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Determination of potential sulfate in denatured ethanol using modified ASTM D7328 method

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Goal

Validate the modified ASTM D7328 procedure for determining potential sulfate in denatured ethanol using a compact high-pressure ion chromatography (HPIC™) system with suppressed conductivity detection

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 engine performance.

This application update describes a simple ion chromatography (IC) method to determine potential sulfate in denatured ethanol. This method is consistent with the modified procedure described in ASTM D7328-17,[1] which covers an IC procedure for the determination of the total and potential inorganic sulfate and total inorganic chloride content in hydrous and anhydrous denatured ethanol to be used in motor fuel applications. To determine potential sulfate, an aliquot of hydrogen peroxide is added to the ethanol sample, which is then evaporated to dryness using a nitrogen stream, and reconstituted with deionized (DI) water. If the hydrogen peroxide is added after evaporation, the sulfate precursors might already be lost, resulting in a low recovery. This revision adds hydrogen peroxide prior to evaporation. The sample is then analyzed using IC.

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Our IC method allows for the analysis of denatured ethanol samples according to ASTM D7328-17 using a Thermo Scientific™ Dionex™ IonPac™ AS22 column set on a compact IC system (Thermo Scientific™ Dionex™ Integrion™ HPIC™ system). This document updates Thermo Scientific Application Update 194[2] and validates the revision to ASTM D7328[1].

Experimental

Equipment

- Thermo Scientific™ Dionex™ Integrion™ HPIC system including:
  - Pump
  - Degasser
  - Conductivity Detector
  - Column oven temperature control
  - Detector-suppressor compartment temperature control
  - Tablet control
- Thermo Scientific™ Dionex™ AS-AP Autosampler with Sample Syringe, 250 µL (P/N 074306) and Buffer line, 1.2 mL (P/N 074989)

HPIC consumables

- Thermo Scientific™ Dionex™ AERS™ 500 Anion Electrolytically Regenerated Suppressor, 4 mm (P/N 082540)
- Thermo Scientific™ Dionex™ IC PEEK Viper™ Fitting Tubing Assembly Kit (P/N 088798)

Software

- Thermo Scientific™ Chromeleon™ Chromatography Data System software version 7.2.8

Reagents and standards

Reagents

- Deionized (DI) water, Type I reagent grade, 18 MΩ·cm resistivity or better filtered through a 0.2 µm filter immediately before use
- Thermo Scientific™ Dionex™ AS22 Eluent Concentrate; Sodium Carbonate/Bicarbonate Concentrate (100x), 250 mL (P/N 063965)
- Hydrogen peroxide, 30% (Certified ACS), Fisher Chemical™ (Fisher Scientific P/N H325-500)

Standards

- Thermo Scientific™ Dionex™ Combined Seven Anion Standard II, 100 mL (P/N 057590)
- Sodium sulfate anhydrous, (Granular/Certified ACS), Fisher Chemical™ (Fisher Scientific P/N S421-500)

Samples

- Twenty denatured ethanol samples

IC conditions	
Columns:	Dionex IonPac AG22 Guard, 4 × 50 mm (P/N 064139) Dionex IonPac AS22 Analytical, 4 × 250 mm (P/N 064141)
Eluent source:	Dionex AS22 Eluent Concentrate (Sodium Carbonate/Bicarbonate Concentrate, 100x)
Eluent:	4.5 mM Sodium Carbonate/1.4 mM Sodium Bicarbonate
Flow rate:	1.2 mL/min
Column temperature:	30 °C
Detector compartment temperature:	20 °C
Detector temperature:	35 °C
Injection volume:	25 µL (Full Loop)
Detection:	Suppressed conductivity, Dionex AERS 500 Anion Electrolytically Regenerated Suppressor* (4 mm), recycle mode, 31 mA
System backpressure:	~1780 psi (100 psi = 0.6894 MPa)
Background conductance:	~20 µS/cm
Run time:	14 min

*Note: this can also be run with a Dionex AERS 500 Carbonate (4 mm) or Dionex ADRS 600 (4 mm) suppressor.

