Application Note

Energy and Chemicals

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Increased sensitivity and reproducibility in the analysis of trace fatty acid methyl esters in jet fuel

Applying the Energy Institute Method IP 585 with an Agilent J&W DB-HeavyWAX GC column

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Abstract

This Application Note demonstrates the increased sensitivity of the analysis of fatty acid methyl esters (FAMEs) in jet fuel by coupling the Agilent J&W DB-HeavyWAX GC column with the Energy Institute Method IP 585. The increased temperature range of the DB-HeavyWAX thick-film column (270 or 280 °C) has ultralow bleed, making it ideal for GC/MS applications. The increased thermal stability of the DB-HeavyWAX column makes it ideal for use with selective ion monitoring mode. This is possible because the column provides for more repeatable retention times over longer periods of time, even when taken to final temperatures above the traditional 250 °C maximum of other WAX-type columns.

Introduction

The analysis of fatty acid methyl esters (FAMEs) in biodiesel, by method IP 585, is necessary to determine if a sample of jet fuel has become contaminated during the transportation process. It is best to do this analysis on a WAX-type column[1]. Gas chromatography columns based on 100 % polyethylene glycol (PEG) stationary phase can be used for a wide variety of applications such as industrial chemical analysis. Compared to polysiloxane stationary phases, the maximum operating temperature of a traditional WAX GC column is much lower, up to 250 °C for thick-film columns.

When a traditional WAX GC column is taken above the stated maximum allowed operating temperature (MAOT), it exhibits poor thermal stability and high bleed levels[2]. At the final temperature of 252 °C required by IP 585, some loss of thermal stability is to be expected with traditional WAX columns. The Agilent J&W DB-HeavyWAX thick-film column has an extended upper temperature limit, up to 270 °C when used isothermally, or 280 °C when programmed. This makes the DB-HeavyWAX ideal for analyzing FAMEs in jet fuel by IP 585.

With the extended temperature limit of the DB-HeavyWAX column, it is possible to maintain a final temperature of 252 °C without damaging the phase. It is also possible to increase the final temperature to 270 °C for extended periods of time, and up to 280 °C, when programmed to decrease the possibility of carryover from higher molecular weight compounds, and to increase reproducibility. The increased thermal stability of the DB-HeavyWAX provides more stable retention times and longer periods of time without needing to update SIM windows due to loss of column phase.

The DB-HeavyWAX does not suffer from poor column bleed, often seen with traditional WAX columns at temperatures at or above 250 °C. This presents a decreased baseline, and enables more accurate quantitation of lower concentration FAMEs.

Experimental

Materials and methods

An Agilent 7890 GC/FID equipped with a split/splitless inlet, an Agilent 7010 MSD, and an Agilent 7693 autosampler with Agilent MassHunter control software was used for the GC/MSD experiments.

Instrument conditions

GC Conditions	
Column	Agilent J&W DB-HeavyWAX, 60 m × 0.25 mm, 0.5 µm (p/n 122-7163) Traditional commercially available WAX column, 60 m × 0.25 mm, 0.5 µm
Carrier	Helium, constant flow, 12 mL/min
Oven	150 °C (5.0 minutes), Ramp 12 °C/min to 200 °C (17.0 minutes), Ramp 3 °C/min to 252 °C (10 minutes)
Inlet	Split mode, 260 °C, split ratio 50:1
Inlet liner	Agilent Ultra Inert, split, low pressure drop, glass wool (p/n 5190-2295)
GC/FID	Agilent 7890B GC equipped with FID
Sampler	Agilent 7693 autosampler
Flowpath supplies	
Septum	Bleed and temperature optimized (BTO) 11 mm septa (p/n 5183-4757, 50/pk)
Gold seal	Agilent Ultra Inert gold seals (p/n 5190-6145, 10/pk)
Vials	2 mL, screw top, amber, write-on spot, certified, (p/n 5182-0716, 100/pk)
Vial inserts	250 µL glass inserts, deactivated (p/n 5181-8872, 100/pk)
Vial caps	9 mm blue screw cap, PTFE/RS (p/n 5185-5820, 500/pk)
Inlet/FID/MSD	85:15 Vespel:graphite ferrules (p/n 5062-3508, 10/pk)
FID Conditions	
Temperature	280 °C
Hydrogen	30 mL/min
Air	400 mL/min
Column + make up	25 mL/min
MSD Conditions	
Mode	SIM/Scan
Scan range	33–320 amu
Solvent delay	20.0 minutes
Source temperature	230 °C
Quad temperature	150 °C

Sample preparation

Calibration standards were purchased from AccuStandard, and working standards were prepared according to IP 585 at nominal concentrations of 2, 10, 25, 50, and 75 mg/g in hexane (Sigma).

