Designation: D7328 – 16

Standard Test Method for Determination of Existent and Potential Inorganic Sulfate and Total Inorganic Chloride in Fuel Ethanol by Ion Chromatography Using Aqueous Sample Injection[1]

This standard is issued under the fixed designation D7328; 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 an ion chromatographic procedure for the determination of the existent inorganic and potential sulfate and total inorganic chloride content in hydrous and anhydrous denatured ethanol to be used in motor fuel applications. It is intended for the analysis of ethanol samples containing between 0.55 mg ⁄kg and 20 mg ⁄kg of existent inorganic sulfate, 4.0 mg ⁄kg to 20 mg ⁄kg of potential inorganic sulfate, and 0.75 mg ⁄kg to 50 mg ⁄kg of total inorganic chloride.

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
D7319 Test Method for Determination of Existent and Potential Sulfate and Inorganic Chloride in Fuel Ethanol and Butanol by Direct Injection Suppressed Ion Chromatography

2.2 *Other Standard:*

ISO/CEN15492 Ethanol as a Blending Component for Petrol—Determination of Inorganic Chloride—Ion Chromatographic Method [3]

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 species present as sulfuric acid, ionic salts of this acid, or mixtures of these.

3.1.4 *potential sulfate, n*—total 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 chloride, a small volume of a sample is evaporated to dryness and reconstituted to the initial sample volume with deionized water, and injected into an ion chromatograph consisting of appropriate ion exchange columns, suppressor and a conductivity detector. For

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

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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 International Organization for Standardization (ISO), 1 rue de Varembé, Case postale 56, CH-1211, Geneva 20, Switzerland, http://www.iso.ch.

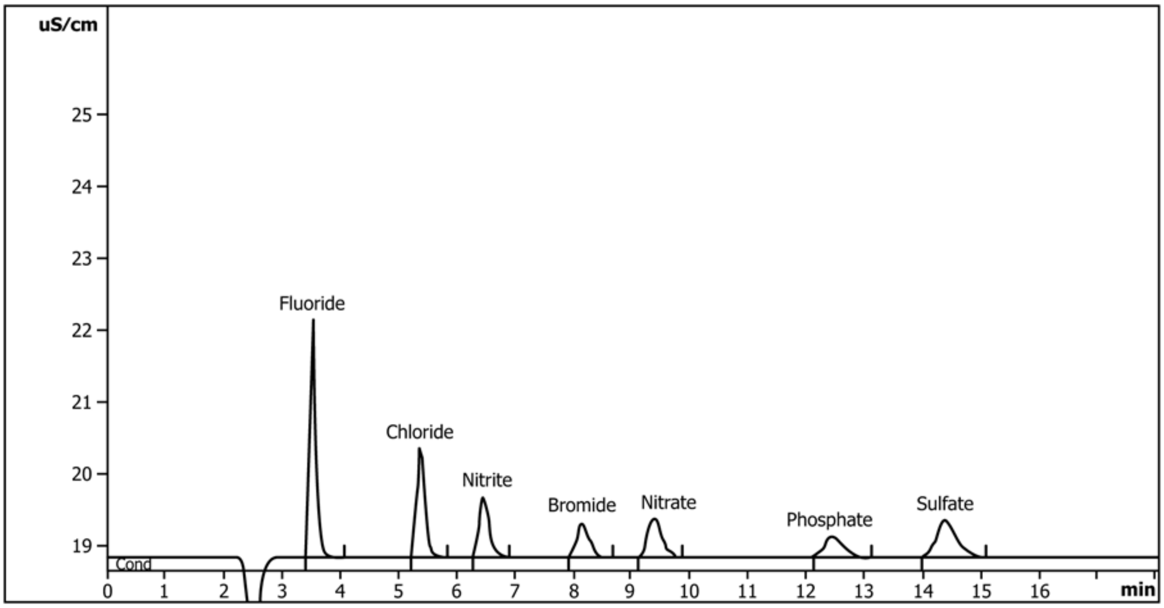

FIG. 1 Typical Ion Chromatogram of a Solution Containing 1 mg/kg of Various Anions in Water

