

JIS

JAPANESE
INDUSTRIAL
STANDARD

Translated and Published by
Japanese Standards Association

☞ JIS K 1475 : 1996

Poly aluminium chloride for water works

ICS 71. 060. 50

Descriptors : aluminium inorganic compounds, chlorides, waterworks, water supply

Reference number : JIS K 1475 : 1996 (E)

K 1475 : 1996

This translation has been made based on the original Japanese Industrial Standard revised by the Minister of International Trade and Industry through deliberations at Japanese Industrial Standards Committee in accordance with the Industrial Standardization Law:

Date of Establishment: 1978-10-01

Date of Revision: 1996-12-20

Date of Public Notice in Official Gazette: 1996-12-20

Investigated by: Japanese Industrial Standards Committee
Divisional Council on Chemical Products

JIS K 1475:1996, First English edition published in 1997-07

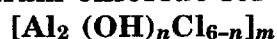
Translated and published by: Japanese Standards Association
4-1-24, Akasaka, Minato-ku, Tokyo, 107 JAPAN

In the event of any doubts arising as to the contents,
the original JIS is to be the final authority.

© JSA 1997

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from the publisher.

Printed in Japan

Poly aluminium chloride for water works

1 Scope This Japanese Industrial Standard specifies poly aluminium chloride for water works.

Remarks: The standards cited in this Standard are listed in Attached Table 1.

2 Quality The quality, when being tested according to 4, shall conform to the requirements shown in Table 1.

The judgement method of flocculation property shall be shown in Informative reference.

Table 1 Quality

Appearance		Colorless to clear light yellowish brown liquid
Specific gravity (20 °C)		1.19 min.
Aluminium oxide (Al ₂ O ₃)	wt%	10.0 to 11.0
Basicity	wt%	45 to 65
pH value (10 g/l solution)		3.5 to 5.0
Sulfate ion (SO ₄ ²⁻)	wt%	3.5 max.
Ammoniacal nitrogen (N)	wt ppm	100 max.
Arsenic (As)	wt ppm	1.0 max.
Iron (Fe)	wt ppm	100 max.
Manganese (Mn)	wt ppm	15 max.
Cadmium (Cd)	wt ppm	1.0 max.
Lead (Pb)	wt ppm	5 max.
Mercury (Hg)	wt ppm	0.1 max.
Chromium (Cr)	wt ppm	5 max.

3 Sampling method Sampling shall be carried out so as to make the sample represent whole body according to rational method based on the agreement between the parties concerned with delivery.

4 Test method

4.1 General matters General matters applicable commonly to tests shall follow JIS K 0050, those to absorptiometry follow JIS K 0115, those to atomic emission spectrometry follow JIS K 0116, those to atomic absorption spectrometry follow JIS K 0121, and those to ion chromatography follow JIS K 0127.

The water for tests shall be A2 specified in 3 of JIS K 0557 or superior one, except when the test specifies the water to be used.

4.2 Specific gravity

(1) **Summary** Keep sample at 20 °C, and measure it using a specific gravity hydrometer.

(2) **Implements** Implements shall be as follows:

- (a) **Specific gravity hydrometer** No. 9 (effective scale range: 1.180 to 1.240) or No. 10 (effective scale range: 1.240 to 1.300) in a set composed of large-sized 19 hydrometers specified in JIS B 7525.
- (b) **Cylinder** Made of glass, having no distortion to give misreading scales on a hydrometer, and its size shall be spacious enough that when the hydrometer is floated in liquid, there is at least 1 cm clearance between outside of a hydrometer and inside wall or bottom of the cylinder.
- (c) **Stirring rod** Capable of stirring sufficiently liquid in order to make the liquid in a cylinder uniform.

