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## Determination of Sulfate and Chloride in Ethanol Using Ion Chromatography

### INTRODUCTION

In Application Note 175, Dionex presented two ion chromatography (IC) methods that, using direct injection, can determine whether ethanol used as a blending agent in gasoline meets the sulfate and chloride concentration limits defined in the American Society for Testing and Materials (ASTM) Specification D 4806. These methods measure mg/L concentrations of chloride and sulfate anions in ethanol in 15 min by direct injection. Both methods were validated by Dionex during participation in the ASTM interlaboratory collaborative study to determine precision and bias for a new Standard Test Method. At the time of this update (February 2007), the ASTM method had not received final approval.

While both Dionex methods have been widely adopted for testing ethanol used for fuel, Dionex noted that there were drawbacks common to both methods. First, when using electrolytic suppression (ASRS<sup>®</sup> ULTRA II or equivalent) there was a baseline rise that could interfere with low-level chloride determinations. While the Anion MicroMembrane Suppressor (AMMS<sup>®</sup> III) with a sulfuric acid regenerant performs well for both methods, electrolytic suppression with the ASRS permits easier operation, reduces analyst exposure to corrosive

sulfuric acid, and eliminates the waste generated when using an acid regenerant. Second, sulfate concentrations higher than 10 mg/L in ethanol exhibited a rapid loss in peak area/height with time, which can result in the underreporting of sulfate data.

The method in this application update addresses both drawbacks of the previous method. The AS Autosampler performs a direct inject on a TAC-ULP1 anion concentrator, installed in place of the injection loop, and then washes off the ethanol. The elimination of the ethanol allows the use of electrolytic suppression in the recycle mode for the highest level of convenience. The method also exhibits good sulfate stability even when 20 mg/L of sulfate is spiked into gasoline-denatured ethanol. Sulfate and chloride are separated on an IonPac<sup>®</sup> AS22 column. This column is optimized for fast separation of common anions such as chloride and sulfate using an easy to prepare carbonate/bicarbonate eluent.

This improved method for determining sulfate and chloride in ethanol allows the analyst to easily determine if their ethanol meets ASTM Specification D 4806. This method is also easier to operate and more rugged than existing methods.

## EXPERIMENTAL

### Equipment

Dionex IC system:

ICS-3000, ICS-2000, ICS-1500, ICS-1000,  
or ICS-90

AS Autosampler

Chromeleon® Chromatography Management Software, ver. 6.8

Consumables:

IonPac AS22 Analytical, 4 × 250 mm  
(Dionex P/N 064141)

IonPac AG22 Guard, 4 × 50 mm  
(Dionex P/N 064139)

Anion Self-Regenerating Suppressor (ASRS  
ULTRA II), 4 mm (Dionex P/N 061561)

TAC-ULP1 Ultra Low Pressure Trace Anion  
Concentrator (5 × 23 mm) (Dionex P/N 061400)

Vial Kit, 10 mL, polystyrene (Dionex P/N 055058)

Syringe filters (Gelman IC Acrodisc® 0.2 µm,  
P/N 4483)

### Conditions

Columns:	IonPac AS22 and AG22
Concentrator Column:	TAC-ULP1
Eluent:	4.5 mM sodium carbonate/ 1.4 mM sodium bicarbonate
Flow Rate:	1.2 mL/min
Column Temperature*:	30 °C
Cell Temperature:	35 °C
Inj. Volume:	200 µL
Reagent Flush†:	1000 µL deionized water
Detection:	Suppressed conductivity, ASRS Ultra II, recycle mode
Suppressor Current:	31 mA
Background Conductance:	~20 µS
Noise:	~5-6 nS/min peak-to-peak
Backpressure:	2100 psi
Run Time:	15 min

\*For optimum performance a 30 °C column temperature is recommended, but this method can also be run on systems without column temperature control (ICS-90 and ICS-1000). This temperature should also be used in the DC compartment when using an ICS-3000.

†In this application the AS is operated in the Concentrate mode (for more information on this mode of operation see either the AS Operator's Manual or Dionex Technical Note 64) with the sample loaded onto the concentrator at an aspirate speed of 3 and a dispense speed of 3. For reagent flush, the aspirate and dispense speeds were 5 and 3, respectively.

