

Testing Method of Component and Element for Natural Rubber

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1. Scope of Application

This specification specifies the quantitative analysis method of non-organic and organic matters contained in natural rubber.

2. Ingredients Subject to Analysis

- (1) Non-organic matter: copper, manganese, iron, nitrogen, sulfur, lead, carbon black
- (2) Organic matter: rubber hydrocarbon, polymer, monomer, organic ingredient
- (3) Others: volatile ingredient, lime, dust ingredient, acetone extraction, chloroform extraction, acetone chloroform extraction, grade, alcohol KOH extraction

3. Sample

3.1 Terminology

- (1) Lot: A bundle of bale, classified by its clearly distinguishable common characteristic.
- (2) Sample: sample taken from the lot to be used in the test

3.2 Sampling Method

Take little quantities from each portion, by dividing the sample into 16 or 32 pieces.

4. Non-Volatile Ingredient

4.1 Scope of Application

This specification is used in measuring the moisture content contained in the sample. However, it also includes other matter which evaporate at 100°C.

4.2 Operation

- (1) Weigh the sample precisely, up to 0.1g (A), and weigh the rubber precisely up to 0.1g, which shall be uniform by passing it through a roller, 10 times (B).
- (2) Take two 10gr samples and weigh, up to 1mg (C).
In case the sample is not weighed immediately, wrap it up in polyethylene film and store it, to prevent the loss of the volatile ingredient.
- (3) Make each sample in a sheet 2mm thick or less by passing it through a tightened cold roller, two times, or cut into small pieces 2mm of maximum size or less, and desiccate for an hour at 100±5°C and then weigh. Desiccate while weighing and for every 30 minutes, until the weight decrease and becomes 1mg or less, and then measure the weight (D).
- (4) Calculate the volatile ingredient (%) by the following formula:

$$\text{Volatile ingredient} = \left(\frac{A-B}{A} - \frac{C-D}{C} \right) \times 100$$

5. Ash Content

5.1 Scope of Application

This specification is applied to the total contents analysis method of non-organic additives contained in natural rubber.

5.2 Operation

- (1) Weigh roughly 5gr of the sample, precisely up to 5mg, and put it in a 50ml preheated porcelain melting pot of known weight. Place the melting pot on a round hole of an asbestos piece and heat gradually. Prevent ignition of rubber at this time, and in case it becomes liquid, pay attention, to prevent splashing of the liquid.
- (2) If the rubber becomes a black mass by complete decomposition, put it in a heating furnace and heat at $550 \pm 25^\circ\text{C}$, and cool down and then weigh, and calculate the percentage of the ash content by the following formula:

$$\text{Ash content (\%)} = \frac{A_w}{S} \times 100$$

where, A_w : weight of ash content (gr)

S : weight of sample (gr)

6. Dust Ingredient

6.1 Scope of Application

Dust ingredient refers to the dust contained in rubber, and this specification specifies the dust ingredient analyzing method.

6.2 Testing Method

- (1) Weigh roughly 10gr of the sample, precisely up to 0.1gr, and cut into a long shape, and put it in a 250ml conical flask and add 150ml of rubber solvent. The rubber solvent refers to a solvent 130°C over the boiling point, with a compound such as xylene.
- (2) After adding 0.5gr of rubber peptizer, melt by heating to $125-130^\circ\text{C}$. The temperature is that of the inside of the flask, and it is desirable to shake, from time to time, to help the melting.
- (3) After melting (normally 2.5-3 hours), pour the solution on a standard body with a known weight. Use 44um of KS A 5101 (test sieves) as the standard body.
- (4) Clean the rubber inside the flask, with 20-30ml of warm industrial gasoline, three times, and pour on the standard body. Suction is allowed, if required.
- (5) Clean the standard body until the rubber is removed, since dust is transferred to the standard body through industrial gasoline.
- (6) Desiccate the standard body and dust at 100°C and weigh the dust precisely up to 0.1mg.
- (7) Test twice or more, and obtain the arithmetic average, and calculate the amount of dust, by the following formula:

$$\text{Dust (\%)} = \frac{D_w}{S} \times 100$$

where, Dw: weight of dust (gr)
 S: weight of sample (gr)

7. Copper (Cu)

7.1 Scope of Application

This specification specifies the non-organic copper analyzing method contained in natural rubber.

7.2 Analyzing Method

7.3.1 Equipment

- (1) Light-absorbing spectrometer: Capable of measuring at 435nm.

