

Determination of Sulfate and Chloride in Ethanol by Ion Chromatography

Ethanol used as a blending agent in gasoline can be contaminated with chloride and sulfate that form plugging deposits and cause corrosion in automobile engines. If sulfate and chloride concentrations exceed the limits defined in ASTM Specification D 4806, then the ethanol may be rejected as unacceptable for use in automotive spark-ignition engine fuel. ASTM International has proposed that a new ion chromatography (IC) method be adopted to measure this critical product specification for ethanol intended for automotive spark-ignition engine fuel use.¹

There are several sample preparation methods available to determine anions in various organic solvents such as ethanol. Those include:

- Direct injection (the method presented here).²
- Dilution with 1:1 (v:v) deionized water or mild oxidizing agent (1–2% hydrogen peroxide solution) for trace level (ppb–ppm) dilution.²
- Evaporation and reconstitution in deionized water for trace level (ppb–ppm) depending on the amount evaporated.³
- Matrix elimination/preconcentration for ultra trace level (ppt–ppb) anion determinations.⁴

Reagent-Free™ Ion Chromatography (RFIC™) and IC methods capable of in-line elimination of the organic solvent.

This application note describes the simplest, most direct method to measure mg/L concentrations of chloride and sulfate anions in ethanol. Sulfate and chloride are determined in 15 min by using IC with eluent generation and suppressed conductivity detection, on either an IonPac® AS14A or IonPac AS18 column. The ion chromatography method allows direct injection of the sample and is sensitive enough to monitor compliance with ASTM Specification D 4806.

The methods described in this application note were validated by Dionex during participation in the ASTM interlaboratory collaborative study to determine precision and bias for the new Standard Test Method.

EQUIPMENT

A Dionex IC system consisting of:

ICS-3000, ICS-2000 (if eluent generation is used), or ICS-3000, ICS-2000, ICS-1500, ICS-1000, or ICS-90 (if eluent is manually prepared)

AS Autosampler (an AS40 can also be used)

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EXPERIMENTAL I (HYDROXIDE ELUENT)

Consumables for the IonPac AS18 Method

IonPac AS18, 4 mm, Analytical, 4 × 250 mm
(Dionex P/N 060549)
IonPac AG18, 4 mm, Guard, 4 × 50 mm
(Dionex P/N 060551)
EluGen® II Potassium Hydroxide Cartridge (EGC II
KOH) (Dionex P/N 058900)
CR-ATC (Dionex P/N 060477)
Anion MicroMembrane Suppressor (AMMS® III)
(Dionex P/N 061561)
Vial Kit, 10 mL, polystyrene (Dionex P/N 055058)
Syringe filters (Gelman IC Acrodisc 0.2 µm, P/N 4483)

Reagents and Standards For The IonPac AS18 Method

Prepare all solutions from analytical reagent grade
chemicals (when available).
Deionized water with a specific resistance of
17.8 MΩ-cm or greater. Filter through a 0.2-µm
filter immediately before use.
Chloride Standard, 1000 mg/L, (Dionex P/N 037159)
Sulfate Standard, 1000 mg/L, (Dionex P/N 037160)
Ethanol, reagent alcohol, EM Science AX0445-1
Sodium hydroxide, NaOH, 50% w/w (Fisher Scientific
SS254-500)
Sulfuric acid, 98% (J.T. Baker InstraAnalyzed 9673-33)

IonPac AS18 Eluent Solution

Fill the plastic eluent reservoir with reagent water
and maintain an inert helium atmosphere of 3–5 psi in
the eluent reservoir. Generate 30 mM KOH eluent on-
line by using the EG Eluent generator system with an
EGC II KOH cartridge.

