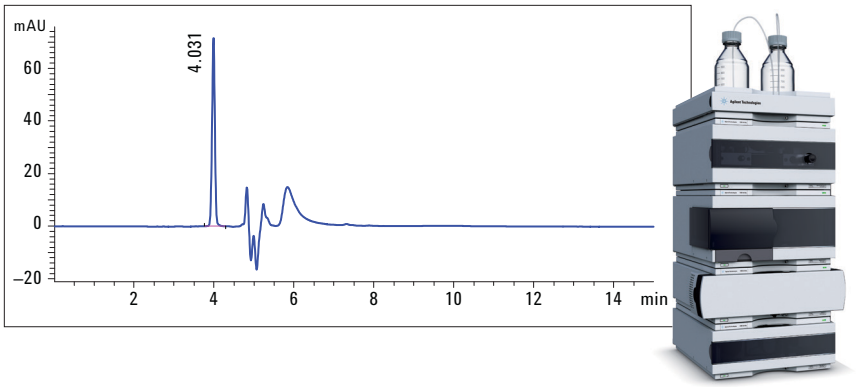
Determination of static dissipater additives in aviation turbine fuel and middle distillate fuels by HPLC

Suitable for Agilent
1260 Infinity III LC

Application Note

Energy and Fuels



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Abstract

This Application Note describes a procedure to determine the static dissipater additive (SDA) content of aviation turbine fuel and middle distillate fuels over the range 1 mg/L to 12 mg/L. Sample preparation is done by enrichment on amino-bonded silica cartridges from Agilent Technologies. Typically used static dissipater additives in aviation turbine fuel are long alkyl chained sulfonic acids, here dinonylnaphthalene sulfonic acid (DINNSA) and dodecylbenzene sulfonic acid (DDBSA). The isocratic HPLC method shows good linearity and precision for each SDA. The precision was better than 0.05 % RSD for the retention times, better than 0.5 % RSD for the area precision, and the linearity was better than 0.999 over the range from 0.32 to 16 mg/mL.

Verified for Agilent
1260 Infinity II LC

Agilent Technologies

Introduction

Static dissipater additives (SDA) are used in the aviation industry to ensure that jet fuel that is distributed, pumped, and transferred to the aircraft will not become charged. These materials are also known as antistatic additives or conductivity improver additives. The SDA material authorized for aviation jet A-1 use is STADIS 450 or STADIS 425. These are long chained hydrocarbons with an anionic polar head group which is typically a sulfonic acid salt. The addition and level of dosing SDA into jet fuels is very closely specified.

Due to the surface active nature of the SDA, the level of additive in certain conditions of distributions (corroded surfaces), may be initially dosed at the correct level and then drop off significantly. In such cases, when checking further at the airport fuel storage depots, the refueling supplier may allow one final dosage after approval[1-3].

One of the main issues in the past, and still of concern, is the determination of the conductivity of the jet fuel which is measured, and then equated back to the level of SDA still present in the fuel. The robustness of this simple test is sometimes questionable, since it is not selectively measuring the SDA, but purely the conductivity of the fuel that may be due to other ionic components that are not active SDA, and therefore may not offer any protection against preventing a static discharge.

The HPLC methods published by IP[4] and ASTM[5] are guidelines for the determination of SDA content by separating the SDA components chromatographically using HPLC and RP-columns. This Application Note describes the method for detection and subsequent determination of the concentration of SDA to very low ppm levels covering the range of SDA expected in distillate fuels.

Sample preparation was done using enrichment on amino-bonded silica cartridges from Agilent Technologies.

