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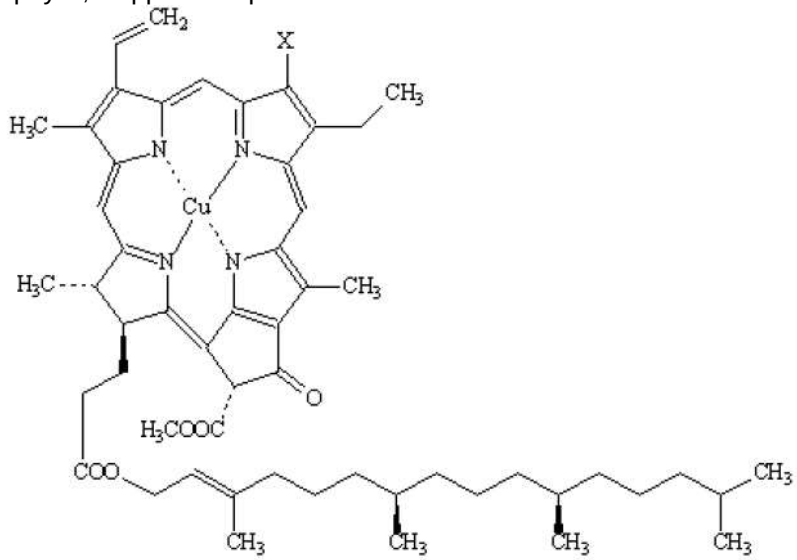
Copper Complexes of Chlorophylls and Chlorophyllins

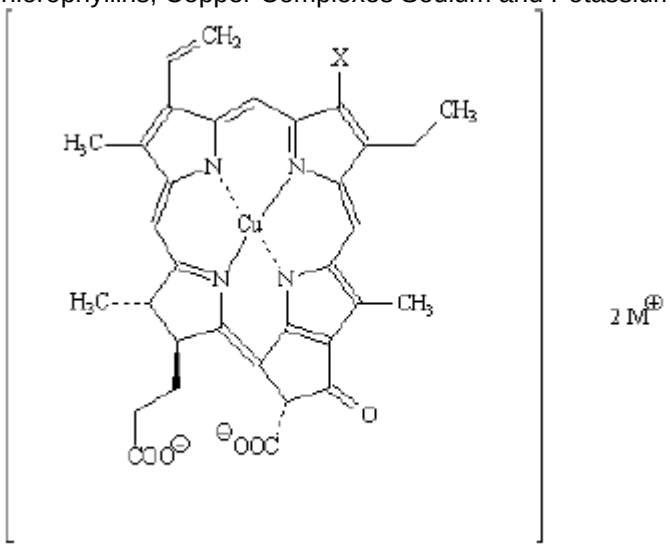
Molecular formula:	$C_{55}H_{72}Cu\ N_4O_5$ (Copper chlorophyll a) $C_{55}H_{70}Cu\ N_4O_6$ (Copper chlorophyll b) $C_{34}H_{32}Cu\ N_4O_5$ (Copper chlorophyllin a (acid form)) $C_{34}H_{30}Cu\ N_4O_6$ (Copper chlorphyllin b (acid form))
Molecular mass:	932.75 (Copper chlorophyll a) 946.73 (Copper chlorophyll b) 640.20 (Copper chlorophyllin a) 654.18 (Copper chlorophyllin b) Each may be increased by a 18 Daltons if the cyclopentenyl ring is cleaved.
CAS Registry Number	65963-40-8 (Chlorophylls, copper complexes)
Chemical name:	Copper chlorophyll a: [Phytl (13^2R,17S,18S)-3-(8-ethyl-13^2-methoxycarbonyl-2,7,12,18-tetramethyl-13^1-oxo-3-vinyl-13^1-13^2-17,18-tetra-hydrocyclopenta[at]-prophyrin-17-yl)propionate]copper (II) Copper chlorophyll b: [Phytl (13^2R,17S,18S)-3-(8-ethyl-7-formyl-13^2-methoxycarbonyl-2,12,18-trimethyl-13^1-oxo-3-vinyl-13^1-13^2-17,18-tetrahydro-cyclopenta[at]-prophyrin-17-yl)propionate]copper (II) The major coloring principles in their acid forms are 3-(10-Carboxylato-4-ethyl-1,3,5,8-tetramethyl-9-oxo-2-vinylphorbin-7-yl)propionate, copper complex (Copper chlorophyllin a) and 3-(10-carboxylato-4-ethyl-3-formyl-1,5,8-trimethyl-9-oxo-2-vinylphorbin-7-yl)propionate, copper complex (Copper chlorophyllin b) Depending on the degree of hydrolysis the cyclopentenyl ring may be cleaved with the resultant production of a third carboxyl function.
EINECS Number	239-830-5 (Copper chlorophyll a) 246-020-5 (Copper chlorophyll b)
Synonyms/Identifiers:	Copper complexes of chlorophylls -CI Natural Green 3 -Copper Chlorophyll -Copper Phaeophytin -CI No 75810 -E 141 (i) -INS No. 141(i) Copper complexes of chlorophyllins -Sodium Copper Chlorophyllin -Potassium Copper Chlorophyllin CI Natural Green 5 CI No 75815 -E 141 (ii) -INS No. 141(ii)

