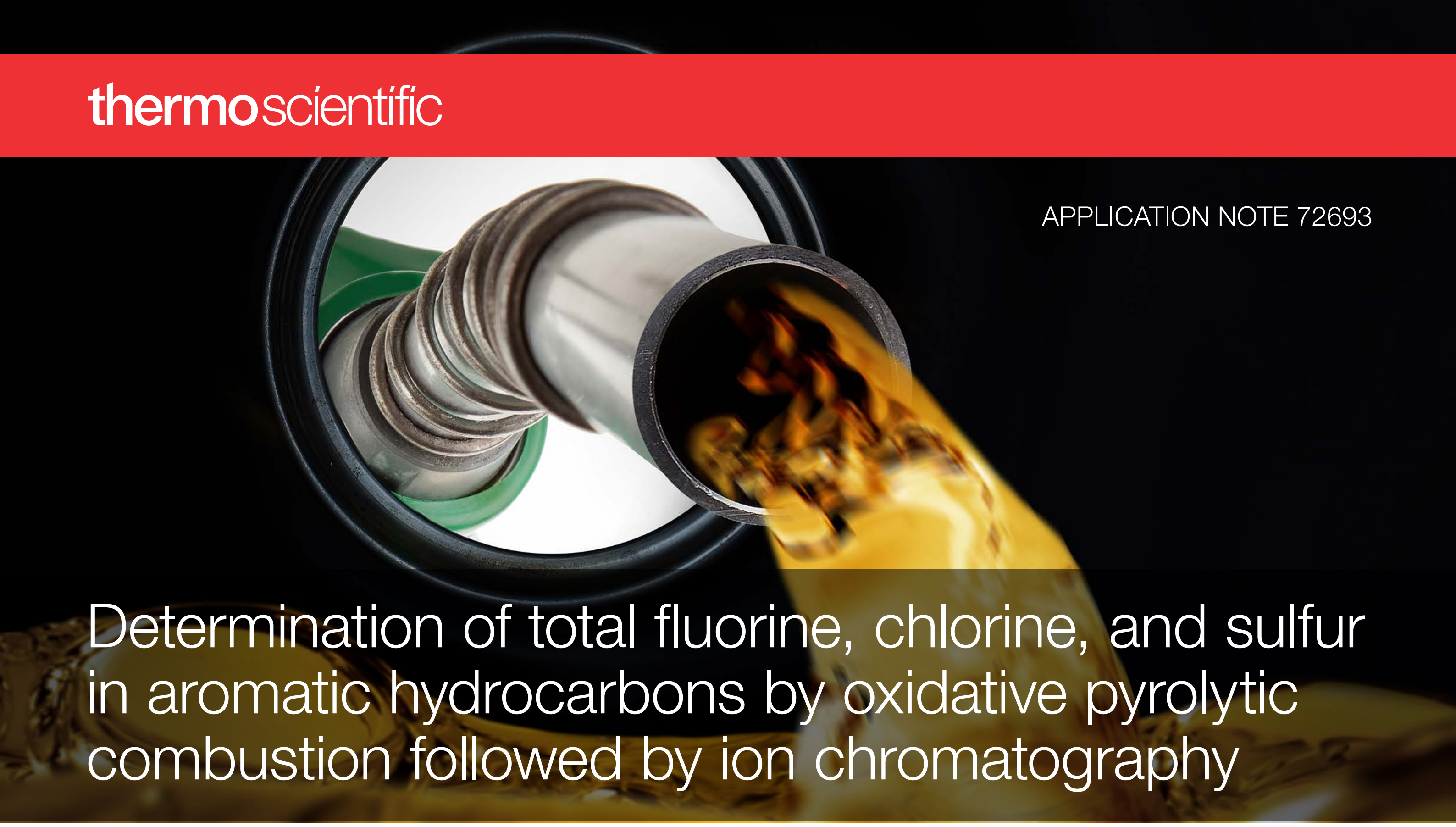

APPLICATION NOTE 72693

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

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Keywords
ASTM method D7359-14a, CIC, Dionex IonPac AS18-4µm column, Dionex Integrion, suppressed conductivity detection

