is obtained at a decreased price, is then sold at a higher price [1]. To prevent tax evasion and fraud of subsidized mineral oils and fuels, governments of the European Union (EU) have adopted regulations phasing in Dow's patented ACCUTRACE Plus S10 fuel marker. This new, commercially branded fuel marker is colorless, removing the visual test barrier that fuel launderers evaded, and can be seen at incredibly low levels, withstanding common marker removal attempts. The European Commission has adopted this fuel marker at the dosage of 2.5 ppm (2.5 µg/mL) in diesel fuel. ACCUTRACE Plus S10 fuel marker (figure 1) contains butoxybenzene as the preferred marker compound in the detection of this fiscal marker [2]. Fuel marker analysis has been performed with two-dimensional GC (GCxGC) analytical methods; however, this application note provides a one-dimensional GC (1D-GC) analysis as an effective alternative.

Figure 1: Structure of the ACCUTRACE Plus S10 Fuel Marker Molecule (2-sec-Butyl-1-(decyloxy)-4-tritylbenzene)

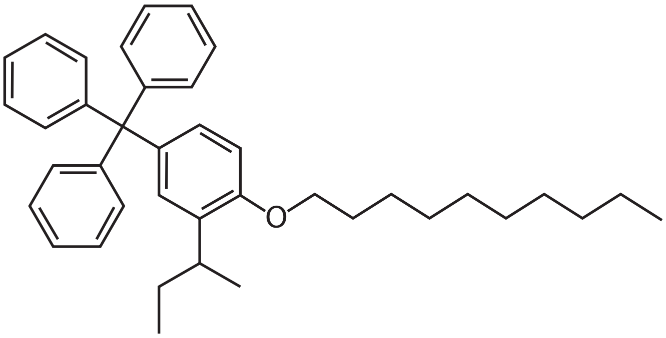
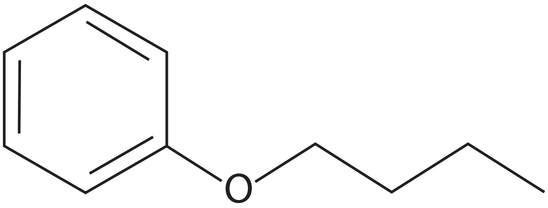


Figure 2: Structure of the Butoxybenzene Molecule



Experimental

Chemicals and Reagents

Butoxybenzene (CAS# 1126-79-0) was purchased from Sigma Aldrich. 2-*sec*-Butyl-1-(decyloxy)-4-tritylbenzene (CAS# 1404190-37-9) was purchased from LCG Standards Ehrenstorfer. All solvents were purchased from ThermoFisher Scientific. Unmarked diesel was obtained from a local gas station.

All standards were prepared in methylene chloride. All analyses were operated with helium as the carrier gas. A seven-point calibration curve was prepared for both butoxybenzene and the 2-*sec*-Butyl-1-(decyloxy)-4-tritylbenzene at the following concentrations: 0.075, 0.1, 0.125, 0.15, 0.2, 0.225, and 0.25 µg/mL. See calibration conditions below in Table I.

Instruments and Method

The instrumentation used includes an Agilent 7890 gas chromatograph (GC) system equipped with a 7693A autosampler with a split/splitless injector and a Restek Rxi-5ms column 30 m x 0.25 mm ID x 0.25 µm (cat.# 13423). A Restek Topaz Precision inlet liner, 4.0 mm x 6.3 x 78.5 (cat.# 23305) was also used.

An Agilent 5975 GC/mass spectrometer detector (MSD) with an extractor source and selected ion monitoring (SIM) mode for m/z 94, 150, 315, 455, 532 at dwell times of 60 milliseconds was used as well.

A 400-to-1 split ratio was used to minimize the amount of diesel reaching the MSD. Dirty matrices can deposit residues in the ion source of the mass spectrometer, affecting its performance and requiring frequent cleaning. Split injection limits the introduction of such residues, thus reducing maintenance needs and downtime See table I for analysis conditions.