7.3.2 Testing chemical and material

- (1) Carbon tetrachloride
- (2) Copper sulfate solution A (1mℓ = 0.1mg Cu): After dissolving 0.393gr of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in water, add 3mℓ of sulfuric acid, and dilute to 1 ℓ . This solution is usable for 1 month.
- (3) Copper sulfate standard solution B (1mℓ = 0.01mg Cu): Take exactly 10mℓ of the standard solution and dilute to 100mℓ. This solution should be used as soon as possible after preparation.
- (4) Nitric acid (1:2)
- (5) Zinc Di bengyl dithio carbamate solution: Dissolve 0.1gr of zinc di bengyl di thio carbamate in 1 ℓ of carbon tetrachloride.

7.3.3 Preparation of measuring line

- (1) Take 0, 1, 2, 3 and 4mℓ of standard solution B and put them in a fluid separating filter, and add 5mℓ of nitric acid (1:2) to each flask, and dilute to 100mℓ.
- (2) Add 25mℓ of zinc dibengyl dithio carbamate solution. In case of using a 1cm cell, add 10mℓ
- (3) Perform the extraction operation in accordance with 7.1.4 and measure the light absorptivity of each. Use a solution with "0" of standard solution B as the comparing fluid.
- (4) Plot the relationship of the concentration and light absorptivity, and use it as the measuring line.

7.3.4 Operation

- (1) Wrap up to 10gr of the sample, with filter paper, and burn at $550 \pm 25^\circ\text{C}$ until carbon is removed. Burn the filter paper in same method and use it as the standard sample.
- (2) Add 10mℓ of nitric acid (1:2), and melt on a steam bath for 30 minutes.
- (3) Transfer to solution to a 100mℓ mass flask, cool down, and dilute with water, up to marking line.
- (4) Take 50mℓ, put it in a fluid separating filter, and dilute to 100mℓ.
- (5) Add 25mℓ of zinc bengyl dithio carbamate solution to this. In case of using a 1cm cell, add 10mℓ.

- (6) After adding 10mℓ of carbon tetrachloride to this, shake vigorously for 1 minute and extract. Repeat this operation twice.
- (7) Subsequently, move to the absorbing cell if copper is extracted, and measure the light absorbility at 435mm, and read the amount of copper at the measuring line.

$$\text{Cu (\%)} = \frac{A}{S} \times 100$$

where, A: amount of copper read in light absorbility (gr)

S: amount of sample (gr)

7.4 Colorimetric Titration Method

7.4.1 Summary

This specification specifies the quantitative analyzing method of copper contained in rubber, using colorimetric method.

7.4.2 Testing chemical

- (1) Sulfuric acid
- (2) Smoke emitting nitric acid
- (3) Peroxide hydrogen solution (30%)
- (4) Ammonia solution
- (5) Arabia rubber solution (5%)
- (6) Dithio carbamate natrium acid (0.1%)
- (7) Sulfuric acid standard solution (1mℓ = 0.00001gr Cu): Put 0.3928gr of sulfuric acid in a mass flask and dilute with 250mℓ of distilled water. Put 25mℓ of this solution in a 1 ℓ mass flask using a pipette and dilute with water, up to the marking line.

7.4.3 Operation

- (1) Cut the sample into a thin film, and take 5gr of the testing chemical and put it in a 500mℓ kjeldahl flask, and add 20mℓ of sulfuric acid and one or two glass beads with care. Place the flask on a tripod, and heat it gradually, until the solution mixture boils.
- (2) Gradually boil until all organic matter is carbonized and decomposed completely, and add up to 5mℓ of sulfuric acid while maintaining the solution mixture at 20mℓ, since sulfuric acid is consumed in oxidization (normally, 30 minutes or more of boiling is required).
- (3) Cool down when carbonization is completed, and heat 5mℓ of smoke emitting nitric acid, little by little, with care. Discontinue addition when the reaction becomes violent. Shake the contents of the flask and wait until the reaction subsides and then, continue the addition.
- (4) Heat the solution mixture with a small flame until the smoking of brown fumes stops, and strongly boil for few minutes, and cool it down. Repeat this operation until the decrease of color, discontinues, for 2 rounds of consecutive nitric acid treatment.
- (5) Dilute the contents of the flask with 100mℓ of distilled water while stirring. Boil this solution until anhydrous sulfuric acid gas is emitted vigorously. Through this, nitrosil sulfuric acid is

hydrolyzed and nitrogen oxide is extracted. If the solution looks yellow, treat the solution as follows since it means existence of iron or non-decomposed organic matter. Add 5mℓ of hydrogen peroxide solution (30%), with care, and gradually heat the solution mixture until anhydrous sulfuric acid gas is emitted, and boil vigorously for 2 minutes, and cool down.

