

Determination of halogens in coal using combustion ion chromatography

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Goal

Combine automated combustion with ion chromatography to quantify halogens in coal.

Introduction

Despite the emergence of alternative energy sources (e.g. natural gas, biofuel, wind, and solar), 40% of the world's electricity is generated using coal.¹ When coal is burned, the exhaust contains halogens that can be released into the atmosphere as acid gases such as hydrogen chloride (HCl) and hydrogen fluoride (HF), which can harm vegetation, animals, and infrastructure directly or cause acid rain.² Mercury (Hg) is another toxic pollutant that is present in coal exhaust. To reduce emissions of Hg and other toxic pollutants by coal burning power plants, the U.S. Environmental Protection Agency (U.S. EPA) published the Mercury and Air Toxics Standards (MATS) rule, which established technology-based emissions limitation standards that reflected the levels achieved by the best-performing sources in operation at that time.³ To meet these standards, power plants have had to incorporate pollutant removal technologies into their design or retrofit existing facilities. The ability of pollution control devices to capture Hg from flue gases is enhanced in the presence of halogens. Coals with higher amounts of chloride are more likely to result in greater concentrations of the oxidized forms of mercury, which are water soluble and can be captured by the wet scrubbers used to reduce sulfur emissions.⁴ Determination of the levels of halogens in coal can be used to predict the efficacy of a particular pollution control strategy and suggest what alterations would be required to meet federal standards.

Because coal is a solid that is not readily solubilized, accessing and quantifying its constituents requires some form of sample preparation prior to analysis.

Combustion methods have been developed that ensure complete decomposition of solid and semi-solid samples and concomitant release of halogens. These methods include the use of the Wickbold apparatus, combustion (oxygen) bombs, the Schöniger flask, microwave-induced combustion (MIC), and automated furnace combustion systems such as the one described here.⁵ After the sample is combusted, detection can include precipitation with silver nitrate followed by gravimetric analysis⁶ or measurement by ion chromatography (IC),⁷ coulometric titration,⁸ or ion selective electrodes⁹.

Combustion IC (CIC) uses the thermochemical decomposition of organic matter in the presence of oxygen (oxidative pyrolysis) to convert the analytes of interest to

gases. The combustion by-product gases, including HX and SO₂/SO₃, are passed through an aqueous absorbing solution and directly injected into the IC instrument, thereby eliminating the sample matrix and any associated interferences (Figure 1). The absorbing solution used is dependent on the anions of interest. Typically, deionized (DI) water is used for halides or an aqueous hydrogen peroxide solution if halides and sulfur are being analyzed. The hydrogen peroxide is required to ensure all the sulfur anions are oxidized to sulfate prior to injection into the IC. The fully automated process of CIC saves time and labor, increases reproducibility, and eliminates the need to dispose of hazardous chemicals used in acid digestions or back extractions.

