



# Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel<sup>1</sup>

This standard is issued under the fixed designation D 4806; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope\*

1.1 This specification covers nominally anhydrous denatured fuel ethanol intended to be blended with unleaded or leaded gasolines at 1 to 10 volume % for use as a spark-ignition automotive engine fuel. The significance of this specification is shown in [Appendix X2](#).

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

- D 86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure
- D 381 Test Method for Gum Content in Fuels by Jet Evaporation
- D 512 Test Methods for Chloride Ion In Water
- D 891 Test Methods for Specific Gravity, Apparent, of Liquid Industrial Chemicals
- D 1152 Specification for Methanol (Methyl Alcohol)
- D 1193 Specification for Reagent Water
- D 1613 Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products
- D 1688 Test Methods for Copper in Water
- D 2622 Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry
- D 3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry

- D 3505 Test Method for Density or Relative Density of Pure Liquid Chemicals
- D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter
- D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products
- D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
- D 4306 Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination
- D 4814 Specification for Automotive Spark-Ignition Engine Fuel
- D 5453 Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence
- D 5501 Test Method for Determination of Ethanol Content of Denatured Fuel Ethanol by Gas Chromatography
- D 5580 Test Method for Determination of Benzene, Toluene, Ethylbenzene, *p/m*-Xylene, *o*-Xylene, C<sub>9</sub> and Heavier Aromatics, and Total Aromatics in Finished Gasoline by Gas Chromatography
- D 5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products
- D 6299 Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance
- D 6423 Test Method for Determination of pH<sub>E</sub> of Ethanol, Denatured Fuel Ethanol, and Fuel Ethanol (Ed75-Ed85)
- D 6428 Test Method for Total Sulfur in Liquid Aromatic Hydrocarbons and Their Derivatives by Oxidative Combustion and Electrochemical Detection<sup>3</sup>
- D 6550 Test Method for Determination of Olefin Content of Gasolines by Supercritical-Fluid Chromatography
- E 203 Test Method for Water Using Volumetric Karl Fischer Titration
- E 300 Practice for Sampling Industrial Chemicals

<sup>1</sup> This specification is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.A0.01 on Gasoline and Gasoline-Oxygenate Blends.

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<sup>2</sup> 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.

<sup>3</sup> Withdrawn.

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

**E 1064** Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration

### 2.2 Other Standards:

United States Code of Federal Regulations, Title 27, Parts 20 and 21<sup>4</sup>

United States Federal Specification O-E-760b Ethyl Alcohol (Ethanol): Denatured Alcohol: and Proprietary Solvent<sup>5</sup>

Ethanol, volume %, min	92.1
Methanol, volume %, max	0.5
Solvent-washed gum, mg/100 mL, max	5.0
Water content, volume %, max	1.0 (Note 1)
Denaturant content, volume %, min	1.96
volume %, max	5.0
Inorganic Chloride content, mass ppm (mg/L), max	40 (32)
Copper content, mg/kg, max	0.1
Acidity (as acetic acid CH <sub>3</sub> COOH), mass % (mg/L), max	0.007 (56) (Note 3)
pHe	6.5 to 9.0
Sulfur, mass ppm, max	30
Sulfate, mass ppm, max	4
Appearance	Visibly free of suspended or precipitated contaminants (clear and bright)

## 3. Terminology

### 3.1 Definitions:

3.1.1 *ethanol, n*—ethyl alcohol, the chemical compound C<sub>2</sub>H<sub>5</sub>OH.

3.1.2 *gasoline, n*—a volatile mixture of liquid hydrocarbons, generally containing small amounts of additives, suitable for use as a fuel in spark-ignition, internal combustion engines.

**D 4814**

3.1.3 *gasoline-ethanol blend, n*—a fuel consisting primarily of gasoline along with a substantial amount (more than 0.35 mass % oxygen) of denatured fuel ethanol.

**D 4814**

3.1.4 *oxygenate, n*—an oxygen-containing, ashless, organic compound, such as an alcohol or ether, which may be used as a fuel or fuel supplement.

**D 4814**

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

3.2.1 *denaturants*—natural gasoline, gasoline components, unleaded gasoline, or toxic or noxious materials added to fuel ethanol to make it unsuitable for beverage use but not unsuitable for automotive use.

3.2.2 *denatured fuel ethanol*—fuel ethanol made unfit for beverage use by the addition of denaturants.

3.2.3 *fuel ethanol*—ethanol with impurities common to its production (including water but excluding denaturants).

3.2.4 *impurities*—in commercially produced fuel ethanol, compounds other than ethanol or denaturants present, such as methanol and fusel oil (for example, amyl and isoamyl alcohols).

3.2.5 *pHe*—a measure of the acid strength of alcohol fuels.

## 4. Performance Requirements

4.1 *Denatured Fuel Ethanol*—When fuel ethanol is denatured as specified in Section 5, it shall conform to the following requirements at the time of blending with a gasoline.

NOTE 1—In some cases, a lower water content may be necessary to avoid phase separation of a gasoline-ethanol blend at very low temperatures. This reduced water content, measured at the time of delivery, shall be agreed upon between the supplier and purchaser.

NOTE 2—If denatured fuel ethanol is prepared by the addition of denaturants to undenatured fuel ethanol after it has been produced rather than during the dehydration process, the 15.56/15.56°C (60/60°F) specific gravity in air of the undenatured fuel ethanol shall be in the range from 0.7937–0.7977.

NOTE 3—Denatured fuel ethanol may contain additives, such as corrosion inhibitors and detergents, that may affect the titratable acidity (acidity as acetic acid) of the finished fuel ethanol. Although the base fuel ethanol may meet the acidity specification, the effect of these additives may produce an apparent high titratable acidity of the finished product. Contact the ethanol supplier if there is a question regarding the titratable acidity of your denatured fuel ethanol to verify that the base ethanol meets the acidity requirements of 4.1.

4.2 *Other Properties*—Limits more restrictive than those specified above, or the specification of additional properties such as color, may be agreed upon between the supplier and the purchaser.

