Determination of Existent and Potential Sulfate and Total Inorganic Chloride in Denatured Ethanol by Direct Injection Using an RFIC System

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Dionex IonPac AS22 Column, Dionex EGC III K_2CO_3 Cartridge, Dionex AERS 500 Suppressor, Biofuel, ASTM

Introduction

Ethanol, a renewable alternative energy source made from grain and other biomass resources, can be used as a fuel either by itself or blended with gasoline. When used as a fuel, ethanol is denatured with a small addition of methanol, butanol, or gasoline to make it unfit for human consumption. Contamination of fuel ethanol with nonvolatile ions, such as chloride and sulfate, can cause corrosion problems and affect the performance of engine systems. According to American Society for Testing and Materials (ASTM) Standard D4806-13a, the concentrations of chloride and sulfate in denatured fuel ethanol used as a blending agent in gasoline are required to be <40 mg/L and <4 mg/L, respectively.[1]

Among the analytical techniques for the determination of chloride and sulfate, ion chromatography (IC) is at the leading edge. ASTM Standard D7319-13 describes a direct injection IC method to determine existent and potential sulfate and inorganic chloride in fuel ethanol and butanol.[2] As IC technologies have progressed over the years, a number of Dionex (now part of Thermo Scientific) application notes (ANs) and application updates (AUs) have been developed to improve IC determination of chloride and sulfate in denatured ethanol.

AN 175 describes two IC methods that use a Thermo Scientific™ Dionex™ IonPac™ AS14A column and a Dionex IonPac AS18 column, respectively.[3] However, with electrolytic suppression and direct injection of ethanol samples, a baseline rise can interfere with the determination of low concentrations of chloride. To remove the baseline rise, a Thermo Scientific™ Dionex™ AMMS™ 300 Anion MicroMembrane™ Suppressor is used with a sulfuric acid regenerant. To improve the method, AU 161 uses a Dionex IonPac AS22 column, a column that achieves superior separation of common anions using carbonate/bicarbonate eluent.[4] The AU 161 method also uses a Thermo Scientific Dionex IonPac TAC-ULP1 Trace Ultralow Pressure Anion Concentrator to perform a matrix elimination, thus preventing ethanol from entering the system and enabling convenient operation by allowing use of electrolytic suppression in the recycle mode.

Whereas AN 175 and AU 161 describe methods to measure chloride and existent sulfate in ethanol, AN 290 demonstrates a method to measure both existent and potential sulfate and chloride in ethanol.[5] In the AN 290 method, a Dionex IonPac AS4A-SC column is used for separation after direct injection of the ethanol samples and a Dionex AMMS 300 Anion MicroMembrane Suppressor is operated with a sulfuric acid regenerant.

More recently, AN 1052 demonstrates good column ruggedness for chloride and sulfate determination in gasoline-denatured ethanol.[6] That method also utilizes direct sample injection and a Dionex AMMS 300 Anion MicroMembrane Suppressor with manually prepared sulfuric acid regenerant.

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The method discussed here addresses the drawbacks of all the previous methods that use chemical suppression instead of electrolytic suppression to obtain a stable baseline for accurate chloride determination. This work uses a Thermo Scientific™ Dionex™ AERS™ 500 Anion Electrolytically Regenerated Suppressor operated in recycle mode. This improved electrolytic suppressor allows recyle-mode self-regeneration for direct injection of denatured ethanol samples for determination of existent and potential sulfate, as well as inorganic chloride.

Goal

To develop an IC method for the determination of existent and potential sulfate, as well as inorganic chloride, in denatured ethanol by direct injection with recycle-mode electrolytic suppression in a Reagent-Free™ IC (RFIC™) system

Equipment

- A Thermo Scientific Dionex ICS-2100 system,* including:
  - Pump
  - Vacuum Degasser
  - EO Eluent Organizer
  - CD Conductivity Detector
- Thermo Scientific Dionex AS-AP Autosampler with Sample Syringe, 250 µL (P/N 074306), and 1.2 mL buffer line assembly (P/N 074989)
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System software, version 7.2

*This method can be run on any Dionex ICS system capable of eluent generation or any Dionex ICS system if manually prepared eluents are used.

