Designation: D7319 – 13

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]

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

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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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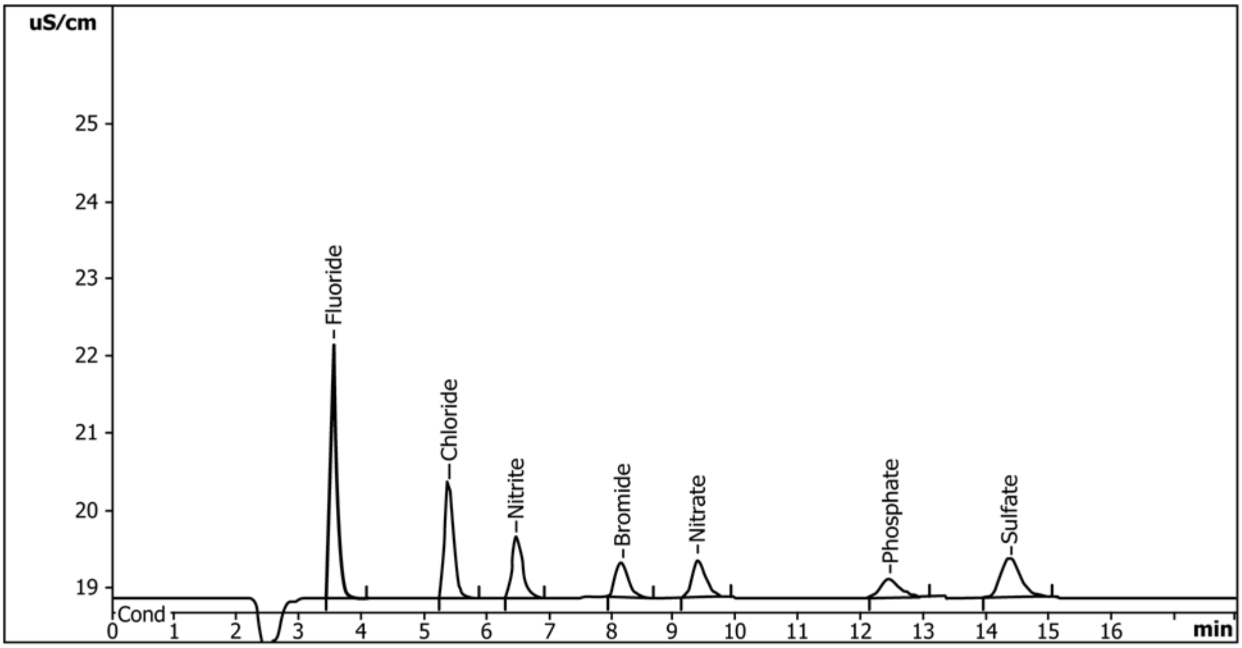
[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[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 ± 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, 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 online 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 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 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 *Tetrabutylamonium Bisulfate*—Technical or reagent grade, 99 % minimum purity.

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[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.

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

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 wt % 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.

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

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.

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

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.

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

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

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 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 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

