Determination of Fluoride in Tea Using a Combustion Ion Chromatography (CIC) System

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ABSTRACT

Purpose: To develop a simple method to determine fluoride in tea using combustion ion chromatography (CIC) to replace the current Chinese national method.

Methods: CIC includes a combustion system and an ion chromatography (IC) system. A known amount of tea sample is oxidized by oxygen (oxidative pyrolysis) at temperatures of about 1000 °C in the combustion system. The combustion byproduct gases are passed through an aqueous absorbing solution, and then directly injected into the IC system for analysis. The fluoride in tea is calculated from the fluoride concentration in the injected sample.

Results: Using the CIC system, fluoride in tea is determined in 11 to 20 min, a significant time savings of more than one hour compared to the current Chinese national method. The CIC method is sensitive (MDL =1 ppm), precise, and accurate. The only sample preparation required is that the tea be ground and dried[1].

INTRODUCTION

When excessive amounts of fluoride are consumed, it can lead to dental fluorosis, bone fractures, and skeletal fluorosis. Currently, the U.S. Environmental Protection Agency (EPA) has an enforceable drinking water standard of 4.0 ppm for fluoride with a non-enforceable secondary standard of 2.0 ppm to protect children against tooth discoloration and/or pitting[1].

Tea is an important product for China's economy. However, all tea plants have an affinity for fluoride. Indiscriminate consumption of tea can lead to soaring levels of fluoride in the body, especially if it is brewed with fluoridated water. According to China national standard NY659-2003, 200 ppm fluoride is the limit for tea[2]. The current standard test method of fluoride in tea is NY/T 838-2004 [3], which is an ion-selective electrode method. It requires preparation of a strong oxidizing perchloric acid solution and Total Ionic Strength Adjustment Buffer (TISAB) solution before measurement. For each measurement, more than 60 min of lab work is needed: weigh the tea sample, add into 25 mL perchloric acid solution, stir for 30 min, add 25 mL TISAB solution, stir for another 30 min, and then determine the fluoride concentration using a fluoride-selective electrode. The electrode also needs to be thoroughly washed and reconditioned before each new measurement. This method is lengthy, potentially unsafe, and cumbersome.

IC is the most sensitive and versatile method for the determination of halides (including fluoride), but determining fluoride in tea using brewed tea is problematic because 1) organic acids that elute near fluoride can impact quantification, 2) brewing time and water hardness affect fluoride release from tea[4]. CIC has been demonstrated for many applications, such as the determination of halogens in coal [5]. 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 interferences.

This study[6] shows development of a simple CIC method to determine fluoride in tea. The CIC system used for this method includes a Mitsubishi Automatic Combustion Unit Model AQF-2100H system and a Thermo Scientific™ Dionex™ Integrion™ HPIC™ system equipped with the Thermo Scientific™ Dionex™ IonPac™ AS18-4µm column set (Figure1).

Figure 1. A combustion ion chromatography (CIC) system.

METHODS AND MATERIALS

Methods: A CIC system, including a Mitsubishi Automatic Combustion Unit Model AQF-2100H system and a Thermo Scientific™ Dionex™ Integrion™ HPIC™ compact IC system (Figures 1and 2), is used to determine the fluoride in tea. About 20 mg of tea sample is weighed into the sample boat and combusted according to the combustion conditions (Table 1). The combustion byproduct gases are passed through an aqueous absorbing solution and then injected into the IC system for analysis (analysis conditions in Table 2).

Figure 2. Illustration of a CIC system.

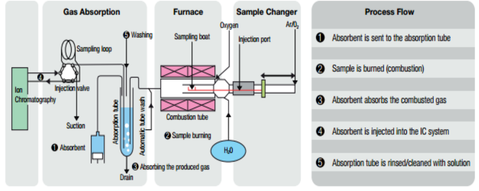


Table 1. Combustion conditions.

