

Determination of Fluoride in Plant Material using Microwave Induced Oxygen Combustion

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Abstract

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Fluorine is essential in human and/or animal nutrition, thus it is important to know its concentration in a diet. One of the important sources of fluorine for humans is tea, containing relatively high amounts of this trace element. A method for fluoride determination in various kinds of tea using microwave supported sample preparation in a high pressure oxygen atmosphere followed by potentiometry with a fluoride ion-selective electrode were described. The parameters of the microwave device for such combustion procedure were checked and optimised in order to find settings ensuring complete sample combustion and/or absorption of the analyte in the absorption solution. For the ion-selective electrode measurement, the technique of standard addition was chosen. The Nernstian slope of the fluoride ion-selective electrode was measured and calculated in the concentration range in which the potential of samples occurred. Concentrations of fluorides in tea in the range from 24.5 mg/kg to 254.5 mg/kg were found. In order to check the accuracy of the method certified reference materials were used. The precision expressed as the relative standard deviation ranged from 3.7% to 15.9%. The method is fast, accurate and reliable for this kind of analysis.

Keywords: ion-selective electrode; sample preparation; tea

Fluorine is an important trace element both for human and animal organism. Because of its reactivity, fluorine is present in the Earth crust only in compound forms, namely fluorite (CaF_2) and cryolite (Na_3AlF_6). In the sea water the concentration of fluorine usually does not exceed 1 mg/l. In the human body, fluorine is present in concentrations comparable with those of iron. The total amount of fluorine ranges from 3.5 g to 4.0 g. As much as 99% of the total body fluorine is present in bones and teeth in the form of hydroxyfluoroapatite. In teeth, fluorine is built into both dentine and enamel. The amount of fluorine in the body depends upon the fluorine intake from food and/or beverages, the age, gender, and

some other factors. In the bones of young people (20–30 years old), 200–800 mg/kg fluorine was found whereas 1000–2500 mg/kg of fluorine was found in the age group 70–80 years. The concentrations are given on the dry matter basis. From the bones, fluorine can be released into the body environment as necessary. Fluorine is usually easily absorbed from its salts in the gastrointestinal tract. Nevertheless, the presence of some ions namely calcium, magnesium, and aluminium could diminish its absorption substantially (up to one half). In the blood, fluorine is present predominately in its inorganic form. The biological half time of fluorine in the blood ranges from 2 h to 9 h and the average concentration was found to be 10–200

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µg/l. The activities of some enzymes can also be affected by fluorine concentrations. Fluorine is eliminated principally in urine. Some small amounts are also excreted by sweat, saliva, and faeces. Additionally a small amount of fluorine is contained in milk. Acute intoxication caused by fluorine is rare. Depending upon the fluorine content in the environment, a long term intake of higher fluorine amounts could be the reason for chronic intoxication with typical manifestations, fluorosis. There are two typical forms of fluorosis, dental and skeletal fluorosis. Also aluminium fluoride complexes were found to be a very dangerous group of substances for both animal and human organisms. (ANKE *et al.* 2004; Report WHO 2006).

From the soil, fluorine is transferred into the plant through its root system. The transferred amount depends on the soil composition and may be also affected by the local environmental conditions. The toxicity of fluorine for plants is relatively low. Intoxication can cause changes in the plant appearance and/or growth. There are some plants in which fluorine is accumulated to a greater extent. The accumulated amount is not regularly distributed throughout the whole plant organism but rather focused in particular parts, e.g. leaves. Tea is an example of plant organisms which are well known to accumulate fluorine (Report WHO 2006). Therefore it was chosen as an example of the plant materials, also representing an important part of human beverages consumption. The fluoride content in various tea sorts has been reported e.g. by CAO *et al.* (2004), JIN *et al.* (2006), MAHVI *et al.* (2006), some authors also discussed the impact of aluminium (RUAN *et al.* 2003; STREET *et al.* 2007).

Since the introduction of the fluoride ion-selective electrode (F-ISE) into analytical chemistry, potentiometry with F-ISE has become the method of choice in many applications, among them the food analysis (SEMLER 1990; MALDE *et al.* 2001; LI *et al.* 2006). Alongside potentiometry, other methods have been used for the fluoride determination, e.g. polarography (GUANGHAN *et al.* 1991; LU *et al.* 1999), spectrophotometry (TUŠL 1968; KHALIFA & HAFEZ 1998), gas chromatography (ČÁPKA *et al.* 2004), or activation analysis (CHAUDHRI *et al.* 2007).

An important part of the analytical system is the sample preparation step. Many procedures have been described (KRAKOVSKÁ & KUSS 2001)

based upon dry ashing and/or wet digestion methods. The use of various microwave techniques in analytical chemistry is still growing, especially in the field of the sample preparation. Microwaves supported techniques have become sophisticated, reliable, fast, and robust methods which meet the requirements of instrumental analytical techniques.

The goal of this work was to elaborate a method for fluoride determination in a plant material (tea) using microwave supported combustion in an oxygen atmosphere, followed by potentiometric measurement using a fluoride ion-selective electrode.

MATERIAL AND METHODS

All reagents were of Suprapur Grade (Merck, Darmstadt, Germany). Ultrapure water NANO-pure (Branstead, Dubuque, USA), having specific conductance less than 1 µS/m, was used for the sample and/or standard solutions preparation.

The microwave digestion system Multiwave 3000 (A. Paar GmbH, Graz, Austria) was used equipped with thick-wall quartz vessels XQ80 (100 ml).

Samples. Fourteen different tea sorts were used for analysis. The tea samples were randomly bought through the trade network. In order to check the accuracy of the results two Certified Reference Materials have been used. GBW 07605 Tea Leaves, produced by National Research Center for CRMS (Langfang, China). The other material was SRM Fluoride in Vegetation NIST 2695 (High Level).

