

# Assay of Fuel-Grade Butanol for Total and Potential Sulfate and Total Chloride Per ASTM D7328-07

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## Introduction

Increasing demand for petroleum and concerns over climatic changes associated with carbon emissions have led to new government and company policies focused on producing sustainable fuels made from renewable organic materials. In recent years, the focus has been on using bioethanol and biodiesel as alternate energy sources. The European Union and many countries, including the U.S., Brazil, China, Thailand, and Japan, have embraced the use of biofuels to decrease their dependence on imported petroleum. However, the production of biofuels, i.e., ethanol and biodiesel, places greater demand on the food and feed commodity markets, i.e., grain, sugar, natural oils, fats, and processing byproducts.<sup>1</sup> While these biofuels have many beneficial properties as alternatives to petroleum and diesel fuel, there are some major drawbacks. For example, ethanol has higher vapor pressure, affinity for water, and lower energy content than gasoline, which increases the complexity for blending, transport, and use. In addition, the high blending ratios of ethanol with gasoline require modified engines, and the lower energy content of blended fuels reduces vehicle gas mileage.<sup>2</sup>

These major shortcomings of existing biofuels have prompted the development of second generation biofuels, which include cellulosic ethanol, biobutanol, and mixed alcohols. Biobutanol overcomes many of the drawbacks associated with ethanol and is believed to have the most potential for significant growth.<sup>3</sup> Butanol has a higher molecular weight than ethanol and therefore has reduced vapor pressure, lower water solubility, and higher energy density. In addition, biobutanol can be blended at any point in the supply chain, requires less adjustment in gasoline blendstocks, and increases vehicle gas mileage.<sup>4</sup>

Sulfate and chloride concentration limits have not yet been defined for biobutanol by ASTM International. However, specifications for ethanol are a good benchmark for the quality of butanol. According to standard ASTM D4806-11A, a maximum concentration limit of 4 mg/L sulfate and 40 mg/L chloride is permissible in ethanol.<sup>4</sup>

Described here is a simple ion chromatography (IC) method to determine total and potential sulfate and total chloride in butanol used as a gasoline additive. It is consistent with the procedure described in ASTM D7328-07, which is intended for the analysis of ethanol samples containing 0.55–20.0 mg/L total sulfate, 4.0–20 mg/L potential sulfate, and 0.75–50.0 mg/L chloride, but can also be applied to butanol samples.<sup>5</sup> To determine total sulfate and chloride, evaporate a sample to dryness and reconstitute in the initial sample volume with deionized (DI) water. Inject 5  $\mu$ L of the reconstituted sample onto a Thermo Scientific Dionex IonPac AS4A-SC Carbonate Eluent Anion-Exchange Column. To determine potential sulfate follow this same procedure, but reconstitute the sample with 0.90% hydrogen peroxide solution in DI water. Linearity, limits of detection and quantification, and precision of potential and total sulfate and total chloride at different concentrations are demonstrated. This IC method allows for the analysis of butanol samples according to ASTM D7328-07 and has the sensitivity to meet the specifications described in ASTM D4806-11A.

## Key Words

- Renewable Energy
- ASTM D4806-11A
- Ion Chromatography (IC)
- Biofuels
- Suppressed Conductivity Detection
- High Octane Rating

## Equipment

- Thermo Scientific Dionex ICS-2100\* Ion Chromatography System including:
  - Single isocratic pump
  - Vacuum degasser
  - High-pressure, 6-port injector
  - Column heater enclosure
  - Conductivity cell and detector
  - EO Eluent Organizer, including pressure regulator and 2 L plastic bottle

\* This method can also be run using a Dionex ICS-1100, -1600, or -5000 IC system.

