

Determination of fuel system icing inhibitor content of aviation turbine kerosine by HPLC

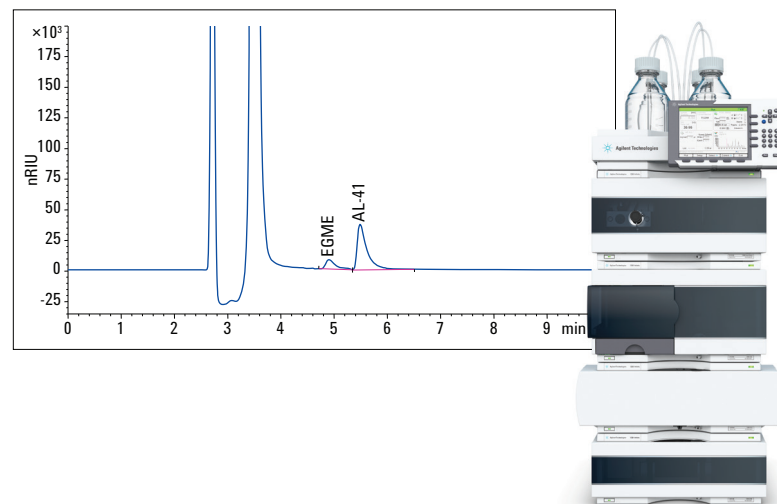
Application Note

Energy and Fuels

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Abstract

This Application Note describes the determination of fuel system icing inhibitor (FSII) content of aviation turbine fuel for a content range between 0% (v/v) and 0.2% (v/v) by high performance liquid chromatography. Sample preparation is done by diluting the aviation turbine kerosine (AVTUR).

The determination covers the previously used ethylene glycol monomethyl ether (EGME) and the now used diethylene glycol monomethyl ether (AL-41) in both aviation turbine kerosine for aircraft carriers (AVCAT) and AVTUR. The isocratic HPLC method shows good linearity and precision for each FSII. The precision was better than 0.05% RSD for the retention times and better than 0.5% RSD for the area. The linearity was better than 0.999 over the range from 0.03% to 0.2% of the typical FSII content in aviation turbine kerosine.



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Introduction

FSII is an additive to aviation fuels that prevents the formation of ice in fuel lines. Jet fuel can contain a small amount of dissolved water that does not appear in droplet form. As an aircraft gains altitude, the temperature drops and jet fuel's capacity to hold water is diminished. Dissolved water can separate and could become a serious problem if it freezes in fuel lines or filters, blocking the flow of fuel and shutting down an engine. Additionally, FSII retards the growth of microorganisms present in the fuel and prevents microbial corrosion to plastics and rubber parts. Typical icing inhibitors are the previously used ethylene glycol monomethyl ether (EGME), which was withdrawn because of toxicity (certified as pesticide) and replaced by diethylene glycol monomethyl ether (AL-41)^{1,2}. Large aircraft do not require FSII as they are usually equipped with electric fuel line heaters that keep the fuel at an appropriate temperature to prevent icing. However, if the fuel heaters are inoperable, the aircraft may still be declared fit to fly, if FSII is added to the fuel³.

The methods published by IP 424/96⁴ and ASTM D5006 - 11⁵ are guidelines for the determination of FSII content. The IP 424/96⁴ describes the separation of the components chromatographically using HPLC and RP-columns in normal phase mode without any extraction. This Application Note describes the method for detection and subsequent determination of the concentration of FSII to very low percentage range covering the range of FSII expected in aviation turbine kerosine. Sample preparation is not required prior to injection into the HPLC system.

The chromatographic method was adapted and transferred to an Agilent 1260 Infinity LC system.

Experimental

Instrumentation

The Agilent 1260 Infinity LC System included the following modules:

- 1260 Infinity Binary Pump (G1312B)
- 1260 Infinity Degasser (G1379B)
- 1260 Infinity High Performance Autosampler (G1367E)
- 1260 Infinity Thermostatted Column Compartment (G1316A)
- 1260 Infinity Refractive Index Detector (G1362B)

Software

OpenLAB CDS ChemStation Edition C.01.03

Preparation of samples and solutions

Reagents and materials

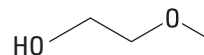
Hexane (dried, Sigma-Aldrich) and 2-propanol (dried, Sigma-Aldrich) must be free of water or dried with materials typically used to dry solvents for normal phase chromatography.

Ethylene glycol monomethyl ether (EGME, Sigma Aldrich) should contain less than 0,15% of water and less than 0,025% of ethylene glycol. Diethylene glycol monomethyl ether (AL-41, Sigma Aldrich) should conform to Defence Standard 91-91¹.