Table I: GC-MS Method with a Calibration Curve that Ranges from 0.075 to 0.25 µg/mL to Demonstrate the Ability to Detect the Fuel Markers Even with Diluted Fuel

Agilent 7890 GC			
Oven	**°C/min**	**Hold (°C)**	**Hold (min)**
		40	1
	30	320	0
	16	330	8
Inlet (Split/Splitless)			
Liner	Topaz, Precision Inlet Liner, 4.0 mm x 6.3 x 78.5 (cat.#: 23305)		
Temperature	250 °C		
Mode	Split		
Split Ratio	400:1		
Analytical Column			
Column	Restek Rxi-5ms 30 m x 0.25 mm ID x 0.25 µm (cat.#: 13423)		
Mode	Constant Flow		
Flow	1 mL/min		

Agilent 5975C MSD	
Acquisition Mode	SIM
Gain Factor	1
SIM Ions	
m/z	**Dwell Time**
94	60
150	60
315	60
455	60
532	60

Chemicals and Reagents	
Analyte	Butoxybenzene (1126-79-0) ACCUTRACE PLUS S10 fuel marker (2-*sec*-Butyl-1-(decyloxy)-4-tritylbenzene (1404190-37-9))
Solvent (Standard Preparation)	Methylene Chloride; Diesel
Calibration Curve Concentration	0.075, 0.1, 0.125, 0.15, 0.2, 0.225, 0.25 µg/mL

Results and Discussion

Figure 3 exhibits the SIM (Single Ion Monitoring) analysis in diesel matrix (m/z 94, 150, 315, 455, 532) showing both butoxybenzene and ACCUTRACE Plus S10 fuel marker under 19 minutes using the above conditions. Notice that the sulfur compound found in the diesel fuel does not interfere with the compounds of interest. Figure 4 shows an overlay of the SIM (orange) and SCAN (green) chromatograms to demonstrate where the peaks of interest elute within the diesel matrix spiked sample; diesel sample was spiked with butoxybenzene and ACCUTRACE Plus S10 fuel marker at a concentration of 0.25 µg/mL.

Figure 3: The SIM (Single Ion Monitoring) Analysis in Diesel Matrix (M/Z 94, 150, 315, 455, 532), Showed Both Butoxybenzene and ACCUTRACE Plus S10 Fuel Marker at a Run Time Under 19 Minutes. A Sulfur Compound Found in the Diesel Fuel Does Not Interfere with the Other Two Compounds of Interest

