

Determination of Chloride and Sulfate in Gasoline-Denatured Ethanol

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Key Words

Renewable Energy, Alternative Fuels, Biofuel, Natural-Gas Condensate, Ion Chromatography, Eluent Generation, Dionex IonPac AS22 Column

Introduction

Ethanol is made from renewable energy sources and an alternative to traditional fossil fuels. Fermentation and distillation of biomass (e.g., cornstalks, vegetable waste, and any starch crop) produce fuel-grade ethanol. Although automobile manufacturers have designed flexible-fuel vehicles that can run on blends of up to 85% ethanol, most vehicles in the U.S. today operate with blends of up to 10% ethanol without the need for modification to the engine or fuel system.

Fuel-grade ethanol is denatured with 2–5% (v/v) of natural gasoline condensate to make it unsuitable for human consumption. In addition, a corrosion inhibitor is added to the denatured ethanol prior to transportation.^{1,2} When combined with gasoline, denatured fuel ethanol increases octane levels and promotes better fuel burning, which reduces harmful emissions.³ Fuel ethanol can be contaminated with inorganic anions such as chloride and sulfate, which form precipitates that can corrode engine components. Therefore, denatured fuel ethanol is required to have <4 mg/L sulfate and <40 mg/L chloride as specified by ASTM International in Standard D4806; ASTM Standard D7319-12 describes a direct injection ion chromatography (IC) method to determine chloride and sulfate in ethanol.^{4,5}

Dionex (now part of Thermo Scientific) Application Note (AN) 290 demonstrates a direct-injection IC method consistent with ASTM D7319-12 and can be used to determine if methanol-denatured ethanol used as a blending agent in gasoline meets the chloride and sulfate specifications in ASTM D4806.⁶ ASTM D7319-12 recommends methanol as the first of four possible denaturants, but it is common industry practice to denature ethanol with natural gas condensate (i.e., gasoline, although not the type a consumer would purchase from a modern gas station) to make it unsuitable for human consumption. Corrosion inhibitors (i.e., a combination of cyclohexyldimethylamine, xylene, and ethylbenzene) are also added to the denatured ethanol to



prevent corrosion of pipelines during transportation. Because the gasoline and/or the corrosion inhibitors can impact the robustness of the method described in AN 290, this study describes ruggedness testing of the AN 290 method by directly injecting 25 μ L of gasoline-denatured ethanol from two different industry sources. This method demonstrates the use of carbonate/bicarbonate eluent generation for the determination of chloride and sulfate in gasoline-denatured ethanol. A complete set of analytical data is presented to verify that the method is appropriate for these samples.

Goal

To evaluate the determination of total chloride, sulfate, and potential sulfate in gasoline-denatured ethanol samples and the robustness of the Thermo Scientific™ Dionex™ IonPac™ AS22 column for this analysis

Equipment

- Thermo Scientific Dionex ICS-2100 system,* including:
 - Pump
 - Degasser
 - Injection Valve
 - Column Heater
 - Conductivity Detector
 - EO Eluent Organizer, including pressure regulator and 2 L plastic bottle
- Thermo Scientific™ Dionex™ AS-DV Autosampler with PolyVials™ for 5 mL vials (P/N 038008)
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System software, version 7.1
- Vacuum Pump

*This method can also be used with a Dionex ICS-1100, -1600, or -5000+ system.

Consumables

- Dionex IonPac AG22 Guard, 4 × 50 mm (P/N 064139)
- Dionex IonPac AS22 Analytical, 4 × 250 mm (P/N 064141)
- Thermo Scientific Dionex EGC III K₂CO₃ Carbonate Eluent Generator Cartridge (P/N 074536)
- Thermo Scientific Dionex EPM III Electrolytic pH Modifier (P/N 080135)
- Dionex EGC Carbonate Mixer Kit, 4 mm (P/N 079943)
- Thermo Scientific™ Dionex™ AMMS™ 300 Anion MicroMembrane™ Suppressor, 4 mm (P/N 064559)
- Filter Unit, 0.2 µm nylon
- Vial Kit, 1.5 mL, Glass with Caps and Septa (P/N 055427)
- 4 Liter Plastic Reservoir for chemical regeneration (P/N 063292)
- Helium or nitrogen, 4.5 grade (99.995%) or better, <5 ppm oxygen

