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Ion Chromatograph Nexera™ IC

raBit

Application News

Analysis of Chloride and Sulfate Ions in Bioethanol Using the Nexera IC Ion Chromatograph

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User Benefits

- Analysis of chloride and sulfate ions in fuel ethanol can be conducted in accordance with ASTM D7319-22[1].
- Accurate quantitative determination, exhibiting excellent linearity and repeatability, can be achieved at concentration levels significantly below the limits specified by the ASTM criteria.

■ Introduction

First-generation bioethanol produced from raw materials such as corn and sugarcane has been utilized to achieve carbon neutrality. However, research and development for second-generation bioethanol produced from non-food, cellulose-based raw materials is also underway to avoid competition with food crops. In Japan, eight companies, including Toyota Motor Corporation, have formed the "Research Association of Biomass Innovation for Next Generation Automobile Fuels" (raBit) to advance research on next-generation bioethanol technologies. Shimadzu participates as a supporting member and promotes research and development through analytical technology cooperation.

It is known that the presence of chloride and sulfate ions in fuel ethanol can form engine residue, leading to reduced engine performance. ASTM D4806-25[2] specifies fuel ethanol quality as criterion of chloride ion must not exceed 6.7 mg/kg and that of sulfate ion must not exceed 4 mg/kg. ASTM D7319-22 includes test methods for chloride and sulfate ions in fuel ethanol using ion chromatography.

In this application, we present an example of the analysis of chloride and sulfate ions in bioethanol using the Nexera IC in accordance with ASTM D7319-22.

■ Analysis of mixed standard solution

Table 1 shows the analytical conditions, and Fig. 1 shows the resulting chromatogram of mixed standard solution of chloride and sulfate ions. The instrument used was a Nexera IC suppressor-type ion chromatograph.

Table 1 Analytical conditions

System	:	Nexera IC
Column	:	Shim-pack IC-SA2 *1 (250 mm×4.0 mm I.D., 9 µm)
Guard Column	:	Shim-pack IC-SA28(G)*2 (10 mm×4.6 mm I.D., 9 µm)
Mobile Phase	:	1.8 mmol/L sodium carbonate 1.7 mmol/L sodium hydrogen carbonate
Flow Rate	:	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

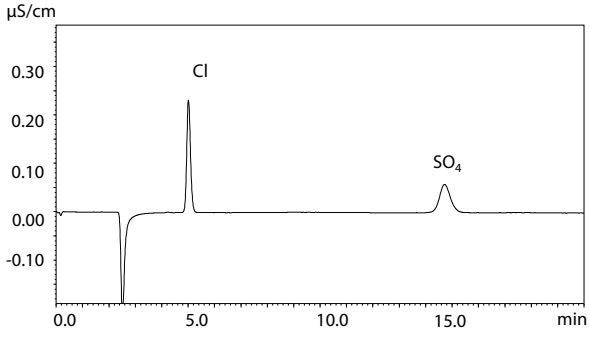

Fig. 1 Chromatogram of mixed standard solution at 1 mg/L of chloride and sulfate ions

■ Linearity

A calibration curve was created using seven calibration levels for chloride ion and six for sulfate ion within the concentration ranges specified in ASTM D7319-22. Table 2 shows the respective calibration levels and coefficients of determination (r^2) for chloride and sulfate ions. It was confirmed that the r^2 values of the calibration curves for both ions were 0.99 or more, as specified in ASTM D7319-22.

Table 2 Calibration levels and coefficients of determination (r^2)

ions	Calibration levels (mg/L)	Coefficients of determination (r^2)
Cl	0.3, 0.5, 1, 5, 10, 20, 50	≥ 0.999
SO_4	0.3, 0.5, 1, 5, 10, 20	≥ 0.999

■ Pretreatment

ASTM D7319-22 states that samples can be analyzed without any pretreatment for chloride and sulfate ions in fuel ethanol.

However, a pretreatment of the addition of hydrogen peroxide is required to analyze sulfur compounds (potential inorganic sulfate) that are oxidized to sulfate ions in the presence of the oxidant. The pretreatment method is shown in Fig. 2, and the notation of ion species in accordance with ASTM D7319-22 is shown in Table 3.

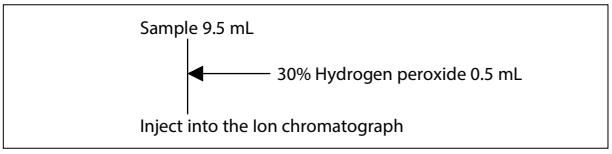

Fig. 2 Pretreatment procedure (For potential inorganic sulfate measurement)

Table 3 Notation of ion species in accordance with ASTM D7319-22

Ion species	Description	Pretreatment
Total inorganic chloride	Chloride ion without pretreatment	None
Total inorganic sulfate	Sulfate ion without pretreatment	
Potential inorganic sulfate	Sulfate ion with oxidant	Addition of hydrogen peroxide

■ Analysis of bioethanol samples and spike and recovery test

Fig. 3 shows the analytical results for bioethanol sample and standard-spiked bioethanol sample, to which a mixed standard solution of chloride and sulfate ions was spiked to make concentration of 1 mg/L for each in the sample solution. The concentrations and recovery rates obtained for the spiked sample are shown in Table 4. Calibration curves for quantitative determination were prepared for both chloride and sulfate ions using six levels less than 20 mg/L as shown in Table 2 to consider the quantitative accuracy in the low-concentration range.