Structural formula: Chlorophylls, Copper Complexes:



where
X = CH_3 for the "a" compound
X = CHO for the "b" compound

Chlorophyllins, Copper Complexes Sodium and Potassium Salts:



where
X = CH_3 for the “a” compound
X = CHO for the “b” compound
M = Potassium and/or sodium

Common Uses

Typical applications include confectionery, desserts, beverages, dairy products, ice cream, fruit preparation, bakery products, soups, sauces, snack food, seasonings, and convenience food.

US FDA Identity & Specifications

§73.125 Sodium copper chlorophyllin.

Identity. (1) The color additive sodium copper chlorophyllin is a green to black powder prepared from chlorophyll by saponification and replacement of magnesium by copper. Chlorophyll is extracted from alfalfa (Medicago sativa) using any one or a combination of the solvents acetone, ethanol, and hexane.

(2) Color additive mixtures made with sodium copper chlorophyllin may contain only those diluents that are suitable and are listed in this subpart as safe for use in color additive mixtures for coloring foods.

Specifications. Sodium copper chlorophyllin shall conform to the following specifications and shall be free from impurities other than those named to the extent that such impurities may be avoided by good manufacturing practice:

- Moisture, not more than 5.0 percent.
- Solvent residues (acetone, ethanol, and hexane), not more than 50 parts per million, singly or, in combination.
- Total copper, not less than 4 percent and not more than 6 percent.
- Free copper, not more than 200 parts per million.
- Lead (as Pb), not more than 10 parts per million.
- Arsenic (as As), not more than 3 parts per million.
- Mercury (as Hg), not more than 0.5 part per million.
- Ratio of absorbance at 405 nanometers (nm) to absorbance at 630 nm, not less than 3.4 and not more than 3.9.
- Total copper chlorophyllins, not less than 95 percent of the sample dried at 100 °C for 1 hour.

Uses and restrictions. Sodium copper chlorophyllin may be safely used to color citrus-based dry beverage mixes in an amount not exceeding 0.2 percent in the dry mix.

Labeling requirements. The label of the color additive and any mixtures prepared therefrom shall conform to the requirements of §70.25 of this chapter.

Exemption from certification. Certification of this color additive is not necessary for the protection of the public health, and therefore batches thereof are exempt from the certification requirements of section 721(c) of the act.

EU Specifications

Commission Regulation (EU) No 231/2012

Copper Complexes of Chlorophylls

Definition Copper chlorophylls are obtained by addition of a salt of copper to the substance obtained by a solvent extraction of strains of edible plant material, grass, Lucerne, and nettle. The product, from which the solvent has been removed, contains other pigments such as carotenoids as well as fats and waxes derived from the source material. The principal coloring matters are the copper phaeophytins. Only the following solvents may be used for the extraction: acetone, methyl ethyl ketone, dichloromethane, carbon dioxide, methanol, ethanol, propan-2-ol and hexane.

Assay Content of total copper chlorophylls is not less than 10 %
$E_{1cm}^{1\%}$ 540 at ca. 422 nm in chloroform
$E_{1cm}^{1\%}$ 300 at ca. 652 nm in chloroform

Description Waxy solid ranging in color from blue green to dark green depending on the source material

Identification

Spectrometry Maximum in chloroform at ca. 422 nm and at ca. 652 nm

Purity

Solvent residues Not more than 50 mg/kg, singly or in combination:
Acetone
Methyl ethyl ketone
Methanol
Ethanol
Propan-2-ol
Hexane
Dicholoromethane: not more than 10 mg/kg

Arsenic Not more than 3 mg/kg

Lead Not more than 2 mg/kg

Mercury Not more than 1 mg/kg

Cadmium Not more than 1 mg/kg

Copper ions Not more than 200 mg/kg

Total copper Not more than 8.0% of the total copper phaeophytins

Aluminum lakes of this color may be used.

Copper Complexes of Chlorophyllins

Definition The alkali salts of copper chlorophyllins are obtained by addition of copper to the product obtained by the saponification of a solvent extraction of strains of edible plant material, grass, lucerne, and nettle; the saponification removes the methyl and phytol ester groups and may partially cleave the cyclopentenyl ring. After addition of copper to the purified chlorophyllins, the acid groups are neutralized to form the salts of potassium and/or sodium.

Only the following solvents may be used for the extraction: acetone, methyl ethyl ketone, dichloromethane, carbon dioxide methanol, ethanol, propan-2-ol and hexane.