Accessories

- Upgrade Kit* for Carbonate and Bicarbonate Eluent (P/N 064333), including:
 - PEEK tubing, 35 cm (14 in.) of black 0.25 mm (0.010 in.) i.d. (white labels) (P/N 064346)
 - PEEK tubing, 60 cm (24 in.) of black 0.25 mm (0.010 in.) i.d. (white labels) (P/N 064343)
 - Fittings 10-32 (P/N 043275)
 - Ferrules 10-32 (P/N 043276)
 - Fittings 1/8 in. fittings (P/N 052267)
 - Ferrules 1/8 in. ferrules (P/N 048949)
 - PEEK tubing, 35 cm (14 in.) of black 0.25 mm (0.010 in.) i.d. (yellow labels) (P/N 064340)
 - PEEK tubing, 30 cm (12 in.) of black 0.25 mm (0.010 in.) i.d. (red labels) (P/N 064334)
 - Polytetrafluoroethylene tubing, 28 cm (11 in.) of clear 1.58 mm (0.062 in.) i.d. (blue labels) (P/N 064337)
- Yellow PEEK 1000 psi backpressure coil, 0.5 mL/min (P/N 053765)

*Parts also can be ordered separately.

Reagents and Standards

- Deionized (DI) water, Type I Reagent Grade, 18 MΩ-cm resistance or better
- Chloride Standard (1000 mg/L), 100 mL (P/N 037159)
- Sulfate Standard (1000 mg/L), 100 mL (P/N 037160)
- Anion Regenerant Concentrate (20×) 200 mL (P/N 037164)
- Sulfuric Acid, ACS Reagent Grade (Fisher Scientific P/N RABS0030500)
- Hydrogen Peroxide, 30% ACS Reagent Grade (Fisher Scientific P/N 3821716)
- 7-Anion Standard (P/N 056933)

Samples

Ethanol samples denatured with natural gas condensate containing corrosion inhibitors (i.e., a combination of cyclohexyldimethylamine, xylene, and ethylbenzene) were generously donated by two different sources. These samples are referred to as Samples A and B.

Conditions

Columns:	Dionex IonPac AG22 Guard, 4 × 50 mm Dionex IonPac AS22 Analytical, 4 × 250 mm
Eluent:	4.5 mM Potassium Carbonate/1.4 mM Potassium Bicarbonate
Eluent Source:	Dionex EGC III K ₂ CO ₃ Cartridge/Dionex EPM III
Flow Rate:	1.2 mL/min
Inj. Volume:	25 µL
Temperature:	30 °C
Detection:	Suppressed Conductivity, Dionex AMMS 300 Suppressor, 4 mm, with 50 mM Sulfuric Acid (Chemical Regeneration)
Background Conductance:	~25 µS
Noise:	3–5 nS peak-to-peak
Backpressure:	2300 psi
Run Time:	20 min

Anion Concentration (mg/L)	Volume of 1000 mg/L Chloride Stock (mL)	Volume of 1000 mg/L Sulfate Stock (mL)	Volume of Deionized Water (mL)	Total Volume (mL)
0.3	0.03	0.03	9.94	100
0.5	0.05	0.05	9.90	100
1.0	0.10	0.10	9.80	100
5.0	0.50	0.50	9.00	100
10.0	1.00	1.00	8.00	100
20.0	2.00	2.00	6.00	100
50.0	5.00	—	5.00	100

Preparation of Solutions and Reagents

Sulfuric Acid, 0.5 N

Carefully transfer 13.7 mL of reagent-grade sulfuric acid to approximately 500 mL of filtered and degassed DI water in a 1 L volumetric flask. Allow the solution to cool before bringing to volume with DI water. Mix by inverting the flask 10 to 20 times.

Sulfuric Acid, 50 mN

Dilute 200 mL of the above described 0.5 N sulfuric acid concentrate in a 2 L volumetric flask by adding approximately 1700 mL of filtered and degassed DI water. Invert the flask to mix the contents and bring the volume to 2000 mL using DI water. Repeat this process to fill three 4 L regenerant bottles.

If using the regenerant concentrate, add the 200 mL concentrate to 1700 mL of filtered and degassed DI water. Invert to mix and bring the volume to 2000 mL using DI water. Repeat this process to fill three 4 L regenerant bottles.

Stock Standard Solutions

Chloride and sulfate standards at concentrations of 1000 mg/L were purchased from Thermo Fisher Scientific.

Preparing Calibration Standards

To prepare chloride and sulfate calibration standards, deliver appropriate volumes of the 1000 mg/L stock standards using calibrated pipettes (Table 1).

