Designation: ~~D7319 – 17~~ D7319 – 22

Standard Test Method for
Determination of Existent and Potential Sulfate and Inorganic Chloride in Fuel Ethanol and Butanol by Direct Injection Suppressed Ion Chromatography[1]

This standard is issued under the fixed designation D7319; 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 a direct injection ion chromatographic procedure for determining existent and potential inorganic sulfate and total inorganic chloride content in hydrous and anhydrous denatured ethanol and butanol to be used in motor fuel applications. It is intended for the analysis of ethanol and butanol samples containing between 1.0 mg⁄kg to 20 mg/kg of existent or potential inorganic sulfate and 1.0 mg⁄kg to 50 mg/kg of inorganic chloride.

NOTE 1—Tertiary butanol is not included in this test method. 1-butanol, 2-butanol, and isobutanol are included in the testing and research report for 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 *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.* Material Safety Data Sheets are available for reagents and materials. Review them for hazards prior to usage.

1.4 *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]
D1193 Specification for Reagent Water
D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter
D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants
D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
D5827 Test Method for Analysis of Engine Coolant for Chloride and Other Anions by Ion Chromatography
D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

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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 D02.03 on Elemental Analysis.

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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**

D6792 Practice for Quality Management Systems in Petroleum Products, Liquid Fuels, and Lubricants Testing Laboratories
D7318 Test Method for Existent Inorganic Sulfate in Ethanol by Potentiometric Titration
D7328 Test Method for Determination of Existent and Potential Inorganic Sulfate and Total Inorganic Chloride in Fuel Ethanol by Ion Chromatography Using Aqueous Sample Injection

2.2 *European Norm Standards:*[3]

EN 15492 Ethanol as a blending component for petrol—Determination of inorganic chloride and sulfate content—Ion chromatographic method

3. Terminology

3.1 *Definitions:*

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

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *existent inorganic sulfate, n*—inorganic sulfate species actually present in the sample at the time of analysis with no oxidation treatment.

3.2.2 *inorganic chloride, n*—chloride present as hydrochloric acid, ionic salts of this acid, or mixtures of these.

3.2.3 *inorganic sulfate, n*—sulfate (SO_4^{-2}) species present as sulfuric acid, ionic salts of this acid, or mixtures of these.

3.2.4 *potential sulfate, n*—inorganic sulfate species present after the sample has been reacted with an oxidizing agent.

4. Summary of Test Method

4.1 For existent inorganic sulfate and total chloride, a small volume of an ethanol or butanol sample is directly injected into a suitably configured ion chromatograph in accordance with manufacturer's recommendations for this test method. For potential sulfate, 0.5 mL of 30 % hydrogen peroxide solution is added to 9.5 mL of the ethanol or butanol sample, and then injected into the ion chromatograph. Ions are separated based on their affinity for exchange sites of the resin with respect to the resin's affinity for the eluent. The suppressor increases the sensitivity of the test method by both increasing the conductivity of the analytes and decreasing the conductivity of the eluent. It also converts the eluent and analytes to the corresponding hydrogen forms of anions. Anions are quantified by integration of their responses compared with an external calibration curve, and are measured as milligrams/litre, then converted to milligrams/kilograms. The calibration standards are prepared in an aqueous matrix.

4.1.1 The use of acid suppression technology is more significant for the precision of sulfate measurement than for chloride. Sulfate precision will be worse if acid suppression is not used.

4.2 Similar methods for chloride and sulfate determinations can be found in EN 15492 for total chloride, in Test Method D7328 for total chloride and existent and potential inorganic sulfate by ion chromatography with aqueous sample injection, and in Test Method D7318 for existent inorganic sulfate by potentiometric lead titration and Test Method D5827 for chloride and other anions in engine coolants by ion chromatography.

NOTE 2—Butanol has limited solubility in water, do not dilute samples with water prior to analysis. In addition, any remnant water from the sample delivery device or glassware may lead to low recoveries of sulfate and chloride. Avoid unintended water contamination of the sample. Added water can lead to phase separation of the sample. The chloride and sulfate ions can migrate to the water dominate phase and lower the recovery from the butanol.

5. Significance and Use

5.1 Sulfates and chlorides can be found in filter plugging deposits and fuel injector deposits. The acceptability for use of the fuel components and the finished fuels depends on the sulfate and chloride content.

