Determination of total fluorine, chlorine, and sulfur in aromatic hydrocarbons by oxidative pyrolytic combustion followed by ion chromatography

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ABSTRACT

Purpose: Demonstrate a simple method based on ASTM method D7359-14a to determine total fluorine, chlorine, and sulfur in aromatic hydrocarbons.

Methods: Total fluorine, chlorine, and sulfur in gasoline were determined by combustion of samples in a combustion oven followed by quantification in an ion chromatography system using a Thermo Scientific™ Dionex™ IonPac™ AS18-4μm column set.

Results: The method demonstrated excellent resolution and sensitivity. Precision was good at 0.11–3.7 peak area relative standard deviation (RSD). Recoveries of ranged from 86–102%.

INTRODUCTION

The total fluorine, chlorine, and sulfur contained in aromatic hydrocarbon matrices can contribute to emissions that cause pollution, be harmful to many catalytic processes, and lead to corrosion. Ion chromatography (IC) is a sensitive and versatile method for the determination of halides and sulfate. Direct injection of these samples into an IC system presents a challenge because the organic components present can interfere with analysis and may not be compatible with the separation media used. Combustion ion chromatography (CIC) eliminates these potential interferences. Using CIC, the samples are oxidized by oxygen (oxidative pyrolysis) at temperatures of about 1000 ˚C, the combustion byproduct gases, including HX and SO_2 /SO_3, are passed through an aqueous absorbing solution, and then directly injected into the IC instrument, thereby eliminating the sample matrix and any associated interference (Figures 1 and 2).

ASTM method D7359-14a[1] describes use of the CIC method for quantifying halogens and sulfur in aromatic hydrocarbons and their mixtures. This application note describes determination of fluorine, chlorine, and sulfur in aromatic hydrocarbon samples based on this method.
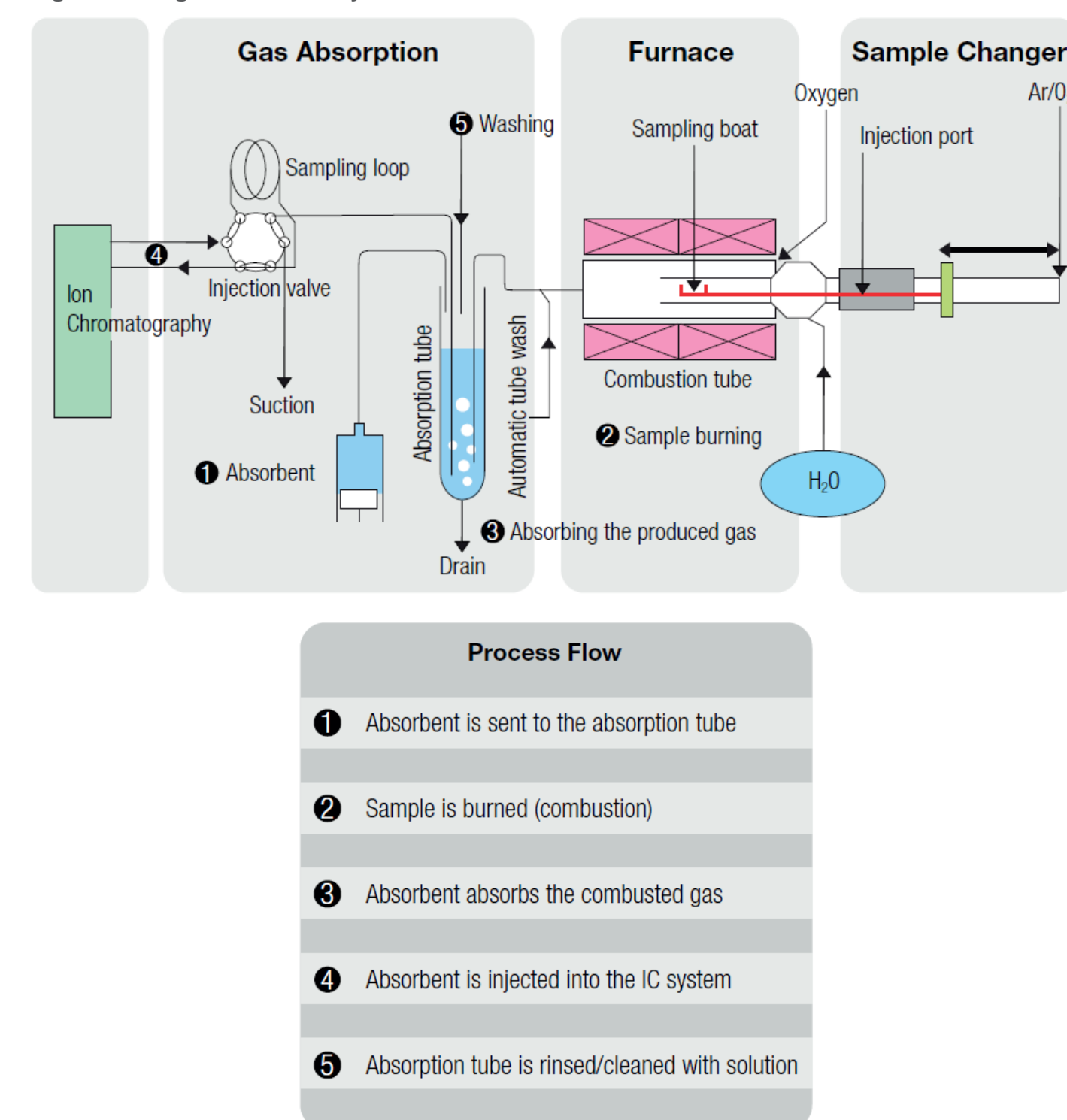
Figure 1. Diagram of a CIC system.