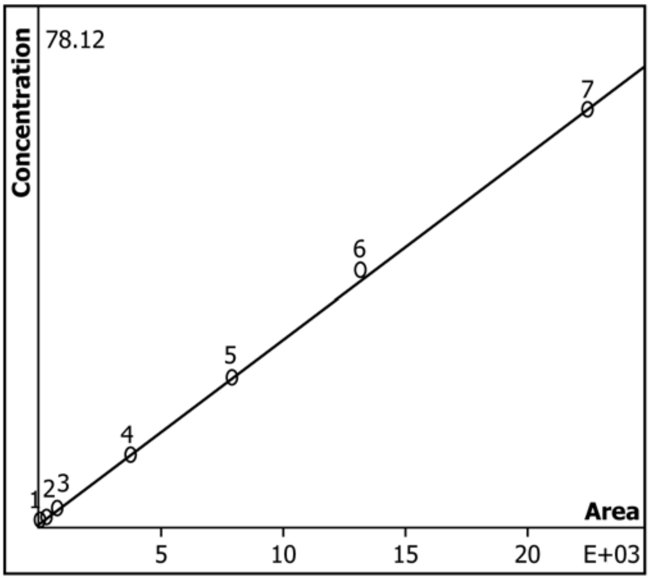

FIG. 2 Typical Chloride Calibration Plot

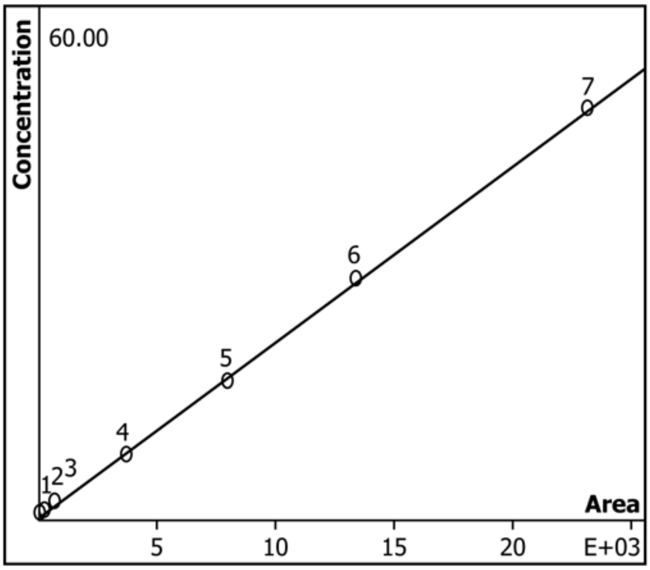

FIG. 3 Typical Sulfate Calibration Plot

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).

10.5.1 If the plot of the peak area values against the ion concentrations is not linear (the correlation factor should be at least 0.99), the procedure should be checked for errors, and if necessary, the calibration should be repeated starting from Section 9.

11. Procedure

11.1 Obtain samples in accordance with Practice D4057 or Practice D4177. Samples should be well mixed to ensure homogeneity. Take a representative portion for analysis. Collect samples in containers with closures that seal well to prevent evaporation of ethanol or butanol. Samples containers should be clean and not contain any residual sulfate or chloride. If containers have been cleaned and rinsed with water, rinse them with water and dry them prior to use.

NOTE 7—Take care to ensure that all glassware and containers are thoroughly dry before introduction of samples. If cleaned and/or rinsed with water, this can also include a follow up rinse with a chloride and sulfate-free organic solvent.

11.1.1 Thoroughly mix the samples in their containers immediately prior to withdrawal of a test specimen.

11.1.1.1 Mixing samples using sonication or mechanical shaking for least 5 min is suggested to ensure sample homogeneity.

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

11.2.1 When analyzing butanol using an autosampler equipped with a syringe injector that uses a water rinse, take care to thoroughly flush the syringe with the sample prior to injection. This will ensure that errors resulting from chloride and sulfate partitioning into the water phase are avoided during/prior to injection.

11.2.2 Equilibrate the system by pumping eluent for 15 to 30 min, until a stable baseline is obtained.

11.2.3 Start the ion chromatographic run in accordance with the manufacturer's instructions.

11.3 *Existent Inorganic Sulfate and Total Chloride:*

TABLE 2 Possible Sulfate and Chloride Check Samples

Chloride and Sulfate Standards mg Chloride and Sulfate (each) /1 L water	Volume of final solution, L	Chloride Stock Solution, mL	Sulfate Stock Solution, mL
50 mg/L, Cl^- only	1.00	25	...
20	1.00	10	10
10	1.00	5	5
5	1.00	2.5	2.5
1	1.00	0.5	0.5
0.5	1.00	0.25	0.25
0.3	1.00	0.15	0.15

11.3.1 Obtain the denatured ethanol or butanol sample to be analyzed, no sample preparation is necessary.

11.3.2 The dilution factor D_f equals 1.0, since the sample is not diluted.

11.3.3 Go to 11.6, if not analyzing for potential sulfate.

11.4 *Potential Sulfate:*

11.4.1 Add 9.5 mL of the denatured ethanol or butanol test specimen to a clean, dry, tared 10-mL glass volumetric cylinder.