potential sulfate, a small volume of a sample is evaporated to dryness and reconstituted to the initial sample volume with 0.90 % hydrogen peroxide solution in water, and injected into an 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 method by both increasing the conductivity of the analytes and decreasing the conductivity of the eluent. The suppressor converts the eluent and the analytes to the corresponding hydrogen form acids. Anions in the aqueous sample are quantified by integration of their responses compared with an external calibration curve, calculated as mg/L for each ion. The calibration standards are prepared from suitable salts dissolved in water solutions. Existent or potential inorganic sulfate and chloride concentrations may be calculated as mg/kg by measuring the density of the original sample.

4.2 Similar methods for chloride and sulfate determinations can be found in Test Method D5827 for engine coolant, and for ethanol in ISO/CEN15492, Test Method D7319 by ion chromatography with direct sample injection, and for sulfate only in Test Method D7318 by potentiometric lead titration.

5. Significance and Use

5.1 Sulfates and chlorides may 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 or standard addition can be used to minimize or resolve most interference problems.

6.2 A water dip (system void, negative peak as shown in Fig. 1) may 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 enough away from the water dip.

6.3 Given the trace amounts of chloride and sulfate determined by this method, interferences can be caused by contamination of glassware, eluents, reagents, etc. Great care must be taken 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,* at least 2000 g capacity, capable of weighing accurately to 0.01 g.

7.1.1 *Analytical Balance,* at least 100 g capacity, capable of weighing accurately to 0.0001 g.

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

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

7.4 *Pipettes or Volumetric Transferring Devices,* Class A glass pipettes or their equivalent of 2.0 cc capacity or automatic pipettes fitted with disposable polypropylene tips.

7.4.1 *Plastic Syringe,* 10 cc disposable, optionally fitted with a 0.2 µm syringe filter (must be chloride and sulfate-free).

7.5 *Volumetric Flask,* Class A of 1 L capacity and Class A of 10 mL capacity.

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

7.6.1 *Injection System,* capable of delivering 25 µL with a precision better than 1 %.

7.6.2 *Pumping System,* capable of delivering mobile phase flows between 0.5 mL/min and 1.5 mL/min with a precision better than 5 %.

7.6.3 *Guard Column,* for protection of the analytical column from strongly retained constituents. Better separations are obtained with greater separating power.

7.6.4 *Anion Separator Column,* capable of producing satisfactory analyte separation (see Fig. 1).

7.6.5 *Anion Suppressor Device,* micro membrane suppressor or equivalent. A cation exchange column in the hydrogen form has been used successfully, but it will periodically need to be regenerated as required. This is indicated by a high background conductivity and low analyte response.

7.6.6 *Conductivity Detector,* low volume (<2 µL) and flow, temperature compensated, capable of at least 0 µS/cm to 1000 µS/cm on a linear scale.

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

7.7 *Gloves,* powder-free examination type.

7.8 *Hot Block,* aluminum, capable of being heated to 65 °C with suitable holes to hold 15 mL glass vials, with a method of flowing nitrogen over inserted samples.

7.9 *Glass Vials,* 15 mL with screw top.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade or higher purity chemicals shall be used for the preparation of all samples, standards, eluents, 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 in Specification D1193. For eluent preparation and handling, comply with all ion chromatograph instrument and column vendor requirements (for example, filtering, degassing, etc.).

8.3 *Eluent Buffer Solution*—The eluent solution used depends on the systems or analytical columns that are used (contact instrument and column vendors). For the chromatograms in Fig. 1, the following eluent buffer was used: Sodium bicarbonate ($NaHCO_3$) 1.7 mM and sodium carbonate (Na_2CO_3) 1.8 mM. Dissolve 2.8563 g ± 0.0005 g of $NaHCO_3$ and 3.8157 g ± 0.0005 g of Na_2CO_3 in reagent water in a 1 L Type A volumetric flask and dilute to volume. Dilute 100 mL of this concentrate to 2000 mL with reagent water for the final working eluent solution. 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. Alternatively, this solution can be purchased from a qualified vendor.