## 5. Denaturants

5.1 The only denaturants used for fuel ethanol shall be natural gasoline, gasoline components, or unleaded gasoline at a minimum concentration of two parts by volume per 100 parts by volume of fuel ethanol. One denatured formula specifically designed for fuel use by the Alcohol and Tobacco Tax and Trade Bureau (TTB) of the U.S. Treasury Department is Formula C.D.A. 20. It requires that for every 100 gal of ethanol of not less than 195 proof, a total of 2.0 gal of denaturant be added. Another fuel alcohol rendered unfit for beverage use and manufactured at an alcohol fuel plant (AFP) requires the addition of 2 gal or more of materials listed by the director to each 100 gal of ethanol. The fuel ethanol formulas approved by the U.S. Treasury Department include materials, which are not allowed by this ASTM specification. This specification prohibits the use of hydrocarbons with an end boiling point higher than 225°C (437°F) as determined by Test Method **D 86**, although they may be permitted by TTB regulations. Some kerosines, for instance, promote piston scuff in automotive

<sup>4</sup> Order as Code of Federal Regulations Title 27 Parts 200-End: from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401.

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engines. The denaturants permitted by this specification may be included as part of the 10 volume % denatured fuel ethanol blended with a gasoline if they do not exceed five volume % of fuel ethanol. Any part of these denaturants that are present at concentrations higher than five volume % of fuel ethanol are considered as part of the base gasoline. The maximum denaturant limits are specified by United States Internal Revenue Service (IRS) regulations.

NOTE 4—TTB regulations concerning the preparation, use, and handling of denatured ethanols are published in the [United States Code of Federal Regulations, Title 27](#), Parts 19, 20, and 21. 27 CFR 19.1005 contains regulations for rendering fuel alcohol unfit for beverage use by an AFP. 27 CFR 21.24 contains the formula for manufacturing completely denatured alcohol, C.D.A. 20.

**5.2 Prohibited Denaturants**—Although this specification permits only hydrocarbons in the gasoline boiling range to be used as denaturants, specific mention must be made of some materials that have extremely adverse effects on fuel stability, automotive engines, and fuel systems. These materials shall not be used as denaturants for fuel ethanol under any circumstances. They are as follows: methanol which does not meet Specification [D 1152](#), pyrroles, turpentine, ketones, and tars (high-molecular weight pyrolysis products of fossil or nonfossil vegetable matter). While any significant amount of methanol will lower the water tolerance and increase the vapor pressure of a gasoline-ethanol blend, these effects become more serious when methanol is present at more than 2.5 parts by volume per 100 parts by volume of fuel ethanol. Also, methanol, which does not meet Specification [D 1152](#), frequently contains impurities, such as turpentine and tars. Similarly, ketone denaturants tend to degrade fuel stability or increase the tendency of a gasoline-ethanol blend to corrode metals and attack elastomers. These effects become more serious if the concentration of a ketone such as 4-methyl pentanone (methyl isobutyl ketone) exceeds one part by volume per 100 parts by volume of fuel ethanol. There is no information available on the effects of denaturants other than those mentioned above; but unless a denaturant, such as a higher aliphatic alcohol or ether, is known to have no adverse effect on a gasoline-ethanol blend or on automotive engines or fuel systems, it shall not be used.

## 6. Workmanship

6.1 The fuel ethanol shall be visually free of sediment and suspended matter. It shall be clear and bright at the ambient temperature or 21°C (70°F), whichever is higher.

6.2 The specification defines only a basic purity for this product. The product shall be free of any adulterant or contaminant that may render the material unacceptable for its commonly used applications.

## 7. Sampling, Containers, and Sample Handling

7.1 The reader is strongly advised to review all intended test methods prior to sampling to understand the importance and effects of sampling technique, proper containers, and special handling required for each test method.

7.2 Correct sampling procedures are critical to obtain a sample representative of the lot intended to be tested. Use appropriate procedures in Practice [D 4057](#) or Practice [E 300](#)

for manual method sampling and in Practice [D 4177](#) for automatic method sampling, as applicable.

7.3 The correct sample volume and appropriate container selection are important decisions that can impact test results. Refer to Practice [D 4306](#) for aviation fuel container selection for tests sensitive to trace contamination. Refer to Practice [D 5854](#) for procedures on container selection and sample mixing and handling. Where practical, fuel ethanol should be sampled in glass containers. If samples must be collected in metal containers, do not use soldered metal containers. This is because the soldering flux in the containers and the lead in the solder can contaminate the sample. Plastic containers should be avoided.

7.4 *Sample Size*—A minimum of about 1 L or 1 U.S. qt is recommended. If specific gravity is to be determined by a hydrometer method, additional volume may be required. This depends on the size of the hydrometer.

7.5 *Lot Size*—A lot shall normally consist of the amount contained in a tanker compartment or other bulk container in which it is delivered. If this definition does not apply, the definition of a lot must be agreed upon between the supplier and purchaser.

NOTE 5—See Sections 5, 6, and 7 on Significance, Safety, and Statistical Considerations, respectively, of Practice [E 300](#) for a detailed discussion of the statistics of sampling.

## 8. Test Methods

8.1 The scope of some of the test methods specified in [8.2-8.10](#) do not include denatured fuel ethanol. The precisions of those test methods may differ from the reported precisions when testing denatured fuel ethanol.

8.2 *Water Content*—Test Methods [E 203](#) or [E 1064](#).

8.3 *Solvent-Washed Gum Content*—Test Method [D 381](#), air jet apparatus.

8.4 *Acidity*—Test Method [D 1613](#).

8.5 *pHe*—Test Method [D 6423](#).

8.6 *Appearance*—The product shall be visibly free of suspended or precipitated contaminants (clear and bright). This shall be determined at indoor ambient temperature unless otherwise agreed upon between the supplier and the purchaser.