Sample size	~ 20 mg
Sample boat	Ceramic
Pyrolysis tube	Quartz tube with ceramic insert and quartz wool
Absorption solution	DI water
Mode	Constant volume
Furnace inlet temp	900 °C
Furnace outlet temp.	1000 °C
Argon flow (Carrier)	200 mL/min
Oxygen flow (Combustion agent)	400 mL/min
Absorption tube	10 mL
Sample loop	100 µL
Final absorption solution vol.	10 mL
Combustion position/time	Programmed

Table 2. Chromatographic conditions.

Columns:	Dionex IonPac AG18-4µm guard (4 × 30 mm) and Dionex IonPac AS18-4µm analytical (4 × 150 mm)
Eluent:	20 mM KOH
Eluent Source:	Dionex EGC 500 KOH Eluent Generator Cartridge with a Dionex CR-ATC 600 Continuously Regenerated Anion Trap Column and high pressure EG degasser
Flow Rate	1.00 mL/min
Column. Temp.	30 °C
Compartment Temperature	25 °C
Detector Temperature	35 °C
Injection Volume	100 µL, (Full loop)
Detection	Suppressed conductivity, Dionex AERS 500 suppressor, 4 mm, 50mA, recycle mode,
Run time (min)	10 min

Data Analysis: By Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS), version 7.2 SR4.

With the Constant Volume mode, Fluoride in tea = Fluoride in absorbing solution x the dilution factor. The fluoride in absorbing solution was determined using a calibration curve produced with eight concentration levels ranging from 0.002 to 2.00 ppm. The dilution correction factor is determined following instructions in the Mitsubishi Automatic Combustion Unit Model AQF-2100H manual[7]. The dilution factor is around 10000 when a 10 mL absorption tube is used.

Sample Preparation

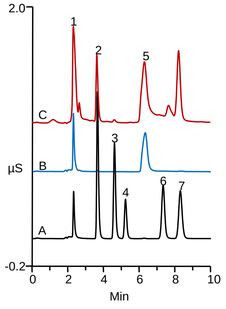
Three tea samples were obtained from stores in China.
Grind at least 25 g of each tea using an electric coffee grinder
Dry sample at 100 °C overnight (>14 h)
Brew tea: Soak 5 g of the dried tea in 50 g of boiled DI-water (~ 100 °C) for 5 min, filter the tea solution and reserve for analysis. Rinse the brewed tea (solid) twice with DI water, then dry it at 100 °C overnight, and grind it.
To assess recovery, 20 µL of a 50 mg/L or 100 mg/L ammonium fluoride solution is added into the 20 mg tea sample in the sample boat using a 100 µL syringe.

RESULTS

Distribution of Fluoride When Brewing Tea

Figure 3 shows a comparison of the chromatograms of the brewed tea solution when directly injected into the IC and when introduced through combustion IC by the Liquid Sample Changer Model ASC-250L. The chromatogram of the tea solution without combustion shows a number of peaks, presumably organic acids, eluting either near or co-eluting with fluoride. This will result in the determined amount of fluoride in tea exceeding the actual value. The combustion process converts organic acids to carbon dioxide and water, therefore fluoride analysis is simplified. As shown in Figure 3, the CIC chromatogram of the same tea solution shows a clean fluoride peak which leads to accurate quantitation of fluoride. Table 3 shows fluoride distribution when brewing 5 g of dried Tea 3 in 50 g of boiled DI water (~ 100 °C) for 5 min. A significant portion (41.1%) of the fluoride remained in the brewed tea leaf. Therefore, the solid tea sample, not the brewed tea solution, should be used to determine the total fluoride content.

Figure 3. Comparison of the chromatograms of tea solution with and without combustion.



Sample :
A 0.02 ppm Fluoride in DI water (Direct inj.)
B 20 µL tea solution* through CIC
C 1000x diluted tea solution (Direct inj.)

