



Designation: D8567 – 24

Standard Test Method for Analysis of Engine Coolant for Organic Additives by High Performance Liquid Chromatograph¹

This standard is issued under the fixed designation D8567; 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 chemical analysis of engine coolant for azoles and organic acids by high performance liquid chromatography (HPLC).

1.2 This test method is applicable to both new and used engine coolant.

1.3 Analysis can be performed directly by this test method without pretreatment other than dilution and filtration, as required by the calibration ranges of the equipment.

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

1.5 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*²

D1176 Practice for Sampling and Preparing Aqueous Solutions of Engine Coolants or Antirusts for Testing Purposes

D1193 Specification for Reagent Water

3. Summary of Test Method

3.1 A sample of engine coolant is prepared by dilution with water. This diluted sample is placed into a sample vial which is

¹ This test method is under the jurisdiction of ASTM Committee D15 on Engine Coolants and Related Fluids and is the direct responsibility of Subcommittee D15.21 on Extended Life Coolants.

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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.

then run through the instrument. The outcome will yield the concentration of organic-based coolant additives, specifically carboxylate-, triazole-, and thiazole-based additives.

4. Significance and Use

4.1 This test method provides for the qualitative and quantitative determination of common organic additives in engine coolant in milligrams per liter and only requires a few milliliters of sample per test, with results typically available in 12 min.

5. Interferences

5.1 The example methods have been vetted to provide the least number of interferences.

5.2 Method interferences can be caused by contamination of glassware, eluent, reagents, etc. Care must be taken to ensure that contamination is kept at the lowest possible level.

5.3 Interferences will have to be determined by each system.

NOTE 1—The use of latex or nitrile gloves is highly recommended to prevent contamination during sample and eluent preparation.

6. Apparatus

6.1 *Analytical Balance*, capable of weighing accurately to 0.0001 g.

6.2 *Ultrasonic Bath*.

6.3 *High Performance Liquid Chromatograph*.

6.4 *Gradient Pump*.

6.5 *Appropriate Analytical HPLC Column*.

6.6 *Column Heater (Optional)*.

6.7 *Ultraviolet Detector*.

6.8 *Optional Light Scattering Detector*.

6.9 *Integrator or Chromatography Data System Software*.

6.10 **Table 1** shows some of the specification needs for the example methods.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade or higher purity chemicals should be used for the preparation of all samples,

TABLE 1 Method Settings and Requirements^A

	HPLC		UHPLC	
	Method A		Method B	
Instrument Settings	Column	Thermo mixed mode WAX-1	Phenomenex C18 reverse phase	Thermo C18 reverse phase
	Column bore and length	4.6 mm by 150 mm	4.6 mm by 75 mm	2.1 mm by 100 mm
	Column temperature	30.0 °C	30.0 °C	40.0 °C
	Eluent A	100 mM KH ₂ PO ₄ in water	0.1 % (v/v) Glacial Acetic acid in water	0.1 % (v/v) Glacial acetic acid in water
	Eluent B	Acetonitrile	Acetonitrile w/ 0.1 % (v/v) glacial acetic acid	Acetonitrile w/ 0.1 % (v/v) glacial acetic acid
	Analysis program	gradient	gradient	gradient
	Flow rate (mL/min)	1.2	1	0.34
	System pressure (kPa)	7000 to 11 000 (1015 to 1600 psi)	12 500 to 14 500 (1800 to 2100 psi)	55 000 to 62 000 (8000 to 9000 psi)
	Injection volume (µL)	50	4.5	1
		UV		
Detector Settings	Wavelength	210 nm	207 nm	207 nm
	Resolution	4 nm	1.2 nm	4.8 nm
	Data collection rate	5 Hz	5 Hz	10 Hz
	Wavelength	214 nm	n/a	n/a
	Resolution	2 nm	n/a	n/a
	Data collection rate	5 Hz	n/a	n/a
	Wavelength	220 nm	n/a	n/a
	Resolution	4 nm	n/a	n/a
	Data collection rate	5 Hz	n/a	n/a
	Wavelength	260 nm	n/a	n/a
	Resolution	4 nm	n/a	n/a
	Data collection rate	5 Hz	n/a	n/a
		Light Scattering		
	Gain	n/a	2	500
	Nebulizer gas pressure	n/a	11 psi	40.0 psi
	Gas flow	n/a	2.0 mL/min	n/a
	Drift tube temperature	n/a	52.0 °C	50.0 °C
	Data collection rate	n/a	5 Hz	10 Hz

^A The above are examples of methods that have been found to work. Any equivalent method meeting the minimum quantification limits is also valid.

standards, and eluents. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.³ Other grades may be used provided it is first ascertained that the reagent is of a purity to permit its use without lessening the accuracy of the determination.

7.2 Purity of Water—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type I of Specification D1193. For the HPLC systems without in-line vacuum degassers, the water used for eluent preparation should be degassed.

7.3 Acetonitrile (ACN), HPLC grade.

7.4 Potassium phosphate, monobasic reagent grade.

7.5 85 % phosphoric acid, HPLC grade.

7.6 Methanol (CH₃OH), HPLC grade.

7.7 Propylene glycol, HPLC grade.

7.8 Glacial acetic acid (CH₃COOH), HPLC grade.

7.9 2-ethylhexanoic acid, 99 % purity.