8.4 *Suppressor Solution for Membrane Suppressor,* 0.025 N sulfuric acid. Carefully add 13.7 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 0.50 N sulfuric acid. Dilute 100 mL of this concentrate to 2000 mL with reagent water for the final working suppressor solution. 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.

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

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

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

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

8.9 *Nitrogen Gas,* 99.99 mol % pure, free of hydrocarbons.

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 Type II water to dissolve the sodium sulfate and make to volume. Calculate the concentration of sulfate in the solution according to Eq 1. Other volumes of stock solution may be prepared using the appropriate ratio of reagents.

$$\text{stock sulfate}\left(\text{mg/L}\right) = \left(\text{g Na}_2\text{SO}_4\right)(0.6764)\left(1000\ \text{mg/g}\right)/1\ \text{L} \quad (1)$$

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

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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., Dorset, U.K., and the *United States Pharmacopeia and National Formulatory*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

TABLE 1 Volumetric Preparation of Chloride and Sulfate Standards in Type II Water

Chloride and Sulfate Standards mg Chloride and Sulfate (each)/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

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 Type II water to dissolve the sodium chloride and make to volume. Calculate the concentration of chloride in the solution according to Eq 2. Other volumes of stock solution may be prepared using the appropriate ratio of reagents.

$$\text{stock chloride}\,(\text{mg/L}) = (\text{g NaCl})\,(0.6068)\,(1000\ \text{mg/g})/1\ \text{L} \qquad (2)$$

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*—Type II water and sulfate and chloride stock solutions are added to a 1 L glass volumetric flask according to Table 1 to achieve the desired standard. These standard solutions should be discarded and remade every month.

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

$$\text{sulfate in standard}\,(\text{mg/L}) = Va \times Ca/V \qquad (\text{a}) \qquad (3)$$

$$\text{chloride in standard}\,(\text{mg/L}) = Vb \times Cb/V \qquad (\text{b})$$

where:

Va = volume of sulfate stock solution (for example, Table 1, Column 3), in mL,
Ca = concentration of sulfate stock (Eq 1), in mg/L,
Vb = volume of chloride stock solution (for example, Table 1, Column 2), in mL,
Cb = concentration of chloride stock (Eq 2), in mg/L, and
V = final volume of standard solution, in L.

9.2.2 Multiples or fractions of Table 1 values can be used to prepare different total volumes (V) of standards, using Eq 3(a) and Eq 3(b) to calculate standard ion concentrations.

NOTE 1—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.

9.3 *Hydrogen Peroxide Solution, 0.90 %*—Carefully pipette 3.0 mL of the 30 % hydrogen peroxide reagent into a 100 mL volumetric. Add Type II water to make to volume.

NOTE 2—Hydrogen peroxide will degrade in aqueous solution, therefore prepare fresh 0.90 % solution daily.

10. Calibration

10.1 Set up the ion chromatograph according to the manufacturer's instructions. No specific parameters are given here since different instruments may require different eluents, 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 to be analyzed. The concentrations of calibrant solutions used shall bracket the expected range for the samples to be analyzed. One or more mid-range standards shall be used to verify the linearity of the calibration plot.

10.1.1 Typical ion chromatographic conditions (conditions used to generate Fig. 1 chromatograms):

Flow: 1.5 mL/min
Sample loop: 25 µL
Suppressor flow: 2 mL/min

10.1.1.1 Other analytical conditions may be used per the manufacturer's instructions. It is important that the resulting chromatogram contain chloride and sulfate peaks with baseline separation like that shown in Fig. 1. If present in sufficient quantity, other anions can interfere with the chloride and sulfate measurements.

NOTE 3—The sample loop volume will vary based on the column capacity, sensitivity, and other factors. Refer to vendor ion chromatography equipment manuals and column information for machine-specific details.

10.1.2 Analytical calibration plots shall be established at only one detector scale setting in order to prevent a change of slope affecting the analytical curve.

10.2 The analytical calibration plot shall be verified 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 The sulfate and chloride calibration plots shall be rerun after any change of the ion chromatography eluent solution (8.3), to reestablish ion retention times and resolution.

