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Application News

Ion Chromatograph HIC-ESP

Analysis of Chloride and Sulfate Ions in Fuel Ethanol

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User Benefits

- Easily evaluate chloride and sulfate ions in fuel ethanol in accordance with ASTM D 7319-07.
- Data with good linearity and reproducibility can be obtained.
- Reduces analysis time and improves usability.

■ Introduction

Ethanol for fuel is an alternative fuel derived from plants and is an environmentally friendly renewable energy source. It is mixed with gasoline and used as a fuel for automobiles. However, when chloride and sulfate ions are present in fuel ethanol, they form residues in the engine and cause engine malfunction.

ASTM D 4806-08a[1)] specifies standards for fuel ethanol, which specify that the concentration of chloride ion in fuel ethanol is 40 mg/kg or less and that ASTM D 7319-07[2)] describes an analytical method for measuring chloride and sulfate ions in fuel ethanol using ion chromatography.

of sulfate ion is 4 mg/kg or less. This article introduces chloride and sulfate ions analysis using the suppressor ion chromatograph HIC-ESP in accordance with ASTM D 7319-07.

■ Analysis of Standard Samples

Table 1 shows the analytical conditions, and Fig. 1 shows the measurement results for standard solutions of chloride ion and sulfate ion. The ion chromatograph HIC-ESP is equipped with an ICDS-40A suppressor for anion analysis. ICDS™-40A is an electrodialysis suppressor using an ion exchange membrane. By regenerating the suppressor in parallel with the analysis, the analysis cycle time can be reduced, and the simple flow path configuration improves operability.

Table 1 Analytical Conditions

System:	HIC-ESP
Column:	Shim-pack™ IC-SA2*1 (250 mm × 4.0 mm I.D., 9 µm)
Guard Column:	Shim-pack IC-SA2(G)*2 (10 mm × 4.6 mm I.D., 9 µm)
Mobile Phase:	0.6 mmol/L sodium carbonate 12.0 mmol/L sodium hydrogen carbonate
Flowrate:	1.0 mL/min
Column Temp.:	30 °C
Injection Volume:	5 µL
Vial:	Shimadzu Vial, LC, 4 mL polypropylene*3
Detection:	Conductivity

*1 P/N: 228-38983-91
*2 P/N: 228-38983-92
*3 P/N: 228-31537-91

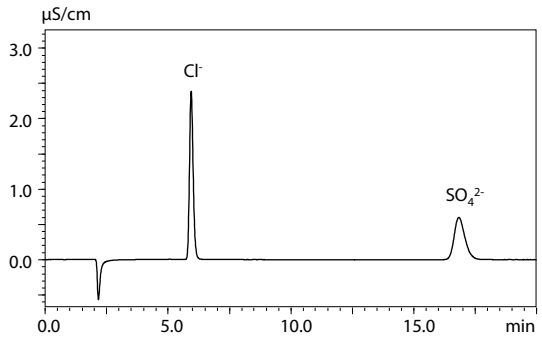

Fig. 1 Chromatogram of Chloride ion and Sulfate Ion Standard Solutions

■ Linearity

Calibration curves were prepared using 7 calibration points for chloride ion and 6 calibration points for sulfate ion in the concentration range in accordance with ASTM D 7319-07. Table 2 shows the calibration curve range and contribution ratio (r^2) for chloride and sulfate ions, and Fig. 2 shows the calibration curve for chloride and sulfate ions. The contribution ratio (r^2) of the calibration curve was over 0.999 for both chloride ion and sulfate ion, and good linearity was obtained.

Table 2 Calibration Curve Range and Contribution Ratio (r^2) for Chloride and Sulfate Ions

	Calibration Curve Range (mg/L)	Contribution Ratio (r^2)
Cl	0.3 - 50	≥ 0.999
SO_4	0.3 - 20	≥ 0.999

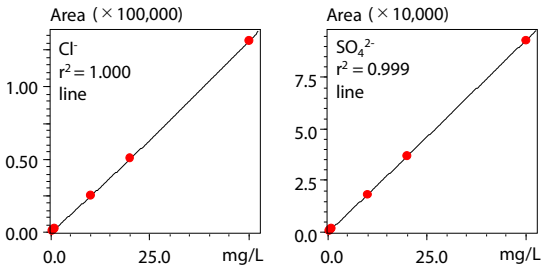

Fig. 2 Calibration Curves for Chloride and Sulfate Ions

■ Sample Preparation

ASTM D 7319-07 specifies the following two analyses for fuel ethanol.

Item 1: Analysis of the sulfate ion and chloride ion are to be conducted using direct injection of the ethanol fuel without pretreatment.

Item 2: The total amount of sulfate ion formed from oxidation of a sulfur compound in the presence of an oxidant is to be analyzed.

In this article, in order to compare the quantitative values of items 1 and 2, the same amount of ethanol as the hydrogen peroxide of item 2 was added to the sample of item 1, which was not originally pretreated, and the amount of fuel ethanol was made the same. Figure 3 shows the sample preparation method for item 2, and Table 3 shows the notation of ion species according to ASTM D 7319-07.

