Standard Test Method for Determining the Concentration of Pipeline Drag Reducer Additive in Aviation Turbine Fuels[1]

This standard is issued under the fixed designation D7872; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the measurement of high molecular weight polymers, in particular pipeline drag reducer additive (DRA), in aviation turbine fuels with a 72 µg/L lower detection limit. The method cannot differentiate between different polymers types. Thus, any non-DRA high molecular weight polymer will cause a positive measurement bias. Further investigation is required to confirm the polymer detected is DRA.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 **Warning—**Mercury has been designated by many regulatory agencies as a hazardous material that can cause central nervous system, kidney and liver damage. Mercury, or its vapor, may be hazardous to health and corrosive to materials. Caution should be taken when handling mercury and mercury containing products. See the applicable product Material Safety Data Sheet (MSDS) for details and EPA's website — http://www.epa.gov/mercury/faq.htm — for additional information. Users should be aware that selling mercury and/or mercury containing products into your state or country may be prohibited by law.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

2.2 *Other Reference:*

CRC Report No. 642 Investigation of Pipeline Drag Reducers in Aviation Turbine Fuels

3. Terminology

3.1 *Definitions:*

3.1.1 *bumping, v*—violent boiling which displaces liquid into the distillation flask.

3.1.2 *drag reducing additive (DRA), n*—a material comprised of very high molecular weight hydrocarbon polymers that is soluble in petroleum products and used to reduce the fluid friction during pipeline transportation.

3.1.3 *rotary evaporation, n*—a distillation process utilizing heat, reduced pressure and a rotating flask which evaporates fluid to reduce the volume of a sample of material.

3.1.3.1 *Discussion*—The apparatus, consisting of a round-bottomed flask in a heated bath, is operated under vacuum (reduced pressure) to lower the boiling point of the fluid, and the rotational motion accelerates evaporation of the liquid by creating additional surface area of the fluid being distilled off.

3.1.4 *sheared DRA, n*—the very long hydrocarbon polymers of drag reducing agent that have been shortened by severe physical processes such that the resulting material is no longer effective at reducing fluid friction.

3.1.4.1 *Discussion*—Severe physical and mechanical processes include large pressure changes which can occur at control valves, pumps, meters, reductions in pipe diameter which affect fluid velocity, and ultrasonication in a laboratory process, resulting in shorter polymeric chains which are still very large compared to the fuel molecules and are non-distillable.

3.1.5 *total exclusion, n*—polymers larger than the pore size cannot enter the pores and elute together as the first peak in the chromatogram.

3.2 *Abbreviations:*

3.2.1 *DRA*—drag reducing additive

3.2.2 *GPC*—gel permeation chromatography

3.2.3 *RI*—refractive index

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.J0.01 on Jet Fuel Specifications.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3.2.4 *THF*—tetrahydrofuran

4. Summary of Test Method

4.1 The method employs a rotary evaporator (also called a rotovap) to concentrate the DRA in a base sample followed by GPC to separate and quantify the DRA from the remaining jet fuel. Rotovaping is a rapid vacuum distillation process used to reduce the volume of jet fuel which effectively increases the relative DRA concentration. The GPC method uses heptane or THF as the mobile phase, a single separation column and refractive index detection. The separation column contains particles with pore sizes that totally exclude sheared and unsheared DRA polymers to give a sharp chromatographic DRA peak.

4.2 An approximate 400 g sample of jet fuel is concentrated through rotary evaporation and analyzed by GPC. The DRA concentration is quantified by integrating the area under the DRA peak. Comparing this area to a calibration curve allows a determination of the weight fraction of the DRA component in the concentrated jet fuel. The original concentration is obtained by correcting for the concentrating in the rotary evaporation of the jet fuel. The detector is calibrated using standards of sheared DRA in jet fuel in the low mg/L concentration range.

5. Significance and Use

5.1 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.

6. Interferences

6.1 This test method has no particular specificity for DRA and will also measure any other high molecular weight compounds present in the sample making it susceptible to interferences. However, no high molecular weight polymers are approved for blending into aviation fuels. Stadis 450 has a low molecular weight polymer and was checked. No interference was found. The presence of non-DRA high molecular weight polymers would create a positive measurement bias. However, detection sensitivity of the non-DRA high molecular weight polymers may not be the same because of polymer type differences. Thus, non-DRA high molecular weight polymers should not be quantified by this test method.

7. Apparatus

7.1 *Vacuum source,* such as a vacuum pump capable of reducing the pressure in a rotary evaporator to 6.77 kPa (28 in. of mercury below atmospheric pressure).