Assay Content of total copper chlorophyllins is not less than 95 % of the sample dried at 100°C for 1 h.
$E_{1cm}^{1\%}$ 565 at ca. 405 nm in aqueous phosphate buffer at pH 7.5
$E_{1cm}^{1\%}$ 145 at ca. 630 nm in aqueous phosphate buffer at pH 7.5

Description Dark green to blue/black powder

Identification

Spectrometry Maximum in aqueous phosphate buffer at pH 7.5 at ca. 405 nm and at 630 nm

Purity

Solvent residues Not more than 50 mg/kg, singly or in combination:
Acetone
Methyl ethyl ketone
Methanol

Ethanol
Propan-2-ol
Hexane
Dicholoromethane: not more than 10 mg/kg

Arsenic	Not more than 3 mg/kg
Lead	Not more than 5 mg/kg
Mercury	Not more than 1 mg/kg
Cadmium	Not more than 1 mg/kg
Copper ions	Not more than 200 mg/kg
Total copper	Not more than 8.0% of the total copper chlorophyllins

Aluminum lakes of this color may be used.

Japanese Specifications

Copper Chlorophyll

Description Copper Chlorophyll occurs as blue-black to green-black powder, flakes, lumps, or viscous substances, having a characteristic odor.

Identification

(1) Proceed as directed under (ii) of Identification (1) for Sodium Copper Chlorophyllin.
(2) Dissolve 10 mg of Copper Chlorophyll in 50 ml of ether, add 2 ml of a solution of sodium hydroxide in methanol (1→100), and shake. Equip with a reflux condenser, and heat on a water bath for 30 minutes. Cool, perform extraction 3 to 5 times with 10 ml of water each time, combine the extracts, add phosphate buffer (pH 7.5) to make 200 ml, and measure the absorbance of this solution. The solution exhibits absorption maxima at wavelengths of 403-407 nm and 630-640 nm. When the absorbances at the absorption maxima are expressed as A_1 and A_2, respectively, A_1/A_2 is not more than 4.0.

Purity

(1) Specific absorbance
$E^{1\%}_{1cm}$ (absorption maximum at around a wavelength of 405 nm)=Not less than 62.0 (on the dried basis).
Weigh accurately about 0.1g of Copper Chlorophyll, dissolve in 50 ml of ether, add 10 ml of a solution of sodium hydroxide in methanol (2→100), and shake. Equip with a reflux condenser, and heat on a water bath for 30 minutes. Cool, perform extraction four times with 20 ml of water each time, combine the extracts, and add water to make exactly 100 ml. Filter this solution, measure exactly 5.0 ml of the filtrate, add phosphate buffer (pH 7.5) to make exactly 100 ml, and quickly measure absorbance. For this procedure, avoid direct sunlight, and use a light-resistant container.

(2) Inorganic copper salt Not more than 300 µg/g as Cu.
Test Solution Weigh 1.0g of Copper Chlorophyll, and dissolve in 60 ml of acetone.
Procedure Proceed as directed under Purity (3) for Sodium Copper Chlorophyllin.

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

(4) Chlorophyllin salt
Weigh 1.0g of Copper Chlorophyll, dissolve in 30 ml of ether, add 20 ml of water, and shake. After standing, filter the water layer through a filter paper moistened with water. The filtrate is colorless.

Loss on Drying
Not more than 3.0% (105°C, 2 hours).

Sodium Copper Chlorophyllin

Description Sodium Copper Chlorophyllin occurs as blue-black to green-black powder. It is odorless or has a slight, characteristic odor.

Identification
(1) Place 1 g of Sodium Copper Chlorophyllin into a porcelain crucible, moisten with a small amount of sulfuric acid, and heat gradually. After it is almost completely incinerated at the lowest possible temperature, allow to cool. Add 1 ml of sulfuric acid, heat gradually until fumes of sulfuric acid have almost completely ceased, and allow to cool. Add 10 ml of diluted hydrochloric acid (1→4) to the residue, dissolve while heating on a water bath, filter if necessary, and add water to make 10 ml. Perform the tests, given below, using this solution as the test solution.
(i) Perform the Flame Coloration Test on the test solution. The color of the flame is first green and then changes to yellow.
(ii) To 5 ml of the test solution, add 0.5 ml of sodium diethyldithiocarbamate solution (1→1,000). A brown precipitate is formed.
(2) To 1 ml of Sodium Copper Chlorophyllin solution (1→1,000), add phosphate buffer (pH 7.5) to make 100 ml, and measure the absorbance. The solution exhibits absorption maxima at wavelengths of 403-407 nm and 627-633 nm. When the absorbances at these absorption maxima are expressed as A_1 and A_2, respectively, A_1/A_2 is not more than 4.0.

