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# Simultaneous Determination of Fluorine and Chlorine in Marine and Stream Sediment by Ion Chromatography Combined with Alkaline Digestion in a Bomb

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**Abstract:** Fluorine and chlorine are important tracers for geochemical and environmental studies. In this study, a rapid alkaline digestion (NaOH) method for the simultaneous determination of fluorine and chlorine in marine and stream sediment reference samples using ion chromatography is developed. The proposed method suppresses the volatilization loss of fluorine and chlorine and decreases the matrix effects. The results are in good agreement with fluorine ~100%, chlorine ranging from 90 to 95% of the expected concentrations. The detection limits of this method were 0.05 µg/g for fluorine and 0.10 µg/g for chlorine. This method is simple, economical, precise and accurate, which shows great potential for the rapid simultaneous determination of fluorine and chlorine in large batches of geological and environmental samples commonly analyzed for environmental geochemistry studies.

**Keywords:** fluorine and chlorine; marine and stream sediment; ion chromatography; alkaline digestion; high pressure bomb

## 1. Introduction

Fluorine and chlorine are of great interest in geological and environmental studies due to their special, highly mobile and volatile properties [1,2]. Fluorine is a minor constituent in a wide range of sedimentary minerals including phosphorites, phosphates, carbonates, silicates and clay minerals [3–6]. Chlorine is the dominant ligand that enables metal transport in the majority of hydrothermal solutions [6–8]. Thus, the content of fluorine, chlorine and ratios of element/Cl in sediment can be used as tracers for chemical evolution of fluids and water/rock interactions in low temperature sediment alteration [9,10] and high temperature hydrothermal systems [11–14], element recycling during subduction-related sediment melting [4,15], and early diagenesis of sediment [3]. Therefore, recent studies have focused on the precise determination of fluorine and chlorine in sediment. Several analytical techniques have been applied to the determination of fluorine and chlorine: by specific ion selective electrode [16–18], instrumental neutron activation analysis (INAA) [16], radiochemical neutron activation analysis (RNAA) [19–22], prompt gamma neutron activation

analysis (PGNA) [23] or X-ray fluorescence spectrometry [24–27]. However, an ion selective electrode requires a rather complex preparation stage and the difficulties of other techniques are the requirement of special instruments and/or time-consuming processes [28]. Moreover, the detection limits of the determination by INAA or X-ray Fluorescence Spectrometry (XRFS) are generally too high, relative to usual abundances [29]. In contrast, ion chromatography, a compact and inexpensive instrument, is commonly used in many laboratories and is the most suitable method for sensitive and simultaneous determination of fluorine and chlorine [5,6,28–35]. However, it is difficult to quantitatively extract fluorine and chlorine from geological materials for ion chromatography analysis. So far, only a few methods have been used to extract fluorine and chlorine from geological samples, including pyrohydrolysis [5,6,29,31,32], alkaline fusion [5,17,28,30], microwave digestion [36], combustion [35] and NH<sub>4</sub>HF<sub>2</sub> digestion with subsequent ammonium dilution [37]. However, the pyrohydrolysis method is not suitable for the analysis of a large batch of samples [37]; alkali fusion requires a high flux-to-sample ratio which results in high blank levels, total dissolved solids (TDS) content and matrix effects [5,28], microwave digestion has poor recoveries caused by incomplete digestion of sediment samples containing zircon or other refractory minerals [38], and the NH<sub>4</sub>HF<sub>2</sub> digestion method cannot extract fluorine from geological materials [37]. Recently, a high-pressure digestion technique has been generally applied [8,36,39–41]. However, there are no reports about the simultaneous determination of fluorine and chlorine in sediment using this technique.

In this paper, a rapid alkaline digestion method for the simultaneous determination of fluorine and chlorine in marine and stream sediment reference samples using the high-pressure digestion bomb with a double inner arc seal design is described. The effects of the digestion parameters on the recoveries of fluorine and chlorine in sediment reference samples are described in detail. A small amount of the sample was digested, and the fluorine and chlorine were extracted completely. This method is practical and simple and can deal with a large number of samples simultaneously.

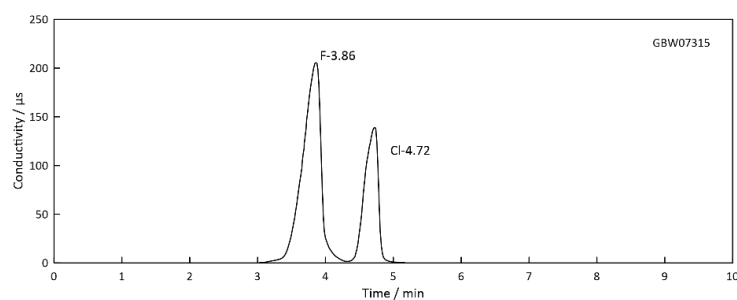
## 2. Experimental

### 2.1. Instrumentation

Experiments were carried out using ion chromatography (DX600, Dionex, CA, USA) at the Laboratory of Spartacus Testing Center, equipped with an anion exchange column in the suppression mode. Analytical conditions are reported in Table 1. Generally, the F<sup>-</sup> peak appeared at about 3.8 min after sample injection. Then, the Cl<sup>-</sup> peak appeared at about 4.7 min after the injection (Figure 1). One measurement cycle could be completed in ~10 min.