(3) **Operations** Operations shall be carried out as follows:

- (a) Clean sufficiently the hydrometer and cylinder prior to use.
- (b) Place suitable quantity of sample in the cylinder, and keep its temperature at 20 °C.
- (c) After enough stirring with a stirring rod, hold the hydrometer by its upper end, and float it slowly in liquid so as not to bring bubbles on it.
- (d) When it gets standing, immerse it into the liquid by about 2 scales, and then let it be free.
- (e) After it gets standing, read the scale at the upper end of meniscus.
- (f) Repeat 2 or 3 times the procedure at (e), obtain averaged value of readings, and make it specific gravity of the liquid⁽¹⁾.

Note ⁽¹⁾ The discrepancy between the measurements given by 2 or 3 trials and the averaged value must be within the interval of one scale.

4.3 Aluminium oxide The determination of aluminium oxide shall follow either titrimetry or ICP atomic emission spectrometry.

4.3.1 Titrimetry

- (1) **Summary** Treat sample with nitric acid to make polymerized aluminium decompose into aluminium ion, add excessively dihydrogen disodium ethylenediaminetetraacetate, complete the formation of chelate, add xylenol orange indicator, carry out back titration with zinc solution, and obtain the content of aluminium oxide.
- (2) **Reagents** Reagents shall be as follows:
 - (a) **Nitric acid** Specified in JIS K 8541.
 - (b) **0.05 mol/l EDTA solution** Weigh 18.61 g of dihydrogen disodium ethylenediamine tetraacetate dihydrate specified in JIS K 8107, add 1000 ml of water to dissolve it, and store it in an air-tight polyethylene bottle.
 - (c) **Sodium acetate buffer solution** Dissolve 272 g of sodium acetate trihydrate specified in JIS K 8371 in water to make 1000 ml.
 - (d) **Xylenol orange solution (1 g/l)** Dissolve 0.1 g of xylenol orange specified in JIS K 9563 in water to make 100 ml.

- (e) **Aluminium standard solution (1 mgAl/ml)** Weigh 1.000 g of aluminium (purity: 99.99 wt% or more) specified in JIS K 8069, put it in a 100 ml beaker, cover its upper with a watch glass, add carefully a small quantity of nitric acid (1+1), and dissolve it with heating. After allowing it to cool, transfer whole liquid into a 1000 ml measuring flask, and add nitric acid (1+30) up to the marked line.
- (f) **0.02 mol/l zinc solution** Weigh 1.308 g of zinc specified in JIS K 8005, put it in a 100 ml beaker, add 6 ml to 7 ml of hydrochloric acid and small quantity of water, and dissolve it with heating. Evaporate water on a water bath nearly to dry up, add water to dissolve it, transfer it into a 1000 ml measuring flask, and add water up to the marked line.

Take 20 ml of 0.05 mol/l EDTA solution into a 200 ml beaker, add 2 ml of nitric acid (1+12), carry out the procedures shown in (c) to (e) in below (3), and the used quantity (ml) of 0.02 mol/l zinc solution shall be made a_1 . Take 20 ml of aluminium standard solution (1 mgAl/ml) and 20 ml of 0.05 mol/l EDTA solution into another 200 ml beaker, add 2 ml of nitric acid (1+12), cover it with a watch glass, boil it for 1 min, allow it to cool, carry out the procedures shown in (c) to (e) in below (3), and the used quantity (ml) of 0.02 mol/l zinc solution shall be made a_2 .

Calculate amount of aluminium equivalent to 1 ml of 0.02 mol/l zinc solution according to the following formula:

$$f = \frac{0.001 \times 20}{a_1 - a_2}$$

where, f : amount of aluminium equivalent to 1 ml of 0.02 mol/l zinc solution (g)

(3) **Operations** Operations shall be carried out as follows:

- (a) Weigh about 10 g of sample to the nearest 1 mg, transfer it into a 500 ml measuring flask, and add water up to the marked line.
- (b) Take 20 ml of this solution into a 200 ml Erlenmeyer flask, add 2 ml(2) of nitric acid (1+12), cover it with a watch glass, boil it for 1 min, allow it to cool, and add 20 ml of 0.05 mol/l EDTA solution.
- (c) Adjust its pH value to be about 3 (confirm it using Thymol Blue test paper) by adding sodium acetate buffer solution, and boil it for about 2 min.
- (d) After cooling it, add about 10 ml⁽³⁾ of sodium acetate buffer solution and 2 drops to 5 drops of xylenol orange solution (1 g/l).
- (e) Titrate it with 0.02 mol/l zinc solution, and make it an end point when color of the liquid turns to faint red.
- (f) Take 20 ml of 0.05 mol/l EDTA solution, transfer it into another 200 ml Erlenmeyer flask, add about 20 ml of water and 2 ml of nitric acid (1+12), and thereafter carry out procedures as shown in (c) to (e).