5.2 Existent and potential inorganic sulfate and total chloride content, as measured by this test method, can be used as one measure of the acceptability of gasoline components for automotive spark-ignition engine fuel use.

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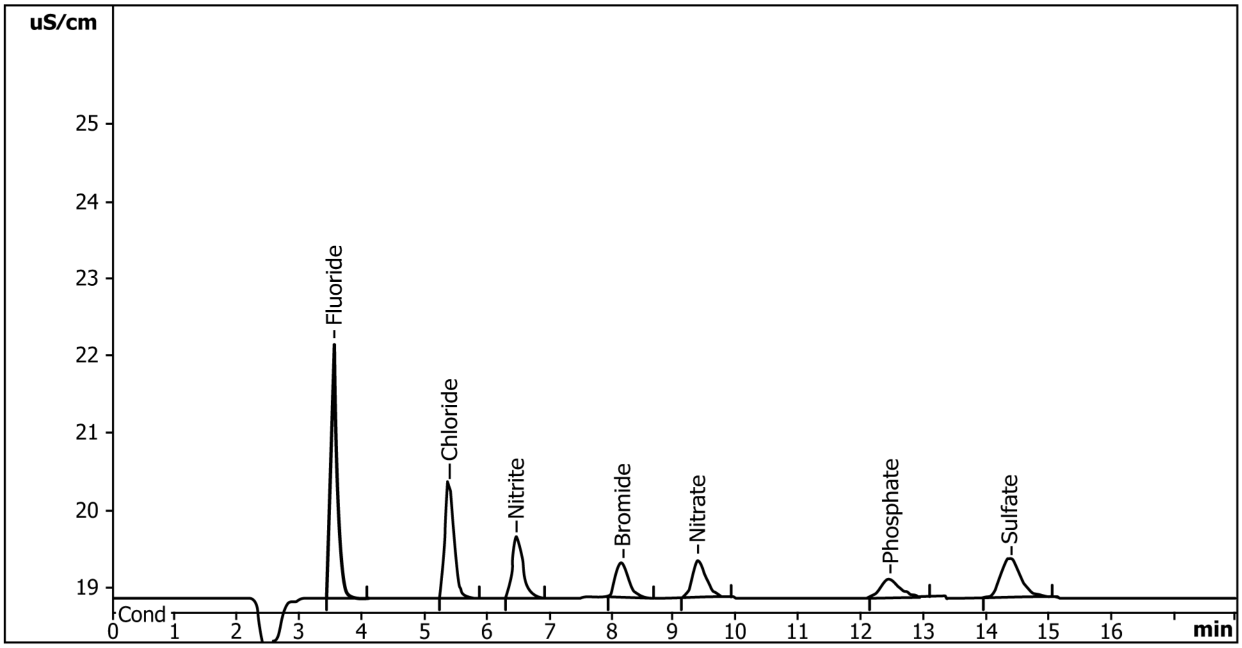
[3] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.



NOTE 1—Chromatogram retention times may be different depending on instruments or columns used.

FIG. 1 Typical Ion Chromatogram of a Solution Containing 1 mg/L of Various Anions in Water

6. Interferences

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

6.2 A water dip (system void, negative peak as shown in Fig. 1) can cause interference with some integrators. Usually, for chloride and sulfate determinations, the water dip should not be a problem since the chloride and sulfate peaks are far away from the water dip.

6.3 Given the trace amounts of chloride and sulfate determined in this test method, interferences can be caused by contamination of glassware, eluent, reagents, and the like. For example, sodium leaching from glassware can precipitate with sulfate giving low sulfate results. Take care to ensure that contamination is kept at the lowest possible levels. The use of powder-free gloves is highly recommended to prevent sample contamination.

7. Apparatus

7.1 *Analytical Balance,* capable of weighing up to 100 g accurately to 0.0001 g.

7.2 *Drying Oven,* controlled at 110 °C ± 5 °C for drying sodium sulfate and sodium chloride.

7.3 *Desiccator,* containing freshly activated silica gel (or equivalent desiccant) with moisture content indicator.

7.4 *Pipets or Volumetric Transferring Devices,* appropriately sized Class A glass pipets or their equivalent or variable volume automatic pipets fitted with disposable polypropylene tips.