MATERIALS AND METHODS

Standard Preparation

Stock solutions of fluorobenzoic acid, trichlorophenol, and dibenzothiophene sulfur were prepared by dissolving weighed quantities in methanol to obtain 1 mg/L concentrations. Calibration standards were prepared by diluting as appropriate from the stock solutions.

Sample Combustion

Mitsubishi Automatic Quick Furnace AQF-2100H. Samples were transferred to the sample boats using the Mitsubishi Liquid Sample Changer Model ASC-250L.

Combustion Conditions	
Volume Combusted	50 μL
Furnace Inlet Temp.	900 ˚C
Furnace Outlet Temp.	1000 ˚C
Argon Flow (Carrier)	200 mL/min
Oxygen Flow (Combustion Agent)	400 mL/min
Humidified Argon Flow	100 mL/min
Pyrolysis Tube	Quartz tube with ceramic insert and quartz wool
Sample Boat	Quartz
Absorption Solution	30 ppm hydrogen peroxide
Absorption Solution Volume	3.5 mL

Figure 2. CIC system components.

Ion Chromatography

Thermo Scientific™ Dionex™ Integrion™ HPIC™ System.

IC Conditions	
Columns	Dionex IonPac AG18-4μm column, 4 × 30 mm, and Dionex IonPac AS18-4μm column, 4 × 150 mm
Eluent Source	Thermo Scientific™ Dionex™ 500 KOH Eluent Generator Cartridge
Elution Conditions	4 mM KOH from 0 to 2 min, 18.5 mM KOH from 2 to 10 min, 4 mM KOH from 10 to 14.5 min
Flow Rate	1.0 mL/min
Column Temp.	30 ˚C
Inj. Volume	100 μL
Detection	Suppressed conductivity

Data Analysis

Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS), version 7.2.

See Application Note 72693[2] for complete materials and methods.

RESULTS

Sample analysis

The standards and gasoline samples were combusted using conditions described in Methods. The combustion products absorbed in hydrogen peroxide solution were injected directly onto a Dionex IonPac AS18-4 μm 4 × 150 mm column set. The target anions fluoride, chloride, and sulfate were eluted using concentration step change elution conditions. Figure 3 shows a representative chromatogram obtained using a 1 mg/L standard sample prepared using fluorobenzoic acid, trichlorophenol, and dibenzothiophene sulfur. All three target anion peaks are well resolved and the separation is completed in 14.5 min.