Notes ⁽²⁾ Make pH value 1 to 2.

⁽³⁾ Adjust pH value to 5 to 6.

- (4) **Calculation** Calculate the concentration (wt%) of aluminium oxide in the sample according to the following formula:

$$A = \frac{1.8895 \times (b' - b) \times f}{S \times \frac{20}{500}} \times 100 - (c \times 0.9129 \times 10^{-4})$$

where, A : concentration of aluminium oxide in sample (wt%)

1.8895 : conversion factor from 1 g aluminium to aluminium oxide

f : amount of aluminium equivalent to 1 ml of 0.02 mol/l zinc solution (g)

b : volume of 0.02 mol/l zinc solution consumed for sample solution (ml)

b' : volume of 0.02 mol/l zinc solution consumed at (3) (f) (ml)

c : iron obtained at 4.9 (ppm)

0.9129 : conversion factor from iron to aluminium

S : mass of sample (g)

4.3.2 ICP atomic emission spectrometry

- (1) **Summary** Measure the emission strength of diluted sample at the wavelength of 396.152 nm by means of ICP atomic emission spectrometry, and obtain the content of aluminium oxide making use of internal standard method.
- (2) **Reagents** Reagents shall be as follows:
 - (a) **Nitric acid** Specified in JIS K 8541.
 - (b) **Internal standard stock solution (1 mgY/ml)** Weigh 0.318 g of yttrium oxide (Y_2O_3), put it into a 100 ml beaker, add 3 ml of hydrochloric acid and a small quantity of water, heat to dissolve it, allow it to cool, transfer it into a 250 ml measuring flask, and add water up to the marked line. Store it in a dark and cool place.
 - (c) **Internal standard solution (10 µgY/ml)** Take 10 ml of internal standard stock solution (1 mgY/ml), transfer it into a 1000 ml measuring flask, and add water up to the marked line.
 - (d) **Aluminium standard solution (1 mgAl/ml)** Follow 4.3.1 (2) (e).
- (3) **Implements and apparatus** Implements and apparatus shall be as follows:
 - (a) **Beaker** Made of quartz or polytetrafluoroethylene.
 - (b) **Measuring flask** Made of polyethylene.
 - (c) **Funnel** Made of polyethylene.
 - (d) **ICP atomic emission spectrometer**
 - (e) **Carrier gas** Argon class 2 specified in JIS K 1105.
- (4) **Operations** Operations shall be carried out as follows:

- (a) Weigh about 10 g of sample to the nearest 1 mg, transfer it into a beaker, add about 30 ml of water and 5 ml of nitric acid, cover it with a watch glass, boil it gently for about 1 min, allow it to cool, pour it into a 100 ml measuring flask through filter paper, and add water up to the marked line.
- (b) Take 2 ml of this solution, transfer it into a 100 ml measuring flask, add 2 ml of nitric acid and 20 ml of internal standard solution, and add water up to the marked line.
- (c) Introduce it into an ICP atomic emission spectrometer according to 5.8 of JIS K 0116, measure emission strength of both aluminium at the wavelength of 396.152 nm and yttrium at the wavelength of 371.029 nm, and obtain an emission-strength ratio of aluminium to yttrium.

Remarks: Carry out sufficient washing of a nebulizer.