Sample Preparation

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

Total Sulfate and Chloride

Directly inject denatured ethanol samples.

Potential Sulfate

Add 9.5 mL of denatured ethanol to a 10 mL volumetric flask, then add 0.5 mL of a 30% hydrogen peroxide solution. Shake for at least 30 s to ensure good mixing. The final hydrogen peroxide concentration of this mixture will be 1.5%.

Total Sulfate and Chloride (1:5 Diluted)

Using DI water, dilute a 1 mL sample of gasoline-denatured ethanol spiked with 5 mg/L each of chloride and sulfate to 5 mL. The final concentrations of spiked chloride and sulfate in the diluted samples will be 1 mg/L.

Potential Sulfate (1:5 Diluted)

Prepare samples for potential sulfate by spiking 5 mg/L of sulfate in 9.5 mL of gasoline-denatured ethanol, then add 2.5 mL of a 30% hydrogen peroxide solution. Shake for at least 30 s to ensure good mixing. Dilute the mixture in a volumetric flask to 50 mL using DI water. The final hydrogen peroxide concentration of this mixture will be 1.5% and the final concentration of spiked sulfate will be 1 mg/L.

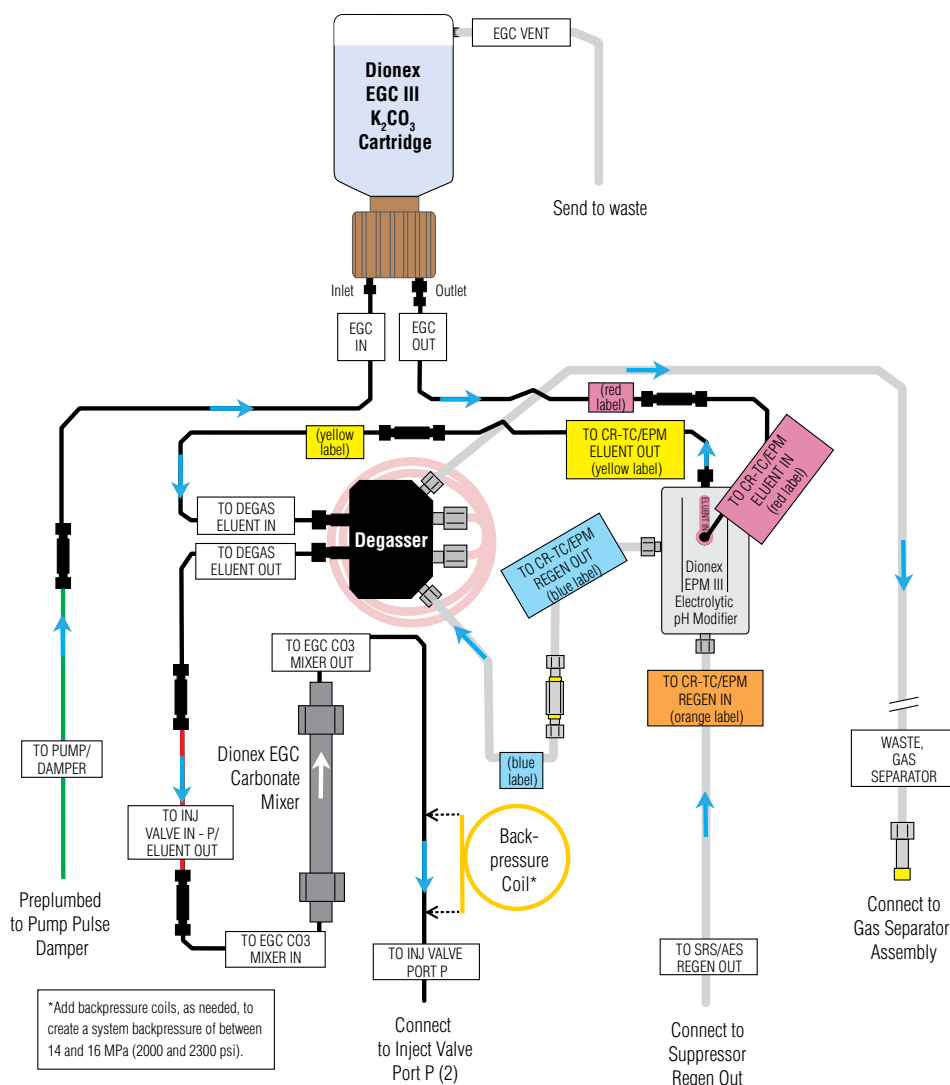


Figure 1. Dionex EGC III K₂CO₃ Cartridge and Dionex EPM III plumbing for a carbonate/bicarbonate eluent generation system.