- Thermo Scientific Dionex AS Autosampler and 2 mL vial tray or Dionex AS-DV Autosampler with 5.0 mL PolyVials (plain caps)
- Thermo Scientific Dionex Chromeleon Chromatography Data System (CDS) 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 (Nalgene Nunc International, P/N 164-00200 or equivalent)
- Vacuum pump for degassing eluents (Gast Manufacturing Corp. P/N DOA-P104-AA or equivalent)
- Reacti-Therm™ III Heating/Stirring Module, triple block (Thermo Fisher Pierce P/N 18935)
- Reacti-Vap™ Evaporator, 9-port (Pierce P/N 18780)
- Plastic Needle 18 GA x 1 1/2" (P/N 039996)
- Vial Kit, 1.5 mL glass with caps and septa (P/N 055427)
- Glass scintillation vials, 20 mL (VWR P/N 66021-624)
- Three 4 L plastic bottle assemblies for chemical regeneration mode of operation

## Consumables

- Dionex IonPac™ AS4A-SC Analytical, 2 × 250 mm (P/N 043125)
- Dionex IonPac AG4A-SC Guard, 2 × 50 mm (P/N 043126)
- Thermo Scientific Dionex AMMS 300 Anion MicroMembrane Suppressor, 2 mm (P/N 064559)

## Reagents and Standards

- DI water, Type I reagent-grade water, 18 MΩ-cm resistance or better
- Thermo Scientific Dionex Chloride Standard, 1000 mg/L (P/N 037159)
- Thermo Scientific Dionex Sulfate Standard, 1000 mg/L (P/N 037160)
- Thermo Scientific Dionex AS4A Eluent Concentrate (P/N 039513)
- Thermo Scientific Dionex Anion Suppressor Regenerant Concentrate 0.50 N Sulfuric Acid, 4 Pack (P/N 37164)
- Sulfuric Acid, ACS Reagent Grade (J.T Baker, P/N 11-9681-05)
- Hydrogen Peroxide, 30% ACS Grade (Mallinckrodt, P/N V340-04)
- Isobutanol, ACS Grade, 99+% (Cat # AA36643K7 Fisher Chemical)
- Tetrabutylammonium Bisulfate, ≥ 99.0% (AT) (Sigma-Aldrich, P/N 86868)
- Tetrabutylammonium Chloride, ≥ 97.0% (AT) (Sigma-Aldrich, P/N 86870)

Samples were obtained from a leading biofuels manufacturer.

## Conditions

- Column: Dionex IonPac AS4A-SC Analytical, 2 × 250 mm  
Dionex IonPac AG4A-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
- Temperature: 30 °C
- Detection: Suppressed Conductivity, Dionex AMMS™ 300 2 mm in the chemical regeneration mode with 50 mN sulfuric acid
- Background: ~ 20 µS
- Noise: 3–5 nS peak-to-peak
- Backpressure: 1200 psi
- Run Time: 10 min

## Preparations of Solutions and Reagents

### 0.5 N Sulfuric Acid

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 volume to 1000 mL using DI water. Invert the solution several times to mix.

### 50 mN Sulfuric Acid

Dilute 200 mL of the prepared 0.5 N sulfuric acid concentrate in a 2 L volumetric flask by adding approximately 1700 mL of filtered and degassed DI water or use Thermo Scientific Dionex Anion Regenerant Concentrate (PN 37164). Invert the flask several times to mix the contents and bring volume to 2000 mL using DI water. Repeat this several times to fill three 4 L regenerant bottles.

### 0.90% Hydrogen Peroxide Solution

Carefully pipette 3.0 mL of 30% hydrogen peroxide reagent into a 100 mL volumetric flask and dilute to the mark with DI water.

*Note: Hydrogen peroxide degrades in an aqueous solution. Therefore, the 0.90% hydrogen peroxide solution needs to be prepared fresh daily.*

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

Transfer 10 mL of the AS4A Eluent Concentrate to a volumetric flask containing approximately 700 mL of filtered and degassed DI water. Invert to mix several times and bring to volume using DI water.

### Stock Standard Solutions

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

### 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).

Table 1. Preparation of calibration 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

### Precautions:

1. Butanol is immiscible in water, which can lead to low recoveries of sulfate due to its poor solubility in the organic phase. If using rinsed glassware for sample preparation, be sure that the glassware is dry. Rinsing all glassware twice with butanol containing chloride and sulfate concentrations below 0.1 mg/L and 0.3 mg/L, ensures that all the water from the rinsing is removed.\* Failing to rinse washed glassware in butanol will lead to low recoveries.