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 K_2CO_3 Carbonate Eluent Generator Cartridge (P/N 074536)
- Thermo Scientific Dionex EPM III Electrolytic pH Modifier (P/N 080135)
- Thermo Scientific Dionex EGC Carbonate Mixer Kit, 4 mm (P/N 079943)
- Dionex AERS 500 Anion Electrolytically Regenerated Suppressor, 4 mm (P/N 082540)
- Thermo Scientific™ Dionex™ ASRS™ 300 Anion Self-Regenerating Suppressor, 4 mm (P/N 064554)
- Vial Kit, Polystyrene with Caps and Blue Septa, 10 mL (P/N 074228)

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)
- Combined Seven Anion Standard II, 100 mL (P/N 057590)
- Hydrogen Peroxide, 30% (w/w), ACS Reagent Grade (Fisher Scientific P/N 3821716)
- Dionex IonPac AS22 Eluent Concentrate (100×), 250 mL (P/N 063965; optional: for manual eluent preparation only)
- Sodium Carbonate, Anhydrous, Powder/Certified ACS (Fisher Scientific P/N S263; optional: for manual eluent preparation only)
- Sodium Bicarbonate, Powder/Certified ACS (Fisher Scientific P/N S233; optional: for manual eluent preparation only)

Sample

Alcohol, HPLC Grade, Anhydrous, 91% ethanol, 4.6% methanol, 4.7% *iso*-propanol (Fisher Scientific P/N A995)

Conditions (Applicable to Figures 1, 3, and 4)

Columns:	Dionex IonPac AG22 Guard, 4 × 50 mm Dionex IonPac AS22 Analytical, 4 × 250 mm
Eluent Source:	Dionex EGC III K_2CO_3 Cartridge with Dionex EPM III Modifier
Eluent:	4.5 mM Potassium Carbonate/ 1.4 mM Potassium Bicarbonate
Flow Rate:	1.2 mL/min
Injection Volume:	25 µL
Temperature:	30 °C
Detection:	Suppressed conductivity, Dionex AERS 500 Suppressor (4 mm), recycle mode, 31 mA
System Backpressure:	~2300 psi
Background Conductance:	~20 µS
Noise:	~5 nS/min peak-to-peak
Run Time:	14 min

Preparation of Solutions and Reagents

Chloride and Sulfate Working Standard Solutions

Prepare working standard solutions by diluting the 1000 mg/L chloride and sulfate standard solutions to the appropriate concentrations with DI water in polyethylene containers.

Sample Preparation

Caution: Ethanol is flammable; therefore, sample preparation must be performed in a fume hood. Given the trace amount of chloride and sulfate determined in this method, do not use glassware to prepare and store standard and sample solutions.

Existent Sulfate and Total Inorganic Chloride

Directly inject denatured ethanol samples.

Potential Sulfate

Mix 9.5 mL of denatured ethanol and 0.5 mL of a 30% hydrogen peroxide solution in a 20 mL polyethylene vial. Shake for at least 30 s to ensure good mixing prior to injection. The final hydrogen peroxide concentration of this mixture will be 1.5%.

Spiked Ethanol Samples for Existent Sulfate and Total Inorganic Chloride

Spike the denatured ethanol samples with appropriate volumes of 1000 mg/L chloride and sulfate standards to obtain 1, 5, and 10 mg/L each of chloride and sulfate.

Spiked Ethanol Samples for Potential Sulfate

Spike the peroxide-treated denatured ethanol samples with appropriate volumes of 1000 mg/L sulfate standards to obtain 1, 5, and 10 mg/L sulfate.

System Configuration

Refer to the product manual, Document No. 065018-04, for detailed instructions on installation of the Dionex EGC III K_2CO_3 cartridge, Dionex EPM III modifier, and Dionex EGC Carbonate Mixer. Detailed system configuration instructions are also provided in AN 1052.[6]

Refer to the product manual, Document No. 031956-08, for detailed instructions on hydration and installation of the Dionex AERS 500 suppressor.

Refer to the product manual, Document No. 065119-08, for complete instructions on installation of the Dionex IonPac AG22/AS22 column set.

For systems using manually prepared eluent, prepare the eluent solution (4.5 mM sodium carbonate/1.4 mM sodium bicarbonate) by transferring 10 mL of the Dionex IonPac AS22 Eluent Concentrate to a 1 L volumetric flask, then bring to volume using DI water. Mix well, then transfer the solution to the eluent reservoir. To prepare the eluent solution using individual sodium salts, dissolve 0.4770 g sodium carbonate and 0.1176 g sodium bicarbonate using DI water in a 1 L volumetric flask. Mix well, then transfer the solution to the eluent reservoir.

Results and Discussion

Summary of Method

This work demonstrates the performance of a Dionex AERS 500 suppressor in recycle mode for determination of chloride and sulfate in denatured ethanol by direct injection using an RFIC system. For separation, the Dionex IonPac AS22 column set was used with the same eluent conditions as in AN 1052. Figure 1, an overlay of five chromatograms, shows separation of seven common anions, indicating excellent system precision.