11.4.2 Add 0.5 mL of 30% hydrogen peroxide solution to the sample (final concentration of 1.5% hydrogen peroxide), and shake it thoroughly for at least 30 s.

11.4.3 The dilution factor D_f equals 1.05.

11.5 Inject 20 µL of sample solution from 11.3 or 11.4 into the ion chromatograph, and measure the areas of the peaks corresponding to chloride and sulfate ions.

11.6 If the concentration of the anion of interest exceeds that of the highest calibration solution, dilute the sample solution with denatured ethanol (for denatured fuel ethanol samples) or butanol (for butanol samples) containing no measurable sulfate or chloride as appropriate, and repeat the sample measurement. Take into account the dilution factor in the calculation of sulfate content in the ethanol sample, and calculate the dilution factor *F* as shown in Eq 5.

$$F = V_f / V_i \qquad (5)$$

where:

F = the dilution factor,
V_i = the volume of the initial sample diluted, in mL, and
V_f = the volume of the final solution, in mL.

12. Calculation

12.1 Calculate the concentrations of sulfate or chloride in the ethanol or butanol sample as mg/L (µg/mL) as shown in Eq 6.

$$C = A \times R_f \times F \times D_f \qquad (6)$$

where:

C = concentration of anion in the original ethanol sample, in mg/L,
A = anion peak area, from the ion chromatogram in 11.5, in counts,
R_f = calibration plot response factor from 11.6, in mg/L/counts,
F = dilution factor from Eq 5 (= 1.0 if no dilution), and
D_f = dilution factor equals 1.0 for existent inorganic sulfate and total chloride from 11.3, 1.05 for potential sulfate from 11.4.

12.2 The units of mg/L (volume) can be converted to mg/kg (weight) using the density of the same denatured ethanol or butanol as is present in the sample, as in Eq 7. Denatured ethanol or butanol density can be measured using Test Method D4052.

$$\text{Sulfate (mg/kg)} = \text{Sulfate (mg/L)}/D \qquad (7)$$

where:

D = density of denatured ethanol, in g/mL for existent inorganic sulfate, or
D = density of the ethanol/peroxide diluted sample, in g/mL for potential sulfate.

12.2.1 Any amount of water present in the ethanol samples will affect the sample density. Measurement of the sample density is necessary to achieve the most accurate results, especially in the case of the potential sulfate where the water content is approximately 5 % of the injected sample volume.

13. Report

13.1 Report the chloride and sulfate content (either existent or potential, or both) results to nearest 0.1 mg/kg over the calibration range. Specify that these results were obtained using ASTM Test Method D7319.

14. Quality Control (QC)

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 X1.5) that is analyzed repetitively by procedures in 11.2-11.6. These results are plotted in control charts to check the system for statistical stability, as in X1.3.

14.1.1 Check samples can be prepared in water. Aqueous stock sulfate and chloride aliquots are added to water in accordance with Table 2 and the total volume of the resulting solution. The ion concentrations are calculated in accordance with Eq 8 and Eq 9. Check samples generated from Table 2 are then analyzed by the procedures in 11.2-11.6. These results are plotted in a control chart to check the system for statistical stability, as in X1.3.

$$\text{Sulfate in Standard (mg/L)} = V_a \times C_a \times 10^{-3} \qquad (8)$$

$$\text{Chloride in Standard (mg/L)} = V_b \times C_b \times 10^{-3} \qquad (9)$$

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.