Goal

To demonstrate a simple method based on ASTM method D7359-14a to determine total fluorine, chlorine, and sulfur in aromatic hydrocarbons

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. Application of combustion IC (CIC) has been demonstrated for many applications that determine the total amounts of these elements in samples, such as the determination of low levels of fluorine in water.[1] Further, CIC has been used to determine potentially corrosive or environmentally damaging halogens and sulfur in complex sample matrices such as intractable solids, semisolids, liquids, and even gasses.[2] Samples can be as diverse as petrochemicals, coal-based chemicals, construction materials, chemicals, polymers, and pharmaceutical intermediates and finished formulations. For example, CIC was used for determination of halogens in coal.[3] Using CIC, the samples are oxidized by oxygen (oxidative pyrolysis) at temperatures of about 1000 °C, the combustion by-product 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 interferences.

ASTM method D7359-14a[4] 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 ASTM method D7359-14a. A gasoline sample is used here as an example of an aromatic hydrocarbon sample to demonstrate method capabilities. The CIC system used for this method includes a Mitsubishi™ Automatic Combustion Unit Model AQF-2100H system and a Thermo Scientific™ Dionex™ Integrion™ HPIC™ compact IC system equipped with the Thermo Scientific™ Dionex™ IonPac™ AS18-4µm column set. Results for linearity, precision, and accuracy are described here.

Experimental

Chromatography conditions

Columns:	Dionex IonPac AS18-4 µm column, 4 mm × 150 mm column (P/N 076034) Dionex IonPac AG18-4 µm column, 4 mm × 30 mm guard column (P/N 076035)
Column temp.:	30 °C
Compartment temp.:	25 °C
Flow rate:	1 mL/min
Eluent:	KOH
Eluent source:	Thermo Scientific™ Dionex™ EGC 500 KOH potassium hydroxide eluent generator cartridge with Thermo Scientific™ Dionex™ CR-ATC 600 continuously regenerated anion trap column (P/N 088662) and high-pressure degasser
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
Run time:	14.5 min
Sampler tray temp.:	Ambient

Chromatography conditions (continued)

Injection volume:	100 µL (Mode: Manual or CIC)
Detection:	Suppressed conductivity, using Thermo Scientific™ Dionex™ AERS™ 500, 4 mm suppressor in recycle mode, 45 mA current
Absorption solution:	30 mg/L hydrogen peroxide

Equipment

- A Dionex Integrion HPIC system was used in this work. The system is an integrated ion chromatograph that includes:
  - Dionex Integrion HPIC System Pump
  - Detector Compartment Temperature Control
  - Conductivity Detector
  - Dionex EGC 500 KOH Eluent Generator Cartridge (P/N 075778)
  - Dionex CR-ATC 600 (P/N 088662)
  - Thermo Scientific™ Dionex™ AERS™ 500 Anion Electrolytically Regenerated Suppressor, 4 mm (P/N 082540)

Table 1 lists the consumable products needed for the Dionex Integrion HPIC system configured for suppressed conductivity detection.

- Mitsubishi Automatic Combustion Unit Model AQF-2100H system, including:
  - Automatic Boat Controller Model ABC-210
  - Liquid Sample Changer Model ASC-250L
  - Horizontal Furnace Model HF-210
  - Gas Absorption Unit GA-210
  - External Solution Selector ES-210
- Software
  - Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) Software, version 7.2 SR4 MUb (8525)
  - Mitsubishi NSX-2100 version 2.1.6.0

