Designation: D8528 – 24

Standard Test Method for Determination of Fluoride and Glycol Degradation Products in Engine Coolants by Ion Chromatography[1]

This standard is issued under the fixed designation D8528; 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 determination of fluoride in engine coolants by ion chromatography. Several glycol degradation products (different carboxylates including, but not limited to, formate and glycolate) can be determined by this test method.

1.2 This test method applies to both new and used engine coolants.

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

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

1.5 *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

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions:*

3.1.1 *eluent, n*—solution used to carry sample material through an ion chromatography system.

4. Summary of Test Method

4.1 A prepared sample is pumped through analytical columns and a suppressor into a conductivity detector. Analytes are separated based on their interaction with the stationary phase (column resin) and mobile phase (eluent). The suppressor increases the sensitivity of the method by both increasing the conductivity of the analytes and decreasing the conductivity of the eluent. Analytes are quantitated by the integration of their conductivity compared with a calibration curve.

5. Significance and Use

5.1 This test method is for the quantitative determination of fluoride and glycol degradation products in engine coolants. By this method, analysis can be performed directly without pretreatment, other than dilution, as required by the linear ranges of the equipment. Table 1 indicates applicable analytes and approximate detection limits.

6. Interferences

6.1 Method interferences can be caused by chemicals with similar retention times, especially if they are in high concentration compared to the analyte of interest. Sample dilution will be used to minimize or solve most interference problems.

6.2 Cross-contamination interferences can be caused by the contamination of glassware, eluent, reagents, etc. Great care must be taken to ensure that these interferences are kept at the lowest possible levels.

7. Apparatus

7.1 *Analytical Balance,* capable of measuring to the nearest 0.0001 g.

7.2 *Ion Chromatograph*—Analytical system with all required accessories. Column life and performance are improved by the use of a gradient pump, if available.

7.3 *Analytical Column*—A high-capacity, hydroxide selective anion exchange column designed for the separation of

[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 D15.04 on Chemical Properties.

Current edition approved Jan. 1, 2024. Published January 2024. DOI: 10.1520/D8528-23.

[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.

TABLE 1 Analytes and Minimum Quantification Limits

Analyte	Detection Limit, mg/L[A]
Fluoride (F^-)	0.4
Glycolate ($HCOO^-$)	2
Formate ($HCOO^-$)	1

[A]Sample diluted 1/10 with reagent water, suppressed conductivity detection, IonPac AS20 column with AG20 guard column. Other systems will require MQL determinations using chosen dilution factors, eluents, columns, and detector.

polarizable anions in a variety of sample matrices. Temperature-controlled column compartment helps with peak reproducibility and baseline stability.

7.4 *Guard Column*—An expandable column placed before the analytical column to prevent column damage, sample contamination, or to aid in sample concentration.

7.5 *Suppressor*—Electrolytically regenerated suppressors that remove the eluent and sample counterions and replace them with regenerant ions, reducing the eluent conductivity. The analytes are converted to the more conductive acid form, which enhances the conductivity, thereby increasing detection sensitivity.

7.6 *Conductivity Detector*—The flow-through conductivity cell that measures the electrical conductance of analyte ions as they pass through the cell. Temperature control and compensation help with peak reproducibility and baseline stability.

7.7 *Drying Oven,* controlled at 105 °C, and 120 °C.

7.8 *Desiccator.*

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade or higher purity chemicals shall be used for the preparation of all samples, standards, and eluents.

8.2 *Purity of Water*—Reagent water as defined by Type II of Specification D1193. It is recommended that all water be filtered through a 1 µm filter. For eluent preparation, if no in-line degasser is available, degas the water by sparging with helium or vacuum degassing and sonication.

8.3 *Eluent Stock Solution*—Prepare 4 mM potassium hydroxide (KOH) solution. Dissolve 4.4884 g of KOH in reagent water in a 1 L volumetric flask and fill up to 1000 mL. Dilute 100 mL of this concentrated solution (80 mM KOH) to 2000 mL in a 2 L volumetric flask with degassed reagent water. The eluent solution used may be different if another system or analytical column is used.

8.4 *Stock Fluoride Solution*—Prepare a 1000 mg/L fluoride solution. Dry approximately 3 g of sodium fluoride (NaF) at 120 °C ± 5 °C for 4 h in an oven and cool to room temperature in a desiccator. Weigh and dissolve 2.2101 g and dilute to 1 L with reagent water. Store in a polyethylene bottle.

8.5 *Stock Formate Solution*—Prepare a 1000 mg/L formate solution. Dry approximately 2 g of sodium formate ($NaHCO_2$) at 105 °C for 6 h in an oven and cool to room temperature in a desiccator. Weigh and dissolve 1.5107 g and dilute to 1 L with reagent water. Store in a polyethylene bottle.

8.6 *Stock Glycolate Solution*—Prepare a 1000 mg/L glycolate solution. Weigh and dissolve 1.0134 g of glycolic acid ($C_2H_4O_3$) and dilute to 1 L with reagent water. Store in a polyethylene bottle.

8.7 Stock solutions with different concentrations may be used.

8.8 Commercially available stock solutions and eluent generator cartridges may be used.

8.9 *Stability*—Standard stock solutions are stable for at least one month when stored at 4 °C. For standard stock solutions obtained commercially, the expiration date and Instructions for Use set by the manufacturer shall be followed.

9. Hazards

9.1 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.

9.2 Read all equipment manuals before attempting to operate the ion chromatograph. Special attention should be given to all warnings.

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

10. Sampling

10.1 Collect samples by following Practice D1176.

11. Preparation of Apparatus

11.1 Equilibrate the system by pumping eluent until a stable baseline is obtained.

11.2 Adjust instrument operating conditions, if possible, to achieve better peak separation.

12. Calibration and Standardization

12.1 Analyze each standard solution separately to determine the analyte retention time.

12.2 Set the chromatograph up as per the manufacturer-specified instructions.

12.3 Analyze a blank containing only the reagent water used for the preparation of the calibration standards.

12.4 Prepare calibrations standards of fluoride at 0.08 mg/L, 0.2 mg/L, 0.4 mg/L, 2.0 mg/L, and 4. mg/L, glycolate at 0.2 mg/L, 0.5 mg/L, 1.0 mg/L, 5.0 mg/L, and 10.0 mg/L, and formate at 0.1 mg/L, 0.25 mg/L, 0.5 mg/L, 2.5 mg/L and 5.0 mg/L from the stock solutions using reagent water. Calibrate the ion chromatograph using all five concentration standards. If it is desirable to calibrate for another analyte, these may be combined in the preceding five calibration standards once the retention times have been established individually. Concentrations of the other analytes in the calibration standards must bracket the expected range.

12.5 Integrate the peak area for determination of the concentrations. Plot the peak area against concentration. A linear calibration curve is generated for each analyte of interest.