Designation: D7546 – 15

Standard Test Method for
Determination of Moisture in New and In-Service Lubricating Oils and Additives by Relative Humidity Sensor[1]

This standard is issued under the fixed designation D7546; 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 quantitative determination of water in new and in-service lubricating oils and additives in the range of 10 mg/kg to 100 000 mg/kg (0.001 wt./wt. to 10 % wt./wt.) using a relative humidity (RH) sensor. Methanol, acetonitrile, and other compounds are known to interfere with this test method.

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—**Samples tested in this test method can be flammable, explosive, and toxic. Use caution when handling them before and after testing.

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]

D4175 Terminology Relating to Petroleum, Petroleum Products, and Lubricants

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology D4175.

4. Summary of Test Method

4.1 An aliquot of sample is heated to a temperature between 25 °C to 200 °C with 1 °C resolution. The sample is maintained at a constant temperature for the duration of the test. Dry inert gas flows over the heated sample and carries the thermally evolved moisture past a relative humidity sensor. The sensor signal is integrated over time to provide a measurement of total mass of water in the sample.

4.2 The sample injection may be done either by mass or by volume.

4.3 This test method utilizes anhydrous compressed gas or ambient air passed through a desiccant to prevent contamination from moisture present in the atmosphere.

4.4 Viscous samples can be analyzed by preheating them to place them in a more fluid state allowing them to be drawn into a syringe, or by dissolving them in a compatible anhydrous solvent. Care should be taken to minimize time spent preheating samples to prevent moisture loss.

5. Significance and Use

5.1 Knowledge of the water content of lubricating oils, additives, and similar products is important in the manufacture, purchase, sale, transfer, or use of such petroleum products to help in predicting their quality and performance characteristics.

5.2 For lubricating oils, the presence of water can lead to premature corrosion and wear, an increase in the debris load resulting in diminished lubrication and premature plugging of filters, impedance to the effect of additives, and undesirable support of deleterious bacterial growth.

6. Interferences

6.1 Methanol and acetonitrile are known to interfere with the determination of moisture by this test method. These substances contribute to a high bias in the final results. More generally, some short-chained polar molecules mimic the effect of water at the RH sensor resulting in a positive interference. Strong polar solvents, such as n-methyl-pyrrolidone, can severely damage the RH sensor.

7. Apparatus

7.1 *Sample Injection Moisture Analyzer Apparatus:*

7.1.1 *Flow Regulator,* capable of maintaining the carrier gas flow rate within the manufacturer's specified conditions.

7.1.2 *Flow Meter,* capable of measuring the carrier gas flow rate within the manufacturer's specified conditions.

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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 D02.96.02 on Chemistry for the Evaluation of In-Service Lubricants.

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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.

***A Summary of Changes section appears at the end of this standard**

7.1.3 *Stainless Steel Sample Coil,* for heating the sample as it is transported from the sample inlet to the sump.

7.1.4 *Sample Coil Heater,* capable of maintaining the sample coil temperature within 1 °C of the programmed temperature between 25 °C and 200 °C.

7.1.5 *Sample Delivery System,* provides programmable variable speed injection of the sample into the coil.

7.1.6 *Sump,* allows for collection of the sample at the bottom of the sample coil during testing and discharge of the sample to a waste container after testing is completed.

7.1.7 *Manifold,* which provides:

7.1.7.1 A thermally stable port for mounting and operation of the relative humidity sensor.

7.1.7.2 Inlet and outlet ports for the carrier gas.

7.1.8 *Relative Humidity (RH) Sensor,* a capacitive sensing element that measures the relative humidity of the carrier gas.

7.1.9 *Microcontroller,* which provides:

7.1.9.1 Capability of integrating and converting the RH sensor signal.

7.1.9.2 Capability of controlling the temperature of the coil heater, and the sensor manifold.

7.1.9.3 Capability of controlling the speed of the sample delivery system.

7.1.10 *Balance,* external, with 1 mg precision for weighing sample.

7.2 *Headspace Vial Moisture Analyzer Apparatus:*

7.2.1 *Flow Regulator,* capable of maintaining the carrier gas flow rate within the manufacturer's specified conditions.

7.2.2 *Flow Meter,* capable of measuring the carrier gas flow rate within the manufacturer's specified conditions.