**Table 1.** Instrumental operating parameters used for ion chromatography analysis.

Operating Parameters	
Volume of Sample Injection Loop	25 µL
Column	IonPac AS14
Column Size	4 mm × 250 mm
Eluent	3.5 mmol/L Na <sub>2</sub> CO <sub>3</sub> + 1 mmol/L NaHCO <sub>3</sub>
Detector	Suppressed conductivity detector
Flow Rate	1.2 mL/min



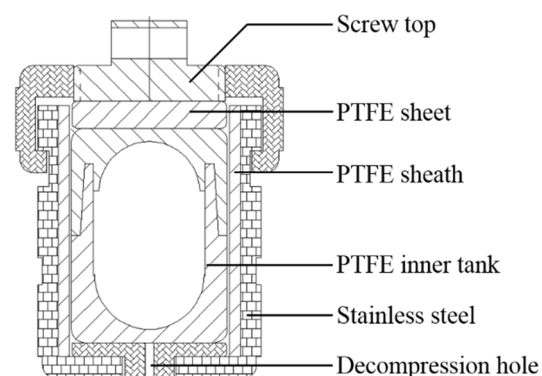
**Figure 1.** Chromatogram of marine sediment GBW07315.

### 2.2. Reagents and Certified Reference Materials

Alkaline digestion solution was prepared by diluting NaOH (AR, Aladdin, Shanghai, China) with pure water (18.2 M $\Omega$ ·cm grade). Eluent solution was prepared just before analysis by diluting Na<sub>2</sub>CO<sub>3</sub> (AR, Sinopharm, Shanghai, China) and NaHCO<sub>3</sub> (AR, Sinopharm, Shanghai, China) reagents with pure water. The calibration solutions were prepared by dilution from 1000 mg/L fluorine and chlorine standard solutions (National Research Center for Reference Materials, Beijing, China) with pure water. Three domestic reference materials GBW07315 (marine sediment from the CC area in the east pacific basin), GSD-9 (stream sediment from the Yangtze River) and GSD-10 (stream sediment from the catchment basin in Yishan, Guangxi Province) were used as reference samples. All these samples were in powder form with size less than 75  $\mu\text{m}$  as originally prepared. Reference GBW07315 was used to optimize the alkaline digestion temperature and time.

### 2.3. Laboratory Ware

A screw-top PTFE-lined, corrosive-resistant digestion bomb with a volume of ~15 mL was used for this research (Figure 2). This bomb has a double inner arc seal design, the inner tank has an oval cross-section, the upper part of the inner tank plugs into the top of the lower part. The inner tank was pre-cleaned with 10% HNO<sub>3</sub> and heated to boiling for about 12 h at 120 °C, then rinsed with pure water.



**Figure 2.** Sketch of the corrosive-resistant digestion bomb (Reproduced with permissions from Ref. [39], Copyright © 2018 Atomic Spectroscopy).

### 2.4. Sample Preparation

A total of 40 mg aliquot of sample powder was accurately weighed into the PTFE bombs and NaOH was added. The sealed bombs were then placed in an electric oven at 240 °C for 12 h. After cooling, 6 mL pure water was added, then the bombs were heated again in the electric oven at 180 °C for 12 h. After cooling again, the sample solution was transferred to a 15 mL centrifuge tube and diluted to 10 mL with pure water. After centrifuging for 8 min at 3000 rpm, 2 mL sample of the supernatant was transferred to a new polyethylene tube. The supernatant was measured by ion chromatography.

### 2.5. Calibration Curves and Limit of Detection

Fluoride and chloride calibration curves in the range of 1–10 µg/g and 1–200 µg/g were prepared respectively by dilution from 1000 mg/L standard solutions (National Research Center for Reference Materials, Beijing, China) with pure water (Figure 3). The correlation coefficient ( $R^2$ ) of the linear calibration is 0.9999 for fluorine and 0.9997 for chlorine, respectively. The method’s limit of detection (LOD, three times the standard deviation of the 6% NaOH blank solution for seven preparation blanks assuming a dilution factor of 250) for F and Cl were 0.05 µg/g and 0.10 µg/g, respectively.

