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Application News

Determining the concentration of pipeline Drag Reducer Additive in Aviation Turbine Fuels as per ASTM D7872

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User Benefits

- Simple GPC method for quantitation of DRA in jet fuel.
- Shorter and sensitive method for DRA

■ Introduction

A small amount of polymer additive is added to the fluid which causes the reduction in friction and increases the pumping capacity of fluids. The addition of such polymeric additive is called Drag Reducing Agent (DRA). The DRA is added in relatively small amounts but may cause some serious impacts on the jet engine performance if that is found in higher concentrations in jet fuels.

DRA is frequently added into multiproduct pipelines to increase throughput or reduce energy requirements of fuel movement. Although these additives are not used in jet fuel, contamination can occur from other products if proper batching guidelines are not followed or by other cases of human error. CRC Report No. 642 reviewed the impact of DRA on jet fuel fit-for-purpose performance and concluded that the fuel spray angle and atomization capability of several engine-type fuel nozzles can be adversely affected impacting high altitude relight performance at elevated concentrations. A method that accurately quantifies the amount of DRA in jet fuel can be useful in confirming the absence of significant contamination to protect the safety of aviation operations. This test method is designed to measure down to sub-100 µg/L levels of DRA in aviation fuel. The sensitive and reproducible method was developed on Nexera GPC system shown in Figure 1.

Figure 1. Nexera GPC system

■ Experimental

Preparation of Standard stock:- Received 10000 mg/kg FLO XS DRA solution form market. Prepared 200 mg/L stock solution DRA from it by diluting by DRA free jet fuel.

Standard calibration levels:- Calibration standards of DRA with concentrations 2, 4, 10, 20 and 100 mg/L were prepared by diluting stock solution using jet fuel.
Each level of standard solution was injected in replicates create calibration curve.

Sample preparation:- Taken around 400 g of jet fuel in 1 L rotary evaporator round bottom flak. Noted the empty round bottom flask weight before transferring the jet fuel sample into it. Jet fuel was then concentrated to around 4-6 g by slowly increasing oil bath temperature to 170 °C at high vacuum. The evaporator parameters are shown in Table 1.
Allowed flask to cool down to room temperature. Taken weight of residue. The residue then taken in HPLC vial to inject on HPLC and calculated the DRA concentration based on priorly acquired the calibration curve. The detailed HPLC parameters are shown in Table 2.

Spiked sample preparation:- Taken around 400 g of jet fuel in 1 L rotary evaporator round bottom flask. Noted the empty round bottom flask weight before transferring the jet fuel sample into it. To that added 200 µL of 200 mg/L stock solution of DRA. Jet fuel was then concentrated to around 4-6 g by slowly increasing oil bath temperature to 170 °C at high vacuum. The detailed Rotovap parameters are given in Table 1.
Allowed flask to cool down to room temperature. Taken weight of residue. The residue then taken in HPLC vial to inject on HPLC and calculated the DRA concentration based on priorly acquired the calibration curve.

Table 1. Rotovap Conditions

Pressure	: 3.1 kPa to 6.5 kPa
Temperature	: 120 °C to 180 °C
Approximate time	: 1 h to 3 h (depending on vacuum pressure and temperature)

Table 2. HPLC Instrument Parameters

Column	: Shodex GPC KF-804 L (250 mm x 7.5 mm I.D., 5 µm)
Mobile phase	: n- Heptane
Detector	: Refractive index detector (RID-20A)
Mode	: Isocratic
Flow rate	: 1.5 mL/min
Column temperature	: 40 °C
Injection volume	: 100 µL
Flow cell temp.	: 40 °C
Run time	: 20 min

■ Results

The GPC should be equilibrated, and column temperature should be allowed to stabilized before starting of analysis. As per the requirement stated by ASTM, the signal to noise ratio was determined at 10 mg/L, which was found to be greater than 10. The coefficient of determination for the DRA was achieved more than 0.99. The Linearity graph is prepared as shown in Figure 2 and the linearity results are shown in Table 3. Samples were analyzed following the linearity acquisition. The very little presence of DRA was found in Jet fuel. The DRA calculation is shown in Equation 1. The same sample was used for spike study. The detailed results of the sample analysis and the sample spike experiment are shown in Table 4.
As shown in Figure 3. S/N is 12.1. This ensures the system is suitable for lower quantitation of DRA in jet fuel.
Spiked 20 mg/L equivalent of DRA stock in jet fuel before evaporation in previously analyzed jet fuel sample to check method recovery. The sample blank and spiked recovery chromatograms are shown in Figure 4.