Figure 3. Combustion IC chromatogram of a 1 mg/L standard containing fluoride, chloride, and sulfate.
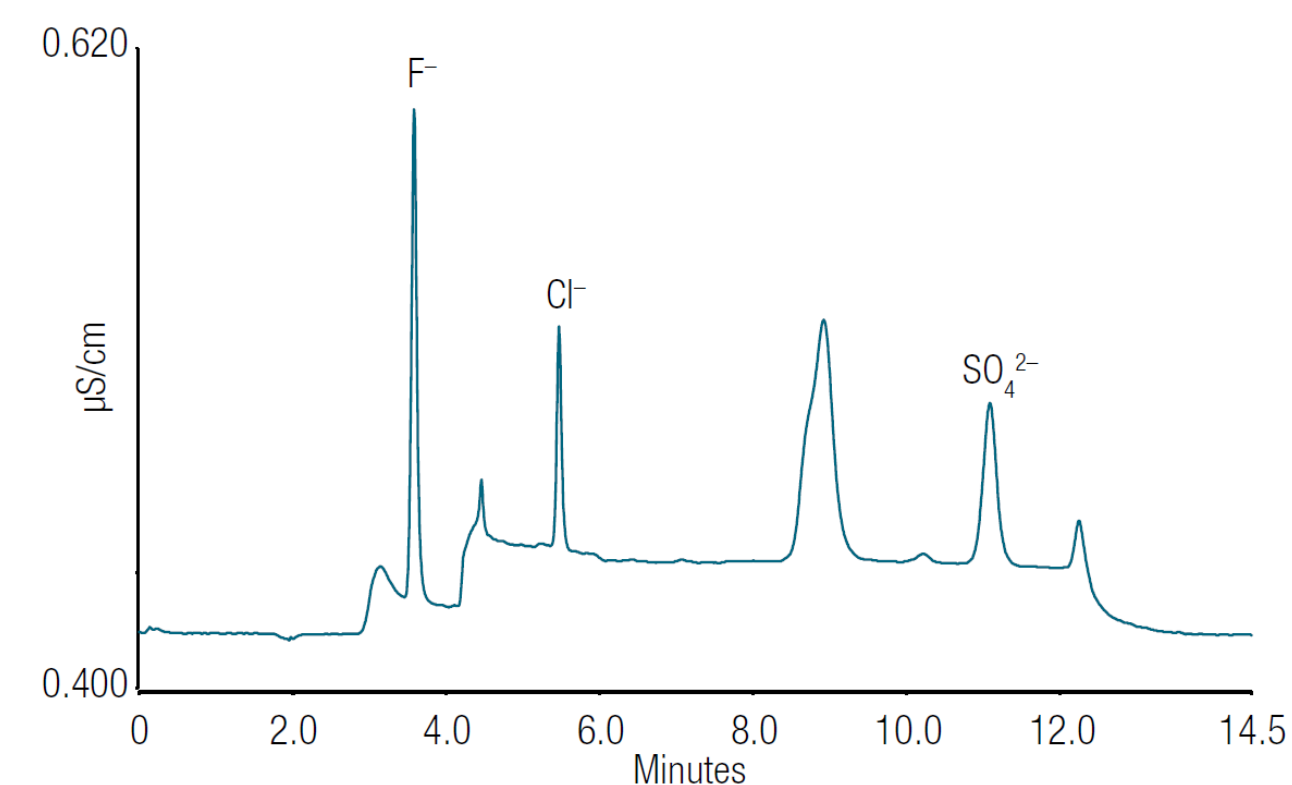
Comparison of the solvent blank with a low concentration standard solution (Figure 4) shows evidence of some background ionic contaminants that could impact the detection limits achieved with this method.