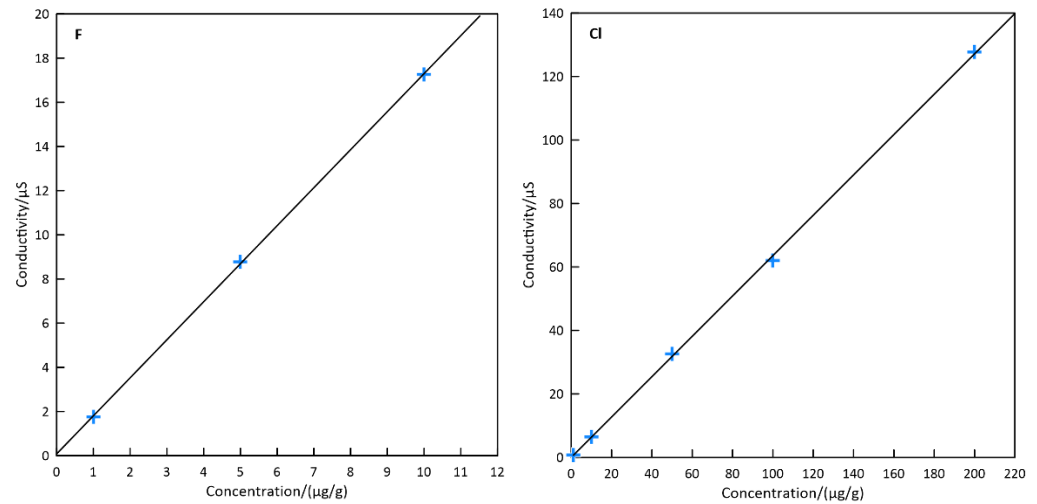


Figure 3. Fluoride and chloride calibration curves performed by ion chromatography.

### 3. Results

The measured concentrations of chlorine and fluorine were compared to the reference values provided for the standard material, GW07315, GSD-9 and GSD-10-1 (Table 2). Generally, the results are in good agreement with F- being ~100%, Cl ranging from 90–95% of the expected concentrations. The relative standard deviation between replicates was <6% and <10% for fluorine and chlorine, respectively.

Table 2. Results for GBW07315, GSD-9-1 and GSD-10-1, and Comparison with Certified Data.

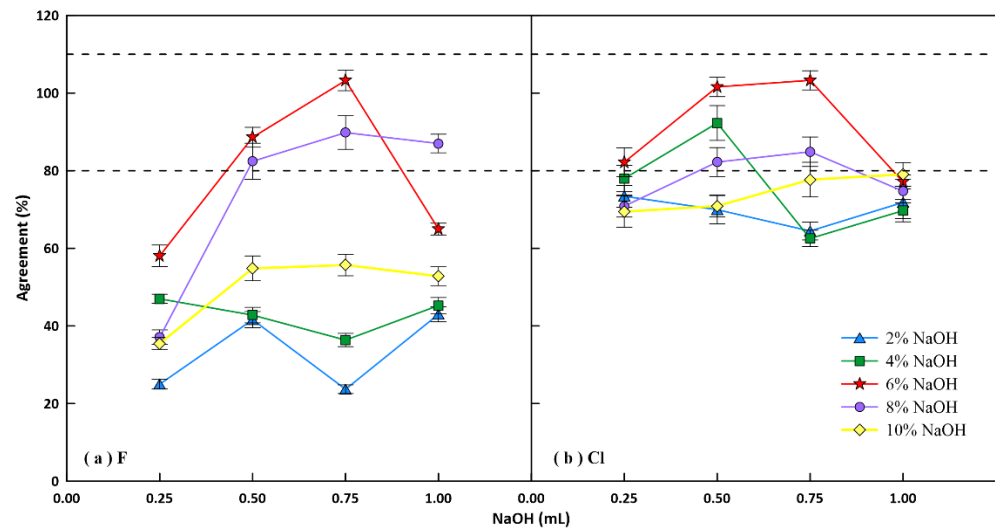
	GBW07315		GSD-9-1		GSD-10-1	
	F (µg/g)	Cl (µg/g)	F (µg/g)	Cl (µg/g)	F (µg/g)	Cl (µg/g)
1	1055	33,037	467	49	149	41
2	1176	34,452	503	43	140	48
3	1099	34,992	482	46	151	45
4	1152	33,982	518	56	161	49
5	1058	36,987	503	45	144	49
6	1034	31,972	525	44	157	45
7	1156	33,650	490	48	142	40
Measured Average Value	1104	34,153	498	47	149	45
Reference Value	1100	36,000 ± 3000	494 ± 39	52 ± 11	149 ± 38	50
Relative Standard Deviation	5.2%	4.6%	4.0%	9.5%	5.2%	8.0%
Accuracy	100%	95%	101%	90%	100%	90%

### 4. Discussion

#### 4.1. Effect of the Amount of NaOH

Although acid digestion has been commonly used for the decomposition of geological samples [38], mineral acids should be avoided to prevent losses of volatile halogens [37]. Alkaline fusion with NaOH can quantitatively extract fluorine [17] and chlorine [20–22] from geological materials, and the high-pressure digestion bomb requires a small amount of reagent, therefore NaOH was used as the digestion reagent. Figure 4 shows the agreements of F and Cl as a function of added NaOH amount for the digestion of 40 mg of GBW07315.