Alternatively, prepare 30 mM NaOH by pipetting
2.40 g of 50% (w/w) aqueous NaOH from the middle
portion of the reagent bottle into a 1-L volumetric flask
containing about 500 mL of degassed reagent water. Do

not shake the 50% (w/w) NaOH bottle or pipette from
the top of the solution where sodium carbonate may have
formed. Dispense the aliquot of NaOH below the surface
of the water to avoid the introduction of carbon diox-
ide from the air into the eluent. Bring to volume with
degassed reagent water, mix, and degas by sparging with
helium or sonicating under vacuum for 10 min. Transfer
to a plastic eluent reservoir and maintain an inert helium
atmosphere of 3–5 psi in the reservoir. (Atmospheric
carbon dioxide readily dissolves in dilute basic solutions,
forming carbonate. Carbonate contamination of eluents
can affect the retention times of the analytes, resulting
in performance that may not be as high as that achieved
with the eluent generator).

Regenerant Solution

Prepare 50 mN H₂SO₄ by adding 5.7 mL
(10.2 g) of concentrated sulfuric acid (18 M) to
4 L of reagent water. Transfer cautiously to the 4-L
pressurizable plastic bottle included in the Suppressor
External Regen Kit.

Conditions for the IonPac AS18 method

Columns	IonPac AS18 Analytical and Guard
Eluent:	30 mM potassium hydroxide (EG or manually prepared 30 mM NaOH)
Flow Rate:	1 mL/min
Temperature:	30 °C
Inj. Volume:	10 µL
Detection:	Suppressed conductivity, AMMS III with 50 mN sulfuric acid
Conductance:	1–2 µS
Noise:	<3 nS/min peak-to-peak
Backpressure:	1600 psi (adjust to ~2300 psi for EG)
Run Time:	15 min

EXPERIMENTAL II (CARBONATE/BICARBONATE ELUENT)

Consumables for IonPac AS14A method

IonPac AS14A, 7 μ m, Analytical,
4 \times 250 mm (Dionex P/N 056904)
IonPac AG14A, 7 μ m, Guard, 4 \times 50 mm
(Dionex P/N 056897)
EluGen II Carbonate Cartridge (EGC II K₂CO₃)
(Dionex P/N 058904)
EGC Carbonate Mixer Kit, 4 mm (Dionex P/N 061686)
EPM Electrolytic pH Modifier (Dionex P/N 063175)
Suppressor, AMMS III (Dionex P/N 061561)
Vial Kit 10-mL polystyrene (Dionex P/N 055058)
Syringe filters (Gelman IC Acrodisc 0.2 μ m, P/N 4483)

Reagents and Standards For IonPac AS14A Method

Prepare all solutions from analytical reagent grade chemicals (when available).
Deionized water, chloride standard, sulfate standard, ethanol, and sulfuric acid as listed for the IonPac AS18 method
AS14A Eluent Concentrate; Sodium Carbonate/Bicarbonate (100x) (Dionex P/N 056937)

IonPac AS14A Eluent Solution

Fill the plastic eluent reservoir with reagent water. Generate 8 mM sodium carbonate/1 mM sodium bicarbonate eluent on-line by using the EG Eluent generator system with an EGC II K₂CO₃ cartridge, EPM and EGC Carbonate Mixer Kit.

Alternatively, pipet 10.0 mL of AS14A eluent concentrate into a 1-L volumetric flask and dilute to a final volume of 1 L using deionized water with a specific resistance of 17.8 M Ω -cm or greater. Mix well and transfer to the eluent reservoir.

Conditions for IonPac AS14A method

Columns: IonPac AS14A, 7 μ m Analytical, 4 mm
IonPac AG14A, 7 μ m Guard, 4 mm
Eluent: 8 mM sodium carbonate/1 mM sodium bicarbonate (EG or manually prepared)
Flow Rate: 1.2 mL/min

Temperature: 30 $^{\circ}$ C
Inj. Volume: 25 μ L
Detection: Suppressed conductivity, AMMS III with 50 mN sulfuric acid
Conductance: 24–26 μ S
Noise: 1–2 nS/min peak-to-peak
Backpressure: ~1900 psi (adjust to ~2300 psi for EG)
Run Time: 35 min

EXPERIMENTAL I AND II

Stock Standard Solutions

Purchase certified 1000 mg/L chloride or sulfate anion standards from Dionex or another reputable source. Or, to prepare a 1000 mg/L solution of chloride anion, dissolve 1.6485 g of sodium chloride in reagent water and dilute to 1 L. To prepare a 1000 mg/L solution of sulfate anion, dissolve 1.8141 g of potassium sulfate in reagent water and dilute to 1 L. Store in high-density polyethylene or polypropylene bottles at 4 $^{\circ}$ C. These stock standards are stable for at least one month.