System Configuration

Figure 1 shows a schematic of the configuration.

- Place the Dionex EGC III K₂CO₃ Cartridge on top of the Dionex ICS-2100 system. Connect the EGC IN line to the Dionex EGC III K₂CO₃ Cartridge INLET port, and connect the EGC OUT line to the Dionex EGC III K₂CO₃ Cartridge OUTLET port. Slide the Dionex EGC III K₂CO₃ Cartridge into the holder, remove the vent cap, and fasten a BD Luer-Lok™ connector and vent line.
- Install the Dionex EPM III onto the ball studs on the mounting bracket. Lift the Dionex EGC cartridge slightly from its holder and slide the Dionex EPM III bracket onto the side of the cartridge holder.
- Connect the following:
 - Connect the line labeled TO CR-TC/EPM ELUENT IN (red label) to the ELUENT IN port on the Dionex EPM III.
 - Connect the line labeled TO CR-TC/EPM ELUENT OUT (yellow label) to the ELUENT OUT port on the Dionex EPM III.
 - Connect the line labeled TO CR-TC/EPM REGEN OUT (blue label) to the REGEN OUT port on the Dionex EPM III.

- Connect the line labeled TO CR-TC REGEN IN (orange label) to the REGEN IN port on the Dionex EPM III. Connect the Dionex EPM III electrical cable to the connector labeled EGC III.

System Configuration for the Dionex EGC III K₂CO₃ Cartridge and Dionex EPM III Conditioning

- Use a 10-32 to 10-32 coupler to connect a yellow 0.5 mL/min (100 psi) backpressure coil to the TO INJECT VALVE IN-P line. Connect a 10-32 to 1/4-28 coupler to the free end of the backpressure coil. Connect the TO SRS/AES REGEN OUT line to the 10-32 to 1/4-28 coupler. Install this backpressure coil for the conditioning process only.
- Prime the pump at a flow rate of 1.00 mL/min using filtered ASTM Type I DI water with the liquid going to waste for 5 min.
- On the system panel, verify that the cartridge type for EGC-1 is set for Carbonate, and the type for EGC-2 is set for pH Modifier. Set EGC-1 concentration to 9 mM and EGC-2 concentration to 1 mM. Turn on EGC-1 and EGC-2. Run the Dionex EGC III K₂CO₃ Cartridge and Dionex EPM III at these settings for 30 min.

Installing and Conditioning the Dionex EGC Carbonate Mixer

- To install the Dionex EGC Carbonate Mixer, install the larger diameter mounting clips on the inside of the door panel on the Dionex ICS-2100 system. Orient the mixer with the outlet pointing up and mount the mixer onto the clips. The mixer outlet must point up to ensure thorough mixing of the eluent.
- Use a 35 cm length of black PEEK tubing to connect the end labeled TO EGC CO₃ MIXER IN to the mixer inlet. Use the 60 cm length of black PEEK tubing to connect the end labeled TO EGC CO₃ MIXER OUT to the mixer outlet.
- Verify that EGC-1 and EGC-2 currents are off and disconnect the Dionex EGC III K₂CO₃ Cartridge inlet line (labeled TO PUMP/DAMPER).
- Once the mixer is installed, fill it with DI water by connecting the EGC K₂CO₃ MIXER IN inlet to the PUMP/DAMPER outlet and the EGC K₂CO₃ MIXER OUT line to a temporary waste container.
- Set the pump flow rate to 5.00 mL/min and run the pump until there is a consistent flow of water exiting the EGC K₂CO₃ MIXER OUT (~5 min for a 4 mm mixer). Turn off the pump after the mixer is filled.
- To condition the mixer with eluent, disconnect the EGC K₂CO₃ MIXER IN from the PUMP/DAMPER outlet, then reconnect the PUMP/DAMPER outlet and the Dionex EGC III K₂CO₃ Cartridge inlet. Connect a 10-32 to 10-32 coupler and a yellow PEEK backpressure coil. Connect the backpressure coil to the EGC K₂CO₃ MIXER IN. Temporarily add this backpressure coil during the conditioning of the mixer.
- Connect the EGC K₂CO₃ MIXER OUT to the TO SRS/AES REGEN OUT line. Set the pump flow rate to 1.2 mL/min and start the pump. The backpressure of the system must be between 2000 and 2300 psi; add or remove backpressure tubing to maintain the pressure within this range. Set EGC-1 and EGC-2 concentrations to 4.5 mM K₂CO₃ and 1.4 mM KHCO₃, respectively. Run at the selected settings until the mixer is filled with the eluent. At the flow rate of 1.2 mL/min, this will take approximately 40 min.
- Turn off EGC-1 and EGC-2 as well as the pump, then remove the yellow PEEK backpressure coil between the TO INJ VALVE IN-P line and the mixer inlet.
- Disconnect the mixer outlet from the TO SRS/AES REGEN OUT line, remove the 10-31 to 1/4-28 coupler, and reconnect the TO SRS/AES REGEN OUT line to the SRS/AES REGEN OUT port. Connect the TO INJ VALVE IN-P line to the EGC K₂CO₃ MIXER IN line.
- Install the guard and analytical column set. Verify that the system pressure displayed by the pump is between 2000 and 2300 psi when pumping eluent under the method conditions to enable the degas assembly to effectively remove electrolysis gases from the eluent. If necessary, install backpressure coils supplied with the Dionex EGC cartridge ship kit to adjust the system pressure to between 2000 and 2300 psi. Because the system pressure can rise over time, trim the backpressure coil as necessary to maintain system pressure under 2300 psi.