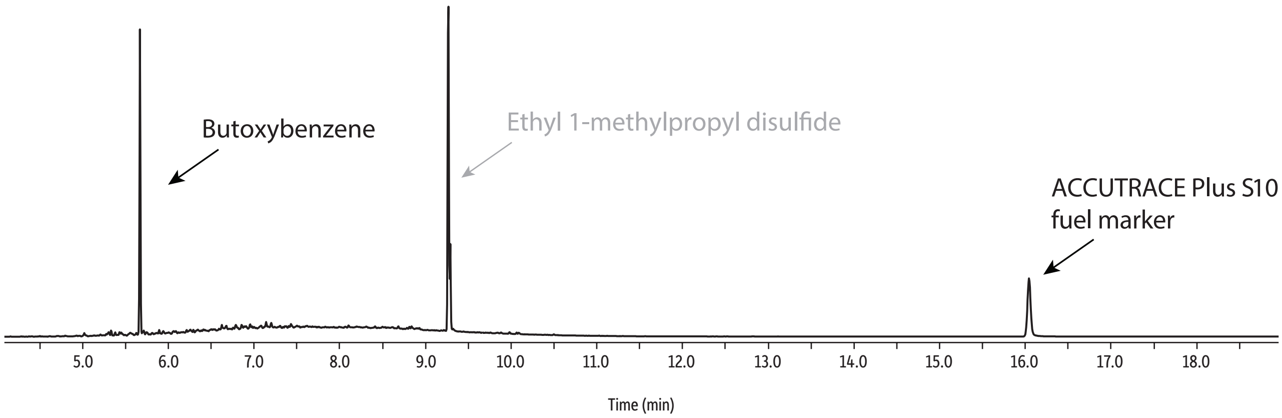
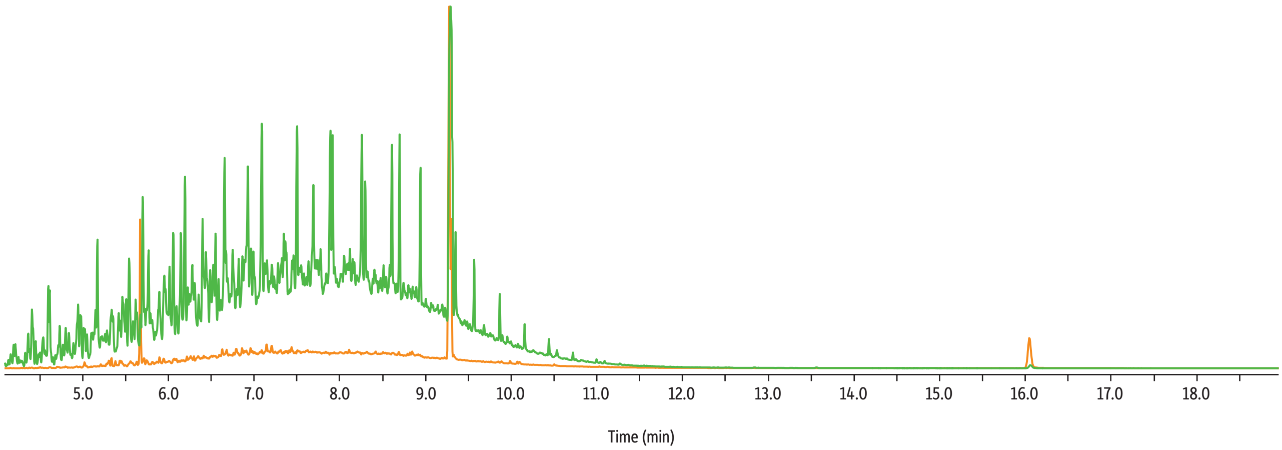
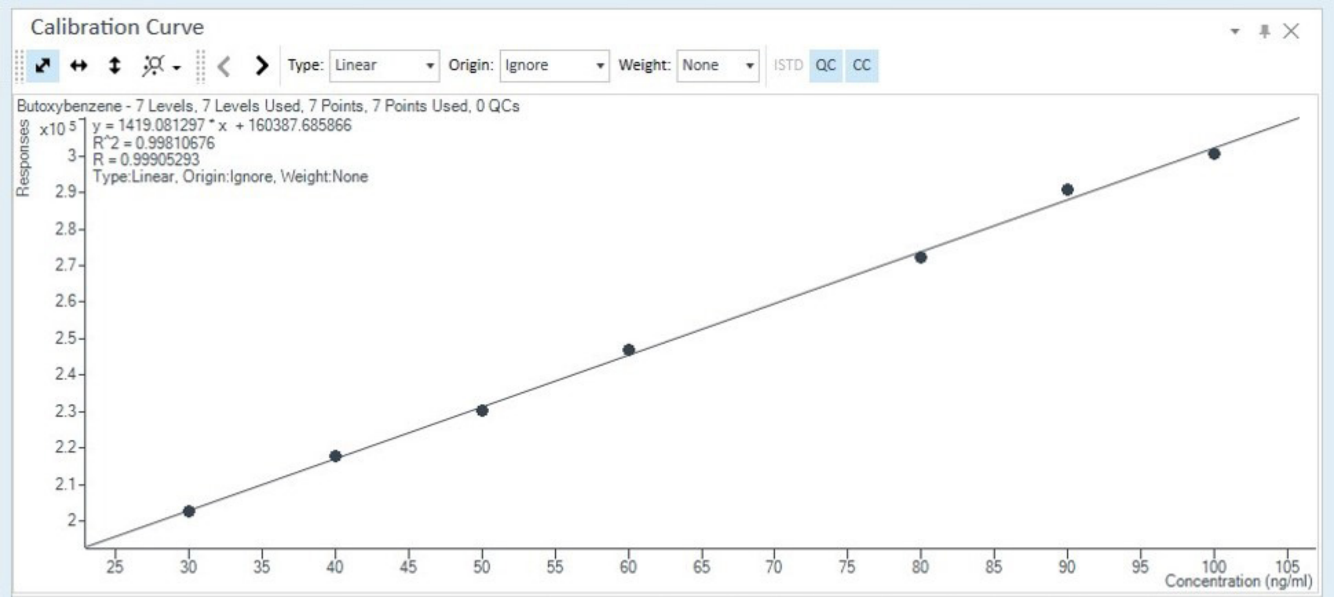


