

KES

Testing Method of Component and Element for Natural Rubber

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1. Scope of Application

This standard shall specify quantitative analysis method of inorganic and organic substance contained in natural rubber.

2. Concerned Component of Analysis

- (1) Inorganic substance : Copper, manganese, iron, nitrogen, zinc, sulfur, lead, carbon black
- (2) Organic substance : Rubber hydrocarbon, synthesis, monomer, and organic component
- (3) Others : Volatile component, ash component, impure component, Acetone extract, chloroform extract, Acetone-Chloroform extract, unsaturated rate, Grade, Alcoholic KOH extract

3. Sample

3.1 Terminology

- (1) Lot : Bundle of Bale classified with some common characteristics being able to be distinguished clearly.
- (2) Sample : Sample extracted from lot to use in test

3.2 Extracting method of sample

Collect sample by a little amount from respective part by dividing equally in 16 or 32 parts.

4. Volatile Component

4.1 Scope of application

This standard shall be applied to measurement of water contents contained in sample.
But, other substances volatilized at 100 °C.

4.2 Treatment

- (1) Measure sample down to 0.1 gr precisely (A) and then measure rubber made uniform by passing it through roller down to 0.1 gr precisely again. (B).
- (2) Collect 2 samples of which mass is approximate 10 gr and measure down to 1 mg (C). When it doesn't measure this sample soon, keep by wrapping with polyethylene film to avoid loss of volatile component.
- (3) Pass each sample through cool roller fixed tightly twice and make it sheet of which thickness is less than 2 mm or cut it into tiny particles of which maximum dimension is less than 2 mm and dry it at 100 ± 5 °C for an hour and then measure and measure at every 30 minutes as drying continuously and measure weight after drying until decrease of becomes less than 1mg. (D)
- (4) Volatile component (%) is calculated from following equation.

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

5. Ash Component

5.1 Scope of application

This standard shall be applied to the whole contents analysis method of inorganic annex contained in natural rubber.

5.2 Treatment

- (1) Measure 5 gr of sample down to 5 mg precisely and put it in crucible of 50 mg knowing weight by heating in advance and place crucible at circular hole of asbestos plate and heat it slowly.

At the moment, make it do not fire and in case of liquid phase, be careful so that liquid doesn't bounce out of.
- (2) When rubber becomes black lump as decomposed completely, make it ash completely at temperature of 550 ± 25 °C by putting in heating furnace and measure after cooling and calculate percentage of ash component according to following equation.

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

Where, A_w : Weight of ash component (gr)

S : Weight of sample (gr)

6. Impure Component

6.1 Scope of application

What is impure component says dust contained in rubber and this standard shall specify analysis method of impure component contents.

6.2 Testing method

- (1) Weigh 10 gr of reagent down to 0.1 gr and cut it long and put it in the conical flask of 250 ml and apply 150 ml of rubber solvent.

Here, rubber solvent means solvent of which boiling point is higher than 130 °C and as an example, there are composite Xylene and etc.

- (2) Apply 0.5 gr of rubber peptizer and then melt it by heating in 125 ~ 130 °C.

At the moment, temperature means temperature of inside flask and it may be good to shake it so that melting is taken well.

- (3) When melting has been completed (Usually 2.5 ~ 3 hours), pour solution on standard strainer of known weight. The standard strainer is used as 44 μm of KS A 5101 (Standard strainer).

- (4) Pour rubber in the flask on the standard strainer by washing with 20 ~ 30 ml of warm industrial gasoline 3 times.

- (5) Since impure component is moved to the standard strainer with industrial gasoline, wash the standard strainer until rubber disappears.

- (6) Thereafter dry the standard strainer and impure component until they become containing amount and weigh weight of impure component down to 0.1 mg precisely.

- (7) Take arithmetic mean after testing more than 2 times and calculate containing amount

of impure component according to following equation.

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

Where, DW : Weight of impure component (gr)

S : Weight of sample (gr)

7. Copper (Cu)

7.1 Scope of application

This standard shall be applied to analysis method for inorganic copper contained in natural rubber.