- (d) **Working curve** Take stepwise, 0, 1, up to 20 ml, of aluminium standard solution (1 mgAl/ml) into as many 100 ml measuring flasks, add 2 ml of nitric acid and 20 ml of internal standard solution respectively, and add water up to the marked line. Thereafter, carry out the procedure as in (c), obtain the ratio between emission strengths, and plot the working curve making use of the relation between the amount of aluminium and the emission-strength ratio.
- (5) **Calculation** On the working curve prepared at (4) (d), find the amount (mg) of aluminium which is equivalent to the emission-strength ratio measured at (4) (c), and calculate the concentration (wt%) of aluminium oxide in the sample according to the following formula:

$$A = \frac{d}{S \times \frac{2}{100}} \times \frac{100}{1000} \times 1.8895$$

where, A : concentration of aluminium oxide in sample (wt%)

d : amount of aluminium (mg)

1.8895 : conversion factor from aluminium to aluminium oxide

S : mass of sample (g)

4.4 Basicity

- (1) **Summary** Add hydrochloric acid into sample, boil it, precipitate aluminium by adding potassium fluoride, add phenolphthalein indicator, titrate it with sodium hydroxide solution, and obtain its basicity.
- (2) **Reagents** Reagents shall be as follows:
 - (a) **Ethanol solution of Methyl Red-Bromocresol Green** Dissolve 0.02 g of Methyl Red specified in JIS K 8896 and 0.1 g of Bromocresol Green specified in JIS K 8840 in 100 ml of ethanol (99.5) specified in JIS K 8101.
 - (b) **Carbonate-free water** Boil the redistilled water to remove such as carbon dioxide or other volatile substances, and allow it to cool to get ordinary temperature with care not to absorb carbon dioxide in air.

- (c) **Ethanol solution of phenolphthalein (5 g/l)** Dissolve 0.5 g of phenolphthalein specified in JIS K 8799 in 100 ml of ethanol (99.5) specified in JIS K 8101, and drip sodium hydroxide (0.02 mol/l) until the liquid gets faint red.
- (d) **Potassium fluoride solution (500 g/l)** Dissolve 250 g of potassium fluoride (anhydride) specified in JIS K 8815 in water to make 500 ml solution, and then filtrate it through a filter paper (class 2).
- (e) **0.5 mol/l hydrochloric acid** Dilute 45 ml to 50 ml of hydrochloric acid specified in JIS K 8180 with water to make 1000 ml solution. Its standardization shall be carried out as follows:

Standardization Place sodium carbonate (anhydride) specified in JIS K 8005 in a platinum crucible, dry it at 500 °C to 650 °C for 40 min to 50 min, allow it to cool in a desiccator, weigh its 0.5 g to 0.7 g to the nearest 1 mg, put it in a 100 ml beaker, add 20 ml of water to dissolve it, add several drops of ethanol solution of Methyl Red-Bromocresol Green, titrate this with the hydrochloric acid, and make it an end point when color of the solution turns from blue to purplish red.

$$f = \frac{e}{g \times 0.0265}$$

where, f : factor of 0.5 mol/l hydrochloric acid
 e : taken amount of sodium carbonate (g)
 g : consumed volume of 0.5 mol/l hydrochloric acid (ml)
 0.0265 : amount of sodium carbonate equivalent to 1 ml of 0.5 mol/l hydrochloric acid (g)

- (f) **0.5 mol/l sodium hydroxide solution** Put gradually about 100 g of sodium hydroxide specified in JIS K 8576 in a 200 ml Erlenmeyer flask, in which about 100 ml of water has been put, with care of its exothermic reaction, stir it with a glass rod to dissolve and make saturated solution, and after stoppering with a rubber stopper, allow it to stand a whole day and night. Take about 25 ml of supernatant solution, and dilute it with carbonate-free water to make total 1000 ml. Its standardization shall be carried out as follows:

Standardization Take 25 ml of 0.5 mol/l hydrochloric acid into a porcelain evaporating dish, add 2 drops to 3 drops of ethanol solution of phenolphthalein (5 g/l), titrate it with the sodium hydroxide solution, stir it with a glass rod toties quoties, and make it an end point when color of solution turns to faint red.