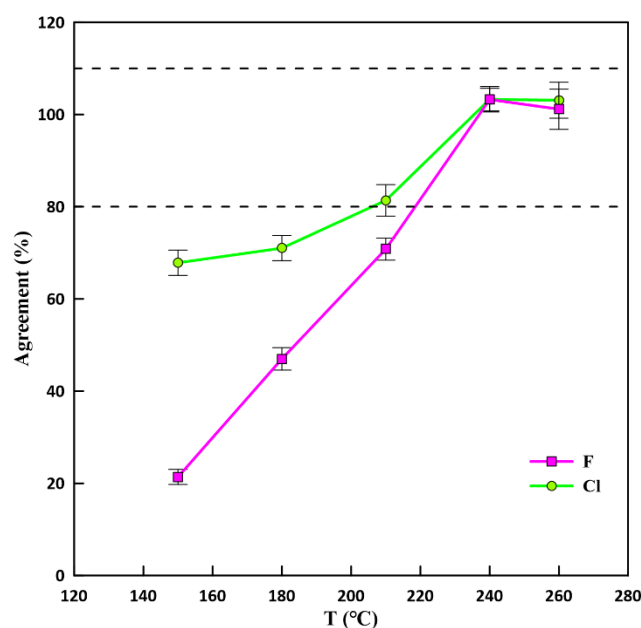
The agreements are expressed as ratios of the measured values relative to their reference values. It can be seen that F was completely recovered with 0.75 mL 6% NaOH, and the agreement for Cl was good with both 0.75 mL 6% NaOH and 0.50 mL 6% NaOH. Thus, the adopted optimum amount is 0.75 mL 6% NaOH.



**Figure 4.** Agreement of (a) fluorine and (b) chlorine as a function of the amount of NaOH. The dotted lines delimit recoveries between 80% and 110%. The agreement is the ratio of the measured value relative to reference values. Error bars represent relative standard deviation ( $n = 3$ ).

#### 4.2. Effect of Digestion Temperature

Figure 5 illustrates the variation of the agreements for F and Cl in GBW07315 at different digestion temperatures (150–260 °C) with 0.75 mL 6% NaOH. The observation demonstrates that the digestion temperature is the critical factor for the complete recovery of F and Cl. The recoveries of both F and Cl increased from 150 °C to 240 °C and they were completely recovered at 240 °C and 260 °C. Therefore 240 °C was used as the optimum for further extractions.



**Figure 5.** Agreement of fluorine and chlorine as a function of the digestion temperature with 0.75 mL 6% NaOH. The dotted lines delimit recoveries between 80% and 110%. The agreement is the ratio of the measured value relative to reference values. Error bars represent relative standard deviation ( $n = 3$ ).

#### 4.3. Method Efficiency

The recovery of the pyrohydrolysis method is not stable [8], probably due to the loss of the halogens or the incomplete extraction during the pyrohydrolysis process [21,22]. In contrast, the digestion bomb used in this study has a double inner arc seal design, allowing the evaporating material from the top to the bottom without clinging onto the inner tank wall, which provides an effective circulation and suppresses the volatilization loss of fluorine and chlorine. The present method consumes a small amount of alkaline (0.75 mL 6% NaOH can extract fluorine and chlorine from 40 mg sample completely) and decreases the matrix effects in comparison to the alkaline fusion method, which requires a large amount of flux and the matrix separation step leading to a high procedural blank [5,28,30]. The  $\text{NH}_4\text{HF}_2$  digestion method has been proposed recently, which suppresses the volatilization loss of chlorine effectively owing to the formed ammonium salts with high boiling points, however, this method cannot determine fluorine and chlorine simultaneously [37]. In addition, compared to the complicated pyrohydrolysis, alkaline fusion and combustion methods [5,6,17,28–32,35], the rapid alkaline digestion method is simple and can deal with a large batch of samples.

## 5. Conclusions

Our results show that NaOH digestion in a high-pressure bomb with double inner arc seal design can be used for the quantitative extraction of fluorine and chlorine in sediments. The proposed method is economical and requires a small amount of the sample and reagent. This effective and simple method has no contamination problems, with good accuracy, and shows great potential for the determination of fluorine and chlorine in large batches of geological and environmental samples.

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