Preparation of standards

Stock solution

To prepare the 1000 mg/L sulfate stock solution, accurately weigh 147.87 mg of sodium sulfate anhydrous, transfer to a 100 mL volumetric flask, and fill to the mark with DI water. Mix thoroughly and store at 4 °C.

Working standard solutions calibration

Prepare the 1.0, 2.0, 5.0, 8.0, and 10 mg/L calibration standard solutions by diluting the 1000 mg/L stock standard with DI water. When the standard solutions are not in use, store at 4 °C.

Sample preparation

Caution: Ethanol is flammable; therefore, sample preparation must be performed in a fume hood.

Preparation of 7.5% hydrogen peroxide solution

Add 25 mL of 30% w/w H_2O_2 to 75 mL of degassed DI water to prepare 100 mL of 7.5% H_2O_2.

Potential sulfate

Carefully add 2.00 mL of the ethanol test specimen into a clean, dry, tared 15 mL glass vial without its screw cap closure. Add 0.5 mL of 7.5% hydrogen peroxide (final concentration of 1.5% hydrogen peroxide). Cap and shake it thoroughly for at least 30 s.

Place the uncapped vial with sample in a hot block at 65 ˚C and blow a steady stream of nitrogen over the sample. Allow the sample to dry completely; this may take 5 to 10 min. When the liquid is gone, remove the vial from the hot block and allow it to cool to room temperature (60 to 80 ˚F). According to Note 5 in ASTM D7328: "It is possible that a slight oily residue from the ethanol denaturant could remain. Do not worry about this residue if it is a thin film, as any sulfide or chloride in it will be extracted into the water phase."[1] *Note: we believe that sulfide should be sulfate.*

Carefully add 2.00 mL DI water to the dried sample. Seal the vial with a screw cap, and shake the vial vigorously to dissolve all of the solid salts.

System preparation and configuration

HPIC Integrion system

Install, hydrate, and condition the Dionex AERS 500 suppressor. Finish the system setup according to the product manuals and the Dionex Integrion system operator's manual.[3] Install and condition the guard and separation columns for 30 min prior to installing the column in line with the suppressor.

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, and then bring to volume using DI water. Mix well, and 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, and then transfer the solution to the eluent reservoir.

Results and discussion

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.