Table 1. Consumables list for the Dionex Integrion HPIC system

Product Name	Description	Part Number
Thermo Scientific™ Dionex™ IC PEEK Viper™ fitting tubing assembly kit	Dionex IC Viper fitting assembly kit for the Dionex Integrion RFIC system with CD: Includes one each of P/Ns: 088805–088811	088798
Dionex IC PEEK Viper fitting tubing assemblies	Guard Column Out to Separator Column In: 0.007 in i.d., 4.0 in long (102 mm)	088805
	Injection Valve, Port C (Port 2) to Guard Column In: 0.007 in i.d., 5.5 in long (140 mm)	088806
	Dionex EGC Eluent Out to Dionex CR-TC Eluent In: 0.007 in i.d., 6.5 in long (165 mm)	088807
	Separator column Out to Suppressor Eluent In: 0.007 in i.d., 7.0 in (178 mm)	088808
	Suppressor Eluent Out to CD In: 0.007 in i.d., 9.0 in long (229 mm)	088810
	Dionex CR-TC Eluent Out to Degasser Eluent In: 0.007 in i.d., 9.5 in long (241 mm)	088811
Dionex EGC 500 KOH Eluent Generator cartridge	Eluent generator cartridge	075778
Dionex CR-ATC 600 Electrolytic trap column	Continuously regenerated trap column used with Dionex EGC KOH 500 cartridge	088662
HP EG Degasser Module	Degasser installed after Dionex CR-TC trap column and before the Injection Valve, used with eluent generation	075522
Dionex AERS 500 suppressor	Suppressor for 4 mm columns	082540
Dionex IonPac AG18-4µm Guard Column	Anion guard column, 4 × 30 mm	076035
Dionex IonPac AS18-4µm Analytical Column	Anion analytical column, 4 × 150 mm	076034
Thermo Scientific™ Nalgene™ Syringe filter	Syringe filters, 25 mm, PES membrane, 0.2 µm. This type is compatible with IC analysis.	Thermo Scientific 7252520*

* Fisher Scientific P/N 09-740-113

Reagents

- Thermo Scientific™ Dionex™ Seven Anion Standard II (P/N 057590)
- 4-Fluorobenzoic acid (Sigma® P/N 128384)
- 2,4,6-Trichlorophenol (Fisher Scientific™ P/N AC139481000)
- Dibenzothiophene sulfur (Fisher Scientific P/N AC112540250)
- 1000 mg/L solutions of Cl (Thermo Scientific P/N 037159), SO_4 (Thermo Scientific P/N 0371609), and F (Thermo Scientific P/N 037158)
- 30% Hydrogen peroxide solution (Sigma P/N 95321)
- Deionized (DI) water, 18 MΩ·cm resistivity or better

It is important to use DI water for CIC, including in the preparation of standards, eluents, absorption solution, wash solution, and the carry solution. This minimizes system contamination and thus improves method sensitivity.

Stock standard solution

Prepare a 1000 µg/mL standard stock solution by accurately weighing an amount within 10% of the target weight for any or all the target compounds, as listed below, into a 100-mL volumetric flask. Use methanol as the solvent.

- Fluorobenzoic acid: 0.7375 g target weight
- Trichlorophenol: 0.1856 g target weight
- Dibenzothiophene sulfur: 0.5748 g target weight
- First dissolve and then make the volume to 100 mL with methanol.

Then, use the following formula to calculate the actual concentration of each target element.

Stock standard solution (µg/mL) = $(A)\,(B)\,(10^6)\,(P)\,/\,(V)\,(K)$

Where:

A = weight of the target compound in grams

B = % concentration of the elements in the respective target compounds

V = final diluted volume

P = % purity of target standard compounds

K = 100 (to convert % into µg/g)

Working standard solution

Calculate the correct stock standard solution concentration using the formula above. Prepare a 10.0 µg/mL working standard by diluting 1 mL of 1000 µg/mL stock standard solution to 100 mL using a volumetric flask.

Calibration standard solution

Prepare 0.1, 0.2, 0.3, 0.5, 0.75, 1, 2, 5, and 10.0 µg/mL calibration standards by diluting the appropriate amount of 10 µg/mL working stock standard solution to 100 mL using a volumetric flask.