- Install the Dionex AMMS 300 suppressor in the external pressurized bottle mode by following the instructions in the product manual, Document No. 031727. Adjust the head pressure on the external regenerant reservoir to deliver a flow rate of 5–8 mL/min. To do this, couple a 3 in. piece of 0.01 in. i.d. PEEK tubing to the end of the suppressor waste line, then trim the tubing until a pressure of 10–15 psi in the regenerant reservoir provides a flow of 5–8 mL/min. Prepare the Dionex AMMS 300 suppressor for use by hydrating the eluent chamber. Transfer approximately 5 mL of regenerant (50 mN sulfuric acid) through the REGEN IN port and approximately 5 mL of eluent through the ELUENT IN port. Allow the suppressor to sit for approximately 20 min to fully hydrate the suppressor screens and membranes.
- Equilibrate the column with eluent for 30 min and run a system blank. The system will display the background conductance and noise listed under Conditions. Inject a standard containing 2.0 mg/L of fluoride; 3.0 mg/L of chloride; 10 mg/L each of nitrite, bromide, and nitrate; and 15 mg/L each of phosphate and sulfate. The column is equilibrated when three consecutive injections of the standard produce the same retention times for all the analytes. Confirm that the resulting chromatogram resembles the 7-Anion Standard shown in Figure 2.

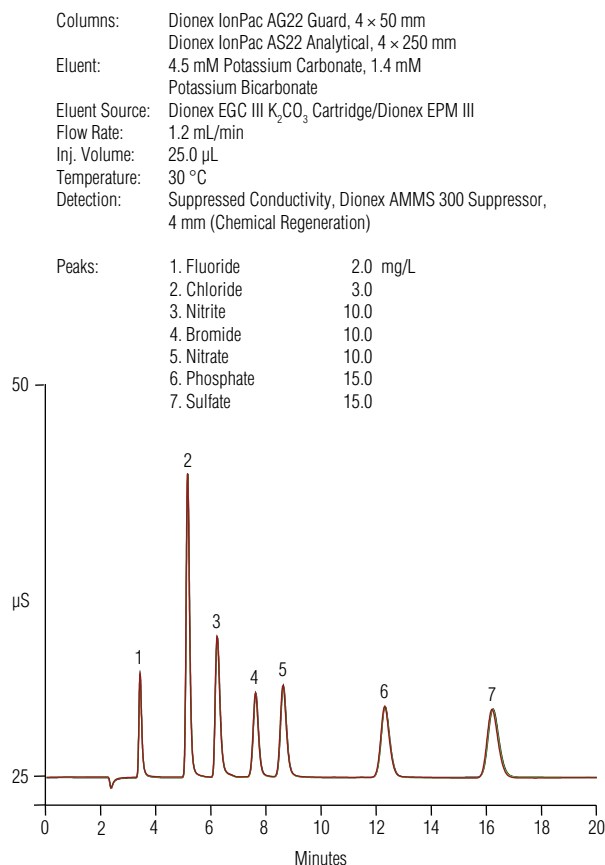


Figure 2. Overlay of three chromatograms showing the separation of the 7-Anion Standard on the Dionex IonPac AS22 column.

