Diesel fuel marker analysis

Analysis of ACCUTRACE™ Plus Fuel Marker

- Fiscal fuel marker analysis in diesel
- 2D-GC/MS method
- Robust analysis

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Fiscal markers and fuel dyes are added to fuels in order to distinguish between reduced taxed fuels and normal fuels. The European Commission has selected Dow ACCUTRACE™ Plus Fuel Marker as the new common fiscal marker for tax rebated fuels in the European Union (EU). The decision to adopt a new fiscal marker, also known as Euromarker, aims to provide member states a safer, more resilient marker to support governments fuel fraud prevention programs.

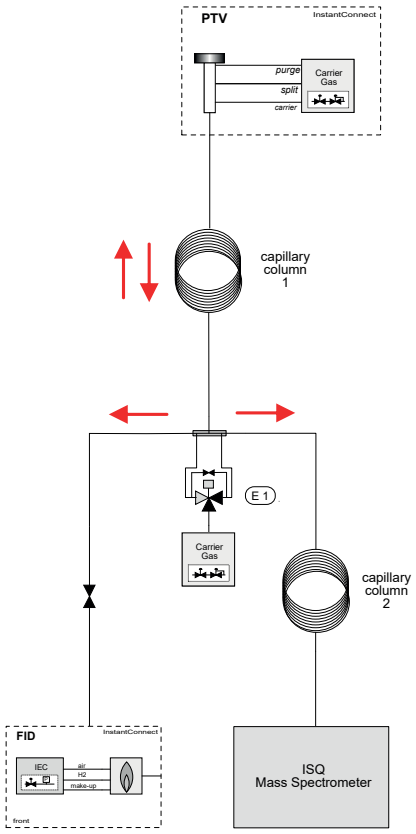

Figure 1. Diagram 2D-GC/MS system for diesel euromarker analysis

Diesel fuel marker

ACCUTRACE™ Plus or butyl phenyl ether (BPE) or butoxybenzene is recently introduced as the new euromarker for 'red' diesel. It will be added in the nominal concentration range of 9,5-14,25 mg/L. For tracing tax fraud, the limit of quantification (LOQ) is set to 2% of the nominal value, meaning 190 ppb. To analyse this low concentration level in a diesel matrix, 2-dimensional gaschromatography and mass spectrometer detection (2D-GC/MS) is the preferred choice.

Principle

The diesel sample is analysed by direct injection into the GC/MS without any sample preparation. To avoid contamination of the mass spectrometer ion source, (in case of illegal additives like engine oil, lubricating oil or vegetable oil), a Deans heartcut/backflush column switching option is applied.

Heartcut and backflush

Contamination of the ion source can lead to a drop in sensitivity and requires frequent ion source cleaning. With the configuration shown in figure 1, the majority of the sample is directed to FID, while only a small fraction containing the marker is directed to the MS. This diagram also facilitates backflush of higher boiling components from the first capillary column after BPE (butyl phenyl ether) has entered the second analysis column. FID is used to determine the correct column switching times, and also shows a profile of the diesel fuel, to indicate possible addition of higher boiling oils.

Results

Figure 2 shows the FID chromatogram with heartcut *and* backflush option enabled. The small (missing) fraction around 3 minutes is diverted to the MS, and therefore not visible on FID; the high boiling components above approximate 4 minutes are backflushed to the split-outlet of the injector, resulting in a clean baseline.

Figure 3 shows a MS chromatogram. To establish the sensitivity, a 50 ppb standard was prepared by spiking a commercial diesel aliquot (checked for zero marker content) with butyl phenyl ether. Mass 94 was used for quantification while mass 150 was the qualifier. The signal to noise ratio for this 50 ppb peak is 128, demonstrating excellent achievement of the required LOD (190 ppb).

Figure 4 shows good linearity over 100 ppb to 20 ppm concentration range. (R^2 =0.9999).