7.5 *Volumetric Flasks (with Glass Stoppers),* Class A of 10 mL, 25 mL, 50 mL, 100 mL, 1000 mL, 2000 mL capacity.

7.5.1 *Container,* equipped with a closure to prevent ethanol evaporation, 1 L (for sample collection). See 6.3 for additional information.

7.6 *Ion Chromatograph,* analytical system with all required accessories including syringes, columns, suppressor, and detector which can be demonstrated to obtain the precision and detection limits and requirements of the method.

7.6.1 *Injection System,* capable of delivering 20 µL with a precision better than 1 %, or as recommended for this determination by the manufacturer.

7.6.2 *Pumping System,* capable of delivering mobile phase flows between 0.2 mL/min and 2.5 mL/min with a precision better than 2 %, or as recommended for this determination by the manufacturer.

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

7.6.4 *Anion Separator Column,* 100 % solvent compatible and capable of producing satisfactory analyte (sulfate and chloride) separation (Fig. 1).

7.6.5 *Anion Suppressor Device,* vendor specific and capable of using acid suppression technology.

7.6.5.1 *Tri-Chamber Approach,* 100 % solvent compatible tri-chamber micro packed bed with cation exchange resin (or equivalent). Suppressor device should simultaneously be on-line continuously chemically regenerated to its hydrogen form using any mineral acid providing H+ ion.

7.6.5.2 *Continuous Approach,* The regenerant channels are flushed with a mineral acid (sulfuric) to supply hydronium ions required for the suppression reaction. The solvent compatible ion exchange membranes provide the transport pathway for the hydronium ions into the eluent channel and the transport of sodium and other cations out of the eluent channel.

7.6.6 *Conductivity Detector,* (low volume), temperature controlled to 0.01 °C, capable of at least 0 µS/cm to 1000 µS/cm on a linear scale.

7.6.7 *Integrator or Chromatography Data System Software,* capable of measuring peak areas and retention times, and correcting the data in accordance with the baseline of the chromatogram.

7.7 *Gloves,* powder-free examination type.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade or higher purity chemicals shall be used for the preparation of all samples, standards, eluent, 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 specifications are available.[4] 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.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water as defined by Type I or better in Specification D1193. For eluent preparation and handling, comply with all ion chromatograph instrument and column vendor requirements (for example, filtering, degassing, and the like).

8.3 *Eluent Buffer Stock Solution*—Sodium bicarbonate ($NaHCO_3$) 1.0 mM and sodium carbonate (Na_2CO_3) 3.2 mM. Dissolve 8.4 g ± 0.0005 g of $NaHCO_3$ and 33.92 g ± 0.0005 g of Na_2CO_3 in reagent water in a 1 L Type A volumetric flask and dilute to volume. Dilute 10.0 mL of this stock solution to 1 L in a 1 L Type A volumetric flask with degassed reagent water. The eluent solution used may be different if other system or analytical columns are used.

NOTE 3—Other volumes of stock solution can be prepared using appropriate ratios of reagents. Follow the specific guidelines for this solution from the vendor of the column being used. Alternatively, this solution can be purchased from a qualified vendor.

8.4 *Suppressor Regenerant Solution for Suppressor*—0.1 M sulfuric acid. Carefully add 334 mL of reagent grade sulfuric acid

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[4] ~~*Reagent Chemicals, American Chemical Society Specifications,*~~*ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials,* American Chemical Society, Washington, DC. For ~~Suggestions~~suggestions on the testing of reagents not listed by the American Chemical Society, see ~~*Annual*~~*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.

(relative density 1.84) to approximately 500 mL reagent water in a 1 L volumetric flask. (**Warning—**This will generate a very hot solution. Allow it to cool before diluting to 1000 mL volume. Never add water to concentrated acid.) Dilute to 1000 mL with reagent water, and label this solution as 10.0 M sulfuric acid. Dilute 10.0 mL of this concentrate to 1000 mL with reagent water for the final 0.1 M working suppressor solution. The regenerate solution used may be different if other system or analytical columns are used.

NOTE 4—Other volumes of this solution can be prepared using appropriate ratios of reagents. Follow the specific guidelines for this solution from the vendor of the suppressor being used.

