Authorization of Calcium Saccharin as Food Additives and Revision of the Standards of Sodium Saccharin

The government of Japan will designate Calcium Saccharin as authorized food additives, and revise the existing use standards for Sodium Saccharin.

Summary

Under Article 10 of the Food Sanitation Law, food additives may not be used on marketed without the authorization by the Minister of Health, Labour and Welfare. Where standards for use of additives and/or their compositional specifications are established based on Article 11 of the law, those additives may not be used or marketed when they do not meet these standards and/or specifications.

In response to a request from the Minister of Health, Labour and Welfare, the Committee on Food Additives of the Food Sanitation Council that is established under the Pharmaceutical Affairs and Food Sanitation Council has discussed the adequacy of the designation of Calcium Saccharin as a food additive and the revision of the existing use standards for Sodium Saccharin. The conclusion of the committee is outlined below.

Outline of the conclusion

The Minister of Health, Labour and Welfare, based on Article 10 of the Food Sanitation Law, should designate Calcium Saccharin, as food additives unlikely to harm human health, and establish compositional specifications and other necessary standards for this substance, based on Article 11 of the law (see Attachments 1). Also, the Minister should revise use standard for Sodium Saccharin, based on Article 11 of the law (see Attachments 2)

Attachment 1

Calcium Saccharin

Standard for use

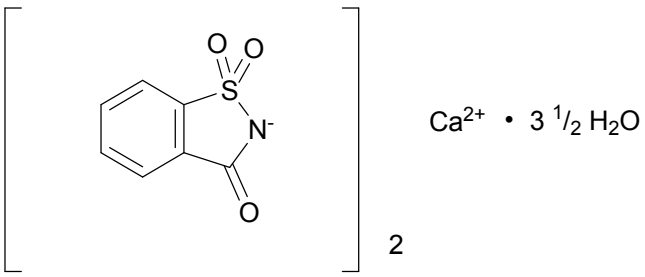
See the Appendixe 1.

Compositional specifications

Substance name

Calcium Saccharin

Structural formula



Molecular formula $C_{14}H_8CaN_2O_6S_2 \cdot 3½H_2O$

Mol. Weight 467.48

Chemical name [CAS number]

Calcium bis(3-oxo-3*H*-1,2-benzothiazol-2-ide) 1,1-dioxide hemiheptahydrat [6381-91-5]

Content Calcium Saccharin, when dried, contains not less than 98.0% of calcium saccharin ($C_{14}H_8CaN_2O_6S_2$).

Description Calcium Saccharin occurs as white crystals or crystalline powder. It has a strong sweet taste.

Identification

(1) To 10 ml of a solution of Calcium Saccharin (1 in 10), add 1 ml of hydrochloric acid, collect the resulting crystalline precipitate by filtration, and wash well with cold water. Dry the washed precipitate for 2 hours at 105°C, and measure the melting point. It starts to melt at a temperature above 226°C and melts completely at below 230°C.

(2) Mix 0.02 g of Calcium Saccharin with 0.04 g of resorcinol, add 10 drops of sulfuric acid, and heat for 3 minutes at 200°C. Cool, and add 10 ml of water and 10 ml of sodium hydroxide solution (1 in 25). The resulting solution emits a green fluorescence.

(3) To 0.1 g of Calcium Saccharin, add 5 ml of sodium hydroxide solution (1 in 25),

evaporate to dryness while gently heating, and fuse the residue, being careful not to carbonize it. Keep heating until it no longer evolves the odor of ammonia, and cool. To the residue, add about 20 ml of water, make slightly acidic with diluted hydrochloric acid (1 in 10), and filter. Add a drop of iron chloride(III) solution (1 in 10) to the filtrate. A purple to red-purple color develops.

(4) Calcium Saccharin responds all tests for Calcium Salt in the Qualitative Tests.

Purity

(1) Lead Not more than 1.0μg/g as Pb.