*\*Isobutanol with the Cat # AA36643K7 purchased from Fisher Chemicals met this criterion.*

2. All samples must be sonicated for at least 15 min prior to placing into the autosampler vials to ensure that the sample is homogenous. Insufficient sonication will lead to improperly mixed samples with varying amounts of chloride and sulfate in each aliquot.

### Total Sulfate and Chloride

Carefully add 2.0 mL of butanol to a clean and dry 20 mL glass scintillation vial without the lid. Place a clean Reacti-block™ aluminum block into the evaporator module. Place a 35 mm immersion depth thermometer into the aluminum block thermometer well. Switch the power on and set the temperature to 65 °C. Allow 30 min for the temperature to stabilize after the indicator light begins flickering. Actual times required for the unit to reach equilibrium for a given temperature may vary depending on the block used and the room temperature. Attach the 18 GA plastic needle onto the port on the evaporator. Attach a nitrogen line onto the evaporator manifold that is connected to a regulator set at about 20 psi. Place a vial with 2 mL of sample onto the heat block, and purge nitrogen over the sample to maintain an inert atmosphere and keep oxygen out. Allow the sample to dry completely, which may require 25–30 min. Once the liquid is entirely evaporated, allow the vial to cool to room temperature, and add 2 mL of DI water to the dried sample. Close the vial with its lid and vortex vigorously to dissolve the solids. Sonicate the resuspended sample for 5 min, and inject the sample immediately or use within a week when stored at room temperature.

## Potential Sulfate

Treat 2 mL of butanol in the same manner as for total sulfate and chloride until the liquid is entirely evaporated. But after drying the vial and allowing it to cool to room temperature, add 2 mL of 0.90% hydrogen peroxide solution. Close the vial with its lid and vortex vigorously to dissolve the solids. Sonicate the resuspended sample for 5 min and inject the sample immediately. Prepare a fresh sample daily.

## Sample Preparation for Spike Recovery Work

### 5000 ppm Organic Chloride Stock in Butanol (100 mL)

Weigh 3.217 g of tetrabutylammonium chloride and add to approximately 70 mL of butanol. Sonicate the mixture for 15 min. When dissolution is complete, allow the mixture to reach room temperature, transfer to a 100 mL volumetric flask, and bring to volume using butanol.

### 2000 ppm Organic Sulfate Stock in Butanol (100 mL)

Weigh 0.70796 g of tetrabutylammonium bisulfate and add to approximately 70 mL of butanol. Sonicate the mixture for 15 min. When dissolution is complete, allow the mixture to reach room temperature, transfer to a 100 mL volumetric flask, and bring to volume using butanol.

### 10, 5, and 1 ppm Butanol Spikes

Prepare these three solutions by pipetting 1, 0.5, and 0.1 mL of the 5000 ppm tetrabutylammonium chloride stock into three 500 mL volumetric flasks. Add 2.5, 1.25, and 0.25 mL of the 2000 ppm tetrabutylammonium bisulfate stock into the flasks, respectively (i.e., the first flask contains the 1 mL chloride stock and 2.5 mL bisulfate stock). Dilute to the mark with butanol. Sonicate for 5 min to mix the contents.

## System Preparation and Setup

Install the analytical and guard columns. Install the Dionex AMMS 300 in the chemical regeneration mode by connecting the eluent line from the column outlet to the ELUENT IN port of the Dionex AMMS 300 and the ELUENT OUT port of the Dionex AMMS 300 to the Cell In of the conductivity detector. Connect a regenerant line to the REGEN IN port of the Dionex AMMS 300 from the regenerant reservoir and connect a line from the REGEN OUT port of the Dionex AMMS 300 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 ELUENT IN port and 5 mL of regenerant through the REGEN IN port. Stop the eluent and regenerant flow to the suppressor, allowing the suppressor to hydrate for approximately 15–20 min. After the suppressor is properly hydrated, restart the liquid flow to the Dionex AMMS 300 and equilibrate the column with eluent for at least 30 min prior to analyzing a system blank. The system background conductance and noise should be what is displayed 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 overlaid chromatograms shown in Figure 1.