10.4 Measurement of the calibration standards. Inject 25 µL of each calibration standard solution (9.2) into the ion chromatograph, and measure the areas of the peaks corresponding to the 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).

10.5 Construct the calibration plots from the peak area measurements 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 coefficients of 0.99 or greater, see Figs. 2 and 3. The response factor for each ion, *Rf*, is the slope of the calibration plot straight line, in mg/L/(area count).

NOTE 4—If the plot of the peak area values least squares correlation is less than 0.99, the instrument and calibration solutions should be checked for errors, and if necessary, the calibration procedure should be repeated starting from Section 9.

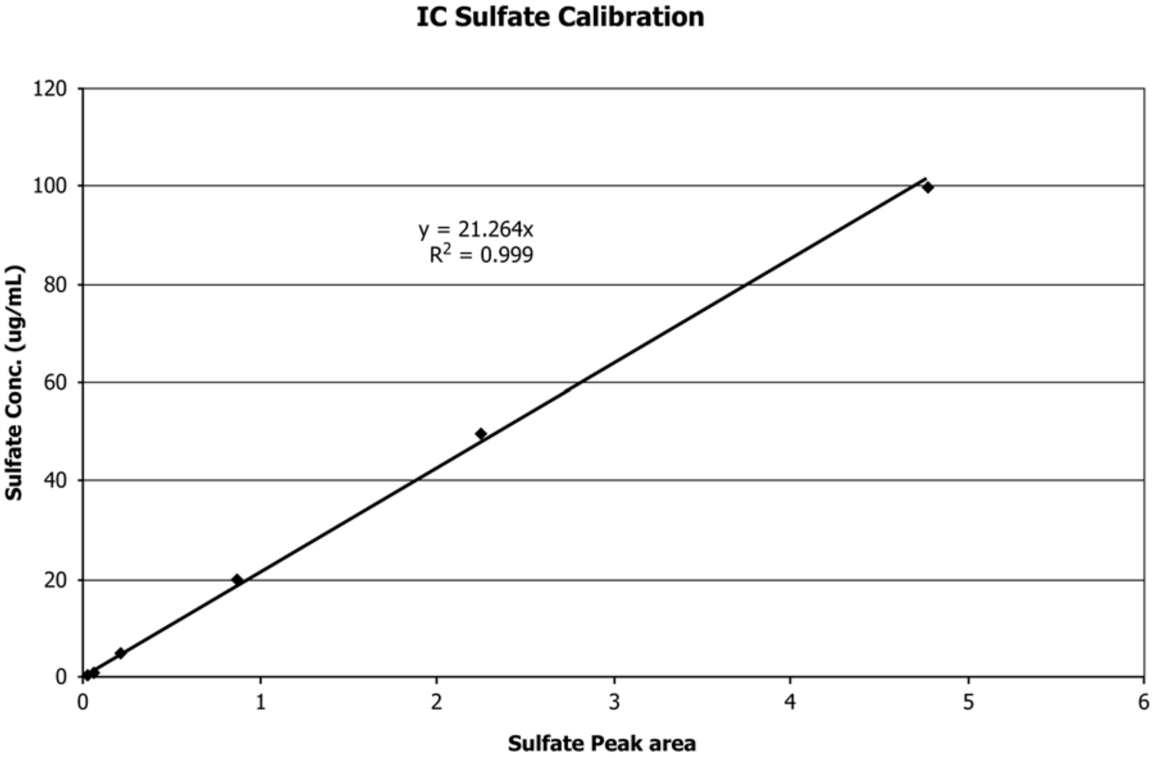

FIG. 2 Typical Sulfate Calibration Plot

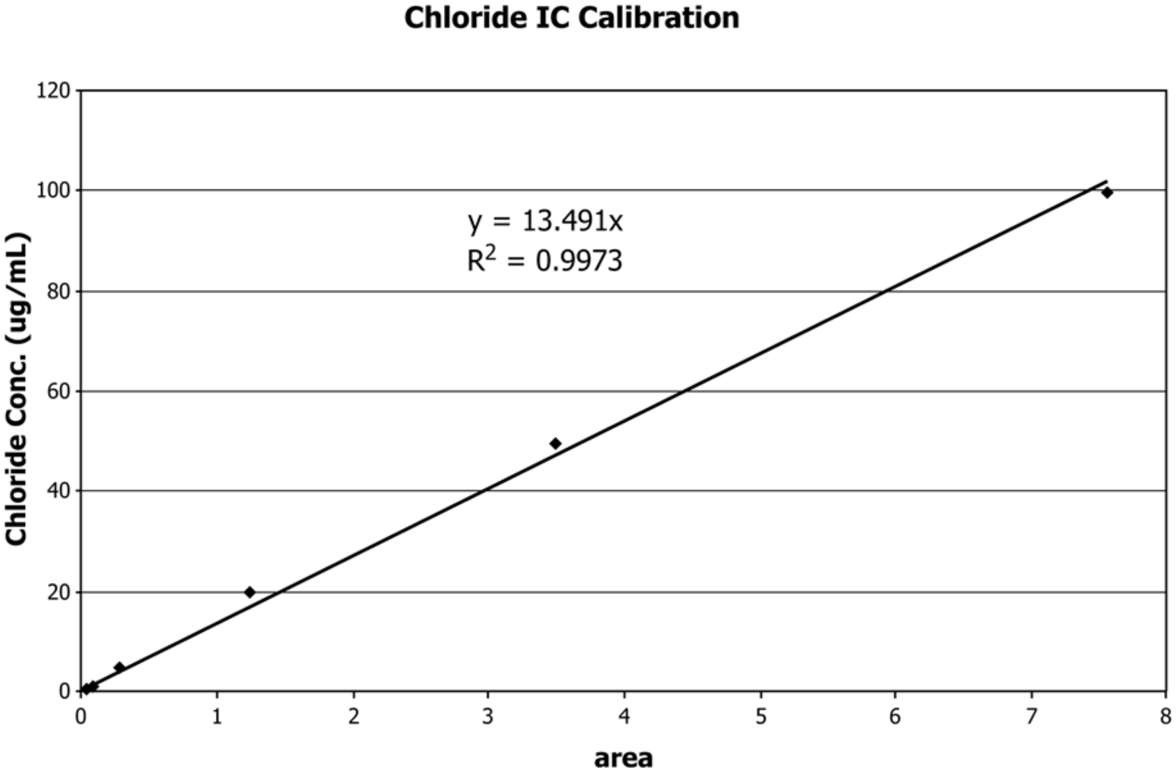

FIG. 3 Typical Chloride Calibration Plot

11. Procedure

11.1 Obtain samples in accordance with Practice D4057 or Practice D4177. Samples should be well-mixed to ensure homogeneity. A representative portion shall be taken from each sample for analysis. Samples should be collected in (preferably glass or polyethylene) containers with closures that seal well to prevent evaporation. Sample containers shall not contain any residual or extractable sulfate or chloride. If containers have been cleaned and rinsed with water, they shall be thoroughly rinsed with Type II reagent water and dried prior to use.

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

11.1.2 Samples may be analyzed for either or both existent and potential inorganic sulfate, as well as total chloride.

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

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

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

11.4 *Existent Inorganic Sulfate and Total Chloride:*

11.4.1 Carefully add 2.00 mL of the ethanol test specimen into a clean, dry, tared 15 mL glass vial without its screw cap closure.

11.4.2 Place the vial with sample in a hot block at 65 °C and blow a steady stream of nitrogen gas over the sample at 2 mL⁄min to 3 mL⁄min flow. Allow the sample to dry completely, this may take 5 min to 10 min. When all of the liquid is gone, remove the vial from the hot block and allow it to cool to room temperature (60 °F to 80 °F).

NOTE 5—It is possible that a slight oily residue from the ethanol denaturant could remain. Do not worry about this residue if it is a thin film, as any sulfide or chloride in it will be extracted into the water phase.

NOTE 6—Various commercial apparatus are used to evaporate the sample. Depending on the apparatus used, the flow can be adjusted to optimize the evaporation.