Results and discussion

Standards of a mixture of FAMEs were injected onto a DB-HeavyWAX, and run according to IP 585, with a final oven temperature of 252 °C. The mixture was initially analyzed by a flame ionization detector (FID) to measure the column bleed. Figure 1 demonstrates the decrease in column bleed of the DB-HeavyWAX compared to a traditional thick-film WAX column. The decrease in column bleed at high temperatures of the DB-HeavyWAX, compared to the traditional WAX-type column, demonstrates the overall increase in thermal stability of the DB-HeavyWAX.

Table 1. SIM windows.

SIM Group	Target compound	Synonym	Symbol	SIM Ions	Dwell
1	Methyl hexadecanoate	Methyl palmitate	C16:0	227* 239 270 271	75 75 75 75
2	Methyl heptadecanoate-d33	Methyl margarate-d33	C17:0-d33 (IS)	317	300
3	Methyl hepadecanoate	Methyl margarate	C17:0	241* 253 284	100 100 100
4	Methyl octadecanoate	Methyl stearate	C18:0	255* 267 298	100 100 100
5	Methyl octadecenoate	Methyl oleate	C18:1	264* 265 296	100 100 100
6	Methyl octadecadienoate	Linoleate	C18:2	262 263* 264 294 295	60 60 60 60 60
7	Methyl octadectrienate	Linolenate	C18:3	236* 263 292 293	75 75 75 75

* Indicates quant ion.