$$f' = \frac{25f}{h}$$

where, f' : factor of 0.5 mol/l sodium hydroxide solution
 f : factor of 0.5 mol/l hydrochloric acid
 h : consumed volume of 0.5 mol/l sodium hydroxide solution (ml)

(3) Operations Operations shall be carried out as follows:

- (a) Weigh about 2 g of sample to the nearest 1 mg, and transfer it into a 200 ml conical beaker with 20 ml to 30 ml of water.
- (b) Take 25 ml of 0.5 mol/l hydrochloric acid, transfer it into the beaker, cover it with a watch glass, heat it for 10 min on a water bath, cool it to room temperature, and add 25 ml of potassium fluoride solution (500 g/l) at one time.
- (c) Add 4 drops to 5 drops of ethanol solution of phenolphthalein (5 g/l), immediately titrate it with 0.5 mol/l sodium hydroxide solution, and make it an end point when color of solution turns to faint red.
- (d) Separately, take 25 ml of water in a 200 ml conical beaker, and carry out the procedures at (b) and (c).

(4) Calculation Calculate the basicity (wt%) of the sample according to the following formula:

$$B = \frac{\frac{(i' - i) \times f' \times 0.008504}{17}}{\frac{S \times A \times 0.5293}{8.994 \times 100}} \times 100$$

where,

 B : basicity of sample (wt%) i : volume of 0.5 mol/l sodium hydroxide solution consumed for sample solution (ml) i' : volume of 0.5 mol/l sodium hydroxide solution consumed at (3) (d) (ml) f' : factor of 0.5 mol/l sodium hydroxide solution

0.008504 : mass of hydroxyl group equivalent to 1 ml of 0.5 mol/l sodium hydroxide solution (g)

17 : gram equivalent of hydroxyl group

 S : mass of sample (g) A : concentration of aluminium oxide obtained at 4.3 (wt%)

0.5293 : conversion factor of aluminium in aluminium oxide

8.994 : gram equivalent of aluminium

4.5 pH value**(1) Summary** Measure pH value of 10 g/l sample solution by glass-electrode method.**(2) Apparatus****Glass-electrode pH meter** Type II specified in JIS Z 8802.**(3) Operations** Operations shall be carried out as follows:

- (a) Weigh 1.0 g of sample, transfer it into a 100 ml measuring flask, and add water up to the marked line.

- (b) While keeping it at about 20 °C temperature, measure its pH value according to 7 of JIS Z 8802.

4.6 Sulfate ion The determination of sulfate ion shall follow either ion chromatography or titrimetry.

4.6.1 Ion chromatography

- (1) **Summary** Inject diluted sample together with eluent into an ion chromatograph, separate sulfate ion by passing through the column of anion-exchange resin, detect it by an electric conductivity detector, and obtain the content of sulfate ion.

- (2) **Reagents** Reagents shall be as follows:

- (a) **Water** The water filtrated through a membrane filter with 0.45 µm or less, and having no peak in the retention time of target ion when a chromatogram is plotted.
- (b) **Eluent** Its type is influenced by both the kind of anion-exchange resin packed in a separation column and the type of apparatus, but it is necessary to carry out previous confirmation on separation condition by the procedures at (4) (e) and (f).

Suppressor type: Prepare both 1.2 m mol/l to 4 m mol/l solution by dissolving sodium hydrogencarbonate specified in JIS K 8622 and 0.75 m mol/l to 4 m mol/l solution by dissolving sodium carbonate specified in JIS K 8625, and mix them.

Nonsuppressor type: Prepare both 8 m mol/l solution of *p*-hydroxybenzoic acid and 3.2 m mol/l solution of bis (2-hydroxyethyl) iminotris (hydroxymethyl) methane, and mix them; or prepare both 2.5 m mol/l solution of phthalic acid and 15 m mol/l solution of sodium tetraborate, and mix them.