NOTE 7—The purpose of the nitrogen is to sweep the ethanol vapors away from the sample tube so they do not condense back into the sample. There should be enough flow to sweep the ethanol vapors without creating turbulence in the sample and possible loss of analyte. When the flow gets too high, the cooling effect from the nitrogen gas can work against the intent. If the temperature in the sample block does not reach 65 °C, this can also extend the time to evaporate. Typical nitrogen flows are two to three milliliters per minute. The flow may be varied to accommodate available laboratory apparatus.

11.4.3 Carefully add 2.00 mL of Type II water to the dried sample. Seal the vial with a screw cap, and shake the vial vigorously to dissolve all of the solid salts.

11.4.4 Inject the resulting solution into the ion chromatograph as in 11.6.

11.5 *Potential Sulfate:*

11.5.1 Carefully add 2.00 mL of the ethanol test specimen into a clean, dry, tared 15 mL glass vial without its screw cap closure.

11.5.2 Place the vial with sample in a hot block at 65 °C and blow a steady stream of nitrogen over the sample. Allow the sample to dry completely, this may take 5 min to 10 min. When all of the liquid is gone, remove the vial from the hot block and allow it to cool to room temperature (60 °F to 80 °F). See Note 5.

11.5.3 Carefully add 2.00 mL of 0.90 % hydrogen peroxide solution (9.3) to the dried sample. Seal the vial with a screw cap, and shake the vial vigorously to dissolve all of the solid salts.

11.5.4 Inject the resulting solution into the ion chromatograph as in 11.6.

11.6 Inject 25 µL of sample solution from 11.4 or 11.5 into the ion chromatograph, and measure the areas of the peaks corresponding to chloride and sulfate ions.

11.7 If the concentration of the anion of interest exceeds that of the highest calibration solution, dilute the sample solution with denatured ethanol 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 as shown in Eq 4.

$$F = \frac{Vf}{Vi} \tag{4}$$

where:

F = dilution factor,
Vi = volume of the initial sample diluted, mL, and
Vf = volume of the final solution, mL.

12. Calculations

12.1 The concentrations of sulfate or chloride in the ethanol sample as mg/L (mg/mL) are calculated as shown in Eq 5.

$$C = A \times Rf \times F \tag{5}$$

where:

C = concentration of anion in the original ethanol sample, mg/L,
A = anion peak area, from the ion chromatogram in 11.6, counts,
Rf = calibration plot response factor from 10.5, mg/L/counts, and
F = dilution factor from Eq 4 (= 1.0 if no dilution).

12.2 The units of mg/L (volume) can be converted to mg/kg (weight) using the density of the same denatured ethanol as is present in the sample, as shown in Eq 6. Denatured ethanol density (*d*) at room temperature may be measured using Test Method D4052.

$$\text{sulfate}\,(\text{mg/kg}) = \text{sulfate}\,(\text{mg/L})/d \tag{6}$$

where:

d = density of denatured ethanol, g/mL.

13. Report

13.1 *Existent Inorganic Sulfate and Total Chloride*—Report the total chloride and existent inorganic sulfate content results to nearest 0.1 mg⁄kg for samples containing more than 3.0 mg⁄kg, to the nearest 0.01 mg⁄kg below 3.0 mg⁄kg. Specify that these results were obtained using Test Method D7328.

13.2 *Potential Sulfate*—Report the potential sulfate content results to nearest 0.1 mg⁄kg for samples containing more than 8.0 mg⁄kg, to the nearest 0.01 mg⁄kg below 8.0 mg⁄kg. Specify that these results were obtained using Test Method D7328.