Combustion conditions

Table 2. Combustion conditions (part 1)

AQF-2100H	
Sample size:	50 µL
Sample boat:	Quartz
Pyrolysis tube:	Quartz tube with ceramic insert and quartz wool
Absorption solution:	30 ppm hydrogen peroxide
Mode:	Constant volume
HF210	
Furnace inlet temperature:	900 °C
Furnace outlet temperature:	1000 °C
Argon flow (Carrier):	200 mL/min
Oxygen flow (Combustion agent):	400 mL/min
GA-210	
Absorption tube:	10 mL
Sample loop:	100 µL
Final absorption solution volume:	10 mL
Absorption solution volume*	3.5 mL
Water supply scale:	3
Argon flow for humidification:	100 mL/min

*This is the starting absorption volume. Final absorption volume is adjusted to a constant about 10 mL and is determined accurately according to the manual.[5]

Table 2. Combustion conditions (part 2)

GA-210 washing parameters		
Water injection time:	25 s	
Drain time:	15 s	
Washing times:	4	
Gas line washing time:	1 s	
Gas line washing interval:	6 s	
Gas line washing times:	6	
Washing time of sample absorption line:	20 s	
Syringe washing times:	6	
GA-210 gas line collection parameters		
Collection time:	0.5 s	
Collection interval:	3 s	
Times:	3	
GA-210 injection parameters		
Washing time for injection start:	0 s	
Sample purge time:	5 s	
Sample absorption time:	10 s	
ABC210/ASC-250L		
Argon time:	10 s	
Oxygen time:	600 s	
Position (mm)	*Wait time (s)*	*Speed (mm/s)*
65	60	20
100	60	0.4
130	120	0.4
End	60	20
Cool	60	40
Home	120	40

Instrument setup and installation

Follow TN72211 to set up a system for this application.[6] The Mitsubishi Automatic Combustion Unit Model AQF-2100H system was connected to the Dionex Integrion HPIC system as depicted in Figure 1.

The Dionex Integrion HPIC system is a high-pressure-capable integrated RFIC system designed for high-pressure eluent generation conditions up to 5000 psi.

The details on preparing an IC system for the analysis can be found in TN 175.[7] Here are the key steps:

- Configuring the modules in Chromeleon CDS
- Plumbing the high-pressure Dionex Integrion HPIC system
- Conditioning electrolytic devices and columns according to their product manuals
- Starting the Dionex Integrion HPIC System, Integrion RFIC Model
- Creating an Instrument Method
- Creating a Data Processing Method

Determination of anions in gasoline

Anions in a gasoline sample are determined by CIC with the Constant Volume mode. There are two methods for calibration: Method 1 uses direct injection of liquid standards through the External Solution Selector ES-210. For this method, a dilution factor needs to be entered into the data sequence pane of the Chromeleon CDS software console window to calculate the concentration in the sample. But because the solvent for standards used in this work is methanol, this method cannot be used. Method 2 uses injection of liquid standards through the Liquid Sample Changer Module ASC-250L. Because both the standards and samples are combusted in the same way, the dilution correction factor is not needed. The Chromeleon CDS software automatically calculates sample anion concentration based on the calibration curve. This method was used for determining the concentrations of anions in the gasoline sample.