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

Experimental

Instrumentation

An Agilent 1260 Infinity LC System consisting of the following modules was used:

- Agilent 1260 Infinity Binary Pump with vacuum degasser (G1312B)
- Agilent 1260 High Performance Autosampler (G1367E)
- Agilent 1260 Infinity Column Compartment (G1316A)
- Agilent 1260 Infinity Diode Array Detector (G4212B)

Software

OpenLAB CDS ChemStation Edition, rev. C.01.03

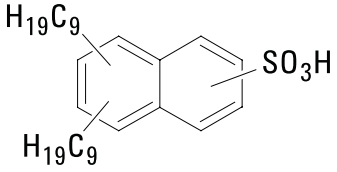
Preparation of solutions and samples

Preparation of solutions

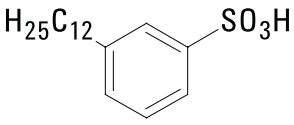
- Buffered phosphoric acid:
  2 mL orthophosphoric acid (85%) was added to 1,000 mL of HPLC grade water and buffer to pH = 2.5 with sodium hydroxide solution.
- Sodium hydroxide solution:
  4 g of sodium hydroxide pellets were dissolved in 100 mL of HPLC grade water

Calibration and reference samples

The DINNSA stock solution was prepared by weighing 80 mg of the DINNSA solution (50% m/m in heptane, Santa Cruz Biotechnology Inc.) in a 100-mL volumetric flask, which was then filled with heptane. The DDBSA stock solution was prepared in a similar manner by weighing 30 mg (70 % m/m in 2-propanol, Sigma Aldrich) in a 100 mL volumetric flask and filled with heptane or mobile phase. From the stock solutions, six calibration standards were prepared (see Table 1). The preparation of the first calibration level for DINNSA was done by pipetting 1 mL of the DINNSA stock solution into a 25-mL flask and then filling it with mobile phase. The preparation of the first level of DDBSA is similar; pipet 1 mL of DDBSA stock solution into a 25-mL volumetric flask and fill it with mobile phase. The other calibration standards were prepared in a similar manner by pipetting aliquots of the stock solution or the standards with high concentrations and diluting it to the final concentration with mobile phase.



Structure of DINNSA



Structure of DDBSA

The reference solution to check the calibration containing 2.0 mg/L for DINNSA was prepared by weighing 50 mg of the DINNSA 50% solution into a 50-mL volumetric flask and diluting to the mark with heptane. Pipetting 1 mL of this solution into a 25-mL volumetric flask and diluting to the mark with heptane will yield the 20-mg/L DINNSA solution. Additional pipetting of 1 mL of this solution into a 10-mL volumetric flask and diluting to the mark with mobile phase will yield the 2-mg/L check solution for DINNSA.

The reference solution to check the calibration contained 2.8 mg/L for DDBSA and was prepared by weighing 50 mg of the DDBSA 70% solution into a 50-mL volumetric flask and diluting to the mark with heptane. Pipetting 1 mL of this solution into a 25-mL volumetric flask and diluting to the mark with heptane will yield the 28-mg/L DDBSA solution. Additional pipetting of 1 mL of this solution into a 10-mL volumetric flask and diluting to the mark with mobile phase will give the 2.8-mg/L check solution for DDBSA.

The calibration solutions were diluted to their final concentration with mobile phase, in order to determine the signal-to-noise rations needed to determine the limit of detection.

Sample preparation

For sample preparation, SPE columns filled with amino-bonded silica (AccuBond Amino, Agilent Technologies) were used. Depending on size, different calibration concentrations and sample volumes were needed (Tables 2, 3).

Two solutions to wash the SPE columns were prepared:

- 2-methyl-pentane or heptane wash for the first wash
- Methanol for the second wash

The required volume (see Table 3) was transferred to the SPE column and the sample was allowed to percolate through the column at a flow rate of less than 2 mL/min. The eluate was discarded and the column was rinsed with the wash solutions, discarding the eluates. The sulfonic acids were eluted using the respective elution volumes in a volumetric flask and were diluted with mobile phase.

Calibration level	DINNSA (mg/L)	DDBSA (mg/L)
1	16	7.84
2	8	3.90
3	3.2	1.57
4	1.6	0.78
5	0.8	0.16
6	0.32	0.157

Table 1
Concentration of calibration levels.