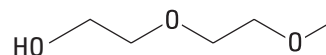
Aviation turbine kerosine (AVTUR, Sigma Aldrich) should conform to Defence Standard 91-91¹ and should be free of icing inhibitor additives.

Calibration and reference samples

The first calibration solution containing 0.15% (v/v) EGME and 0.15% (v/v) AL-41 is prepared by pipetting 150 μ L pure EGME and pure AL-41 into a 100-mL volumetric flask and adding AVTUR to the mark. Standard or reference solution can be prepared in the same manner by adding eluent instead of AVTUR to the volumetric flask. The standard for calibration of the second level containing 0.03% (v/v) EGME and 0.03% (v/v) AL-41 is prepared by pipetting 10 mL of the first calibration solution into a 50-mL volumetric flask and adding AVTUR to the mark. Both solutions must be shaken to mix the components. Standard solution can be stored in dimmed light at room temperature for three months.



Structure of Ethylene glycol monomethyl ether (EGME)



Structure of Diethylene glycol monomethyl ether (AL-41)

The reference solutions to check the sensitivity of the method and the system were prepared in the same manner. The solution of 0.015% (v/v) content of each FSII was prepared by pipetting 5 mL of the first standard solution into a 50-mL flask and filling to the mark with AVTUR, the solution with 0.0075% content of FSII by pipetting 12.5 mL of the second standard solution into a 50-mL volumetric flask and filling to the mark with AVTUR.

Sample preparation

Sample preparation is not usually required prior to injection, only the sampling procedure according to IP 475⁷ must be taken into account. To prevent clogged capillaries and column frits in the HPLC system, filter the samples with a microfilter of 0.45 µm porosity, which is chemically inert to hydrocarbon (for example, PTFE, 30 mm diameter, 0.45 µm, Agilent Technologies, Part-No. A4134).

Chromatographic conditions

Column for method setup

Agilent ZORBAX Eclipse XDB-CN, 4.6 × 250 mm, 5 µm

The standard XDB-CN column is tested and shipped with a mobile phase containing water. This column will not give the required performance for this application. A custom made column for use under normal phase conditions (without water) has to be used.

Mobile phase (v/v)

950 mL hexane/50 mL 2-propanol (v/v), adjusted to meet the required resolution of 1.5 between EGME and AL-41.

Calibration level	EGME (%, v/v)	AL-41 (%, v/v)
1	0.15	0.15
2	0.03	0.03

Table 1
Concentration of the calibration levels.

Chromatographic conditions	
Column	Agilent ZORBAX Eclipse XDB-CN, 4.6 × 250 mm, 5 µm (custom made)
Flow:	1.00 mL/min
Type:	isocratic
Temperature:	25 °C (or room temperature, be sure to maintain constant conditions for the refractive index detector)
Data rate:	2.5 Hz
Injection volume:	100 µL
Maximum pressure:	90 bar

Table 2
Chromatographics conditions.

Chromatograms and calculation

When the operating conditions are steady, inject a fixed volume of 100 µL of the calibration standard 1 of FSII and ensure the chromatogram resembles the one shown in Figure 1.

Both FSII components elute well separated showing the required resolution of 2.0 (must be > 1.5). The resolution can be recalculated using the following equation:

$$R = 2(t_2 - t_1) / 1.699(\gamma_2 + \gamma_1)$$

where:

t_2 = retention time in seconds of the AL-41 peak

t_1 = retention time in seconds of the EGME peak

γ_2 = width in seconds at half height of the AL-41 peak

γ_1 = width in seconds at half height of the EGME peak

If the resolution requirements are not met, check the equipment and adjust if necessary the composition or flow rate of the mobile phase. Interference from fuel components can be checked by injecting the additive free fuel.

Based on the calculation that the same injection volumes for calibration standards and samples are used the formulation standards for the FSII's are calculated as following:

(m=slope, i=intercept)

$$m = (Y - Z) / 0,12$$

$$i = Z - (0,03 m)$$

where:

Y = peak area for the 0.15% (v/v) calibration standard

Z = peak area for the 0.03% (v/v) calibration standard

If not calculated automatically by the data system, calculate the content of FSII (C) in a sample as a percentage by volume. For this calculation, the peak areas of the sample must be compared with areas of the standards by using the following equation:

$$C = (A - i) / m$$

where:

A = peak area for the sample

i = intercept of the calibration curve

m = slope of the calibration curve

Setup for testing precision and linearity

According to values defined in IP 367⁶ the precision for repeatability and reproducibility must be met:

Repeatability: < 0.01% (v/v)

Reproducibility: < 0.01% (v/v)