Purity
(1) Specific absorbance
$E^{1\%}_{1cm}$ (at the absorption maximum near a wavelength of 405 nm): Not less than 508 (on the dried basis). Weigh accurately about 0.1g of Sodium Copper Chlorophyllin, dissolve in water to make exactly 100 ml, and measure exactly 1 ml of this solution. Add phosphate buffer (pH 7.5) to make exactly 100 ml, measure the absorbance. Avoid direct sunlight during the procedure, and use light-resistant containers.

(2) pH 9.5-11.0 (1.0g, water 100 ml).

(3) Inorganic copper salt Not more than 300 µg/g as Cu.
Test Solution Weigh 1.0g of Sodium Copper Chlorophyllin, and dissolve in 60 ml of water.
Procedure Measure 2 µl of the test solution, and perform Thin-Layer Chromatography without using a control solution. Use a *n*-butanol-water-acetic acid mixture (4:2:1) as the developing solvent. No light brown spots are observed. For the thin-layer plate, use silica gel for thin-layer chromatography dried at 110°C for 1 hour. Stop the development when the solvent front rises about 10 cm, air-dry, and spray with sodium diethyldithiocarbamate solution (1→1,000).

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

Loss on Drying
Not more than 5.0% (105°C, 2 hours).

JECFA Specifications

Chlorophylls, Copper Complexes

Prepared at the 31st JECFA (1987), published in FNP 38 (1988) and in FNP 52 (1992). Metals and arsenic specifications revised at the 59th JECFA (2002). An ADI of 0-15 mg/kg was established at the 13th JECFA (1969).

Definition Obtained by addition of an organic salt of copper to the substance obtained by solvent extraction of grass, Lucerne, nettle and other plant material; the product, from which the solvent has been removed, contains other pigments such as carotenoids as well as fats and waxes derived from the source material; the principal coloring matters are the copper phaeophytins. Only the following solvents may be used for the extraction: Acetone, dichloromethane, methanol, ethanol, propan-2-ol and hexane.

Assay Not less than 10% of total copper phaeophytins

Description Waxy solid ranging in color from blue green to dark green depending on the source material.

Identification

Solubility (Vol. 4): Insoluble in water; soluble in ethanol, diethyl ether, chloroalkanes, hydrocarbons and fixed oils

Spectrometry (Vol. 4): A (1%, 1 cm) at 422 cm in chloroform is not less than 54.

Thin-layer chromatography: Apply a 1 in 20 solution of the sample in chloroform as a band of the length of 2 cm to a Silica 60C plate. After drying, develop the plate by a mixture of 50% hexane, 45% chloroform and 5% ethanol (general purpose reagent grade chloroform is supplied with 2% of added ethanol as a stabilizer. The 5% ethanol in the solvent mixture is in addition to this), until the solvent ascends to a point 15 cm above the initial spots. Allow the solvent to evaporate, then visually chromatography examine the separated spots and identify the components of interests by their R_f values and colors. Approximate R_f values and color of the spots are as follows:
Copper phaeophytin a: 0.5, green
Copper phaeophytin b: 0.73, yellow/green

In addition spots may be visible for β-carotene at Rf 0.81 and xanthophyll at R_f 0.47 and 0.23.

Purity

Residual solvents (Vol. 4)

Acetone, methanol, ethanol, propan-2-ol, hexane: Not more than 50 mg/kg, singly or in combination

Dichloromethane: Not more than 10 mg/kg

Determine *gas chromatographically* using either the method of entrainment distillation (*Determination of Residual Solvents*) or headspace analysis (*Limit Test for Solvent Residues*).

Free ionizable copper

Not more than 200 mg/kg

Accurately weigh about 1 g of the sample and dissolve in 20 ml of arachid oil, with the aid of gentle heat. Add exactly 200 ml of water, stir mechanically, and adjust to pH 3.0 by careful addition of 0.5 N hydrochloric acid (avoid over-shooting). Allow the mixture to stand for 10 min. If necessary readjust to pH 3.0 by careful addition of 0.5 N hydrochloric acid. Transfer to a separating funnel and allow to stand for about 20 min. Filter the aqueous phase through a No. 50 Whatman filter paper, rejecting the first 10 ml. Subject this solution to analysis for copper by *atomic absorption spectrometry* (see Volume 4).

Total copper

Not more than 8% of the total copper phaeophytins
Ignite about 0.1 g, accurately weighed, of the sample contained in a silica dish, at a temperature not exceeding 500°, until all carbon is removed; moisten with one or two drops of concentrated sulphuric acid and re-ash. Dissolve the ash by boiling with 3 portions (each of 5 ml) of 10% (w/w) hydrochloric acid, filtering each addition through the same small filter paper into a 100 ml volumetric flask. Cool, and make up to volume with purified water. Subject this solution to analysis for copper by *atomic absorption spectrometry* (see Volume 4).

Arsenic (Vol. 4)

Not more than 3 mg/kg (Method II)

Lead (Vol. 4)

Not more than 5 mg/kg

Determine using an atomic absorption technique appropriate to the specified level. The selection of sample size and method of sample preparation may be based on the principles of the method described in Volume 4, “Instrumental Methods.”

