Determination of Total and Potential Sulfate and Total Chloride in Ethanol According to ASTM Method D 7319

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Application Note 290

Key Words
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Introduction

Ethanol is increasingly being used as a gasoline additive, due to rising crude oil prices and a global effort to reduce greenhouse gas emissions.[1] The Energy Policy Act of 2005 increased the amount of biofuel, such as ethanol, that must be mixed with petroleum-based gasoline, providing tax incentives and loan guarantees for the production of blended gasoline.[2] Since 2005, the United States (U.S.) has been the world's largest producer of ethanol fuel. The U.S. produced 13.2 billion gallons of ethanol fuel in 2010 and, when combined with the production in Brazil, the two countries accounted for nearly 90% of the ethanol produced that year.[3,4] Most vehicles in the U.S. can operate with blends of up to 10% ethanol and motor vehicle manufacturers already produce vehicles designed to run on much higher ethanol blends.

Ethanol is produced from the fermentation of any starch crop, such as corn, sorghum, potatoes, wheat, and sugar cane. Biomass, such as cornstalks and vegetable waste, is also used for ethanol production. When combined with gasoline, ethanol increases octane levels and promotes better fuel burning, which reduces harmful emissions.[5] However, ethanol can be contaminated with chloride and sulfate, which can contribute to plugging and corrosion of automobile engines.

Ethanol that is used as a blending agent in gasoline is required to meet sulfate and chloride concentration limits defined by the American Society for Testing and Materials (ASTM) specification D 4806. According to this specification, the maximum permissible concentrations of sulfate and chloride in ethanol are 4 mg/L and 40 mg/L, respectively.[6]

Thermo Scientific Application Note 175 and Application Update 161 describe two ion chromatography (IC) methods to determine whether ethanol used as a blending agent in gasoline meets the total chloride and sulfate specifications set by ASTM D 4806.[7,8] Although both methods are widely used for testing ethanol, neither method describes the determination of potential sulfate in ethanol. Total sulfates are the inorganic sulfate species present in a sample at the time of analysis with no oxidation treatment, whereas potential sulfates are the species of sulfate present in a sample that has been treated with an oxidizing agent.

This study describes a simple and direct injection IC method to determine total and potential sulfate and chloride in ethanol used as a gasoline additive. This method is consistent with ASTM method D 7319, which is intended for the analysis of ethanol samples containing 1.0–20.0 mg/L of total or potential sulfate and 1.0–50.0 mg/L of chloride.[9]

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Total sulfate and chloride were determined by directly injecting 5 µL of ethanol onto a Thermo Scientific™ Dionex™ IonPac™ AS4A-SC column followed by chemical suppression with an analysis time of 10 min. Potential sulfate was determined by adding 0.5 mL of 30% hydrogen peroxide to 9.5 mL of the ethanol sample, then injecting 5 µL onto the Dionex IonPac AS4A-SC column. Linearity, limits of detection and quantification, and precision of potential and total sulfate and total chloride at different concentrations were demonstrated. As described in Thermo Scientific Application Note 201, which shows direct injection of methanol samples, this IC method allows the direct injection of ethanol samples to determine chloride and sulfate and has the sensitivity to meet ASTM specification D 4806.[10]

Equipment

- Thermo Scientific™ Dionex™ ICS-2100 system* including:
  - Single isocratic pump
  - Vacuum degasser
  - High pressure, 6-port injector
  - Column heater enclosure
  - Conductivity cell detector
  - EO Eluent Organizer, including pressure regulator and 2 L plastic bottle
- Thermo Scientific™ Dionex™ AS Autosampler and 2 mL vial tray or an AS-DV Autosampler with 5.0 mL PolyVials with plain caps
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) software, Version 6.8 or higher
- Helium or nitrogen, 4.5 grade (99.995%) or better, <5 ppm oxygen (Praxair)
- Filter unit, 0.2 µm nylon (Thermo Scientific™ Nalgene™ P/N 164-00200 or equivalent nylon filter)
- Vacuum pump (Gast Manufacturing Corp. P/N DOA-P104-AA or equivalent for degassing eluents)
- Vial Kit, 1.5 mL glass with caps and septa (P/N 055427)
- Three 4 L plastic bottle assemblies for chemical regeneration mode of operation

*The method also can be run using a Thermo Scientific™ Dionex™ ICS-1100, -1600, or -5000 system.