- (c) **Removing liquid** This is the same one as in (b), but in case of suppressor type, 10 m mol/l to 25 m mol/l sulfuric acid or the like shall be used.
- (d) **Nitric acid (1+25)** The one prepared by using nitric acid specified in JIS K 8541.
- (e) **Sulfate-ion standard stock solution (1 mgSO₄/ml)** Heat sodium sulfate specified in JIS K 8987 at 110 °C for 2 h, and allow it to cool in a desiccator. Weigh its 1.479 g into a 100 ml beaker, dissolve it in a small quantity of water, transfer it into a 1000 ml measuring flask, and add water up to the marked line. Alternatively, employ sulfate-ion standard solution, SO₄²⁻ 1000, specified in JIS K 0028.
- (f) **Sulfate-ion standard solution (0.1 mgSO₄/ml)** Take 10 ml of sulfate-ion standard stock solution (1 mgSO₄/ml), transfer it into a 100 ml measuring flask, and add water up to the marked line.

- (3) **Implements and apparatus** Implements and apparatus shall be as follows:

- (a) **Filtrating apparatus with membrane filter** Equipped with a membrane filter with about 0.45 µm or less pore diameter (nearly the same pore diameter as that of the filter which is equipped with the ion chromatograph itself).

- (b) **Syringe** With volume of 1 ml to 2 ml, or automatic sample injecting device.
 - (c) **Ion chromatograph** There are two types; a type combining a separation column and removing column, and a type with separation column alone; but the following conditions must be satisfied, and sulfate ion can be separately detected from other anions.
 - (d) **Separation column for anions** In case of suppressor type, styrenedivinyl polymer on whose surface anion-exchange resin is coated (pellicular type), measuring 4 mm to 4.6 mm in inside diameter and 10 cm to 25 cm in length. In case of nonsuppressor type, polyacrylate or silica material on whose surface anion-exchange resin is coated, measuring 4 mm to 4.6 mm in inside diameter and 5 cm to 25 cm in length. In front of separation column, precolumn shall be set to prevent the contamination by suspensoids or organic substances.
 - (e) **Flow rate for eluent** The optimum flow rate is the one specified in the employed apparatus, but in standard 1 ml/min to 2 ml/min.
 - (f) **Flow rate for removing liquid** The same as that in (e), but in standard, 0.5 ml/min to 4 ml/min (for suppressor type only).
 - (g) **Detector** Electric conductivity detector installed inside a thermostat, or the one equipped with the device for temperature compensation.
- (4) **Operations** Operations shall be carried out as follows:
- (a) Weigh about 10 g of sample to the nearest 1 mg, transfer it into a 500 ml measuring flask, and add water up to the marked line.
 - (b) Take 5 ml out of this solution, transfer it into a 200 ml beaker, add 10 ml of water and 1 ml of nitric acid (1+12), heat it, allow it to cool, transfer it into a 100 ml measuring flask, and add water up to the marked line.
 - (c) Take 10 ml out of this solution, transfer it into a 100 ml measuring flask, and add water up to the marked line.
 - (d) Filtrate this through the membrane filter with 0.45 µm pore diameter.
 - (e) Inject a definite quantity of sample which has passed through the procedure at (d) into the ion chromatograph, and record its chromatogram.
 - (f) Measure the peak height or peak area of the peak which corresponds to that made by sulfate ion on the chromatogram.
 - (g) **Working curve** Take stepwise, 0, 2, up to 5 ml, of sulfate-ion standard solution (0.1 mgSO₄/ml) into as many 100 ml measuring flasks, add water up to the marked line. Thereafter carry out the procedures as in (e) and (f), and plot the working curve making use of the relation between the amount of sulfate ion (mg) and either peak height or peak area.
- (5) **Calculation** On the working curve prepared at (4) (g), find the amount (mg) of sulfate ion which is equivalent to the peak height or peak area measured at (4) (f), and calculate the concentration (wt%) of sulfate ion in the sample according to the following formula:

$$C = \frac{j \times \frac{1}{1000}}{S \times \frac{5}{500} \times \frac{10}{100}} \times 100$$

where, C : concentration of sulfate ion in sample (wt%)
 j : amount of sulfate ion (mg)
 S : mass of sample (g)

