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APPLICATION NOTE 73280

Determination of fluorine and chlorine in iron ore using combustion ion chromatography

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Dionex IonPac AS18-Fast-4µm column, suppressed conductivity detection, AQF-2100H, ADRS 600 suppressor, Dionex Integrion HPIC system, CIC, mining

Goal

To develop a method for the determination of fluorine and chlorine in iron ore using combustion ion chromatography

Introduction

Iron ore—a rock or mineral from which iron can be extracted—is the primary source of iron for the steel industry. Fluorine and chlorine contaminants in iron ore are of great concern. During iron ore processing, fluorine combustion products exist as gases or aerosols, which can be inhaled by humans and cause fluorine poisoning.[1] Chlorine in iron ore can form carcinogens such as dioxin during combustion.[2] Halogens are also very corrosive to iron-containing products such as steel. Thus, the content of halogens is an important iron ore quality index.

Halogen compounds in iron ore cannot be directly determined by ion chromatography (IC). Automated combustion ion chromatography (CIC) is often used to determine these halogen contaminants. In CIC, the samples containing halogen-containing compounds are first combusted and the resultant gas is released into an absorption solution, which is then directly injected into an IC system.

As shown in Figure 1, for this application pyrolysis takes place in the combustion system at a temperature above 900 °C. Halogen-containing substances are transformed into hydrogen halides (X–) or elemental halogens (X_2). These gaseous combustion products are fed into an absorption solution

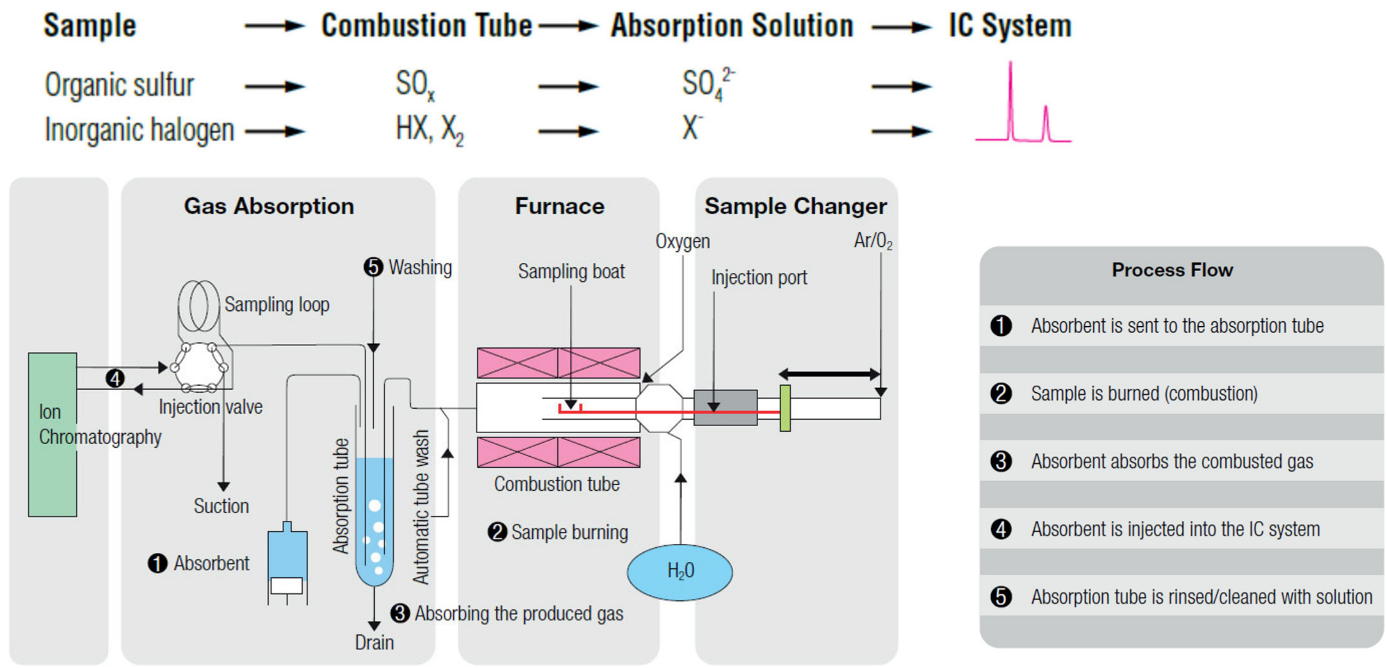


Figure 1. Diagram of a CIC system

(deionized water) and are subsequently detected as the halide (e.g. chloride) by the IC system. While one chromatogram is being recorded, pyrolysis of the next sample is already underway.