Calibration Standard Solutions

Caution: Ethanol is flammable. Work under a hood.

To prepare chloride and sulfate calibration standards, use a calibrated pipet to deliver the appropriate volume (Table 1) of the 1000 mg/L stock standard into a 100-mL volumetric flask and dilute to volume with reagent grade ethanol. Prepare calibration standards daily; our observation is that ethanolic solutions containing greater than 10 mg/L sulfate exhibit a loss in sulfate peak area within one day.

Table 1. Preparation of Calibration Standards

Anion Concentration (mg/L)	Volume of 1000 mg/L chloride stock standard (mL)	Volume of 1000 mg/L sulfate stock standard (mL)	Final Volume (mL)
50 (Cl ⁻ only)	5.000	—	100
20	2.000	2.000	100
10	1.000	1.000	100
5	0.500	0.500	100
1	0.100	0.100	100
0.5	0.050	0.050	100
0.1	0.010	0.010	100

Samples

Caution: Ethanol is flammable. Work under a hood.

Obtain samples in accordance with ASTM Practice D 4057 or Practice D 4177. Store in high-density polyethylene (HDPE) containers rinsed with deionized water until free of ionic contamination, with tight sealing closures to prevent evaporation. Filter samples through IC Acrodisk filters into clean autosampler vials prior to injection.

System Preparation and Setup

Verify that the pump flow rate is within specifications and recalibrate if necessary. Verify that the conductivity cell constant is within specifications and recalibrate if necessary. Consult the pump or detector manuals for procedural details.

Install and condition the EluGen II cartridge as directed in the manual. (For instructions on installation and use, see the Product Manual for the EGC II K_2CO_3 Cartridge, Eluent pH modifier and Carbonate/Bicarbonate Mixer, Document No. 031840, or QuickStart for the EGC II KOH Cartridge, Document No. 031909).

Install the analytical and guard columns. If using eluent generation, make sure that the system pressure displayed by the pump is between 2300 and 2800 psi when pumping eluent under the method conditions, so the degas assembly can effectively remove electrolysis gas from the eluent. If necessary, install backpressure coils supplied with the EGC ship kit to adjust the system pressure to between 2300 and 2800 psi. Because the system pressure can rise over time, trim the backpressure coil as necessary to maintain system pressure under 3000 psi. Do not exceed 3000 psi or the degas assembly tubing may rupture.

Prepare the AMMS III for use by hydrating the eluent chamber. Pump approximately 5 mL of regenerant (50 mN H_2SO_4) through the REGEN IN port. Pump approximately 5 mL of eluent through the ELUENT IN port. Allow the suppressor to sit for approximately 20 min to fully hydrate the suppressor screens and membranes. Install the AMMS III in the external pressurized

bottle mode by following the Installation and Troubleshooting Instructions for the AMMS III, Document No. 031727. (The Displacement Chemical Regenerant Mode can also be used; it is described in the same document). Adjust the head pressure on the external regenerant reservoir to deliver a flow rate of 5–8 mL/min. (If convenient, couple a three-inch piece of 0.01-inch i.d. PEEK tubing to the very end of the suppressor waste line, then trim it until a pressure of 10–15 psi in the regenerant reservoir provides a flow of 5–8 mL/min.)

Equilibrate the column with eluent for 30 min, and analyze a system blank of reagent alcohol. The system should display the background conductance and noise listed above under “Conditions” for the appropriate column.

