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Report Name: National Food Safety Standard for Food Additive Chlorophyllin Copper Complex Sodium Salts Notified to WTO

Country: China - People's Republic of

Post: Beijing

Report Category: FAIRS Subject Report, Sanitary/Phytosanitary/Food Safety, WTO Notifications

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Report Highlights:

On October 25, 2023, China notified the National Food Safety Standard for Food Additive Chlorophyllin Copper Complex Sodium Salts to the World Trade Organization (WTO) under G/SPS/N/CHN/1289. The proposed date of entry into force is to be determined. Comments may be submitted to China's SPS National Notification and Enquiry Center at sps@customs.gov.cn until December 24, 2023. The report provides an unofficial translation of the draft standard.

Report Summary:

On October 25, 2023, China notified the National Food Safety Standard for Food Additive Chlorophyllin Copper Complex Sodium Salts to the World Trade Organization (WTO) under G/SPS/N/CHN/1291. The proposed date of entry into force is to be determined. Comments may be submitted to China's SPS National Notification and Enquiry Center at sps@customs.gov.cn until December 24, 2023.

This standard applies to food additive chlorophyllin copper complex sodium salts processed through saponifying, copper substitution reaction, neutralizing, etc. using extracted chlorophyll from raw materials such as folium mori, silkworm excrement, grass, or plants, or using chlorophyll directly. The standard specifies the technical requirements and testing methods for food additive chlorophyllin copper complex sodium salts.

This notified draft standard will replace the current implementing national standard GB 26406-2011 (link in Chinese). The report provides an unofficial translation of the draft standard notified to WTO.

BEGIN TRANSLATION

National Food Safety Standard
The Food Additive Chlorophyllin Copper Complex Sodium Salts
(Draft for Comments)
Foreword

This standard replaces GB 26406-2011 National Food Safety Standard for Food Additive Chlorophyllin Copper Complex Sodium Salts.

As compared with GB 26406-2011, the following major changes are made to this standard:

- The scope, molecular formula, and relative molecular mass are revised,
- The requirements for indicators of free copper (Cu) and lead (Pb) are revised,
- The identification tests and determination methods for total copper (Cu) are revised,
- The absorbance ratio from the physical and chemical indicators is included in the identification tests,
- The absorbance $E_{1cm}^{1\%}$ (405 ± 3nm) is deleted,
- Three physical and chemical indicators for content of chlorophyllin copper complex sodium salts (on dry basis), basic dyes, and solvent residues are added,
- Descriptions of commercial products are added.

1. Scope

This standard applies to the food additive chlorophyllin copper complex sodium salts made of chlorophyll extracted from raw materials of silkworm excrement, grass (for example tall fescue, alfalfa, nettle, etc.), or plants such as spinach, spirulina, and folium mori, or directly with chlorophyll, through the processes of saponification, copper replacement, and neutralization. The solvents used are acetone, dichloromethane, methanol, ethanol, isopropanol, n-hexane, petroleum ether (with a boiling range of 90℃ to 120℃), and (or) plant oil extraction solvent.

2. Molecular Formula and Relative Molecular Mass

2.1 Molecular formula

Disodium copper chlorophyllin ($C_{34}H_{30}O_5N_4CuNa_2$)

Trisodium copper chlorophyllin ($C_{34}H_{31}O_6N_4CuNa_3$)

2.2 Relative molecular mass

Disodium copper chlorophyllin: 684.16 (according to international relative atomic mass in 2021).

Trisodium copper chlorophyllin: 724.16 (according to international relative atomic mass in 2021).

3. Technical Requirements

3.1 Sensory Requirements

Sensory requirements shall comply with provisions in Table 1.

Table 1: Sensory Requirements

Items	Requirements	Testing Methods
Color	Blackish green to black	Take a reasonable amount of the sample, place it in a clean dry white porcelain plate, and observe its color and form under the natural light.
Form	Powder	

3.2 Physical and Chemical Indicators

Physical and chemical indicators shall comply with provisions in Table 2.