Results and Discussion

The method described in this study determines total and potential sulfate and total chloride in ethanol denatured with natural gas condensate containing corrosion inhibitors. Because these samples have the potential to deteriorate the column, column ruggedness was studied. Ruggedness was tested by repetitive sample injections from two different sources. Intermittent injection of a sample spiked with 5 mg/L of chloride and sulfate was used to evaluate retention time stability and peak area response. The samples studied were fuel-grade ethanol denatured with 2–5% (v/v) of natural gas condensate. This study analyzed samples from both sources by direct injection and injection after a 5-fold dilution.

Diluting natural gas condensate-denatured samples in DI water can cause the gasoline to separate from the aqueous phase. If this phase-separated gasoline is injected onto the column, it can lead to column deterioration. To test this possibility, >400 diluted and undiluted sample injections were performed over the course of the study with no effort made to ensure the sample was well mixed just prior to injection (i.e., the vial was not removed from the autosampler prior to mixing and then returned to the autosampler). The >400 sample injections caused no noticeable column degradation.

Figure 3 shows overlays of six chromatograms from different points in the study that demonstrate the reproducibility of the separation of spiked Sample A gasoline-denatured ethanol. The peak area RSDs for chloride and sulfate from these six injections were 1.1% and 1.6%, respectively, and the retention time RSDs were 0.15% and 0.25%, respectively, exhibiting good column robustness during this study.

After method ruggedness was confirmed, this method was qualified for suitability with gasoline-denatured ethanol samples. The linearity in the calibrated concentration range, limits of detection (LOD), and limits of quantification (LOQ) were measured as part of the evaluation of method suitability. ASTM D7319-09 was used to set the appropriate calibration ranges.

Table 2 summarizes the evaluation of the relationship between peak area response and concentration obtained by injecting standards from 0.3 to 50 mg/L for chloride and 0.3 to 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 6.5 $\mu\text{g/L}$ and 21.8 $\mu\text{g/L}$, and the LOQs were 18.2 $\mu\text{g/L}$ and 65.3 $\mu\text{g/L}$, respectively. The study showed that this method can reliably quantify sulfate and chloride at concentrations that are well below the ASTM D4806 specifications of 4 mg/L for sulfate and 40 mg/L for chloride.

Column: Dionex IonPac AG22 Guard, 4 $\times$ 50 mm
Dionex IonPac AS22 Analytical, 4 $\times$ 250 mm
Eluent: 4.5 mM Potassium Carbonate, 1.4 mM Potassium Bicarbonate
Eluent Source: Dionex EGC III K₂CO₃ Cartridge/Dionex EPM III
Flow Rate: 1.2 mL/min
Inj. Volume: 25.0 μL
Temperature: 30 $^{\circ}\text{C}$
Detection: Suppressed Conductivity, Dionex AMMS 300 Suppressor, 4 mm (Chemical Regeneration)

Peaks: 1. Chloride 5.3 mg/L
2. Sulfate 5.9

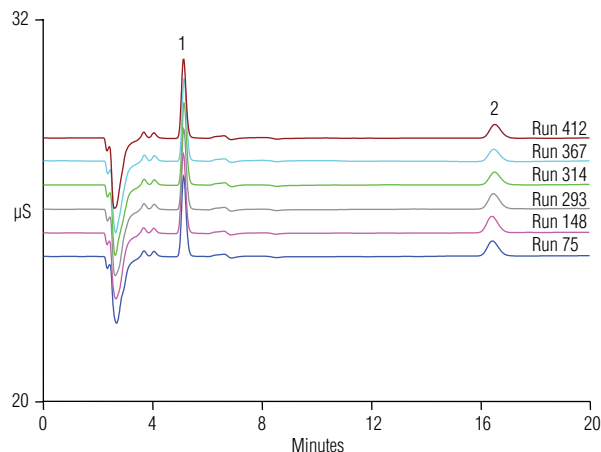


Figure 3. Overlay of six chromatograms showing the separation of spiked gasoline-denatured ethanol Sample A.

Table 2. Method linearity, LOD, and LOQ.