This application note developed a CIC method for determining fluorine and chlorine in iron ore samples. Key performance parameters were evaluated including separation, linearity, limits of detection, and precision. Fluorine and chlorine concentrations were determined in six iron ore samples.

Experimental

Equipment

- Thermo Scientific™ Dionex™ Integrion™ HPIC system including:
  - Eluent generation
  - Dionex Integrion HPIC system pump
  - Conductivity Detector (P/N 079829)
  - Degasser
  - Column oven temperature control
  - Detector compartment temperature control
  - Consumables device tracking capability
- Mitsubishi Chemical Analytech Automatic Combustion Unit Model AQF-2100H system, including
  - Automatic Boat Controller Model ABC-210
  - Horizontal Furnace Model HF-210
  - Gas Absorption Unit GA-211
  - External Solution Selector ES-210/211

Consumables

- Thermo Scientific™ Dionex™ EGC 500 KOH Cartridge (P/N 075778)
- Thermo Scientific™ Dionex™ CR-ATC 600 Continuously Regenerated Anion Trap Column (P/N 088662)
- Thermo Scientific™ Dionex™ ADRS™ 600 Anion Dynamically Regenerated Suppressor, 2 mm (P/N 088667)

Software

- Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) Software, version 7.2.9
- Mitsubishi NSX-2100, version 10.2.3.0

Reagents and standards

- Deionized (DI) water, Type I reagent grade, 18 MΩ-cm resistance or better
- Sodium and potassium salts, A.C.S. reagent grade or better, for preparing anion standards
- Tungsten (VI) oxide, (WO_3), Acros Organic (P/N 214211000)
- Oxygen, ultrahigh purity, GR 4.4
- Argon, ultrahigh purity, GR 5.0

Samples

Six iron ore samples were kindly provided by a company headquartered in Australia. (S1-S6)

Chromatographic conditions

Columns:	Thermo Scientific™ Dionex™ IonPac™ AG18-Fast-4µm Guard, 2 × 30 m (P/N 076037) Thermo Scientific™ Dionex™ IonPac™ AS18-Fast-4µm Analytical, 2 × 150 mm (P/N 076036)
Eluent:	30 mM KOH
Eluent source:	Dionex EGC 500 KOH cartridge with Dionex CR-ATC 600
Flow rate:	0.25 mL/min
Injection volume:	100 µL (Full loop)
Column temp.:	30 ˚C
Detection:	Suppressed conductivity
Suppressor:	Dionex ADRS 600 (2 mm) suppressor, recycle mode, 19 mA
Detection compartment:	20 °C
Cell temp.:	35 ˚C
Background conductance:	<0.5 µS/cm
System backpressure:	~2500 psi
Noise:	<1.5 nS/cm
Run time:	15 min

Combustion conditions

Mass combusted:	10–15 mg sample with 10–15 mg tungsten oxide (burning aid)
Furnace inlet temp.:	1000 °C
Furnace outlet temp.:	1100 °C
Argon flow (Carrier):	100 mL/min
Oxygen flow (Combustion agent):	400 mL/min
Humidified argon flow:	100 mL/min
Water supply scale:	4
Pyrolysis tube:	Quartz tube with ceramic insert and quartz wool
Sample boat:	Ceramic with nickel liner
Absorption solution:	Water
Absorption tube size:	10 mL
Absorption solution volume:	3.5 mL
AQF mode:	Constant volume
Automatic boat controller program:	Table 1

Table 1. ABC-210 program

Position	Wait time (s)	Speed (mm/s)
135 (mm)	60	10
End	300	
Cool	200	
Home	200	

Preparation of solutions and reagents

Anion stock standard solution

Prepare stock standard solutions (1000 mg/L) by dissolving the appropriate amounts of the required compounds in 100 mL of DI water according to Table 2.

Table 2. Masses of compounds used to prepare 100 mL of 1000 mg/L ion standards

Analyte	Compound	Amount (mg)
Fluoride	Sodium fluoride (NaF)	221.0
Chloride	Sodium chloride (NaCl)	164.9
Bromide	Sodium bromide (NaBr)	128.8
Sulfate	Sodium sulfate (Na_2SO_4)	147.9
Carbonate	Sodium carbonate (Na_2CO_3)	176.6
Tungstate	Sodium tungstate (Na_2WO_4)	118.6

Calibration standard solutions

Six calibration levels were used to cover the expected concentration range found in iron ore samples. (Table 3). Prepare the highest concentration working standard solution (level 6) by pipetting the appropriate amount of 1000 mg/L stock (fluoride 0.5 mL, chloride 1 mL) into a 100 mL volumetric flask and diluting to the mark with DI water. Prepare levels 1–5 standard solutions by mixing the appropriate amount of standard solution level 6 with DI water. For example, prepare the level 1 standard solution by adding 0.5 mL of standard solution level 6 in DI water and adjust the volume to 100 mL. Store at 4 °C.

