



## Standard Test Method for Analysis of Engine Coolant for Chloride and Other Anions by Ion Chromatography<sup>1</sup>

This standard is issued under the fixed designation D 5827; 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 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 the standard. The values given in parentheses are for information only.

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:

D 1193 Specification for Reagent Water<sup>2</sup>

D 1176 Test Method for Sampling and Preparing Aqueous Solutions of Engine Coolants or Antirusts for Testing Purposes<sup>3</sup>

### 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

TABLE 1 Analytes and Minimum Detection Limits

Analyte	Detection Limit, mg/L <sup>A</sup>
Chloride (Cl <sup>-</sup> )	2.0
Nitrite (NO <sub>2</sub> <sup>-</sup> )	5.0
Bromide (Br)	4.0
Nitrate (NO <sub>3</sub> <sup>-</sup> )	7.1
o-Phosphate (HPO <sub>4</sub> ) <sup>2-</sup>	20.0
Sulfate (SO <sub>4</sub> ) <sup>2-</sup>	8.0
Oxalate (C <sub>2</sub> O <sub>4</sub> ) <sup>2-</sup>	12.0

<sup>A</sup> 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.

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 concentrate to the sample such that the sample is not diluted

<sup>1</sup> 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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<sup>2</sup> Annual Book of ASTM Standards, Vol 11.01.

<sup>3</sup> Annual Book of ASTM Standards, Vol 15.05.

significantly and the resulting test solution matches the eluant used in the system. One method is the addition of 100  $\mu\text{L}$  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.<sup>4</sup>

6.5 *Anion Suppressor Device*—Micro membrane suppressor or equivalent.<sup>5</sup> 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  $\mu\text{L}$ ) and flow, temperature compensated, capable of at least 0 to 1000  $\mu\text{S}/\text{cm}$  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  $600 \pm 5^\circ\text{C}$ .

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 is available.<sup>6</sup> Other grades may be used, provided it is first

<sup>4</sup> Analytical column PN AS4ASC and AG4ASC guard columns manufactured by Dionex Corp., 1228 Titan Way, Sunnyvale CA 94088-3603, have been found satisfactory for this purpose.

<sup>5</sup> AMMS P.N. 37106 manufactured by Dionex Corp., 1228 Titan Way, Sunnyvale CA 94088-3603, has been found satisfactory for this purpose.

<sup>6</sup> *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

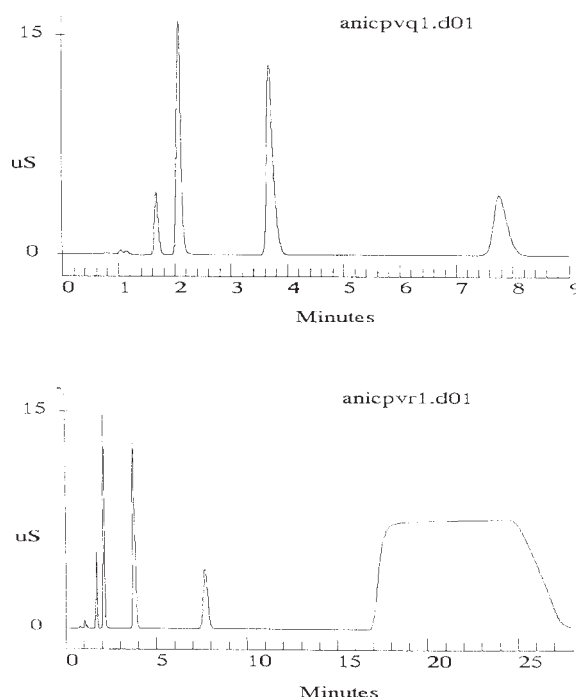


FIG. 1 Sample Run—Chloride Peak at 1.7 min

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 D 1193. It is recommended that all water be filtered through a 0.2- $\mu\text{m}$  filter. For eluant preparation, degas the water by sparging with helium or vacuum degassing and sonication.