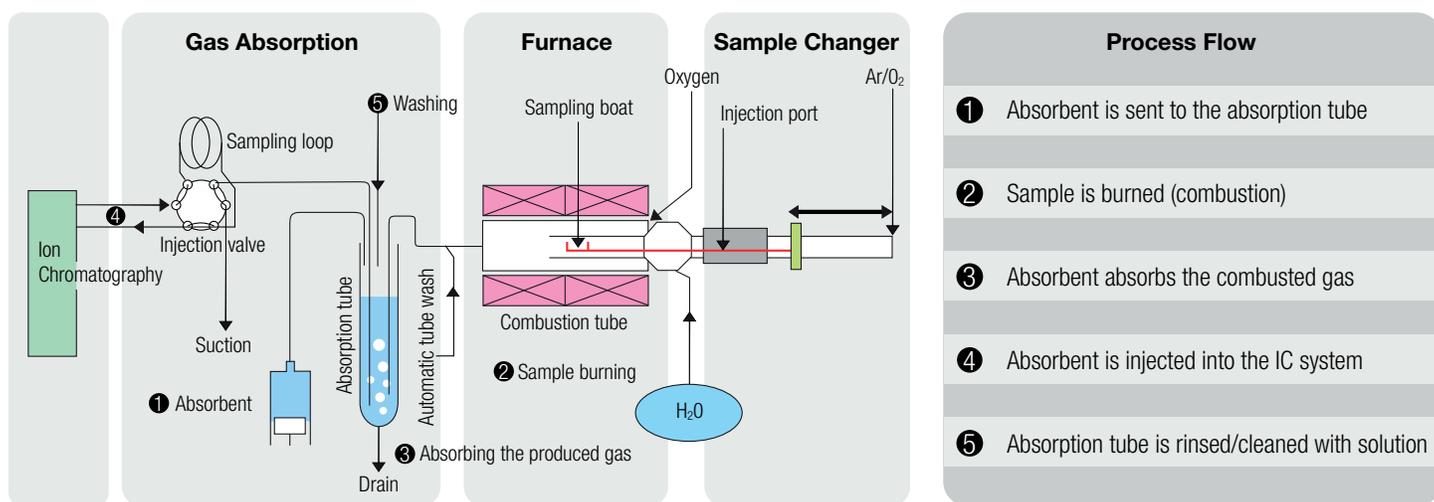


Figure 1. Diagram of a CIC system.

In this application note, coal samples were combusted in the Mitsubishi® AQF-2100H system and then fluoride and chloride were accurately and precisely determined using the Thermo Scientific Dionex ICS-2100 Ion Chromatography System with a Thermo Scientific™ Dionex™ IonPac™ AS15 anion-exchange column set.

Equipment

- Mitsubishi Automatic Quick Furnace AQF-2100H
 - Solid Auto Sampler ASC-240S
 - Horizontal Furnace HF-210
 - AQF-2100H Mullite Pyrolysis Set (P/N AQ3QM5)
 - Gas Absorption Unit GA-210
 - External Solution Selector ES-210
- Dionex ICS-2100 Ion Chromatography System (The Thermo Scientific™ Dionex™ Integriion™ HPIC™ system can also be used for this application)

- Thermo Scientific Dionex EGC III KOH cartridge (P/N 074532)
- Thermo Scientific Dionex CR-ATC Continuously Regenerated Anion Trap Column (P/N 060477)
- Thermo Scientific™ Dionex™ AERS™ 500 Anion Electrolytically Regenerated Suppressor, 4 mm (P/N 082540)

Software

- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) software, version 7.2
- Mitsubishi NSX-2100 version 2.0.2.0

Reagents and Standards

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

- Fisher Scientific, ACS Grade
 - Sodium bromide (P/N S255)
 - Sodium chloride (P/N S271)
 - Sodium fluoride (P/N S299)

Sample

Coal samplers were obtained in powder form and were stored at room temperature.

IC Conditions

Columns:	Dionex IonPac AG15 Guard, 4 × 50 mm (P/N 053942) Dionex IonPac AS15 Separation, 4 × 250 mm (P/N 053940)
Eluent Source:	Dionex EGC III KOH cartridge with Dionex CR-ATC column
Eluent Conc.:	38 mM KOH
Flow Rate:	1.2 mL/min
Column Temp.:	30 °C
Inj. Volume:	200 µL (Full loop)
Detection:	Suppressed conductivity, Dionex AERS 500 suppressor, 4 mm, recycle mode, 113 mA

Background

Total Conductance:	~ 1.1 µS
Noise:	< 1 nS
System Backpressure:	~1800 psi

Combustion Conditions

Mass Combusted:	10–55 mg
Furnace Inlet Temp.:	900 °C
Furnace Outlet Temp.:	1050 °C
Argon Flow (Carrier):	200 mL/min
Oxygen Flow (Combustion Agent):	400 mL/min
Humidified Argon Flow:	100 mL/min
Humidified Argon Pump Setting:	2
Pyrolysis Tube:	Ceramic insert
Sample Boat:	Ceramic
Absorption Solution:	Water
Absorption Tube Size:	10 mL
Absorption Solution Volume:	10 mL
AQF Mode:	Constant Volume

Preparation of Standards

Stock Solutions

To prepare 1000 mg/L stock solutions, accurately weigh the amounts of standard compounds listed in Table 1, transfer to a 100 mL volumetric flask, and fill to mark with DI water. Mix thoroughly. Concentrated standards should be stable for at least one month when stored at 4 °C.

Table 1. Mass of standard compound to prepare 100 mL of a 1000 mg/L stock halide solution.

Analyte	Compound	Mass (g)
Bromide	Sodium bromide	0.129
Chloride	Sodium chloride	0.164
Fluoride	Sodium fluoride	0.221

Working Standard Solutions

Prepare the highest concentration working standard solutions [1.0 mg/L (F, Br) and 5.0 mg/L (Cl)] by pipetting the appropriate amount of 1000 mg/L stock into a 100 mL volumetric flask and diluting to the mark with DI water. Prepare the 0.1, 0.25, 0.5 mg/L (F, Br) and 0.1, 0.5, 1.0 mg/L (Cl) standard solution mixes by diluting the highest concentration working standards with DI water. When the standard solutions are not in use, store at 4 °C.

