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Determination of Chloride and Sulfate in Methanol Using Ion Chromatography

INTRODUCTION

The increase in costs and demand for petroleum combined with potential supply shortages have led to renewed concerns about worldwide dependence on oil.¹ In addition, burning fossil fuels produces carbon monoxide and other pollutants hazardous to human health. One strategy to alleviate some of these concerns is the use of alternative fuels, such as methanol, ethanol, biodiesel, or other similar fuel products.

Methanol, the simplest alcohol, is normally produced from natural gas or methane. Production from biomass has recently been explored as an alternative, and interest has been growing for production of methanol from coal.^{2,3} Natural gas is more uniformly spread throughout the world compared to oil and there is an abundance of coal, which could support the energy needs of the world for hundreds of years. Therefore, the economics of methanol is more favorable versus oil, which makes it a viable replacement for petroleum fuels used for transportation.⁴ China has committed to using methanol as an alternative to petroleum fuel, and is implementing production on a large scale to take advantage of their coal reserves.⁵

Contamination of methanol fuel with inorganic anions, such as chloride and sulfate, may lead to reduced engine performance due to the formation of plugging deposits and cause corrosion in engine components that are in contact with the fuel. Ion chromatography (IC) with suppressed conductivity detection is the simplest

approach for determining inorganic anions in alcohol fuels, enabling the detection of the target anions with a single injection, reasonable analysis times, and minimal or no sample preparation.

Dionex provides a wide range of solutions for the determination of anions from parts per billion (ppb) to parts per million (ppm) concentrations in alcohols. Dionex Application Update 161 and Application Note 175 demonstrate that IC, with and without eluent generation, easily determines chloride and sulfate in neat and blended ethanol fuels.^{6,7} Dionex Application Update 163 demonstrates the determination of low ppb concentrations of inorganic anions in organic solvents using preconcentration and matrix elimination.⁸

This application note presents a simple and direct approach for determining chloride and sulfate in methanol using a Reagent-Free™ IC system with eluent generation (RFIC-EG™ system). Chloride and sulfate are determined in less than 12 min using an IonPac® AS24 column with an electrolytically generated potassium hydroxide eluent and suppressed conductivity detection. The described method permits the direct injection of the sample with detection limits in the single digit ppb concentration range. The linearity, limits of detection and quantitation, and precision of chloride and sulfate determination in methanol are demonstrated. This RFIC-EG system method delivers a fast and automated assay of chloride and sulfate in methanol.

EQUIPMENT

Dionex ICS-3000 Reagent-Free™ Ion Chromatography system with Eluent Generation (RFIC-EG™ system)^a consisting of:

- SP Single Pump or DP Dual Pump module
- EG Eluent Generator module
- DC Detector/Chromatography module (single or dual temperature zone configuration)
- AS Autosampler

EluGen® EGC II KOH cartridge (P/N 058900)

Continuously-Regenerated Anion Trap Column, CR-ATC (P/N 060477)

Chromeleon® 6.8 Chromatography Workstation

Polystyrene injection vials with caps and septa, 10 mL (Dionex P/N 055058)

REAGENTS AND STANDARDS

Deionized water, Type I reagent grade, 18 MΩ-cm resistivity or better

Chloride Standard, 1000 mg/L, (Dionex P/N 037159)

Sulfate Standard, 1000 mg/L, (Dionex P/N 037160)

Methanol, HPLC grade, Burdick and Jackson (Cat.# 230-4)

CONDITIONS

Columns: ^b	IonPac AS24 Analytical, 2 × 250 mm (P/N 064153) IonPac AG24 Guard, 2 × 50 mm (P/N 064151)
Eluent:	28 mM KOH
Eluent Source:	EGC II KOH with CR-ATC
Flow Rate: ^b	0.3 mL/min
Injection Volume:	5 µL (full loop)
Temperature:	30 °C (column compartment) 30 °C (detector compartment)
Detection:	Suppressed conductivity, ASRS® 300 (2 mm), AutoSuppression® external water mode, 21 mA
Background	
Conductance:	<0.80 µS
Noise:	1–2 nS
System	
Backpressure:	~2200 psi

^aAny Dionex RFIC-EG system can be used for this application.