TABLE 3 Test Method Precision

Analyte	mg/kg	Repeatability (*r*)	Reproducibility (*R*)
Total Chloride	1.0	0.07	0.42
	20.0	0.56	3.40
	50.0	1.06	6.45
Existent Inorganic Sulfate	1.0	0.09	1.23
	4.0	0.21	2.92
	20.0	0.58	7.95
Potential Sulfate	1.0	0.14	1.41
	4.0	0.36	3.51
	20.0	1.32	12.85

14.1.2 When there is no QC/QA protocol established in the testing facility, Appendix X1 can be used as the QC/QA system.

15. Precision and Bias[5]

15.1 *Precision*—The precision of this test method was determined by the statistical evaluation of the interlaboratory test results. For measuring total chloride, both methods of suppression provided a single precision statement. For existent and potential inorganic sulfate, the data indicated two distinct statistical populations, reflecting use of the packed bed tri-chamber suppressor regeneration approach and the continuous suppressor membrane regeneration approach. Repeatability and reproducibility statements for total chloride and existent and potential inorganic sulfate are provided with calculated values in Table 3 and Table 4.

15.1.1 *Repeatability (r)*—The difference between successive test results, obtained by the same operator using the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of this test method provide the following repeatability values:

15.1.1.1 *Total Chloride*—The pooled limit of quantitation (PLOQ) and repeatability *r* along with applicable range for chloride measured in ethanol and butanol is calculated as follows:

	Ethanol	Butanol
Repeatability (*r*):	$6.851E-02 \times X^{0.7000}$	$9.55E-03 \times (X + 16)$
Applicable range:	0.75 and 50 mg/kg	0.1–31.6 mg/kg
PLOQ estimate:	0.75 mg/kg	0.56 mg/kg

15.1.1.2 *Existent Inorganic Sulfate*—The pooled limit of quantitation (PLOQ) and repeatability *r* along with applicable range for existent inorganic sulfate measured in ethanol and butanol is calculated as follows:

	Ethanol	Butanol
Repeatability (*r*):	$0.09030 \times (X + 1.000E-04)^{0.623}$	$0.01134 \times (X+25)$ mg/kg
Applicable range:	1.0 and 20 mg/kg	0.3–12.1 mg/kg
PLOQ estimate:	0.01 mg/kg	1.1 mg/kg

15.1.1.3 *Potential Sulfate*—The pooled limit of quantitation (PLOQ) and repeatability *r* along with applicable range for potential sulfate measured in ethanol and butanol is calculated as follows:

TABLE 4 (a) Total Chloride Precision—Butanol

mg/kg	Repeatability (*r*)	Reproducibility (*R*)
0.6	0.1759	0.9536
1	0.1819	0.9865
5	0.2426	1.3154
10	0.3184	1.7264
15	0.3942	2.1375
20	0.4700	2.5485
25	0.5458	2.9596
30	0.6216	3.3706
32	0.6519	3.5350

TABLE 4 (b) Existent Inorganic Sulfate Precision—Butanol *(continued)*

mg/kg	Repeatability (*r*)	Reproducibility (*R*)
1	0.1819	0.9865
2	0.1971	1.0687
3	0.2122	1.1509
4	0.2274	1.2332
5	0.2426	1.3154
6	0.2577	1.3976
7	0.2729	1.4798
8	0.2880	1.5620
9	0.3032	1.6442
10	0.3184	1.7264
11	0.3335	1.8086
12	0.3487	1.8908

TABLE 4 (c) Potential Sulfate Precision—Butanol *(continued)*

mg/kg	Repeatability (*r*)	Reproducibility (*R*)
0.6	0.1759	0.9536
1	0.1819	0.9865
2	0.1971	1.0687
3	0.2122	1.1509
4	0.2274	1.2332
5	0.2426	1.3154
6	0.2577	1.3976
7	0.2729	1.4798
8	0.2880	1.5620
9	0.3032	1.6442
10	0.3184	1.7264
11	0.3335	1.8086

	Ethanol	Butanol
Repeatability (*r*):	$0.09645 \times (X + 0.59494)^{0.8642}$	$0.01516 \times (X + 11)$ mg/kg
Applicable range:	1.0 and 20 mg/kg	0.3–11.7 mg/kg
PLOQ estimate:	0.01 mg/kg	0.61 mg/kg

15.1.2 *Reproducibility (R)*—The difference between two single and independent test results, obtained by different operators working in different laboratories on identical test material, would in the long run, in normal and correct operation of this test method provide the following reproducibility values:

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[5] Supporting data will be filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1614.