7.2 Analysis method

Copper analysis in natural rubber shall conform to Referee Colorimetric method, titration colorimetric method.

7.3 Referee Colorimetric method

7.3.1 Equipments

(1) Extinction photometric scale : It is to be able to measure at 435 mm.

7.3.2 Reagent and material

(1) Carbon tetrachloride

(2) Copper sulfate solution A (1 mL = 0.1 mg Cu) : Melt 0.393 gr of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in water and then dilute with 1 L after adding 3 mL of sulfuric acid.

This solution shall be useful for a month.

(3) Copper Sulfate standard solution B (1 mL = 0.01 mg Cu) : Collect standard solution A with 10 mL precisely and dilute with 100 mL.

This solution should be used as soon as possible after preparation.

(4) Nitric acid (1 : 2)

(5) Zinc Di Bengyl dithio carbamate solution : Melt 0.1 gr of Zinc DiBengyl dithio Carbamate in 1 L of carbon tetrachloride.

7.3.3 Estimating line preparation

(1) Collect 0, 1, 2, and 3, 4 mL of standard solution B and put them in separating liquid filter and put nitric acid (1 : 2) in respective flask by 5 mL and dilute them to approximate 100 mL.

(2) Apply 25 mL of Zinc Di Bengyl dithio Carbamate solution.

At the moment, apply 10 mL at using Cell of 1 cm.

(3) Precede extraction treatment by 7.1.4 and measure extinction rate of each.

At the moment, use solution that standard solution B is "O" as comparative solution.

(4) Take as estimating line by plotting relation between density and extinction rate.

7.3.4 Treatment

(1) After wrapping approximate 10 gr of sample with filtering paper, make it ash until carbon disappears at 550 ± 25 °C.

By means of the same method, use it empty sample to make filtering paper ash only.

(2) Apply 10 mL of nitric acid (1 : 2) and melt it in steam bath phase for approximate 30 minutes.

(3) Move solution to mass flask of 100 mL and cool it and then dilute with water up to marked line.

(4) Collect 50 mL separately and put it in separating liquid filter and dilute to approximate 100 mL.

(5) Apply 25 mL of zinc DiBengyl dithio Carbamate solution in filter.

At the moment, apply 10 mL at using Cell of 1 cm.

(6) Apply 10 mL of carbon tetrachloride in here and then extract through shaking strongly for approximate 1 minute.

Repeat this treatment 2 times approximately.

(7) When copper is extracted, move it absorbing Cell and measure extinction rate at 435 nm and then read amount of copper in estimating line.

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

Where, A : Amount of copper read from extinction rate (gr)

S : Amount of sample (gr)

7.4 Titration colorimetric method

7.4.1 Introduction

This standard shall be applied to method to analyze amount of copper contained in rubber quantitatively based on colorimetric method.

7.4.2 Reagent

- (1) Sulfuric acid
- (2) Fuming nitric acid
- (3) Hydrogen peroxide (30 %)
- (4) Ammonia water
- (5) Arabia rubber solution (5 %)
- (6) Di-ethyl dithio carbamate solution (0.1 %)
- (7) Copper sulfuric acid standard solution (1 ml = 0.00001 gr Cu) : Put 0.3928 gr of copper sulfuric acid in mass flask and melt it in 250 ml of distilled water.
Collect 25 ml of this solution with pipette in mass flask of 1 l and make it thin up to marked line with water.

7.4.3 Treatment

- (1) Cut sample as thin film phase and thereafter collect 5 gr of reagent adequately and move it to kjildahl flask of 500 ml and add 20 ml of sulfuric acid and 1 ~ 2 of glass gem in that and place flask on three-legged platform and heat it slowly until it boils.
- (2) Boil it slowly and continuously until organic material has been carbonized and separated completely and keep amount of sulfuric acid with approximate 20 ml as sulfuric acid is consumed by oxide and add 5 ml of sulfuric acid again as necessary.
(It is needed to boiling more than 30 minutes generally.)