- (6) Repeat this operation until the decrease of color, discontinues, when treated with hydrogen peroxide solution, twice, successively. Dilute the content of the flask with distilled water and mix well while stirring. If the solution contains insoluble ingredients, heat to a boil and filter with class 1 filter paper, while it is still warm. Clean the filter paper with distilled water, and dilute the 250mℓ mass flask up to the marking line, and mix well.

If there is a lot of copper and manganese, divide and measure the solution written above.

- (7) Take exactly 25mℓ of the above solution and put it into a triangular flask or beaker, and add ammonia solution to make it alkali. Heat and boil after adding 1-2mℓ of ammonia solution again.
- (8) Place it on a steam bath until hydrated iron is coagulated and precipitated completely, and filter it in a 100mℓ nessler tube using class 1 filter paper. Clean the filter paper two or three times with a little, warm distilled water.
- (9) Successively add 21mℓ of arabia rubber solution, 10mℓ of ammonia solution, and 10mℓ of diethyl dithio carbonyl acid sodium solution into the solution in the nessler tube as the protective colloid.
- (10) Dilute up to the marking line with distilled water and mix well. Take the base testing solution prepared in the same operation, up to the amount of the sample in the nessler tube, and add the same amount of the same testing chemical, and dilute to 90mℓ and mix well.
- (11) Add the copper sulfate standard solution to this testing nessler tube, using a burette until the color becomes the same as that of the sample diluted with the same amount of this.
- (12) Calculate the copper content by the following formula:

$$\text{Cu (\%)} = \frac{V_c \times 0.00001}{W} \times 100$$

where, V_c : amount of copper sulfate standard solution used (mℓ)

W : sampling amount (gr)

8. Manganese (Mn)

8.1 Scope of Application

This specification specifies the analysis of manganese content contained in rubber.

8.2 Analyzing Method

Mn analyzing method of rubber should conform to colorimetric method, light absorbing spectrometer method, and colorimetric titration..

8.3 Colorimetric Method

8.3.1 Summary

After reducing to ashes of sample, melt, dissolve and colorize the ash content, and analyze by colorimetric method.

8.3.2 Testing fluid

- (1) Sulfuric acid kalium
- (2) H_2SO_4
- (3) Phosphoric acid
- (4) Iodine acid

8.3.3 Operation

- (1) Weigh roughly 10g of the sample and put in a porcelain melting pot, and reduce to ashes by heat decomposing, gradually.
- (2) Add 5-15gr of acid kalium sulfate to the lime and melt until boiling is completed.
- (3) Burn carbon completely by heating again, cool down, and melt in 80ml of 5% sulfuric acid, then filter, and add 5ml of phosphoric acid and 0.5gr of iodine acid, and heat until colorized.
- (4) Subsequently, boil for 15 minutes and cool down, and move it to a 100ml mass flask, and dilute with water, up to the marking line.
- (5) Colorimetry coloring fluid with the standard solution using a nessler tube or photospectrometer, and calculate by the following formula:

$$\text{Mn (\%)} = \frac{\text{analyzed amount of Mn}}{\text{sample amount}} \times 100$$

8.3.4 Reparation of standard solution

Dilute 0.05N permanganese acid kalium solution with thin acidic distilled water, thus making 0.02mg of manganese per 1ml, and add periodine acid to this solution, and boil and cool down.

8.4 Light Absorbing Photometer Method

8.4.1 Summary

This method is the weight analysis of Mn contained in rubber using the light absorbing photometer method.

8.4.2 Device

Light absorbing photometer: Tester capable of adjusting 5.25mm and using a 1-5cm cell.

8.4.3 Testing chemical

- (1) Manganese sulfate standard solution AC 1ml = (mg Mn): Melt 0.77gr of manganese sulfate in water, and add 2ml of sulfuric acid and dilute to 250ml. This solution should be stable for at least 1 month.
- (2) Manganese sulfate standard solution B (1ml = 0.02 mg Mn): Take 10ml of standard solution A, and move it to a 500ml mass flask, and dilute it with water.
- (3) Orthophosphoric acid

- (4) Potassium hydrogen sulfate (KHSO_4)
- (5) Potassium periodate (KIO_4)
- (6) Potassium permanganate rinse solution (0.03 gr/ℓ): Melt 0.03gr of potassium permanganate (KMnO_4) in water and make 1 ℓ.
- (7) Sulfuric acid (1:19)

8.4.4 Preparation of measuring line

- (1) Take the appropriate amount of standard solution B, in a 0-20mℓ range, add 25mℓ of water, and add 20mℓ of sulfuric acid (1:19), then add 0.3g of KIO_4 , and heat each solution according to 8.4.5 (3).
- (2) Cool down and move the solution to a 50mℓ flask, and dilute. Measure the light absorbability of each, at 525nm. Use a solution where 0mℓ of the standard solution is added, as the base solution.
- (3) Plot the concentration and light absorbability, as the measuring line.