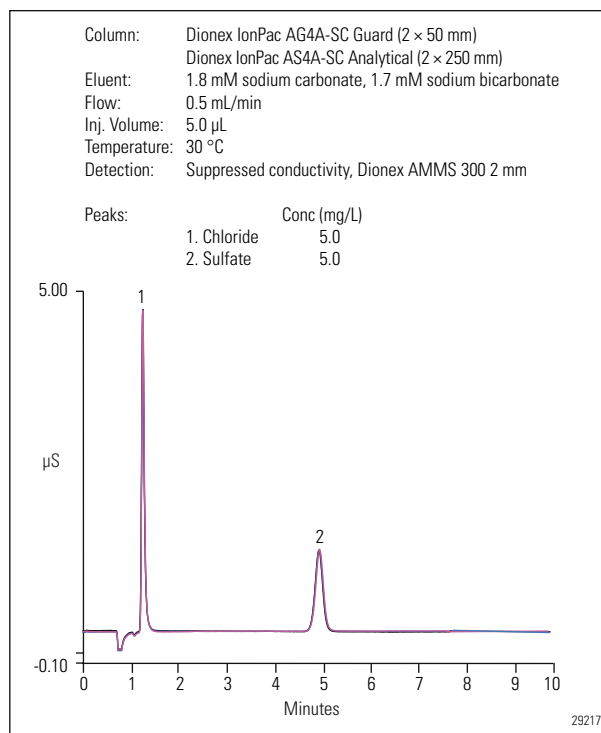


Figure 1. Overlay of three chromatograms of chloride and sulfate in water determined on the Dionex IonPac AS4A-SC column.

## Results and Discussion

This procedure demonstrates an IC method to determine whether butanol used as a blending agent in gasoline meets the chloride and sulfate specifications described in ASTM D4806-11A.<sup>6</sup> A method to determine total chloride and sulfate in butanol is also described, as well as a procedure to determine potential sulfates in butanol. Total inorganic sulfate and chloride can be determined by evaporating a sample to dryness and reconstituting in DI water followed by injection onto a Dionex IonPac AS4A-SC column. To determine potential sulfate, the butanol samples are evaporated to dryness and reconstituted in a 0.90% hydrogen peroxide solution that is injected onto the Dionex IonPac AS4A-SC column. The oxidizing agent (i.e., hydrogen peroxide) is used to convert all the sulfur species to sulfate. Figures 2A and 2B compare replicate injections of a butanol sample containing 0.03 mg/L of chloride and 0.93 mg/L of sulfate (2A) to a butanol sample containing 3.2 mg/L of chloride and 4.4 mg/L of sulfate (2B). As shown, chloride and sulfate demonstrate stable retention times and peak area responses at different concentrations.

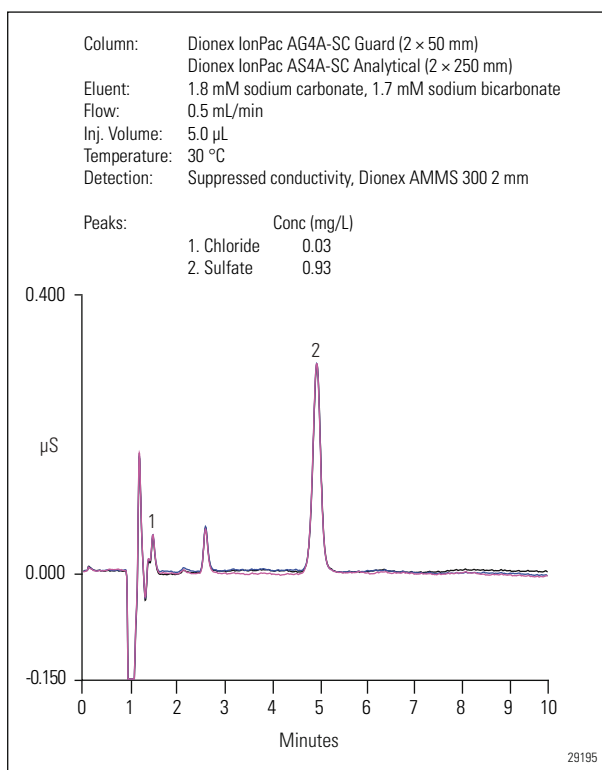


Figure 2A. Overlay of three chromatograms showing total chloride and sulfate in butanol sample A.