Table 2: Physical and Chemical Indicators

Items		Indicators	Testing Methods
Sodium copper chlorophyllin content (on dry basis), *w*/%	≥	95.0	A.3 in Appendix A
Total copper (Cu), *w*/%	≤	8.0	GB 5009.13
Free copper (Cu), *w*/%	≤	0.020	A.4 in Appendix A
Loss on drying, *w*/%	≤	5.0	Direct drying method [a] in GB 5009.3
pH		9.5～11.0	A.5 in Appendix A
Basic dyes		Passed tests	A.6 in Appendix A
Solvent residue [b]			A.7 in Appendix A
Dichloromethane (mg/kg)	≤	10	
Methanol, isopropanol, n- hexane, and total heptane/(mg/kg)	≤	100 (silkworm excrement) 50 (plant)	
Lead (Pb)/ (mg/kg)	≤	3.0	GB 5009.75 or GB 5009.12
Arsenic (As)/ (mg/kg)	≤	2.0	GB 5009.76 or GB 5009.11
Note 1: Silkworm excrement and plants represent chlorophyllin copper complex sodium salts			

extracted from silkworm excrement and plants respectively.

Note 2: Commercialized chlorophyllin copper complex sodium salts products should use the chlorophyllin copper complex sodium salts in compliance this standard as raw materials, added with food auxiliary materials such as edible plant oils, maltodextrin, and water, and /or emulsifier, antioxidant, acidity regulator, etc. that meets quality standards of food additives, with the content in compliance with its claimed values, in form of powder or liquid.

[a] Temperature and drying time are 105℃ and 2 hours respectively.
[b] Determine relevant solvent residues (use petroleum ether to determine heptane and use plant oil extraction solvent to determine n-hexane) according to solvent used for the product.

Appendix A

Testing Methods

A.1 General Rules

Analytically pure reagents and level three water in compliance with provisions in GB/T 6682 are used in this standard unless otherwise specified. The standard solution, standard solution for impurity determination, preparations, and products used in the tests should be prepared according to GB/T 601, GB/T 602, and GB/T 603 if not otherwise specified. Solutions used in the tests of the standard refer to aqueous solutions if it is not indicated which solvent should be used for preparation.

A.2 Identification Tests

A.2.1 Solubility

It can be dissolved in water, almost insoluble in ethanol, propyl alcohol, acetone, and ether, and insoluble in chloroform. If the aqueous solution is in the acid condition (pH<6.5) or with existence of calcium ions, sediments can be shown.

A.2.2 Maximum absorption wavelength and absorbance ratio

With a sample solution as specified in A.3.3.1 for determining contents of chlorophyllin copper complex sodium salts, maximum absorption peaks show within scope of both two wavelengths of 405 nm±3 nm and 630 nm±3 nm and the absorbance ratio A_{405nm}/A_{630nm} measured at the two maximum wavelengths is within the range of 3.2~4.0.

A.2.3 Copper Ions and Sodium Ions Tests

A.2.3.1 Reagents and materials

A.2.3.1.1 Sulfuric acid.

A.2.3.1.2 Hydrochloric acid solution: 1+3.

A.2.3.1.3 Ammonia solution: 10%.

A.2.3.1.4 Sodium diethyldithiocarbamate solution: 1 g/L.

A.2.3.2 Analytic steps

Measure 1 g of the sample, place it in a crucible that has been heated at temperature of 800℃ ± 25 ℃ and obtain a constant weight. Slowly heat up until the sample is completely carbonized. Cool the carbonized sample, use 0.5 mL - 1 mL of sulfuric acid to wet the residues, continue to heat until the sulfuric acid steam disappears. Heat the residues with a furnace at temperature of 800℃ ± 25℃ until weight of the residues is constant. Add 10 mL of hydrochloric acid solution to the residue, heat, and dissolve in a water bath, and filter it. Put filtrate into a measuring flask, add water until the volume reaches the mark, and use it as the sample solution to conduct the following tests:

a) Identification of copper ions: measure 2 mL of the sample solution and add in ammonia solution. The color of the solution will turn blue.

b) Identification of copper ions: measure 5 mL of the sample solution and add in 0.5 mL of sodium diethyldithiocarbamate solution. Reddish brown sediment will appear.

c) Identification of sodium ions: use the sample solution to do flame tests. The color will be yellow.

