Designation: D5827 – 09$^{\varepsilon 1}$

StandardTest Method for Analysis of Engine Coolant for Chloride and Other Anions by Ion Chromatography[1]

This standard is issued under the fixed designation D5827; 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.

ε^1 NOTE—Updated research report information in Footnote 5 editorially in May 2009.

1. Scope*

1.1 This test method covers the chemical analysis of engine coolant for chloride ion by high-performance ion chromatography (HPIC). Several other common anions found in engine coolant can be determined in one chromatographic analysis by this test method.

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

1.3 Coelution of other ions may cause interferences for any of the listed anions. In the case of unfamiliar formulations, identification verification should be performed by either or both fortification and dilution of the sample matrix with the anions of interest.

1.4 Analysis can be performed directly by this test method without pretreatment, other than dilution, as required by the linear ranges of the equipment. Table 1 indicates several applicable anions and approximate detection limits.

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

1.6 *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 its use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

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

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

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

3. Summary of Test Method

3.1 A small volume of working sample is prepared by dilution of the sample with the method eluant. This diluted sample is filtered and pumped through two ion exchange columns and a suppressor and into a conductivity detector. Ions are separated based on their affinity for exchange sites of the resin with respect to the resin's affinity for the eluant. The suppressor increases the sensitivity of the method by both increasing the conductivity of the analytes and decreasing the conductivity of the eluant. The suppressor converts the eluant and the analytes to the corresponding hydrogen form acids. Anions are quantitated by integration of their response compared with an external calibration curve and are reported as milligrams per litre (mg/L).

4. Significance and Use

4.1 This test method provides for the qualitative and quantitative determination of common anions in engine coolant in the milligrams per litre to low percent range and requires only a few millilitres or microlitres of sample per test, with results available in less than 30 min. Acceptable levels of chloride and other anions vary with manufacturer's blending specifications and applicable ASTM minimum or maximum specifications.

5. Interferences

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

5.2 A water dip (solvent system peak) can cause interference with some integrators. This is eliminated by dilution with the eluant if the sample dilution factor is 49 + 1 (v/v) or greater. Below this dilution, it is best to add a spike of eluant

[1] This test method is under the jurisdiction of ASTM Committee D15 on Engine Coolants and is the direct responsibility of Subcommittee D15.04 on Chemical Properties.

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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

TABLE 1 Analytes and Minimum Detection Limits

Analyte	Detection Limit, mg/L[A]
Chloride (Cl^-)	2.0
Nitrite (NO_2^-)	5.0
Bromide (Br)	4.0
Nitrate (NO_3^-)	7.1
o-Phosphate $(HPO_4)^{2-}$	20.0
Sulfate $(SO_4)^{2-}$	8.0
Oxalate $(C_2O_4)^{2-}$	12.0

[A] Determined using 100-µL sample volume. Sample diluted 99 + 1 (v/v) with chromatographic eluant 30-µS/cm full scale, suppressed conductivity detection. Dionex AS4ASC column with AG4ASC guard columns. Other systems will require MDL determinations using chosen dilution factors, eluants, columns, and detector.

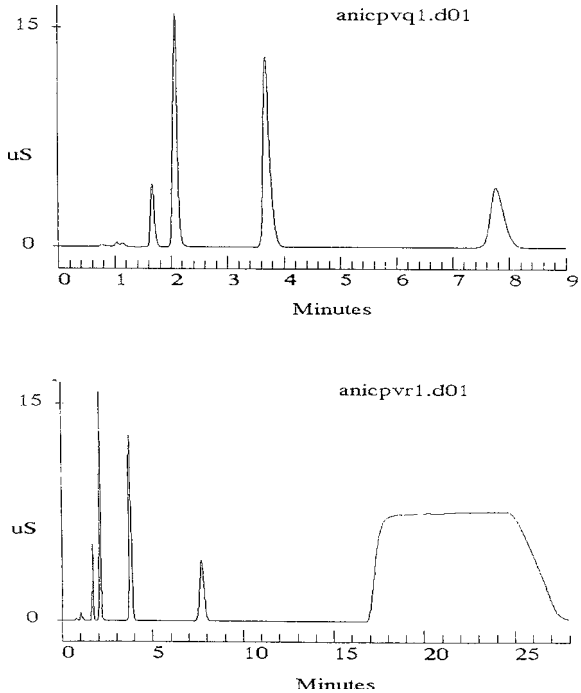

FIG. 1 Sample Run—Chloride Peak at 1.7 min

concentrate to the sample such that the sample is not diluted significantly and the resulting test solution matches the eluant used in the system. One method is the addition of 100 µL of 100X eluant concentrate to 10.0 mL of sample or standard.