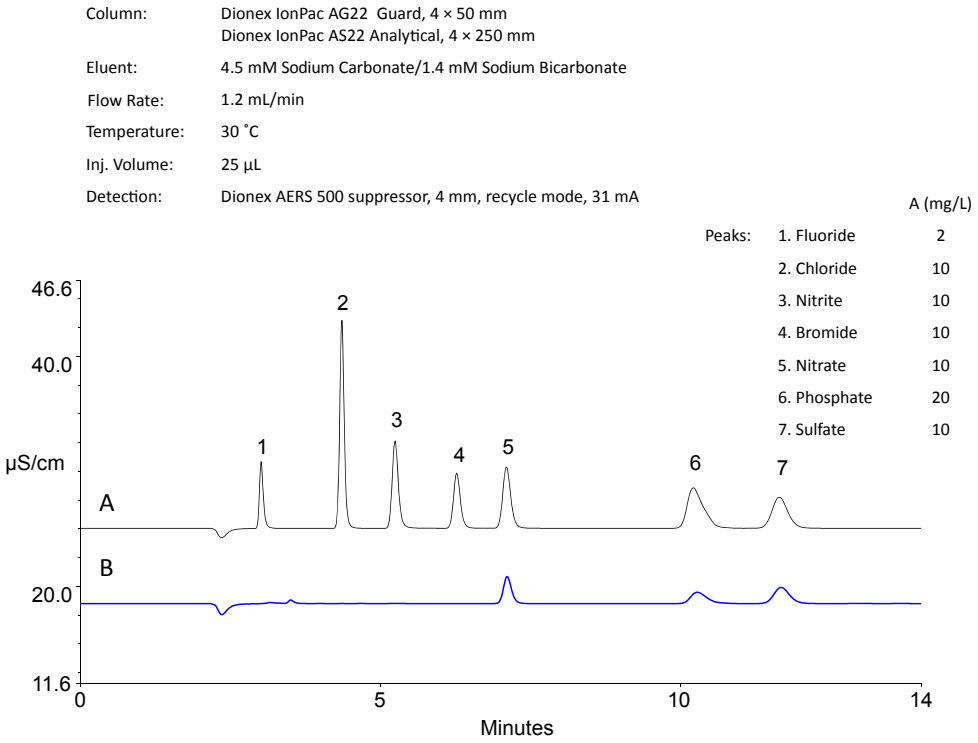

Figure 1. Separation of (A) seven common anions and (B) a denatured ethanol sample

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).

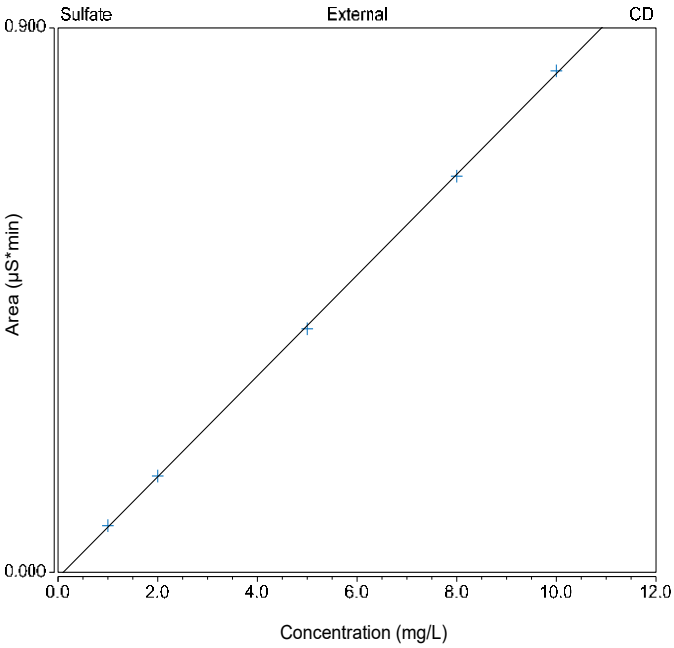

Figure 2. Sulfate calibration curve

Determination of potential sulfate in denatured ethanol

To determine potential sulfate, hydrogen peroxide was added to a denatured ethanol sample, which was then evaporated to dryness using a nitrogen stream and reconstituted with DI water. The oxidizing agent (i.e., hydrogen peroxide) is used to convert all the sulfur species to sulfate. In our study, twenty denatured ethanol samples were analyzed using a compact high-pressure ion chromatography system. The amounts of measured potential sulfate in the samples are reported in Table 1.

Table 1. The contents of potential sulfate in denatured ethanol samples

Sample ID	Potential Sulfate (mg/L)
Sample 1	5.39
Sample 2	5.35
Sample 3	5.35
Sample 4	5.34
Sample 5	5.33
Sample 6	5.39
Sample 7	5.32
Sample 8	5.38
Sample 9	6.09
Sample 10	5.56
Sample 11	5.42
Sample 12	5.38
Sample 13	5.42
Sample 14	5.37
Sample 15	5.30
Sample 16	5.40
Sample 17	5.35
Sample 18	5.35
Sample 19	5.40
Sample 20	5.50

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.

References

1. ASTM D7328 – 17, Standard Test Method for Determination of Existent and Potential Inorganic Sulfate and Total Inorganic Chloride in Fuel Ethanol by Ion Chromatography Using Aqueous Sample Injection.
2. Thermo Fisher Application Update 194: Determination of Existent and Potential Sulfate and Total Inorganic Chloride in Denatured Ethanol by Direct Injection Using an RFIC System. Sunnyvale, CA, 2014.
3. Thermo Fisher Scientific. Product Manual for Dionex ERS 500 suppressor. Doc No. 031956, Sunnyvale, CA, 2017.

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