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National Food Safety Standard - Flourine

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Report Highlights:
On November 20, 2009, China notified the WTO of "National Food Safety Standard of the People's Republic of China for the Determination of Flourine in Foods" as SPS/N/CHN/181. The date for submission of final comments to the WTO is January 1, 2010. The proposed date of entry into force has not been specified.

Executive Summary:
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Thanks go to the consortium of industry and 3rd country Embassies in Beijing for their assistance in

translating and reviewing this standard.

This report contains an UNOFFICIAL translation of National Standard on Determination of Fluorine in Foods.

General Information:

BEGIN TRANSLATION

ICS 67.040
C

GB National Food Safety Standard
GB 5009.18 – XXXX
To replace GB/T 5009.18 – 2003

Determination of Fluorine in Foods

(Draft for Comment)

Issued on xx-xx-xxxx Implemented on xx-xx-xxxx

Issued by the Ministry of Health

of the People's Republic of China

Preface

This standard is to replace GB/T 5009.18 – 2003 Determination of Fluorine in Foods.
This standard is proposed and administrated by Ministry of Health of P. R. China.
The issuance status of all the previous editions replaced by this standard are:
GB/T 5009.18 – 1985, GB/T 5009.18 – 1986 and GB/T 5009.18 – 2003.

1. Scope

This standard stipulates the method to determine fluorine in foods such as grain, vegetable, fruit, beans and bean product, meat, fish and egg, etc.

The standard is applicable to the determination of fluorine in foods. Fluorine ion selection electrode method is not suitable for the test sample with high fat content and not be incinerated (such as peanuts and fat meat, etc.).

The detection limit of the method: Method I: 0.10mg/kg and method II: 1.25mg/kg

Method I: Diffusion-fluorine reagent colorimetry

2. Principle

The fluoride in food reacts with acid in a diffusion box to generate hydrogen fluoride gas, which is absorbed by sodium hydroxide via diffusion. The fluorine ion, lanthanum (III) and fluorine reagent (alizarin complexan) generate blue ternary complex under appropriate PH value and the color turns darker as the concentration of fluorine ion increases. The abstraction is conducted with or without organic solvent containing amine and the constant quantity should be compared with standard series.

3. Reagent

The water used in this method is the de-ionized water containing no fluorine, the reagents are analytically pure and all reagents are stored in polyethylene plastic bottles.

3.1 Acetone

3.2 Silver-sulfate-sulfuric acid solution (20g/L): Weigh 2g silver and dissolve it in 100mL sulfuric acid (3+1).

3.3 Sodium hydroxide-absolute alcohol solution (40g/L): Take 4g sodium hydroxide and dissolve it in absolute alcohol and dilute the solution to 100mL.

3.4 Acetic acid solution (1 mol/L): Take 3 mL glacial acetic acid, add water to dilute to 50mL.

3.5 Alizarin complexan solution: Take 0.19g alizarin complexan, add a small amount of water and sodium hydroxide solution (40g/L) to dissolve it, add 0.125g sodium acetate, adjust the pH value with acetic acid solution (3.4) to 5.0 (red), add water to dilute the solution to 500mL and store the diluted solution in refrigerator.

3.6 Sodium acetate solution (250g/L)

3.7 Lanthanum nitrate solution: Weigh 0.22g lanthanum nitrate, use a small amount of acetic acid solution (3.4) to dissolve, add water to about 450mL, adjust the pH value with acetic acid solution (3.4) to 5.0, add water to dilute the solution to 500mL and store the diluted solution in refrigerator.

3.8 Buffer solution (pH 4.7): Weigh 30g anhydrous sodium acetate, dissolve it in 400mL water add 22mL glacial acetic acid, adjust pH to 4.7 via adding glacial acetic acid slowly, and then add water to dilute the solution to 500mL.

3.9 Diethylaniline - isoamyl alcohol solution (5 + 100): Take 25mL diethylaniline and dissolve it in 500mL isoamyl alcohol.

3.10 Magnesium nitrate solution (100g/L)

3.11 Sodium hydroxide solution (40g/L): Weigh 4g sodium hydroxide, dissolve it in water and dilute to 100mL.

3.12 Fluorine standard solution: Accurately weight 0.221g cold sodium chloride which has been dried at 95℃-105℃ for 4h, dissolve it in water, move it into a 100mL volumetric bottle, add water to the scale and blend. Store the solution in refrigerator. This solution is equivalent to 1.0mg fluorine.