Linearity (R²) > 0.999

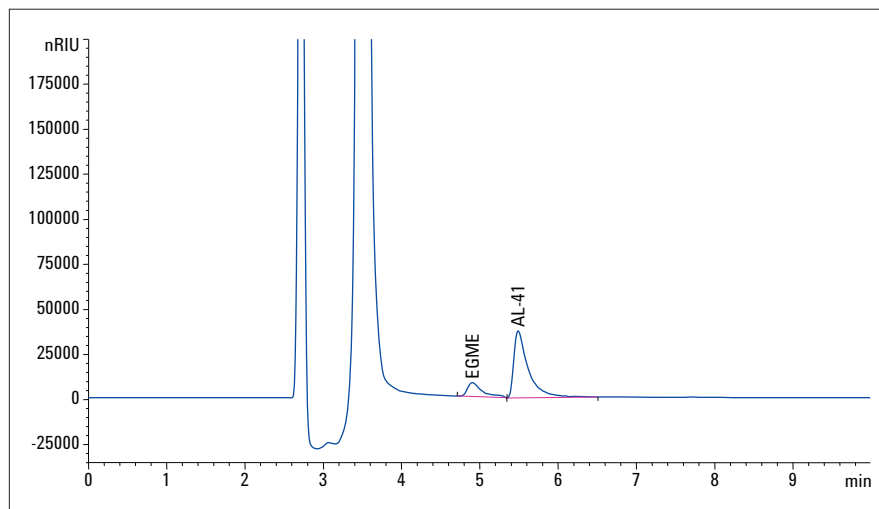


Figure 1
Calibration standard 1, 0.15% of each FSII in AVTUR.

Results and discussion

The chromatograms in Figure 2 show great similarity with those presented in the IP 424/96⁴. The values for the precision of the chromatographic method are shown in Table 3.

Table 3 shows the data for the precision of the method according to the separation with the ZORBAX Eclipse XDB-CN, 4.6 × 250 mm, 5 µm with a flow rate of 1.0 mL/min. The retention time precision (RSD) was for all samples and analytes better than 0.05%, the RSD for the area precision was less than 0.5% for all analytes in all samples.

To determine the limit of detection, the solutions for the calibration standard level 1 were diluted by AVTUR.

Run	EGME		AL-41	
	Retention time	Area	Retention time	Area
1	4.947	5113	5.554	22702
2	4.946	5117	5.553	22775
3	4.949	5116	5.557	22854
4	4.951	5104	5.558	22805
5	4.945	5089	5.551	22886
6	4.949	5093	5.556	22865
Mean	4.948	5105	5.555	22814
SD	0.002	11.02	0.0024	62.62
RSD (%)	0.04	0.22	0.04	0.27

Table 3
Results for the reproducibility of the chromatographic method.

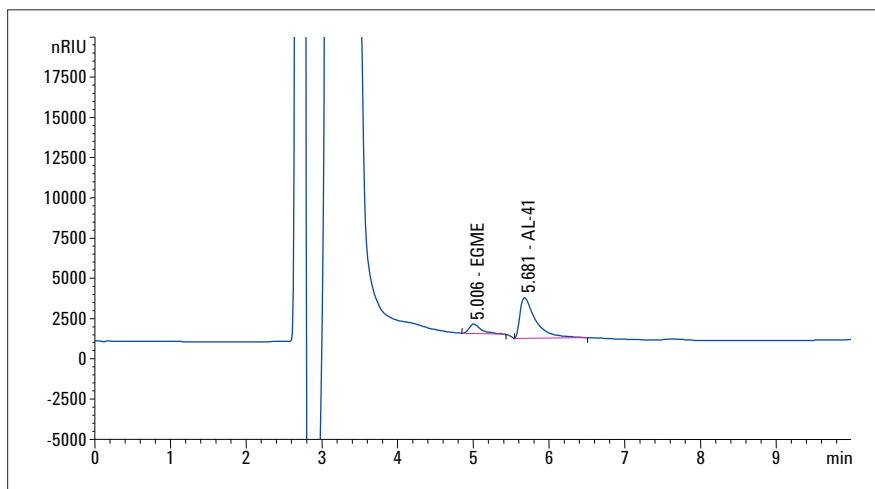


Figure 2
Injection of 0.0015% (v/v) standard, S/N-ratio: 15.5 for EGME and 68.0 for AL-41.

Calibration

Good linearity was determined for both analytes shown in Figure 3 with correlation coefficients better than 0.9999. According to the requirements for checking precision and linearity (see page 4) all demands were fulfilled.

Conclusions

The 1260 Infinity LC System is designed to provide highest resolution and sensitivity even with conventional columns and materials as well as with columns suitable for UHPLC.

