



Standard Test Method for Determination of Existent and Potential Sulfate and Inorganic Chloride in Fuel Ethanol and Butanol by Direct Injection Suppressed Ion Chromatography¹

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 to 20 mg/kg of existent or potential inorganic sulfate and 1.0 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 and health 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.

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](#)

[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](#)

[D6792 Practice for Quality System in Petroleum Products 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 of Terms Specific to This Standard:

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

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

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

3.1.4 *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

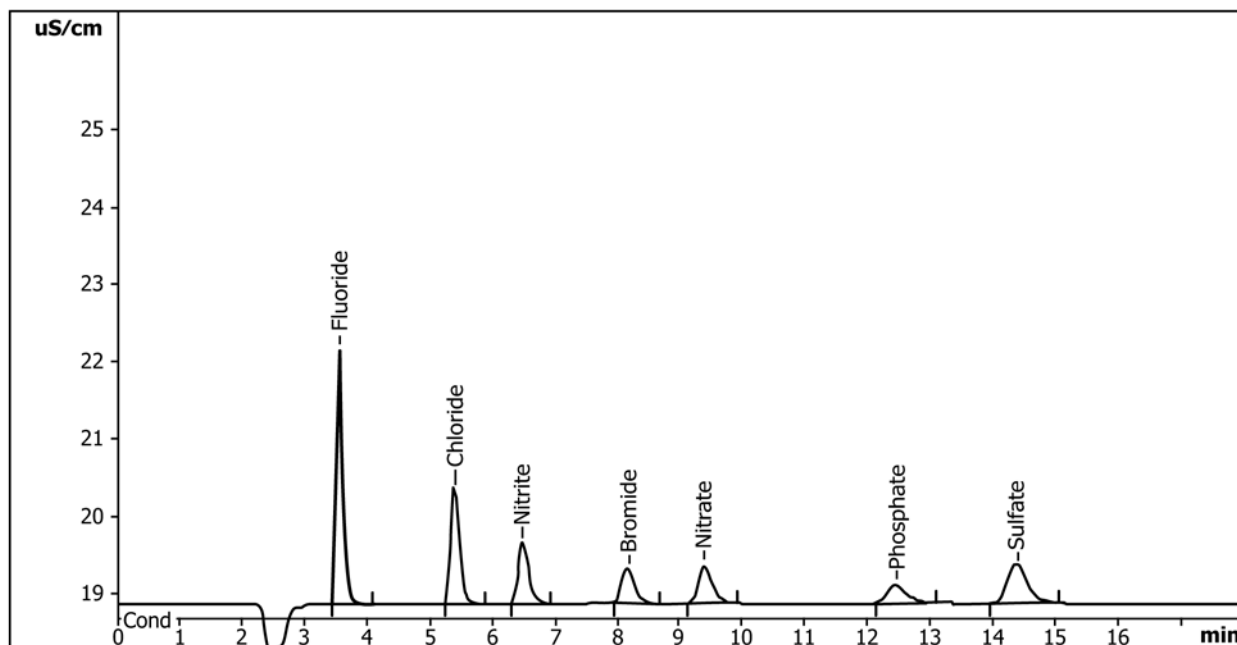
¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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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.

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

*A Summary of Changes section appears at the end of this standard



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

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.

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 $110 \pm 5^\circ\text{C}$ 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, 25, 50, 100, 1000, 2000-cc 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 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 to 1000 $\mu\text{S}/\text{cm}$ 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 II 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 ± 0.0005 g of NaHCO_3 and 33.92 ± 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 (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 *Tetrabutylammonium Bisulfate*—Technical or reagent grade, 99 % minimum purity.

⁴ *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 *Annual 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.