SPE Column size	DINNSA	DDBSA
500 mg	0.8–16 mg/L	0.7–8.5 mg/L
100 mg	0.32–9 mg/L	0.35–4.5 mg/L

Table 2
Calibration range depending on the SPE column size.

	500 mg SPE column	100 mg SPE column
Sample volume	50 mL	10 mL
First wash step	2 × 5 mL	2 × 2 mL
Second wash step	5 mL	2 mL
DINNSA/DDBSA eluate	5 mL	2 mL

Table 3
SPE sample, wash and elution volumes.

	Agilent ZORBAX Stable Bond C8, 250 × 4.6 mm, 5 µm	Agilent ZORBAX Stable Bond C8, 100 × 4.6 mm, 1,8 µm
Flow:	0.50 mL/min	0.50 mL/min
Type:	Isocratic	Isocratic
Temperature:	40 °C	40 °C
DINNSA detection:	234/4 nm (Ref.: 450/100 nm)	234/4 nm (Ref.: 450/100 nm)
DDBSA detection:	225/4 (Ref.: 450/100 nm)	225/4 (Ref.: 450/100 nm)
Data rate:	2.5 Hz	20 Hz
Cell:	10 mm, 1 µL Agilent Max-Light Cartridge Cell	10 mm, 1 µL Agilent Max-Light Cartridge Cell
Injection volume:	20 µL	20 µL
Maximum pressure:	90 bar	140 bar

Table 4
Apparatus conditions.

Chromatographic conditions

Column for method setup

- Agilent ZORBAX Stable Bond C8, 250 × 4.6 mm, 5 µm, (p/n 880975-906)
- Agilent ZORBAX RRHT Stable Bond C8, 100 × 4.6 mm, 1.8 µm, (p/n 828975-906)

Mobile phase: v/v

400 mL methanol/400 mL THF/50 mL buffered phosphoric acid

Chromatograms and calculation

When the operating conditions were stable, a fixed volume of the calibration standard of DINNSA or DDBSA was injected ensuring that the chromatograms resemble those shown in Figure 1 (DINNSA) and Figure 2 (DDBSA).

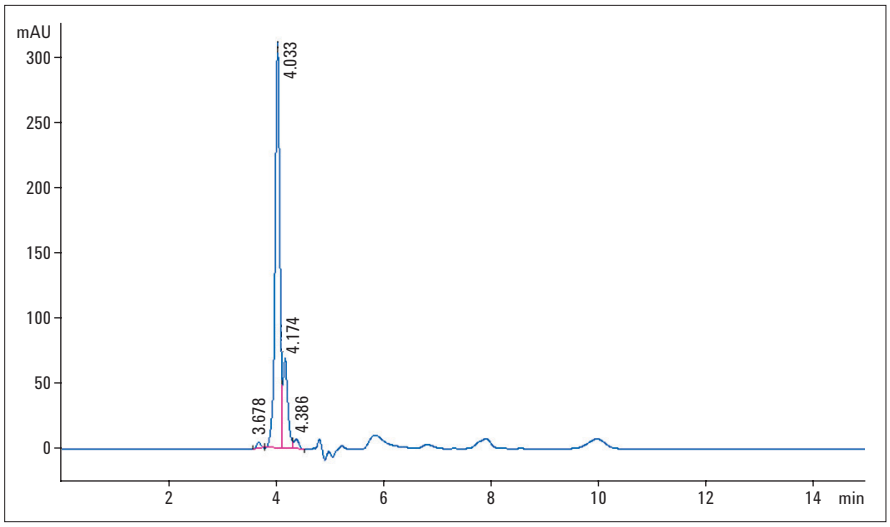


Figure 1
DINNSA calibration standard, 8 mg/L.

