# Determination of fluoride in tea using a combustion ion chromatography system

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## Goal

To develop a simple method to determine fluoride in tea using combustion ion chromatography (CIC), including a Mitsubishi Automatic Combustion Unit Model AQF-2100H system and a Thermo Scientific™ Dionex™ Integrion™ HPIC™ system.

## Introduction

Consumption of excessive amounts of fluoride can lead to dental fluorosis, bone fractures, and skeletal fluorosis. Currently, the U.S. 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 increased levels of fluoride in the body, especially if the tea is brewed with fluoridated water. China national standard NY659-2003 sets a limit of 200 ppm fluoride for tea.[2] The current standard method for determining

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fluoride in tea is NY/T 838-2004,[3] which is an ion-selective electrode method. It requires preparations of 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, unsafe, and tedious.

Ion chromatography (IC) is the most sensitive and versatile method for the determination of halides (including fluoride). However, determining fluoride in brewed tea is problematic because organic acids that elute near fluoride can impact quantification and brewing time and water hardness affect fluoride release from tea.[4] Combustion IC (CIC) has been demonstrated for many applications, such as the determination of halogens in coal.[5] Using CIC, samples are oxidized (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 application note shows development of a simple CIC method to determine fluoride in tea. The CIC system used for this method is comprised of a Mitsubishi® Automatic Combustion Unit Model AQF-2100H system and a Dionex Integrion HPIC system equipped with the Thermo Scientific™ Dionex™ IonPac™ AS18-4μm column set.

## Experimental
### Equipment
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

Dionex Integrion HPIC system including:

- Dionex Integrion HPIC system pump

- CD Conductivity Detector

- Detector Compartment Temperature Control

- Column Oven Temperature Control

- Tablet Control

- Consumables Device Tracking Capable

- Eluent Generation

* Equivalent results can be achieved using an Automatic Boat Controller with solid sample changer.

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

**Table 1. Consumables list for the Dionex Integrion HPIC system.**

| Product Name | Description | Part Number |
|---|---|---|
| Thermo Scientific™ Dionex™ IC PEEK Viper™ Fitting Tubing Assembly Kits | Dionex IC Viper fitting assembly kit for the 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 |
| | EGC Eluent Out to 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 |
| | CR-TC Eluent Out to Degasser Eluent In: 0.007 in i.d., 9.5 in long (241 mm) | 088811 |
| Thermo Scientific™ Dionex™ EGC 500 KOH Eluent Generator Cartridge | Eluent generator cartridge | 075778 |
| Thermo Scientific™ Dionex™ CR-ATC 600 Continuously Regenerated Anion 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 |
| Thermo Scientific™ Dionex™ AERS™ 500 Carbonate Electrolytically Regenerated Suppressor | Suppressor for 4 mm columns | 082540 |
| Thermo Scientific™ Dionex™ IonPac™ AG18-4µm Guard Column | Anion guard column, 4 × 30 mm | 076035 |
| Thermo Scientific™ 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

## Software
• Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) Software, version 7.2 SR4 MUb (8525)

• Mitsubishi NSX-2100 version 2.1.6.0

## Reagents and standards
• Deionized (DI) water, 18 MΩ·cm resistivity or better

• Dionex IC Standard, Fluoride Standard (1000 mg/L), 100 mL, P/N 037158

• Ammonium fluoride, (Sigma-Aldrich®, ≥99.99%)

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

To prepare the 2000 ppm fluoride stock standard, 389.9 ± 0.1 mg of ammonium fluoride was accurately weighed into a 100 mL volumetric flask and ~50 mL of DI water was added. The flask was swirled to dissolve the ammonium fluoride, filled to the mark with DI water, and then mixed thoroughly. The stock standard was stored at 4 °C and was stable for one month. Because ammonium fluoride sublimates when heated, this fluoride stock standard can be used for either IC or CIC.

## Working standard solutions

Working standard solutions were prepared for the External Solution Selector ES-210 by diluting the Dionex IC Fluoride Standard (1000 mg/L) or the 2000 ppm ammonium fluoride stock standard with DI water (Table 2).

Working standard solutions were prepared for the Liquid Sample Changer Model ASC-250L by diluting the 2000 ppm ammonium fluoride stock standard with DI water (Table 3). The Dionex IC Fluoride Standard is not recommended here because it is prepared from its sodium form, which causes quartz devitrification at high concentration.

## Samples

Three tea samples were obtained from stores in China and were stored at room temperature:

• Tea 1 was in an individually sealed vacuum package, about 7 g/package.