4.6.2 Titrimetry

- (1) **Summary** Add nitric acid into sample, heat it, add ethanol and lead nitrate solution to produce the precipitate of lead sulfate, dissolve the precipitate in ammonium acetate-acetic acid buffer solution, add Cu-PAN indicator, titrate it with dihydrogen disodium ethylenediaminetetraacetate solution, and obtain the content of sulfate ion.
- (2) **Reagents** Reagents shall be as follows:
 - (a) **Nitric acid (1+12)** Follow 4.3.1 (2) (a).
 - (b) **Lead nitrate solution (17 g/l)** Dissolve 17 g of lead nitrate specified in JIS K 8563 in water to make 1000 ml solution.
 - (c) **Ammonium acetate-acetic acid buffer solution** Dissolve 15.42 g of ammonium acetate specified in JIS K 8359 in about 500 ml of water, add 35 ml of acetic acid specified in JIS K 8355, and then add water to make total 1000 ml (pH value of this solution is about 4.2).
 - (d) **Cu-PAN indicator** Mix 1-(2-pyridylazo)-2-naphthol and disodium copper ethylenediaminetetraacetate tetrahydrate by the mass ratio of 1 : 11.1, dissolve 1 g of this mixture in ethanol (60 vol% to 70 vol%) to make 100 ml solution, and use its supernatant.
 - (e) **0.05 mol/l EDTA solution** Follow 4.3.1 (2) (b). Standardize it as follows:
Standardization Take 50 ml of 0.02 mol/l zinc solution into a 300 ml beaker, add about 80 ml of ammonium acetate-acetic acid buffer solution, heat it, immediately add 4 drops to 5 drops of Cu-PAN indicator, titrate it with 0.05 mol/l EDTA solution, and make it an end point when color of the solution turns from red to yellow.

$$f'' = \frac{50}{k} \times \frac{\frac{1}{50}}{\frac{1}{20}}$$

where, f'' : factor of 0.05 mol/l EDTA solution
 k : consumed volume of 0.05 mol/l EDTA solution (ml)

- (f) **0.02 mol/l zinc solution** Follow 4.3.1 (2) (f).
- (3) **Operations** Operations shall be carried out as follows:
 - (a) Weigh about 10 g of sample to the nearest 1 mg, transfer it into a 500 ml measuring flask, and add water up to the marked line.
 - (b) Take 20 ml out of this solution, transfer it into a 200 ml beaker, add 2 ml of nitric acid (1+12), and heat it.

- (c) Add water to make about 40 ml, immerse it in a water bath kept at 80 °C, add gradually 30 ml of ethanol (99.5) and about 10 ml of lead nitrate solution (17 g/l) to make the white precipitate of lead sulfate, and keep the temperature as it is for about 10 min to age the precipitate.
 - (d) Cool it with running water, filtrate it through a filter paper (class 6), and wash the beaker and precipitate with 20 ml to 30 ml of ethanol (20 vol%). Repeat this washing 3 times, and gather all precipitate on the filter paper.
 - (e) Put the precipitate together with the filter paper into original beaker, add about 80 ml to 100 ml of ammonium acetate-acetic acid buffer solution, and dissolve the precipitate completely by heating.
 - (f) Add 4 drops to 5 drops of Cu-PAN indicator while keeping the temperature at 80 °C to 100 °C, titrate it with 0.05 mol/l EDTA solution, and make it an end point when color of solution turns from red to yellow.
- (4) **Calculation** Calculate the concentration (wt%) of sulfate ion in the sample according to the following formula:

$$C = \frac{0.004803 \times m \times f''}{S \times \frac{20}{500}} \times 100$$

where, C : concentration of sulfate ion in sample (wt%)

0.004803 : mass of sulfate ion equivalent to 1 ml of 0.05 mol/l EDTA solution (g)

m : consumed volume of 0.05 mol/l EDTA solution (ml)

f'' : factor of 0.05 mol/l EDTA solution

S : mass of sample (g)