7.2 *Rotary evaporator,* equipped with a silicone oil heating bath that can accommodate flasks capable of holding 400 g of jet fuel. A bump trap may be connected to the evaporation flask. Any silicone oil bath capable of reaching 180°C is suitable. There are a variety of high temperature silicone bath oils that may be used and are commercially available. Water may be used to cool the rotovap condenser. Details of the rotovap are described in Table 1.

NOTE 1—Bumping can cause loss of polymer from the flask that would create a lower than actual detection value.

7.3 *Gel permeation chromatography system,* described in Table 2. The method includes flexibility in the selection of GPC hardware and conditions; however, a refractive index detector is required.

7.4 Any GPC apparatus may be used, provided the RI detector response to the DRA peak has a signal to noise (S/N) ≥ 10 for a 50 µg/L DRA in jet fuel sample after rotary evaporation (this translates into 10 mg/L if rotary evaporation provided a reduction of 400 g to 2 g for a jet fuel sample containing 50 µg/L DRA).

7.5 To achieve sub 100 µg/L DRA detection, a column that exhibits total exclusion of the sheared DRA is required. Total exclusion leads to sharper elution peaks providing easier detection. In addition, polymers are susceptible to shearing while passing through a GPC column. Columns packed with large particle size stationary phase avoid shearing, 5 or 10 µm particle sizes are recommended.

8. Reagents and Materials

8.1 All chemicals are American Chemical Society grade chemicals or better unless specified otherwise.

8.2 Drag reducing additive, available from appropriate additive supplier in "sheared" form for use in preparing standards.

9. Sampling

9.1 Fuel samples are typically drawn from pipelines. Consult Practice D4057 for guidance on proper sampling procedures. Consult Practice D4177 for guidance on auto sampling.

10. Preparation of Apparatus

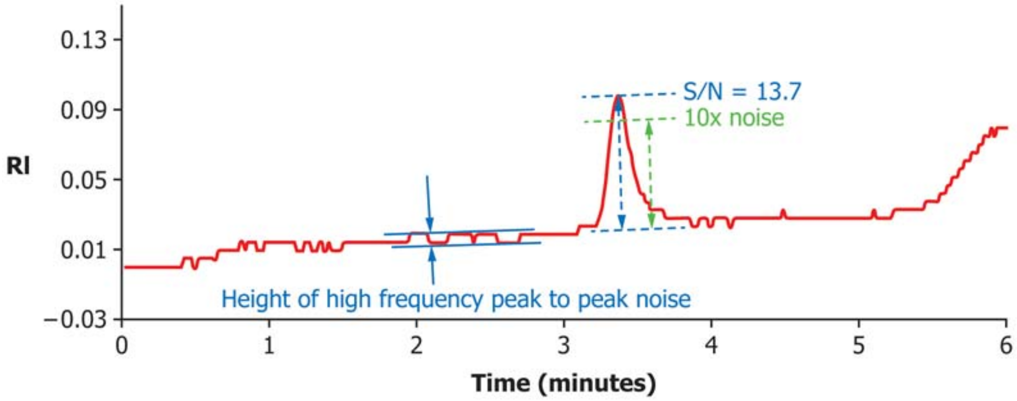
10.1 The GPC should be equilibrated for 1 h and the column temperature stabilized to the temperature of the analysis prior to analyzing samples.

11. Calibration and Standardization

11.1 Prepare standards of sheared DRA in jet fuel by dilution of a concentrated stock solution supplied by an appropriate additive supplier in the range of 0 to 100 mg/L.

TABLE 1 Rotovap Conditions

Pressure	3.1 kPa to 6.5 kPa (28 to 29 in. Hg below atmospheric pressure)
Temperature	120 to 180°C
Approximate time	1 to 3 h (depending on vacuum pressure and temperature)



NOTE 1—Chromatogram of a concentrated jet fuel sample originally containing 50 µg/L of sheared DRA acquired using a GPC apparatus described in Table 2 (GPC column, 10 µm particles with 500 Å pore size, heptane mobile phase). Noise is the height of the high frequency peak to peak displacement taken near the peak through a range which is at least the width of the base of the DRA peak. Signal is the peak height. Chromatogram example exhibits a DRA signal that satisfies the S/N > 10.