Figure 4: Overlay of the Same Diesel Matrix Spiked Sample Figure 3) Containing Both Butoxybenzene and ACCUTRACE Plus S10 Fuel Marker at a Concentration of 0.25 µg/mL in Scan (Green) and SIM (Orange)



A calibration curve ranging from 0.075 to 0.25 µg/mL demonstrated the low levels of detection that are possible to reach with a one-dimensional GC approach. In Figure 5 and Figure 6, the linear regression of 0.998 of the method is shown. In Table II and Table III, the calibration accuracy of all calibration points is shown to be below 4%.

Figure 5: The 0.998 R2 Value and Calibration Curve (0.075, 0.1, 0.125, 0.15, 0.2, 0.225, 0.25 µg/mL) for Butoxybenzene, Including a 0.061 µg/mL LOD



Calibration Curve

Type: Linear Origin: Ignore Weight: None ISTD QC CC

Butoxybenzene - 7 Levels, 7 Levels Used, 7 Points, 7 Points Used, 0 QCs

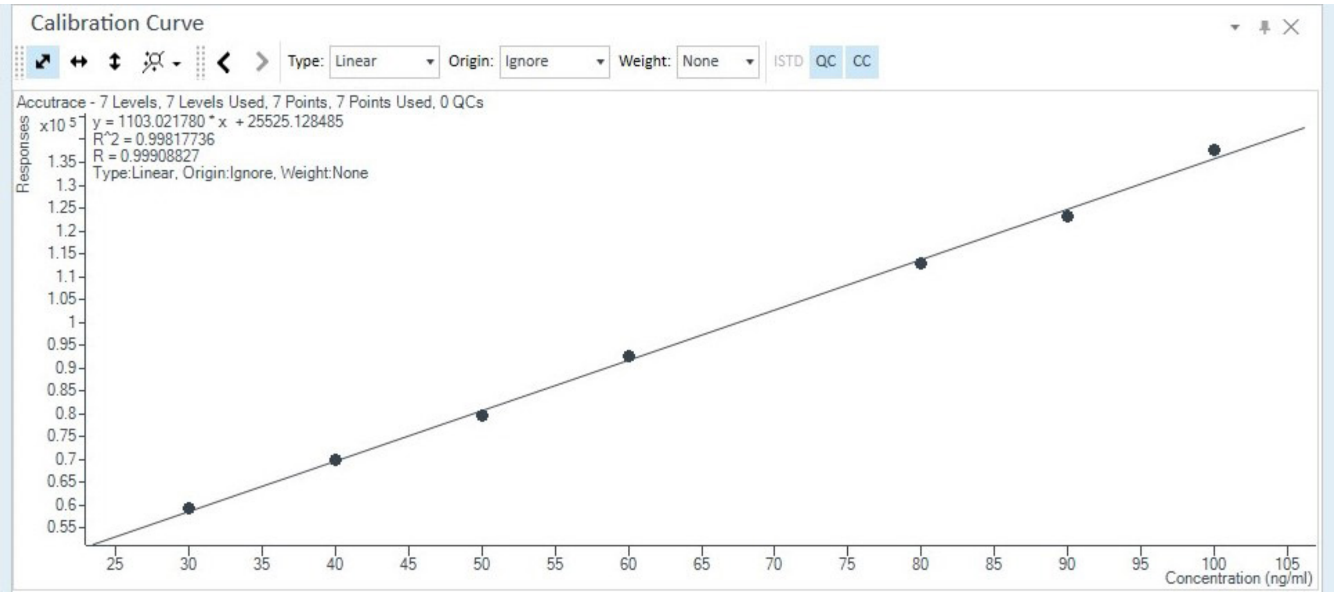
$y = 1419.081297 * x + 160387.685866$

$R^2 = 0.99810676$

$R = 0.99905293$

Type:Linear, Origin:Ignore, Weight:None

Figure 6: The 0.998 R2 Value and Calibration Curve (0.075, 0.1, 0.125, 0.15, 0.2, 0.225, 0.25 µg/mL) for ACCUTRACE Plus S10 Fuel Marker, Including a 0.4 µg/mL LOD



Calibration Curve

Type: Linear Origin: Ignore Weight: None ISTD QC CC

Accutrace - 7 Levels, 7 Levels Used, 7 Points, 7 Points Used, 0 QCs

$y = 1103.021780 * x + 25525.128485$

$R^2 = 0.99817736$

$R = 0.99908827$

Type:Linear, Origin:Ignore, Weight:None

Table II: Calibration Curve Accuracy (in Diesel Matrix) for Butoxybenzene