A.3 Determination for Content of Chlorophyllin Copper Complex Sodium Salts (on dry basis)

A.3.1 Reagents and materials

A.3.1.1 0.15 mol/L disodium phosphate solution: measure 53.7 g of disodium hydrogen phosphate ($Na_2HPO_4 \cdot 12H_2O$), add water to dissolve, and dilute until volume reaches 1,000 mL.

A.3.1.2 0.15 mol/L potassium dihydrogen phosphate solution: measure 20.4 g of potassium dihydrogen phosphate (KH_2PO_4), add water to dissolve, and dilute until volume reaches 1,000 mL.

A.3.1.3 Phosphate buffer solution (pH 7.5): mix 0.15 mol/L disodium phosphate solution and 0.15 mol/L potassium dihydrogen phosphate solution in a ratio of 21:4.

A.3.2 Instruments and equipment

Spectrophotometer

A.3.3 Analytic steps

A.3.3.1 Preparation of sample solution

Measure 0.1 g of the sample, accurate to 0.0002g, add water to dissolve, and dilute it until the volume reaches 500 mL. Accurately measure 5 mL of the above-prepared solution and use phosphate buffer solution (pH 7.5) to dilute it until the volume reaches 100 mL.

A.3.3.2 Determination

Put sample solution into a 1cm cuvette, use phosphate buffer solution (pH 7.5) as the blank contrast solution, and determine the absorbance with a spectrophotometer at the maximum absorption wavelength within the range of 405 nm ± 3 nm. The absorbance should be controlled within the range of 0.3~0.7, otherwise, the concentration of the sample solution should be adjusted before the absorbance is determined again.

A.3.4 Results calculation

The mass fraction w_1 for content of chlorophyllin copper complex sodium salts (on dry basis) is calculated according to formula (A.1):

$$w_1 = \frac{A \times 10^4}{565 \times 100 \times m \times (1 - w_0)} \times 100\% \quad \text{.....(A.1)}$$

Where:

A -- absorbance value in the sample solution,

10^4 -- volume conversion factor,

565 -- extinction value of the 1% solution (100 mL of solvent contains 1g of chlorophyllin copper complex sodium salts) in 1cm cuvette,

100 -- concentration conversion factor,

m -- mass of the sample, expressed in g,

w_0 -- weight loss of the sample during drying, expressed in %.

The arithmetic mean of the results from parallel determinations is taken as the test result. The absolute value of the differences between the two independently determined results obtained under repetitive conditions should be no more than 2.0% of the arithmetic mean.

A.4 Determination of Free Copper (Cu)

A.4.1 Reagents and materials

Same as GB 5009.13.

A.4.2 Instruments and equipment

Same as GB 5009.13.

A.4.3 Sample treatment

Measure 0.1 g of the sample, accurate to 0.0002 g, add about 75mL of water to dissolve. Use 1mol/L hydrochloric acid solution to adjust pH value to 3.0, add water until the volume reaches 100 mL, and filter it with double-layer filter paper.

A.4.4 Analytic steps

Except for sample treatment, other steps comply with methods specified in GB 5009.13.

A.5 Determination of pH Value

Prepare concentration of 1% sample solution and use an acidity meter to determine its pH value.

A.6 Determination of Basic Dyes

Prepare 5 mL of 0.05% sample solution, add 1mL of 1mol/L hydrochloric acid solution and 5 mL of n-hexane, mix well, then separate. If the color of n-hexane layer is not darker than light green, it means the sample passes the test.

A.7 Determination of Solvent Residues (dichloromethane, methanol, isopropanol, n-hexane, and heptane)

A.7.1 Reagents and materials

A.7.1.1 Water: Level one water meeting with requirements in GB/T 6682.