8.7 *Specific Gravity*—Test Methods [D 891](#), Procedure B or Test Method [D 4052](#). For Test Methods [D 891](#), Procedure B (hydrometer), no formal precision statement is available, but practical experience indicates that precision is no better than 0.0005. Test Methods [D 891](#) Procedure C (pycnometer), with an interlaboratory precision (reproducibility) of 0.0002, should be used as a referee method.

8.8 *Inorganic Chloride Content*—Modification of Test Methods [D 512-81\(1985\)](#)<sup>e1</sup>, Method C.

8.8.1 The modification of Test Methods [D 512-81\(1985\)](#)<sup>e1</sup>, Method C consists of using 5 mL of sample diluted with 20 mL of water in place of the 25-mL sample specified in the standard procedure. The water shall meet Specification [D 1193](#), Type II. The volume of the sample prepared by this modification will be slightly larger than 25 mL. To allow for the dilution factor, report the chloride ion present in the fuel ethanol sample as the chloride ion present in the diluted sample multiplied by five.

8.8.2 The precision of this modified method has not been determined, but for the actual amount of chloride ion found in the diluted sample, it is expected to be similar to the precision of Test Methods D 512–81(1985)<sup>e1</sup>, Method C.

8.9 *Copper Content*—Modification of Test Methods D 1688, Test Method A.

8.9.1 The modifications of Test Methods D 1688, Test Method A (atomic absorption, direct) consists of mixing reagent-grade ethanol (which may be denatured in accordance with BATF of the U.S. Treasury Department Formula 3A or 30) in place of water as the solvent or diluent for the preparation of reagents and standard solutions. However, this must not be done to prepare the stock copper solution described in the section on Copper Solution, Stock in Test Method D 1688. Because a violent reaction may occur between the acid and the ethanol, use water, as specified, in the acid solution part of the procedure to prepare the stock copper solution. Use ethanol for the rinse and final dilution only.

8.9.2 The precision of this modified method has not been determined, but it is expected to be similar to the precision of Test Method D 1688, Test Method A.

8.10 *Ethanol Content*—Test Method D 5501.

8.11 *Sulfur Content*—Test Methods D 2622, D 3120, D 5453, or D 6428. California specifies that compliance with

the California sulfur standard for denatured ethanol shall be determined using Test Method D 5453–93. EPA allows Test Methods D 3120, D 5453, or D 6428 for measuring sulfur in gasoline as long as these alternative test method results are correlated to the EPA designated Test Method D 2622 when determining compliance with Federal EPA sulfur standards.

8.12 *Sulfate Content*—See Annex A1-Annex A3 for the test methods.

8.13 *Denaturant Content*—Denaturant is added in the specified range to comply with federal regulations. The content is set by volumetric addition during the denaturing process. There is no standardized test procedure to directly determine the denaturant content in fuel ethanol. Current analytical procedures only provide a calculated estimate of the denaturant content, which is not sufficiently accurate for determining compliance.

## 9. Keywords

9.1 acidity; automotive spark-ignition engine fuel; base gasoline; chloride ion content; copper content; corrosion inhibitors; denaturants; denatured fuel ethanol; ethanol; ethanol content; ethanol purity; fuel; fuel ethanol; gasoline; gasoline-ethanol blend; impurities; oxygenate; solvent-washed gum; sulfate ion content; sulfur content; water content

## ANNEXES

(Mandatory Information)

### A1. TEST METHOD FOR INORGANIC SULFATE IN ETHANOL BY POTENTIOMETRIC LEAD TITRATION

#### A1.1 Scope

A1.1.1 This test method describes a potentiometric titration procedure for determining the inorganic sulfate content of hydrous, anhydrous ethanol, and anhydrous denatured ethanol, which is added as a blending agent with spark ignition fuels. It is intended for the analysis of ethanol samples containing between 0.5-20 µg/g inorganic sulfate.

A1.1.2 *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.

#### A1.2 Referenced Documents

A1.2.1 *ASTM Standards*.<sup>2</sup>

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D 6299 Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical System Measurement Performance

#### A1.3 Terminology

A1.3.1 *Definitions of Terms Specific to This Standard:*

A1.3.1.1 *inorganic sulfate, n*—sulfate species present as sulfuric acid, ionic salts of this acid, or mixtures of these. Specifically in this method, inorganic sulfate is present as sulfate in ethanol.

#### A1.4 Summary of Test Method

A1.4.1 An ethanol sample containing inorganic sulfate is titrated in ethanolic medium with a standard lead solution. Lead sulfate precipitate is formed during the titration. Perchloric acid is added to remove possible interference from carbonate. The endpoint is signaled by an increase in lead ion activity, as measured by a lead-selective electrode.

#### A1.5 Significance and Use

A1.5.1 Ethanol is used as a blending agent added to gasoline. Sulfates are indicated in filter plugging deposits and fuel injector deposits. When fuel ethanol is burned, sulfates can contribute to sulfuric acid emissions. Ethanol acceptability for use depends on the sulfate content. Sulfate content, as measured by this test method, can be used as one measure of determination of the acceptability of ethanol for automotive spark-ignition engine fuel use according to Specification D 4806.

#### A1.6 Apparatus

A1.6.1 *Potentiometric Titration Assembly*—A titration assembly consisting of an automatic titrator fitted with a lead

ion-selective electrode, a double-junction reference electrode, buret and stirring is used. Stirring may be accomplished by means of magnetic or propeller type stirrer mechanisms. The buret size should ideally be 10 mL or 20 mL.

**A1.6.2 Reference Electrode**—A double junction reference electrode with the inner electrode composed of silver/silver chloride with a potassium chloride solution as internal electrolyte. The external solution is composed of 1 M lithium chloride in ethanol. This configuration is used to prevent silver ion, a lead electrode poison, from leaching into the analyte solution during titration. Preferred electrolytes for use in double junction electrodes may vary with the manufacturer; use the manufacturer recommended electrolytes for the application. Other types of reference electrodes may be considered with some caveats (for example, single junction, combination or glassy carbon), but the data presented in this method was generated using exclusively a double junction electrode, which is the best choice for this determination.