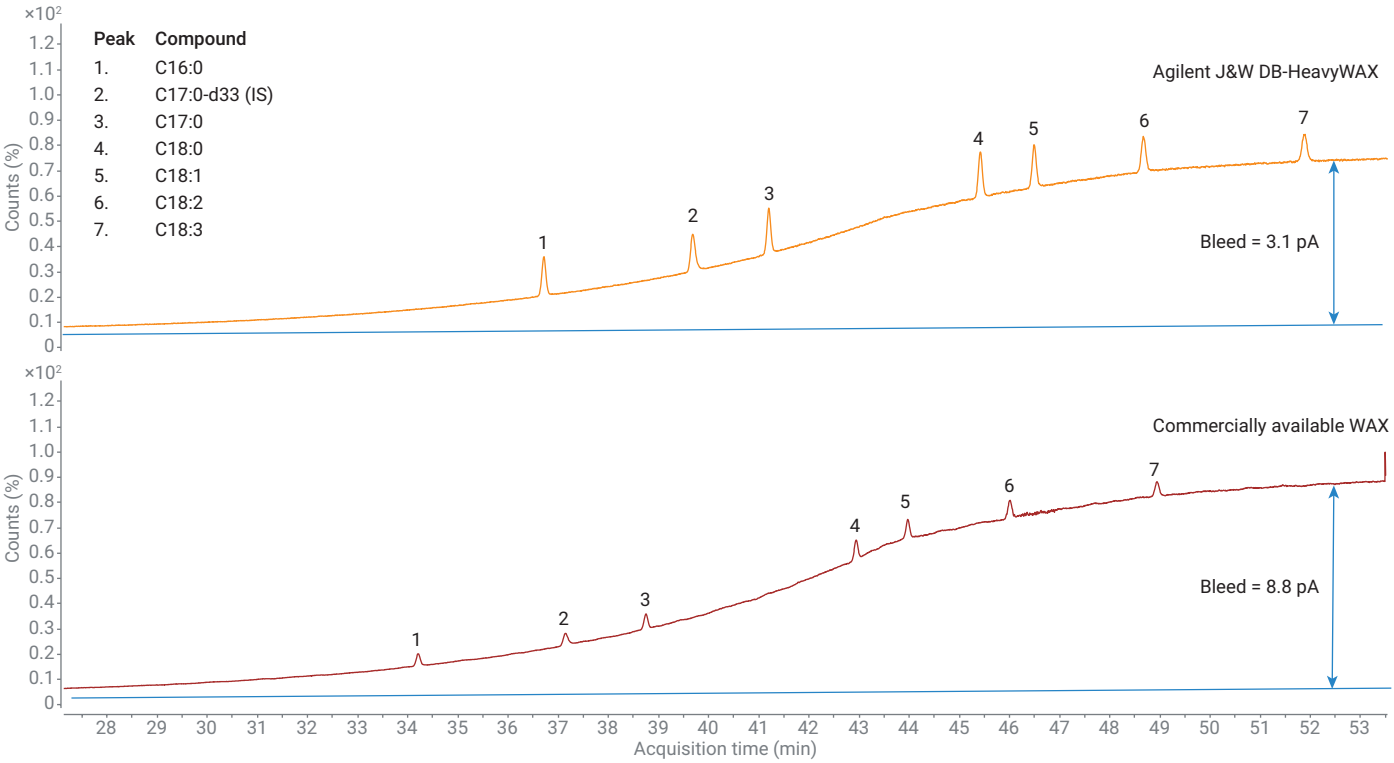

Figure 1. Standard of 10 mg/g FAMEs collected by FID on an Agilent J&W DB-HeavyWAX column and a commercially available WAX column.

Figure 2 shows that the low bleed of the DB-HeavyWAX measured by FID achieves a higher signal-to-noise ratio (S/N) when the column is used with a mass spectrometer. The increased DB-HeavyWAX S/N compared to traditional WAX columns provides greater sensitivity and more accurate quantitation of FAMEs in biodiesel over extended periods of use at temperatures greater than 250 °C.

Figure 3 demonstrates how the low bleed level of DB-HeavyWAX benefits the analysis of FAMEs analyzed in SIM or Scan mode. Even at concentrations as low as 2 mg/g, it is possible to detect analytes of interest on the DB-HeavyWAX column in Scan mode.