- (3) When carbonization has completed, cool it and heat fuming nitric acid of 5 ml by a little amount carefully and when intense reaction appears, stop adding and wait for reaction to calm down by shaking contents of flask and continue addition.
- (4) Heat composite solution with a small flame until brown smog doesn't come out and boil it for several minutes hard and then cool it.
- Repeat this treatment until decrease of color doesn't appear with 2 continuous nitride treatment.
- (5) Dilute contents of flask with 100 ml of distilled water as shaking
- Boil this solution until anhydrous sulfuric acid comes out strongly and then cool it.
- Nitrosyl sulfuric acid is hydrolyzed by this and extracts nitric oxide.
- In case that solution shows yellow, treat solution like following since it shows existence of iron or non-decomposed organic material. That is, add 5 ml of peroxide (30 %) carefully and heat composite solution until anhydrous sulfuric acid comes out and then boil it strongly and cool it.
- (6) Repeat this treatment until decrease of color doesn't appear though it takes 2 continuous treatments by peroxide.
- As shaking, dilute content of flask with distilled water and mix sufficiently.
- If solution contains non-decomposed material, heat it until it boils and then filter it by using filtering paper of 1 type at warm state.
- Wash filtering paper with heated distilled water and dilute in mass flask of 250 ml up to marked line and mix well.
- When copper and manganese contains, quantify solution written above by several equal parts.
- (7) Collect 250 ml of above solution in conic flask or beaker precisely and put it in and then make it alkalinity by adding ammonia.
- Add 1 ~ 2 ml of extreme ammonia and make it boil by heating.
- (8) Place it on steam double boiling bath until iron hydroxide has solidified and deposited

completely and filter it in nestler pipe of 100 ml by using filtering paper of 1 type and wash filtering paper with a small amount of warm distilled water 2 ~ 3 times.

- (9) Add 21 ml of Arabia rubber solution, 10 ml of ammonia and 10 ml of diethyl dithio carbamate sodium solution to solution of nestler pipe as protective colloid.
- (10) Dilute with distilled water up to marked line and mix well and then collect background testing solution taken with same treatment with nestler pipe as much as sample and add same reagent with same amount and dilute with approximate 90ml and mix well.
- (11) Add copper sulfate acid standard solution to this testing nestler pipe with burette and titrate with amount same to that until color same to one of diluted sample appears.
- (12) Calculate contain of copper with following equation.

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

Where, V_c : Used amount of copper sulfuric acid standard solution (ml)

W : Collected amount of sample (gr)

8. Manganese

8.1 Scope of application

This standard shall specify analysis of content of manganese contained in rubber.

8.2 Analysis method

Mn analysis in rubber shall conform to colorimetric method, extinction photometric method, and colorimetric titration method.

8.3 Colorimetric method

8.3.1 Introduction

Make sample ash and color after melting and solution of ash component and then analyze with colorimetric method.

8.3.2 Reagent

- (1) Potassium sulfuric acid
- (2) H_2SO_4
- (3) Phosphoric acid
- (4) Periodate acid

8.3.3 Treatment

- (1) Measure 10 g of sample and put it in ceramic furnace and make it ash through decomposing by heating slowly.
- (2) Add 5 ~ 15 gr of acid potassium sulfate to ash component and melt it until boiling ends.
- (3) Burn carbon completely by heating again and cool it and then melt it in 80 ml of 5 % sulfuric acid and filter and heat it colors by adding 5 ml of 85 % phosphoric acid and 0.5 gr of periodate acid.
- (4) Then, make it boil continuously for 15 minutes and cool it and move it to mass flask of 100 ml and dilute with water up to marked line.
- (5) Take colored solution colorimetric measurement by using nestler pipe or photoelectricity spectrum photometric scale and then calculate as following equation.

