

Guideline on Specifications for Carbon Black

2010. 05.

<Introduction>

1. Background

With revision of the Regulation on Designation of Raw Materials for Cosmetics (MFDS Notice No. 2010-24, 2010.04.30), the KFDA developed this guideline on specifications for carbon black to help the industry and other interested parties effectively control raw materials for cosmetic products.

2. Purpose

- A. To provide specifications for carbon black used in the manufacture of cosmetics products and to contribute to safety of cosmetic products;

- B. To help the cosmetics industry and other related testing laboratories perform effective quality control.

Carbon Black

Carbon Black contains not less than 95.0% of carbon (C:12.01), when assayed with a color prepared by adding aromatic crude oil into a combustion tube, injecting natural gas to perform heat-degradation and cooling it with water.

Description Carbon Black occurs as black powders and it is odorless and tasteless.

Identification When 1.0 g of Carbon Black is carbonized at 500°C for 4 hours, it is completely or nearly reduced to ashes. When hydrochloric acid, nitric acid and sodium hydroxide test solution are added to 2.0 g of Carbon Black, it is not soluble.

Specific surface area Take 0.10–0.20 g of Carbon Black into a sample tube, vacuum-dry it at 110°C for 12 hours, add a small amount of dried nitrogen, stopper the sample tube and accurately weigh the test sample. Attach the sample tube to the measuring system and carefully reduce the pressure of the sample tube to the degree of 2–10 Pa. If necessary, measure the sample tube's empty volume. Lift the Dewar bottle containing liquid nitrogen to the specified position above the sample tube, introduce sufficient amount of nitrogen until the relative pressure (P/P_0) becomes about 1.0, measure the volume of the adsorbed nitrogen (V_a) at the relative pressure levels of 0.10, 0.20 and 0.30 and obtain the following BET (Brunauer, Emmet,

Teller) adsorption isotherm equation. The regression equation's correlation coefficient (r^2) should be not less than 0.995.

$$\frac{1}{V_a \left(\frac{P_0}{P} - 1 \right)} = \frac{(C-1)}{V_m C} \times \frac{P}{P_0} + \frac{1}{V_m C}$$

P : partial pressure (Pa) of adsorption gas in equilibrium with sample surface at -195.8°C (liquid nitrogen's boiling point).

P_0 : adsorption gas's vapor pressure

V_a : volume of adsorption gas under standard conditions (0°C , 1.013×10^5 Pa) (mL)

V_m : volume of adsorption gas under standard conditions which forms apparent monomolecular layer on sample surface (mL)

C: integral number relating to adsorption enthalpy of adsorption gas on sample surface

With V_m from this equation, calculate the sample's specific surface area (S) according to the following equation. ($200 \sim 260 \text{ m}^2/\text{g}$).

$$S = (V_m N_a) / (m \times 22400)$$

N: Avogadro's number, $6.022 \times 10^{23}/\text{mol}$

a: Effective cross section of one adsorption gas molecule (m^2)

$$N_2 : 0.162 \times 10^{-18}$$

m: mass of sample powder (g)

Loss on ignition Not more than 2.0% (1.0 g after drying at 125°C for 1 hour, with cover, ignition at 950°C for 7 minutes)

Residue on ignition Not more than 0.15% (ignition at 800°C for 6 hours)

Purity 1) **Lead** Add 20 mL of hydrochloric acid and 5 mL of bromine test solution to 1.0 g of Carbon Black, heat it for 5 minutes, filter the solution, wash the residues with 50 mL of boiling water, sum it with the filtrate and evaporate it to dryness. To this, add 1 mL of 1 N hydrochloric acid, 20 mL of water and 5 mL of sulfurous acid and filter it while stirring. Boil the filtrate, cool it and add water to make 50 mL. Take 10 mL of this solution and use it as sample solution (not more than 10 ppm).

2) **Arsenic** Add 20 mL of nitric acid to 1.0 g of Carbon Black and concentrate it to about 5 mL by heating. After cooling, add 5 mL of sulfuric acid, heat it until white fumes are evolved, add a small amount of nitric acid and heat it again until white fumes are evolved. Repeat this procedure until red fumes are not evolved. Then, add 5 mL of a mixture of nitric acid and perchloric acid (1:1) and heat it. Repeat this procedure until the solution becomes colorless to light yellow. After cooling, add 10 mL of saturated ammonium oxalate solution and heat it until white fumes are evolved. Repeat this procedure three times. After cooling, add water to make 30 mL and use it as sample solution. Take 20 mL of sample solution and perform the test using apparatus C (not more than 3 ppm).

3) **Sulfur:** Perform this test by appropriate method among the following test methods.

A) Titration method

Accurately take about 25 mg of Carbon Black and process it according to the oxygen flask combustion method using 10 mL of a mixture of hydrogen peroxide and water (1:100) as the absorbing liquid. Use the resultant solution as the sample solution. Add 40 mL of methanol to sample solution, accurately add 15 mL of 0.002 N barium perchlorate solution, allow it to stand for 10 minutes, add 0.15 mL of Arsenazo III test solution and perform titration with 0.002 N sulfuric acid until the solution's color is changed from blue-purple to red. Perform blank test in the same manner to correct the result (not more than 0.65%).

$$1 \text{ mL of } 0.002 \text{ N barium perchlorate solution} = 0.032062 \text{ mg S}$$

B) Method using automatic elemental analyzer

Determine the amount of sulfur in test sample according to the following assay method (not more than 0.65%).