Analyte	Range (mg/L)	Coefficient of Determination (r^2)	LOD ^a ($\mu\text{g/L}$)	LOQ ^b ($\mu\text{g/L}$)
Chloride	0.3–50	0.9999	6.5	18.2
Sulfate	0.3–20	0.9997	21.8	65.3

^a Estimated from $3 \times S/N$

^b Estimated from $10 \times S/N$

Native amounts of total chloride and sulfate were determined in gasoline-denatured ethanol samples from two different industry sources, followed by confirmation of the peak identities by spiking in known amounts of chloride and sulfate. Figures 4 and 5 compare unspiked Samples A and B to the same samples spiked with 5 mg/L each of chloride and sulfate. Figure 4a shows the detection of trace (0.6 mg/L) sulfate in the unspiked sample, while Figure 5a shows trace chloride (0.7 mg/L) and sulfate (1.8 mg/L). In the spiked samples, Sample A shows detection of 5.3 mg/L of chloride and 5.9 mg/L of sulfate, and Sample B shows 6.1 mg/L of chloride and 7.3 mg/L of sulfate. As shown in the unspiked samples in Figures 4 and 5, the gasoline-denatured ethanol had no peaks that interfered with the determinations of chloride and sulfate.

Potential sulfates are the reduced inorganic sulfur species present in a sample, which generate sulfate when treated with an oxidizing agent. Potential sulfates were determined in gasoline-denatured ethanol by adding 0.5 mL of 30% hydrogen peroxide solution to 9.5 mL of denatured ethanol. Figure 6 shows a chromatogram that determined potential sulfate in Sample A gasoline-denatured ethanol spiked with 5 mg/L of sulfate followed by the addition of hydrogen peroxide. The chromatogram in Figure 6 shows 5.9 mg/L of sulfate in the sample. It also shows that the presence of the oxidizing agent does not interfere with the separation or integration of the sulfate peak.

Column: Dionex IonPac AG22 Guard, 4 × 50 mm
Dionex IonPac AS22 Analytical, 4 × 250 mm
Eluent: 4.5 mM Potassium Carbonate, 1.4 mM Potassium Bicarbonate
Eluent Source: Dionex EGC III K₂CO₃ Cartridge/Dionex EPM III
Flow Rate: 1.2 mL/min
Inj. Volume: 25.0 µL
Temperature: 30 °C
Detection: Suppressed Conductivity, Dionex AMMS 300 Suppressor, 4 mm (Chemical Regeneration)

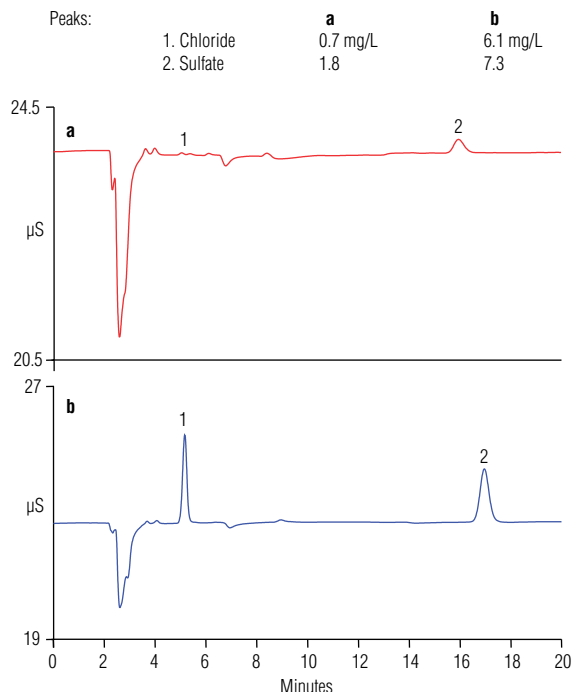


Figure 5. Separation of chloride and sulfate in both (a) unspiked and (b) spiked gasoline-denatured ethanol Sample B.

Column: Dionex IonPac AG22 Guard, 4 × 50 mm
Dionex IonPac AS22 Analytical, 4 × 250 mm
Eluent: 4.5 mM Potassium Carbonate, 1.4 mM Potassium Bicarbonate
Eluent Source: Dionex EGC III K₂CO₃ Cartridge/Dionex EPM III
Flow Rate: 1.2 mL/min
Inj. Volume: 25.0 µL
Temperature: 30 °C
Detection: Suppressed Conductivity, Dionex AMMS 300 Suppressor, 4 mm (Chemical Regeneration)