3.13 Standard fluorine solution for use: Accurately weight 1.0mL standard fluorine solution, put it in a 200mL volumetric bottle, add water to the scale and blend. Every milliliter of such solution is equivalent to 5.0μg fluorine.

3.14 Round filter paper: Cut filter paper into Φ4.5cm, soak it in sodium hydroxide solution (40g/L) – anhydrous alcohol solution, dry it at 100℃ for use.

4. Instrument

4.1 Plastic diffusion box: Inside diameter 4.5cm, depth 2cm, the internal wall top of the cover is smooth and with a convex ring (for containing sodium hydroxide absorbing solution) and the box should be air tight after the lid is tightly covered. Other types of plastic box can also be used.

4.2 Thermostat: 55℃±1℃

4.3 Visible spectrophotometer

4.4 Acidometer

4.5 Muffle roaster

5. Analysis procedure

5.1 Diffusion mono-color method

5.1.1 Test sample processing

5.1.1.1 Test sample of grain type: Paddy husking and visible impurities of other grains should be removed, 50g – 100g representative test sample should be taken, crushed and sieved with a 40 mesh sieve.

5.1.1.2 Vegetable and fruit: Take edible part, wash, dry in the air, cut them into pieces and blend. Weigh 100g – 200g test sample, dry at 80℃ with a blower, crush, sieve with a 40 mesh sieve and the result is expressed in fresh weight; Meanwhile, water content should be measured.

5.1.1.3 Special test sample (high fat content test sample and test samples that are not easy to crush and sieve, such as peanuts, fat meat and fruit with high sugar content, etc.): Weigh 1.00g – 2.00g grinded test sample and put the sample in a crucible (nickel, silver and porcelain, etc.), add 4mL magnesium nitrate solution (100g/L), add sodium hydroxide solution (100g/L), to make the solution alkaline. After blending, soaking for 0.5h, fix the fluorine in test sample and then wave it to dry on a water bath, heat to carbonize till no smoke and ash at 600℃ in a Muffle roaster. When it completely incinerated, take it out and leave it for cooling. Take the ashes for diffusion.

5.1.2 Determination

5.1.2.1 Take several plastic boxes, add 0.2mL sodium hydroxide – anhydrous alcohol solution (40g/L) at the centers of the box lids, apply smoothly in the ring and dry them at 55℃±1℃ in a thermostat to form a layer of film. Take the film out for use or paste the filter paper (3.14) in the boxes.

5.1.2.2 Weigh 1.00g – 2.00g processed test sample and put the sample in a plastic box, add 4mL water the make the sample well-distributed and not lumped. Add 4mL silver sulfate – sulfuric acid solution (20g/L), tightly cover the lid immediately and then gently shake to homogeneous. If the test sample has been processed via incineration, the ashes should be all moved into the plastic box firstly, use 4mL water to clean the crucible for several times, the washing water should all be poured into the plastic box and the ashes are made evenly diffused. If the crucible is not completely cleaned, add 4mL silver sulfate – sulfuric acid solution (20g/L) into the crucible and continue to clean. The washing water should all be poured into the plastic box and the lid should be tightly covered immediately and then the solution should be gently shaken to homogeneous. The solution should be kept in a 55℃±1℃ thermostat for 20h.

5.1.2.3 Respectively add 0, 0.2, 0.4, 0.8, 1.2 and 1.6 mL standard fluorine solution for use in plastic boxes (equivalent to 0, 1.0, 2.0, 4.0 and 8.0μg fluorine). Add water to 4 mL (respectively add 4mL (20g/L) silver sulfate – sulfuric acid solution and then tightly cover the lids immediately, gently shake the solution till homogeneous (never to splash any acid onto the lids) and place the boxes in thermostat and maintain the temperature for 20h.

5.1.2.4 Take out the boxes, take off the box lids, dissolve the sodium hydroxide films in the lids respectively with 20mL water several times (a small amount of water every time), move the solution carefully into 100mL separator funnels with a dropper .