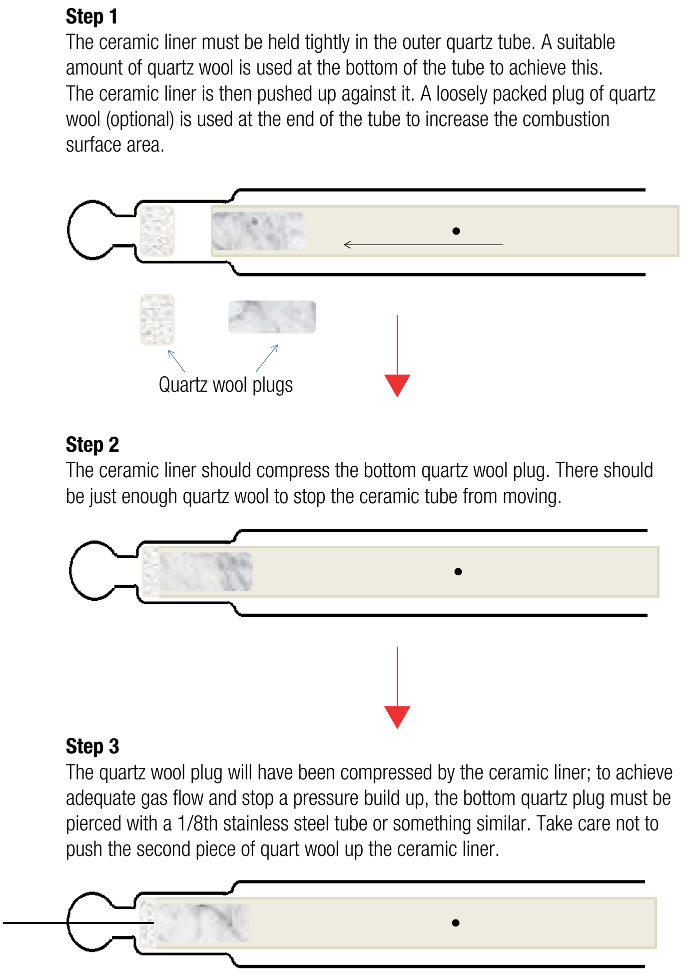
System preparation and configuration

IC system

Install, hydrate, and condition the Dionex EGC 500 KOH eluent generator cartridge as described in the product manual. Install and hydrate the Dionex CR-ATC 600 trap column and the Dionex ADRS 600 suppressor. Finish the system setup according to the product manuals and the Dionex Integrion system operator's manual and technical note.[3] Install and condition the guard and separation columns for 30 min as described in the column manual prior to installing the column in line with the suppressor.

Combustion system

Iron ore contains high levels of alkali and alkaline earth metals such as sodium, potassium, and calcium that can cause rapid devitrification of quartz components and combustion tubes, necessitating their frequent replacement and resulting in higher system maintenance costs. Additionally, accuracy and recovery of halides are compromised by high temperature combustion in a quartz pyro-tube. Thus, this application requires the use of a ceramic pyro-tube insert. Install the ceramic tube insert as described in Figure 2. Refer to the Mitsubishi AQF-2100H instrument manual[4] for complete system setup.



Step 1
The ceramic liner must be held tightly in the outer quartz tube. A suitable amount of quartz wool is used at the bottom of the tube to achieve this. The ceramic liner is then pushed up against it. A loosely packed plug of quartz wool (optional) is used at the end of the tube to increase the combustion surface area.

Step 2
The ceramic liner should compress the bottom quartz wool plug. There should be just enough quartz wool to stop the ceramic tube from moving.

Step 3
The quartz wool plug will have been compressed by the ceramic liner; to achieve adequate gas flow and stop a pressure build up, the bottom quartz plug must be pierced with a 1/8th stainless steel tube or something similar. Take care not to push the second piece of quart wool up the ceramic liner.

Figure 2. Installation of the ceramic tube

Note: The ceramic liner installation guide was kindly provided by Paul Taylor from a1-envirosciences GmbH.

