

JAPANESE
INDUSTRIAL
STANDARD

Translated and Published by
Japanese Standards Association

JIS K 0102 : 2019

Testing methods for industrial
wastewater
(Amendment 1)

JIS K 0102:2016 was revised under date of March 20, 2019.
This Amendment includes the revised items and is to be used
in conjunction with **JIS K 0102:2016**.

This document has incorporated the erratum to the Japanese
version issued in December, 2019.

ICS 13.060.25;13.060.30;13.060.50

Reference number : JIS K 0102 : 2019 (E)

Foreword

This Japanese Industrial Standard has been revised by the Minister of Economy, Trade and Industry through deliberations at the Japanese Industrial Standards Committee in accordance with the Industrial Standardization Law.

This Amendment partially replaces the previous edition (**JIS K 0102:2016**), which has been technically revised.

Date of Establishment: 1964-02-01

Date of Revision: 2019-03-20

Date of Public Notice in Official Gazette: 2019-03-20

Investigated by: Japanese Industrial Standards Committee
Standards Board for ISO area
Technical Committee on Chemical Products and
Analytical Methods

JIS K 0102:2019, First English edition published in 2020-04

Translated and published by: Japanese Standards Association
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In the event of any doubts arising as to the contents,
the original JIS is to be the final authority.

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Printed in Japan

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Testing methods for industrial wastewater (Amendment 1)

Introduction

This Amendment aims to increase convenience of users of **JIS K 0102** by incorporating in its contents new technologies and new types of measuring devices that have been designed in recent years in the field of environmental analyses for the purpose of achieving labour saving, cost reduction and reduction of environmental load.

In the clauses listed in the contents page, this Amendment:

- a) introduces the small distillation apparatus that requires only a small portion of sample for analysis of phenols, fluorine compound, total cyanide, and ammonium ion, and reduction of reagent and sample volumes for thermal decomposition pre-treatment in analysis of total nitrogen and total phosphorus;
- b) introduces the sodium and potassium analysis method using inductively coupled plasma atomic emission spectrometry;
- c) introduces the alkylmercury analysis method using gas chromatography-mass spectrometry;
- d) introduces the hexavalent chromium analysis method using liquid chromatography-inductively coupled plasma mass spectrometry;
- e) moves the beryllium analysis methods from Annex to the main body;
- f) adds the method for preventing false-positives in residual chlorine analysis.

JIS K 0102:2016 is revised as follows.

2 o) 2)

Replace “For reference solutions, as well as those prepared according to the method specified in each test item, either the reference solutions with traceability ensured to meet the National Metrological Standard (Article 134 of the Measurement Act) or these solutions diluted to a definite concentration shall be used ⁽³⁾.” by “For reference solutions, as well as those prepared according to the method specified in each test item, either the reference solutions traceable to the National Metrological Standard or these solutions diluted to a definite concentration shall be used ⁽³⁾.”

2 o) 2)

Replace the Information by the following:

Information: Representative traceability-ensured reference solutions are those bearing a JCSS (Japan Calibration Service System) mark.

2 o) 3)

Replace “The concentration of reference solution is expressed by mass in 1 ml (mg/ml, µg/ml or ng/ml), except for the concentration of chloride reference solution used in residual chloride measurement and those of the reference solutions used in ion-selective electrode method and flame photometry, which is expressed by mass in 1 L (mg/L).” by “The concentration of reference solution is expressed by mass in 1 ml or 1 L (mg/ml, µg/ml, ng/ml, g/L, mg/L or µg/L).”

7.1 a) 1)

Replace “**JIS B 7411-1**” by “**JIS B 7414**”.

7.2 a) 1)

Replace “**JIS B 7411-1**” by “**JIS B 7414**”.

12.1 c) 2)

Replace “**JIS B 7411-1**” by “**JIS B 7414**”.

12.1

In Note (3), replace “**JIS B 7411-1**” by “**JIS B 7414**”.

13 b) 2)

Replace “**JIS B 7411-1**” by “**JIS B 7414**”.

28.1

Replace the entire subclause by the following:

28.1 Phenols The test of phenols is carried out by applying either the 4-aminoantipyrine absorptiometry described in **28.1.2** or the 4-aminoantipyrine coloring flow injection analysis (FIA) described in **28.1.3** on the sample which has been pretreated (distilled) as specified in **28.1.1**. The results in this case are expressed by the determination value obtained using phenol reference solution. Alternatively, the continuous flow analysis (CFA) specified in **28.1.3** where distillation and 4-aminoantipyrine coloring absorptiometry are performed in a continuous flow may be applied.