Concentration of DRA in jet fuel =
(DRA concertation in jet fuel concentrate) (W2/W1)

W1 = Weight of jet fuel in a tared 1 L round bottom flask prior to evaporation
W2 = Weight of residue after evaporation

Equation 1. Formula for DRA in concentrated sample

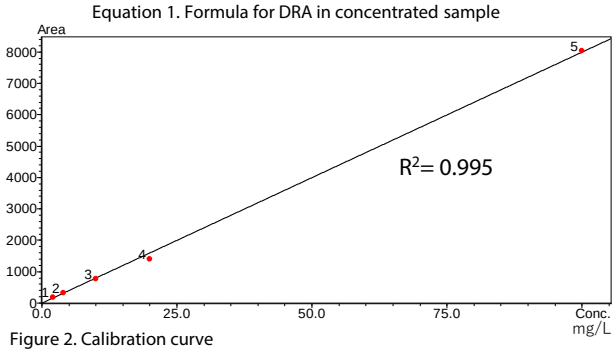

Figure 2. Calibration curve

Table 3. Calibration curve details

Std Conc. mg/L	Found conc. mg/L	Linearity	% Accuracy
2.0	2.008	0.995	100.4
4.0	4.022		100.55
10.0	10.002		100.02
20.0	18.302		91.51
100.0	107.504		107.5

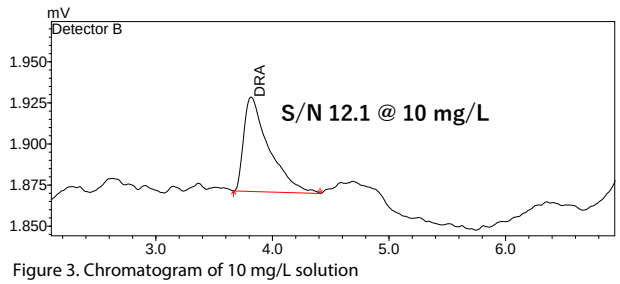

Figure 3. Chromatogram of 10 mg/L solution

This method is not particularly specific to DRA, hence it may also measure any high molecular weight compound present in the sample. Higher care need to be taken to avoid contamination and potential interference with DRA peak. Jet fuel evaporation is very critical step of the process. The weight of residue should be as low as possible to get better sensitivity and quantitation. There is no chance of any high molecular weight compound added in jet fuel except DRA, however care need to be taken to remove grease used for Rotovap.

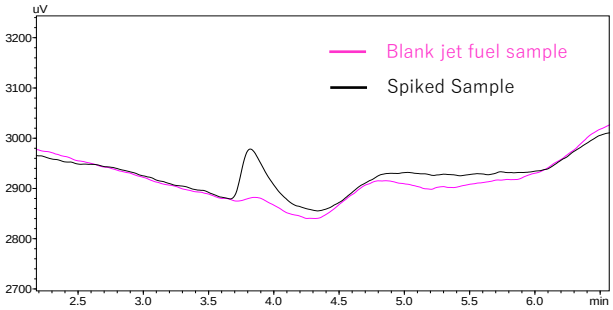

Figure 4. Overlaid chromatograms of blank and spiked sample

Table 4. Sample spiked results

Sample	Conc. (mg/L)	Cal. Conc. of DRA (mg/L)	% Recovery
Sample 1	1.497	0.025	
Spike 1	19.3	0.287	89.00%
Spike 2	20.5	0.291	95.02%

■ Conclusion

This application note demonstrates ASTM D7872 for the determination of DRA in jet fuels. The sample preparation steps pose challenges; however, Shimadzu Nexera GPC system is capable to analyze DRA even at trace levels with superior S/N ratio.

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