**A1.6.3 Lead Electrode**—A lead sulfide-based crystalline sensor type lead ion selective electrode (ISE) is used.

**A1.6.4 Drying Oven**—A drying oven for drying sodium sulfate at 110°C is required.

**A1.6.5 Pipets or Volumetric Transferring Devices**—Class A glass pipets or their equivalent.

**A1.6.6 Volumetric Flasks**—Class A volumetric flasks.

**A1.6.7 Polishing Material**—Lead sulfide-based crystalline sensor electrodes require polishing to remove oxidation products. These materials are supplied with the electrode from the manufacturer.

**A1.6.8 pH Test Strips**—Test strips in the range of pH 1 to pH 7.

**A1.6.9 Titration Vessels**—Standard glass beakers or titration vessels supplied with titration equipment.

## A1.7 Reagents

**A1.7.1 Lead Nitrate**, reagent grade, 99 % minimum purity. (**Warning**—Poison; harmful by inhalation and if ingested; avoid contact with the skin. Dispose of this material in accordance with accepted local requirements.)

**A1.7.2 Sodium Sulfate**, anhydrous, reagent grade, 99 % minimum purity. (**Warning**—Do not ingest; avoid unnecessary exposure.)

**A1.7.3 Perchloric Acid 70 %**, A.C.S. reagent grade minimum purity with sulfate concentration <0.001 % (m/M). Dispose of this material in accordance with accepted local requirements. (**Warning**—Corrosive; keep away from skin and eyes. Perchloric acid is a strong oxidizer.)

**A1.7.4 Ethanol**, denatured with methanol, formula 3A, or histological grade ethanol, anhydrous, denatured with ethyl acetate, methyl isobutyl ketone, and hydrocarbon naphtha. (**Warning**—Flammable; toxic; may be harmful or fatal if ingested or inhaled; avoid skin contact.)

**A1.7.5 Ethanol**, absolute, 200 proof, 99.5 %, A.C.S. reagent grade.

**A1.7.6 Lithium Chloride**, 99+ %, A.C.S. reagent grade.

**A1.7.7 Water**, Type III reagent water conforming to Specification **D 1193**.

**A1.7.8 Anhydrous Calcium Sulfate Desiccant**.

**TABLE A1.1 Preparation of Sulfate Standards in Ethanol**

Ethanol Standard µg sulfate/g Ethanol	Ethanol, g	Sulfate Stock Solution, mL
50	975	25
20	990	10
10	995	5
5	997.5	2.5
1	999.5	0.5

## A1.8 Preparation of Standard Solutions

**A1.8.1 Lead Titrant, 0.0025 M**—Dissolve 0.833 g lead nitrate in 300 mL water. Pour into a 1-L bottle, fill with denatured ethanol and mix well. Standardize in accordance with **A1.10.1**.

**A1.8.2 Sulfate Standard, 0.01 M**—Dry 5 g anhydrous sodium sulfate at 110°C for 1 h. Remove from the oven and allow to cool in a desiccator over anhydrous calcium sulfate desiccant. Accurately weigh about 0.70 g on an analytical balance to the nearest tenth of a milligram and place in a 500-mL volumetric flask. Add water to dissolve the sodium sulfate then dilute to volume. Calculate the exact concentration in accordance with Eq A1.1.

$$\frac{G}{(142.02)(0.500)} = \text{Molarity} \quad (\text{A1.1})$$

where:

$G$  = weight in grams of  $\text{Na}_2\text{SO}_4$  dissolved in 500 mL,  
and  
142.02 = its gram molecular weight.

**A1.8.3 Sulfate Stock Solution for Standards in Ethanol, 2000 mg/L**—Accurately weigh 2.95 g anhydrous sodium sulfate to the nearest tenth of a milligram and transfer to a 1-L volumetric flask (dried anhydrous sodium sulfate should be stored in a desiccator). Add water to dissolve the sodium sulfate and make to volume. Calculate the concentration of sulfate in the solution in accordance with Eq A1.2.

$$\text{Aqueous Stock Sulfate (mg/L)} = (\text{g Na}_2\text{SO}_4) (0.6764) (1000 \text{ mg/g}) / 1 \text{ L} \quad (\text{A1.2})$$

where:

$\text{g Na}_2\text{SO}_4$  = weight in grams of  $\text{Na}_2\text{SO}_4$  dissolved in 1 L,  
and  
0.6764 = fraction of sulfate in  $\text{Na}_2\text{SO}_4$ .

**A1.8.4 Sulfate Standards in Ethanol**—Ethanol is weighed into a container equipped with a closure to prevent evaporation in accordance with **Table A1.1** to achieve the desired standard. Sulfate stock solution from **A1.8.3** is transferred to the solution according to **Table A1.1** and the final weight of the solution is recorded. The concentration of the standard is calculated by dividing the number of milligrams sulfate from the sulfate stock solution and dividing by the final solution weight in accordance with Eq A1.3.

$$\text{Ethanol Sulfate Standard } (\mu\text{g/g}) = V \times C / W \quad (\text{A1.3})$$

where:

$V$  = volume of Aqueous Sulfate Stock (**A1.8.3**), mL,

$C$  = concentration of Aqueous Sulfate Stock (A1.8.3),  $\mu\text{g/mL}$  (equal to  $\text{mg/L}$ ), and  
 $W$  = final weight of ethanol and Aqueous Sulfate Stock aliquot, g.

A1.8.5 *Sulfate Blank Solution, 0.01 M*—Same solution as in A1.8.2.

A1.8.6 *Dilute Perchloric Acid, 0.1 M*—Dissolve 8.8 mL perchloric acid in 250 mL water in a 1-L volumetric flask, mix well and dilute to the mark with water.

A1.8.7 *Lithium Chloride in Ethanol, 1 M*—Lithium chloride (8.49 g) is added to absolute ethanol (200 mL) with stirring until dissolved.