Figure 4. Comparison of CIC chromatograms of a solvent blank (methanol, A) and a 0.5 mg/L standard containing fluoride, chloride, and sulfate.
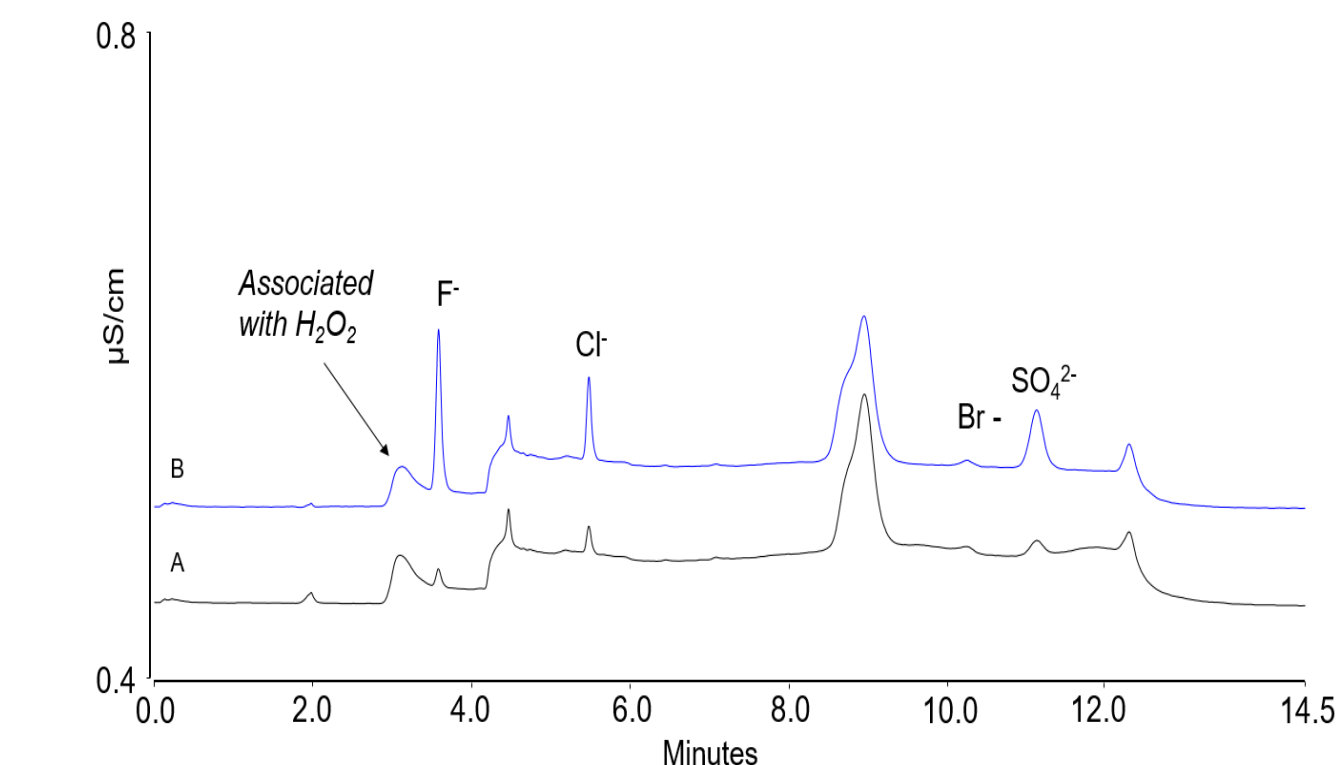
Linearity and precision

Method linearity was determined for all three anions using nine concentration levels from 0.2 to 10 mg/L. The calibration data contained in Table 1 show coefficient of determination values from 0.999 to 1 indicating linear response to analyte concentration. A second order polynomial curve fit was used for fluoride and a linear curve fit was used for chloride and sulfate.

Table 1. Calibration data for three anions.

Analyte	Retention Time (min)	Range (mg/L)	Coefficient of Determination
Fluoride	3.55		1.000
Chloride	5.46	0.2–10	0.999
Sulfate	11.0		0.999

Method precision was determined using seven replicate injections at three concentration levels. The data are summarized in Table 2. Both retention time and peak area RSD values were below 4% indicating good method precision.

Table 2. Precision data for the anions at three different concentrations (n=7).

Standard Conc. (mg/L)	Retention Time RSD			Peak Area RSD		
	F	Cl	SO₄	F	Cl	SO₄
0.2	0.11	0.02	0.02	3.65	3.56	2.54
0.5	0.11	0.04	0.01	2.57	2.01	1.15
2.5	0.16	0.03	0.02	0.49	0.45	0.11

Determination of F, Cl, and S in gasoline

Figure 5 shows analysis of a gasoline sample using the method described here. The gasoline sample contains other anions besides fluoride, chloride, and sulfate but they do not interfere.

Accuracy

Method accuracy was determined by first calculating base amounts of target anions present in the gasoline sample and then spiking a known amount of anion in to the sample. Three concentration levels were used for the spiking experiment. Good recoveries ranging from 85 to 102% were obtained for all three spike levels which shows that the method can accurately calculate the amounts of target anions present in the sample (Table 3).

