



Designation: 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<sup>1</sup>

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:<sup>2</sup>

**D1193** Specification for Reagent Water

<sup>1</sup> 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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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

**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

**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:*<sup>3</sup>

**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**.

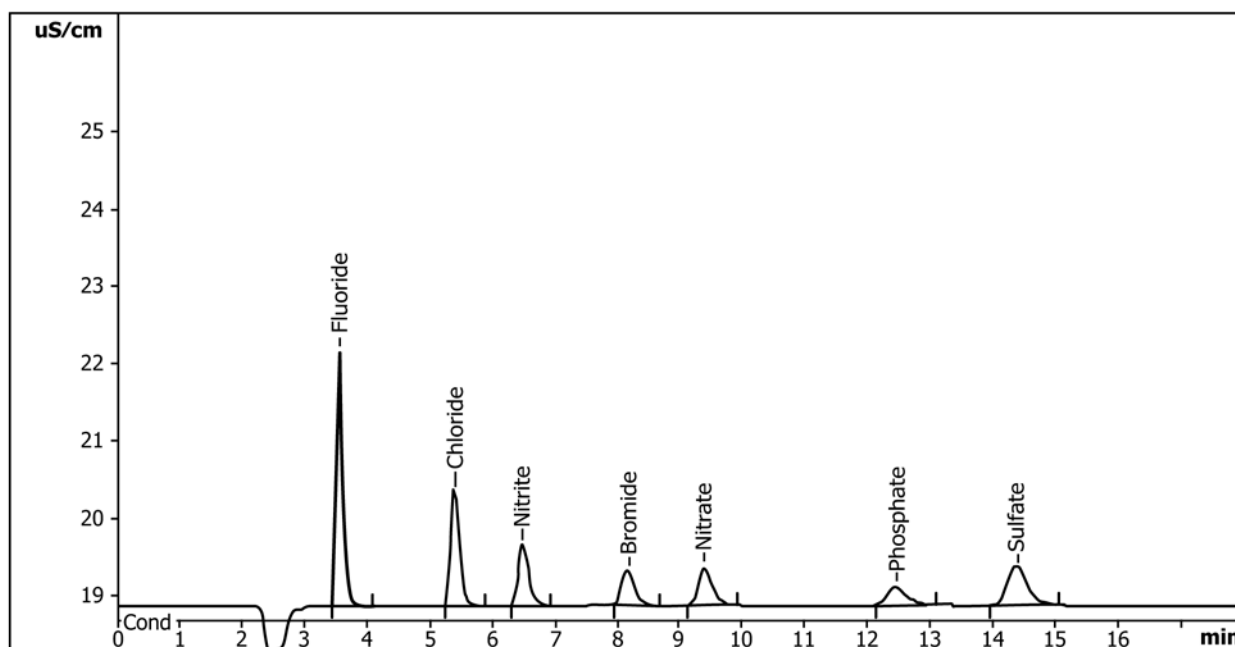
### 3.2 Definitions of Terms Specific to This Standard:

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.

<sup>3</sup> 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

3.2.3 *inorganic sulfate*, *n*—sulfate ( $\text{SO}_4^{2-}$ ) 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.

#### 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.