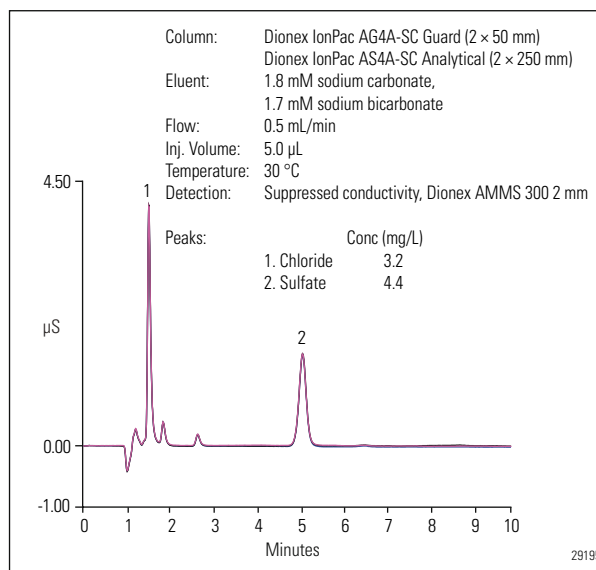


Figure 2B. Overlay of three chromatograms of chloride and sulfate in butanol sample B.

To demonstrate that chloride and sulfate are well resolved from other common anions that may leach from labware into the sample, a butanol sample with known amounts of chloride and sulfate was spiked with each of the common anions. The spiked samples were then transferred to a clean and dry 20 mL glass scintillation vial without the lid. The sample was dried by purging nitrogen over the sample for 25–30 min in a heat block set to 65 °C to maintain an inert atmosphere and keep oxygen out. Once the liquid evaporated, the vial was allowed to cool to room temperature and the sample was resuspended in DI water. Figure 3 demonstrates that other 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 and a run time of 10 min.

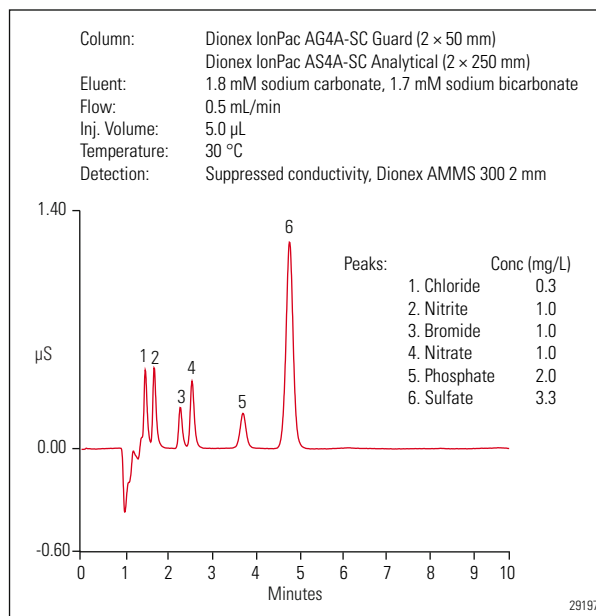


Figure 3. Separation of common anions spiked in butanol.

The linearity, limits of detection (LODs), and limits of quantification (LOQs) were evaluated to determine the suitability of the method for this analysis. ASTM D7328-07 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 a coefficient of determination ( $r^2$ ) greater than 0.999. The LODs for chloride and sulfate were 5.0  $\mu\text{g/L}$  and 20  $\mu\text{g/L}$ , respectively, and the LOQs were 14.7  $\mu\text{g/L}$  for chloride and 60  $\mu\text{g/L}$  for sulfate.

Table 2: Data for linearity, LOD and LOQ of chloride and sulfate.