5.1.2.5 Respectively add 3mL alizarin complexan solution, 3.0mL buffer solution, 8.0mL acetone, 3.0mL lanthanum nitrate solution, 13.0mL water in separator funnels, blend and place for 10min, respectively add 10.0mL diethylaniline - isoamyl alcohol solution (5 + 100), shake for 2 min and after stratification, dispose of the water layer, take the organic layer, filter the solution into a 10mL plugged comparison tube by filter paper.

5.1.2.6 Regulating the zero point with a 1cm comparison cup at 580nm wave length based on a standard zero tube, measure the absorbance and draw the curve. The content is obtained via comparing the absorbance of the test sample with the curve.

5.1.3 Result calculation

The content of fluorine in test sample is calculated according to formula (1)

Where:

X --- The content of fluorine in test sample, the unit is mg/kg.

A --- The mass of fluorine in test sample used for determination, the unit is μg.

m --- The mass of test sample, the unit is g.

Two significant digits should be reserved for the calculation result.

5.1.4 Precision

The difference between the absolute values of the two independent determination results obtained under the repeatability condition must not exceed 10% of the average arithmetic value.

5.2 Diffusion multiple method

5.2.1 Test sample processing

The same as that in 5.1.1.

5.2.2 Determination

5.2.2.1 The same as that in 5.1.2.1.

5.2.2.2 The same as that in 5.1.2.2.

5.2.2.3 The same as that in 5.1.2.3

5.2.2.4 Take the boxes out, take off the box lids, dissolve the sodium hydroxide film in the lids for several times with 10mL water respectively, completely move the solution carefully into 25mL plugged comparison tubes with a dropper.

5.2.2.5 Respectively add 2.0 mL alizarin complexan solution, 3.0mL buffer solution, 6.0mL acetone, 2.0mL lanthanum nitrate solution in comparison tubes, add water to scale, blend and place for 20min, regulate the zero point with a zero tube in 3 cm comparison cup (reference wave length 580nm), measure the absorbance of the tubes and draw standard curves for comparison.

5.2.3 Result calculation

The same as that in 5.1.3.

5.2.4 Precision

The difference between the absolute values of the two independent determination results obtained under the repeatability conditions must not exceed 10% of the average arithmetic value.

Method II: Incineration distillation - fluorine reagent colorimetry

6. Principle

The fluorine in test sample is fixed with magnesium nitrate and after high temperature incineration, under acidic condition, fluorine is separated via distillation. The distilled fluorine is absorbed by sodium hydrogen solution and the fluorine reacts with fluorine reagent and lanthanum nitrate to generate blue ternary complex and the constant quantity should be compared with standard.

7. Reagent

The water used in this method is de-ionized water containing no fluorine, the reagents are analytic pure and all reagents are stored in polyethylene bottles.

7.1 Acetone

7.2 Hydrochloric acid (1+11): take 10mL hydrochloric acid and add water to dilute to 120mL.

7.3 Sodium acetate solution (250g/L)

7.4 Acetic acid solution: the same as that in 3.4.

7.5 Alizarin complexan solution: the same as that in 3.5.

7.6 Magnesium nitrate solution (100g/L)

7.7 Lanthanum nitrate solution: the same as that in 3.7

7.8 Buffer solution (pH 4.7): the same as that in 3.8.

7.9 Sodium hydroxide solution (100g/L)

7.10 Phenolphthalin – alcohol indicator (10g/L)

7.11 Sulfuric acid (2+1)

7.12 Sodium hydrogen solution (40g/L): the same as that in 3.11

7.13 Standard fluorine solution for use: the same as that in 3.13.

8. Instrument

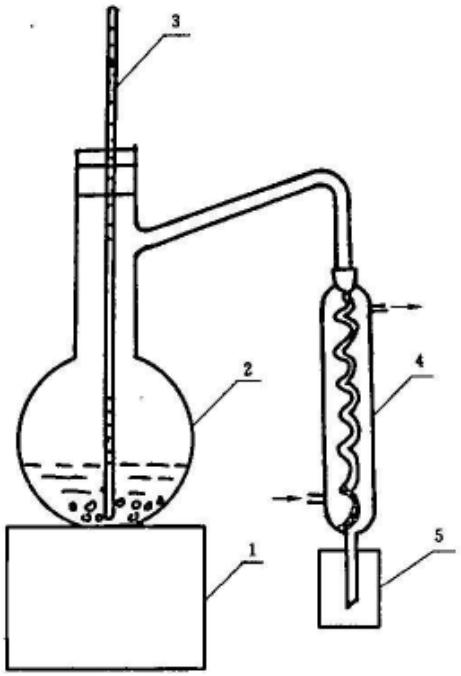
8.1 Electrothermal constant temperature water bath