Method of Assay

Accurately weigh about 100 mg of the sample and dissolve in diethyl ether, making the volume to 100 ml. Dilute 2 ml of this solution to 25 ml with diethyl ether. The concentration of the sample should not give an absorbance at 660.4 nm that is in excess of the working range for Absorbance measurements, i.e., not in excess of 0.7.

Measure the absorbances (A) of the solution in a 1 cm cell against a diethyl ether blank at 667.2 nm, 654.4 nm, 649.8 nm and 628.2 nm. (The latter two wavelengths being the absorbance maxima in diethyl ether for copper phaeophytin a and copper phaeophytin b respectively).

Calculate the concentration of the individual compounds in micromoles per liter from the following equations:

Copper phaeophytin a = 45.6 A (649.8nm) – 2.75 A (6288.2nm) + 3.10 A (667.2nm) – 35.4 A (654.4nm)

Copper phaeophytin b = -8.46 A (649.8nm) + 20.7 A (628.2nm) – 1.69 A (667.2nm) + 5.13 A (654.4nm)

Convert the figures in micromoles per liter to percentages using the following equations:

$$\%\text{copper phaephytin a} = \frac{\text{micromoles} \times 0.9327 \times 12.5 \times 100}{\text{mass of sample (mg)}}$$

$$\%\text{copper phaeophytin b} = \frac{\text{micromoles} \times 0.9467 \times 12.5 \times 100}{\text{mass of sample (mg)}}$$

Chlorophyllins, Copper Complexes Sodium and Potassium Salts

Prepared at the 31st JECFA (1987), published in the Combined Compendium of Food Additive Specifications, FAO JECFA Monographs 1 (2005). Corrected at the 69th JECFA (2008). An ADI of 0-15 mg/kg was established at the 22nd JECFA (1978).

Definition The alkali salts of Copper Chlorophyllins are obtained by the addition copper to the product obtained by the saponification of a solvent extraction of grass, lucerne, nettle and other plant material; the saponification removes the methyl and cyclophytol ester groups and may partially cleave the pentenyl ring; after addition of copper to the purified chlorophyllins, the acid groups are neutralized to form the salts of potassium and/or sodium; the commercial products may be presented as aqueous solutions or dried powders. Only the following solvents may be used for the extraction: acetone, dichloromethane, methanol, ethanol, propan-2-ol and hexane.

Assay Not less than 95% total copper chlorophyllins after drying (100°, 1 h).

Description Dark green to blue/black powder or dark green solution.

Identification

Solubility (Vol. 4): Soluble in water; very slightly soluble in lower alcohols and ketones and diethyl ether; insoluble in chloroalkanes, hydrocarbons and fixed oils

Spectrometry (Vol. 4): A (1%, 1 cm) of the sample, dried at 100° for 1 h, at 405 nm in pH 7.5 phosphate buffer is not less than 540.

Test for copper: Dissolve the sulfated ash of the sample (using 1 g of sample, Method I) in 10 ml of dilute hydrochloric acid TS by heating on a water bath. Filter if the solution is not clear, and dilute to 10 ml with water. Use this solution as the test preparation for the following tests.

To 5 ml of the test preparation add ammonia TS to make the solution alkaline. Blue color should appear.

To 5 ml of the above test preparation add 0.5 ml of a 1 in 1000 sodium diethyldithiocarbamate solution. A brown precipate should be formed.

Test for sodium (Vol. 4): Passes test

Test the solution described under TESTS, IDENTIFICATION TESTS Test for copper

Test for potassium (Vol. 4): Passes test

Test the solution described under TESTS, IDENTIFICATION TESTS Test for copper

Purity

Basic dyes

To 5 ml of a 0.5 aqueous solution of the sample in a test-tube add 1 ml of 1 N hydrochloric acid and add 5 ml of diethyl ether. Mix thoroughly and allow to separate. The ether layer should be no darker than pale green.

Residual solvents (Vol. 4)

Acetone, methanol, ethanol, propan-2-ol, hexane: Not more than 50 mg/kg, singly or in combination

Dichloromethane: Not more than 10 mg/kg

Determine *gas chromatographically* using either the method of entrainment distillation (*Determination of Residual Solvents*) or headspace analysis (*Limit Test for Solvent Residues*).

Free ionizable copper

Not more than 200 mg/kg

Accurately weigh about 1 g of the sample and dissolve in 20 ml of arachid oil, with the aid of gentle heat. Add exactly 200 ml of water, stir mechanically, and adjust to pH 3.0 by careful addition of 0.5 N hydrochloric acid (avoid over-shooting). Allow the mixture to stand for 10 min. If necessary readjust to pH 3.0 by careful addition of 0.5 N hydrochloric acid. Transfer to a separating funnel and allow to stand for about 20 min. Filter the aqueous phase through a No. 50 Whatman filter paper, rejecting the first 10 ml. Subject this solution to analysis for copper by *atomic absorption spectrometry* (see Volume 4).