5.3 Method interferences can be caused by the contamination of glassware, eluant, reagents, etc. Great care must be taken to ensure that contamination, especially by chloride, is kept at the lowest possible levels.

5.4 Pre-rinsing of the sample preparation containers with deionized water is mandatory.

5.5 The use of latex gloves is highly recommended to prevent contamination.

6. Apparatus

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

6.2 *Ion Chromatograph*—Analytical system with all required accessories including syringes, columns, suppressor, gasses, and detector. Column life and performance are enhanced by the use of a two-eluant channel gradient pump, if available.

6.3 *Guard Column,* for protection of the analytical column from strongly retained constituents. Better separations are obtained with additional plates.

6.4 *Anion Separator Column,* capable of producing analyte separation equivalent to or better than that shown in Fig. 1.

6.5 *Anion Suppressor Device*—Micro membrane suppressor or equivalent. A cation exchange column in the hydrogen form has been used successfully, but it will periodically need to be regenerated as required, being indicated by a high background conductivity and low analyte response.

6.6 *Conductivity Detector,* low volume (<2 µL) and flow, temperature compensated, capable of at least 0 to 1000 µS/cm on a linear scale.

6.7 *Integrator or Chromatography Data System Software,* capable of obtaining approximately the same detection limits as are listed in Table 1.

6.8 *Drying Oven,* controlled at 105, 150, and 600 ± 5°C.

6.9 *Desiccator.*

7. Reagents

7.1 *Purity of Reagents*—Reagent grade or higher purity chemicals shall be used for the preparation of all samples, standards, eluants, and regenerator solutions. 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 specification are available.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high 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 II of Specification D1193. It is recommended that all water be filtered through a 0.2-µm filter. For eluant preparation, degas the water by sparging with helium or vacuum degassing and sonication.

7.3 *Eluant Buffer Stock Solution*—Sodium bicarbonate ($NaHCO_3$) 1.5 mM and sodium carbonate (Na_2CO_3) 1.2 mM. Dissolve 2.5203 ± 0.0005 g of $NaHCO_3$ and 2.5438 ± 0.0005 g of Na_2CO_3 in reagent water in a 1000-mL Type A volumetric flask and dilute to 1 L. Dilute 100.0 mL of this stock solution to 2000 mL in a 2-L Type A volumetric flask with degassed reagent water. The pH of the stock solution is 10.1 to 10.3 (based on pK_a calculation). The eluant solution used may be different if other system or analytical columns are used.

[3] *Reagent Chemicals, American Chemical Society Specifications* , 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.

7.4 *Stock Bromide Solution*—Dry approximately 2 g of sodium bromide (NaBr) for 6 h at 150°C and cool in a desiccator. Weigh and dissolve 1.2877 g of the dried salt in reagent water and dilute to 1 L (1.00 mL = 1.00 mg bromide).

7.5 *Stock Chloride Solution*—Dry approximately 2 g of sodium chloride (NaCl) for 1 h at 600°C and cool in a desiccator. Weigh and dissolve 1.6485 g and dilute to 1 L with reagent water (1.00 mL = 1.00 mg Cl^-).

7.6 *Stock Formate Solution*—Dry approximately 2 g of sodium formate ($NaHCO_2$) at 105°C for 6 h and cool in a desiccator. Weigh and dissolve 1.4775 g of the salt in reagent water and dilute to 1 L (1.00 mL = 1.00 mg formic acid).

7.7 *Stock Glycolic Acid Solution*—Weigh and dissolve 1.0000 g of the solid acid in reagent water and dilute to 1 L (1.00 mL = 1.00 mg glycolate).

7.8 *Stock Nitrate Solution*—Dry approximately 2 g of sodium nitrate ($NaNO_3$) for 24 h at 105°C and cool in a desiccator. Weigh and dissolve 1.3707 g and dilute to 1 L with reagent water (1.00 mL = 1.00 mg NO_3^-).

7.9 *Stock Nitrite Solution*—Dry approximately 2 g of sodium nitrite ($NaNO_2$) for 24 h in a desiccator containing concentrated sulfuric acid (relative density of 1.84). Weigh and dissolve 1.4998 g and dilute to 1 L with reagent water (1.00 mL = 1.00 mg NO_2^-). Refrigerate and prepare weekly because nitrite is oxidized easily.