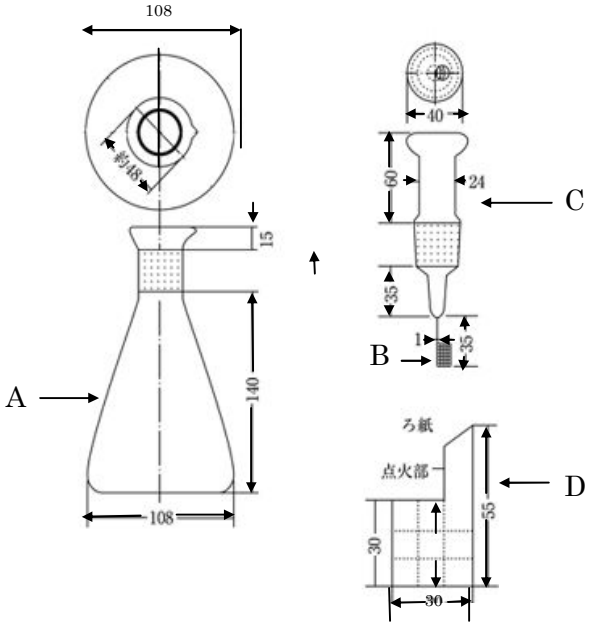
Test Solution Place 2.0 g of Calcium Saccharin in a 300 ml Kjeldahl flask, and add 10 ml of nitric acid and 5 ml of sulfuric acid. Heat until brown fumes are produced and then the solution turns light yellow. After cooling, add 10 ml of diluted hydrochloric acid (1 in 4), boil for 15 minutes, and cool. Use the resulting solution as the sample solution. To the sample solution, add 10 ml of diammonium hydrogen citrate solution (1 in 2), make slightly alkaline with ammonia solution, and cool. Transfer the solution to a 200-ml separating funnel, wash the inside of the Kjeldahl flask with water into the separating funnel, and further add water to make about 100 ml. Add 5 ml of ammonium pyrrolidine dithicarbamate solution (3 in 100), and allow to stand for 5 minutes. Then, add 10 ml of butyl acetate, shake for 5 minutes, and allow to stand. Use the butyl acetate layer as the test solution.

Control Solution Measure exactly 1 ml of Lead Standard Solution, and add water to make exactly 100 ml. Measure exactly 2 ml of this solution, and proceed as directed for the sample solution.

Procedure Proceed as directed in Method 1 in the Lead Limit Test.

(2) Selenium Not more than 30 μg/g as Se.

(i) Use the apparatus outlined in the Figure.



A: Colorless, hard-glass, thick-walled flask with a flared mouth (2 mm in wall thickness and 500-ml in capacity)

B: Platinum basket or platinum gauze cylinder (hung from the bottom of stopper C with a platinum wire)

C: Hard-glass, ground stopper

D: Filter paper (Cut out a filter paper to make the shape given in the Figure, and make folding lines as described by dot lines. The long end is used for light-off.)

(ii) Procedure

Sample Solution Place 0.20 g of Calcium Saccharine, previous dried and weighed accurately, on the center of the filter paper, and wrap carefully along with the folding lines without spilling. Place the parcel into B (a platinum basket or platinum mesh cylinder), leaving the long end on the outside. Put 25 ml of diluted nitric acid (1 in 30) as the absorbing liquid into flak A. Fill the flask with air, moist the ground part of stopper C, light off the long end, and immediately place it into the flask. Keep the flask airtight until the combustion is completed. Allow it to stand for 15–30 minutes with occasional shaking until the white fumes inside the flask completely disappear. Pour a small amount of water to the upper part of the flask, carefully remove the stopper, and transfer the solution in A to a beaker. Wash C, B, and the inside wall of A with 25 ml of water, and add the washings to the beaker. Boil the resulting solution gently for 10 minutes. Cool to room temperature, add water to make exactly 100 ml, and use the sample solution.

Standard Solution Weigh 0.060 g of selenium, add 100 ml of diluted nitric acid (1

in 2) to dissolve while heating on a water bath if necessary, and dilute with water to exactly 1,000 ml. To exactly measured 5 ml of this solution, add water to make exactly 200 ml. Take exactly 2 ml of the resulting solution, and add diluted nitric acid (1 in 60) to make exactly 50 ml.