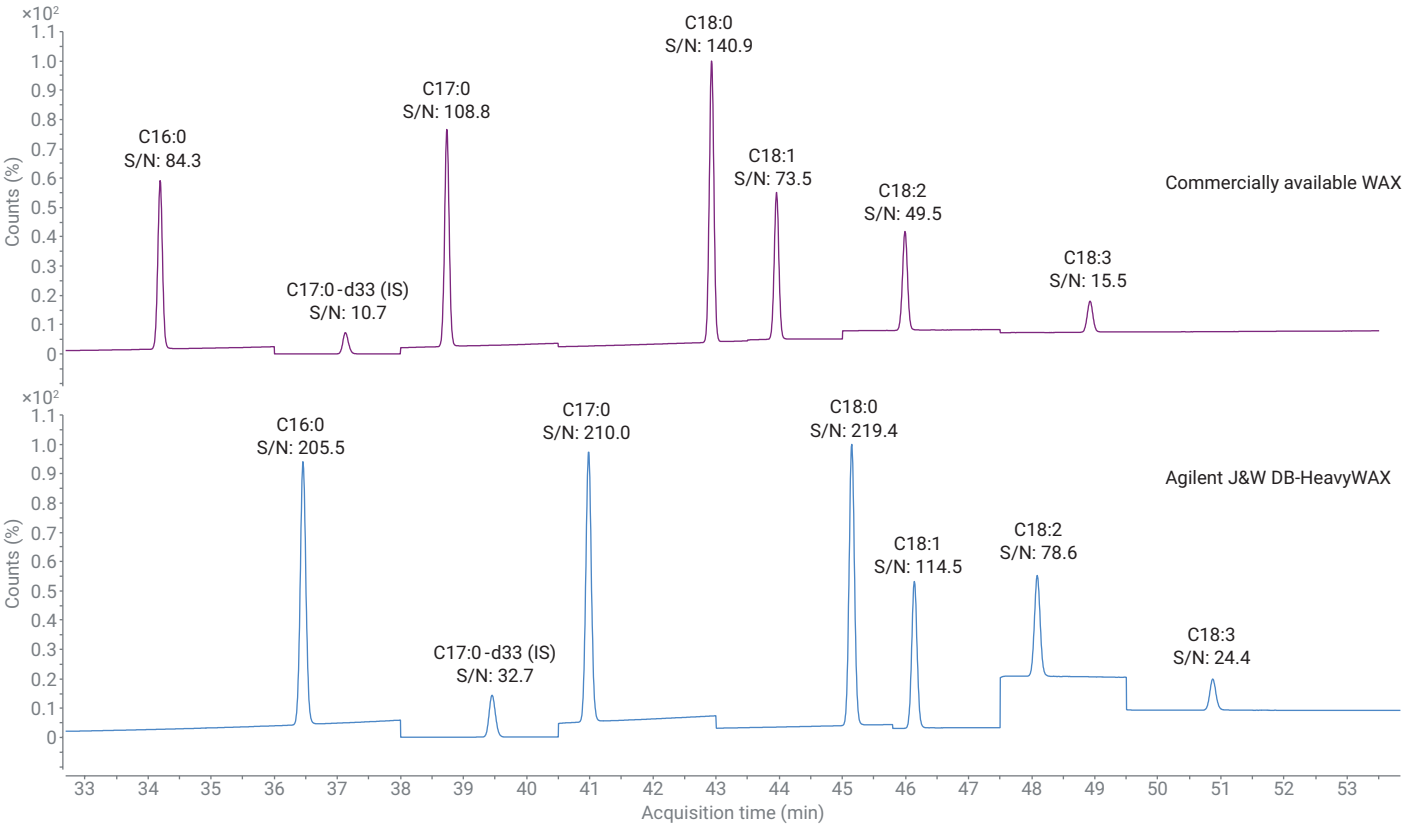

Figure 2. Standard of 25 mg/g FAMEs collected in SIM mode on an Agilent J&W DB-HeavyWAX column and a commercially available WAX column.