Phenols are easily decomposed by phenol decomposing bacteria. Because they are easily attacked by oxidizing substances, reducing substances, alkali, etc., the test shall be carried out immediately after sampling. When immediate testing is impracticable, the sample shall be preserved in accordance with **3.3**, and tested as soon as possible.

In this test, the phenols to be targeted are hydroxyl derivatives of benzene and its analogue which produce the colored compound by reacting with 4-aminoantipyrine according to the specified method.

The methods shown in **28.1.1** and **28.1.2** are in consistency with the second edition of **ISO 6439** published in 1990, and the flow analysis is in consistency with the first edition of **ISO 14402** published in 1999.

NOTE: The corresponding International Standards relevant to this test method are as follows.

The symbols which denote the degree of correspondence in the contents between the corresponding International Standards and **JIS** are **IDT** (identical), **MOD** (modified), and **NEQ** (not equivalent) according to **ISO/IEC Guide 21-1**.

ISO 6439:1990 *Water quality—Determination of phenol index—4-Aminoantipyrine spectrometric methods after distillation* (MOD)

ISO 14402:1999 *Water quality—Determination of phenol index by flow analysis (FIA and CFA)* (MOD)

The value of “phenols” reported in this method is equivalent to the “phenol index” as defined in **ISO 6439**.

28.1.1 Pretreatment (distillation method) The phenols are separated by thermal distillation under the presence of copper (II) sulfate in acidity of phosphoric acid (approximately pH 4).

a) **Reagents** The following reagents shall be used.

- 1) **Water**, of A3 specified in **JIS K 0557**. Preserve it in a borosilicate glass bottle.
- 2) **Phosphoric acid (1+9)**, prepared using the phosphoric acid specified in **JIS K 9005**.
- 3) **Copper (II) sulfate solution** Dissolve 10 g of copper (II) sulfate pentahydrate specified in **JIS K 8983** in water to make 100 ml.
- 4) **Methyl orange solution (1 g/L)**, in accordance with **24.1 a) 2)**.

b) **Apparatus** The following apparatus shall be used.

- 1) **Distillation apparatus**, as specified in **38.1.1.2 b) 1)**.
- c) **Distillation** Distillation shall be carried out as follows. The pretreatment (distillation method) may be omitted if the sample has no color or turbidity, and contains no material that may interfere with the 4-aminoantipyrine absorptiometry. If this is the case, the sample may be immediately tested without receiving the treatment for storage specified in **3.3**.

The distillation procedure described in NOTE 2 or NOTE 3 may be used if proven to achieve a recovery rate of 80 % to 120 % by testing a sample to which a definite volume of phenol reference solution has been added. The distillate obtained by the procedure in NOTE 2 or NOTE 3 is applicable to the FIA method specified in **28.1.2.1**, **28.1.2.3**, and **28.1.3**.

- 1) In a 500-ml distillation flask, place 250 ml of sample, or if the phenol concentration in the sample is 50 mg/L or more, 250 ml of diluted sample prepared by adding water to a suitable volume of sample to make 250 ml. Add to this flask five to seven drops of methyl orange solution (1 g/L), add phosphoric acid (1+9) until methyl orange changes its color so that the pH is approximately 4, and add 2.5 ml of copper (II) sulfate solution. If the phenol concentration in the sample is 25 µg/L or less, place 500 ml of sample in a 1 000-ml distillation flask and add 5 ml of copper (II) sulfate solution. In this case, the capacity of the receiver stated in **2)**, the volume of distillate stated in **3)** and the volume of water and total distillate stated in **4)** shall all be doubled. If, for preservation purposes, phosphoric acid

and copper (II) sulfate pentahydrate have been added to the sample, addition of these may be omitted.

- 2) After adding boiling chips (2 mm to 3 mm in grain size) to the distillation flask, mount the distillation flask on the distillation apparatus, and perform distillation while receiving the distillate in a 250-ml measuring cylinder (with a stopper).
- 3) As soon as the amount of the distillate in the measuring cylinder has reached 225 ml, stop the heating.
- 4) When the boiling of the sample in the distillation flask has ceased, add 25 ml of water to the distillation flask, and restart the distillation to get another 25 ml of distillate, so that the total of 250 ml of distillate is obtained. If the distillate has white turbidity, add phosphoric acid (1+9) again to the distillate until the pH is approximately 4, add 2.5 ml of copper (II) sulfate solution, and carry out distillation again. When this redistillation is not effective in clearing the turbidity, treat it according to 4) of NOTE 1.