8.5 *Sodium Sulfate*—anhydrous, reagent grade, 99 % minimum purity. (**Warning—**Do not ingest. Avoid unnecessary exposure.)

8.6 *Sodium Chloride*—ACS or reagent grade, 99 % minimum purity.

8.7 *Tetrabutylamonium Bisulfate*—Technical or reagent grade, 99 % minimum purity.

8.8 *Tetrabutylammonium Chloride*—Technical or reagent grade 97 % minimum purity.

8.9 *Butanol*—ACS, 99 % minimum purity. Could consist of isobutanol, sec butanol, or n-butanol. (**Warning—**Flammable, toxic, and may be harmful if ingested or inhaled. Affects central nervous system similar to excessive alcohol exposure.)

8.10 *Ethanol*—denatured with methanol, formula 3A or histological grade ethanol, anhydrous, denatured with ethyl acetate, methylisobutyl ketone and hydrocarbon naphtha. (**Warning—**Flammable, toxic, and may be harmful or fatal if ingested or inhaled. Avoid skin contact.)

8.11 *Hydrogen Peroxide*—ACS reagent grade, 30 % by weight in water.

8.12 *Hydrogen Peroxide Solution, 30 %*—commercially available 30 % hydrogen peroxide solution.

9. Preparation of Standard Solutions

9.1 *Stock Solutions:*

9.1.1 *Sulfate Stock Solution, approximately 2000 mg/L*—To ensure dryness, place anhydrous sodium sulfate (5 g) in a drying oven at 110 °C for at least an hour, cool, and store in a desiccator. Accurately weigh 2.96 g anhydrous sodium sulfate to the nearest tenth of a milligram and transfer to a 1 L volumetric flask. Add water to dissolve the sodium sulfate, and make to volume. Calculate the concentration of sulfate in the solution in accordance with Eq 1. Other volumes of stock solution can be prepared using the appropriate ratio of reagents.

$$\text{Stock Sulfate (mg/L)} = (\text{g } Na_2SO_4)(0.6764)(1000 \text{ mg/g})/1 \text{ L} \quad (1)$$

TABLE 1 Typical Volumetric Preparation of Chloride and Sulfate Standards in Water

Chloride and Sulfate Standards mg Chloride and Sulfate (each)/1 L water	Chloride Stock Solution, mL	Sulfate Stock Solution, mL
50 Cl^- only	25	...
20	10	10
10	5	5
5	2.5	2.5
1	0.5	0.5
0.5	0.25	0.25
0.3	0.15	0.15

where:

g Na_2SO_4 = weight in grams of Na_2SO_4 dissolved in 1 L, and
0.6764 = weight percent sulfate in Na_2SO_4.

9.1.2 *Chloride Stock Solution (approximately 2000 mg/L)*—To ensure dryness, place sodium chloride (5 g) in a drying oven at 110 °C for at least an hour, cool, and store in a desiccator. Accurately weigh 3.30 g dried sodium chloride to the nearest tenth of a milligram and transfer to a 1 L volumetric flask. Add water to dissolve the sodium chloride and make to volume. Calculate the concentration of chloride in the solution in accordance with Eq 2. Other volumes of stock solution can be prepared using the appropriate ratio of reagents.

$$\text{Stock Chloride (mg/L)} = (\text{g NaCl})\,(0.6068)\,(1000\text{ mg/g})/1\text{ L} \tag{2}$$

where:

g NaCl = weight in grams of NaCl dissolved in 1 L, and
0.6068 = weight percent chloride in NaCl.

9.2 *Chloride and Sulfate Standards in Water*—Add water and sulfate and chloride stock solutions are added to a 1 L glass volumetric flask in accordance with Table 1 to achieve the desired standard.

9.2.1 Chloride and sulfate stock solutions from 9.1 are added quantitatively into the flask and mixed quantitatively with water in accordance with Table 1. Be very careful to measure the exact volumes of the sulfate and chloride stock solutions that are added to the flask, and fill the flask to 1.00 L with water. The sulfate and chloride concentrations of each standard are calculated in accordance with Eq 3 and Eq 4.

$$\text{Sulfate in Standard (mg/L)} = V_a \times C_a / V \tag{3}$$

$$\text{Chloride in Standard (mg/L)} = V_b \times C_b / V \tag{4}$$

where:

V_a = volume of sulfate stock solution (9.1.1), in mL,
C_a = concentration of sulfate stock (Eq 1), in mg/L,
V_b = volume of chloride stock solution (9.1.2) in mL,
C_b = concentration of chloride stock (Eq 2), in mg/L,
V = final volume of standard solution, in L.