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

8.3.4 Preparation of standard solution

Dilute 0.05 N potassium permanganese acid solution with distilled water of thin sulfuric acid and add a small amount of periodate acid prepared so as to contain 0.02 mg of manganese within approximate 1 ml and make it boil and cool and prepare precisely.

8.4 Extinction photometric method

8.4.1 Introduction

This method is method to analyze amount of Mn contained in rubber quantitatively

by extinction photometric method.

8.4.2 Equipments

Extinction photometric scale : It is to be able to use 1 ~ 5 cm Cell as tester able to adjust 5.25 mℓ.

8.4.3 Reagent

- (1) Manganese Sulfate standard solution A (1 mℓ = 0.02 mg Mn)

Melt 0.77 gr of manganese sulfate in water and then add 2 mℓ of sulfuric acid and dilute with water of 250 mℓ.

This solution is stable for a month at least

- (2) Collect 10 mℓ of manganese sulfate standard solution B (1 mℓ = 0.02 mg Mn)

standard solution A and move it to mass flask of 500 mℓ and dilute with water.

This solution should be used immediately.

- (3) Orthophosphoric acid

- (4) Potassium Hydrogen Sulfate (KHSO_4)

- (5) Potassium Periodate (KIO_4)

- (6) Potassium Permanganate Rinse Solution (0.03 gr / ℓ)

Make it 1 ℓ by melting 0.03 gr of Potassium Permanganate (KmnO_4) in water.

- (7) Sulfuric acid (1 : 19)

8.4.4 Estimating line preparation

- (1) Collect sufficient amount of standard solution B in range of 0 ~ 20 mℓ respectively and

add 25 mℓ of water and then add 20 mℓ of sulfuric acid (1 : 19) and add 0.3 gr of KIO_4 and ten heats each solution by 8.4.5 (3) clause.

- (2) Cool solution and move it to mass flask of 50 mℓ and dilute.

Measure extinction rate of each at 525 mm. At the moment, make it added by standard solution 0 mℓ as standard solution.

- (3) Plot density and extinction rate and prepare with estimating line.

8.4.5 Treatment

- (1) After wrapping 10 ~ 12 gr of sample with filtering paper containing no ash component, place it on ceramic furnace in which 5 gr of KHSO_4 contains.

Make it ash at 550 ± 25 °C until there is no carbon.

Prepare empty sample without sample through same method.

- (2) Add 20 ml of H_2SO_4 (1 : 19) and heat it for approximate 30 minutes in steam bath.

After heat, filter it in beaker of 150 ml and wash furnace with water and then add washing solution and filtering solution.

- (3) Add 3 ml of H_3PO_4 and add 0.3 gr of KIO_4 and evaporate it so that it becomes approximate 50 ml as heating carefully. At the moment, time requires approximate +5 minutes.

- (4) Move solution to volumetric flask of 50 ml and cool down to environmental temperature and then dilute up to marked line with water.

- (5) Wash Cell with KmnO_4 solution and wash with water again and then wash with testing solution finally.

- (6) Put testing solution in Cell and measure extinction rate around 525 nm.

At the moment, use empty sample as reference solution

- (7) Calculate amount of Mn according to following equation from estimating line.

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

Where, A : Amount of Mn read from estimating line (gr)

S : Amount of collected sample (gr)

8.5 Colorimetric titration method

8.5.1 Decomposition of organic material

It follows from clause (1) to (6) clause of 7.2.2.

8.5.2 Quantification

- (1) Move sufficient amount of sample (Remaining amount used in copper measurement from 250 ml) from decomposition sample solution by measuring and evaporate until it

becomes 75 mL. (When content of Mn is very few, evaporate it in order to compare the last solution after oxidizing and decomposing by using additional sample.)