NOTE 1 The biochemical decomposition of phenols is restricted by the addition of phosphoric acid and copper (II) sulfate pentahydrate in the preservation of sample. In 4-aminoantipyrine absorptiometry, oxidizing substance, reducing substance, metallic ion, aromatic amines, oils, tars and so on can interfere. Most of the interferences can be removed by distillation operation, but when the sample contains oxidizing substance, reducing substance, sulfur compounds, or oils or tars, the following should be performed.

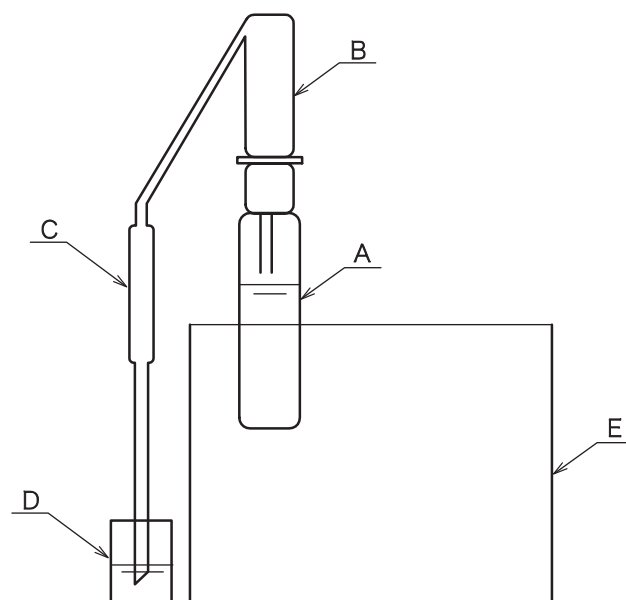
- 1) **Oxidizing substance** When the sample contains oxidizing substances such as residual chlorine or when iodine is isolated by addition of potassium iodide to the sample made acidic, add a small volume of excessive L(+)-ascorbic acid specified in **JIS K 9502** or a small volume of excessive iron (II) sulfate heptahydrate specified in **JIS K 8978** immediately after sampling. For the preservation of sample, add phosphoric acid to adjust the pH to about 4 and add 1 g of copper (II) sulfate pentahydrate specified in **JIS K 8983** per 1 L of sample.
- 2) **Reducing substance** When reducing substance is present in the sample, add an excess of potassium hexacyanoferrate (III) specified in **JIS K 8801**. For the preservation of sample, add phosphoric acid specified in **JIS K 9005** to adjust the pH to about 4 and add 1 g of copper (II) sulfate pentahydrate specified in **JIS K 8983** per 1 L of sample.
- 3) **Sulfur compound** When the sample contains hydrogen sulfide and sulfite ion, perform the following: Immediately after sampling, add phosphoric acid to adjust the pH to about 4, blow air carefully in the sample or agitate it to expel hydrogen sulfide and sulfur dioxide and then add 10 ml of copper (II) sulfate solution per 1 L of sample. Alternatively, precipitate copper (I) sulfide by adding an excess of copper (II) sulfate solution, and add phosphoric acid to adjust the pH to about 4.

- 4) **Oils and tars** When the sample contains oils and tars, perform either of the following.
- 4.1) Immediately after sampling, without adding copper (II) sulfate solution, add sodium hydroxide solution (100 g/L) [prepared in accordance with **19 a) 2)**] to adjust the pH to 12 to 12.5, transfer to a separatory funnel, add chloroform specified in **JIS K 8322** to extract oils and tars and discard the chloroform layer. Heat the water layer on boiling water bath and remove the residual chloroform. For the preservation, add phosphoric acid to adjust the pH to about 4 and add 1 g of copper (II) sulfate pentahydrate per 1 L of sample.
- 4.2) At the time of distillation, take 250 ml of the sample, add several drops of methyl orange solution (1 g/L), and make it acidic with sulfuric acid (0.5 mol/L) (prepared by using sulfuric acid specified in **JIS K 8951**). Transfer it to a separatory funnel and add 75 g of sodium chloride specified in **JIS K 8150**. Carry out extractive separation using 20 ml of chloroform at the first time and then using 12.5 ml for each of the following four times. Collect and transfer the chloroform layers to another separatory funnel, and carry out back extraction using 2.0 ml of sodium hydroxide solution (100 g/L) [prepared in accordance with **19 a) 2)**] at the first time and using 1.5 ml for each of the following two times. Collect the water layers and heat on the water bath until chloroform disappears. Cool it and make it 250 ml with water, and carry out the distillation in **c)**.
- 5) **Amines** Some amines are determined as phenol under certain reaction conditions. The interference can be minimized by distillation at pH under 0.5.

NOTES 2 A smaller distillation flask, 100 ml or 200 ml, may be used, in which case the distillation procedure shall be as follows.