Procedure Measure exactly 40 ml each of the sample solution and the standard solution into separate beakers, and adjust the pH to 1.8–2.2 with ammonia solution. To each, add 0.2 g of hydroxylamine hydrochloride to dissolve while gently shaking, add 5 ml of a solution that is prepared by dissolving 0.10 g of 2,3-diaminonaphtharine and 0.5 g of hydroxylamine hydrochloride in 0.1 mol/L hydrochloric acid and then diluting to 100 ml. Shake and allow to stand for 100 minutes. Transfer them into separate separating funnels, wash the beakers with 10 ml each of water, and add the washings to the corresponding separating funnels. To each, add 5.0 ml of cyclohexane, and shake well for 2 minutes to extract selenium. Collect the cyclohexane layer, and centrifuge to remove the water. Use the resulting solutions as the test solution and the control solution, respectively. Against the reference solution that is prepared in the same manner using 40 ml of diluted nitric acid (1 in 60) instead of the test solution, measure the absorbance at maximum absorption wavelength near 378 nm. The absorbance of the test solution is not greater than that of the control solution.

(3) Arsenic Not more than 4.0 μg/g as As_2O_3 (0.50 g, Method 1, Apparatus B).

(4) Benzoic acid and salicylic acid Dissolve 0.5 g of Calcium Saccharine in 10 ml of water, and add 5 drops of acetic acid and 3 drops of iron(III) chloride solution (1 in 10). No precipitate is produced, and a violet to red-violet color is not formed.

(5) Toluenesulfonamides Not more than 25 μg/g.

Test Solution Dissolve 10.0 g of Calcium Saccharine in 50 ml of water. Extract three times with 30 ml of ethyl acetate each time, combine the ethyl acetate layers, wash with 30 ml of sodium chloride solution (I in 4), and transfer the ethyl acetate layer to a dry flask. Add about 10 g of anhydrous sodium acetate, shake, and filter into an eggplant-shape flask. Wash the residue on the filter twice with 10 ml of ethyl acetate each time, and add the washings to the flask. Concentrate under reduced pressure to remove the ethyl acetate. To the residue, add exactly 1.0 ml of a solution of caffeine in ethyl acetate (1 in 4,000), shake, and allow to stand for 1 minute. Use the resulting supernatant as the test solution. If necessary, centrifuge to obtain the supernatant.

Standard Solution Dissolve about 0.025 g each of *o*-toluenesulfonamide and *p*-toluenesulfonamide, accurately weighed, in ethyl acetate to make exactly 100 ml. Concentrate exactly 1 ml of the resulting solution under reduced pressed to remove the ethyl acetate, and to the residue, add a solution of caffeine in ethyl acetate (1 in 4,000)

to dissolve it.

Procedure Analyze 1 μl portions of the test solution and the standard solution by gas chromatography using the operating conditions given below. Measure the peak area ratios of *o*-toluenesulfonamide to caffeine and *p*-toluenesulfonamide to caffeine for both test solution and standard solution, and designate the ratio as Q_{T1} and Q_{T2} for the test solution and as Q_{S1} and Q_{S2} for the standard solution, respectively. Determine the amount of toluenesulfonamides by the formula:

$$\text{Amount of toluenesulfonamides (\%)} = \frac{Q_{T1}}{Q_{S1}} \times W_{S1} + \frac{Q_{T2}}{Q_{S2}} \times W_{S2} \times \frac{1}{\text{Weight of the sample}} \times 100$$

W_{S1}= weight (g) of *o*-toluenesulfonamide in 1 ml of the standard solution

W_{S2}= weight (g) of *p*-toluenesulfonamide in 1 ml of the standard solution

Operating conditions

Detector: Flame ionization detector.

Column: Use a silicate-glass capillary tube (0.32 mm internal diameter and 30 m length) coated with a 0.25 μm thick layer of a mixture of 5%diphenyl and 95%dimethylpolysiloxane for gas chromatography.

Column temperature: 185°C.

Inlet temperature: 250°C.

Injection: Sprit ratio (10:1).

Carrier gas: Helium or nitrogen.

Flow rate: Adjust so that the peak of caffeine appears about 10 minutes after injection.

(6) Readily carbonizable substances Dissolve 0.20 g of Calcium Saccharine in 5 ml of sulfuric acid for readily carbonizable substances determination, and keep for 10 minutes at 48–50°C. The color of the resulting solution is not deeper than that of Matching Fluid A.