8.4.5 Operation

- (1) After wrapping 10-12g of the sample with paper, having no ash, place it on top of a porcelain melting pot containing 5gr of KHSO_4 . Reduce to ashes this at $550 \pm 25^\circ\text{C}$ until there is no carbon. Prepare the standard sample without any of the sample by the same method.
- (2) Add 20mℓ of H_2SO_4 (1:19) and heat for 30 minutes on a steam bath. After heating, filter in a 150mℓ beaker, and clean the melting pot with water, detergent fluid, and filtered fluid.
- (3) Add 3mℓ of H_3PO_3 and 0.3gr of KIO_4 , and heat with care. Evaporate until it becomes 50mℓ. Roughly +5 minutes of time is required.
- (4) Move the solution to a 50mℓ volumetric flask, and cool down to the normal temperature, and dilute with water up to the marking line.
- (5) Clean the cell with KMnO_4 solution. Clean again with water, and finally, clean with the testing solution.
- (6) Add the testing solution and measure the light absorbability at around 525nm.
- (7) Read the amount of Mn at the measuring line and calculate by the following formula:

$$\text{Mn (\%)} = \frac{A}{S} \times 100$$

where, A: amount of Mn read at measuring line (gr)

S: amount of sample taken (gr)

8.5 Colorimetric Titration Method

8.5.1 Decomposition of organic matter

Shall conform to 7.2.2 (1) through (6).

8.5.2 Quantitative measurement

- (1) Weigh an appropriate amount of the sample (remnants from 250mℓ used in quantitative measurement of copper) and form the decomposition sample solution and move it to a 250mℓ beaker.

Vaporize until it becomes 75mℓ. (If the contents of Mn is very little, vaporize to compare with the solution after oxide-decomposition using a separate sample.)

- (2) In case iron, discolorize by adding 10mℓ of phosphoric acid.
- (3) After adding 0.5gr of iodine kalium, boil the solution and the cool down a little, and add 0.1gr of iodine kalium again, and boil again, and heat the beaker on a double steam boiler for 15 minutes if a thick color appears. Add iodine kalium again if the reaction is not sufficient, at this time. Subsequently, heat the sample on a double steam boiler for 15 minutes and cool down. If color is thick when colorimeter, put it in a 25mℓ mass flask and dilute with distilled water up to the marking line.
- (4) Put an appropriate amount of this, into a 100mℓ nessler tube, and dilute with distilled water up to the marking line.
- (5) Take as much of the sample as possible from the base testing solution treated in same way as the sample, and put into a 100mℓ nessler tube, and dilute with distilled water up to the marking line.
- (6) Add the manganese standard solution to the nessler tube of the base test using a burette, and put the same amount in a 100mℓ nessler tube, and dilute with distilled water up to the marking line.
- (7) Titrate until the color becomes the same as the sample when diluted by adding the manganese standard solution to the nessler tube of the base test using a burette. Put the contents of the nessler tube in a small beaker and stir. However, do not shake the tube with the cap or use a finger as a cap.
- (8) Calculate Mn by the following formula:

$$\text{Mn (\%)} = \frac{V \times 0.0001}{W} \times 100$$

Where, V: amont of permanganese kalium standard solution used (mℓ)

W: weight of sample (gr)

9. Iron (Fe)

9.1 Summary

This method specifies to the quantitative analysis of iron contained in natural rubber by the colorimetric method.

9.2 Sampling

Shall conform to 3.2.

9.3 Device

Photoelectric photometer: Use a spectrophotometer or filter photometer with a 1-3cm absorbing cell length capable of measuring the absorbility at 510mm.