7.3 *Eluant Buffer Stock Solution*—Sodium bicarbonate ( $\text{NaHCO}_3$ ) 1.5 mM and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) 1.2 mM. Dissolve  $2.5203 \pm 0.0005$  g of  $\text{NaHCO}_3$  and  $2.5438 \pm 0.0005$  g of  $\text{Na}_2\text{CO}_3$  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  $\text{pK}_a$  calculation). The eluant solution may be different if other system or analytical columns are used.

7.4 *Stock Bromide Solution*—Dry approximately 2 g of sodium bromide ( $\text{NaBr}$ ) for 6 h at  $150^\circ\text{C}$  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 ( $\text{NaCl}$ ) for 1 h at  $600^\circ\text{C}$  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  $\text{Cl}^-$ ).

7.6 *Stock Formate Solution*—Dry approximately 2 g of sodium formate ( $\text{NaHCO}_2$ ) at  $105^\circ\text{C}$  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 ( $\text{NaNO}_3$ ) for 24 h at  $105^\circ\text{C}$  and cool in a desiccator. Weigh and dissolve 1.3707 g and dilute to 1 L with reagent water ( $1.00\text{ mL} = 1.00\text{ mg NO}_3^-$ ).

**7.9 Stock Nitrite Solution**—Dry approximately 2 g of sodium nitrite ( $\text{NaNO}_2$ ) 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 ( $1.00\text{ mL} = 1.00\text{ mg NO}_2^-$ ). 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 ( $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) in reagent water and dilute to 1 L ( $1.00\text{ mL} = 1.00\text{ mg oxalic acid}$ ).

**7.11 Stock Phosphate Solution**—Weigh and dissolve 1.4330 g of potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) and dilute to 1 L with reagent water ( $1.00\text{ mL} = 1.00\text{ mg PO}_4^{3-}$ ).

**7.12 Stock Sulfate Solution**—Dry approximately 2 g of anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) for 1 h at  $105^\circ\text{C}$  and cool in a desiccator. Weigh and dissolve 1.4790 g and dilute to 1 L with reagent water ( $1.00\text{ mL} = 1.00\text{ mg SO}_4^{2-}$ ).

**7.13 Suppressor Solution for Membrane Suppressor**—0.025 N  $\text{H}_2\text{SO}_4$ . 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  $4^\circ\text{C}$ . 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 D 1176. 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.

**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	Flow: 2 mL/min
Detector: see 6.6	Suppressor flow: 2 mL/min
Eluant: see 7.3	Sample loop: 50 $\mu\text{L}$

**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.

## 10. Procedure

**10.1** Set the ion chromatograph up in accordance with the manufacturer's instructions.

**10.2** Equilibrate the system by pumping eluant for 15 to 30 min, until a stable baseline is obtained. Sample preparation is usually performed by 99 + 1 (v/v) dilution with eluant.

**10.3** Flush the injection loop with 2 to 3 mL of sample using a 10-mL disposable plastic syringe fitted with a 0.2- $\mu\text{m}$  syringe filter.<sup>7</sup>

**10.4** Start the chromatographic run in accordance with the manufacturer's instructions.

**10.5** At least one duplicate and one fortified coolant sample must be analyzed with each batch of ten or fewer samples. Results must be recorded in the laboratory manual. The fortified sample is to be prepared by addition of a mixed analyte mid-range standard. Addition of 100  $\mu\text{L}$  of fortification

**TABLE 2 Chromatographic Conditions**

Analyte	Peak No.	Retention Time, min
Chloride	2 <sup>A</sup>	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

<sup>A</sup> 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.

<sup>7</sup> Nalgene Catalogue No. 190-202, or equivalent.