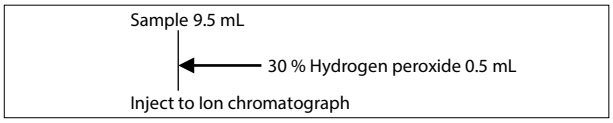

Fig. 3 Sample Preparation Method (Item 2)

Table 3 Description of Ion Species in ASTM D 7319-07

Notation	Ion species
Total inorganic chloride	Chloride ion measured without pretreatment
Total inorganic sulfate	Sulfate ions measured without pretreatment
Potential inorganic sulfate	Sulfate ions measured in the presence of oxidants

■ Analysis of Chloride and Sulfate Ions in Fuel Ethanol

Chloride ion and sulfate ion standard solutions were added to commercial fuel ethanol at 10 mg/L each. Three types of samples were measured, and the results were compared: those without pretreatment (Item 1), those with pretreatment (Item 2), and those without added ions. Table 4 shows the samples and the ion species described in ASTM, Fig. 4 shows the comparison of fuel ethanol chromatograms, Table 5 shows the quantitative results for fuel ethanol before the addition of chloride and sulfate ions (sample 1), and Table 6 shows the quantitative results and recovery rate of fuel ethanol after addition of chloride and sulfate ions (sample 2, sample 3).

Both chloride and sulfate ions showed good peak shapes with and without oxidizing agents. The peak at the retention time of about 4 minutes is derived from impurities in fuel ethanol.

The repeatability of each sample was evaluated by the relative standard deviation (%RSD) of the concentrations analyzed five times in a row. Table 6 shows the results. Good reproducibility was confirmed for both chloride and sulfate ions. The reproducibility of sulfate ion measured in the presence of an oxidizing agent tended to be better than that of sulfate ion measured without pretreatment. Fig. 5 shows the superimposition of the chromatogram obtained by five consecutive analyses of the sample in item 2.

The sample injection volume was measured at 5 µL, which is less than 20 µL as described in ASTM, and sufficient reproducibility was obtained.

Table 4 Samples and the Ion Species Described in ASTM

Sample		Ion Species Described in ASTM	
		Cl^-	SO_4^{2-}
Sample 1	Fuel ethanol only	-	-
Sample 2	Item 1 + chloride and sulfate 10 mg/L	Total inorganic chloride	Total inorganic sulfate
Sample 3	Item 2 + chloride and sulfate 10 mg/L	-	Potential inorganic sulfate

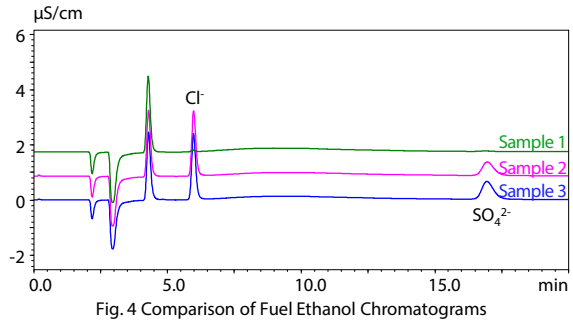

Fig. 4 Comparison of Fuel Ethanol Chromatograms

Table 5 Quantitative Results for Fuel Ethanol before Addition of Chloride and Sulfate Ions (Sample 1)

	Concentration (mg/L)	Conversion value*4 (mg/kg)
Chloride	0.473	0.577
Sulfate	0.377	0.460

*4 To convert from 4 mg/L to mg/kg, we used 0.82 as the specific gravity of fuel ethanol.

Table 6 Quantitative Results and Recovery Rate of Fuel Ethanol after Addition of Chloride and Sulfate Ions (Sample 2, Sample 3)

	Concentration (mg/L)	Conversion value*4 (mg/kg)	Recovery rate (%)
Total inorganic chloride	9.92	12.1	94.5
Total inorganic sulfate	8.38	10.2	80.1
Potential inorganic sulfate	10.9	13.3	105

Table 7 Repeatability of Quantitative Results (N = 5)

	Repeatability of quantitative results (%RSD)
Total inorganic chloride	0.31
Total inorganic sulfate	8.10
Potential inorganic sulfate	0.29

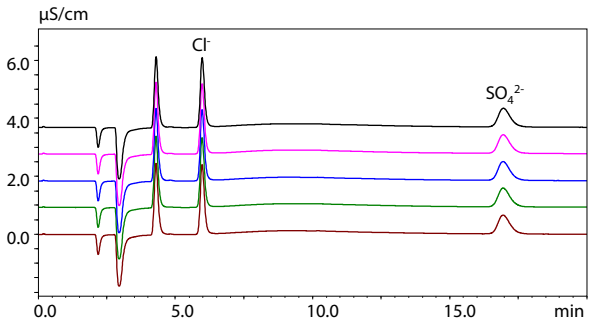

Fig. 5 Chromatograms Analysis Five Times (Sample 3)

■ Conclusion

This article introduced the analysis of chloride and sulfate ions in fuel ethanol based on ASTM D 7319-07. By using the ion chromatograph HIC-ESP, chloride and sulfate ions could be measured in accordance with the specifications. In addition, by using an electrodialysis suppressor ICDS-40A using an ion exchange membrane, peak diffusion generated in the suppressor can be suppressed, and analysis can be performed stably.

<Reference>
1) ASTM D4806-08a, Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel, ASTM International, West Conshohocken, PA, 2008, www.astm.org
2) ASTM D7319-07, Standard Test Method for Determination of Total and Potential Sulfate and Inorganic Chloride in Fuel Ethanol by Direct Injection Suppressed Ion Chromatography, ASTM International, West Conshohocken, PA, 2007, www.astm.org

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