- (2) In case that there is iron component, discolor it by adding 10 mL of phosphoric acid.
- (3) Add 0.5 gr of potassium iodinate and then boil solution and cool slightly and then add approximate 0.1 gr of potassium iodinate and boil again and when it shows most thick color, heat beaker on steam double boiling bath for 15 minutes
When reaction is incomplete, add potassium iodinate again.
In case that color is too thick at the time of colorimeter, put in mass flask of 15 mL slowly and dilute up to marked line with distilled water.
- (4) Collect sufficient amount in nestler pipe of 100 mL from that and dilute up to marked line with distilled water.
- (5) Collect amount same as sample from background testing solution treated equally with sample in other nestler pipe of 100 mL and make distilled water close to marked line and dilute with water.
- (6) Add manganese standard solution to nestler pipe of background test with a burette and collect in 100 mL nestler pipe of same amount and dilute through adding distilled water up to marked line.
- (7) Add manganese standard solution to nestler pipe of background test with a burette and titrate until it becomes color same as one at the time of diluting with same amount. At the moment, put content of nestler pipe in small beaker and shake. But, must not shake in pipe with cork or shake with finger corked.
- (8) Mn is calculated according to following equation.

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

Where, V : Used amount of potassium permanganate standard solution (mL)

W : Mass of sample (gr)

9. Iron

9.1 Introduction

This method shall be applied to method of quantitative analysis of iron component contained in natural rubber through colorimetric method.

9.2 Collection of sample

Based on 3.2

9.3 Equipment

Photoelectric Photometer : use spectrophotometer or filter photometer able to measure extinction rate at 510 nm with length of extinction Cell 1 ~ 3 cm.

9.4 Reagent

(1) Buffer solution : Melt 164 gr of anhydrous sodium in water and then add 28.5 mL of Acetic Acid and make it 500 mL with water.

(2) HCL

(3) Hydroxylamine Hydro Chloride solution (100 g / L)

Melt 10 gr of Hydroxylamine Hydro Chloride in water and then make it 100 mL.

(4) Fe standard solution A (1 mL = 0.1 mg Fe)

Add 3 mL of chloride acid to specific amount of distilled water and melt 0.7021 gr of Ferrous Ammonium Sulfate in here and then make it 1 L.

This solution is usable for a month at least.

(5) Fe standard solution B (1 mL = 0.01 mg Fe)

Collect 10 mL of Fe standard solution A and dilute with 100 mL.

This solution should use by preparing at every test.

(6) 1.10 Phenathroline solution (1 g / L)

Melt 0.5 gr of 1.10 Phenathroline Monno Hydrate in hot water and dilute with 500 mL.

9.5 Preparation of estimating line

(1) Collect and put Fe standard solution B in volume flask of 50 mL by 0, 5, 10, 15, 20 mL and then apply each 1 mL of HCl.

(2) Treat each solution according to 9.6(3) ~ 9.6(7) and prepare estimating line through

measuring extinction rate.

9.6 Treatment

- (1) Measure 10 ~ 12 gr of sample down to 1 mg and put it in furnace and make it ash.

At the moment, wrap it with filter paper of no ash and make it ash at 525 ± 25 °C until carbon disappears.

- (2) Make filter paper ash as empty sample with same method.

- (3) Add 5 ml of chloride acid and add 5 ml of water and then decompose on steam plate from 30 minutes to 60 minutes approximately.

If solution shows thick yellow, it is thought that Fe exists.

- (4) Add 5 ml of chloride acid and decompose for approximate 30 minutes more.

- (5) Add less than 2 ml of chloride acid in volume flask of 50 ml and add 1 ml of Buffer Solution 10 ml Hydroxyl Amine solution.

Add 10 ml of 1.10 Phenanthroline and fill up to marked line with water and then leave for approximate 15 minutes and make it as Reference solution.

- (6) Get setting by using Reference solution around 510 nm and thereafter measure extinction rate of each sample.

- (7) Read extinction rate of each sample and then read amount of Fe by estimating line prepared at 9.5 and calculate according to following equation.

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

Where, A : Fe amount of sample read from extinction rate (gr)

B : Fe amount of Filter Paper empty sample (gr)

S : Sample collected amount

10. Nitrogen

10.1 Introduction

- (1) This method shall specify analyzing method of synthesis nitrogen in natural or