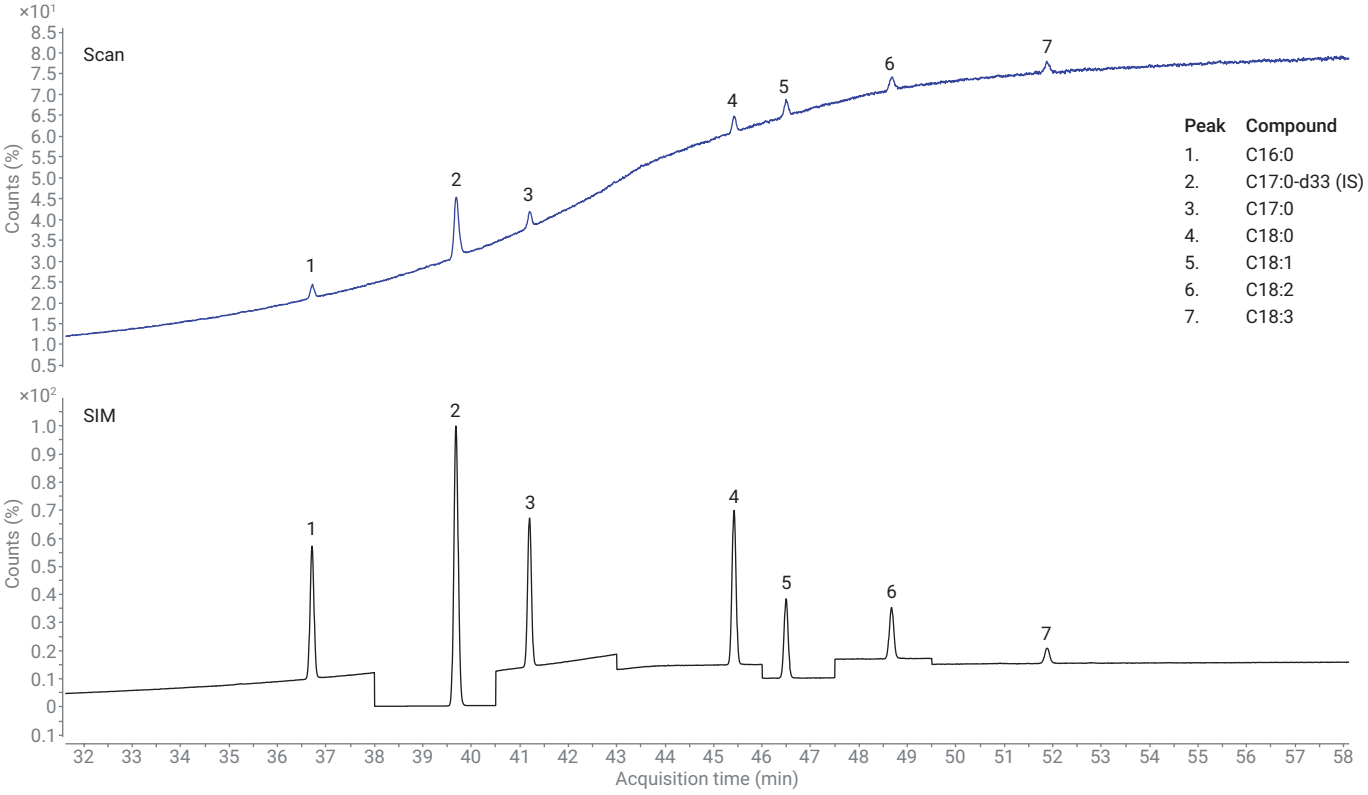

Figure 3. Standard of 2 mg/g FAMEs acquired in Scan and SIM modes on an Agilent J&W DB-HeavyWAX column.

Reproducibility and longevity

Table 2 shows nine replicates of a 2 mg/g standard of FAMEs, collected in SIM mode over 200 total injections and a period of 50 hours operating at 260 °C. All the compounds had a %RSD below 0.15 %, illustrating the stability and ruggedness of the DB-HeavyWAX over extended periods of time.

Table 2. Nine replicates of a standard of 2 mg/g FAMEs collected in SIM mode on an Agilent J&W DB-HeavyWAX column over 50 hours operating at 260 °C.

Compound	Operating hours at 260 °C									Average	%RSD
	1	5	7	13	22	39	42	46	49		
C16:0	36.58	36.47	36.45	36.44	36.43	36.43	36.43	36.43	36.42	36.45	0.13 %
C17:0 d33 (ISTD)	39.57	39.47	39.45	39.44	39.44	39.44	39.44	39.44	39.44	39.46	0.11 %
C17:0	41.09	40.99	40.98	40.96	40.97	40.97	40.97	40.97	40.96	40.98	0.10 %
C18:0	45.26	45.16	45.15	45.13	45.14	45.15	45.15	45.15	45.14	45.16	0.08 %
C18:1	46.25	46.15	46.14	46.12	46.13	46.13	46.13	46.13	46.13	46.15	0.09 %
C18:2	48.20	48.10	48.09	48.07	48.08	48.07	48.08	48.08	48.07	48.09	0.09 %
C18:3	51.01	50.89	50.87	50.85	50.84	50.86	50.86	50.87	50.86	50.88	0.10 %

Conclusions

The Agilent J&W DB-HeavyWAX column provides an increased maximum temperature range of 270/280 °C for a thick-film column and low bleed. This expanded range offers increased sensitivity and improved thermal stability. The increased thermal stability and ruggedness of the DB-HeavyWAX makes it ideal for SIM methods such as IP 585, where retention time reproducibility is important to productivity. The ultralow bleed of the DB-HeavyWAX achieves an increase in S/N for the analytes of interest, providing an increase in sensitivity and flexibility to collect data in SIM or Scan mode.

References

1. McCurry, J. GC/MS Analysis of Trace Fatty Acid Methyl Esters (FAME) in Jet Fuel Using Energy Institute Method IP585, *Agilent Technologies*, publication number 5990-9432EN, **2011**.
2. Abercrombie, V.; Provoost, L. Increased Thermal Stability and Maximum Temperature of the Agilent J&W DB-HeavyWAX Column, *Agilent Technologies*, publication number 5991-9035EN, **2018**.

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