Loss on Drying Not more than 15.0% (120°C, 4 hours).

Assay Weigh accurately about 0.3 g of Calcium saccharine, previously dried, add 40 ml of acetic acid for nonaqueous titration to dissolve, and titrate with 0.1 mol/L perchloric acid. Use a potentipmeter to confirm the endpoint. Separately, perform a blank test to make correction. Each ml of 0.1 mol/L perchloric acid = 20.22 mg of $C_{14}H_8CaN_2O_6S_2$

Reagents

2,3-Diaminonaphthalene Light yellow-brown crystals or powder.

Melting point: 193–198°C.

Sensitivity: Measure exactly 40 ml each of Selenium Standard Solution and diluted nitric acid (1 in 60), and adjust the pH to 1.8–22 with ammonia solution. To each, add 0.2 g of hydroxylamine hydrochloride and dissolve while gently shaking, then add 5 ml of a solution that is prepared by dissolving 0.10 g of 2,3-diaminonaphtharine and 0.5 g of hydroxylamine hydrochloride in 0.1 mol/L hydrochloric acid and then diluting to 100 ml. Shake, and allow to stand for 100 minutes. Transfer them into separate separating funnels, wash the beakers with 10 ml each of water, and add the washings to the corresponding separating funnels. Add 5.0 ml of cyclohexane, and shake well for 2 minutes to extract selenium. Separately, collect the cyclohexane layers, and centrifuge to remove the water. Against the cyclohexane solution from diluted nitric acid (1 in 60), measure the absorbance of the solution from Selenium Standard Solution by ultraviolet-visible spectrophotometry. The absorbance is not less than 0.08 at a wavelength of 378 nm.

Selenium Se [K8598]

Standards Solutions

Selenium Standard Solution Dissolve 0.04 g of selenium in 100 ml of diluted nitric acid (1 in 2) while heat on a water bath if necessary, and add water to make 1,000 ml. Measure exactly 5 ml of this solution, and add water to make exactly 200 ml. To exactly 2 ml of the resulting solution, add diluted nitric acid (1 in 60) to make exactly 50 ml. Prepare fresh before use. Each ml of the standard solution contains 0.04 μg of selenium (Se).

Appendix 1

Standards for use

1. Standards applying generally to all food additives

When a food listed in column 2 of the following table that contains additives listed in column 1 of the same table is used in the process of the manufacturing or processing of any of the foods listed in column 3 in the same table, the additives contained in that food are considered to be used in the food listed in column 3.

Column 1	Column 2	Column 3
Calcium Saccharin Sodium Saccharin	Flour paste (hereinafter in section F, referred to as any paste food which is prepared by adding sugar, fats/oils, powder milk, eggs, or wheat flour to main ingredients such as wheat flour, starch, nuts or their processed products, cocoa, chocolate, coffee, fruit pulps, or fruit juice, pasteurized, and used for bread or confectionery as fillings or toppings).	Confections.

Note: the underlined part is newly added.

2. Calcium Saccharin

Target Foods	Maximum Limit	Other Requirements
An (sweetened bean paste).	maximum residue limit as sodium saccharine Less than: 0.20 g/kg	The maximum limits given left do not apply to foods approved or recognized to have special dietary use labeling.
Confections (including liquid-form and powdered-form as ingredients).	0.10 g/kg	
Edible ices (including sherbets, flavored ices, and other similar	0.30 g/kg	

foods).		When Calcium Saccharin is used with Sodium Saccharine, the sum of the residues of both substances shall be less than the corresponding maximum limits as sodium saccharine.
Fermented milk (excluding those used as ingredients of lactic acid bacterial beverages).	0.20 g/kg	
Fermented milk (only for ingredients of lactic acid bacterial beverages).	1.5 g/kg	
Fish paste.	0.30 g/kg	
Fish/shellfish (processed, excluding fish paste, *tsukudani* (foods boiled down with soy sauce), pickles, and canned or bottled products).	1.2 g/kg	
Fish/shellfish (canned or bottled processed foods).	0.20 g/kg	
Flour pastes.	0.20 g/kg	
Ice cream products (including liquid-form and powdered-form as ingredients).	0.20 g/kg	
Jams.	0.20 g/kg	
Kasu-zuke (lee-pickled foods).	1.2 g/kg	
Koji-zuke (*koji* (*A. oryzae*)-pickled foods).	2.0 g/kg	
Lactic acid bacterial drinks.	0.30 g/kg	
Lactic acid bacterial drinks as ingredients.	1.5 g/kg	