• Tea 2 was in a sealed paper package with a GB/T18650 label.

• Tea 3 was originally in a sealed plastic package but had been previously opened for about a year.

To prepare tea samples for fluoride determination, at least 25 g of tea for each tea sample was ground using an electric coffee grinder and the tea sample was dried at 100 °C overnight (>14 h) if the package was previously opened.

The following samples were also included in this work for comparison:

• Tea samples directly from the package without grinding.

• Freshly ground tea samples without drying. Tea samples 1 and 2 were ground immediately after the package was opened.

• Ground tea sample 3 dried at 100 °C for 1 h.

To understand the fluoride distribution when brewing tea, the tea was dried overnight, 5 g of the dried tea was soaked in 50 g of boiled DI water (~100 °C) for 5 min, the tea solution was filtered, and the fluoride in the tea solution was measured using CIC. The remaining fluoride in the brewed tea (solid) was measured using CIC after rinsing the tea twice with DI water, drying it at 100 °C overnight, and grinding it. For comparison, 1000-fold diluted filtered tea solution was directly injected into the IC through the External Solution Selector ES-210 (i.e. a non-combusted sample).

To assess recovery, 20 µL of a 50 mg/L or 100 mg/L ammonium fluoride solution were added into the 20 mg tea sample in the sample boat using a 100 µL syringe.

Table 2. Concentration of working standards for the ES-210.

| Calibration Level | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Concentration (ppm) | 0.002 | 0.005 | 0.02 | 0.05 | 0.20 | 0.5 | 1.00 | 2.00 |

Table 3. Concentration of working standards for the ASC-250L.

| Calibration Level | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Concentration (ppm) | 4.0 | 10.0 | 50.0 | 100 | 200 | 500 | 1000 | 2000 |

## Combustion conditions

**Table 4. Combustion conditions.**

| AQF-2100H | |
|---|---|
| Sample size | ~ 20 mg |
| Sample boat | Ceramic |
| Pyrolysis tube | Quartz tube with ceramic insert and quartz wool |
| Absorption solution | DI water |
| **HF-210** | |
| Furnace inlet temp. | 900 °C |
| Furnace outlet temp. | 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 |
| Washing parameter | 341 |
| 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 |
| **Gas line collection parameters** | |
| Collection time | 0.5 s |
| Collection interval | 3.0 s |
| Times | 3 |
| **Injection parameters** | |
| Washing time for injection start | 0 s |
| Sample purge time | 5 s |
| Sample absorption time | 10 s |
| **ABC-210/ ASC-250L** | |
| Argon time | 10 s |
| Oxygen time | 600 s |

| Position (mm) | Wait Time (s) | Speed (mm/s) |
|---|---|---|
| 85 | 60 | 10 |
| 130 | 60 | 10 |
| 160 | 120 | 10 |
| 200 | 180 | 10 |
| End | 90 | 10 |
| Cool | 60 | 40 |
| Home | 120 | 40 |

*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.[6]

## Chromatographic conditions

**Table 5. Chromatographic conditions.**

| | |
|---|---|
| Columns | Dionex IonPac AG18-4µm guard (4 × 30 mm) Dionex IonPac AS18-4µm analytical (4 × 150 mm) |
| Eluent | 20 mM KOH |
| Eluent source | Dionex EGC 500 KOH cartridge with Dionex CR-ATC 600 trap column and high pressure EG degasser |
| Flow rate | 1.00 mL/min |
| Column temperature | 30 °C |
| Detector compartment Temperature | 25 °C |
| Detector temperature | 35 °C |
| Injection volume | 100 µL, (Full loop) |
| Detection | Suppressed conductivity, Dionex AERS 500 suppressor, 4 mm, 50 mA, recycle mode, |
| Run time | 10 min |
| Background conductance | < 0.5 µS |
| Typical noise | < 1 nS |
| System backpressure | ~ 2800–2900 psi |

## Determination of fluoride in tea

Fluoride in tea is determined by CIC using 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, the weight of each tea sample and dilution factor need to be entered into the data sequence pane of the Chromeleon CDS software console window to calculate the concentration of fluoride in the tea sample. The dilution correction factor is determined following instructions in the Mitsubishi Automatic Combustion Unit Model AQF-2100H manual[6]. The dilution factor is around 10,000 when a 10 mL absorption tube is used. Method 2 uses injection of liquid standards through the Liquid Sample Changer Module ASC-250L. Because both standards and samples are combusted in the same way, the dilution correction factor is not needed. Only the weight of each tea sample needs to be entered into the data sequence pane of the Chromeleon CDS software.