^bAlternatively, an IonPac AG18, AS18 2 mm column set can be used for this application, using the conditions listed in Figure 3. A 4 mm column set can also be used, but injection volume and flow rate must be increased fourfold.

PREPARATION OF REAGENTS AND STANDARDS

Eluent Solution

Generate the potassium hydroxide eluent online by pumping high quality deionized water (18 MΩ-cm resistivity or better) through the EGC II KOH cartridge. Chromeleon software will track the amount of KOH used and calculate the remaining cartridge lifetime.

Alternatively, prepare 28 mM NaOH by carefully pipetting 2.24 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 deionized water. Dispense the NaOH below the surface of the deionized water to avoid introducing carbon dioxide from the air into the eluent. Bring to volume, mix thoroughly, and degas by sparging with helium or sonicating under vacuum for 10 min. Transfer to a plastic reservoir and maintain an inert helium atmosphere of 3–5 psi in the reservoir. (Note: Carbon dioxide readily dissolves in dilute hydroxide solutions to form carbonate. Carbonate contamination can lead to poor retention time reproducibility of the target analytes, resulting in performance that may not be as high as achieved with an eluent generator.)

Stock Standard Solutions

Purchase certified 1000 mg/L chloride and sulfate standards from Dionex or another reputable source. Alternatively, prepare a 1000 mg/L chloride stock solution by dissolving 0.1648 g of sodium chloride in deionized water and dilute to 100 mL. To prepare a 1000 mg/L sulfate stock solution, dissolve 0.1479 g of sodium sulfate in deionized water and dilute to 100 mL. Store the stock solutions in high-density polyethylene or polypropylene bottles at 4 °C. These stock standards are stable for at least one month.

Calibration Standard Solutions

Caution: Methanol is flammable. Work under a hood.

To prepare chloride and sulfate calibration standards, use a calibrated pipette to deliver the appropriate volume of the 1000 mg/L stock standard into a 100 mL volumetric flask. Add deionized water to a total aqueous volume of 10 mL and bring to volume with HPLC grade methanol (Table 1). For example, to prepare 10 mg/L each of chloride and sulfate, pipette 1 mL of each 1000 mg/L stock standard into a 100 mL volumetric flask, add 8 mL of deionized water, bring to volume with HPLC grade methanol, and mix well. Prepare calibration standards daily. A sulfate standard prepared in methanol will exhibit a loss in peak area response within a day.

SAMPLE PREPARATION AND SETUP

Install backpressure tubing in place of the column set to produce a total backpressure of 2000–2500 psi at a flow rate of 1 mL/min. Install an EGC II KOH cartridge and condition the cartridge by setting the KOH concentration to 50 mM at 1 mL/min for 30 min. After completing the conditioning process, disconnect the backpressure tubing temporarily installed in place of the column set. Install a CR-ATC between the EGC II KOH cartridge and the EGC degas. Hydrate the CR-ATC prior to use by following the instructions outlined in the *EluGen Cartridge Quickstart Guide*.⁹

Prepare the ASRS 300 (2-mm) for use by hydrating the eluent and regen chambers with deionized water. Allow the suppressor to stand for at least 20 min to fully hydrate the suppressor screens and membranes. For more information on installing the ASRS, consult the *SRS 300 Product Manual*.¹⁰ Install the IonPac AG24 and AS24 columns in place of the backpressure tubing and configure the ASRS 300 suppressor for use in the external water mode. (Note: The ASRS 300 in the recycle mode will not work for this application due to a significant rise in the baseline at the beginning of each injection, which interferes with the determination of chloride and sulfate.) Equilibrate the column with 28 mM KOH for at least 30 min prior to performing any injections. Inject the same source of deionized water used for the preparation of the calibration standards. An equilibrated system has background conductance of <0.8 μS and baseline noise <2 nS.