9.2.2 Multiples or fractions of Table 1 values can be used to prepare different volumes of standards, but Eq 3 and Eq 4 are still used to calculate standard ion concentrations.

NOTE 5—Alternatively, commercially available stock calibration solutions can be used, provided that the solutions are traceable to primary stock solutions or certified reference materials and are free from other analytes.

10. Calibration

10.1 Set up the ion chromatograph in accordance with the manufacturer's instructions. No specific parameters are given here since different equipment will require differing eluent, flow conditions, and instrument settings. Calibrate the ion chromatograph with at least five levels of sulfate and chloride, starting near but above the minimum detection limit, and further defining the working

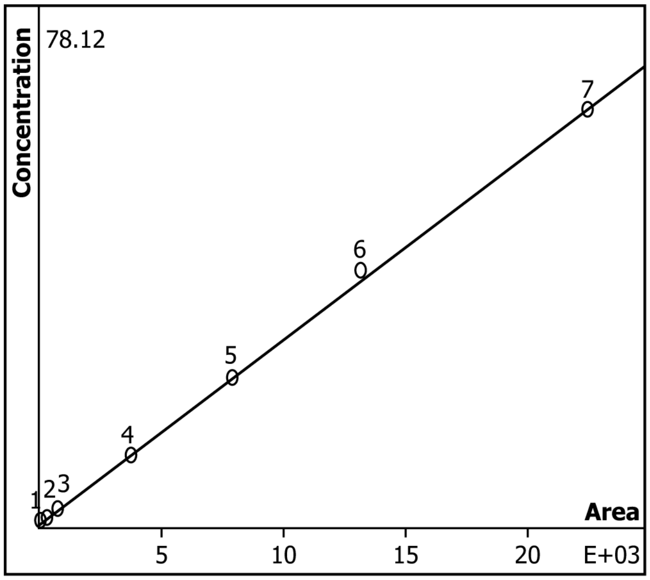

FIG. 2 Typical Chloride Calibration Plot

range in samples subsequently to be analyzed. Use concentrations of calibrant solutions that bracket the expected range for the samples to be analyzed. Use one or more mid-range standards shall be used to verify the linearity of the calibration plot.

10.1.1 Typical ion chromatographic conditions:

Flow: 0.7 mL/min
Suppressor flow: 0.5 mL ⁄min to 1.0 mL/min
Sample loop: 20 μL

10.1.2 Other analytical conditions can be used per the manufacturer's instructions. It is important that the resulting chromatogram contain chloride and sulfate peaks with baseline separation like that shown in Fig. 1. It is the user's responsibility to determine retention times for each analyte ion. If present in sufficient quantity, other anions can interfere with the chloride and sulfate measurements.

NOTE 6—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.

10.1.3 Establish analytical curves at only one detector scale setting in order to prevent a change of slope affecting the analytical curve.

10.2 Verify the analytical calibration plot daily or whenever samples are to be run, prior to the analysis of samples to verify the system resolution, calibration, and sensitivity as part of the quality verification process (see Section 14).

10.3 Rerun the sulfate and chloride calibration plots after any change of the ion chromatography eluent solution from 8.3, to reestablish ion retention times and resolution.

10.4 Measurement of the calibration standards. Inject 20 µL of each calibration solution from 9.2 into the ion chromatograph, and measure the areas of the peaks corresponding to sulfate and chloride ions. An ion chromatogram of a 1 mg/L calibration solution is shown in Fig. 1 (other anions, if present, will elute as shown). It is the user's responsibility to determine retention times for each analyte ion.

10.5 Construct the sulfate and chloride calibration plots by plotting the peak area counts against the sulfate and chloride ion concentrations. Use linear regression to determine the best straight line calibration, the plots should each have a linear least squares correlation coefficient of 0.99 or greater, see Figs. 2 and 3. The response factor for each ion, R_f, is the slope of the calibration plot straight line, in mg/L/(area count).