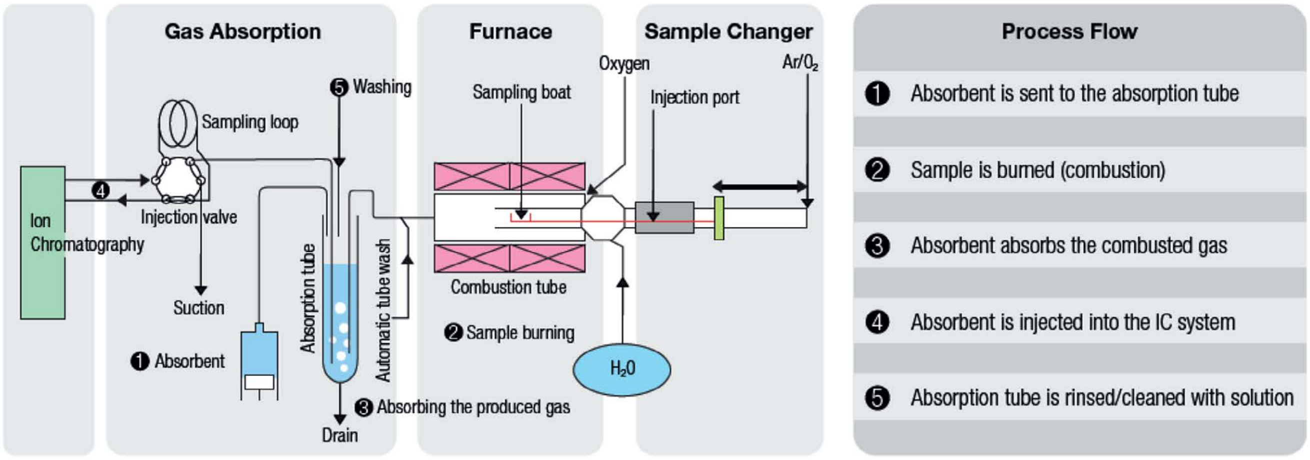

Figure 1. Diagram of a combustion ion chromatography (CIC) system

Results and discussion

Sample analysis

The standards and gasoline samples were combusted using conditions described in Table 2. 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 2 shows a representative chromatogram obtained using a 1 mg/L standard sample prepared using fluorobenzoic acid, trichlorophenol, and dibenzothiophene sulfur as described in the “stock standard” preparation section. All three target anion peaks are well resolved and the separation is completed in 14.5 min. Figure 3 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.

Columns:	Dionex IonPac AS18-4µm column, 4 mm × 150 mm (P/N 076034) Dionex IonPac AG18-4µm guard column, 4 mm × 30 mm (P/N 076035)
Column Temp.:	30 °C
Compartment Temp.:	25 °C
Flow Rate:	1 mL/min
Eluent:	KOH
Eluent Source:	Dionex EGC 500 KOH with Dionex CR-ATC 600 continuously regenerated anion trap column (P/N 088662) and high pressure degasser
Elution Conditions:	See text
Run Time:	14.5 min
Detection:	Suppressed conductivity, Dionex AERS 500 suppressor, 4 mm, recycle mode

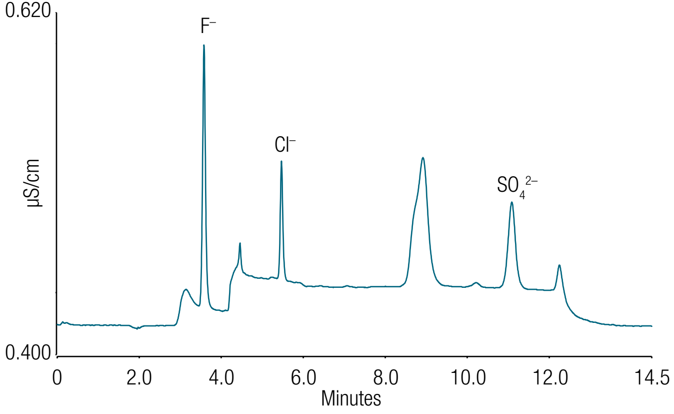

Figure 2. Combustion IC chromatogram of a 1 mg/L standard containing fluoride, chloride, and sulfate

