

Application News

High Performance Liquid Chromatography

No.L384

Determination of Chloride and Sulfate in Fuel Ethanol by Ion Chromatography

Recently, ethanol has received much attention as an alternative fuel. It is mixed with gasoline as a fuel in automobiles.

Residues are known to form in the engine when the ethanol fuel contains chlorides and sulfates, and this causes sluggish performance of the engine.

ASTM D4806-08a (American Society for Testing and

Materials (United States)) is a standard that regulates ethanol fuel, and ASTM D7319-07 specifies that ion chromatography is to be used as the official method for analyzing chlorides and sulfates in ethanol fuel.

Here we present an example of analysis using the Prominence HIC-SP suppressor-type ion chromatograph which pertains only to this analytical method.

■ Analysis of Standard Solution

According to ASTM D4806-08a, the ethanol fuel mixed with gasoline in automobiles is to contain less than 40 mg/kg (32 mg/L) of chlorides, and a concentration of less than 4 mg/kg of sulfates.

ASTM D7319-07, in which ion chromatography is the officially designated analytical method, specifies that analysis be conducted by direct injection into a

suppressor-type ion chromatograph, and that the standard solution be prepared by dissolving sodium chloride and sodium sulfate in ultra pure water.

Fig. 1 shows a chromatogram of the chloride ion and sulfate ion standard solution (10 mg/L each). The analytical conditions that were used are shown in Table 1.

Table 1 Analytical Conditions

Instrument	: Prominence HIC-SP
Column	: Shim-pack IC-SA2 (250 mm L. × 4.6 mm I.D.)
Guard Column	: Shim-pack IC-SA2(G) (10 mm L. × 4.6 mm I.D.)
Mobile Phase	: 12 mmol/L Sodium hydrogencarbonate 0.6 mmol/L Sodium carbonate
Flow Rate	: 1.0 mL/min
Column Temp.	: 30 °C
Injection Vol.	: 20 µL
Detection	: CDD-10A _{SP} (Suppressor)

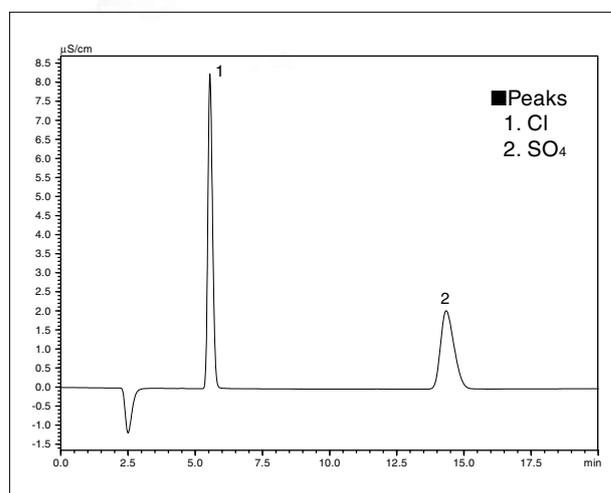


Fig. 1 Chromatogram of a Standard Mixture of Chloride and Sulfate (10 mg/L each)

■ Linearity

Fig. 2 shows the calibration curve for the chloride ion and sulfate ion at concentrations from 0.1 mg/L to 20 mg/L. Excellent linearity was obtained for both the chloride ion and sulfate ion, with a correlation coefficient (R^2) greater than 0.999 for each ion.

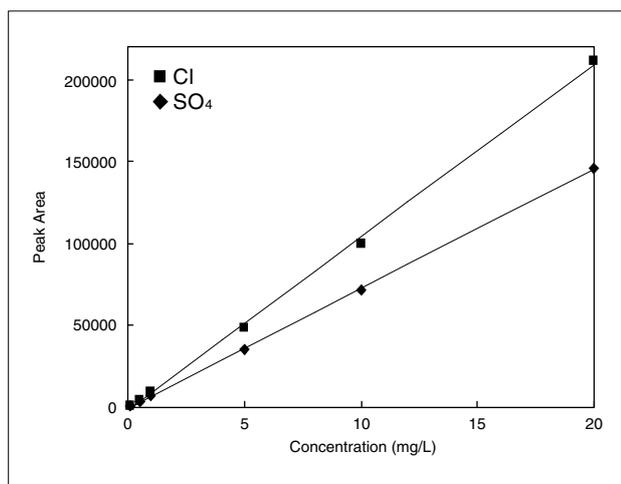


Fig. 2 Calibration Curve

■ Sample Preparation

The following two items are specified with respect to ethanol fuel in ASTM D7319-07.