9.4 Testing Chemical

- (1) Buffer solution: Dissolve 164gr of sodium anhydrous in water, and add 28.5ml of acetic acid, and dilute with water to 500ml.
- (2) Hcl
- (3) Hydroxylamine hydro chloride solution (100g/ l): After dissolving 10gr of hydroxylamine hydrochloride in water, make it 100ml.
- (4) Fe standard solution A (1ml = 0.1mg Fe): Add 3ml of hydrochloric acid to a certain amount of distilled water, and dissolve 0.7021gr of ferrous ammonium sulfate in this, and make it 1 l . This solution should be usable for at least one month.
- (5) Fe standard solution B (1ml = 0.1mg Fe): Take 10ml of the Fe standard solution and dilute it to 100ml. This solution should be prepared for every test.
- (6) 1.10 phenathroline solution (1g/ l): Dissolve 0.5gr of 1.10 phenathroline monohydrate in hot water and dilute to 500ml.

9.5 Preparation of measuring line

- (1) Take and put 0, 5, 15 and 20ml of the Fe standard solution B in a 50ml volumetric flask, and add 1ml of Hcl to each.
- (2) Treat each solution according to 9.5 (2) and (3), and measure the light absorbility and prepare the measuring line.

9.6 Operation

- (1) Measure 10-12gr of the sample, up to 1mg, and put in a melting pot and reduce to ashes. Wrap with filter paper having no lime and, reduce to ashes at $525 \pm 25^{\circ}\text{C}$ until there is no carbon.
- (2) Reduce to ashes filter paper as the standard sample by the same method.
- (3) Add 5ml of hydrochloric acid and 5ml of water, and decompose on a steam plate for 30 to 60 minutes. If the solution looks thick and yellow, it is assumed that Fe exists.
- (4) Add 5ml of hydrochloric acid and decompose for 30 minutes or more. Filter the solution in a 50ml volumetric flask and dilute with water up to the marking line.
- (5) Add 2ml or less of hydrochloric acid to a 50ml volumetric flask, and add 10ml of the buffer solution and 1ml of the hydroxyl amine solution. Add 10ml of 1.10 phenathroline, and fill with water up to the marking line, and put aside for 15 minutes, and use it as the reference solution.
- (6) After setting at around 510nm, use the reference solution, and measure the light absorbility of each sample.
- (7) After reading the light absorbility of each sample, read the amount of Fe, using the measuring line prepared in 9.5, and calculate by the following formula:

$$\text{Fe (\%)} = \frac{A - B}{S} \times 100$$

where, A: Fe amount of sample read in light absorbility (gr)

B: Fe amount of filter paper standard sample

S: amount of sample taken

10. Nitrogen (N)

10.1 Summary

- (1) This method regulates the comprehensive nitrogen analysis method contained in natural or synthetic rubber.
- (2) This method can be applied to raw polymer and sulfur-added rubber.
- (3) Method A is the macro operation and method B is the semimacro operation.

10.2 Device

- (1) Kjeldahl degestion and distillation equipment
- (2) Method A: Macro kjeldahl flask has a 800mℓ capacity and is connected to an electric heating device.
- (3) Method B: Micro kjeldahl flask and device should conform to ASTM E 147 (30-100cm³ in capacity).

10.3 Reagents

- (1) Boric acid solution: Dissolve 40g of boric acid in warm water and dilute it with 1 ℓ of water after cooling down to normal temperature.
- (2) Catalyst compound: Mix K₂SO₄, CuSO₄•5H₂O and selenium powder in the ratio of 30:4:1 in weight or dissolve 110g of K₂SO₄, 14.7g of CuSO₄•5H₂O and 3.7g of selenium in 600mℓ of heated sulfuric acid.
- (3) Indicator (methyl red-methylene blue): Dissolve 0.1g of methyl reder and 0.05g of methylene blue in alcohol making total volume of 100mℓ.
- (4) Indicator (methyl red-bromcresol green): Dissolve 0.08g of methyl reder and 0.4g of bromcresol making total volume of 100mℓ.
- (5) Standard NaOH solution: 0.02N without carbonate
- (6) Standard NaOH solution: 0.1N without carbonate
- (7) NaOH (40%): Dissolve 400g of NaOH in 600mℓ of distilled water
- (8) Sulfuric acid
- (9) Sulfuric acid standard solution: 0.02N without carbonate
- (10) Sulfuric acid standard solution: 0.1N without carbonate
- (11) Zinc: Round bead shape

10.4 Method A (Macro method)

- (1) Cut out 2gr of the sample, measuring up to 1mg, and put in a kjeldahl flask. Add 13gr of the catalyst compound, and add 60mℓ of sulfuric acid or 65mℓ of catalyst sulfuric acid solution. Shake well to insure mixing of the compounds. Heat gradually until the solution becomes transparent, and heat for an hour, continuously.