## Instrument setup and installation

Follow TN72211 to setup the system for this application.[7] The Mitsubishi Automatic Combustion Unit Model AQF-2100H system was connected to the Dionex Integrion HPIC system according to Figure 1.
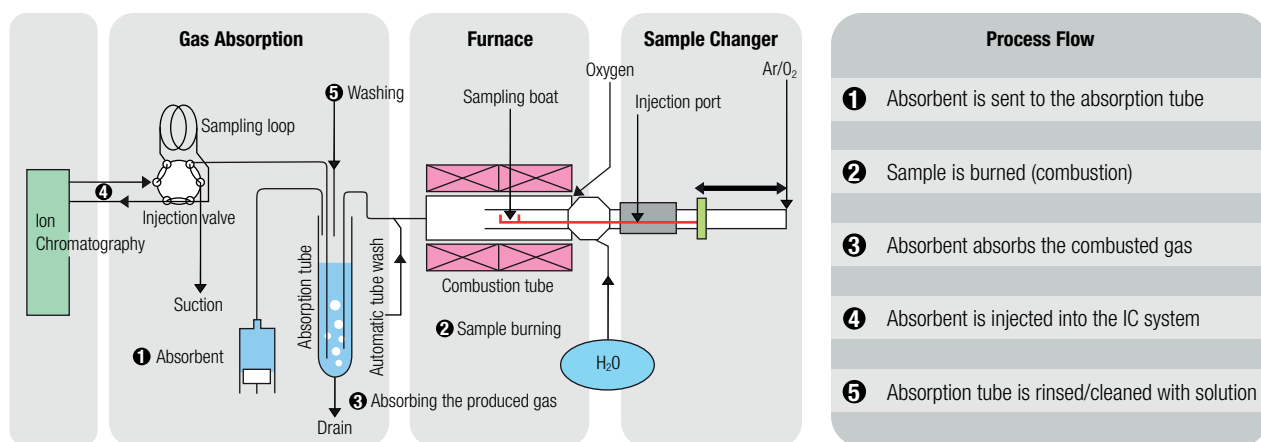


Figure 1. Diagram of a combustion ion chromatography (CIC) setup.

The Dionex Integrion HPIC system is a high-pressure-capable integrated RFIC system designed for high pressure eluent generation under conditions up to 5000 psi. The details on preparing an IC system for the analysis can be found in TN 175.[8] The key steps include:

- Configuring the modules in the Chromeleon CDS software

- Plumbing the high pressure Dionex Integrion HPIC system

- Conditioning electrolytic devices and columns according to their product manuals

- Starting the Dionex Integrion HPIC system

- Creating an Instrument Method

## Results and discussion

Compared to the current standard test method for fluoride in tea (NY/T 838-2004)3, which needs more than one hour with many manual steps for sample preparation, this method is short and simple. As illustrated in Figure 1, after placing the boat containing the weighed tea sample into the sample changer, the sample is sent to the furnace and combusted for about 10 min using the combustion conditions listed in Table 4. The combusted gas is absorbed by DI water and is then analyzed by IC in 10 min (Table 5). This automated method requires about 20 min per sample. By overlapping the functions of the IC and the combustion unit, the time is shortened to about 11 min per sample.

In this application note, calibration method 1 was used to determine fluoride in tea samples. The IC system was calibrated by direct injection of fluoride standards through the External Solution Selector ES-210. To determine the linear calibration ranges, the peak area responses to concentration were determined using a minimum of triplicate injections of calibration standards over the calibration range of 0.002 to 2.00 mg/L. The calibration was linear with $r^2$ = 0.9993. However, a quadratic calibration ($r^2$ = 1.0000) was used here because it was a better fit for the data and should therefore provide a more accurate determination of the fluoride in the tea sample with dilution factor of 10,000. Figure 2 shows the quadratic calibration curve.