The determination of fuel system icing inhibitor (FSII) content of aviation turbine fuel is easy to determine with the 1260 Infinity LC System and the ZORBAX Eclipse XDB-CN material. Since the standard column is tested and shipped with water and gives unsatisfactory results a custom made column tested and shipped without water must be used.

The results for precision show, that the conditions allow a very stable determination of these analytes with RSD's less than 0.5% for area precision and less than 0.05% for retention time precision.

The correlation coefficient for the linearity of the calibration was found to be better than 0.9999 for both analytes.

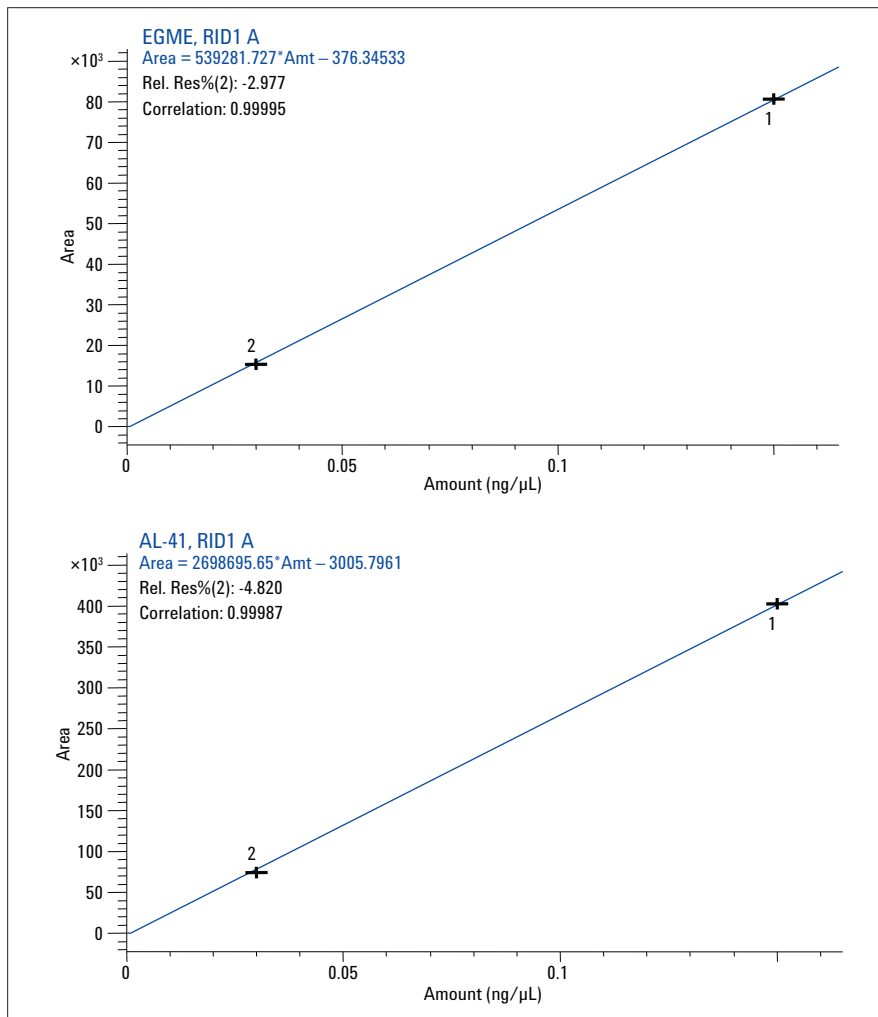


Figure 3
Calibration curves for EGME and AI-41.

References

1.
Defence Standard 68/252/issue
1 (DERD 2451) – Fuel System Icing
Inhibitor, Joint Service Designation:
AL-41.
2.
Defence Standard 91-91/issue 1
(DERD 2494) - Turbine Fuel, Aviation
Kerosene Type, Jet A-1, Joint Service
Designation; AVTUR.
3.
Aviation Jet Fuel Information, Version
3.3.2, [http://www.csgnetwork.com/
jetfuel.html](http://www.csgnetwork.com/jetfuel.html).
4.
IP 424/96-Determination of fuel
system icing inhibitor content of avia-
tion turbine kerosines by high perfor-
mance liquid chromatography, **2010**.
5.
ASTM D5006 - 11 Standard Test
Method for Measurement of Fuel
System Icing Inhibitors (Ether Type) in
Aviation Fuels and D4171: Specification
for Fuel System Icing Inhibitors.
6.
IP 367- Petroleum products –
Determination and application of preci-
sion data in relation to methods of test.
7.
IP 475, Petroleum liquids - Manual
sampling.

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