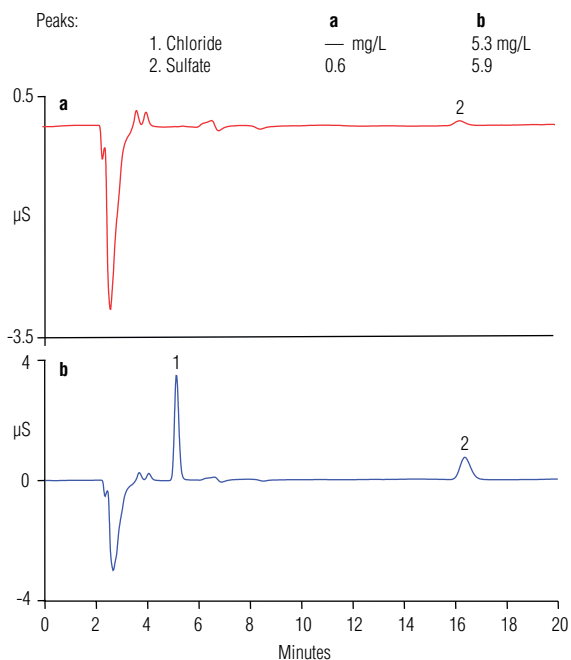


Figure 4. Separation of chloride and sulfate in (a) unspiked and (b) spiked gasoline-denatured ethanol Sample A.

Column: Dionex IonPac AG22 Guard, 4 × 50 mm
Dionex IonPac AS22 Analytical, 4 × 250 mm
Eluent: 4.5 mM Potassium Carbonate, 1.4 mM Potassium Bicarbonate
Eluent Source: Dionex EGC III K₂CO₃ Cartridge/Dionex EPM III
Flow Rate: 1.2 mL/min
Inj. Volume: 25.0 µL
Temperature: 30 °C
Detection: Suppressed Conductivity, Dionex AMMS 300 Suppressor, 4 mm (Chemical Regeneration)

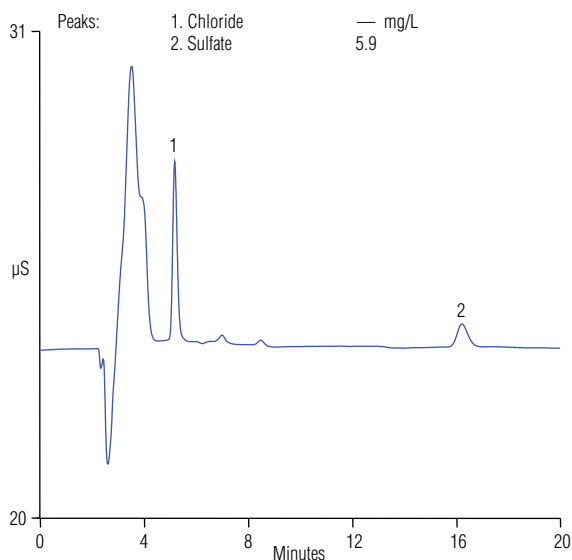


Figure 6. Separation of potential sulfate in a gasoline-denatured ethanol Sample A using a Dionex IonPac AS22 column.

Method Precision and Accuracy

Precision of chloride, sulfate, and potential sulfate were determined by performing six replicate injections of a 1:5 diluted gasoline-denatured ethanol sample spiked with 1 mg/L each of chloride and sulfate. Peak area RSDs for chloride, sulfate, and potential sulfate were 0.22, 0.33, and 0.30, respectively, over six replicate injections.

Recovery studies were performed by spiking 5 mg/L each of chloride and sulfate to determine method accuracy (Figures 4b and 5b show examples of injections used for the recovery studies). Table 3 summarizes the calculated recoveries of chloride and sulfate spiked into Samples A and B. The reported recoveries are an average of duplicate injections from three preparations. Recoveries ranged from 92–97% for chloride and 100–104% for sulfate, suggesting good method accuracy.

Table 3. Recovery of chloride and sulfate in gasoline-denatured ethanol.

Sample	Analyte	Amount Added (mg/L)	% Recovery (n = 6)
Sample A	Chloride	5.0	97.4
	Sulfate	5.0	100
Sample B	Chloride	5.0	92.3
	Sulfate	5.0	104

Conclusion

This study describes a fast, simple, direct-injection IC method with eluent generation to determine total and potential sulfate and total chloride in gasoline-denatured ethanol samples. This approach is consistent with ASTM D7319-12. The study shows good column ruggedness with no column deterioration over more than 400 sample injections. The method described can reliably quantify sulfate and chloride at 65 µg/L and 18 µg/L, respectively—concentrations that are well below the ASTM D4806 specifications of 4 mg/L for sulfate and 40 mg/L for chloride.

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