The method detection limit (MDL) of the IC method was determined following the guidelines outlined in USP General Chapter, Validation of Compendial Methods.[9] 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. Table 6 summarizes the calibration and MDL of the IC method.
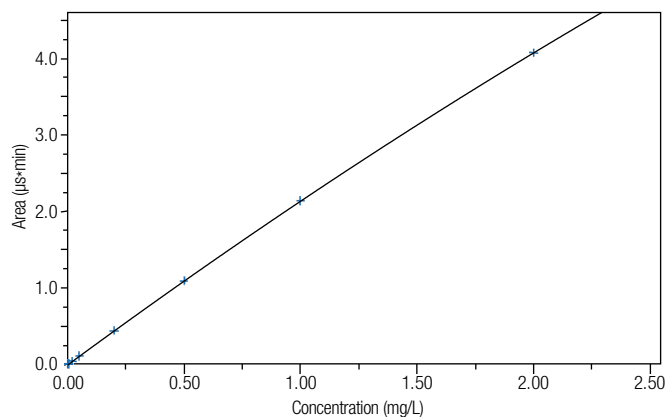


Figure 2. Fluoride calibration curve from 0.002 to 2.00 mg/L.

Table 6. Summary of calibration and the IC method detection limit (MDL) for fluoride.

| 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 |

Figure 3 shows a comparison of the chromatograms of the brewed tea solution when directly injected to IC and when introduced through CIC by the Liquid Sample Changer Model ASC-250L. The chromatogram of the tea solution without combustion shows several peaks, presumably organic acids, either eluting near or coeluting with fluoride. As a result, the determined amount of fluoride in tea exceeds the actual value. The combustion process converts organic acids to carbon dioxide and water; therefore, fluoride analysis is simplified. As seen in Figure 3, the CIC chromatogram of the same tea solution shows a clean fluoride peak, leading to accurate quantitation.

Columns:            Dionex IonPac AG18-4µm, and Dionex IonPac AS18-4µm, 4 mm
Eluent:             20 mM KOH
Eluent Source:      Dionex EGC-500 KOH cartridge,with Dionex CR-ATC 600 trap column,
                    Dionex high pressure degasser
Flow Rate:          1.0 mL/min
Inj. Volume:        100 µL
Column Temp.:       30 °C
Detection:          Suppressed conductivity, Dionex AERS 500, 4 mm,
                    35 °C, 50 mA, recycle mode
                    Compartment Temp. 25 °C
Sample Prep.:       Brew 5 g tea in 50 mL DI-water for 5 min, filter tea through 0.2 µm filter

Sample:             A. 0.02 ppm Fluoride (Direct inj.)
                    B. 20 µL tea solution through CIC
                    C. 1000× diluted tea solution (Direct inj.)

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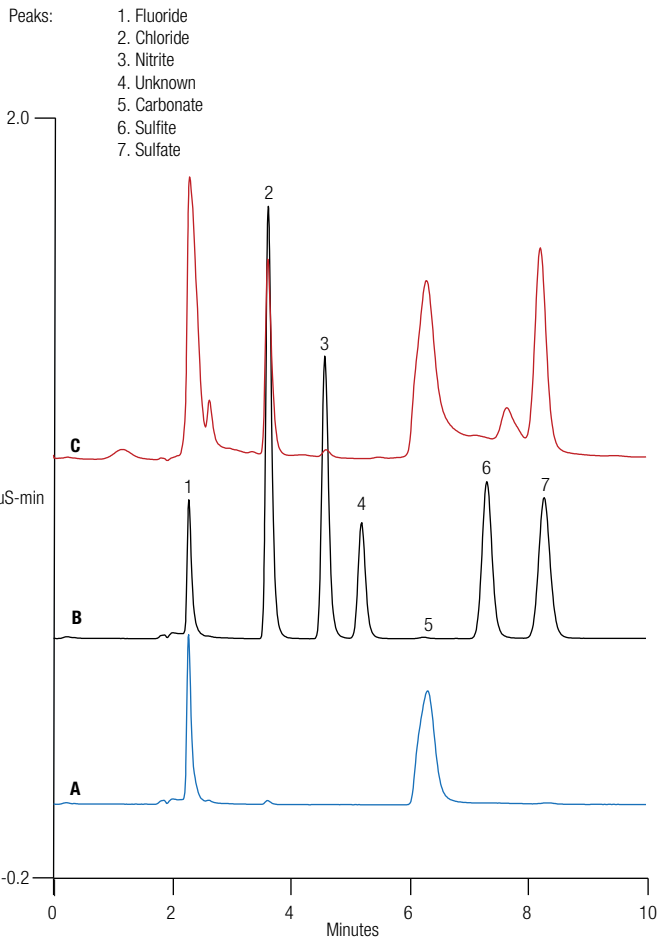                    6. Sulfite
                    7. Sulfate



Figure 3. IC and combustion IC chromatograms of the tea solution.

Table 7 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%) 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.

Table 7. Distribution of fluoride in tea after brewing.