* Tea solution preparation: Brew 5 g tea in 50 mL DI-water for 5 minutes, filter tea through 0.2 µm filter

Peaks:
1. Fluoride
2. Chloride
3. Nitrite
4. Unknown
5. Carbonate
6. Sulfite
7. Sulfate

Table 3. The distribution of fluoride when brewing tea.

	Fluoride (ppm)	% Fluoride
Fluoride in brewed tea (Tea 3)	77±4 (n=3)	59
Fluoride remaining in the tea after brewing	54 ±10 (n=3)	41

Calibration and Method Detection Limit (MDL)

Table 4 summarizes the calibration and MDL of the CIC method. The calibration is linear with r^2=0.9993. But a quadratic calibration (r^2=1.0000) is recommended for better fit and more accurate determination of the fluoride of the tea sample with dilution factor at about 10,000. The method detection limit (MDL) of the IC method was determined following the guidelines outlined in USP General Chapter, Validation of Compendial Methods[8]. It is calculated by > 7 injections of the lowest calibration standard 0.002 mg/L, and MDL = 3.14 × σ (standard deviation) = 0.0002 ppm. Based on the dilution factor of 10,000, the estimated MDL for the CIC method is 2 ppm. The repeat burnings of 4.0 ppm standards were also used to determine the MDL of the combustion CIC method for tea. Following the same guidelines[8], the MDL of the CIC method for tea = 1ppm. In conclusion, the CIC method is sensitive for determining fluoride in tea.

Table 4. Fluoride calibration and method detection limit (MDL).

Calibration Range (ppm)	Calibration Type	Coefficient of Determination (r^2)	MDL (ppm)
0.002–2.00	Quadratic	1.000	0.0002
0.002–2.00	Linear	0.9993	0.0002

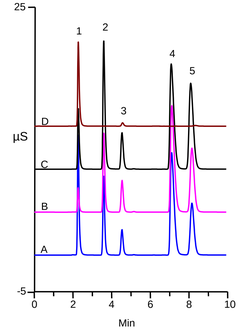
Determination of Fluoride in Tea by CIC

CIC was used to determine fluoride in three tea samples. The CIC method to determine fluoride in tea is simple in that the only sample preparation required is that the tea be ground and dried. The results of fluoride in Tea 1, Tea 2, and Tea 3 are shown in Table 5 and Figure 4.

Table 5. Fluoride in tea samples.

	Fluoride in Tea (ppm)
Tea 1	279+3 (n = 13)
Tea 2	55+4 (n = 20)
Tea 3	129+3 (n = 6)

Figure 4. Combustion ion chromatograms of tea samples



Sample : Fluoride (mg/Kg)
A Tea 1 279
B Tea 2 55
C Tea 3 129
D 200 ppm F^-(NH_4F) 200

Peaks:
1. Fluoride
2. Chloride
3. Nitrite
4. Sulfite
5. Sulfate

As sample matrix may impact the precision and accuracy, method performance was also evaluated by spike recovery in tea samples. Table 6 shows results of the spike recoveries of fluoride in three teas. When spiking either 50 ppm or 100 ppm of fluoride, the calculated recoveries were from 95–116% for all samples. The CIC method to determine fluoride in tea exhibits good precision and accuracy.

Table 6. Recovery of fluoride in tea.

	Fluoride Spiked (ppm)	Recovery (%)
Tea 1	50	111±7 (n=3)
Tea 2	50	103±6 (n=3)
Tea 2	100	99±1 (n=3)

CONCLUSIONS

This study demonstrates:

- A simple CIC method to determine fluoride in tea that the only sample preparation required is the tea be ground and dried.
- Using the CIC system fluoride in tea is determined in 11 to 20 min, a significant time savings over the current Chinese national method.
- The CIC method is sensitive (MDL =1 ppm), precise (RSD<8%), and accurate (recovery 99-111%).

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TRADEMARKS/LICENSING

PO72498-EN 0318S