Table 1. Preparation of Calibration Standards

Anion Concentration (mg/L)	Volume of 1000 mg/L Chloride Stock (mL)	Volume of 1000 mg/L Sulfate Stock (mL)	Volume of Deionized Water (mL)	Total Volume (mL)
0.1	0.01	0.01	9.98	100
0.5	0.05	0.05	9.90	100
1.0	0.10	0.10	9.80	100
5.0	0.50	0.50	9.00	100
10.0	1.00	1.00	8.00	100

Inject a standard containing 5 mg/L each of chloride and sulfate in methanol. The column is equilibrated when two consecutive injections of the standard produce identical retention times for chloride and sulfate. Confirm that the chromatogram resembles the separation shown in Figure 1.

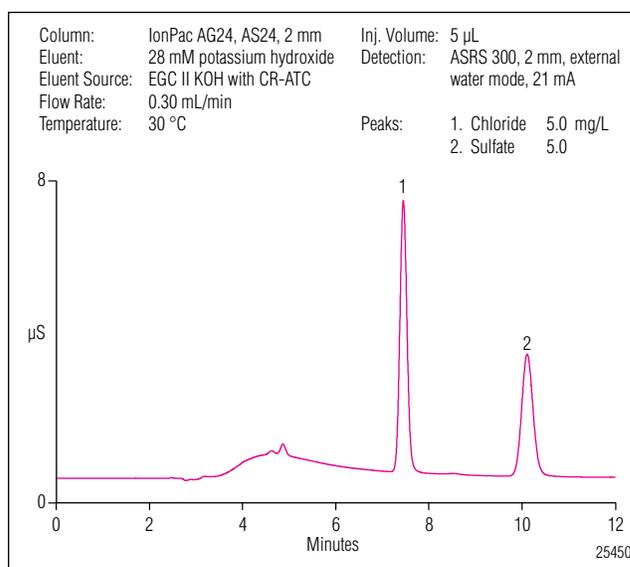


Figure 1. Separation of 5 mg/L chloride and sulfate in HPLC grade methanol on the IonPac AS24 column.

RESULTS AND DISCUSSION

The direct injection of untreated methanol samples is the simplest approach for determining chloride and sulfate. This procedure eliminates costly and time consuming sample preparation commonly used to determine anions in solvents. (See Application Note 175⁷ for a summary of sample preparations.) Figure 2 shows an overlay of 10 injections of 1 mg/L each of chloride and sulfate in methanol obtained using the optimized conditions with the AS24 column and an electrolytically generated potassium hydroxide eluent. The AS24 column allows fast (12 min) runs, but retention time stability may decrease with heavy usage. For long term analysis, the IonPac AS18 is recommended, using the conditions described in Figure 3. Typical run times with the AS18 column are approximately 20 min.

The use of the ASRS 300 in the external water mode further simplifies the method by avoiding the preparation of sulfuric acid regenerent solutions commonly required for chemical suppression with other suppressor devices. The suppressor cannot be used in the recycle mode when performing direct injections of methanol samples, which produce oxidation products that interfere with the determination of chloride and sulfate. To use the suppressor in the recycle mode, follow the matrix elimination procedure described in Application Update 161.

Table 2 summarizes the linearity obtained by injecting calibration standards from 0.1 to 10 mg/L chloride and sulfate in methanol. The calibration curves were linear with correlation coefficients (r^2) greater than 0.999. Due to the poor stability of sulfate in methanol, probably due to poor solubility, a loss of peak area response was observed over time. This decrease in response appeared to occur at a faster rate for sulfate concentrations of 10 mg/L or greater. Therefore, it is strongly recommended to prepare calibration standards fresh daily and immediately analyze samples if possible. The limits of detections (LODs) for chloride and sulfate were determined by analyzing a blank methanol solution and determining the baseline noise. For this application, the noise was <2 nS, which produced LODs of 3 and 8 $\mu\text{g/L}$ for chloride and sulfate, respectively. Table 2 summarizes the LODs and limits of quantification (LOQs) determined using the optimized conditions described earlier.