4.7 Ammoniacal nitrogen

- (1) **Summary** Add sodium carbonate into sample to make precipitate of aluminium as hydroxide, add sodium hypochlorite and then 1-naphthol into its supernatant, measure the absorbance of generated indophenol-type coloring stuff (bluish green) with wavelength of 720 nm vicinity, and obtain the content of ammoniacal nitrogen.
- (2) **Reagents** Reagents shall be as follows:
 - (a) **Sulfuric acid (1+35)** The one prepared using sulfuric acid specified in JIS K 8951.
 - (b) **Sodium carbonate solution (30 g/l)** Dissolve 3 g of sodium carbonate (anhydride) specified in JIS K 8625 in water to make 100 ml solution.
 - (c) **Sodium hydroxide solution (10 g/l)** Dissolve 1 g of sodium hydroxide specified in JIS K 8576 in water to make 100 ml solution.
 - (d) **Sodium hypochlorite solution (available chlorine 1 g/l)** Dissolve 100/C ml (C: concentration of available chlorine) of sodium hypochlorite (on the market) and 15 g of sodium hydroxide in water to make 1000 ml solution.

- (e) **EDTA-sodium hydroxide mixed solution** Dissolve 0.93 g of disodium ethylenediaminetetraacetate dihydrate specified in JIS K 8107 in sodium hydroxide solution (40 g/l) to make 250 ml solution.
- (f) **1-naphthol solution** Dissolve 1.6 g of 1-naphthol specified in JIS K 8698 in acetone-ethanol solution (15 : 85) to make 100 ml solution.
- (g) **Ammoniacal-nitrogen standard stock solution (0.1 mgN/ml)** Allow ammonium chloride specified in JIS K 8116 in a desiccator [keeping magnesium perchlorate specified in JIS K 8228] to stand for at least 16 h, weigh its 0.382 g, put it in a 100 ml beaker, dissolve it in water, transfer it into a 1000 ml measuring flask, and add water up to the marked line.
- (h) **Ammoniacal-nitrogen standard solution (5 µgN/ml)** Take 50 ml of ammoniacal-nitrogen standard stock solution (0.1 mgN/ml), transfer it into a 1000 ml measuring flask, and add water up to the marked line. Prepare this solution when it is used.

(3) **Apparatus Photoelectric spectrophotometer**

(4) **Operations** Operations shall be carried out as follows:

- (a) Weigh about 10 g of sample to the nearest 1 mg, transfer it into a 500 ml measuring flask, and add water up to the marked line.
- (b) Take 25 ml out of this solution, transfer it into a 100 ml measuring cylinder with a stopper, add 1.5 ml of sulfuric acid (1+35), shake it, add 5 ml of sodium carbonate solution (30 g/l), then add water up to the marked line, and shake it gently.
- (c) Allow it to stand quietly to make hydroxide precipitate, take accurately 50 ml of its supernatant, and transfer it into a 100 ml color comparison tube with a ground stopper.
- (d) Add sodium hydroxide solution (10 g/l) to control its pH, and make its pH about 11⁽⁴⁾.
- (e) Add 1 ml of sodium hypochlorite solution (available chlorine: 1 g/l), mix them, 2 min later and within 5 min add 1 ml of EDTA-sodium hydroxide mixed solution, and mix them again. Then, 1 min later and within 5 min⁽⁵⁾ add 5 ml of 1-naphthol solution, mix them, add water up to the marked line, and allow it to stand at 25 °C to 30 °C for 15 min.
- (f) Take its portion into a 10 mm absorption cell, and measure its absorbance at wavelength of 720 nm vicinity.
- (g) **Working curve** Take stepwise, 0, 1, up to 7 ml, of ammoniacal nitrogen standard solution (5 µgN/ml), transfer them into as many 100 ml measuring flasks, and add water to make them about 50 ml. Thereafter, carry out the procedures as in (e) and (f), plot the working curve making use of the relation between the quantity of ammoniacal nitrogen and the absorbance.

Notes ⁽⁴⁾ The blank for working curve and standard solution have a low buffer action, so pH adjustment is not needed.

⁽⁵⁾ The time control needed when reagents are added shall be carried out accurately, including working curve preparation.