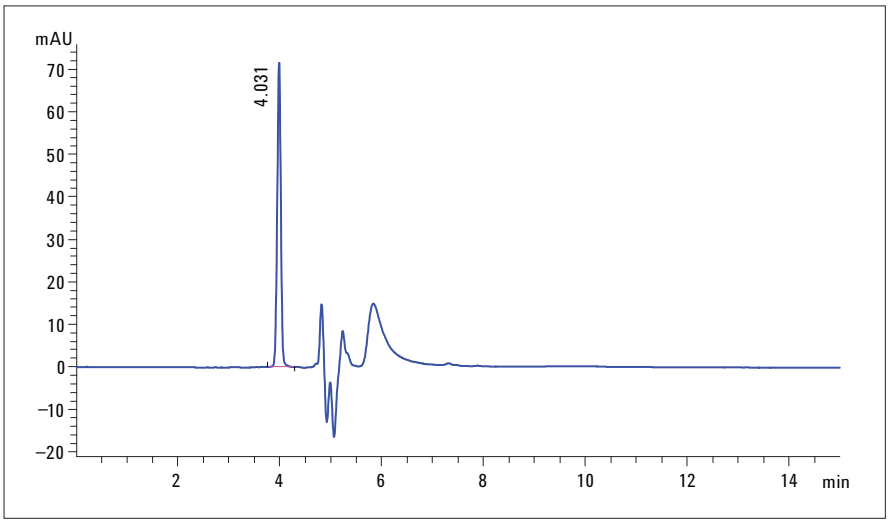


Figure 2
DDBSA calibration standard, 3.9 mg/L.

Both SDA components elute at nearly the same retention time and must not be separated because only one component is always added to the fuel.

Based on the calculation that the same injection volumes are used for the calibration standards and samples, the formulation standards for the SDAs are calculated as follows:

- DINNSA: $C_{SDA} = A_{DINNSA} \times 7.952$
- DDBSA: $C_{SDA} = A_{DDBSSA} \times 14.29$
  - where A_{xx} is the concentration of the corresponding sulfonic acid (mg/L)
  - C_{xx} is the concentration of the corresponding SDA (mg/L)
  - 7.952/14.29 is the SDA formulation standard factor

Testing precision and linearity

With the following setup for the reference sample the adapted method can be checked:

- Precision of areas must be < 1 % RSD
- Precision of retention times must be < 0.5 % RSD
- Linearity should be given at least with $R^2 > 0.999$

With these limits and settings for testing, the samples in Table 5 were prepared and analyzed.

Sample	Purpose	Number of injections
Blank solution	Verify baseline stability and identify artifacts	3
Reference sample	Verify precision of areas and retention times for reference solution for each SDA	10
Calibration	Verify linearity	6 level

Table 5
Setup for evaluation of the chromatographic method.

	DINNSA Sample 1		DDBSA Sample 1	
Run	Retention time	Area	Retention time	Area
1	4.027	583.74	4.027	449.52
2	4.028	582.45	4.028	448.8
3	4.029	583.02	4.029	448.52
4	4.03	583.9	4.03	449.75
5	4.028	583.85	4.028	449.54
6	4.028	583.99	4.028	450.37
7	4.03	584.53	4.03	449.89
8	4.028	585.12	4.028	450.75
9	4.029	585.25	4.029	451.13
10	4.031	585.26	4.031	450.9
MW	**4.03**	**584.11**	**4.03**	**449.92**
SD	**0.001**	**0.944**	**0.001**	**0.873**
RSD	**0.03**	**0.16**	**0.03**	**0.19**

Table 6
Results for the reproducibility of the chromatographic method.

Results and discussion

The chromatograms in Figures 1 and 2 show great similarity with those presented in the IP 568[4]. The values for the precision of the chromatographic method are shown in Table 6.

Table 6 shows the data for the precision of the method according to the separation with the ZORBAX Stable Bond C8, 250 × 4.6 mm, 5 µm with a flow rate of 0.50 mL/min. The retention time precision (RSD) was better than 0.05% for all samples and analytes and the RSD for area precision was less than 0.5%.

To determine the limit of detection, the solutions for the calibration standard level 6 were diluted by eluent.

The chromatograms in Figures 3 and 4 show the high sensitivity with the 1-µL Agilent Max-Light Cartridge Cell of the DAD coupled with a great dynamic range for each analyte (see Figure 5).