## A1.9 Titration Equipment Preparation

A1.9.1 *Titrator*—The titrator is prepared by filling the titrator reservoir with lead titrant (A1.8.1) and following the manufacturer's procedure for filling the buret. Titrations are performed in monotonic titration mode. Either 25  $\mu\text{L}$  or 50  $\mu\text{L}$  titrant addition increments can be used. A 10 mV/min drift condition or 20-s wait time between additions (whichever is achieved first) is employed.

A1.9.2 *Electrode Preparation*—Proper care of the lead-selective electrode is essential for obtaining high-quality titration curves. Preparation of the lead electrode should be performed as specified by the manufacturer. A lead electrode utilizing a solid crystal sensor requires polishing when performance deteriorates. The voltage range for a 10 mg/kg sulfate in ethanol titration should span at least 50 mV and produce an acceptably shaped titration curve (see Fig. A1.1). If this level of electrode performance is not met, this indicates a need for lead electrode polishing. The lead electrode normally comes supplied with a polishing grit and a cloth rectangle. The polishing grit medium is placed on the cloth and wet with ethanol or water and moved over the surface of the cloth for a minute, rinsed with water to remove the polishing medium and wiped dry with a tissue. The electrode is then soaked in lead titrant (A1.8.1) for 2 min to re-equilibrate the electrode surface. The double junction reference electrode is filled with 1 M lithium chloride in ethanol (A1.8.7) in the outer chamber.

## A1.10 Standardization

A1.10.1 The exact concentration of the lead titrant shall be determined experimentally by titration of the sulfate standard (A1.8.2). Transfer 1.00 mL sulfate standard solution into a 150-mL beaker. Add approximately 100 mL ethanol and 1 mL of 0.1 M perchloric acid (A1.8.6). Prepare the autotitrator for operation, immerse the electrodes in the titration solution, initiate stirring and titrate to the potentiometric endpoint with lead titrant. Titration should require approximately 4.0 mL of lead solution to reach the endpoint.

A1.10.2 Titrate a blank in the same manner without addition of sulfate standard.

A1.10.3 The standardization should be repeated until precision comparable to that shown in A1.15 and Table A1.2 has been achieved. Calculate the concentration of the lead titrant as follows:

$$M_{pb} = \frac{V \times S}{T - T_b} \quad (\text{A1.4})$$

where:

$M_{pb}$  = molarity of lead in the titrant, moles/litre,

$V$  = mL of sulfate standard solution added,

$S$  = molarity of the sulfate solution (A1.8.2),

$T$  = mL of lead titrant used to titrate the sulfate solution, and

$T_b$  = mL of lead titrant used for the blank.

## A1.11 Sample Analysis

A1.11.1 Obtain an ethanol sample in accordance with Practice D 4057 or Practice D 4177. The sample should be well mixed to ensure homogeneity. A representative portion shall be taken for analysis. Samples should be collected in containers with closures that seal well to prevent evaporation of ethanol. Samples containers should not contain any residual sulfate. If containers have been cleaned and rinsed with water, they shall be rinsed with Type III reagent water prior to use.

A1.11.2 Determine the blank value by analysis of a denatured ethanol sample used for making standards (100 g) using the procedure described in A1.11.3. An aliquot of sulfate solution will be added to all samples as part of the blank.

A1.11.3 Weigh an ethanol sample (approximately 100 g) into a 150-mL beaker. Pipet 0.200 mL of sulfate blank solution (A1.8.5) into the beaker containing the ethanol solution. Add 1 mL of 0.1 M perchloric acid (A1.8.6). Ensure the sample is acidic to pH paper before titrating with a pH in the range of 3 to 5. The pH may be checked by dipping a glass stirring rod into the sample and testing a droplet on it with a moistened pH test strip. If 1 mL of 0.1 M perchloric acid is insufficient to achieve this, add more acid. To prepare the autotitrator for operation, immerse the electrodes in the titration solution, initiate stirring and titrate to the potentiometric endpoint with lead titrant. The average of three blank values is recorded for use in calculation of sulfate content of samples.

A1.11.4 Run samples run according to the procedure detailed in A1.11.3, including the addition of 0.200 mL of sulfate blank solution. Ensure that duplicate determinations agree to within the repeatability limits in Table A1.3 (see A1.15). If not, perform additional titrations until agreement is achieved. If satisfactory titration curves are not obtained, polish the lead electrode. Typical titration curves for sulfate standards in ethanol are shown in Fig. A1.1, and examples from commercial ethanol samples are shown in Fig. A1.2.

## A1.12 Calculation

A1.12.1 Calculate the inorganic sulfate content of the ethanol sample according to Eq A1.5.

$$\text{Sulfate } (\mu\text{g/g}) = \frac{(V - V_b)(M_{pb})(F)}{G} \quad (\text{A1.5})$$

where:

Sulfate = sulfate concentration,  $\mu\text{g/g}$  ( $\text{mg/kg}$ ),

$V$  = volume of lead titrant for sample, mL,

$V_b$  = volume of lead titrant for blank, mL,

$M_{pb}$  = molarity of lead titrant, mmol/mL,

$F$  = factor (96058  $\mu\text{g}$  sulfate/mmol sulfate), and

$G$  = weight of ethanol sample taken for analysis, g.

A1.12.2 The units of  $\mu\text{g/g}$  can be converted to  $\mu\text{g/mL}$  through the density of ethanol using Eq A1.6. However, for the