4) Polynuclear aromatic hydrocarbons (PAHs) Accurately take about 2.5 g of Carbon Black, add 20 mL of a mixture of dichloromethane and methanol (50:50) and sufficiently disperse the test sample by sonication for 30 minutes. Centrifuge it at 3000 rpm for 15 minutes, take the supernatant and filter it. Use the filtrate as the sample solution. Separately, accurately take 0.1 mL of PAHs standard solution (Polynuclear Aromatic Hydrocarbons Mix, 100–2000 µg/mL, Supelco), add a mixture of dichloromethane and methanol (50:50) to make 1 mL, 10 mL, 50 mL and 100 mL, and use such solutions as standard solutions for construction of standard curve. Test sample and standard

solutions by gas chromatography under the following conditions and determine the sample solution's PAHs content from the standard curve (not more than 0.5 ppm).

<Operating conditions>

Detector: mass analyzer (ionization mode: 70 eV, analysis mode: EI+)

Column: DB-5MS (30 m × 0.25 mm × 0.25 μm) or equivalent one

Column temperature: 70°C (keep this temperature for 3 minutes) → temperature elevation at 20 °C/min → 240 °C → temperature elevation at 7 °C/min → 310 °C (keep this temperature for 3 minutes)

Carrier gas: helium

Injector temperature: 250 °C

Analyzer temperature: 310 °C

Injection volume: 1 μL

5) Benzo(a)pyrene Accurately take about 2.5 g of Carbon Black, add 20 mL of a mixture of internal standard (1 μg/mL 3-methylene chloro anthracene), dichloromethane and methanol (50:50), and sufficiently disperse the test sample by sonication for 30 minutes. Centrifuge it at 3000 rpm for 15 minutes, take the supernatant and filter it. Use the filtrate as the sample solution. Separately, accurately take appropriate amount of benzo(a)pyrene standard, add a mixture of internal standard, dichloromethane and methanol (50:50) to make more than 5 solutions with different concentrations, and use such solutions as standard solutions for construction of standard curve. Prepare such standard solutions to assure that benzo(a)pyrene concentration per 1 mL is in the range of 1–100 ng/mL. Take 10 μL of each of sample

and standard solutions and test them by liquid chromatography under the following conditions and determine the sample solution's benzo(a)pyrene content from the standard curve (not more than 5 ppb).

<Operating conditions>

Detector: fluorometric detector (excitation wavelength: 325 nm, emission wavelength: 400 nm)

Column: Supecosil LC_PAH (4.6 x 250 mm, 5 μ m) or equivalent one

Mobile phase: acetonitrile : water = 94 : 6

Flow rate: 1.0 mL/min

6) Dibenz(a,h)anthracene Accurately take about 2.5 g of Carbon Black, add 20 mL of a mixture of internal standard (1 μ g/mL 3-methylene chloro anthracene), dichloromethane and methanol (50:50), and sufficiently disperse the test sample by sonication for 30 minutes. Centrifuge it at 3000 rpm for 15 minutes, take the supernatant and filter it. Use the filtrate as the sample solution. Separately, accurately take appropriate amount of dibenz(a,h)anthracene standard, add a mixture of internal standard, dichloromethane and methanol (50:50) to make more than 5 solutions with different concentrations, and use such solutions as standard solutions for construction of standard curve. Prepare such standard solutions to assure that dibenz(a,h)anthracene concentration per 1 mL is in the range of 1–100 ng/mL. Take 10 μ L of each of sample and standard solutions and test them by liquid chromatography under the following conditions and determine the sample solution's dibenz(a,h)anthracene content from the standard curve. (not more than 5 ppb).

<Operating conditions>

Detector: fluorometric detector (excitation wavelength: 325 nm, emission wavelength: 400 nm)

Column: Supecosil LC_PAH (4.6 x 250 mm, 5 μm) or equivalent one

Mobile phase: acetonitrile : water = 94 : 6

Flow rate: 1.0 mL/min

Assay Dry Carbon Black at 105 °C for 1 hour and take about 1.0 mg. Separately, accurately take 1.0–2.0 mg of standard for quantitation 2,5-Bis(5-tert-butyl-benzeno xazol-2-yl)thiophene, C₂₆H₂₆N₂O₂S, MW 430.57) and use it in construction of standard curve. Test sample and standard using automatic elemental analyzer and determine carbon content (%) in sample from the standard curve.

<Operating conditions>

Detector: thermal conductivity detector (TCD)

Column: Porapack PQS (PTFE, 2 m, 6 x 5 mm) or equivalent one

Column temperature: 60 °C

Carrier gas: Helium (120–140 mL/min)

Combustion gas: Oxygen (250 mL/min)

Furnace temperature: 900 °C

Reaction tube temperature: 1800 °C