FIG. 1 Signal to Noise Example

TABLE 2 GPC Components and Operation Parameters

Column	5 or 10 µm particle size; between 50 Å (5 nm) and 10^4 Å (1000 nm) pore size
Length:	300 mm
ID:	7.5 mm
Temperature:	20 to 40°C
Flow Rate:	1.5 mL/min
Mobile phase	THF or Heptane
Volume injected	100 µL
Equilibration time	1 h (prior to injections)
Detector	RI

Base jet fuel should be free of DRA and other high molecular weight polymer contamination. For the development of the method a 1 wt% concentrate of sheared FLO XS DRA (10000 mg/kg, 8010 mg/L) in jet fuel was obtained from Baker Hughes for making the calibration samples. The concentrate may also be provided in diesel fuel.

11.2 Prepare a 200 mg/L stock calibration sample by quantitatively blending 4.0 mL of the 8010 mg/L concentrate with 156.2 mL jet fuel. From this, make a series of 100 mL calibration samples in the range of 2.0 to 100 mg/L, by placing volumes of 200 mg/L stock calibration sample, given in Table 3, into the required number of 100 mL capacity volumetric flasks and making them up to 100 mL with jet fuel.

TABLE 3 DRA in Jet Fuel Calibration Standards[A]

	Volume (mL) of 200 mg/L stock calibration sample added to 100 mL capacity volumetric flasks
2 mg/L calibration sample (CS1)	1.0
4 mg/L calibration sample (CS2)	2.0
10 mg/L calibration sample (CS3)	5.0
20 mg/L calibration sample (CS4)	10.0
100 mg/L calibration sample (CS5)	50.0

[A] Record data to the same decimal place indicated in Table 3. Use DRA-free jet fuel for a zero concentration calibration sample.

12. Procedure

12.1 If non-sheared DRA samples were provided or to ensure the DRA in jet fuel is sheared, the sample may be placed in an ultrasonicator or mechanically sheared with a homogenizer. Details on procedures for shearing can be provided by the DRA supplier.

12.2 Accurately weigh approximately 400 g of jet fuel to 0.1 g in a tared 1 L round bottom flask (W1). Concentrate this sample to between 2 g to 10 g on a rotary evaporator and accurately weigh the residue to 0.1 g (W2).

NOTE 2—Oil from the oil bath should be removed from the outside surface of the round bottom flask with volatile solvent and allowed to dry to ensure accurate weighting of the flask with the jet fuel concentrate.

NOTE 3—Avoid the use of silicone vacuum grease on the round bottom flask fitting.

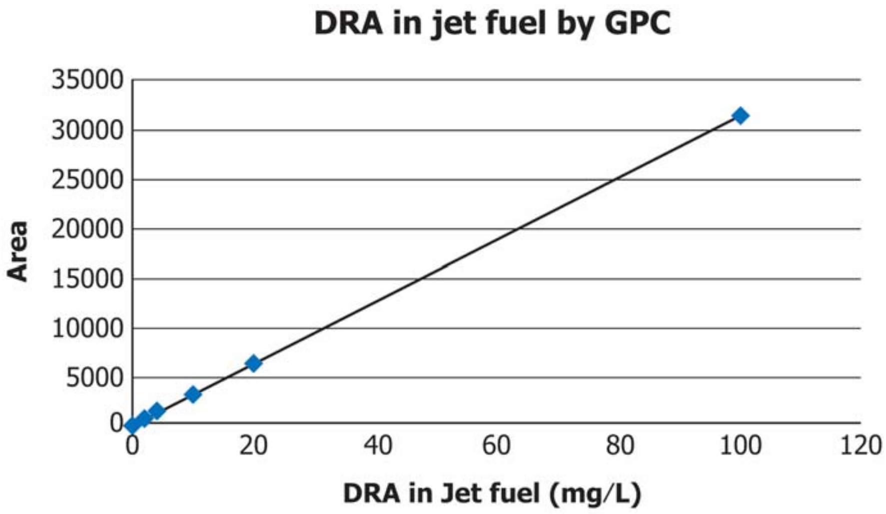
12.3 Transfer some of the concentrated sample to a vial from which a syringe aliquot may be drawn (or into a suitable GPC auto sampler vial). The entire sample does not need to be transferred and the remaining may be saved or discarded.

12.4 GPC operation parameters are summarized in Table 2. The one hour equilibration step (10.1) is done to ensure the baseline is flat prior to sample injection. 100 µL of standards and concentrated sample are injected in the GPC apparatus and the output is recorded on an electronic data collection system.