Consumables

Dionex IonPac AS4A-SC Analytical, 2 × 250 mm (P/N 043125)

Dionex IonPac AS4A-SC Guard, 2 × 50 mm (P/N 043126)

Thermo Scientific™ Dionex™ AMMS™ 300 Anion MicroMembrane Suppressor, 2 mm (P/N 064559)

Reagents and Standards

Deionized water, Type I reagent grade, 18 MΩ-cm resistance or better

Chloride standard, 1000 mg/L (P/N 037159)

Sulfate standard, 1000 mg/L (P/N 037160)

AS4A Eluent concentrate (P/N 039513)

Anion suppressor regenerant concentrate, 0.50 N sulfuric acid (P/N 37164, 4 pack)

Ethanol, reagent alcohol 90.94% ethanol, 5% isopropanol, 4.6% methanol (EM Science VWR P/N EM-AX0445-1)

Sulfuric acid, ACS reagent grade (J.T. Baker P/N 11-9681-05)

Hydrogen peroxide, 30% ACS grade (Mallinckrodt P/N V340-04)

Sodium thiosulfate, (J.T. Baker P/N 3949)

CONDITIONS	
Column:	Dionex IonPac AS4A-SC Analytical, 2 × 250 mm
	Dionex IonPac AS4A-SC Guard, 2 × 50 mm
Eluent:	1.8 mM sodium carbonate/ 1.7 mM sodium bicarbonate
Flow Rate:	0.5 mL/min
Inj. Volume:	5.0 µL
Column Temp.:	30 °C
Detection:	Suppressed conductivity, Dionex AMMS 300, 2 mm with 50 mN sulfuric acid
Background Conductance:	~ 20 µS
Noise:	3–5 nS peak-to-peak
Backpressure:	1200 psi
Run Time:	10 min

Preparation Solutions and Reagents

Sulfuric Acid, 0.5 N

Carefully transfer 13.7 mL of reagent grade sulfuric acid to ~500 mL of filtered and degassed deionized (DI) water in a 1 L volumetric flask. Allow the solution to cool before making up to volume with DI water. Invert the flask several times to mix.

Sulfuric Acid, 50 mN

Dilute 200 mL of the 0.5 N sulfuric acid concentrate prepared above in a 2 L volumetric flask by adding ~1700 mL of filtered and degassed DI water. Invert the flask several times to mix the contents and bring volume to 2000 mL using DI water. Repeat this step several times to fill three 4 L regenerant bottles. If using the regenerant concentrate (P/N 039513), simply add the 200 mL concentrate to 1700 mL of filtered and degassed DI water. Invert several times to mix and bring volume to 2000 mL using DI water. Repeat this step several times to fill three 4 L regenerant bottles.

Eluent Solution (1.8 mM Sodium Carbonate/ 1.7 mM Sodium Bicarbonate)

Transfer 10 mL of the AS4A eluent concentrate to a 1 L volumetric flask and add it to ~700 mL of filtered and degassed DI water. Invert several times to mix and bring to volume to 1000 mL using DI water.

Stock Standard Solutions

Thermo Scientific chloride and sulfate standards at concentrations of 1000 mg/L were used for the study. Alternatively, standards can be purchased from another reliable supplier or be prepared manually. The 1000 mg/L chloride standard can be prepared by dissolving 0.1648 g of sodium chloride in 100 mL filtered and degassed DI water. The 1000 mg/L sulfate standard can be prepared by dissolving 0.1814 g of potassium sulfate in 100 mL filtered and degassed DI water.

Preparing Calibration Standards

To prepare a mixed calibration standard, deliver appropriate volumes of the 1000 mg/L individual stock standards using calibrated pipettes (see Table 1).

Table 1. Preparation if calbration standards.

Anion Concentration (mg/L)	Volume of 1000 mg/L Chloride Stock (mL)	Volume of 1000 mg/L Sulfate Stock (mL)	Total Volume with DI Water (mL)
0.3	0.03	0.03	100
0.5	0.05	0.05	100
1.0	0.10	0.10	100
5.0	0.50	0.50	100
10.0	1.00	1.00	100
20.0	2.00	2.00	100
50.0	5.00	—	100

Sample Preparation

Caution: Ethanol is a flammable, and all sample preparation must be performed under a hood.

Note: Samples of ethanol containing chloride, sulfate, and other species of sulfur were not available. Prepare simulated samples by spiking known amounts of chloride and sulfate in 90% ethanol for total sulfate and chloride determination. For potential sulfate determination, spike 90% ethanol with a known concentration of thiosulfate.

Total Sulfate and Chloride

Directly inject samples of 90% ethanol spiked with chloride and sulfate without further preparation.