System Preparation and Configuration

IC System

Install, hydrate, and condition the Dionex EGC III KOH eluent generator cartridge as described in the product manual.¹⁰ Refer to the Dionex Integrion HPIC System Operator's Manual¹⁴ if you are using that system rather than the Dionex ICS-2100 IC system. Install and hydrate the Dionex CR-ATC trap column¹¹ and the Dionex AERS 500 suppressor.¹² Finish the system setup according to the product manuals and the Dionex ICS-2100 system Operator's Manual.¹³ Install and condition the guard and separation columns for 30 min prior to installing the columns in-line with the suppressor.

Combustion System

Coal, petroleum, and mineral products that contain high levels of alkali and alkaline earth metals (such as sodium, potassium, and calcium) can cause rapid devitrification (crystal formation causing small cracks to form) of quartz components and combustion tubes requiring their frequent replacement, resulting in higher system maintenance costs. Additionally, accuracy and recovery of halides and sulfur are compromised by high temperature combustion in a quartz pyro-tube. As a result, this application requires the use of a ceramic (mullite)

pyro-tube insert. Refer to the Mitsubishi AQF-2100H instruction manual for complete system setup.¹⁵

Calculation of Analyte Concentration in Coal Dilution Correction Factor

Because the IC is calibrated by direct injection of liquid standards, the weight and dilution of each coal sample needs to be entered into the data sequence pane of the Chromeleon CDS software console window to calculate the concentration of analytes that were present in the coal prior to combustion. To determine the dilution, make an aqueous 2–5 mg/L phosphate standard and compare the area counts of the peak via direct injection to that from dilution into the absorption tube of the gas absorption unit (GA-210). Multiply this peak area ratio by the dispense volume of the absorption solution (set in the GA parameters) to get the final volume of the absorption solution before injection into the IC. Multiply the final volume by 1000 when the combustion sample size is in mg.

$$\text{Dilution} = \left(\frac{\text{Area of Direct Injection}}{\text{Area of Dilute Injection}} \right) * (\text{Absorption Solution Volume}) * 1000$$

Dry Coal Calculations

Because coal powder readily absorbs moisture from the atmosphere, which adds to its mass, the analyte values determined by CIC are referred to as wet unless it has been dried. To determine dry values, weigh coal into a heat resistant container and then dry in an oven at >100 °C for ~1.5 h. Reweigh the sample and calculate the moisture content and dry concentration:

$$\% \text{ Moisture} = \frac{(\text{Weight Before Drying}) - (\text{Weight After Drying})}{\text{Weight Before Drying}}$$

$$\text{Dry Concentration} = \frac{\text{Concentration}}{\left(\frac{100 - \% \text{ Moisture}}{100} \right)}$$

Results and Discussion

Method Linear Calibration Ranges

Because National Institute of Standards and Technology (NIST)-certified coal samples were not available with a suitable range of analyte concentrations for calibration by combustion, standard halide solutions were prepared in DI water and directly injected into the IC system (Figure 2) to obtain the required calibration curves.

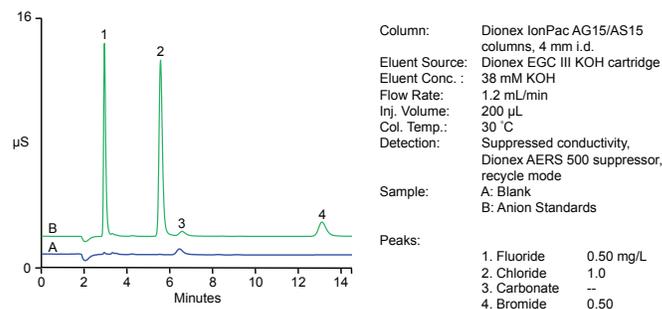


Figure 2. Separation of anion standards.

To determine the linear calibration ranges, the peak responses to concentration were determined using triplicate injections of calibration standards over a 10- or 50-fold dilution range (Table 2). Plotting peak area versus concentration demonstrated linearity for the concentration ranges used, as exemplified by the fluoride calibration curve (Figure 3). Coefficients of determination (r^2) ranged from 0.9987 to 0.9995.

Table 2. Anion calibration ranges and coefficients of determination.