Labware cleaning. All labware was cleaned using 100 g/l HNO₃. The vessels, stoppers, flasks, etc. were first soaked in 100 g/l HNO₃ for at least 12 h, then rinsed with ultrapure water and soaked in ultrapure water for at least another 12 hours. Finally they were thoroughly rinsed with ultrapure water and stored/kept in a closed dust-free housing until used. The combustion cuvettes were cleaned using a special microwave procedure described below.

Microwave cleaning program. This program was used to clean the quartz cuvettes after each combustion procedure. The vessel was filled with 6 ml of concentrated HNO₃. The sample holder was inserted into the vessel which was finally closed with a Teflon stopper. Four cuvettes were then placed into the Multiwave 3000 rotor (A. Paar GmbH, Graz, Austria). The rotor was closed with

Table 1. Cleaning program

Step	Power (W)	Ramp (min)	Hold (min)	Fan level
Heating	800	0	30	1
Cooling	0	0	30	3

the safety cover and placed into the microwave oven. The duration of the cleaning program was one hour (Table 1).

Microwave digestion. The optimised microwave oven program parameters are given in the Table 2.

The tea sample (about 300 mg weight) was wrapped in a cellophane bag, placed on a quartz sample holder and inserted into a thick-walled quartz combustion vessel. In order to initiate the combustion, a small piece of an ash-free filter paper soaked with NH_4NO_3 solution (0.5 g/ml) was used. The paper was placed under the sample bag. The vessel was then closed with a special stopper equipped with a valve system which enabled the vessel to be filled with oxygen. The oxygen filling procedure took approximately 10 s using 10.5 bar oxygen pressure. After the combustion, the products were absorbed in either 10 ml of the Total Ionic Strength Adjustment Buffer (TISAB) pH = 5.3 or in 10 ml of the absorption solution which consisted of 8 mmol/l Na_2CO_3 and 1 mmol/l NaHCO_3 mixture. For the composition of TISAB see e.g. SEMLER (1990).

Potentiometry. For the potentiometric measurements, the 940 pH/ISE Meter, Thermo ORION (Waltham, USA), was used. The electrode system consisted of F-ISE type 9409 BN, Thermo ORION (Waltham, USA) and the reference argentchloride electrode, type RAE 111, Monokrystal (Turnov, Czech Republic). The pH measurements were done using the 82-72BN, PerpHecT[®] ROSS[™] Sure-Flow[®] Electrode, Thermo ORION (Waltham, USA). The TISAB solution was used to adjust the pH (pH = 5.3) and the ionic strength of solutions.

Measurements were evaluated using the method of standard addition.

Table 2. Combustion program

Step	Power (W)	Ramp (min)	Hold (min)	Fan level
Combustion	1400	0	1	1
Absorption	400	0	5	1
Cooling	0	0	15	3

RESULTS AND DISCUSSION

The NIST SRM 2695 (Fluoride in Vegetation) was used in order to find which absorption solution should be used. The results obtained with TISAB were satisfactory. The mean value was 263 mg/kg and the 95% Confidence Interval 23–289 mg/kg was found. The Relative Standard Deviation was 4.9%. Because the certified value is 250–304 mg/kg the use of the TISAB solution is justified. From the whole procedure view point, the use of TISAB is also more convenient.

In order to check the accuracy of the method, the certified Reference Material Tea Leaves GBW 7605 was analysed. The certified value for fluoride concentration was 300–340 mg/kg. Using the above described method with TISAB as the absorption solution, the 95% confidence interval of 292–312 mg/kg based upon 6 replicates was found. The Relative Standard Deviation was 2.6%. It could be seen that the accuracy of the method is satisfactory. The value of the Limit of Detection for the procedure above described is 4.55 mg/kg.

The results of the determination of fluorine in various teas are based upon at least 4 determinations. The Relative Standard Deviation ranged from 3.7% to 23.5% (Table 3). The mean content of fluoride in the sorts of tea under investigation

Table 3. Fluoride content in various sorts of tea

Tea sort	Mean (mg/kg)	95% CI (mg/kg)	RSD (%)	<i>n</i>
Ceylon	24.5	19.9–29.1	13.6	4
Keemun	33.9	30.7–37.1	15.9	4
Nilgiri	36.5	33.2–39.8	11.5	4
Assam	56.5	51.9–61.4	9.7	8
Darjeeling	57.3	52.4–62.2	11.1	4
Formosa Oolong	58.5	53.6–63.4	6.0	8
Earl Grey	62.6	55.6–69.5	14.9	4
Green Curles	64.0	45.5–82.5	15.4	4
Bancha	92.1	83.0–101.2	7.1	8
English Classic	114.7	111.8–117.4	11.6	4
Sayonara	144.0	133.2–154.8	5.4	4
Gunpowder	150.2	142.5–157.9	3.7	4
Georgia	248.1	217.5–278.7	8.9	4
Hanasaki	254.5	230.5–278.5	6.8	4

95% CI – confidence interval; RSD – relative standard deviation; *n* – number of determinations

was found to range from 24.5 mg/kg (Ceylon) to 254.5 mg/kg (Hanasaki). The whole procedure is relatively fast. The analysis of one tea sample (including the sample preparation step and two measurements with ISE by means of the Standard Addition Method) takes 30 minutes. Both the accuracy and precision of the method were satisfactory for this kind of analysis. The main reason for this investigation was to develop and verify a new fast and reliable method for determination of fluoride in various sorts of tea. The result given in Table 3 need not represent a typical fluoride content in various tea sorts. For this reason, many more tea samples should be analysed and additionally classified with respect to different parameters, e.g. the region of the tea origin.

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