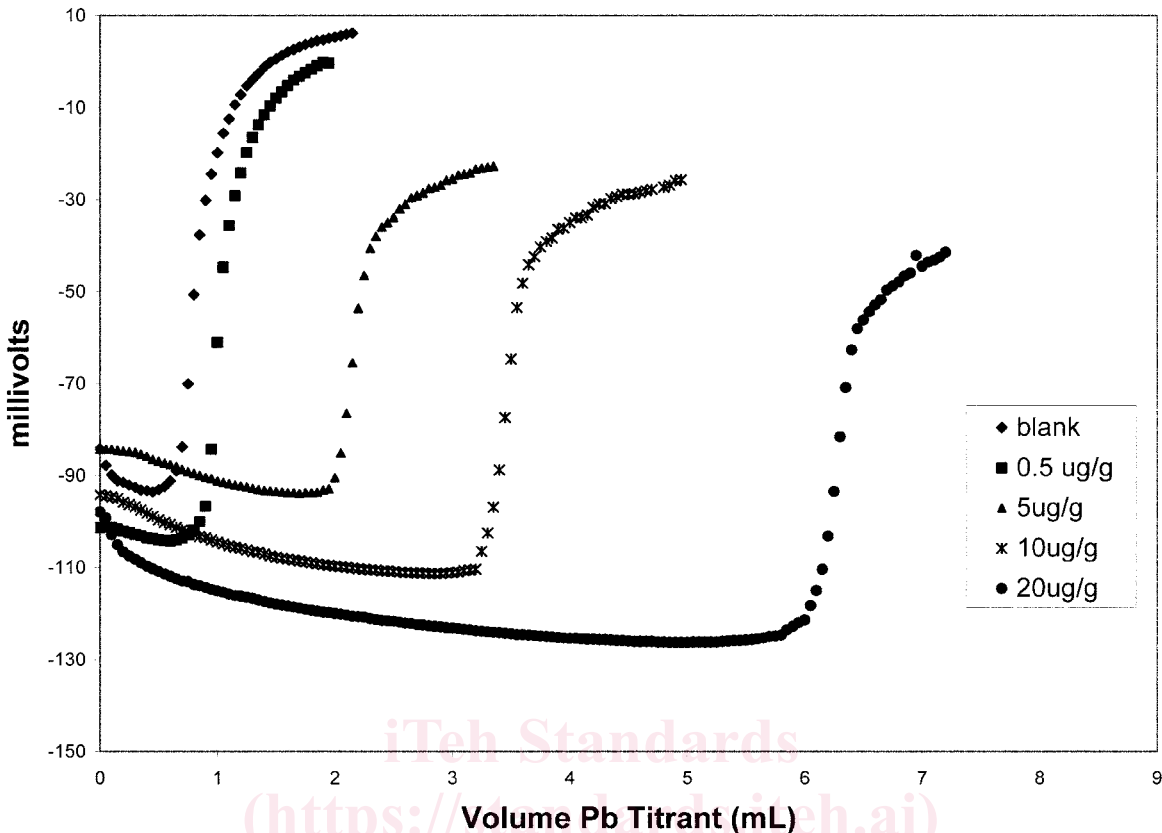


FIG. A1.1 Potentiometric Titration Curves for Sulfate Standards in Ethanol

purposes of this method, all calculations should use the  $\mu\text{g/g}$  (weight/weight) units.

$$\text{Sulfate } (\mu\text{g/mL}) = \text{Sulfate } (\mu\text{g/g}) (0.7893 \text{ g ethanol / mL ethanol}) \quad (\text{A1.6})$$

**A1.13 Report**

A1.13.1 Report the sulfate content results to the nearest 0.1  $\mu\text{g/g}$  over the 0.5–50  $\mu\text{g/g}$  range.

**A1.14 Quality Control**

A1.14.1 Confirm the performance of the instrument or the test procedure by analyzing one or more quality check sample(s) after each calibration and on at least each day of use thereafter. For example, a good check sample could be a single representative ethanol sample (see X1.1.5) that is analyzed repetitively. These results are plotted in control charts to check the system for statistical stability, as in X1.1.3.

A1.14.1.1 When QC/Quality Assurance (QA) protocols are already established in the testing facility, these can be used when they confirm the reliability of the test result.

A1.14.1.2 When there is no QC/QA protocol established in the testing facility, Appendix X1 can be used to define a suitable QC/QA system.

**A1.15 Precision and Bias**

A1.15.1 This precision statement represents replicate analyses performed in one laboratory by the same analyst on the same day on the same instrument.

A1.15.2 *Repeatability*—Two repeat analyses should agree 95 % of the time to within the repeatability values shown in Table A1.3. Titrant standardization precision is also shown in Table A1.2

A1.15.3 *Reproducibility*—At this time, no interlaboratory precision data have been obtained to allow a calculation for reproducibility.

A1.15.4 *Bias*—At this time, bias has not been measured versus any other test method.