### Reagents and Standards

Prepare all solutions from analytical reagent grade chemicals (when available).

Deionized water with a specific resistance of  
17.8 MΩ-cm or greater. Filter through a 0.2-µm  
filter immediately before use.

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

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

OR

Tetrabutylammonium bisulfate (TBABS)  
(Fluka P/N 86868)‡

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

AS22 carbonate/bicarbonate eluent concentrate;  
Sodium Carbonate/Bicarbonate (100×)  
(Dionex P/N 063965)

‡This application work was performed using TBABS, but a brief comparison showed no difference in the results when the Dionex sulfate standard was used in place of the TBABS standard.

### IonPac AS22 Eluent Solution

Pipet 10.0 mL of AS22 eluent concentrate into a 1-L volumetric flask and bring to volume using deionized water with a specific resistance of 17.8 MΩ-cm or greater. Mix well and transfer to the eluent reservoir.

### Stock Standard Solutions

Purchase certified 1000 mg/L chloride or sulfate anion standards from Dionex or another reputable source. Or, to prepare a 1000 mg/L solution of chloride anion, dissolve 1.6485 g of sodium chloride in reagent water and dilute to 1 L. To prepare a 1000 mg/L solution of sulfate anion, dissolve 0.8837 g of TBABS in reagent water and dilute to 250 mL. Store in high-density polyethylene or polypropylene bottles at 4 °C. These stock standards are stable for at least one month.

## Calibration Standard Solutions

Caution: Ethanol is flammable. Work under a hood.

To prepare chloride and sulfate calibration standards, use a calibrated pipet to deliver the appropriate volume of the 1000 mg/L stock standard into a 100-mL volumetric flask. For example, to prepare a calibration standard containing 1 mg/L chloride and sulfate, pipet 0.1 mL of each 1000 mg/L stock standard into the volumetric flask, add 9.8 mL of deionized water and then bring to volume with reagent grade ethanol and mix well. For 4 mg/L and 20 mg/L standards add 0.4 and 2 mL of the stock standard solutions and 9.2 and 6 mL of deionized water, respectively. For standards prepared with 5% gasoline, 5 mL (3.8 g) of unleaded gasoline was added to the volumetric flask prior to adding the reagent grade ethanol. The solution should be mixed thoroughly, sonicated, and then brought to volume with denatured ethanol. Prepare calibration standards daily.

## Sample Preparation

Caution: Ethanol is flammable.

Obtain samples in accordance with ASTM Practice D 4057 or Practice D 4177. Store in high-density polyethylene (HDPE) containers rinsed with deionized water until free of ionic contamination, with tight sealing closures to prevent evaporation. To prepare samples for analysis, pipet 10.0 mL of deionized water into a 100-mL volumetric flask, and then bring to volume with the ethanol sample and mix well. If you observe particulates, filter samples through IC Acrodisc filters into clean autosampler vials prior to injection. A sample of the reagent grade ethanol used to prepare the calibration standards should be prepared in the same manner to evaluate if the amount of sulfate and chloride it contributes to the standard is high enough that it needs to be accounted for.

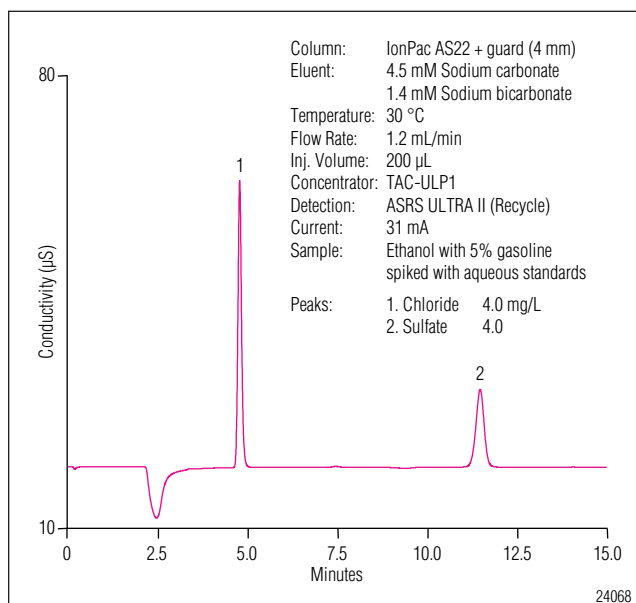


Figure 1. Separation of 4 mg/L sulfate and chloride in reagent grade ethanol containing 5% unleaded gasoline.

