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

Terri T. Christison and Neil G. Rumachik, Thermo Fisher Scientific, 1214 Oakmead Parkway, Sunnyvale, CA, USA, 94085

Abstract

Purpose: To determine potential sulfate in E85 denatured ethanol using a combustion IC system.

Methods: An aliquot of hydrogen peroxide was added to commercial E85 ethanol samples, which were then evaporated to dryness using a nitrogen stream and reconstituted with deionized (DI) water. The sample was then analyzed using ion chromatography (IC) with suppressed conductivity.

Results: The response of chloride and sulfate to concentration were determined to be linear without forcing through zero, with coefficients of determination of r2 = 0.9988 and r2 = 0.9999, for chloride and sulfate, respectively. The accuracy of the method was demonstrated by the 90% and 98% recoveries of 3 mg/L chloride and sulfate.

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] Here, we show the determination of potential sulfate using an updated anion-exchange column and electrolytic suppression.

Materials and methods

Sample Preparation

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 hot block 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 5 mL autosampler vials.

Instrument method parameters

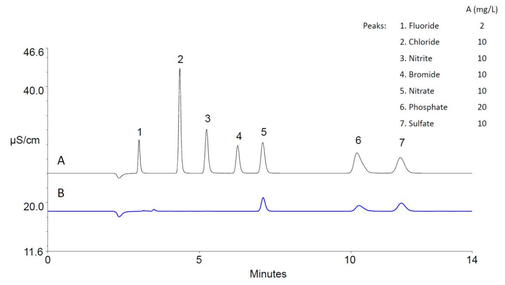
Item	Parameter
Instrument	Thermo Scientific™ Dionex™ IC system, including column heater and pump degas module
Autosampler	Thermo Scientific™ Dionex™ AS-DV autosampler
Columns	Dionex IonPac AS22, 4 mm column set
Eluent	4.5 mM sodium carbonate, 1.4 mM sodium bicarbonate
Flow rate	1.2 mL/min
Inj. volume	25 µL
Column temp.	30 ° C
Detection	Suppressed conductivity, Thermo Scientific™ Dionex™ ADRS 600 (4 mm) suppressor, 31 mA, recycle mode, constant current

Results

Separation

Figure 1 shows the separation of seven common anions and a denatured ethanol sample. Sulfate is well resolved from other common anions including fluoride, chloride, nitrite, bromide, nitrate, and phosphate within 14 min.

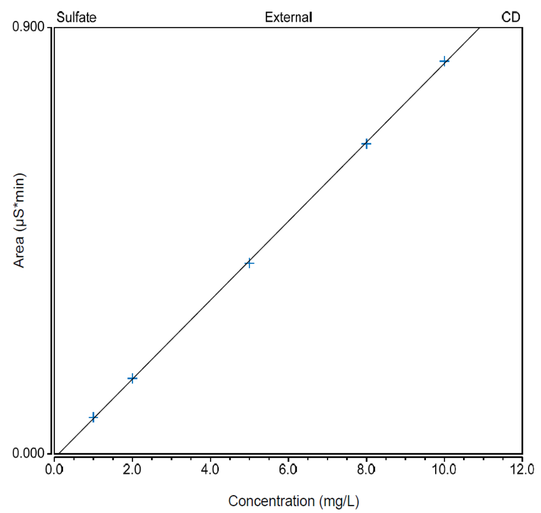
Figure 1. Separation of (A) seven common anions and (B) a denatured ethanol sample.



Calibration

To determine the content of potential sulfate in denatured ethanol samples, the peak responses to concentration were determined using triplicate injections of calibration standards. Initial analyses showed that sulfate concentrations in ethanol samples are within the range of 1–10 mg/L. A calibration curve with five concentration levels was constructed from 1 mg/L to 10 mg/L with a resulting coefficient of determination of 0.9998 (Figure 2).

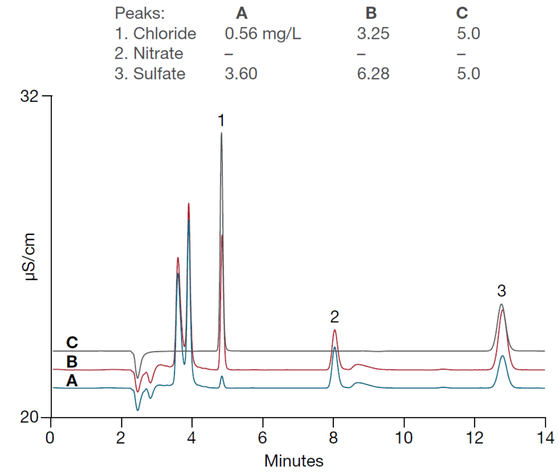
Figure 2. Sulfate calibration curve



Accuracy

Figure 3 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.

Figure 3. 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.



Reproducibility

To determine reproducibility, triplicate samples of laboratory grade denatured ethanol and E85 fuel samples were evaluated. The results shown in Table show excellent retention time and peak area reproducibility with RSDs < 0.1 for retention time and < 0.5 for concentration. Additionally, both samples were well within the ASTM D4806-13a spec of < 40 mg/L chloride and < 4 mg/L sulfate.[2]

Table 1. Accuracy and precision results for retention time and peak area of lab denatured ethanol and with 1 mg/L added chloride and sulfate.

Sample	Chloride				Sulfate			
	Retent. time (min)	RSD (%)	Conc. (mg/L)	RSD (%)	Reten. time (min)	RSD (%)	Conc. (mg/L)	RSD (%)
Denatured ethanol	4.797	0.07	0.0636	0.13	12.794	0.02	0.709	0.34
E85 fuel	4.807	0.0	0.0531	0.16	12.800	0.0	3.459	0.14

n = 3

Conclusion

This study describes a fast, simple method to determine potential sulfate in denatured ethanol according to ASTM D7328-17, an IC method for fuel ethanol. The method uses a Dionex IonPac AS22 column combined with suppressed conductivity detection on a HPIC system to validate the modified ASTM D7328 procedure which revised the potential sulfate method by adding hydrogen peroxide into the ethanol samples prior to evaporation.

More information can be found in Thermo Fisher Scientific application update 72996[3] and application proof note AP 002323.[4] See the QR code below to access these from AppsLab!

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. ASTM D4086-13a Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel.
3. Thermo Fisher Scientific Application Update 72996: Determination of potential sulfate in denatured ethanol using modified ASTM D7328 method.
4. Thermo Fisher Scientific Application Proof Note AP002323: Determination of potential sulfate in E85 denatured ethanol using a compact ion chromatography system.

Trademarks/licensing