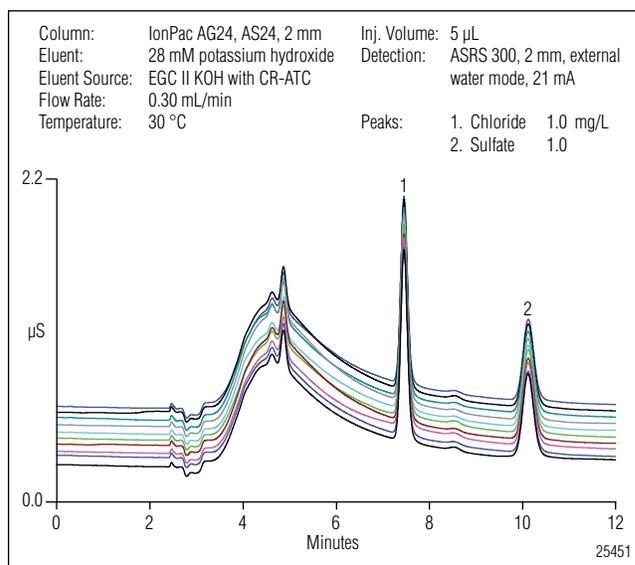


Figure 2. Overlay of 10 chromatograms of chloride and sulfate in HPLC grade methanol on the IonPac AS24 column (chromatograms offset by 2%).

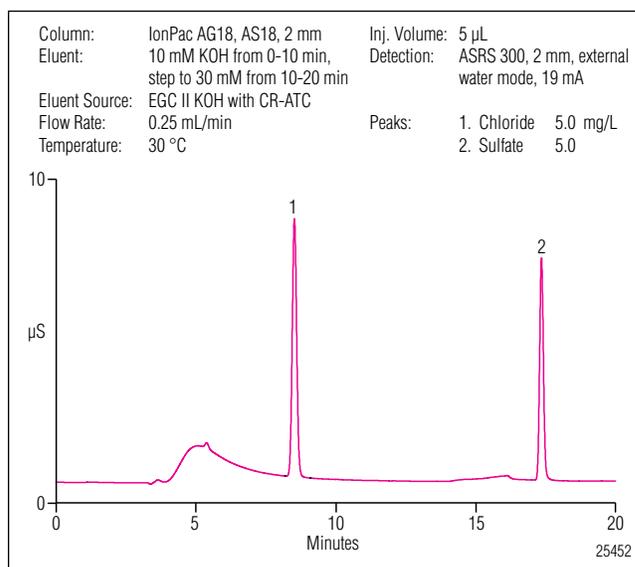


Figure 3. Separation of 5 mg/L chloride and sulfate in HPLC grade methanol on the IonPac AS18 column.

Table 2. Linearity, LODs, and LOQs

Analyte	Range (mg/L)	Linearity (r^2)	Est LOD ^a ($\mu\text{g/L}$)	Est LOQ ^b ($\mu\text{g/L}$)
Chloride	0.1–10	0.9998	3	10
Sulfate	0.1–10	0.9997	8	26

^aestimated from $3 \times \text{S/N}$

^bestimated from $10 \times \text{S/N}$

The retention time and peak area precisions were determined by performing replicate injections of 1 mg/L and 10 mg/L each of chloride and sulfate in methanol. The retention time precisions for chloride and sulfate for 10 replicate injections of the solutions were $\leq 0.03\%$ (data not shown). Table 3 summarizes the peak area precisions for the replicate injections. As expected, the higher sulfate concentration produced a higher peak area RSD due to the gradual peak area loss discussed above. However, the peak area precisions were comparable between chloride and sulfate when prepared at 1 mg/L each.

CONCLUSION

This application note describes a fast, simple, automated direct injection approach for determining chloride and sulfate in methanol. Either the IonPac AS24 or AS18 column can be used successfully for the analysis of methanol samples with run times of 12 min and 20 min, respectively. The eluent generator produces a high purity KOH eluent that together with the ASRS 300 enables the detection of single-digit ppb concentrations of chloride and sulfate in methanol.

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Table 3. Peak Area Precision for Chloride and Sulfate in Methanol

Anion Concentration (mg/L)	Chloride Peak Area Precision (RSD, n = 10)	Sulfate Peak Area Precision (RSD, n = 10)
1	0.61	0.53
10	0.40	1.9

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