## SYSTEM PREPARATION AND SETUP

Install the analytical and guard columns. Fill the reagent flush bottle of the AS with deionized water. Prepare the ASRS ULTRA II for use by hydrating the eluent and regen chambers with deionized water. Wait at least 20 min before pumping eluent through the eluent chamber. For more information on ASRS operation, consult the *ASRS ULTRA II CSRS ULTRA II ASRS MS Quickstart*, Document No. 031951-03. Equilibrate the column with eluent for 30 min, and analyze an injection of the water used for sample preparation. The system should display the background conductance and noise listed above under “Conditions”.

Inject a standard containing 4 mg/L each chloride and sulfate in ethanol. The column is equilibrated when two consecutive injections of the standard produce the same retention time for sulfate. Confirm that the resulting chromatogram resembles the chromatogram of the 4 mg/L standard shown in Figure 1.

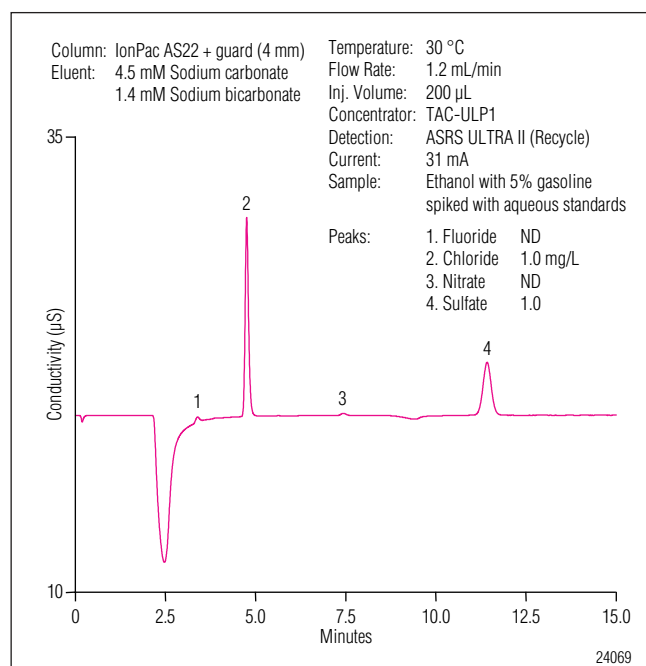


Figure 2. Separation of 1 mg/L sulfate and chloride in reagent grade ethanol containing 5% unleaded gasoline.

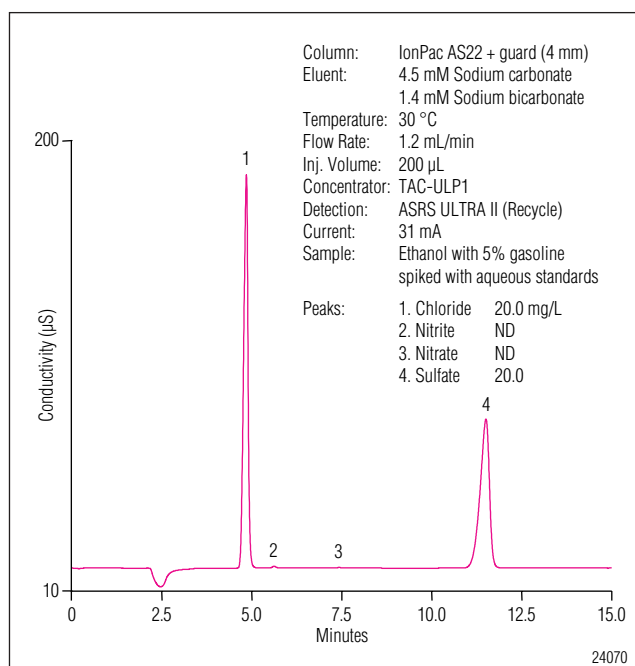


Figure 3. Separation of 20 mg/L sulfate and chloride in reagent grade ethanol containing 5% unleaded gasoline.