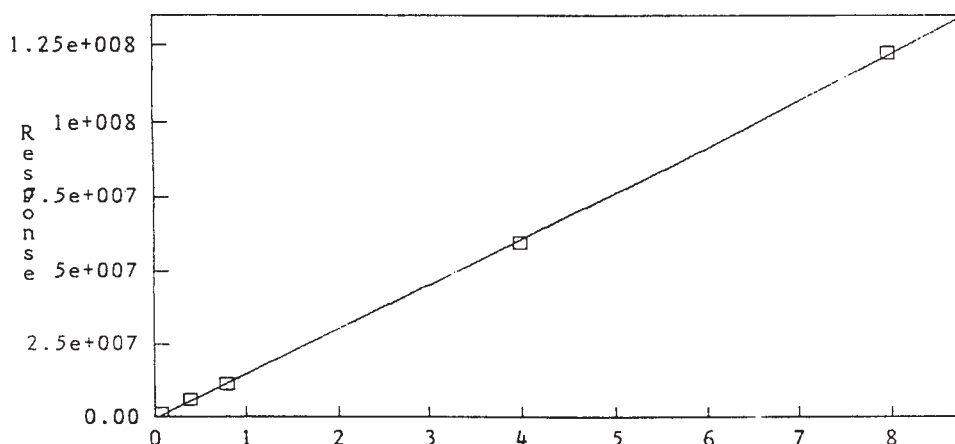
Gradient File: C:\DX\METHOD\ACOOOL.GPM

Anion step gradient run on AS4A-SC column

Lo Pressure Limit = 50  
Hi Pressure Limit = 2600  
Eluant 1 - Carb/Bicarb Buffer  
Eluant 2 - 10x Eluant 1 Conc.  
Eluant 3 -  
Eluant 4 -  
V5 Off - Off  
V5 On - On  
V6 Off - Off  
V6 On -

Time	Flow	%1	%2	%3	%4	V5	V6	Comment
0.0	2.0	100	0	0	0	1	0	Equilibration/Inject
15.0	2.0	100	0	0	0	1	0	Step to 2x ElConc.
15.1	2.0	81	19	0	0	1	0	Column Cleanup
22.7	2.0	81	19	0	0	1	0	Ramp to E1
25.0	2.0	100	0	0	0	1	0	System Equilibration
30.0	2.0	100	0	0	0	1	0	End Run: Anion AS4A-SC

FIG. 2 Test Method Parameters



Method: C:\DX\Method\ACOOOL.MET  
Component: Chloride  
Fit Type: Linear  
r<sup>2</sup>: 0.999774  
Amt - Resp = 6.548e - 008 + 0.03103  
Resp - Amt = 1.527e + 007 + -4.739e - 005  
Standardization: External  
Calibration Area

FIG. 3 Example Calibration Curve

standard solution to 10 mL of prepared sample in eluant will not dilute the sample appreciably.

## 11. Calculation

11.1 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. Calibration is in the concentration range of interest and must have a linear least squares correlation coefficient of 0.9990 or greater (see Fig. 3).

11.2 The concentration of analyte is given by the concentration read from the calibration curve multiplied by the dilution factor used.

11.3 Relative percent difference (RPD) of duplicate runs:

$$RPD = \frac{(A - B)}{(A + B)/2} \times 100 \% \quad (1)$$

where:

A = concentration found in Analysis Run 1, and

B = concentration found in Analysis Run 2.

Results must be within 20 %.

11.4 Spike (fortified) recovery as percent:

$$\text{recovery} = \frac{(A - B)}{C} \times 100 \% \quad (2)$$

where:

A = concentration found in analysis of fortified sample,



$B$  = concentration found in analysis of sample, and  
 $C$  = concentration of analyte added to sample.

Spike recovery must be within a 80 to 120 % range.

## 12. Reporting of Results

12.1 Report the concentration of anions found in the sample, sample analysis date, and analyst.

## 13. Precision and Bias

13.1 *Precision*—The collaborative test of this test method was performed by seven laboratories, with one operator each. The operators made determinations of chloride in various matrices including glycol and common inhibitors on each of four samples in duplicate on two separate days for a total of 112 analyses.

13.1.1 *Repeatability*—The standard deviation of duplicate results by the same analyst on different days should be considered suspect if the results differ by more than 5.8 % absolute.

13.1.2 *Reproducibility*—Results submitted by two or more laboratories should be considered suspect if they differ by more than  $\pm 11$  %.

13.2 *Bias*—No suitable reference material is available for the determination of bias.

## 14. Keywords

14.1 chloride; chromatography methods; engine coolant; ion chromatography

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