8.2 Electric oven: 800W

8.3 Acidometer

8.4 Muffle roaster

8.5 Distillation device: refer to Fig. 1.



1 — Electric oven

2 — Distillation bottle

3 — Thermometer

4 — Condensation tube

5 — Small beaker

Fig. 1 Diagram of Distillation Device

8.6 Visible spectrophotometer

9. Analysis procedure

9.1 Test sample processing

9.1.1 Grain: the same as that in 5.1.1.1.

9.1.2 Vegetable: the same as that in 5.1.1.2.

9.1.3 Fish and meat: Take fresh meat, crush and mix. Bones of fish should be first removed and then the fish should be pounded and blended.

9.1.4 Egg: Remove the shell and then blend the egg white and yolk.

9.1.5 Bean product: Pound and blend the test sample.

9.2 Incineration

Weigh 5.00g mixed test sample (based on fresh weight), add 5.0mL magnesium nitrate (100g/L) and 0.5mL sodium hydroxide solution (100g/L) in a 30mL crucible to make the solution alkaline and soak for 0.5h after blending, place it on a water bath for drying and then low temperature carbonization is conducted till there is no smoke completely. Move the substance into a Muffle roaster, incineration is

conducted at 600℃ for 6h, and then take the substance out and leave it for cooling.

9.3 Distillation

9.3.1 Add 10mL water in a crucible, add several drops of sulfuric acid (2+1) slowly into the crucible, prevent the solution from splashing, neutralize the solution till there is no bubble generated. Move the solution into a 500mL distilling bottle, wash the crucible with 20mL water for several times and put the water into the distillation bottle.

9.3.2 Add 60mL sulfuric acid (2+1) and several small glass pellets with no fluorine into the distillation bottle, connect the distillation device and then heat for distillation. The distillate is absorbed with a 50mL beaker containing 5mL water, 7-20 drops of sodium hydroxide solution (100g/L) and 1 drop of phenolphthalein indicator and when the temperature of the solution in distillation bottle rises to 190℃, stop distillation (the whole distillation time is about 15min – 20min).

9.3.3 Take off the condenser tube, add water with a dropper to wash the condenser tube for 3-4 times and the wash water is also be poured into the beaker. Move the absorption liquid in the beaker into a 50mL volumetric bottle and wash the beaker with a small amount of water for 2-3 times and pour the washing water into the volumetric bottle. Neutralize with hydrochloric acid (1+11) to that red just disappears. Dilute with water to scale and mix homogeneously.

9.3.4 Respectively suck 0, 1.0, 3.0, 5.0, 7.0 and 9.0mL standard fluorine use solution and put the solutions in distillation bottles. Add water to 30mL and then operate according to 9.3.2 and 9.3.3.

9.4 Determination

9.4.1 Respectively suck standard series distillate and test sample distillate 10.0mL into 25mL plugged comparison tubes.

9.4.2 Operate as same as that specified in 5.2.2.5.

9.4.3 Result calculation: the content of fluorine in test sample is calculated according to formula (2).

$$X = \frac{A \times V_2 \times 1\,000}{V_1 \times m \times 1\,000} \qquad \cdots\cdots\cdots\cdots\cdots\cdots (2)$$

Where:

X — The content of fluorine in test sample, the unit is mg/kg;

A — The mass of fluorine in test sample used in determination, the unit is μg;

V1 — Volume of distillate absorbed during color comparison, the unit is mL;

V2 — Total volume of distillate, the unit is mL;

m — Mass of test sample, the unit is g.

The expression of result: the same as that in 5.1.3.