### Alternate Equipment Configurations

The work in this application update was completed with manually prepared eluents but it is possible to generate the 4.5 mM sodium carbonate/1.4 mM sodium bicarbonate eluent using a RFIC™ system (ICS-2000 or ICS-3000). This will require an EluGen® II Carbonate Cartridge (EGC II K<sub>2</sub>CO<sub>3</sub>) (Dionex P/N 058904), EGC Carbonate Mixer Kit, 4 mm (Dionex P/N 061686), and an EPM Electrolytic pH Modifier (Dionex P/N 063175). For instructions on installation and use, see the product manual for the EGC II K<sub>2</sub>CO<sub>3</sub> Cartridge, Eluent pH Modifier and Carbonate/Bicarbonate Mixer, Document No. 031840. Install this system in the configuration where the ASRS ULTRA II is plumbed in the Recycle mode (Section 2.2.4 in the product manual).

While Dionex strongly recommends using the AS autosampler for this application, an AS40 autosampler can be used with the following procedure. Handle vials and caps with gloves to prevent anion contamination. Prior to adding sample, rinse a 5 mL AS40 vial and filterless cap with water to remove possible anion contamination. Do not use filter caps. Dilute 0.5 mL ethanol to 4 mL with DI water in the cleaned vial. A rinse vial is not necessary.

### RESULTS AND DISCUSSION

Figure 1 shows a chromatogram of 4 mg/L each of chloride and sulfate spiked into reagent grade ethanol, containing methanol and isopropanol, to which 5% unleaded gasoline was added. Note the flat baseline obtained without the use of chemical regeneration of the suppressor. Using the ASRS ULTRA II in the convenient Recycle mode allows reproducible integration of the chloride peak. Continuous suppression using the ASRS ULTRA II ensures a stable baseline for each injection. This method also has approximately eight times the sensitivity of the method in Application Note 175 that uses the IonPac AS14A column due to concentration of eight times the sample injected on the AS14A column. This increased sensitivity permits easy determination of 1 mg/L chloride and sulfate in gasoline denatured ethanol (Figure 2). If desired, this method should be able to determine chloride and sulfate at concentrations well below 1 mg/L. If trace-level anion (low to sub-µg/L concentrations) determinations are required, the method in Dionex Application Note 85 should be used.

Dionex Application Note 175 reported the lack of stability of higher concentrations (e.g. 20 mg/L) of sulfate in ethanol samples. We evaluated the stability of 20 mg/L sulfate in ethanol with 5% unleaded gasoline using the method described in this application update. Figure 3 shows a chromatogram of 20 mg/L sulfate and 20 mg/L chloride in ethanol denatured with gasoline. Injecting this sample repetitively for nearly 24 h (99 injections), the sulfate peak area was much more stable (Figure 4) than observed in Application 175. During that study, sulfate peak areas dropped as much as 20% in 2 h and continued to decline.

This application update describes an improved method for determining sulfate and chloride in ethanol. This method is easier to operate, more rugged, and more sensitive than existing methods, and allows the analyst to easily determine if their ethanol meets ASTM Specification D 4806.

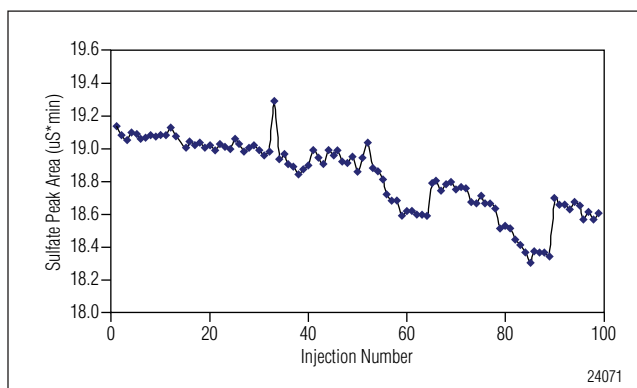


Figure 4. Peak area stability of 20 mg/L sulfate in reagent grade ethanol containing 5% unleaded gasoline over 99 consecutive injections.

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