A.7.1.2 The standard substances for components to be determined are dichloromethane, methanol, isopropanol, n-hexane, heptane, and chromatographically pure.

A.7.1.3 Internal standard substances: 3-methyl-2-pentanone and chromatographically pure.

A.7.1.4 *N*-methylpyrrolidone

A.7.2 Instruments and equipment

A gas chromatograph: with a flame ionization detector (FID) and a headspace sampler.

A.7.3 Reference chromatographic conditions

A.7.3.1 Chromatographic column: quartz capillary (Φ 0.53 mm×30m), coated with dimethylpolysiloxane, 5 μm in thickness, or similar chromatographic column in performance.

A.7.3.2 Carrier gas: nitrogen

A.7.3.3 Carrier gas flow rate: 5 mL/min.

A.7.3.4 Column temperature: 35 ℃ for 5 minutes, heat it to 90 ℃ with an increase of 5 ℃ per minute and maintain the same condition for 6 minutes.

A.7.3.5 Temperature at the sample entry point: 140 ℃.

A.7.3.6 Detector temperature: 300 ℃.

A.7.3.7 Sample size: 1.0 mL.

A.7.4 Reference conditions for headspace sampler

A.7.4.1 Sample heating temperature: 80 ℃.

A.7.4.2 Sample heating time: 10 minutes.

A.7.4.3 Injector temperature: 90 ℃.

A.7.4.4 Transfer temperature: 100 ℃.

A.7.5 Analytic steps

A.7.5.1 Preparation of the internal standard solution

Measure 50.0 mL of water, put it into a 50 mL sample vial, weigh it, and accurate to 0.0001g. Measure 15 μL of 3-methyl-2-pentanone, inject it into the sample vial, and mix well. Weigh the sample vial again and accurate to 0.0001 g.

A.7.5.2 Preparation of blank solution

Measure 5.0 mL of water and 1.0 mL of the internal standard solution separately, move them into a headspace vial. Measure 20 μL of *N*-methylpyrrolidone, inject it into the headspace vial, seal it. Heat the vial at 80 ℃ for 10 minutes and shake vigorously to mix well.

A.7.5.3 Preparation of standard solution

Measure 5.0 mL of water and 1.0 mL of the internal standard solution separately, put into a headspace vial, measure 10 mg of the standard substance to be determined (each solvent is analyzed separately), use *N*-methylpyrrolidone to dissolve and dilute it until the volume reaches 100 mL. Measure 20 μL of the solution and inject it into the headspace vial, seal and heat the vial at 80 ℃ for 10 minutes. Shake vigorously to mix well.

A.7.5.4 Preparation of sample solution

Measure 0.2 g of the sample, accurate to 0.0001 g, put into a headspace vial, and add 5.0 mL of water and 1.0 mL of the internal standard solution. Measure 20 μL of *N*-methylpyrrolidone, inject into the headspace vial, seal it and heat the vail at 80 ℃ for10 minutes, then shake vigorously to mix well.

A.7.5.5 Determination

Conduct chromatographic analyses of the blank solution, the standard solution, and the sample solution respectively after headspace treatment under the reference operating conditions specified in A.7.3 and A.7.4. For the reference gas chromatogram map of the solvent residues in the standard solution, please see Figure B.1.

A.7.6 Results calculation

A.7.6.1 Correction factor f_i

The correction factor f_i is calculated according to formula (A.2):

$$f_i = \frac{m_i \times 50}{m_0 \times (A_f - A_g)} \quad \text{(A.2)}$$

Where:

m_i -- mass of the component to be determined in the standard solution, expressed as mg,

m_0 -- mass of the internal standard substance in the internal standard solution, expressed in mg,

A_f -- ratio between peak areas of the component to be determined and peak areas of the internal standard substance in the chromatogram map of the standard solution,

A_g -- ratio between peak areas of the component to be determined and peak areas of the internal standard substance in the chromatogram map of the blank solution,

50 -- volume conversion factor.