7.10 Benzoic acid, reagent grade.

7.11 4-tert-butylbenzoic acid, 99 % purity.

7.12 Adipic acid, 99 % purity.

7.13 Sebacic acid, 99 % purity.

7.14 Dodecanedioic acid, 99 % purity.

7.15 Benzotriazole, 99 % purity.

7.16 p-toluic acid, 99 % purity.

7.17 Tolyltriazole, CAS # 29385-43-1.

7.17.1 Use of a different isomer of tolyltriazole may generate undesirable results.

7.18 2-mercaptobenzothiazole.

8. Hazards

8.1 Personal protective equipment (such as eye protection, gloves, laboratory coat, etc.) should be used in the handling of all chemicals. All chemicals and solutions should be prepared in a fume hood. Special care should be taken when handling solutions around electrical equipment.

8.2 Read all equipment manuals before attempting to operate HPLC instrumentation. Special attention should be given to all warnings.

8.3 Be familiar with the SDS for all chemicals used in this procedure.

9. Sampling

9.1 Collect the sample in a clean glass or polyethylene bottle in accordance with Practice D1176. Collect at least 100 mL of sample.

³ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

TABLE 2 Minimum Values of Quantification

Analyte (listed in relative retention time)	Minimum Limit of Quantitation ^A (mg/L)
Adipic acid	125
Benzotriazole	15
Tolyltriazole	20
Benzoic acid	25
Sebacic acid	125
p-toluic acid	15
Mercaptobenzothiazole	20
Dodecanedioic acid	125
2-ethylhexanoic acid	1000
t-butyl benzoic acid	25

^A Above is merely the minimum value to meet. Labs should determine actual limit of detection for LOD and LOQ per instrument.

10. Eluent Preparation

10.1 Method A:

10.1.1 Make 4 L of 70/30 mobile phase buffer using the following method:

10.1.1.1 In a 2000 mL volumetric flask, add 27.2 g of potassium phosphate monobasic (KH₂PO₄).

10.1.1.2 Fill the flask to the mark with DI water. Insert a stir bar and mix until fully dissolved.

10.1.1.3 Transfer the mixture and stir bar into a 4000 mL beaker. Insert a pH probe and mix.

10.1.1.4 Using phosphoric acid (H₃PO₄ 85 %), titrate (can use disposable transfer pipet) drop wise until you reach a pH of 3.0.

10.1.1.5 Filter the mixture through a 1.2 µm filter and degas under vacuum and sonication.

10.1.1.6 Slowly add 857 mL of acetonitrile to the buffer and gently mix, avoiding the entrainment of air.

10.1.1.7 Transfer the 70/30 buffer to the appropriate eluent bottle on the instrument.

10.2 Method B and C:

10.2.1 Make 1 L of Eluent A:

10.2.1.1 Using a clean 1 L volumetric flask, pipet 1.000 mL glacial acetic acid.

10.2.1.2 Fill volumetric flask to the line with acetonitrile and mix thoroughly.

10.2.1.3 Transfer the eluent to the appropriate eluent bottle on the instrument.

10.2.2 Make 1 L of Eluent B:

10.2.2.1 Using a clean 1 L volumetric flask, pipet 3 1.068 mL glacial acetic acid.

10.2.2.2 Fill volumetric flask to the line with water and mix thoroughly.

10.2.2.3 Transfer the eluent to the appropriate eluent bottle on the instrument.

NOTE 2—Volumes listed in Section 7 can be adjusted depending on eluent bottle size and needs of the instrument to run properly.

11. Calibration and Standardization

11.1 Analyze each standard solution separately to determine each analyte's retention time. On a completely new system, it may be necessary to establish analyte retention times by preparing and analyzing single-analyte solutions.

NOTE 3—Approximate retention times are shown below in Table 3.

NOTE 4—Additional analytes can be added for analysis, but may cause interferences not accounted for with the example methods.

11.2 The use of other equipment, eluents, or flows requires calculation of suitable dilution factors and instrument settings that permit the analyst to obtain the resolution and detection limits given in Table 3 may also be acceptable.

11.3 Calibrate the chromatograph with at least three levels or concentrations of each analyte.

11.3.1 One standard should be near, but below the desired minimum quantification limit.

11.3.2 A mid-range standard must be used to verify the resolution of each analyte.

11.3.3 A high-analyte standard should be used to provide adequate resolution of analytes.

NOTE 5—More standards can be added to add robustness to the calibration curve.

TABLE 3 Analyte Retention Times and Preferred Detector

Analyte	Method A	Method B	Method C
	Retention Time Per Method (min)		
Adipic acid	2.11	3.15 ^A	3.10 ^A
Benzotriazole	3.10	3.86	3.50
Tolyltriazole	4.12	4.49	4.05
Benzoic Acid	5.64	4.53	4.20
Sebacic Acid	5.98	5.20 ^A	4.60 ^A
p-toluic acid	6.73	5.41	4.70
Mercaptobenzothiazole	6.37	5.63	4.85
Dodecanedioic Acid	8.76	6.09 ^A	5.30 ^A
2-ethylhexanoic acid	7.50	6.47	5.65
t-butyl benzoic acid	9.89	6.89	6.00

^A Found on light scattering detector.