Application proof note | 002323

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Energy

Determination of potential sulfate in E85 denatured ethanol using a compact ion chromatography system

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Introduction

Alternative fuels, such as ethanol from plant sources, have gained popular interest as a substitute for non-renewable petroleum fuels. Because ethanol is also a desirable intoxicant, non-palatable solvents such as gasoline, methanol, or butanol are added to discourage consumption of ethanol fuel. This ethanol fuel is labeled “denatured ethanol.” In addition, because it is obtained from plant sources, the denatured ethanol can contain high concentrations of chloride and sulfate that can damage a vehicle’s engine due to the ions’ corrosivity. Therefore, it is important to determine the chloride and sulfate concentrations and to determine the concentration of sulfur ions that could generate sulfate after treatment with an oxidizing agent (potential sulfate). Ion chromatography (IC) with suppressed conductivity detection is demonstrated as an accurate and sensitive method for these determinations, as shown in the industry standard, ASTM D7328 method[1] and a modified ASTM D7328 method (Thermo Scientific Application Update 72996: Determination of potential sulfate in denatured ethanol)[2].

In this application proof note, the same application is demonstrated on 4 × 250 mm, Thermo Scientific™ Dionex™ IonPac™ AS22 anion-exchange column using manually prepared carbonate eluent with the suppressor upgraded to current technology. The application is facilitated by a Thermo Scientific™ Dionex™ Inuvion™ ion chromatography system.

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Method

Reagents and standards

- DI water, ASTM Type I
- Thermo Scientific™ Dionex™ AS22 Eluent Concentrate; Sodium Carbonate/Bicarbonate Concentrate (100X) (P/N 063965). To prepare eluent, dilute 10 mL of concentrate to 1 L total with DI water.
- 7.5% hydrogen peroxide solution prepared from 30% (w/w) hydrogen peroxide (certified ACS), Thermo Scientific™ (Fisher Chemical P/N H325-500). To prepare 7.5% hydrogen peroxide, add 25 mL of 30% peroxide to 75 mL DI water.
- Thermo Scientific™ Dionex™ Combined Seven Anion Standard II (P/N 057590)
- Thermo Scientific™ Dionex™ Chloride Standard (1,000 mg/L) (P/N 037159). Dilute with DI water to prepare working standards.
- Thermo Scientific™ Dionex™ Sulfate Standard (1,000 mg/L) (P/N 037160). Dilute with DI water to prepare working standards.

Samples and sample preparation

A commercial E85 ethanol fuel was obtained from a local supplier of ethanol fuel (sample A). ACS grade 80% ethanol from our laboratory was also evaluated (not shown). To determine accuracy, the recoveries of added chloride and sulfate standard were determined (3 mg/L was added to the E85 sample and 1 mg/L was added to laboratory ethanol).

The samples were prepared according to the instructions in Application Update 72996. To determine potential chloride and potential sulfate, 0.5 mL of 7.5% hydrogen peroxide was added to 2 mL sample in a 15 mL glass vial, and manually shaken for 30 s. The samples were evaporated to dryness at 65 °C using a Fisherbrand™ Isotemp™ hot block (P/N 88-860-021) and nitrogen flow head space. The dried samples were reconstituted with DI water to 2 mL and analyzed for potential chloride and potential sulfate. In this application, the ethanol samples were prepared in triplicate and blended to fill the 5 mL autosampler vial.

Instrument method parameters

Instrument	Dionex Inuvion system (P/N 22185-60108), includes column heater and pump degas module
Autosampler	Thermo Scientific™ Dionex™ AS-DV autosampler (P/N 068907) with 5 mL Thermo Scientific™ Dionex™ PolyVials™ and filter caps (P/N 038141)
Columns	Dionex IonPac AS22, 4 mm column set (P/N 064141, 064139)
Eluent	4.5 mM sodium carbonate, 1.4 mM sodium bicarbonate
Flow rate	1.2 mL/min
Inj. volume	25 µL
Column temp.	30 °C
Detection	Suppressed conductivity, Thermo Scientific™ Dionex™ ADRS 600 (4 mm) suppressor (P/N 088666CMD or 088666), 31 mA, recycle mode, constant current
Background conductance	~20 µS/cm
System backpressure	~1,800 psi (100 psi = 0.6894 MPa)
Sample prep.	Oxidize available chlorine and sulfur species with hydrogen peroxide to potential chloride and sulfate. Evaporate to dryness and reconstitute to 2 mL with DI water.
Run time	14 min
Software	Thermo Scientific™ Chromeleon™ Data System (CDS) software version 7.3.2

Results

Ethanol E85 fuel and laboratory 80% ethanol samples were analyzed. To quantify the samples, the response of chloride and sulfate to concentration were determined using triplicate injections of 1, 2, 5, 8, and 10 mg/L chloride and sulfate. The responses were shown to be linear without forcing through zero, with coefficients of determination of $r^2 = 0.9988$ and $r^2 = 0.9999$, for chloride and sulfate, respectively.

Figure 1 compares the chromatograms of (A) E85 sample, and (B) Sample A with 3 mg/L of chloride and sulfate added. Chromatogram C shows a 5 mg/L standard for comparison. The accuracy of the method was demonstrated by the 90% and 98% recoveries of 3 mg/L chloride and sulfate. This application proof note demonstrates the determination of potential chloride and sulfate in E85 ethanol fuel following the modified ASTM D7328 method on a Dionex Inuvion IC system.

Peaks:	A	B	C
1. Chloride	0.56 mg/L	3.25	5.0
2. Nitrate	–	–	–
3. Sulfate	3.60	6.28	5.0

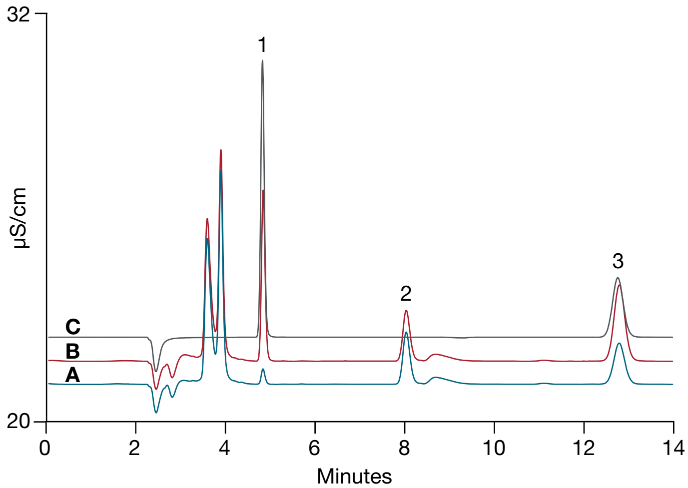

Figure 1. Potential chloride and sulfate in (A) E85 ethanol fuel, and (B) Sample A with 3 mg/L chloride and sulfate added. Compared with (C) 5 mg/L standard.

References

1. ASTM D3278, Standard Test Method for Determination of Existent and Potential Sulfate and Total Inorganic Chloride in Fuel Ethanol by Ion Chromatography Using Aqueous Sample Injection.
2. Thermo Scientific Application Update 72996: Determination of potential sulfate in denatured ethanol using modified ASTM D7328. 2019 (accessed May 2023)

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