**A1.16 Keywords**

ethanol; lead; potentiometric; sulfate; titration

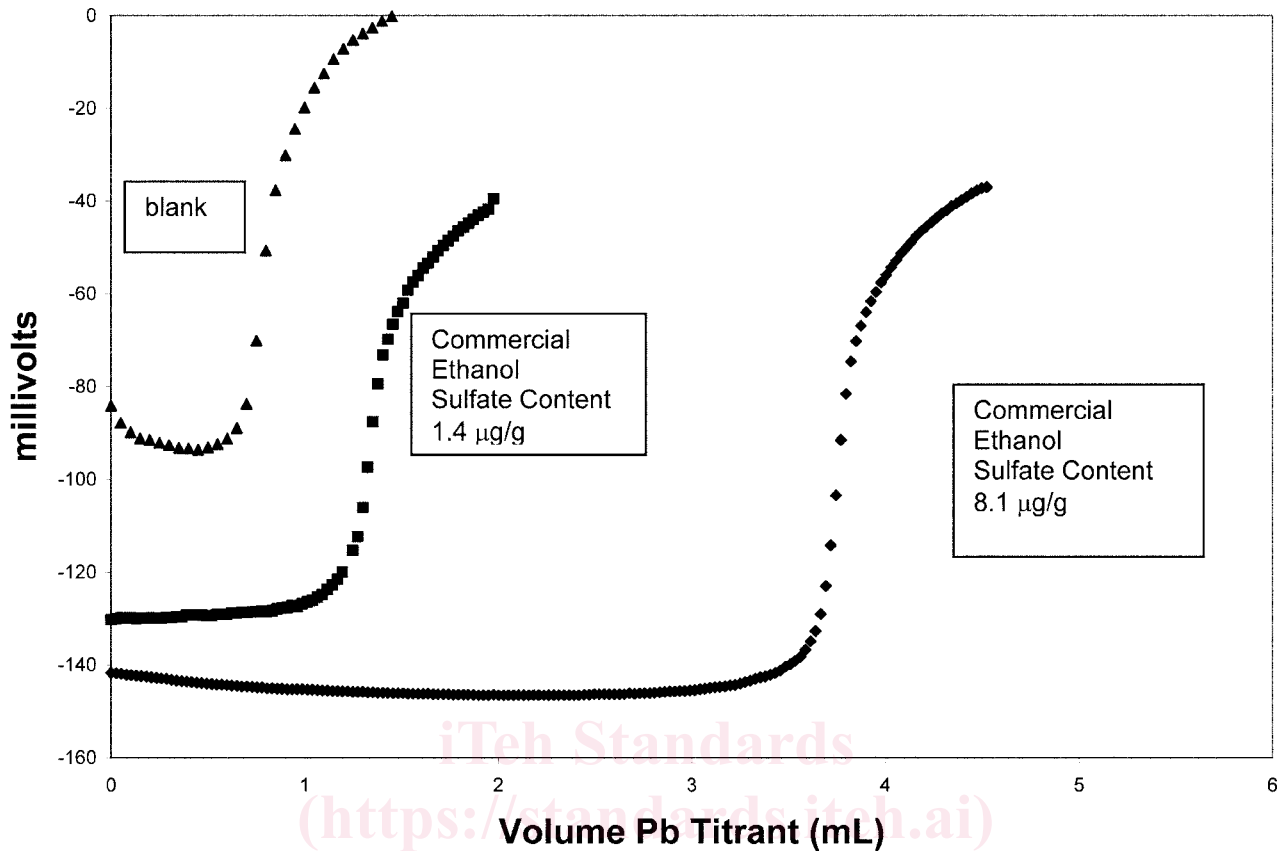


FIG. A1.2 Potentiometric Titration Curves for Sulfate in Commercial Ethanol

TABLE A1.2 Titrant Standardization Precision

Prepared Lead Titrant Molar Concentration	Average Lead Titrant Molar Concentration by Titration	Number of Determinations	Standard Deviation	Repeatability 2.8x Standard Deviation
0.002517	0.002477	10	$9.89 \times 10^{-6}$	0.000277

TABLE A1.3 Method Precision

Prepared Sulfate Concentration, µg/g	Average Sulfate Concentration by Titration, µg/g	Number of Determinations	Standard Deviation, µg/g	Repeatability 2.8x Standard Deviation
20.3	19.2	7	0.270 <sup>A</sup>	0.76
10.1	9.94	6	0.091	0.25
5.07	4.90	8	0.100	0.28
1.01	1.03	8	0.042	0.11
0.50	0.55	4	0.056	0.16

<sup>A</sup> The relatively high value for standard deviation for the 20.3 µg/g sample is believed to arise from variability in the amount of sulfate solution added as part of the blank from a problem with the transfer device used for the transfer.



## A2. TEST METHOD FOR DETERMINATION OF INORGANIC CHLORIDE AND SULFATE IN ETHANOL BY DIRECT INJECTION SUPPRESSED ION CHROMATOGRAPHY

### A2.1 Scope

A2.1.1 This test method describes a direct injection ion chromatographic procedure for determining the inorganic chloride and sulfate content of hydrous and anhydrous denatured ethanol. It is intended for the analysis of ethanol samples containing between 0.5–0 mg/kg inorganic chloride and 0.5–20 mg/kg inorganic sulfate ions.

A2.1.2 Co-elution of other ions may cause interferences in the sulfate determination. Sometimes it will be necessary to avoid this by standard addition analysis for the ion of interest.

A2.1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

A2.1.4 *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.

### A2.2 Referenced Documents

A2.2.1 *ASTM Standards:*<sup>2</sup>

**D 4177** Practice for Automated Sampling of Petroleum and Petroleum Products

**D 5827** Test Method for Analysis of Engine Coolant for Chloride and Other Anions by Ion Chromatography

**D 6299** Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical System Measurement Performance

**D 6792** Guide for Quality System in Petroleum Products and Lubricants Testing Laboratories

### A2.3 Terminology

A2.3.1 *Definitions of Terms Specific to This Standard:*

A2.3.1.1 *inorganic sulfate, n*—sulfate ( $\text{SO}_4^{2-}$ ) species present as sulfuric acid, ionic salts of this acid, or mixtures of these.

A2.3.1.2 *inorganic chloride, n*—chloride ( $\text{Cl}^-$ ) species present as hydrochloric acid, ionic salts of this acid, or mixtures of these.

### A2.4 Summary of Test Method

A2.4.1 A small volume of an ethanol sample is directly injected into a suitably configured ion chromatograph according to manufacturer's recommendations for this method. 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 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 quantitated by integration of their responses compared with an external calibration curve, and are reported as

mg/kg, or may be converted to mg/L. The stock calibration standards are prepared in an aqueous matrix. The injected calibration standards are prepared from suitable compounds in an ethanolic matrix.

### A2.5 Significance and Use

A2.5.1 Ethanol is used as a blending agent in gasoline. Sulfates are found in filter plugging deposits and fuel injector deposits. Ethanol acceptability for use depends on the sulfate and chloride content.

A2.5.2 Sulfate and chloride content, as measured by this test method, can be used as one measure of the acceptability of ethanol for automotive spark-ignition engine fuel use according to Specification D 4806.

### A2.6 Interferences

A2.6.1 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.

A2.6.2 A water dip (system void, negative peak as shown in Fig. A2.1) can cause interference with some integrators. This dip may be eliminated by dilution with the eluent. 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.

A2.6.3 Given the trace amounts of chloride and sulfate determined in this method, interferences can be caused by contamination of glassware, eluent, reagents, etc. Great care must be taken to ensure that contamination is kept at the lowest possible levels. The use of latex gloves is highly recommended to prevent contamination. The use of latex or lint-free gloves is highly recommended to prevent sample contamination.