TABLE 2 Possible Sulfate and Chloride Check Samples

Chloride and Sulfate Standards mg Chloride and Sulfate (each)/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

TABLE 3 Method Precision

Analyte	mg/kg	Repeatability (r)	Reproducibility (R)
Total Chloride	1.0	0.2	1.3
	20.0	0.6	3.5
	50.0	1.3	7.0
Existent Inorganic Sulfate	1.0	0.2	1.1
	4.0	0.5	2.2
	20.0	1.0	4.9
Potential Sulfate	4.0	0.4	1.8
	20.0	0.6	3.5

14. Quality Control

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 the procedures in Section 11. These results are plotted in a control chart 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 Type II water according to Table 2 in a 1 L solution. The ion concentrations are calculated according to Eq 7(a) and Eq 7(b). Check samples generated from Table 2 are then analyzed by the procedures in Section 11. These results are plotted in a control chart to check the system for statistical stability, as in X1.3.

$$\text{sulfate in standard (mg/L)} = Va \times Ca \times 10^{-3} \quad \text{(a)} \qquad (7)$$

$$\text{chloride in standard (mg/L)} = Vb \times Cb \times 10^{-3} \quad \text{(b)}$$

where:

Va = volume of sulfate stock solution (Table 2, Column 4), in mL,

Ca = concentration of sulfate stock (Eq 1), in mg/L,

Vb = volume of chloride stock solution (Table 2, Column 3), in mL, and

Cb = concentration of chloride stock (Eq 2), in mg/L.

14.2 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.

14.3 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 as determined by the statistical evaluation of the interlaboratory test results is as follows:

15.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method exceed the following values only in one case in twenty.

15.1.1.1 *Total Chloride*—The pooled limit of quantitation (PLOQ) is 0.75 mg/kg. Repeatability r between 0.75 mg/kg and 50 mg/kg total chloride measured is calculated as follows:

$$r = 0.02078\,(X + 10.0709) \qquad (8)$$

15.1.1.2 *Existent Inorganic Sulfate*—The pooled limit of quantitation (PLOQ) is 0.55 mg/kg. Repeatability r between 0.55 mg/kg and 20 mg/kg existent inorganic sulfate measured is calculated as follows:

$$r = 0.2319\,(X + 1.000E - 04)^{0.5000} \qquad (9)$$

15.1.1.3 *Potential Sulfate*—The pooled limit of quantitation (PLOQ) is 4.0 mg/kg. Repeatability r between 4.0 mg/kg and 50 mg/kg potential sulfate measured is calculated as follows:

$$r = 0.1763\,(X^{0.4000}) \qquad (10)$$

where:

X = analyte concentration in mg/kg.

15.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method exceed the following values only in one case in twenty.

15.1.2.1 *Total Chloride*—Reproducibility R between 0.75 mg/kg and 50 mg/kg total chloride measured is calculated as follows:

$$R = 0.1173\,(X + 10.0709) \qquad (11)$$

15.1.2.2 *Existent Inorganic Sulfate*—Reproducibility R between 0.55 mg/kg and 20 mg/kg existent inorganic sulfate measured is calculated as follows:

$$R = 1.0963\,(X + 1.000E - 4)^{0.5000} \qquad (12)$$

15.1.2.3 *Potential Sulfate*—Reproducibility R between 4.0 mg/kg and 20 mg/kg potential sulfate measured is calculated as follows:

$$R = 1.0505\,(X^{0.4000}) \qquad (13)$$

where:

X = analyte concentration in mg/kg.

15.2 *Bias*—Since there was no generally accepted reference material available at the time of the interlaboratory testing, no statement of bias can be made at this time.

15.3 Table 3 shows precision values calculated from Eq 8-13.

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR; D02-1611.

16. Keywords

16.1 aqueous injection; denatured ethanol; ethanol; existent inorganic sulfate; fuel ethanol; ion chromatography; potential sulfate; total chloride

APPENDIX

(Nonmandatory Information)

X1. QUALITY CONTROL

X1.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) 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 MNL 7).[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 MNL 7). 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 may be reduced. The QC sample precision should be checked against the ASTM test method precision to ensure data quality.

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 must be homogeneous and stable under the anticipated storage conditions. See Practice D6299, Guide D6792, and MNL 7 for further guidance on QC and control charting techniques.

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[6] *ASTM MNL 7*, Manual on Presentation of Data Control Chart Analysis, 6th ed., available from ASTM International Headquarters.

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D7328 – 13) that may impact the use of this standard. (Oct. 1, 2016.)

(1) Added new Note 6 and Note 7.