Rxi-5ms Column – 400:1 Split Injection						
Name	**RT (min)**	**Area**	**S/N**	**Amount (µg/mL)**	**Calibrated Amount (µg/mL)**	**Accuracy (%)**
Butoxybenzene	5.669	202652	210677	0.075	0.0781	-3.97
	5.669	218564	561.13	0.1	0.0969	3.20
	5.669	230214	34.36	0.125	0.1204	3.82
	5.669	246794	278425	0.15	0.1495	0.33
	5.669	272383	321341	0.2	0.1971	1.47
	5.669	290039	359070	0.225	0.23	-2.17
	5.669	297606	363391	0.25	0.2441	2.42

Table III: Calibration Curve Accuracy (in Diesel Matrix) for ACCUTRACE Plus S10 Fuel Marker

Rxi-5ms Column – 400:1 Split Injection						
Name	**RT (min)**	**Area**	**S/N**	**Amount (µg/mL)**	**Calibrated Amount (µg/mL)**	**Accuracy (%)**
ACCUTRACE Plus S10 fuel marker	16.042	59259	4126.9	0.075	0.0753	-0.40
	16.042	69796	2649	0.1	0.0996	0.40
	16.042	80701	5091.4	0.125	0.1246	0.32
	16.042	92551	3843.9	0.15	0.1519	-1.25
	16.042	112823	7385.4	0.2	0.1985	0.76
	16.042	123251	11541	0.225	0.2225	1.12
	16.042	136321	6746.7	0.25	0.2526	-1.03

Even at the lowest level of calibration (0.075 µg/mL) for both butoxybenzene and ACCUTRACE Plus S10 fuel marker, the signal-to-noise ratio (S/N) remains high, as indicated by the yellow cells in table II and table III. A high S/N allows for the detection of trace levels of analytes that might be present in low concentrations within a sample. It enhances sensitivity, improves quantitative and qualitative accuracy, aids in the reliable identification of compounds, and aids reproducibility.