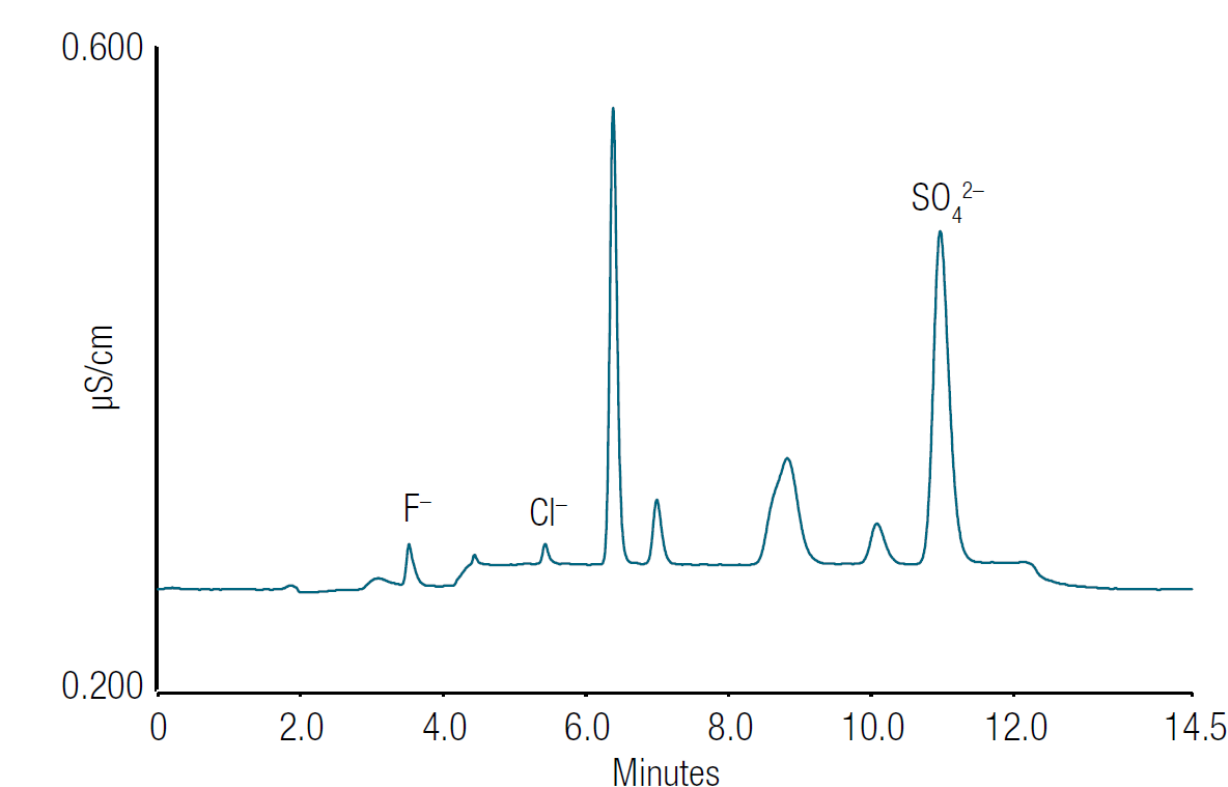**Figure 5. Combustion IC chromatogram of a gasoline sample.**

Table 3. Recoveries of fluoride, chloride and sulfate in premium gasoline (n = 3).

Spike Conc. (mg/L)	F		Cl		SO₄	
	Average Amount (mg/L)	Recovery (%)	Average Amount (mg/L)	Recovery (%)	Average Amount (mg/L)	Recovery (%)
0	0.24	-	0.22	-	4.37	-
0.5	0.75	102	0.71	96.5	4.82	91.0
1	1.22	98.0	1.08	85.9	5.30	93.0
2	2.11	93.7	2.03	90.5	6.30	96.3

CONCLUSIONS

▪ Fluorine, chlorine, and sulfur can be precisely and accurately determined in aromatic hydrocarbons using combustion ion chromatography

▪ Analysis was automated using the Mitsubishi AQF–2100H system in combination with the Dionex Integrion HPIC system with a Dionex IonPac AS18-4μm column

▪ Eluent generation frees the analyst from the need to prepare eluent, eliminates the handling of strong base, and removes a possible source of error

REFERENCES

1. ASTM Method D7359-14a. Standard test method for total fluorine, chlorine, and sulfur in aromatic hydrocarbons and their mixtures by combustion followed by Ion Chromatography detection (Combustion Ion Chromatography-CIC). Published January 2015.

2. Thermo Scientific Application Note 72693: Determination of total fluorine, chlorine, and sulfur in aromatic hydrocarbons by oxidative pyrolytic combustion followed by ion chromatography. Sunnyvale, CA, 2018.

TRADEMARKS/LICENSING

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