Total copper

Not more than 8% of the total copper phaeophytins
Ignite about 0.1 g, accurately weighed, of the sample contained in a silica dish, at a temperature not exceeding 500°, until all carbon is removed; moisten with one or two drops of concentrated sulphuric acid and re-ash. Dissolve the ash by boiling with 3 portions (each of 5 ml) of 10% (w/w) hydrochloric acid, filtering each addition through the same small filter paper into a 100 ml volumetric flask. Cool, and make up to volume with purified water. Subject this solution to analysis for copper by *atomic absorption spectrometry* (see Volume 4).

Arsenic (Vol. 4)

Not more than 3 mg/kg (Method II)

Lead (Vol. 4)

Not more than 5 mg/kg

Determine using an atomic absorption technique appropriate to the specified level. The selection of sample size and method of sample preparation may be based on the principles of the method described in Volume 4, “Instrumental Methods.”

Method of Assay

Accurately weigh about 1 g of the sample, dried previously at 100° for 1 h, then dissolve in 20 ml Phosphate Buffer Solution (pH 7.5) and dilute to 1000 ml with distilled water.

Dilute 10 ml of this solution to 100 ml with Phosphate Buffer Solution (pH 7.5). Measure the optical density of the final solution (0.001% w/v) in a suitable spectrophotometer, using a 1 cm cell and slit width of 0.10 mm at 403-406 nm, recording the maximum within this range.

The percentage of sodium copper chlorophyllin is given by the expression:

$$\frac{\text{Optical density} \times 10^4}{565 \times \text{weight of sample (g)}}$$

This formula was derived on the assumption that 100% pure sodium copper chlorophyllin has a specific absorbance of 565.

General Standard of Food Additives, Maximum Permissible Levels

The provisions that follow are defined at the additive group level, and thus apply to the total content of Chlorophophylls and Chlorophyllins, copper complexes.

Number	Food Category	Max Level (mg/kg)	Notes
01.1.4	Flavored fluid milk drinks	50	Except for use in fermented milk drinks at 500 mg/kg. Excluding chocolate milk.
01.6.1	Unripened cheese	50	Subject to national legislation of the importing country aimed, in particular, at consistency with Section 3.2 of the Preamble.
01.6.2.1	Ripened cheese, includes rind	15	
01.6.2.2	Rind of ripened cheese	75	
01.6.2.3	Cheese powder (for reconstitution; e.g. for cheese sauces)	50	
01.6.4.2	Flavored processed cheese, including containing fruit, vegetables, meat, etc.	50	
01.6.5	Cheese analogues	50	
01.7	Dairy-based desserts (e.g. pudding, fruit or flavored yoghurt)	500	
02.4	Fat-based desserts excluding dairy-based dessert products of food category 01.7	500	
03.0	Edible ices, including sherbet and sorbet	500	
04.1.2.3	Fruit in vinegar, oil, or brine	100	As copper.
04.1.2.4	Canned or bottled (pasteurized) fruit	100	As copper.
04.1.2.5	Jams, jellies, marmalades	200	Subject to national legislation of the importing country aimed, in particular, at consistency with Section 3.2 of the Preamble.
04.1.2.6	Fruit-based spreads (e.g. chutney) excluding products of food category 04.1.2.5	150	
04.1.2.7	Candied fruit	250	
04.1.2.8	Fruit preparations, including pulp, purees, fruit toppings and coconut milk	100	As copper. Excluding coconut milk.
04.1.2.9	Fruit-based desserts, including fruit-flavored water-based desserts	150	
04.1.2.10	Fermented fruit products	100	As copper.
04.1.2.11	Fruit fillings for pastries	100	As copper.
04.1.2.12	Cooked fruit	100	As copper.
04.2.2.5	Vegetable (including mushrooms and fungi, roots and tubers, pulses and legumes, and aloe vera), seaweed, and nut and seed purees and spreads (e.g., peanut butter)	100	As copper.
04.2.2.6	Vegetable (including mushrooms and fungi, roots and tubers, pulses and legumes, and aloe vera), seaweed, and nut and seed pulps and preparations (e.g.	100	As copper. Excluding tomato-based sauces.