Good linearity was determined for both analytes shown in Figure 5 with correlation coefficients better than 0.9999. According to the requirements for checking precision and linearity, all requirements were fulfilled.

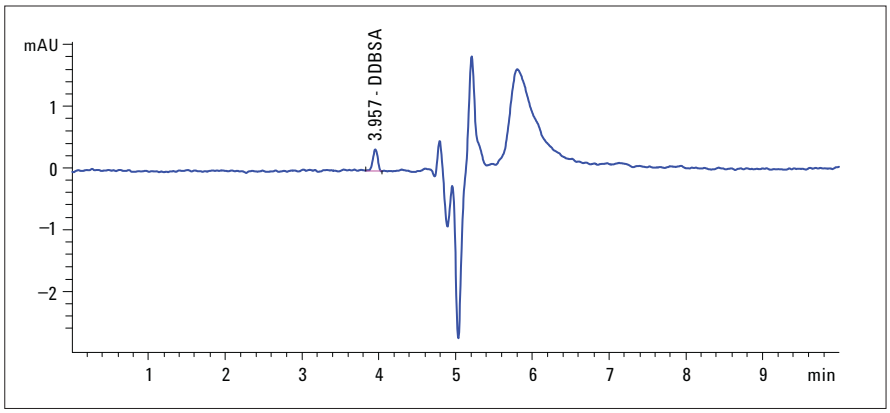


Figure 3
Injection of 20 µL of a 0.157mg/L solution of DDBSA, S/N-ratio: 7.

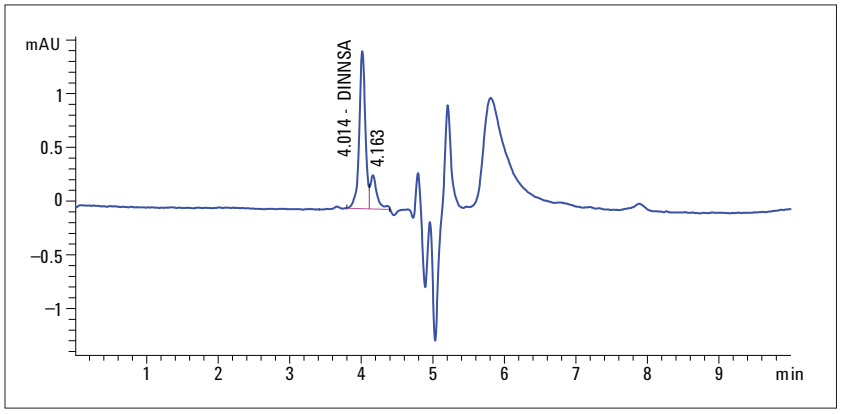


Figure 4
Injection of 20 µL of a 0.32 mg/L solution of DINNSA, S/N-ratio: 70.

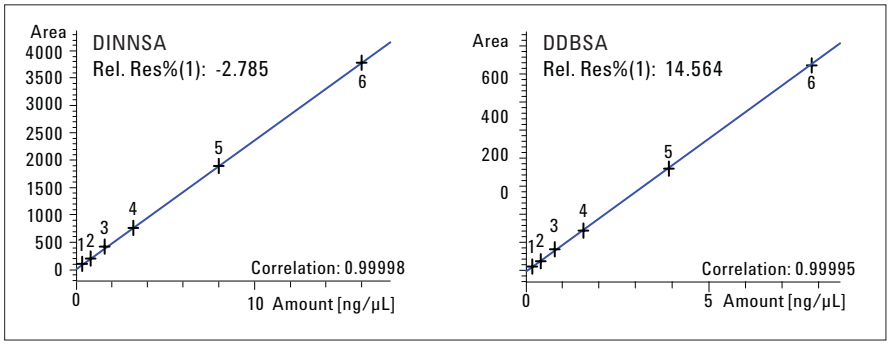


Figure 5
Calibration curves for DINNSA and DDBSA

To check if the determination also runs under UHPLC conditions, the method parameters were transferred to a setup using a RRHT (Rapid Resolution High Throughput) column. The 1260 Infinity LC System with its 600 bar pressure range was used for both setups. Similar chromatograms were obtained, showing the same selectivity with reduced retentions times, proportional to the column length (Figures 6 and 7).