Ethanol Analysis

Figure 2 shows the performance of a Dionex ASRS 300 Anion Self-Regenerating Suppressor with the direct injection of an anion standard mixture and a denatured ethanol sample. Although it shows excellent separation of the anion standard (Figure 2, Chromatogram A), a baseline rise associated with the injection of the ethanol sample was observed (Figure 2, Chromatogram B). This is consistent with the data in AN 1052.

In comparison, a stable baseline was obtained when the Dionex AERS 500 suppressor was used in recycle mode. Figure 3, Chromatogram A shows a direct injection of denatured ethanol. No chloride and sulfate were found in the sample. According to ASTM D7319-13, potential sulfate refers to inorganic sulfate species present after the sample has reacted with an oxidizing agent.[2] After treating with 30% hydrogen peroxide for potential sulfate determination, <0.1 mg/L of chloride and sulfate were found in the sample (Figure 3, Chromatogram B). The denatured sample spiked with 1 mg/L each of chloride and sulfate is shown in Figure 3, Chromatogram C. The sample treated with hydrogen peroxide also did not cause a baseline rise when using the Dionex AERS 500 suppressor in recycle mode.

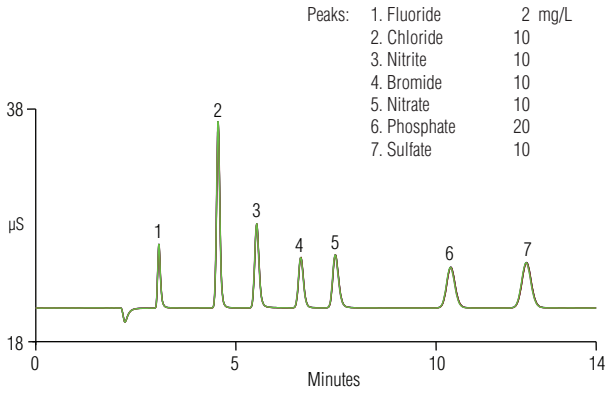

Figure 1. Overlay of five chromatograms showing the separation of seven common anions.

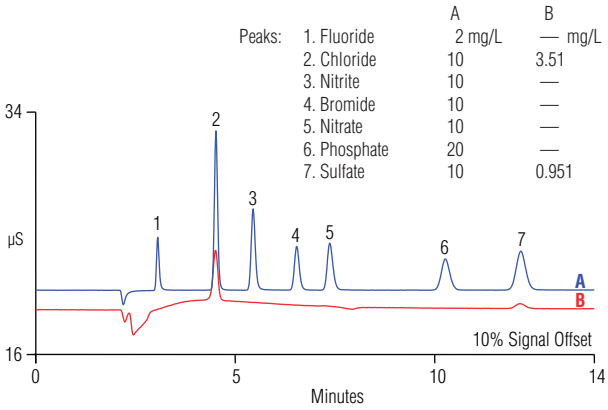

Figure 2. Separation of (A) seven common anions and (B) chloride and existent sulfate in spiked denatured ethanol. Here a Dionex ASRS 300 Suppressor (4 mm) was used in place of the Dionex AERS 500 Suppressor to show the baseline disturbance caused by injection of ethanol; all other parameters were the same as specified in the Conditions.

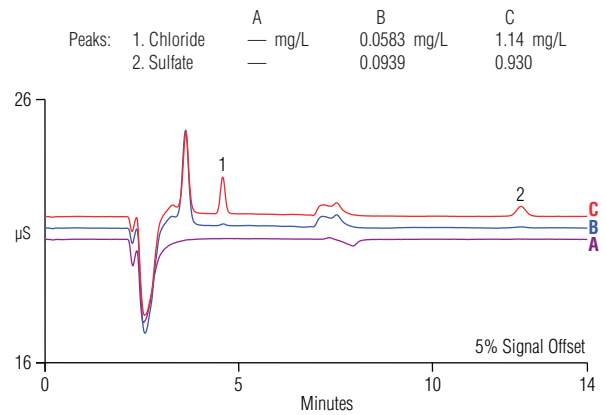

Figure 3. (A) Denatured ethanol (without treatment of hydrogen peroxide) and separation of chloride and potential sulfate in (B) unspiked and (C) spiked denatured ethanol (with treatment of hydrogen peroxide). The Dionex AERS 500 was operated in recycle mode.

Calibration, Limit of Detection (LOD), and Limit of Quantitation (LOQ)

ASTM Method D7319-13[2] was used to set the calibration ranges in this study. The calibration standards were prepared in the same fashion as in AN 1052 and each standard was injected three times.[6] Linear relationships of peak area to concentration were obtained in the range of 0.3–50 mg/L for chloride and 0.3–20 mg/L for sulfate, with coefficients of determination (r^2) of >0.99 (Table 1). The results meet the requirement specified in ASTM Method D7319-13.