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

Figure 4 shows CIC chromatograms of a 200 ppm fluoride standard and about 20 mg of the three tea samples. The peaks of fluoride, chloride, nitrite, sulfite, and sulfate indicated that F, Cl, N, and S are present in all three teas. The fluoride levels vary among samples: 279 ppm in Tea 1, 55 ppm in Tea 2, and 129 ppm in Tea 3.

Columns:            Dionex IonPac AG18-4µm, and Dionex IonPac AS18-4µm, 4 mm
Eluent:             20 mM KOH
Eluent Source:      Dionex EGC-500 KOH cartridge,with Dionex CR-ATC 600 trap column,
                    Dionex high pressure degasser
Flow Rate:          1.0 mL/min
Inj. Volume:        100 µL
Column Temp.:       30 °C
Detection:          Suppressed conductivity, Dionex AERS 500, 4 mm,
                    35 °C, 50 mA, recycle mode
                    Compartment Temp. 25 °C
Sample Prep.:       Brew 5 g tea in 50 mL DI-water for 5 min, filter tea through 0.2 µm filter
Sample size:        ~20 mg

Sample :                                Fluoride (ppm)
                    A. Tea 1                  279
                    B. Tea 2                   55
                    C. Tea 3                  129
                    D. 200 ppm F-(NH$_4$F)    200

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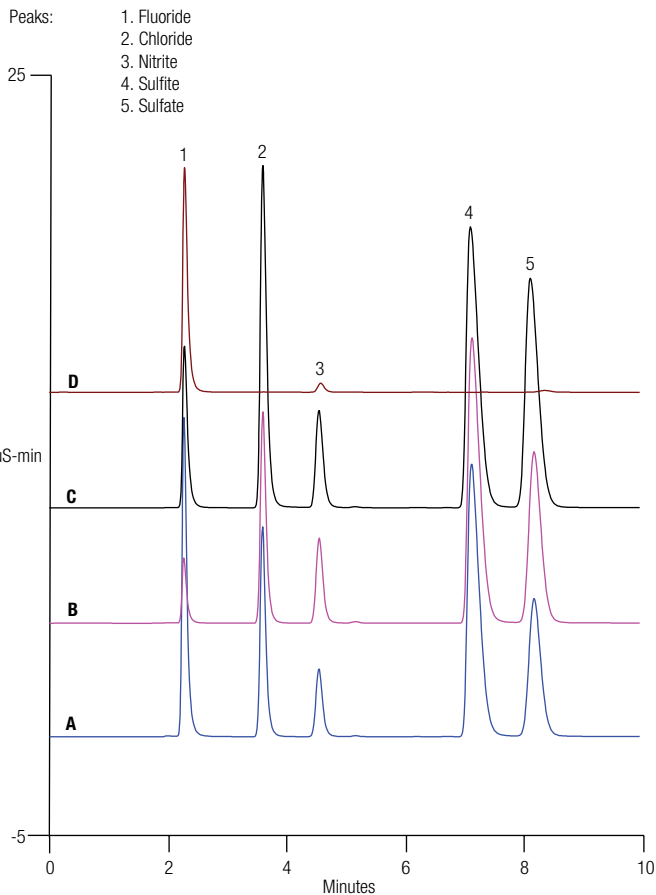                    5. Sulfate



Figure 4. Combustion IC chromatograms of standard and teas.

In the development of this CIC method, different sample preparations were explored. Table 8 shows the results of fluoride in Tea 3 with different preparations. The results suggest that not all of the tea within a single package is homogeneous with respect to fluoride. The most consistent results are achieved by grinding the tea. Therefore, grinding is the recommended sample preparation for this analysis. The drying test also indicated that drying overnight at 100 °C is necessary for fluoride recovery.

The CIC method performance was measured by recovery of known fluoride standards. The standards from 4 to 2000 ppm were introduced using the Liquid Sample Changer Module ASC-250L and combusted. The fluoride concentration was then measured using calibration method 1. Table 9 summarizes the results. From 10 to 2000 ppm, the method is accurate with 100±5% compared to its actual value. The repeated combustion of the 4.0 ppm standard was used to determine the MDL of the combustion CIC method for tea following the same guidelines.[9] The MDL of the combustion CIC method for tea was determined to be 1 ppm.