13. Calculation or Interpretation of Results

13.1 The chromatogram peak area corresponding to the DRA signal in the 3 to 4 min region is integrated. An external calibration curve plotting integrated area of DRA standards verses the mg/L of the standards is used to determine mg/L DRA in sample. Ensure that the correct standard concentrations are entered into the chromatography data system calibrations table and construct a calibration curve for sheared DRA. See Fig. 2 for an example.

13.2 The DRA concentration in the concentrated jet fuel sample is determined by integrating the area of the DRA peak



NOTE 1—Calibration range 0 mg/L to 100 mg/L of sheared DRA in jet fuel.

FIG. 2 Typical Calibration Curve

in the concentrated fuel and using the external calibration curve to determine the associated DRA mg/L level (Fig. 3).

13.3 The level of DRA in the test specimen is determined by multiplying the concentration (in mg/L) of DRA determined by GPC in the concentrated fuel by the dilution factor for the sample which is the ratio of the weight of fuel after and before concentrating.

13.4 Calculate the concentration of DRA in jet fuel (in mg/L) as follows:

$$\text{Concentration of DRA in jet fuel} = (\text{calculated mg/L DRA in jet fuel concentrate}) \times (W2/W1) \quad (1)$$

where:

W1 = weight of jet fuel in a tared 1 L round bottom flask prior to rotovaping, and
W2 = weight of residue after rotovaping (W2).

13.5 Eq 1 reports the level in mg/L. Multiply result by 1000 to report µg/L level of DRA in finished fuel.

14. Report

14.1 Report the concentration of drag reducing additive (DRA) in the fuel sample, in units of µg/L to the nearest whole unit, and reference this test method. If the result is less than 72 µg/L, report "less than 72 µg/L".

15. Precision and Bias

15.1 The precision of this test method is as follows:

Repeatability = 0.01793 (X + 1117.6082) µg/L
Reproducibility = 0.03014 (X + 1117.6082) µg/L
(X is the average of results being compared)

15.1.1 Precision was determined using DP22 software on interlaboratory results in the range of 40 to 200 µg/L.

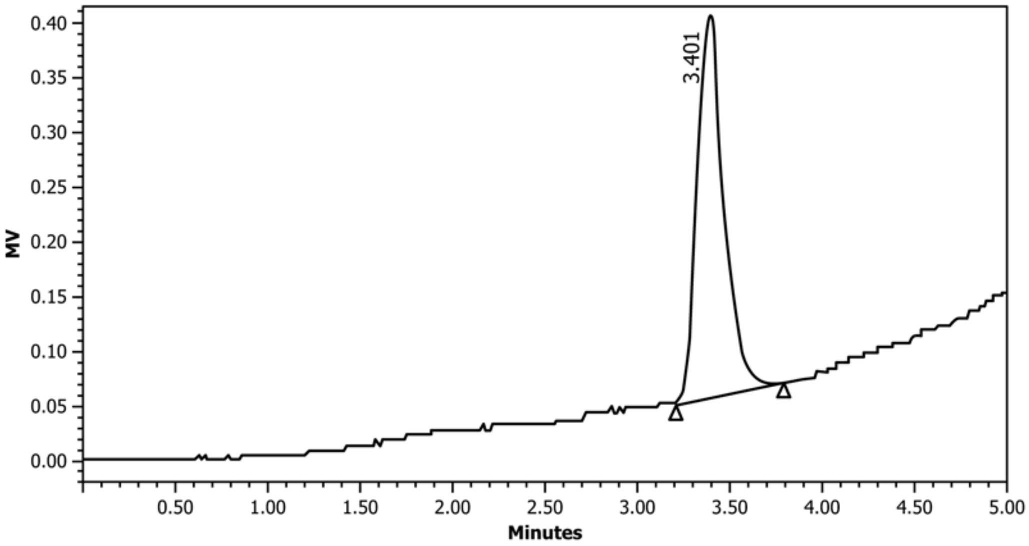


FIG. 3 GPC Chromatogram of a Concentrated Jet Fuel Sample Containing DRA at an Original Concentration of 50 µg/L

15.1.2 The poor repeatability and reproducibility values shown above reflect the challenges in conducting the ILS. It is recommended that in the future by carrying out another ILS that takes into account lessons learnt from the ruggedness trial, ILS detailed in ASTM Research Report RR:D02-1763[3] and field experience the repeatability and reproducibility and bias could be understood/dealt with, and precision improved.

16. Keywords

16.1 DRA; GPC; jet fuel; rotary evaporation; total exclusion

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[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1763. Contact ASTM Customer Service at service@astm.org.

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