Analyte	Range mg/L	Coefficient of Determination $r^2$	LOD <sup>a</sup> ( $\mu\text{g/L}$ )	LOQ <sup>b</sup> ( $\mu\text{g/L}$ )
Chloride	0.3–50	0.9999	5.00	14.7
Sulfate	0.3–20	0.9993	20.0	60.0

<sup>a</sup>Estimated from  $3 \times S/N$

<sup>b</sup>Estimated from  $10 \times S/N$

Figure 4 is an overlay of three chromatograms for determining potential sulfate in a butanol sample. The samples were prepared as described in the sample preparation section by evaporation, followed by resuspension in 0.9% hydrogen peroxide. The peak area responses and retention times were stable over the replicate injection, even in the presence of low concentrations of the oxidizing agent.

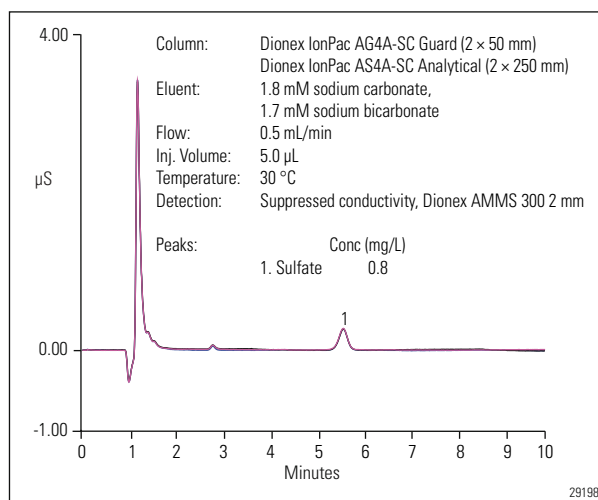


Figure 4. Overlay of three chromatograms determining potential sulfate in butanol.

The Dionex AMMS 300 suppressor in the chemical regeneration mode ensures a stable baseline for each injection. The repeatability obtained with the Dionex AMMS 300 suppressor can clearly be seen in Figures 2A, 2B and 4, where the overlays of seven replicate injections exhibit consistent peak responses with no baseline drift, thereby allowing the determination of low concentrations of chloride. As shown in Table 3, method precision is good for total sulfate and chloride and potential sulfate for triplicate injections within the same sample preparation across samples of varying concentrations. Sample preparation precision was also determined over three preparations of the same sample and peak area response, with RSDs ranging from 1.18 to 3.39.

Table 3. Peak area precision of total and potential sulfate and total chloride in butanol.

Sample	Analyte	Amount mg/L	Within Same Sample Preparation Precision RSD		Between-Sample Preparation Precision
			Ret. Time (n = 3)	Peak Area (n = 3)	Peak Area (n = 9, over 3 Preparations)
A	Chloride	0.03	0.00	1.47	3.39
	Sulfate	0.89	0.04	0.77	2.74
	Potential Sulfate	0.93	0.02	0.40	3.14
B	Chloride	3.7	0.08	0.65	1.57
	Sulfate	3.3	0.07	0.44	1.18
	Potential Sulfate	4.4	0.05	0.19	2.25
C	Chloride	0.89	0.13	0.91	1.56
	Sulfate	0.13	0.08	0.86	1.91
	Potential Sulfate	0.21	0.07	0.93	2.60

Recovery studies were performed on butanol purchased from Fisher Scientific by spiking known amounts of the chloride and sulfate to determine method accuracy. Table 4 summarizes the amounts spiked and the calculated recoveries. The reported recoveries are an average of duplicate injections from three preparations of each of the concentrations. Recoveries ranged from 97–100% for chloride and 101–105% for sulfate, suggesting method accuracy.

Table 4: Recovery of chloride and sulfate at different concentrations in butanol.

Analyte	Amount (mg/L)	% Recovery (n = 6)
Chloride	10.0	99.9
	5.0	97.3
	1.0	98.4
Sulfate	10.0	105.1
	5.0	101.3
	1.0	101.9

## Conclusion

This study describes a fast, simple method to determine total and potential sulfate and total chloride in butanol according to ASTM D7328-07, an IC method for fuel ethanol. The method described here can reliably quantify sulfate and chloride in butanol at 60 µg/L and 15 µg/L, respectively, which is well below the ASTM D4806-11A specification for fuel ethanol of 4 mg/L for sulfate and 40 mg/L for chloride.

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## Suppliers

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

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

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