Inject a standard containing 5 mg/L each chloride and sulfate in ethanol. The column is equilibrated when two consecutive injections of the standard produce the same retention time for sulfate. Confirm that the resulting chromatogram resembles the ion chromatogram of the 10 mg/L standard shown in Figure 1 (if using the AS14A method) or Figure 2 (if using the AS18 method).

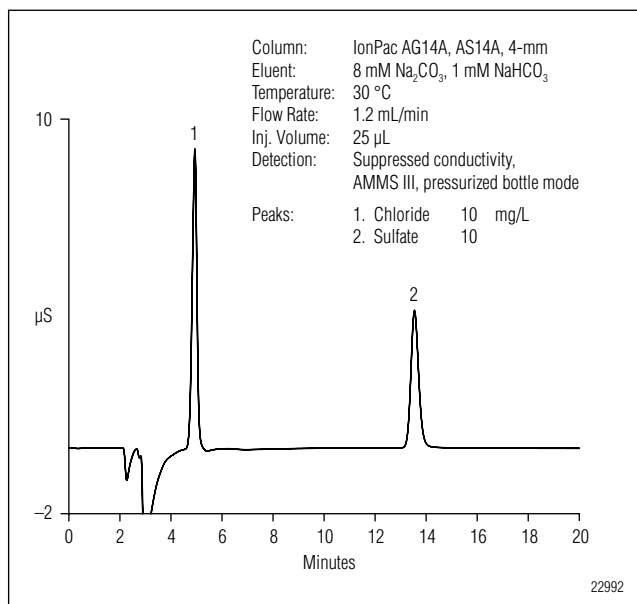


Figure 1. Overlay of three ion chromatograms of chloride and sulfate anions in ethanol determined on the Dionex IonPac AS14A column. Sample is an ethanolic standard containing 10 mg/L each chloride and sulfate. See text for conditions.

RESULTS AND DISCUSSION

Chromatography

Figure 1 is an overlay of three ion chromatograms of a standard containing 10 mg/L each of chloride and sulfate anions in ethanol, obtained by using the optimized conditions described above for the AS14A column set with a manually prepared eluent. Figure 2 was produced on the AS18 column set with an EG produced eluent. Both the AS18 and AS14A columns provide baseline resolution of chloride and sulfate from common anions that might be encountered in ethanol samples. This is demonstrated in Figure 3 with common anions spiked into ethanol and separated on an AS14A column.

Dionex ion chromatography will perform the necessary determination of chloride and sulfate in ethanol by direct injection. Continuous suppression using the AMMS III ensures a stable baseline for each injection and the dynamic nature of the AMMS III ensures sufficient suppression capacity regardless of the eluent strength, unlike other suppressor principles used elsewhere. The reproducibility obtained with the AMMS III is clearly seen in Figures 1 and 2, where overlays of repeated injections exhibit consistent peak heights and no baseline drift.

Users of AutoSuppression® may observe the formation of ethanol oxidation products, formate and acetate, that may interfere with chloride quantitation (not sulfate) when performing undiluted ethanol injections. Sample evaporation/reconstitution⁴ eliminates this phenomena, permitting normal use of AutoSuppression.