7.2.3 *Sample Heating Chamber,* capable of maintaining the sample chamber temperature within 1 °C of the programmed temperature between 25 °C and 200 °C.

7.2.4 *Sample Delivery System,* transports vial into sample heating chamber.

7.2.5 *Manifold,* which provides:

7.2.5.1 A thermally stable port for mounting and operation of the relative humidity sensor

7.2.5.2 Inlet and outlet ports for the carrier gas.

7.2.6 *Relative Humidity (RH) Sensor,* a capacitive sensing element that measures the relative humidity of the carrier gas.

7.2.7 *Microcontroller,* which provides:

7.2.7.1 Capability of integrating and converting the RH sensor signal.

7.2.7.2 Capability of controlling the temperature of the sample heating chamber, and the sensor manifold.

7.2.7.3 Capability of controlling the speed of the sample delivery system.

7.2.8 *Balance,* external, with 1 mg precision for weighing sample.

8. Reagents and Materials

8.1 *Carrier Gas,* any dry inert gas including, but not limited to, dry air, nitrogen, helium, or argon.

8.2 *Water,* deionized.

8.3 *For Sample Injection Moisture Analyzer:*

8.3.1 *Traceable Syringe,* traceable at the desired total mass of water, typically 500 µg (0.5 µL).

8.3.2 *Glass or Plastic Syringe,* 1 mL or 5 mL capacity.

8.3.3 *Needle,* 18 gauge or 22 gauge.

8.4 *For Headspace Vial Moisture Analyzer:*

8.4.1 *Traceable 1 µL microcapillary,* traceable at the desired total mass of water, typically 1000 µg (1.0 µL).

TABLE 1 Suggested Injection Volume Based on Expected Water Content

Expected Water Concentration, (% m/m)	Sample Volume, mL
Less than 0.02	5
0.02 to 0.025	4
0.025 to 0.035	3
0.035 to 0.050	2
Greater than 0.05	1

9. Sampling

9.1 Laboratory sample shall be thoroughly homogeneous before drawing a test specimen.

9.2 *Sample Injection Moisture Analyzer*—Select test specimen size as indicated in Table 1 based on the expected water concentration.

9.3 *Headspace Vial Moisture Analyzer*—Select test specimen size as indicated in Table 2 based on the expected water concentration.

10. Preparation of Apparatus

10.1 Establish carrier gas flow to the analyzer by either opening the source regulator or turning on the dry air generator.

10.2 Turn on analyzer and allow equilibration for at least 15 min.

11. Calibration and Standardization

11.1 *Sample Injection Moisture Analyzer:*

11.1.1 To ensure the integrity of the test results, the RH sensor shall be verified and calibrated using a traceable syringe. Alternatively, the RH sensor may be verified using a traceable standard solution of water in a compatible solvent. Other suitable instrument calibration methods and standards may be used as specified by the instrument manufacturer.

NOTE 1—Examples of suitable water standards include water in propylene carbonate or water in xylenes.

11.1.2 Perform the coil heater calibration in accordance with the manufacturer's instructions. After calibration, the coil shall verifiably maintain an arbitrary set temperature from 25 °C to 200 °C within ±1 °C. Coil heater calibration should be performed at least once annually.

11.1.3 To perform the RH sensor verification, set the instrument to calibration/verification mode and inject 0.5 µL water directly into the sensor chamber of the instrument using the calibrated syringe. Acceptable results are 475 µg to 525 µg water detected.

11.1.3.1 If the RH sensor verification is not within the acceptable range:

TABLE 2 Suggested Sample Mass Based on Expected Water Content

Expected Water Concentration, (% m/m)	Sample Volume, g
Less than 0.02	1.00
0.02 to 0.025	1.00
0.025 to 0.035	0.50
0.035 to 0.050	0.25
Greater than 0.05	0.10

11.1.3.2 Perform at least five injections using the procedure outlined in 11.1.3. If the coefficient of variation between the five injections is <2 %, use the mean result of the five injections to perform a single-point recalibration of the instrument.