A2.6.4 Pre-rinsing of the sample preparation containers with Type II water is mandatory.

### A2.7 Apparatus

A2.7.1 *Analytical Balance*, capable of weighing up to 100 g accurately to 0.0001 g.

A2.7.2 *Drying Oven*, controlled at  $110 \pm 5^\circ\text{C}$  for drying sodium sulfate and sodium chloride.

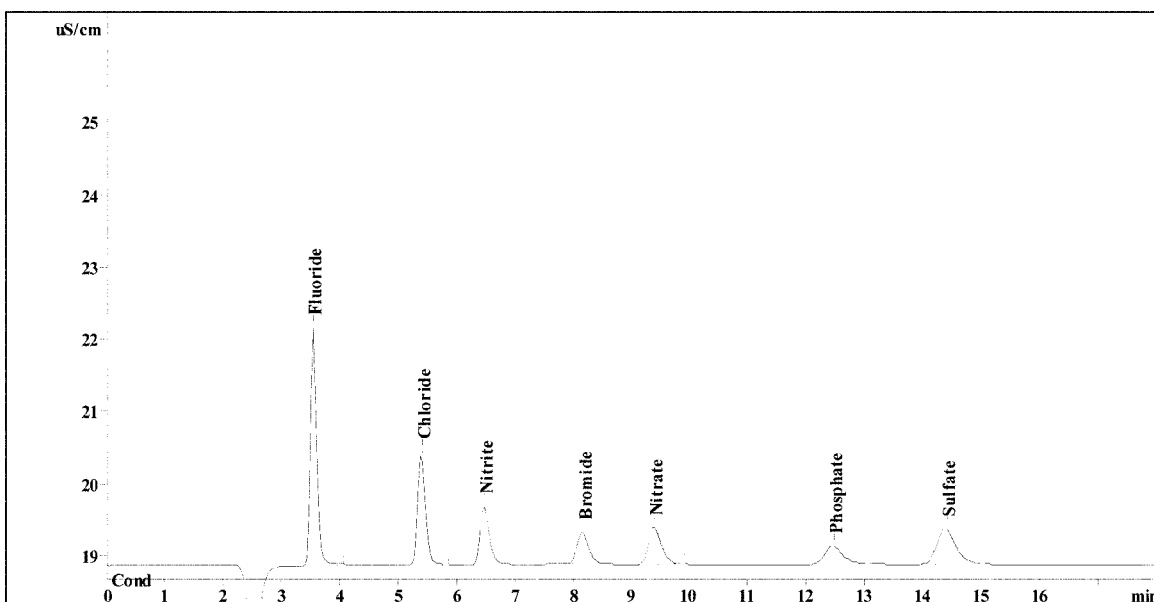
A2.7.3 *Desiccator*, containing freshly activated silica gel (or equivalent desiccant) with moisture content indicator.

A2.7.4 *Pipettes or Volumetric Transferring Devices*—Class A glass pipettes or their equivalent of 1 and 5 mL capacity or variable volume automatic pipettes fitted with disposable polypropylene tips.

A2.7.5 *Volumetric Flasks*—Class A of 25, 50, 100, 1000 mL capacity.

A2.7.5.1 *Container*, equipped with a closure to prevent ethanol evaporation, 1 L.

A2.7.6 *Ion Chromatograph*—Analytical system with all required accessories including syringes, columns, suppressor, and detector.



**FIG. A2.1 Typical Ion Chromatogram of a Solution Containing 1 mg/Kg of Various Anions**

A2.7.6.1 *Injection System*, capable of delivering 20  $\mu\text{L}$  with a precision better than 1 %, or as recommended for this determination by the manufacturer.

A2.7.6.2 *Pumping System*, capable of delivering mobile phase flows between 0.2 and 2.5 cc/min with a precision better than 2 %, or as recommended for this determination by the manufacturer.

A2.7.6.3 *Guard Column*, for protection of the analytical column from strongly retained constituents. Better separations are obtained with additional theoretical plates.

A2.7.6.4 *Anion Separator Column*, 100 % solvent compatible and capable of producing satisfactory analyte separation (Fig. A2.1).

A2.7.6.5 *Anion Suppressor Device*, 100 % solvent compatible tri-chamber micro packed bed with cation exchange resin (or equivalent). Suppressor device should simultaneously be on-line continuously electrolytically/chemically regenerated to its hydrogen form using any mineral acid providing  $\text{H}^+$  ion. Follow ion chromatography instrument vendor recommendations.

A2.7.6.6 *Conductivity Detector*, (low volume), temperature controlled to 0.01 $^{\circ}\text{C}$ , capable of at least 0 to 1000  $\mu\text{S}/\text{cm}$  on a linear scale.

A2.7.6.7 *Integrator or Chromatography Data System Software*, capable of measuring peak areas and retention times, and correct the data according to the baseline of the chromatogram.

A2.7.7 *Gloves*, lint-free or latex.

## A2.8 Reagents

A2.8.1 *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. 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.

A2.8.2 *Purity of Water*, unless otherwise indicated, reference to water shall be understood to mean reagent water as defined by Type II in Specification D 1193. For eluent preparation and handling, comply with all ion chromatograph instrument and column vendor requirements (for example, filtering, degassing, etc.).

A2.8.3 *Eluent Buffer Stock Solution*, Sodium bicarbonate ( $\text{NaHCO}_3$ ) 1.0 mM and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) 3.2 mM. Dissolve  $8.4 \pm 0.0005$  g of  $\text{NaHCO}_3$  and  $33.92 \pm 0.0005$  g of  $\text{Na}_2\text{CO}_3$  in reagent water in a 1-L Type A volumetric flask and dilute to volume. Dilute 10.0 cc 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 A2.1—Other volumes of stock solution may be prepared using appropriate ratios of reagents. Follow the specific guidelines for this solution from the vendor of the column being used.

A2.8.4 *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.

NOTE A2.2—Other volumes of this solution may be prepared using appropriate ratios of reagents. Follow the specific guidelines for this solution from the vendor of the suppressor being used.