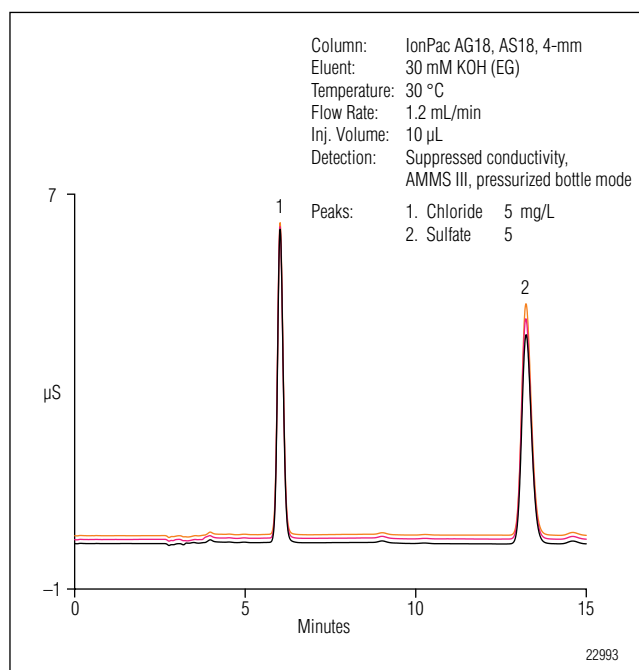


Figure 2. Overlay of three ion chromatograms of chloride and sulfate anions in ethanol determined on the Dionex IonPac AS18 column (chromatograms offset by 1%). Sample is an ethanolic standard containing 5 mg/L each chloride and sulfate. See text for conditions.

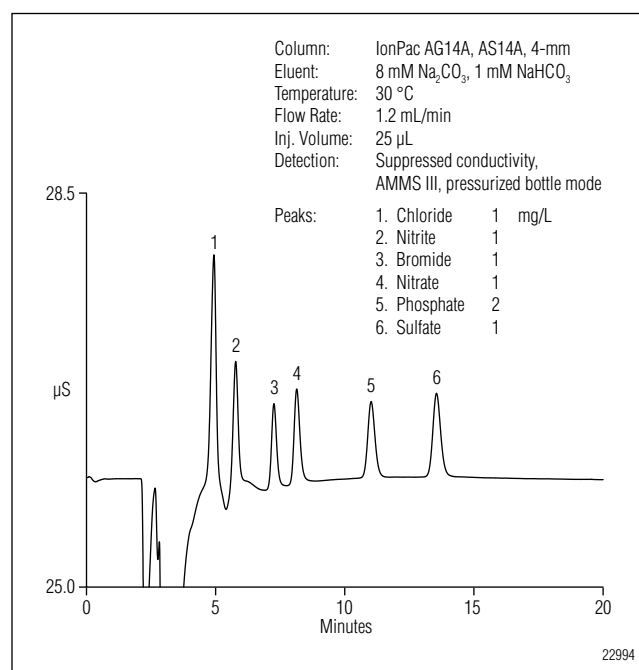


Figure 3. Ion chromatogram of common anions in ethanol determined on the Dionex IonPac AS14A column. Sample is an ethanolic standard containing common anions at the concentrations shown. See text for conditions.

Method Performance

Table 2 summarizes the calibration data for a typical calibration curve for the AS14A application obtained by injecting calibration standards from 0.1 to 10 mg/L for sulfate, and from 0.1 to 20 mg/L for chloride. The calibration curve is linear with a correlation coefficient of 0.99 or better. Concentrations of sulfate greater than 10 mg/L in ethanol exhibited a rapid loss in peak area/height with time, caused by either poor solubility or reactivity of the sulfate anion.

Method precision is good for samples containing less than 10 mg/L sulfate, as shown in Table 3. Precision suffers for solutions containing greater than 10 mg/L sulfate because of the poor solubility or reactivity noted above.

Figures 4 and 5 are examples of ethanol samples analyzed during the ASTM interlaboratory collaborative to validate this method for monitoring compliance with ASTM ethanol specification D 4806. The sample analyzed in Figure 5 was spiked with chloride and sulfate, whereas the sample shown in Figure 4 was not.

Table 2. Calibration Data For Chloride and Sulfate in Ethanol		
	Chloride Peak Area ($\mu\text{S} \cdot \text{min}$)	Sulfate Peak Area ($\mu\text{S} \cdot \text{min}$)
0.1	0.0166	0.0174
0.5	0.0812	0.0678
1	0.1662	0.1546
5	0.8726	0.6850
10	1.8267	1.4959
20	3.9101	—
Linearity (r^2)	0.9981	0.9979