Columns:	Dionex IonPac AS18-4µm column, 4 mm × 150 mm (P/N 076034) Dionex IonPac AG18-4µm guard column, 4 mm × 30 mm (P/N 076035)
Column Temp.:	30 °C
Compartment Temp.:	25 °C
Flow Rate:	1 mL/min
Eluent:	KOH
Eluent Source:	Dionex EGC 500 KOH with Dionex CR-ATC 600 continuously regenerated anion trap column (P/N 088662) and high pressure degasser
Elution Conditions:	See text
Run Time:	14.5 min
Detection:	Suppressed conductivity, Dionex AERS 500 suppressor, 4 mm, recycle mode

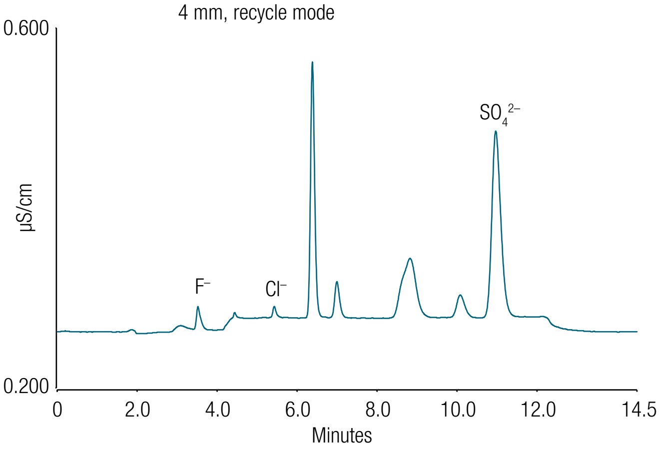

Figure 3. Combustion IC chromatogram of a gasoline sample

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 3 shows 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.

Method precision was determined using seven replicate injections at three concentration levels. The data are summarized in Table 4. Both retention time and peak area RSD values were below 4% indicating good method precision. Intermediate precision was determined for the three concentration levels across three days. As shown in Table 5, the RSD values for this data are also below 4%, implying good intermediate method precision.

Accuracy

A gasoline sample was procured and used for determining method 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. The results for spike recovery are included in Table 6. 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. Calibration data for three anions

Peak No.	Peak Name	Ret. Time (min)	Concentration Range (mg/L)	Coefficient of Determination
1	F	3.55	0.2 to 10	1.000
2	Cl	5.46	0.2 to 10	0.999
3	SO_4	11.03	0.2 to 10	0.999

Table 4. Precision data for the anions at three different concentrations (n=7)

Standard Conc. (mg/L)	Retention Time RSD			Peak Area RSD		
	F	Cl	SO_4	F	Cl	SO_4
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

Table 5. Intermediate precision data (n=7)

Spike Conc. (mg/L)	Day	Retention Time RSD			Peak Area RSD		
		F	Cl	SO_4	F	Cl	SO_4
0.2	1	0.11	0.02	0.02	3.65	3.56	2.54
	2	0.06	0.03	0.03	3.97	3.98	2.21
	3	0.09	0.02	0.04	3.49	2.50	2.77
0.5	1	0.11	0.04	0.01	2.57	2.01	1.15
	2	0.07	0.02	0.01	2.47	1.34	1.13
	3	0.10	0.03	0.03	1.97	2.75	1.62
2.5	1	0.16	0.03	0.02	5.12	3.53	1.56
	2	0.13	0.04	0.01	3.39	0.56	0.56
	3	0.07	0.00	0.04	1.14	1.00	1.02

Table 6. Results for the spike recovery experiment (n=3)

Spike Conc. (mg/L)	F		Cl		SO_4	
	Average Amount (mg/L)	% Recovery	Average Amount	% Recovery	Average Amount (mg/L)	% Recovery
0 (Premium Gasoline)	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

Conclusion

A CIC method based on ASTM Method D7359-14a for routine analysis of anions in aromatic hydrocarbon samples was used to determine fluorine, chlorine, and sulfur in gasoline. A high resolution separation was achieved in 14.5 min. The method shows good linearity and precision and accurately quantifies amounts of anions present in the sample.

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