Table 8. Fluoride in Tea 3 with different sample preparations.

|  | Tea Sample and Replicate | Fluoride (ppm) | Average |
|---|---|---|---|
| No grinding No drying | Tea leaf 1 (19.70 mg) | 137 | |
|  | Tea leaf 2 (22.66 mg) | 68 | 102±29 (n=4) |
|  | Tea leaf 3 (25.78 mg) | 111 | |
|  | Tea leaf 4 (21.44 mg) | 92 | |
| Ground | Tea Powder 1 | 115 | |
|  | Tea Powder 2 | 110 | 114±4 (n=3) |
|  | Tea Powder 3 | 116 | |
| Ground and dried at 100 °C for 1 h | Tea Powder 4 | 113 | |
|  | Tea Powder 5 | 118 | 115±3 (n=3) |
|  | Tea Powder 6 | 114 | |
| Ground and dried at 100 °C overnight | Tea Powder 7 | 125 | |
|  | Tea Powder 8 | 133 | |
|  | Tea Powder 9 | 131 | 129±3 (n=6) |
|  | Tea Powder 10 | 127 | |
|  | Tea Powder 11 | 129 | |
|  | Tea Powder 12 | 128 | |

Table 9. Accuracy for fluoride determination from 4 to 2000 ppm.

| Concentration (ppm) | Measured Conc. (ppm) | Replicates | Recovery (%) |
|---|---|---|---|
| 4.0 | 4±0.4 | 16 | 100±10 |
| 10.0 | 10±0.4 | 10 | 100±4 |
| 50.0 | 51 | 1 | 102 |
| 100.0 | 99 99 | 2 | 99 |
| 200.0 | 202±2 | 4 | 101±1 |
| 500.0 | 496 | 1 | 99 |
| 1000.0 | 1000 | 1 | 100 |
| 2000.0 | 2055 | 1 | 103 |

The results of the fluoride determinations in Tea 1, Tea 2, and Tea 3 are shown in Table 10. Both Tea 1 and Tea 2 were in sealed packages before grinding. As no difference was observed before and after drying Tea 1 and Tea 2 samples, all data points were used to calculate the average fluoride content in these two teas. The determined fluoride concentrations in teas were as follows: 279±3 ppm in Tea 1, 55±4 ppm in Tea 2, and 129±3 ppm in Tea 3.

As sample matrix may impact the precision and accuracy, method performance was also evaluated using spike recovery in tea samples. Table 11 shows the 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% to 116% for all samples. The CIC method to determine fluoride in tea exhibits good precision and accuracy.

**Table 10. Fluoride in Tea 1, Tea 2, and Tea 3.**

| Sample | Measurement Time | Fluoride (ppm) | Average | RSD |
|---|---|---|---|---|
| Tea 1 Freshly ground without drying | Day 1 | 280±3 (n=3) | 279±3 (n=13) | 1 |
| | Day 2 | 278±5 (n=3) | | |
| | Day 3 | 279±2 (n=3) | | |
| Tea 1 Ground and dried at 100 °C overnight | Day 4 | 278±3 (n=4) | 279±3 (n=13 | 1 |
| Tea 2 Freshly ground without drying | Day 2 | 55±5 (n=9) | 55±5 (n=20) | 8 |
| Tea 2 Ground and dried at 100 °C overnight | Day 4 | 57±3 (n=3) | 55±5 (n=20 | 8 |
| | Day 5 | 53±4 (n=8) | | |
| Tea 3 Ground and dried at 100 °C overnight | Day 4 | 129±3 (n=6) | 129±3 (n=6) | 2 |

**Table 11. Recovery of fluoride in tea.**

| Sample | Fluoride (ppm) | Recovery* (%) | Average recovery (%) |
|---|---|---|---|
| Tea 1 (279 ppm F⁻) 50.0 ppm spiked | 337 | 116 | 111±7 (n=3) |
| | 330 | 103 | |
| | 336 | 114 | |
| Tea 2 (55 ppm F⁻) 50 ppm spiked | 109 | 107 | 103±6 (n=3) |
| | 108 | 104 | |
| | 104 | 95 | |
| Tea 2 100 ppm spiked | 155 | 99 | 99±1 (n=3) |
| | 153 | 97 | |
| | 155 | 99 | |
| Tea 3 (129 ppm F⁻) 100 ppm spiked | 229 | 101 | |

## Conclusion

This application note demonstrates a simple CIC method to determine fluoride in tea. Using the CIC system, fluoride in tea is determined in 20 min (11 min if the combustion and chromatography functions are overlapped), a significant time savings over the current Chinese national method. The CIC method is sensitive (MDL=1 ppm), precise, and accurate. The only sample preparation required is to grind and dry the tea.

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