Table 3. Peak Area Precision for Chloride and Sulfate in Ethanol		
Anion Concentration (mg/L)	Chloride Precision (% RSD, n=7)	Sulfate Precision (% RSD, n=7)
1	0.48	0.44
10	0.49	1.64

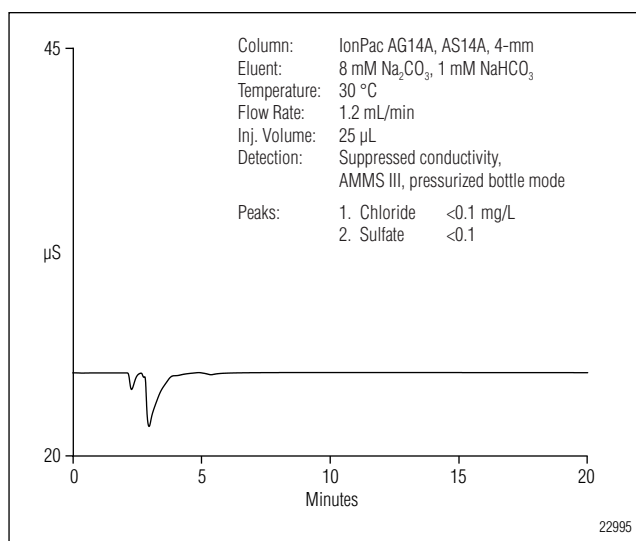


Figure 4. Ion chromatogram of chloride and sulfate anions in ethanol determined on the Dionex IonPac AS14A column. Sample provided for the ASTM interlaboratory collaborative study is ethanol denatured with natural gasoline, unleaded gasoline, or ketone. See text for conditions.

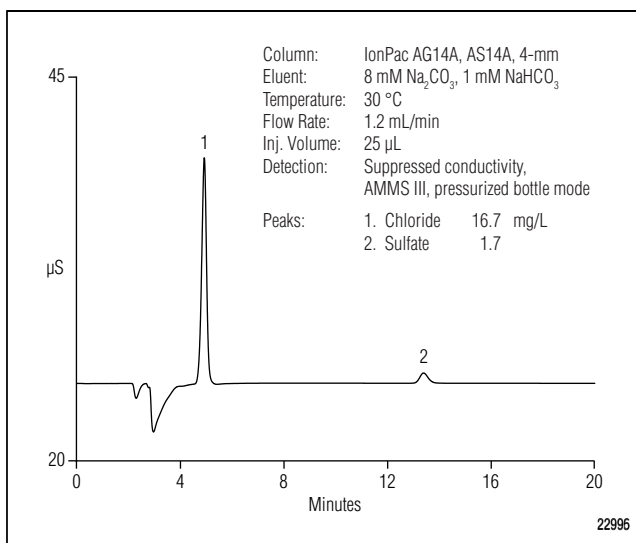


Figure 5. Ion chromatogram of chloride and sulfate anions in ethanol determined on the Dionex IonPac AS14A column. Sample, provided for the ASTM interlaboratory collaborative study, is ethanol denatured with natural gasoline, unleaded gasoline or ketone and spiked with aqueous stock standards containing chloride and sulfate. See text for conditions.

SUMMARY

In less than 15 min, both methods presented here measure chloride and sulfate concentrations in ethanol with sub-mg/L detection limits. Both methods flexibly employ RFIC systems, eluent generation, or manually prepared eluents and regenerants as needed. Each user is free to choose the approach best suited to the individual laboratory.

REFERENCES

1. ASTM Specification D 4806, ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428.
2. Standard Test Method WK9828 for Determination of Inorganic Chloride and Sulfate in Ethanol by Direct Injection Suppressed Ion Chromatography, ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428.
3. Standard Test Method WK9829 for the Determination of Inorganic Chloride and Potential Sulfate in Fuel Ethanol, Finished Spark Ignition Fuels and their Components by Ion Chromatography using Aqueous Sample Injection.
4. *Determination of Trace Anions in Organic Solvents*. Application Note 85; Dionex Corporation, Sunnyvale, CA, 2004.

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