Milk drinks.	0.30 g/kg
Miso (fermented soybean paste).	0.20 g/kg
Miso-zuke (*miso*-pickled foods).	1.2 g/kg
Nonalcoholic beverages.	0.30 g/kg
Nonalcoholic beverages (powdered).	1.5 g/kg
Nonalcoholic beverages (only products consumed in 5-fold or more dilution).	1.5 g/kg
Pickles (preserved or pickled foods, excluding those listed in this column).	0.20 g/kg
Processed sea weeds.	0.50 g/kg
Sauces.	0.30 g/kg
Shoyu-zuke (soy sauce-pickled foods).	1.2 g/kg
Simmered beans.	0.50 g/kg
Soy sauce.	0.50 g/kg
Su-zuke (vinegar-pickled foods).	2.0 g/kg
Syrup.	0.30 g/kg
Takuan-zuke (rice bran-pickled radishes).	2.0 g/kg
Tsukudani (foods boiled down with soy sauce).	0.50 g/kg
Vinegar.	0.30 g/kg
Vinegar (used in	0.90 g/kg

3-fold or more dilution).		
Other foods.	0.20 g/kg	

Attachments 2

Standards for use

Sodium Saccharin

Target Foods	Maximum Limit	note
An (sweetened bean paste).	as maximum residue limit of sodium saccharine Less than: 0.20 g/kg	The maximum limits given left do not apply to foods approved or recognized to have special dietary use labeling.
Confections (including liquid-form and powdered-form as ingredients).	0.10 g/kg	
Edible ices (including sherbets, flavored ices, and other similar foods).	0.30 g/kg	
Fermented milk (excluding those used as ingredients of lactic acid bacterial beverages).	0.20 g/kg	
Fermented milk (only for ingredients of lactic acid bacterial beverages).	1.5 g/kg	When Sodium Saccharin is used with Calcium Saccharine, the sum of the residues of both substances shall be less than the corresponding maximum limits.
Fish paste.	0.30 g/kg	
Fish/shellfish (processed, excluding fish paste, *tsukudani* (foods boiled down with soy sauce), pickles, and canned or bottled products).	1.2 g/kg	
Fish/shellfish (canned or bottled processed foods).	0.20 g/kg	
Flour pastes.	0.20 g/kg	
Ice cream products (including liquid-form and powdered-form as ingredients).	0.20 g/kg	
Jams.	0.20 g/kg	
Kasu-zuke (lee-pickled foods).	1.2 g/kg	
Koji-zuke (*koji* (*A. oryzae*)-pickled foods).	2.0 g/kg	
Lactic acid bacterial drinks.	0.30 g/kg	

Lactic acid bacterial drinks as ingredients.	1.5 g/kg	
Milk drinks.	0.30 g/kg	
Miso (fermented soybean paste).	0.20 g/kg	
Miso-zuke (*miso*-pickled foods).	1.2 g/kg	
Nonalcoholic beverages.	0.30 g/kg	
Nonalcoholic beverages (powdered).	1.5 g/kg	
Nonalcoholic beverages (only products consumed in 5-fold or more dilution).	1.5 g/kg	
Pickles (preserved or pickled foods, excluding those listed in this column).	0.20 g/kg	
Processed sea weeds.	0.50 g/kg	
Sauces.	0.30 g/kg	
Shoyu-zuke (soy sauce-pickled foods).	1.2 g/kg	
Simmered beans.	0.50 g/kg	
Soy sauce.	0.50 g/kg	
Su-zuke (vinegar-pickled foods).	2.0 g/kg	
Syrup.	0.30 g/kg	
Takuan-zuke (rice bran-pickled radishes).	2.0 g/kg	
Tsukudani (foods boiled down with soy sauce).	0.50 g/kg	
Vinegar.	0.30 g/kg	
Vinegar (used in 3-fold or more dilution).	0.90 g/kg	
Other foods.	0.20 g/kg	

Note: the underlined part is newly added.