Potential Sulfate

Add 9.5 mL of 90% ethanol spiked with known amounts of thiosulfate to a 10 mL volumetric flask, then add 0.5 mL of a 30% hydrogen peroxide solution. Shake for ≥30 sec to ensure good mixing. The final hydrogen peroxide concentration of this mixture is 1.5%.

System Configuration

Install the analytical and guard columns. Install the Dionex AMMS 300 suppressor in chemical regeneration mode by connecting the eluent line from the column outlet to the ELUENT IN port of the suppressor and the ELUENT OUT port of the Dionex AMMS 300 suppressor to the CELL IN port of the conductivity detector. Connect a regenerant line to the REGEN IN port of the suppressor from the regenerant reservoir and connect a line from the REGEN OUT port of the Dionex AMMS 300 suppressor to a waste container.

Start the column eluent flow and adjust the head pressure on the chemical regenerant reservoir to deliver a flow rate of 2.5–5 mL/min. If necessary, add restriction tubing to the regenerant waste line to achieve the required flow rate. Allow approximately 5 mL of eluent to flow through the Dionex AMMS 300 suppressor ELUENT IN port and 5 mL of regenerent through the REGEN IN port. Stop the eluent and regenerant flow to the suppressor. Allow the suppressor to hydrate for 15–20 min. After the suppressor is properly hydrated, restart the liquid flow to the suppressor and equilibrate the column with eluent for ≥30 min prior to analyzing a system blank of reagent alcohol.

Verify that the system background conductance and noise are as specified in the Conditions section. Inject a standard containing 5 mg/L of chloride and sulfate in water. The column is equilibrated when at least three of the resulting chromatograms resemble the overlayed chromatograms shown in Figure 1.

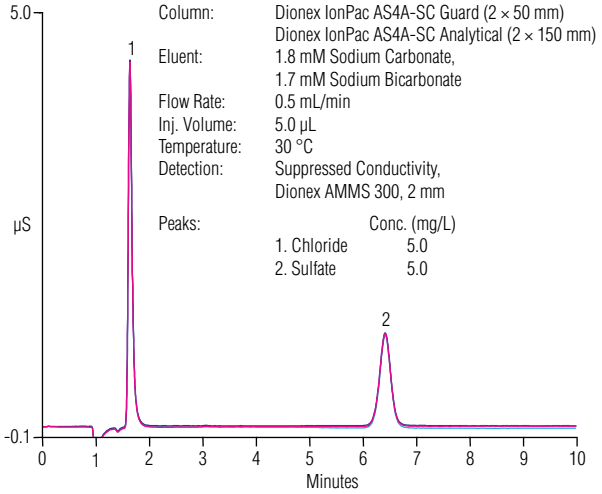

Figure 1. Overlay of three chromatograms of chloride and sulfate anions in water determined using the Dionex IonPac AS4A-SC column.

Results and Discussion

Thermo Scientific Application Note 175 demonstrates two direct injection IC methods to determine whether ethanol used as a blending agent in gasoline meets the chloride and sulfate specifications in ASTM D 4806.[6] Due to the limitations discussed here, an alternative method using preconcentration with matrix elimination was developed, which is described in Thermo Scientific Application Update 161.[8] However, these methods do not discuss the procedure required for determining potential sulfate in ethanol. To determine the potential sulfate in ethanol, an oxidizing agent—hydrogen peroxide—is added to the sample to convert all the sulfur species to sulfate.

The method described in this study uses a direct injection approach, which is a time- and cost-effective method of determining total and potential sulfate and total chloride in ethanol samples. Figure 2A compares an unspiked ethanol sample to replicate injections of the same sample spiked with 5 mg/L each of chloride and sulfate. As shown in Figure 2B, chloride and sulfate demonstrate stable retention times and peak area responses over time.

Interferences can be caused by anions with similar retention times to sulfate and chloride. Interfering anions can be present in the sample or leach from labware into the sample. Figure 3 demonstrates that some common anions do not interfere with the determination of chloride and sulfate. As shown, chloride and sulfate are well resolved with no interferences from the spiked anions with a run time of 10 min.