Conclusions

Fuel laundering is a serious economic, environmental, and safety issue. It undermines legitimate businesses, causes significant tax revenue losses, and poses health and environmental risks. Governments are continuously improving detection technologies, enhancing regulatory measures, and promoting public awareness to combat this illicit activity effectively.

A 1D-GC approach can detect both butoxybenzene and ACCUTRACE Plus S10 fuel marker at extremely low levels. With this method, both compounds can meet regulatory detection limits in under 20 minutes. This method is robust, reliable, and has a high utility in ensuring fuel quality and safety. The established calibration curves demonstrated excellent linearity, and all recoveries of calibration curve and matrix replicates were well within 80%-120%.

Choosing between one-dimensional gas chromatography and two-dimensional gas chromatography depends on the specific requirements of your analysis. While GCxGC offers significant advantages in terms of resolving complex mixtures, 1D-GC analyses offer simplicity, cost-effectiveness, variety, and robustness.

To use 1D-GC over 2D-GC is often based on practical considerations where the added complexity and cost of GCxGC do not provide enough additional benefit to justify its use. For many laboratories, especially those handling routine analyses with relatively simple matrices, 1D-GC provides the necessary analytical performance while being more accessible and manageable.

Acknowledgements

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References

1. Office of the Comptroller & Auditor General, Report on the Accounts of the Public Services 2015: Tackling Fuel Laundering, Dublin, Ireland, 2015, 1555-170. https://www.audit.gov.ie/en/find-report/publications/2016/tackling-fuel-laundering.pdf
2. Commission Implementing Decision (EU) 2022/197, Establishing a Common Fiscal Marker for Gas Oils and Kerosene, Official Journal of the European Union, Brussels, Belgium, January 2022, 52-55. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32022D0197

Rxi-5ms GC Columns

- General-purpose columns that can be used for phenols, residual solvents, drugs of abuse, pesticides, semivolatiles, PCB congeners (e.g., Aroclor mixes), and solvent impurities.
- Tested and guaranteed for ultra-low bleed; improved signal-to-noise ratio for better sensitivity and mass spectral integrity.
- Temperature range: -60 °C to 330/350 °C.
- Equivalent to USP G27 and G36 phases.

ID	Length	df	Units	Cat.#
0.25 mm	30 m	0.25 µm	ea.	13423

Topaz Precision Inlet Liner

- **Deactivation**—unbelievably low breakdown for accurate and precise low-level GC analyses.
- **Reproducibility**—unbeatable manufacturing controls and QC testing for superior reliability across compound classes.
- **Productivity**—unparalleled cleanliness for maximized GC uptime and lab throughput.
-

Cat.#	ID	OD	Length	Units
23305	4.0 mm	6.3 mm	78.5 mm	5-pk.

Short-Cap Vial with Grad Marking Spot

Cat.#	Size	Type	Volume	Color	Units
21142	12 x 32 mm	9-425 Screw-Thread	2 mL	Amber	100-pk.

Short Screw Caps

Cat.#	Cap Size	Type	Septa Material	Units
24488	9-425	Screw Thread	PTFE/Silicone	1000-pk.

GC-MS Mass Spec Cleaning Kit

Poor sensitivity, loss of sensitivity at high masses, or high multiplier gain during an autotune are all indicators that your mass spectrometer source may need to be cleaned. Restek has assembled all of the necessary components for cleaning and polishing your ion source.

Cat.#	Product	Units
27194	GC-MS Mass Spec Cleaning Kit	kit.
27195	GC-MS Mass Spec Cleaning Kit with Rotary Tool	kit.

High-Temperature EI Filament

- EI (electron ionization) filaments meet or exceed original manufacturer's performance
- Every filament is subjected to QC tests, including heat, electrical current, and resistance
- Samples from each filament manufacturing lot are installed in an MSD for in situ testing.

Cat.#	Product	Similar to	Units
23099	High-Temperature EI Filament	Agilent G3170-60050 (obsolete), G7005-60061	ea.

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