To calculate the LOD and LOQ, baseline noise was first determined by measuring the peak-to-peak noise in a representative 1-min segment of the baseline where no peaks elute but close to the peaks of interest. The signal was determined from the average peak height of three injections each of 0.05 mg/L chloride and 0.1 mg/L sulfate. The LOD and LOQ were then calculated by multiplying the signal-to-noise ratio 3× and 10×, respectively. The LODs of chloride and sulfate were 13 and 45 µg/L (Table 1), respectively, approximately 2× that of the LODs reported in AN 290 and AN 1052.[5–6] In general, noise levels are lower with chemical suppression than with electrolytic suppression; however, electrolytic suppression offers simple operation with no need to handle corrosive sulfuric acid to prepare the regenerant, and the LODs are significantly lower than required for this application.[7]

Sample Precision

Short-term method precision was evaluated by seven successive injections of the spiked denatured ethanol. For total inorganic chloride and existent sulfate, the denatured ethanol was spiked with appropriate volumes of 1000 mg/L chloride and sulfate standards to obtain 1, 5, and 10 mg/L each of chloride and sulfate. The peroxide-treated denatured ethanol was spiked with 1, 5, and 10 mg/L sulfate to evaluate method precisions for potential sulfate. As shown in Table 2, retention time (RT) RSDs were <0.2% and peak area RSDs ranged from 0.3 to 5.15%, indicating good method precision.

Method Ruggedness

The baseline stability when using the Dionex AERS 500 suppressor was evaluated by continuous injections of denatured ethanol samples. In this study, a total of >400 injections of denatured ethanol were made, among which there were >300 continuous injections of denatured ethanol samples (without hydrogen peroxide treatment) spiked with 5 mg/L each of chloride and sulfate. No baseline rise or drift was observed in this study. Figure 4 shows the overlay of five chromatograms from the continuous injections of the spiked denatured ethanol.

Table 1. Calibrations, LODs, and LOQs of chloride and sulfate.

Analyte	Linear Range (mg/L)	r^2	LOD (µg/L)	LOQ (µg/L)
Chloride	0.3–50	0.9983	13	43
Sulfate	0.3–20	0.9993	45	151

Table 2. RT and peak area precisions of total inorganic chloride, existent sulfate, and potential sulfate.

Analyte	Spiked Concn (mg/L)	RT RSD (n = 7)	Peak Area RSD (n = 7)
Total Inorganic Chloride	1.0	0.04	1.67
	5.0	0.07	0.35
	10	0.13	0.31
Existent Sulfate	1.0	0.04	2.19
	5.0	0.05	3.59
	10	0.04	1.17
Potential Sulfate	1.0	0.07	3.30
	5.0	0.02	3.58
	10	0.04	5.15

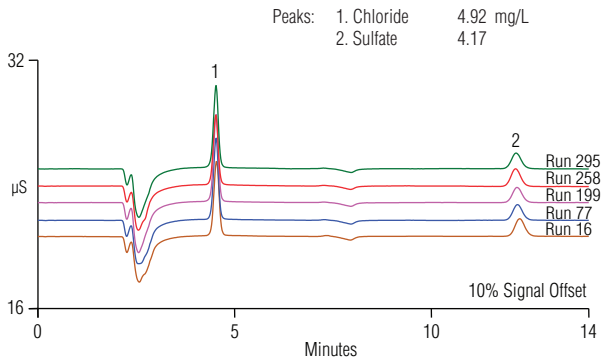

Figure 4. Overlay of five chromatograms showing the separation of chloride and existent sulfate in spiked denatured ethanol.

Conclusion

This study describes an improved method for the determination of total inorganic chloride as well as existent and potential sulfate in denatured ethanol using an RFIC system. To address the drawback of baseline rise associated with electrolytic suppression and direct injection of ethanol samples, the Dionex AERS 500 suppressor is used in place of the chemically regenerated suppressors used in previous ANs. This approach also obviates the need for matrix elimination prior to electrolytic suppression. With the Dionex AERS 500 suppressor operating in recycle mode, an RFIC system requires only a source of DI water, while a traditional IC system requires a source of carbonate/bicarbonate eluent. This allows easier operation and eliminates the handling of corrosive sulfuric acid, the manual preparation of acid regenerant, and the waste associated with suppressor chemical regeneration. This method demonstrates good retention time and peak area precisions, as well as baseline stability after >400 injections of denatured ethanol samples.

References

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