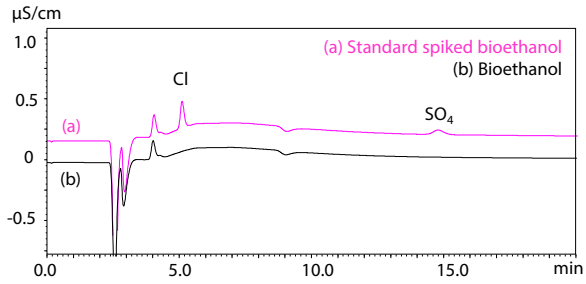

Fig. 3 Comparison of chromatograms of bioethanol and standard spiked bioethanol (without pretreatment)

Table 4 Result of spike and recovery test

Ion species	Conc. (mg/L)	Content *4 (mg/kg)	Recovery (%)
Total inorganic chloride	1.05	1.33	105
Total inorganic sulfate	0.71	0.90	71

*4 Gravity 0.79 for bioethanol was employed for the conversion of unit from mg/L to mg/kg

The sample and the standard spiked sample, which were treated with hydrogen peroxide solution to measure sulfate ion (potential inorganic sulfate) in the presence of the oxidant, were analyzed. The analytical results are shown in Fig. 4, and the concentration and recovery rate obtained are shown in Table 5. The addition of the oxidant resulted in better recovery rate for sulfate ion compared to that of the sample without pretreatment. This would be due to unstable dissociation condition of sulfate ion in organic solvent and/or denaturation.

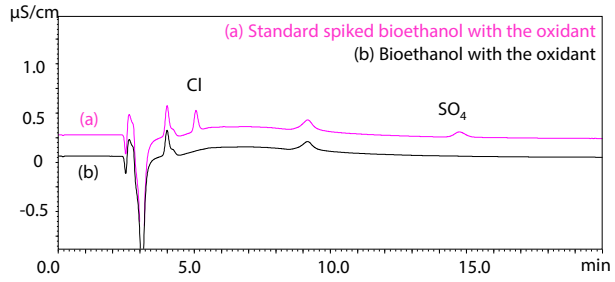

Fig. 4 Comparison of chromatograms for bioethanol and standard spiked bioethanol (with the oxidant)

Table 5 Result of spike and recovery test with the oxidant

Ion species	Conc. (mg/L)	Content*5 (mg/kg)	Recovery (%)
Potential inorganic sulfate	1.01	1.35	95.8

*5 Gravity 0.79 for bioethanol was employed for the conversion of unit from mg/L to mg/kg

■ Repeatability in standard spiked sample

The repeatability of each spiked sample was evaluated using the relative standard deviation (% RSD). Fig. 5 shows the results of six consecutive analyses of spiked bioethanol, and Fig. 6 shows the results of six consecutive analyses of spiked bioethanol with the oxidant. Furthermore, Table 6 shows the retention time and peak area repeatabilities for the six consecutive analyses. The addition of the oxidant improved the repeatability of sulfate ions, as observed in the spike and recovery test.

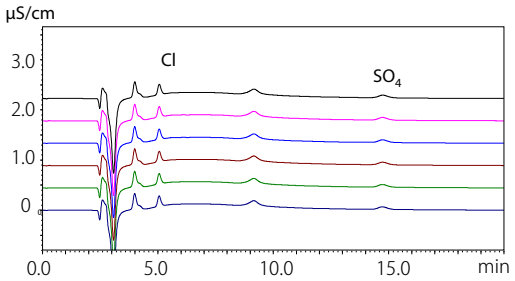

Fig. 5 Result of six consecutive analyses of standard spiked bioethanol

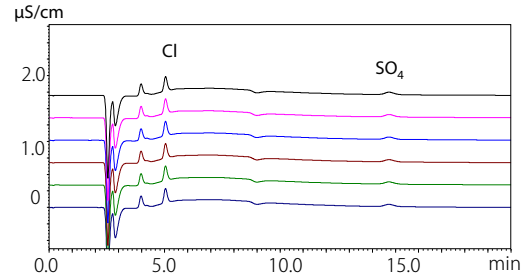

Fig. 6 Result of six consecutive analyses of standard spiked bioethanol with the oxidant

Table 6 Retention time and peak area repeatabilities for six consecutive analyses of standard spiked bioethanol

Ion species	Retention time (%RSD)	Area (%RSD)	Pretreatment
Total inorganic chloride	0.02	0.51	None
Total inorganic sulfate	0.02	5.56	None
Potential inorganic sulfate	0.04	0.77	Addition of hydrogen peroxide

■ Conclusion

Chloride and sulfate ions in bioethanol were determined using a Nexera IC system in accordance with ASTM D7319-22. The method offers high sensitivity, linearity, and repeatability, enabling reliable quantification at concentrations well below ASTM-specified limits, thus supporting effective quality control and regulatory compliance of fuel ethanol.

<Acknowledgements>

We would like to express our sincere gratitude to raBit (Research Association of biomass Innovation for Next Generation Automobile Fuels) for providing the samples and assisting with the interpretation of the analytical results.

<References>

1) ASTM D7319-22, 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
2) ASTM D4806-25a, 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

<Related Applications>

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