- (1) Analysis of the sulfate ion and chloride ion are to be conducted using direct injection of the ethanol fuel without sample preparation.
- (2) The total amount of sulfate ion formed from oxidation of a sulfur compound in the presence of an oxidant is to be analyzed.

The preparation procedure for number (2) is shown in Fig. 3.

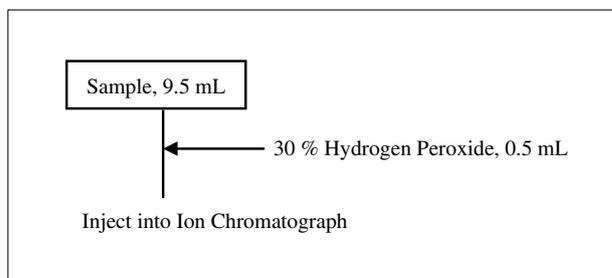


Fig. 3 Sample Preparation

■ Analysis of Chloride and Sulfate in Ethanol

Fig. 4 shows the results of analysis of a commercially available ethanol sample prepared by adding chloride and sulfate standard solution.

(Above-mentioned analysis item (1))

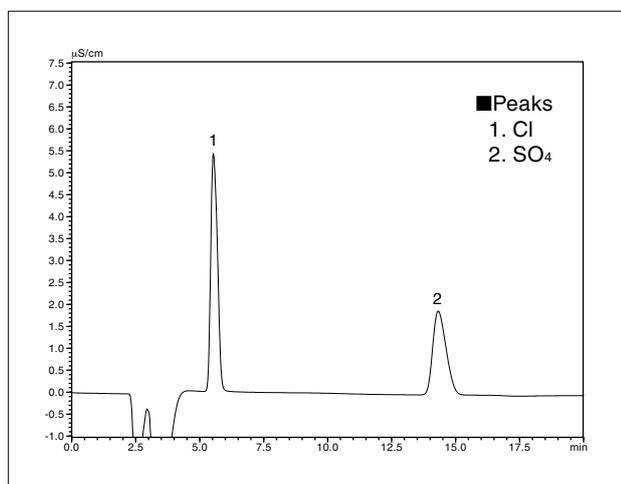


Fig. 4 Chromatogram of Ethanol Sample (spiked at 10 mg/L each)

Fig. 5 shows the results of analysis of a sample consisting of the ethanol prepared according to Fig. 3, to which was added 30 % hydrogen peroxide aqueous solution and a standard solution of chloride and sulfate ions. In this case, analysis was conducted only for the sulfate ion.

(Above-mentioned analysis item (2))

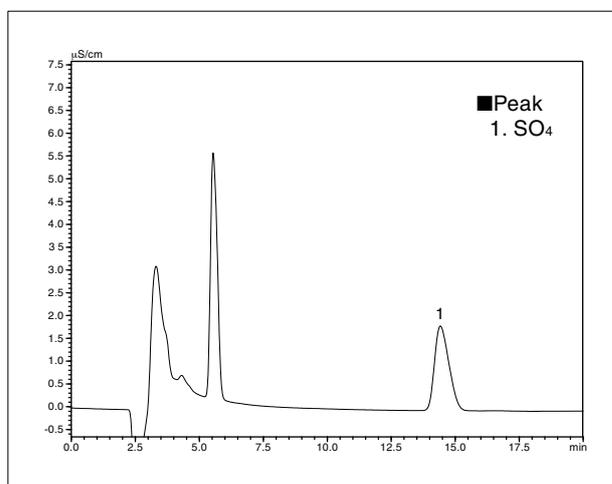


Fig. 5 Chromatogram of Ethanol Sample After Oxidation by Hydrogen Peroxide (spiked at 10 mg/L each)

Reference Materials

- 1) ASTM D 4806-08a : Standard Specification for 4806 Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel
- 2) ASTM D 7319-07 : Standard Test Method for Determination of Total and Potential Sulfate and Inorganic Chloride in Fuel Ethanol by Direct Injection Suppressed Ion Chromatography

NOTES:

*This Application News has been produced and edited using information that was available when the data was acquired for each article. This Application News is subject to revision without prior notice.



SHIMADZU CORPORATION, International Marketing Division

3, Kanda-Nishikicho 1-chome, Chiyoda-ku, Tokyo 101-8448, Japan Phone: 81(3)3219-5641 Fax: 81(3)3219-5710
Cable Add.:SHIMADZU TOKYO