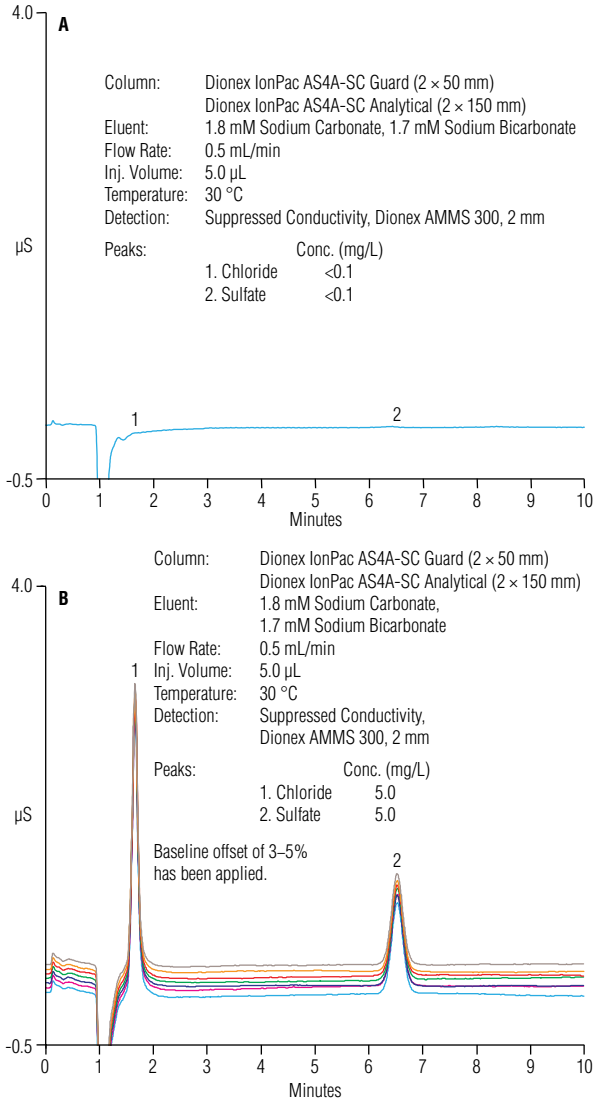

Figure 2. A) Chromatogram of chloride and sulfate anions in ethanol determined using the Dionex IonPac AS4A-SC column. B) Overlay of seven chromatograms of chloride and sulfate anions in ethanol determined using the Dionex IonPac AS4A-SC column.

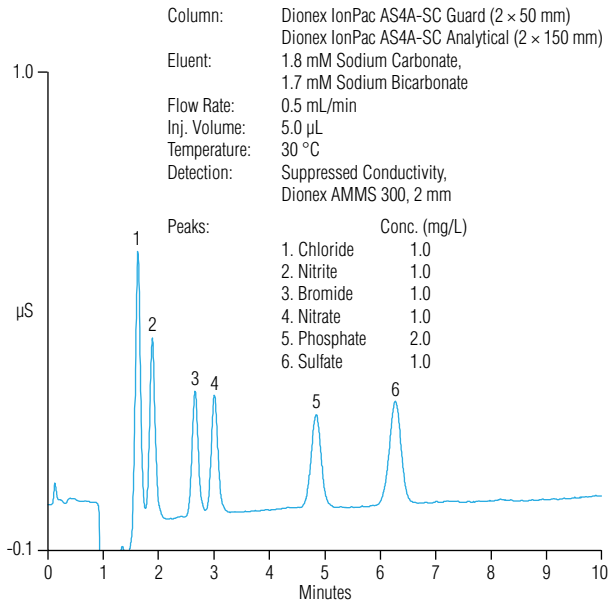

Figure 3. Separation of common anions in ethanol determined using the Dionex IonPac AS4A-SC column.

The linearity, limits of detection (LOD), and limits of quantification (LOQ) were evaluated to determine the suitability of the method for this analysis. ASTM Method D 7319-09 was used to set the appropriate calibration ranges. Table 2 summarizes the linearity obtained by injecting calibration standards from 0.3–50 mg/L for chloride and 0.3–20 mg/L for sulfate. The calibration curves were linear with coefficients of determination (r^2) greater than 0.999. The LODs for chloride and sulfate were 5.0 µg/L and 20 µg/L, respectively, and the LOQs were 14.7 µg/L for chloride and 60 µg/L for sulfate.

Figure 4 is an overlay of seven chromatograms for determining potential sulfate in an ethanol sample spiked with 4 mg/L of thiosulfate followed by the addition of hydrogen peroxide. The peak area responses and retention times are stable over the replicate injections, even in the presence of the oxidizing agent.