A.7.6.2 Component content to be determined

The content w_i (mg/kg) for the components (dichloromethane, methanol, isopropanol, n-hexane, and heptane) to be determined in the sample is calculated according to formula (A.3):

$$w_i = \frac{A_i \times m_0 \times f_i \times 1000}{m \times 50} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \text{(A.3)}$$

where:

A_i -- ratio between peak areas of the component to be determined and peak areas of the internal standard substance in chromatogram map of the sample solution,

m_0 -- mass of the internal standard substance in the internal standard solution, expressed in mg,

f_i -- correction factor,

m -- mass of the sample, expressed in g,

1,000 -- mass conversion factor,

50 -- volume conversion factor.

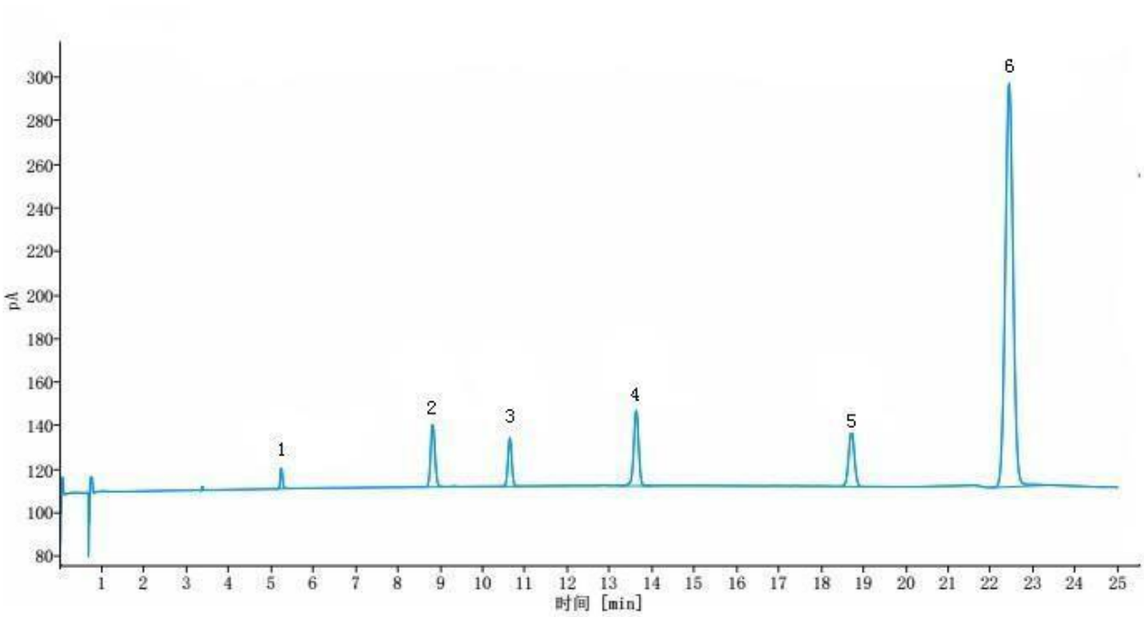
The content of dichloromethane obtained from calculation according to formula (A.3) is w_2, the content of methanol, content of isopropanol, content of n-hexane, and content of heptane are w_3, w_4, w_5, and w_6 respectively, and the sum is the content of solvent residues (sum of methanol, isopropanol, n-hexane, and heptane) in the sample.

The arithmetic mean from parallel determination results is calculated as test result. The absolute value of the differences between the two independently determined results obtained under repetitive conditions should be no more than 10 % of the arithmetic mean.

Appendix B
The reference gas chromatogram map of the solvent residues in the standard solution

For the reference gas chromatogram map of the solvent residues in the standard solution, see Figure B.1.

Figure B.1 The reference gas chromatogram map of the solvent residues in the standard solution



Time [minute]

Note:
1 – methanol,
2 – isopropanol,
3 – dichloromethane,
4 - n-hexane,
5 – heptane,
6 - internal standard substance (3-methyl-2-pentanone).

Attachments:

No Attachments.