Analyte	Concentration (mg/L)	r^2
Bromide	0.1–1.0	0.9987
Chloride	0.1–5.0	0.9999
Fluoride	0.1–1.0	0.9998

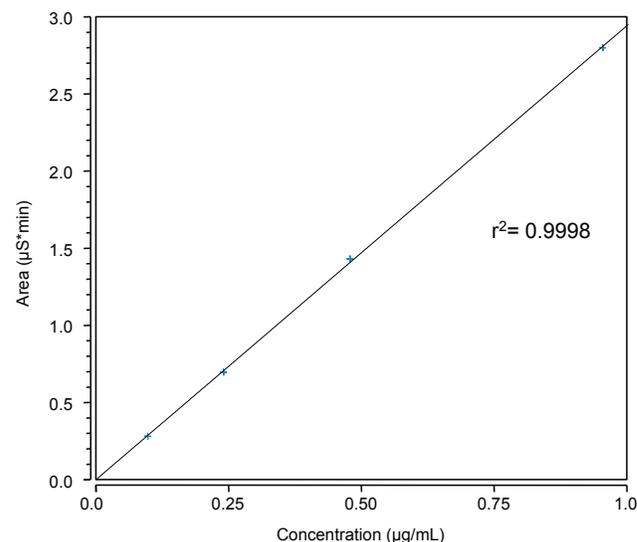


Figure 3. Fluoride calibration curve.

Confirmation of Calibration

To confirm the validity of the IC calibration, fluoride was determined in triplicate 50 mg aliquots of National Institute of Standards and Technology (NIST) standard reference material 1635¹⁶ (subbituminous coal) (Table 3). The 27.6 mg/kg (2.1% RSD) value was in agreement with that of the certified reference material (25.9 ± 3.3 mg/kg). Chloride and bromide were detected in this material, but they were not certified.

Determination of Halogens in Coal

Because the moisture content was not determined, the concentrations reported here are the wet values. Coal samples contained 60–200 mg/kg fluorine, while chlorine was generally present at higher levels and had a broader range (30–1400 mg/kg; Figure 4 and Table 3). Bromine was detected in some of the coal samples but the concentrations were below the lowest level standard (0.1 mg/L).

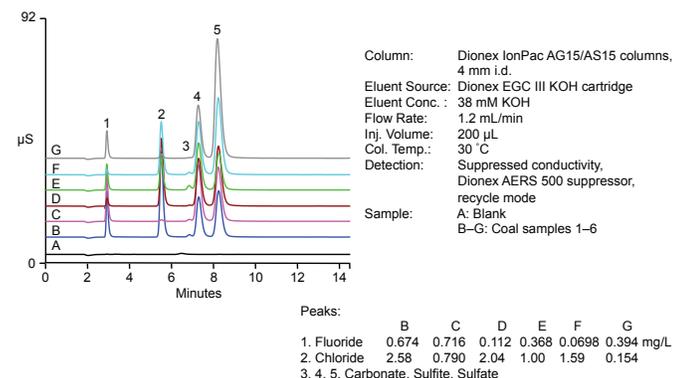


Figure 4. Separation of anions in absorption solution from coal combustion. Analyte concentrations have not been adjusted for the mass and dilution (see Table 3 for these values).

Table 3. Fluorine and chlorine results in coal samples.

Sample	Fluorine		Chlorine	
	mg/kg	RSD	mg/kg	RSD
NIST 1635	27.6	2.1	--	--
1	187	1.5	723	2.5
2	221	0.23	28.6	0.42
3	75.9	3.2	1420	3.3
4	77.5	1.2	211	0.4
5	56.5	5.0	1230	1.2
6	195	3.3	81.7	5.5

n = 3

Good precision was achieved as evidenced by the relative standard deviation (RSD) values calculated from the three replicates (0.2–5.5). In addition to fluoride and chloride, peaks were detected at 7.3 and 8.2 min. These were likely sulfite and sulfate, respectively. The amount of sulfur present in CIC samples can be determined by adding hydrogen peroxide (H₂O₂) to the absorption solution at a concentration that is high enough to ensure complete oxidation of sulfite to sulfate. Caution: g/kg sulfur can be typically found in coal, which would require the use of an absorbent containing H₂O₂ in molar excess (≥ 900 mg/L). Using H₂O₂ at this concentration can result in the appearance of contaminants that interfere with fluoride determination and could damage the column and other instrument components. Because water (with no H₂O₂) was used as the absorbent for the data presented here, multiple peaks corresponding to the sulfur-containing species were observed.

Conclusion

This application note demonstrates that chlorine and fluorine can be precisely and accurately determined in coal using combustion ion chromatography. Analysis was automated by using the Mitsubishi AQF-2100H system in combination with the Dionex ICS-2100 IC system that paired reagent-free IC (RFIC) with a Dionex IonPac AS15 column set.

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