Table 3. Calibration standards (mg/L)

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
Fluoride	0.025	0.25	0.5	1	2.5	5
Chloride	0.05	0.5	1	2	5	10

Constant volume determination

Make a 0.5–1 mg/L phosphate standard and compare the peak 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 as 8 mL in the GA parameter) to get the final volume of the absorption solution before injection into the IC.

$$\text{Constant volume (mL)} =$$

$$(\text{Absorption solution volume})\left(\frac{\text{Area of direct injection}}{\text{Area of dilute injection}}\right)$$

$$= 8\left(\frac{\text{Area of direct injection}}{\text{Area of dilute injection}}\right)$$

Results and discussion

Separation

The Thermo Scientific™ Dionex™ IonPac™ AS18-Fast-4µm anion-exchange column is a high-capacity, high-efficiency column that provides excellent resolution of inorganic anions in diverse sample matrices. This is the hydroxide-selective column of choice for fastest separation of inorganic anions. Compared to the Thermo Scientific™ Dionex™ IonPac™ AS18-Fast column, the new Dionex IonPac AS18-Fast-4µm anion-exchange column uses smaller resin particles for more efficient peaks resulting in faster run times, more accurate peak integration, and more reliable results.[5]

In this study, tungsten oxide is added to the sample as a combustion aid to improve fluorine recovery. Thus, tungstate is formed as a combustion product. Figure 3 shows a separation of fluoride, chloride, carbonate, sulfate, bromide, and tungstate within 15 min using a Dionex IonPac AS18-Fast-4µm column on the Dionex Integrion HPIC system. Fluoride and chloride were well resolved from other peaks.

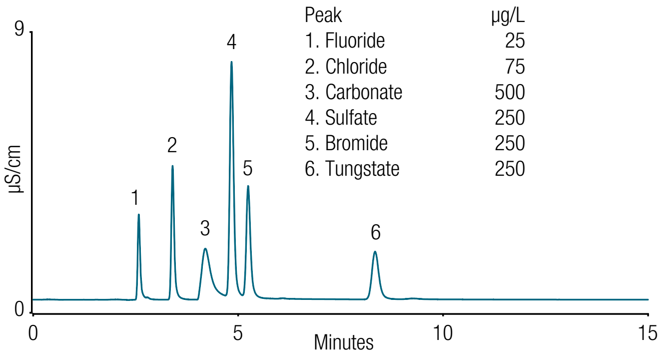


Figure 3. Separation of fluoride, chloride and common anions using a Dionex IonPac AS18-Fast-4µm column

Calibration

Run inorganic fluoride and chloride calibration standards by IC with the external injection mode and build the calibration curves. Table 3 shows the calibration concentration ranges. Plotting peak area versus concentration demonstrated linearity for the concentration ranges used for the chloride calibration curve (Figure 4A) with a coefficient of determination (r^2) of 0.9999. Fluoride exhibited a quadratic relationship to concentration (Figure 4B) with a coefficient of determination (r^2) of 0.9997.

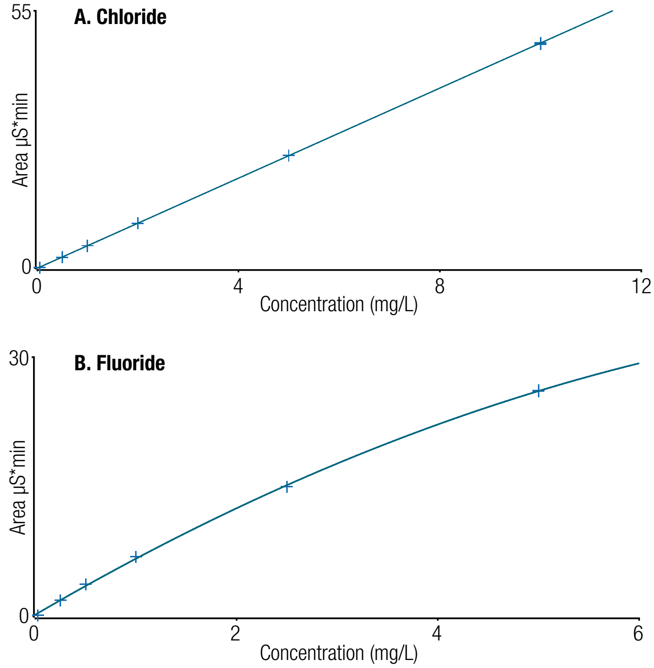


Figure 4. Calibration curves

Limit of detection (LOD)

The LOD was determined based on the signal-to-noise (S/N) ratio. Determination of the S/N ratio is performed by comparing the signal measured from the standard with low concentrations of analyte to those of blank samples and establishing the minimum concentration at which the analyte can be reliably detected. A S/N=3 is used for estimating the detection limit (LOD) and S/N=10 is used for estimating the quantification limit (LOQ)[6]. In this study, the baseline noise was first determined by measuring the peak-to-peak noise in a representative 1 min segment of the baseline where no peaks elute, but close to the peak of interest. The signal was determined from the average height of three injections of standard (fluoride 0.625 mg/L, chloride 1.25 mg/L). The calculated LOD of fluorine in sample is 0.762 µg/g and the calculated LOD of chlorine in sample is 0.738 µg/g. The LOD were calculated based on a sample weight of 10 mg.