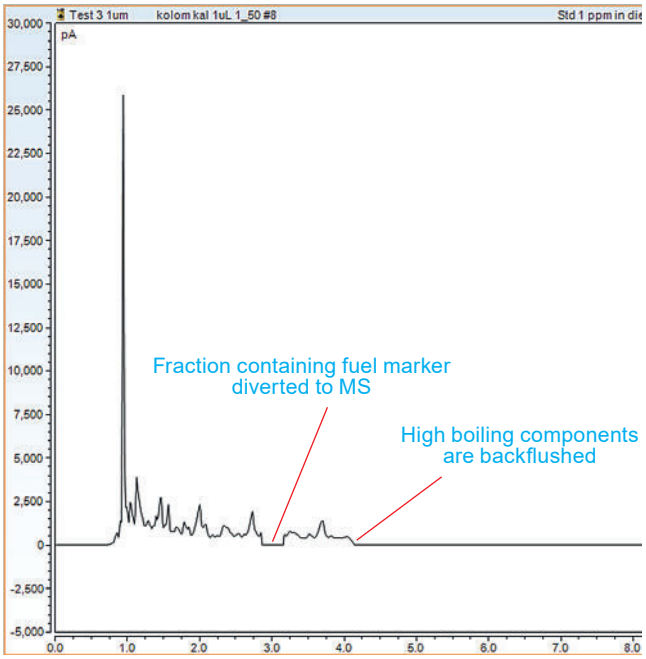

Figure 2. FID chromatogram with heartcut and backflush option enabled

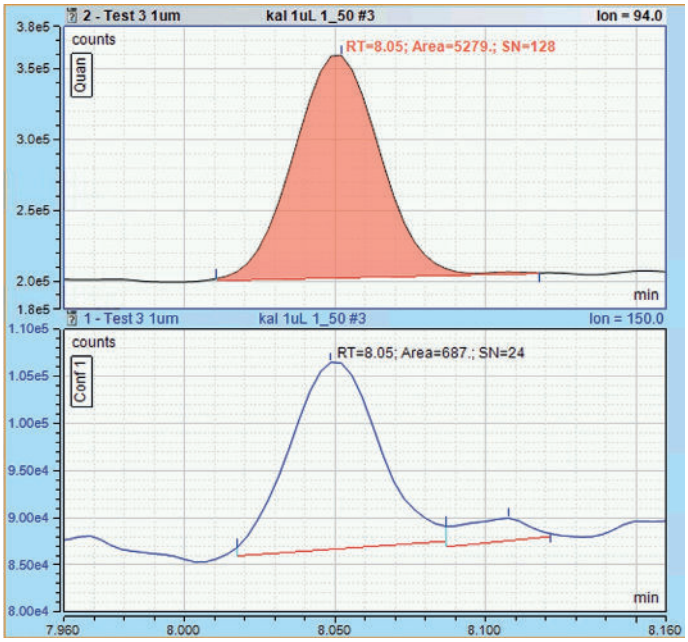

Figure 3. Mass chromatogram diesel sample spiked with 50 ppb butyl phenyl ether

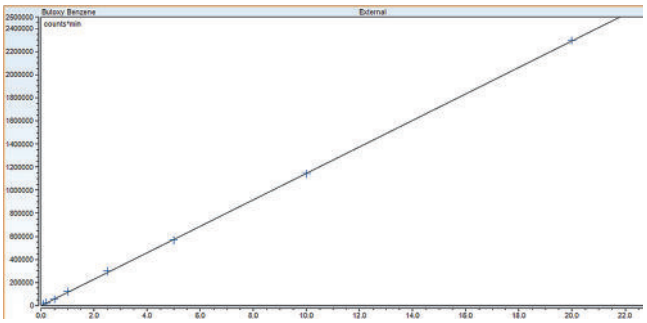

Figure 4. Calibration curve (100 ppb - 20 ppm)

Run #	Retention time (min)	Concentration (ppm)
1	8.02	0.10
2	8.03	0.10
3	8.03	0.10
4	8.03	0.10
5	8.03	0.10
6	8.03	0.10
7	8.02	0.10
8	8.02	0.10
9	8.03	0.10
10	8.02	0.10
RSD	**0.03%**	**1.85%**

Figure 5. Repeatability butoxybenzene at 100 ppb (n=10)

Specification

Configuration:	2D-GC/MS instrument based on Thermo Trace GC 1600 and ISQ 7610
Options:	- AS/AI 1610 liquid autosampler - TriPlus 100 LS / RSH liquid autosampler
Application:	Analysis of euromarker ACCUTRACE™ Plus (butoxybenzene/butyl phenyl ether) in diesel using 2D-GC/MS
Sample requirements:	See our pre-installation guide
Analysis Time:	15 minutes
Carrier gas:	He
Temperature program:	100 °C (0.5 min)-10 °C/min-180 °C (0 min)-30 °C/min-250 °C (4 min)
Injection volume	1 ul
Injector	PTV
Columns	Restek Rxi-17sil ms, 15 m × 0.25 mm × 0.15 µm MEGA-Wax, 30 m x 0.25 mm I.D. x 1.00 µm df Restrictor: 0.63m x 0.1mm ID
Minimum Detectability:	< 50 ppb
Dynamic Range:	> 5 decades
Linearity	R^2=0.9999
Recovery	100% ± 10% ;calibration range (0.1–10 mg/L);
Repeatability:	< 2% RSD at 100 ppb (n=10)
Data systems:	Chromeleon CDS

Figure 7. GC 1610 - ISQ 7610 - AS 1610