	vegetable desserts and sauces, candied vegetables) other than food category 04.2.2.5		
04.2.2.7	Fermented vegetable (including mushrooms and fungi, roots and tubers, pulses and legumes, and aloe vera) and seaweed products, excluding fermented soybean products of food categories 06.8.6, 06.8.7, 12.9.1, 12.9.2.1 and 12.9.2.3	100	As copper.
04.2.2.8	Cooked or fried vegetables (including mushrooms and fungi, roots and tubers, pulses and legumes, and aloe vera), and seaweeds	100	As copper.
05.1.2	Cocoa mixes (syrups)	6	As copper. Subject to national legislation of the importing country aimed, in particular, at consistency with Section 3.2 of the Preamble.
05.1.3	Cocoa-based spreads, including fillings	6	As copper. Excluding products conforming to the Standard for Cocoa Butter (CODEX STAN 86-1981). Subject to national legislation of the importing country aimed, in particular, at consistency with Section 3.2 of the Preamble.
05.1.4	Cocoa and chocolate products	700	For use in surface decoration only.
05.1.5	Imitation chocolate, chocolate substitute products	700	
05.2.1	Hard candy	700	
05.2.2	Soft candy	100	
05.2.3	Nougats and marzipans	100	
05.3	Chewing gum	700	
05.4	Decorations (e.g. for fine bakery wares), toppings (non-fruit) and sweet sauces	100	
06.4.3	Pre-cooked pastas and noodles and like products	100	For use in instant noodles only.
06.5	Cereal and starch based desserts (e.g. rice pudding, tapioca pudding)	75	
07.1.4	Bread-type products, including bread stuffing and bread crumbs	6	As copper. Subject to national legislation of the importing country aimed, in particular, at consistency with Section 3.2 of the Preamble.
07.2	Fine bakery wares (sweet, salty, savory) and mixes	75	
09.2.3	Frozen minced and creamed fish products, including mollusks, crustaceans, and echinoderms	40	For use in surimi and fish roe products only.
09.2.4.1	Cooked fish and fish products	30	As copper. For use in surimi and fish roe products only.
09.2.4.3	Fried fish and fish products, including mollusks, crustaceans, and echinoderms	40	For use in surimi and fish roe products only.
09.2.5	Smoked, dried, fermented, and/or salted fish and fish products, including mollusks, crustaceans, and echinoderms	200	Excluding products conforming to the Standard for Smoked Fish, Smoked-flavored Fish and Smoke-dried Fish

			(CODEX STAN 311-2013).
09.3.1	Fish and fish products, including mollusks, crustaceans, and echinoderms, marinated and/or in jelly	40	For use in glaze, coatings or decorations for fruit, vegetables, meat or fish only.
09.3.2	Fish and fish products, including mollusks, crustaceans, and echinoderms, pickled and/or in brine	40	For use in glaze, coatings or decorations for fruit, vegetables, meat or fish only.
09.3.3	Salmon substitutes, caviar, and other fish roe products	200	
09.3.4	Semi-preserved fish and fish products, including mollusks, crustaceans, and echinoderms (e.g. fish paste), excluding products of food categories 09.3.1 - 09.3.3	75	For use in surimi and fish roe products only.
09.4	Fully preserved, including canned or fermented fish and fish products, including mollusks, crustaceans, and echinoderms	500	For use in surimi and fish roe products only.
10.4	Egg-based desserts (e.g. custard)	300	On the dry ingredient, dry weight, dry mix or concentrate basis.
11.4	Other sugars and syrups (e.g. xylose, maple syrup, sugar toppings)	64	As copper.
12.2.2	Seasonings and condiments	500	
12.4	Mustards	500	
12.5	Soups and broths	400	For use of chlorophylls, copper complexes (INS 141(i)) only in products conforming to the Codex Standard for Bouillons and Consommés (CODEX STAN 117-1981).
12.6	Sauces and like products	100	
13.6	Food supplements	500	For use in surface treatment only.
14.1.4	Water-based flavored drinks, including "sport," "energy," or "electrolyte" drinks and particulated drinks	300	
15.1	Snacks - potato, cereal, flour or starch based (from roots and tubers, pulses and legumes)	350	
15.2	Processed nuts, including coated nuts and nut mixtures (with e.g. dried fruit)	100	
15.3	Snacks - fish based	350	

Regulatory Approvals/Consumption Limits

JECFA: ADI of 0-15 mg/kg bw for chlorophylls, copper complexes (13th Report, 1969) and chlorophyllins, copper complexes sodium and potassium salts (22nd Report, 1978)

USA: Approved for use in citrus-based dry beverage mixes NTE 0.2% in dry mix; extracted from alfalfa (21 CFR 73.125).

EU: ADI withdrawn (2015); Cu-chlorophylls and Cu-chlorophyllins are authorized for use at *Quantum satis* in foods and beverages in Europe.