9.4.4 Precision: the same as that in 5.1.4.

Method III: Fluorine ion selection electrode method

10. Principle

The lanthanum fluoride mono-crystalline film of fluorine ion selection electrode generates selective logarithmic response to fluorine ion and when the fluorine electrode and the saturated mercurous chloride electrode are in the tested solution, the potential difference can change as the activity of fluorine ions in solution changes. For the potential change law complies with Nernst equation, please refer to formula (3).

$$E = E^{0} - \frac{2.303\,RT}{F}\lg C_{F^-} \qquad \cdots\cdots(3)$$

E and igCF forms a linear relationship. 2.303RT/F is the slope of this straight line. (it is 59.16 in 25℃).

The ions such as iron and aluminum, etc. which form complex with fluorine ion interfere the determination but other common ions do not interfere. The acidity of the tested solution is pH5-6, total ion strength buffering agent is used to eliminate the effect interfering ions and acidity.

11. Reagent

The water used in this method is de-ionized water containing no fluorine, the reagents are analytic pure and all reagents are stored in polyethylene bottles.

11.1 Sodium acetate solution (3 mol/L): Weigh 204g sodium acetate (CH3COONa – 3H2O), dissolve it in 300mL water, add acetic acid (1 mol/L) to regulate pH to 7.0, and then add water to dilute to 500mL.

11.2 Sodium citrate solution (0.75 mol/L): Weigh 110g sodium citrate (Na3C6H5O7 – 2H2O), dissolve it in 300mL water, add 14mL perchloric acid, and then add water to dilute to 500mL.

11.3 Total ion strength buffering agent: Equivalent mixture of sodium acetate solution (3 mol/L) and sodium citrate solution (0.75 mol/L), the agent should be prepared when using.

11.4 Hydrochloride acid (1+11): the same as that in 7.2.

11.5 Standard fluorine solution: the same as that in 3.12.

11.6 Standard fluorine use solution: suck 10.0mL standard fluorine solution and put the solution in a 100mL volumetric bottle, add water to dilute to scale. Repeatedly dilute the solution in such a way till the solution per milliliter is equivalent to 1.0μg fluorine.

12. Instrument

12.1 Fluorine electrode

12.2 Acidometer: ±0.01pH (or ionmeter)

12.3 Magnetic agitator

12.4 Mercurous chloride electrode

13. Analysis procedure

13.1 Weigh 1.00g crushed test sample sieved with a 40 mesh sieve and put it in a 50mL volumetric bottle, add 10mL hydrochloride acid (1+11), seal, soak and abstract for 1h (frequently shake gently), try to prevent the test sample from adhering on the bottle wall as far as possible. After abstraction, add 25mL total ion strength buffering agent and add water to the scale, blend for use.

13.2 Suck standard fluorine use solutions of 0, 1.0, 2.0, 5.0 and 10.0 ml (equivalent to 0, 1.0, 2.0, 5.0

and 10.0 μg fluorine), put them respectively in 50mL volumetric bottles, add 25mL total ion strength buffering agent and 10mL hydrochloride (1+11) respectively into the volumetric bottles and then add water to the scale. Blend for use.

13.3 Connect fluorine electrode and mercurous chloride electrode to the negative terminal and positive terminal of the measuring instrument, insert the electrode into a 25mL plastic cup containing water. An iron rod coated with polyethylene tube is placed into the cup and read out the equilibrium potential value while electromagnetic agitation is conducted. After replacing the water for 2-3 times and when the potential value is balanced, the potential determination of the sample solution and the standard solution can be conducted.

13.4 Take electrode potential as the longitudinal coordinate and the fluorine ion concentration as the horizontal coordinate, draw a standard curve on a piece of logarithmic coordinate paper and the content can be obtained from the curve according to the potential value of the test sample.

13.5 Result calculation: The content of fluorine in test sample can be calculated according to formula (4).

$$X = \frac{A \times V \times 1\,000}{m \times 1\,000} \qquad \cdots\cdots (4)$$

Where:

X — Content of fluorine in test sample, the unit is mg/kg;

A — Concentration of fluorine in test sample used for determination, the unit is μg/mL;

m — Mass of test sample, the unit is g;

V — Total volume of test solution, the unit is mL.

Two significant digits are reserved for the calculation result.

13.6 Precision:

The difference between the absolute values of the two independent determination results obtained under the repeatability condition must not exceed 20% of the average arithmetic value.