7.10 *Stock Oxalic Acid Solution*—Weigh and dissolve 1.4002 g of oxalic acid dihydrate ($C_2H_2O_4{\cdot}2H_2O$) in reagent water and dilute to 1 L (1.00 mL = 1.00 mg oxalic acid).

7.11 *Stock Phosphate Solution*—Weigh and dissolve 1.4330 g of potassium dihydrogen phosphate (KH_2PO_4) and dilute to 1 L with reagent water (1.00 mL = 1.00 mg PO_4^{-3}).

7.12 *Stock Sulfate Solution*—Dry approximately 2 g of anhydrous sodium sulfate (Na_2SO_4) for 1 h at 105°C and cool in a desiccator. Weigh and dissolve 1.4790 g and dilute to 1 L with reagent water (1.00 mL = 1.00 mg SO_4^{-2}).

7.13 *Suppressor Solution for Membrane Suppressor*—0.025 *N* H_2SO_4. Carefully add 13.7 mL of reagent sulfuric acid (relative density of 1.84) to approximately 500 mL reagent water in a 1-L volumetric flask. Dilute to 1000 mL with reagent water. Dilute 100 mL of this concentrate to 2000 mL with reagent water for the final working suppressor solution.

7.14 *Stability*—Standard stock solutions are stable for at least one month when stored at 4°C. Fresh nitrite and phosphate standards must be prepared weekly.

8. Sampling

8.1 Collect the sample in a scrupulously clean glass or polyethylene bottle in accordance with Test Method D1176. Collect at least 100 mL of sample.

9. Calibration and Standardization

9.1 Analyze each standard solution separately to determine the analyte's retention time.

9.2 Set the chromatograph up in accordance with the conditions specified in Table 2 and Fig. 2. The use of other equipment, eluants, or flows requires calculation of suitable dilution factors and instrument settings that permit the analyst to obtain the resolution and detection limits given in Fig. 1 and Table 1, respectively.

TABLE 2 Chromatographic Conditions

Analyte	Peak No.	Retention Time, min
Chloride	2[A]	1.7
Nitrite	3	2.1
Bromide	4	3.3
Nitrate	5	3.7
Phosphate	6	7.7
Sulfate	7	10.5
Oxalate	8	13.3

[A] Fluoride, acetate, formate, and glycolate will all elute before chloride, and poor resolution of these species often precludes the quantitation of any, or all four, of them.

9.3 Prepare concentrations of chloride at 0.08, 0.4, 0.8, and 4.0 mg/L from the stock solution. All final solutions should be made with eluant as described in 5.2. Calibrate the ion chromatograph with at least five levels of the analyte, starting near but above the minimum detection limit (MDL) and further defining the working range in samples subsequent to dilution. These chloride analyte examples reflect a dilution of 99 + 1 (v/v) with eluant. If it is desirable to calibrate for another anion species, these may be combined in the preceding five calibration standards once the retention times have been established individually. Concentrations of these other anions in the calibration solutions must bracket the expected range for these species and include a level near the MDL for each species.

NOTE 1—Ion chromatography equipment other than that described in this test method may require that standards be prepared at higher or lower levels.

9.4 Analyze a blank containing only the eluant as described in Section 10.

9.5 A mid-range standard must be used to verify the resolution of anions, regardless of a desire to quantitate all of them.

9.6 Analytical curves must be established at only one detector scale setting in order to prevent a change of slope affecting the analytical curve.

9.7 The analytical calibration curve and an eluant blank shall be verified daily prior to the analysis of samples to verify the system resolution, calibration, and sensitivity.

9.8 The analytical calibration curve, analyte retention times and resolution, and an eluant blank shall be verified subsequent to a change of the system eluant.

9.9 *Conditions:*

Column: ion chromatography
Detector: see 6.6
Eluant: see 7.3
Flow: 2 mL/min
Suppressor flow: 2 mL/min
Sample loop: 50 µL

NOTE 2—If a gradient pump is available, refer to Fig. 2 for an example of a step gradient that has proven successful for cleaning the column of strongly retained species such as polyphosphates and molybdate, which would otherwise elute in subsequent runs.

NOTE 3—The sample loop volume will vary based on the column capacity, sensitivity, and other factors. Refer to ion chromatography equipment manuals and column information for machine-specific details.