European Food Safety Authority, Maximum Permissible Levels

MPLs of Cu-chlorophylls (E 141(i)) and Cu-chlorophyllins (E 141(ii)) in foods according to Annex II to Regulation (EC) No 133/2008

FCS Category Number	FCS food category	E-number/group	Restrictions/exemptions	MPL (mg/l or mg/kg as appropriate)
01.4	Flavored fermented milk products including heat-treated products	Group II		*Quantum satis*
01.5	Dehydrated milk as defined by Directive 2001/114/EC		Except unflavored products	
01.6.3	Other creams		Only flavored creams	
01.7.1	Unripened cheese excluding products falling in category 16		Only flavored unripened cheese	
01.7.2	Ripened Cheese	E 141	Only *sage Derby cheese, green and red pesto cheese, wasabi, cheese and green marbled herb cheese*	
01.7.3	Edible cheese rind	Group II		
01.7.4	Whey cheese			
01.7.5	Processed cheese		Only flavored processed cheese	
01.7.6	Cheese products (excluding products falling in category 16)		Only flavored unripened products	
01.8	Dairy analogues, including beverage whiteners			
03	Edible ices			
04.2.1	Dried fruit and vegetables	E 141	Only preserves of red fruit	
04.2.2	Fruit and vetegetables in vinegar, oil, or brine		Only vegetables (including olives)	

04.2.3	Canned or bottled fruit and vegetables		Only preserves of red fruits	
04.2.4.1	Fruit and vegetable preparations excluding compote		Only seaweed based fish roe analogues	*Quantum satis*
			Only preserves of red fruit	
		Group II	Only *mostarda di frutta*	
04.2.5.2	Jam, jellies and marmalades and sweetened chestnut puree as defined by Directive 2001/113/EC	E 141	Except chestnut puree	
04.2.5.3	Other similar fruit or vegetable spreads	Group II	Except *crème de pruneaux*	
05.2	Other confectionery including breath freshening microsweets			
05.3	Chewing gum			
05.4	Decorations, coatings and fillings, except fruit-based fillings covered by category 4.2.4			
06.3	Breakfast cereals		Only breakfast cereals other than extruded, puffed and/or fruit-flavored breakfast cereals	
06.5	Noodles			
06.6	Batters			
06.7	Pre-cooked or processed cereals			
07.2	Fine bakery wares			
08.3.3	Casings and coatings and decorations for meat		Except edible external coating of *pasturmas*	

09.2	Processed fish and fishery products including molluscs and crustaceans	E 141	Only fish paste and crustacean paste	
			Only precooked crustaceans	
			Only smoked fish	
		Group II	Only surimi and similar products and salmon substitutes	
09.3	Fish roe		Except sturgeons' eggs (caviar)	
12.2.2	Seasonings and condiments		Only seasonings, for example curry powder, tandoori	
12.4	Mustard			
12.5	Soups and broths			
12.6	Sauces		Excluding tomato-based sauces	
12.7	Salads and savory-based sandwich spreads			
12.9	Protein products, excluding products covered in category 1.8			
13.2	Dietary foods for special medical purposes defined in Directive 1999/21/EC (excluding products from food category 13.1.5)			
13.3	Dietary foods for weight control diets intended to replace total daily food intake or an individual meal (the whole or part of the total daily diet)			
14.1.4	Flavored drinks		Excluding chocolate milk and malt products	*Quantum satis*
14.2.3	Cider and perry		Excluding *cidre bouche*	

14.2.4	Fruit wine and made wine		Excluding *wino owocowe markowe*	
14.2.5	Mead			
14.2.6	Spirit drinks as defined in Regulation (EC) No 110/2008		Except: spirit drinks as defined in Article 5(1) and sales denominations listed in Annex II, paragraphs 1-14, of Regulation (EC) No 110/2008 and spirits (preceded by the name of the fruit) obtained by maceration and distillation, London Gin, Sambuca, Maraschino, Marrasquino or Maraskino and Mistra	
14.2.7.2	Aromatized wine-based drinks		Except *bitter soda, sangria, claria, zurra*	
14.2.7.3	Aromatized wine-product cocktails			
14.2.8	Other alcoholic drinks including mixtures of alcoholic drinks with non-alcoholic drinks and spirits with less than 15% of alcohol			
15.1	Potato-,cereal-, flour- or starch-based snacks	Group II		*Quantum satis*
15.2	Processed nuts			
16	Desserts excluding products covered in categories 1,3 and 4			
17.1	Food supplements supplied in a solid form including capsules and tablets and similar forms, excluding chewable forms			

17.2	Food supplements supplied in a liquid form			
17.3	Food supplements supplied in a syrup-type or chewable form			

Safety Reviews

Joint FAO/WHO Expert Committee on Food Additives (JECFA) (1969) JECFA 13th Report. Specifications for the Identity and Purity of Food Additives and Their Toxicological Evaluation. WHO Technical Report Series, No. 445.

Joint FAO/WHO Expert Committee on Food Additives (JECFA) (1978) JECFA 22nd Report. Evaluation of Certain Food Additives and Contaminants. WHO Technical Report Series, No. 631.

EFSA ANS Panel (EFSA Panel on Food Additives and Nutrient Sources Added to Food), 2015. Scientific Opinion on re-evaluation of copper complexes of chlorophylls (E 141(i)) and chlorophyllins (E 141(ii)) as food additives. EFSA Journal 2015;13(6):4151, 60 pp. doi:10.2903/j.efsa.2015.4151