Electrolytic suppression is not used for this method because the rise in baseline observed can interfere with determination of low concentrations of chloride. The Dionex AMMS 300 suppressor in chemical regeneration mode is used to ensure a stable baseline for each injection, which improves the quantification of chloride. The repeatability obtained with the Dionex AMMS 300 suppressor is shown in Figures 2B and 4, where the overlays of seven replicate injections exhibit consistent peak responses with no baseline drift.

Precision measurements at different concentrations of chloride were determined by spiking known concentrations of chloride into 90% ethanol, followed by multiple injections (n = 7). Precision measurements at different concentrations of sulfate were determined by spiking known concentrations of sulfate into 90% ethanol, followed by multiple injections (n = 7). Samples for potential sulfate determinations were prepared by spiking known concentrations of thiosulfate to 9.5 mL of 90% ethanol and then adding 0.5 mL of a 30% hydrogen peroxide solution to make a final concentration of 1.0, 4.0, or 20.0 mg/L of sulfate.

As shown in Table 3, method precision is good for total and potential sulfate over a period of seven injections at concentrations of 1.0, 4.0, and 20 mg/L and at concentrations of 1.0, 20, and 50 mg/L for total chloride determination.

Table 2. Linearity, LOD and LOQs.

Analyte	Range (mg/L)	Coefficient of Determination (r^2)	LOD[a] (µg/L)	LOQ[b] (µg/L)
Chloride	0.3–50	0.9999	5.00	14.7
Sulfate	0.3–20	0.9993	20.0	60.0

[a] Estimated from 3 × S/N

[b] Estimated from 10 × S/N

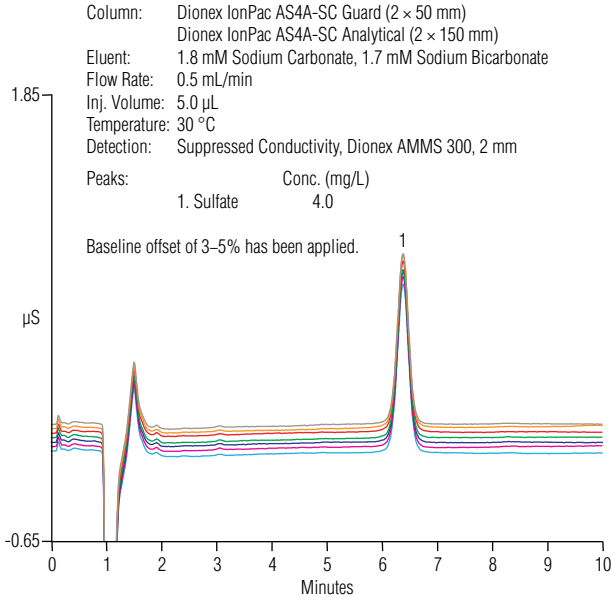

Figure 4. Overlay of seven chromatograms determining potential sulfate in ethanol using the Dionex IonPac AS4A-SC column.

Table 3. Method precision.

Measurement	Anion Concentration mg/L	Precision (RSD, n = 7)
Total Chloride	1.0	0.45
	20.0	0.62
	50.0	0.39
Total Sulfate	1.0	0.86
	4.0	0.65
	20.0	0.72
Potential Sulfate	1.0	0.67
	4.0	0.33
	20.0	0.32

Conclusion

This study describes a fast, simple, and direct injection method to determine total and potential sulfate and total chloride in ethanol according to ASTM D 7319. Thermo Scientific Application Note 175 and Application Update 161 present methods to measure total chloride and sulfate in ethanol at sub-mg/L detection limits; however, the method presented here also measures potential sulfate in ethanol. This method can reliably quantify sulfate and chloride at 60 µg/L and 15 µg/L, respectively, which is well below the ASTM D 4806 specification of 4 mg/L for sulfate and 40 mg/L for chloride.

Suppliers

Sigma-Aldrich, 3050 Spruce Street, St. Louis, MO 63103, U.S.A., Tel: 800-521-8956. www.sigmaaldrich.com

J.T. Baker, A Division of Mallinckrodt Baker, Inc., 222 Red School Lane, Phillipsburg, NJ, 08865, U.S.A., Tel: 908-859-2151; 800-582-2537. www. mallbaker.lookchem.com

Sarstedt Inc., 1025, St. James Church Road, P.O. Box 468, Newton NC 28658-0468, U.S.A., Tel: +1 828 465 4000. www.sarstedt.com

Praxair Specialty Gases and Equipment, 39 Old Ridgebury Road, Dansbury, CT 06810-5113, U.S.A., Tel: 877-772-9247. www.praxair.com

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