Sample analysis

Six iron ore samples were collected in Australia. Figure 5 shows the chromatogram of sample #1, which is a lighter colored sample (Tail) that is comprised mostly of Al_2O_3, CaO, MgO, and SiO_2. Figure 6 shows the chromatogram of sample #2, which is a dark sample (CON) that is comprised 20% Cu, 30% Fe, and 30% S. As the figures show, the Dionex IonPac AS18-Fast-4µm column achieves excellent resolution and sensitive detection for fluoride and chloride. Three replicate analyses were performed for each sample. Tables 4 and 5 summarize the result of fluorine and chlorine, respectively, in the six samples. Good precision was achieved as evidenced by the relative standard deviation (RSD) values calculated from the three replicate analyses (0.73–2.8%).

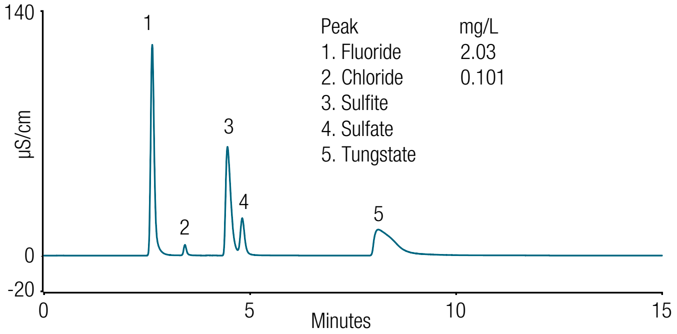


Figure 5. Determination of fluorine and chlorine in iron ore sample #1

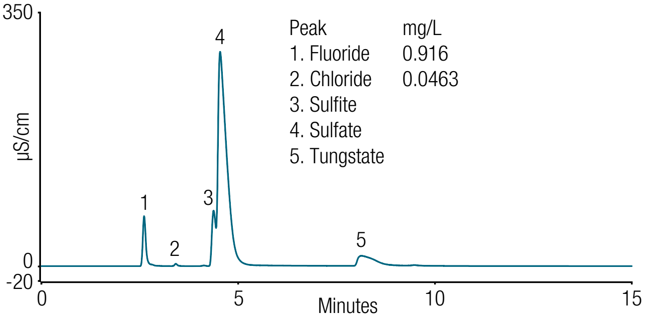


Figure 6. Determination of fluorine and chlorine in iron ore sample #2

Method precision

The precision of the method was determined by triplicate injections of the calibration standard level 5. The peak area precision is <0.05% with retention time precision <0.15% for both fluoride and chloride. The excellent retention time stability and peak area precision are consistent with results typically obtained when using an electrolytically generated high-purity potassium hydroxide eluent. The use of a Reagent-Free™ IC system with an electrolytically generated potassium hydroxide eluent further simplifies the method by eliminating the time required to manually prepare eluents and reducing the time required for method development.

Table 4. Fluorine in iron ore samples, ppm (µg/g)

Sample	S1	S2	S3	S4	S5	S6
Replicate 1	2002	883	1835	413	621	557
Replicate 2	2022	887	1771	410	620	562
Replicate 3	1993	917	1790	408	627	560
Average	2006	896	1798	410	623	560
RSD	0.73	2.1	1.8	0.67	0.58	0.48

Table 5. Chlorine in iron ore samples, ppm (µg/g)

Sample	S1	S2	S3	S4	S5	S6
Replicate 1	99.8	44.6	93.0	25.5	23.4	29.0
Replicate 2	99.3	43.2	91.1	24.2	23.0	30.3
Replicate 3	97.6	44.0	93.3	24.4	22.9	30.2
Average	98.9	44.0	92.5	24.7	23.1	29.8
RSD	1.2	1.7	1.3	2.8	1.2	2.3

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Conclusion

This study demonstrates that fluorine and chlorine can be determined sensitively and precisely in iron ore using combustion ion chromatography. Analysis was automated by using the Mitsubishi AQF-2100H system in combination with the Dionex Integrion HPIC system with a Dionex IonPac AS18-Fast-4µm column. The Reagent-Free ion chromatography system provides excellent reproducibility, thereby yielding greater quantification accuracy and consistently reliable results.

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