Conclusion

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

The determination of static dissipater in aviation fuel is easy to achieve with the 1260 Infinity LC System and the ZORBAX Stable Bond C8 material. The usage of RRHT columns for detecting the sulfonic acids from fuel shows similar resolutions with shorter retention times.

The results for precision show that the conditions allow a very stable determination of these analytes with RSDs 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 0.999 for both analytes.

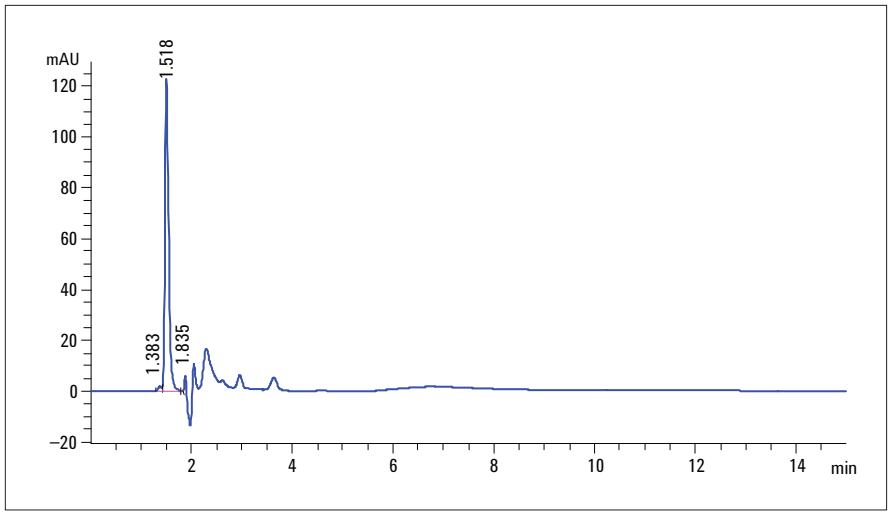


Figure 6
Solution for DINNSA (2.8 mg/L) on the RRHT column.

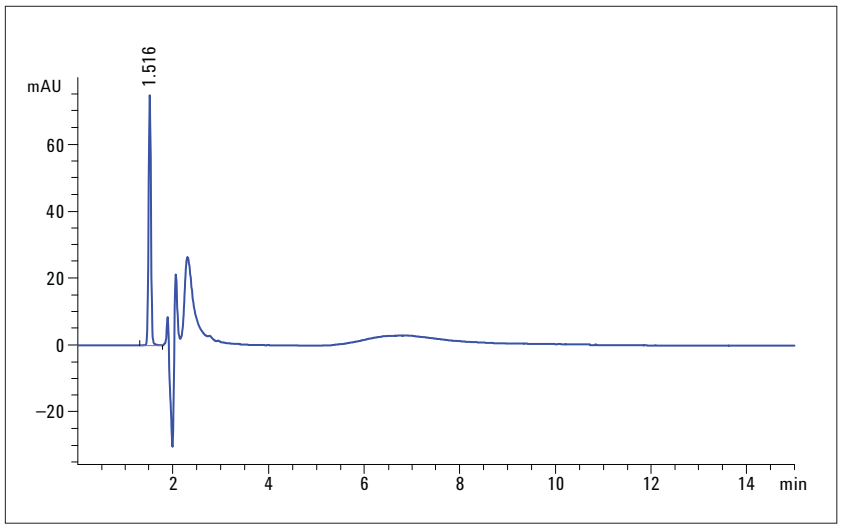


Figure 7
Solution for DDBSA (2.0 mg/L) on the RRHT column.

References

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2.
IP 475, Petroleum liquids–Manual sampling

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IP 476, Petroleum liquids–Automatic pipeline sampling

4.
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