15.1.2.1 *Total Chloride*—The reproducibility R along with the applicable range for total chloride measured in ethanol and butanol is calculated as follows:

	Ethanol	Butanol
Reproducibility (R):	$0.4172 \times X^{0.7000}$	$0.03073 \times (X + 16)$ mg/kg
Applicable range:	0.75 and 50 mg/kg	0.1–31.6 mg/kg

15.1.2.2 *Existent Inorganic Sulfate*—The reproducibility R along with the applicable range for existent inorganic sulfate measured in ethanol and butanol is calculated as follows:

	Ethanol	Butanol
Reproducibility (R):	$1.2291 \times (X + 1.000\text{E}{-}04)^{0.6230}$	$0.04898 \times (X{+}25)$ mg/kg
Applicable range:	1.0 and 20 mg/kg	0.3–12.1 mg/kg

15.1.2.3 *Potential Sulfate*—Reproducibility R along with the applicable range for potential sulfate measured in ethanol and butanol is calculated as follows:

	Ethanol	Butanol
Repeatability (r):	$0.9408 \times (X + 0.59494)^{0.8642}$	$0.08221 \times (X + 11)$ mg/kg
Applicable range:	1.0 and 20 mg/kg	0.3–11.7 mg/kg

where:

X = analyte concentration in mg/kg (mg/kg for butanol).

15.2 *Bias*—Since no generally accepted standard reference materials with known values of sulfate and chloride in ethanol or butanol are available, bias of this test method cannot be determined.

NOTE 8—Should a laboratory decide to perform spike recoveries from butanol as part of their routine operating procedure, be aware that the spikes need to be prepared using 5000 ppm and 2000 ppm stock solutions of organic chloride and sulfate respectively (see 8.7 and 8.8) in butanol free of chloride and sulfate (see 8.9). For long term stability of spiked stock solutions, it was found in the ILS that the analyst shall use the organic chloride and sulfate for preparing the stock solutions.

15.3 Table 3 shows precision values calculated from 15.1.1.1 to 15.1.2.3.

16. Keywords

16.1 anions; chloride; direct injection; ethanol; existent inorganic sulfate; inorganic chloride; potential sulfate; sulfate; suppressed ion chromatography; total chloride

APPENDIX

(Nonmandatory Information)

X1. QUALITY CONTROL (QC)

X1.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control sample.

X1.2 Prior to monitoring the measurement process, the user of the test method needs to determine the average value and control limits of the QC sample (see Practice D6299, Guide D6792, and MNL7[6]).

X1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process (see Practice D6299, Guide D6792, and MNL7[6]). Any out-of-control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

X1.4 In the absence of explicit requirements given in the test method, the frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample is analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency can be reduced. The QC sample precision should be checked against the ASTM test method precision to ensure data quality.

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[6] MNL7, *Manual on Presentation of Data Control Chart Analysis*, 6th ed., ASTM International, W. Conshohocken, PA.

X1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and shall be homogeneous and stable under the anticipated storage conditions. See Practice D6299, Guide D6792, and MNL7[6] for further guidance on QC and control charting techniques.

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D7319–12) that may impact the use of this standard. (Approved May 1, 2013.)

(1) Revised subsections 1.1, 4.1, 7.6, and Sections 8, 11, and 15.
(2) Added Note 2, Note 7, and Note 8.
(3) Added Table 4.
(4) Revised the title of this test method.

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D7319–11) that may impact the use of this standard. (Approved Dec. 1, 2012.)

(1) Updated 7.6.5.2 and 15.1.

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