11.1.3.3 Repeat step 11.1.3 to verify RH sensor calibration.

11.1.3.4 If results are not within acceptable range, contact the analyzer manufacturer.

11.2 *Headspace Vial Moisture Analyzer:*

11.2.1 To ensure the integrity of the test results, the RH sensor shall be verified and calibrated using a traceable syringe. Alternatively, the RH sensor may be verified using a traceable standard solution of water in a compatible solvent. Other suitable instrument calibration methods and standards may be used as a specified by the instrument manufacturer.

11.2.2 Perform the heating chamber calibration in accordance with the manufacturer's instructions. After calibration, the sample heating chamber shall verifiably maintain an set temperature from 25 °C to 275 °C within ±1 °C. Heating chamber calibration should be performed at least once annually.

11.2.3 To perform the RH sensor verification, set the instrument to calibration/verification mode and inject 1.0 µL water directly into the sensor chamber of the instrument using the calibrated syringe. Acceptable results are 950 µg to 1050 µg water detected.

11.2.3.1 If the RH sensor verification is not within acceptable range:

11.2.3.2 Perform at least five injections using the procedure outlined in 11.1.3. If the coefficient of variation between the five injections is <2 %, use the mean result of the five injections to perform a single-point recalibration of the instrument.

11.2.3.3 Repeat step 11.1.3 to verify RH sensor calibration.

11.2.3.4 If results are not within acceptable range, contact the analyzer manufacturer.

12. Procedure A (Syringe Injection Method)

12.1 *Sample Analysis:*

12.1.1 Program the analyzer with appropriate test conditions.

12.1.2 Flush clean syringe and needle 2 to 5 times with the material to be tested.

12.1.3 Place empty syringe on the balance, and tare it.

12.1.4 Draw desired amount of sample into the syringe.

NOTE 2—Suggested test specimen sizes are listed in Table 1.

12.1.5 Place syringe with test specimen back onto balance and reweigh.

12.1.6 Record the sample weight.

12.1.7 Load the syringe with the test specimen in the testing portion of the analyzer.

12.1.8 Begin the program and follow the instrument provided prompts for starting analysis.

12.1.9 Record result displayed at the end of the test.

12.1.10 Repeat 12.1.4 – 12.1.9 for subsequent tests.

13. Procedure B (Headspace Vial Method)

13.1 *Sample Analysis:*

13.1.1 Program the analyzer with appropriate test conditions.

13.1.2 Flush clean syringe and needle 2 to 5 times with the material to be tested.

13.1.3 Place empty sample vial (with septum/cap) on the balance, and tare it.

13.1.4 Pour/inject desired amount of sample into the sample vial.

NOTE 3—Suggested test specimen sizes are listed in Table 2.

13.1.5 Place sample vial with test specimen back onto balance and reweigh.

13.1.6 Record the sample mass.

13.1.7 Load the sample vial with the test specimen in the testing portion of the analyzer.

13.1.8 Begin the program and follow the instrument provided prompts for starting analysis.

13.1.9 Record result displayed at the end of the test.

13.1.10 Repeat to 13.1.4 to 13.1.9 for subsequent tests.

14. Calculation or Interpretation of Results

14.1 Calculate the water concentration in mass or volume % of the sample as follows:

$$\text{water, mass } \% = \frac{R}{10^4 \times W} \text{ or} \tag{1}$$

$$\text{volume } \% = \frac{R}{10^4 \times V}$$

where:

R = total water result for test specimen, µg,
W = sample weight, g, and
V = volume of sample used, mL.

14.2 If results are displayed as percent of water present and conversion to mg/kg is desired, calculate as follows:

$$\text{mg/kg} = \text{water} \left(\% \right) \times 10^4 \tag{2}$$

14.3 No further calculation or interpretation is necessary.

15. Report

15.1 Report the water concentration to the nearest whole mg/kg the nearest 0.01 mass %, the nearest whole µL/mL, or the nearest 0.01 volume %.

16. Precision and Bias[3]

16.1 Precision and bias statements will be established following completion of the round robin analyses in accordance with ASTM requirements.

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[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report: RR:D02-1674.

17. Keywords

17.1 additives; lubricating oils; moisture determination; relative humidity sensor

SUMMARY OF CHANGES

Subcommittee D02.96 has identified the location of selected changes to this standard since the last issue (D7546 – 09) that may impact the use of this standard. (Approved April 1, 2015.)

(1) Updated test method to include headspace sample vial method (Procedure B).

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