If using a 200-ml distillation flask, the volumes of sample, copper (II) sulfate solution, receiver, and distillate shall all be double the volumes for a standard procedure.

- 1) In a 100-ml distillation flask, place 50 ml of sample and 5 ml of water, add one or two drops of methyl orange solution (1 g/L), add phosphoric acid (1+9) until methyl orange changes its color so that the pH is approximately 4, and add 0.5 ml of copper (II) sulfate solution.
 - 2) After adding boiling chips (2 mm to 3 mm in grain size) to the distillation flask, mount the distillation flask on the distillation apparatus, and perform distillation while receiving the distillate in a 50-ml measuring cylinder (with a stopper).
 - 3) Continue distillation until the receiver is full (50 ml).
- 3 The distillation procedure in the case of using a small distillation apparatus is as follows. An example of a small distillation apparatus is shown in figure 28.1.



- A : distillation vessel (made of heat-resistant glass, 50 ml to 80 ml in capacity)
B : distillation tube (capable of gas-liquid separation)
C : cooler
D : receiver (e.g. 50-ml measuring cylinder with a stopper)
E : heating equipment (capable of controlling to 150 °C to 210 °C)

Figure 28.1 Example of small distillation apparatus

- 1) Place 50 ml of sample in a distillation vessel, add one or two drops of methyl orange solution (1 g/L), add phosphoric acid (1+9) until methyl orange changes its color so that the pH is approximately 4, and add 0.5 ml of copper (II) sulfate solution.
- 2) After adding boiling chips (2 mm to 3 mm in grain size), mount a distillation tube on the distillation vessel, and mount this assembly on a heating equipment. Perform distillation while receiving the distillate in a 50-ml measuring cylinder (with a stopper) etc.
- 3) When 90 % of sample volume has been distilled, remove the distillation vessel from the heating equipment. Rinse the inner wall of the cooler with water, add the washings to the receiver, and add water to the 50-ml mark.

28.1.2 4-Aminoantipyrine absorptiometry The pH of the sample is adjusted to about 10, and 4-aminoantipyrine (4-amino-1,2-dihydro-1,5-dimethyl-2-phenyl-3H-pyrazole-3-one) solution and potassium hexacyanoferrate (III) solution are added to the sample. The absorbance of the generated red antipyrine dye is measured near the wavelength of 510 nm and the amount of phenols determined by reference to the working curve of the phenol reference solution (direct method). If sufficient coloration cannot be achieved by this method, the colored solution may be subjected to extraction using chloroform or methyl benzoate (solvent extraction method), or the phenols in the sample may be colored by the same principle as the standard method and then extracted with a hydrophobic column (solid-phase extraction method).

These methods detect, besides phenols ($\text{C}_6\text{H}_5\text{OH}$), both phenol derivatives having a substituent at *o*- and *m*-positions and polycyclic compounds having a substituent of hydroxyl group, owing to generation of antipyrine dye resulting from the reaction with 4-aminoantipyrine. The phenol derivatives with substituent at *p*-position hardly react with 4-aminoantipyrine, so they give nearly no coloring. The intensity of coloring by antipyrine dye is influenced by the type, position, and number of substituents.

Determination range: Direct method $\text{C}_6\text{H}_5\text{OH}$ 50 μg to 500 μg ,

Repeatability: 3 % to 10 %

Solvent extraction method $\text{C}_6\text{H}_5\text{OH}$ 2.5 μg to 50 μg ,

Repeatability: 3 % to 10 %

Solid-phase extraction method $\text{C}_6\text{H}_5\text{OH}$ 0.2 μg to 15 μg ,

Repeatability: 3 % to 10 %

28.1.2.1 Direct method The intensity of color of red antipyrine dye generated in the solution is measured to determine the amount of phenols.

a) **Reagents** The following reagents shall be used.

- 1) **Water**, as specified in **28.1.1 a) 1)**.
- 2) **Ammonium chloride-ammonia buffer solution (pH 10)** Dissolve 67.5 g of ammonium chloride specified in **JIS K 8116** in 570 ml of ammonia solution specified in **JIS K 8085**, and add water to make 1 L.
- 3) **Potassium hexacyanoferrate (III) solution** Take a large crystal, weighing 9 g, of potassium hexacyanoferrate (III) specified in **JIS K 8801**, and after washing its surface with a small amount of water, dissolve in water to make 100 ml. If necessary, filtrate it. This solution should be renewed each week, but solutions younger than 1 week should be replaced if their color has turned dark red.
- 4) **4-Aminoantipyrine solution (20 g/L)** Dissolve 2.0 g of 4-aminoantipyrine specified in **JIS K 8048** in water to make 100 ml. Prepare this solution immediately before use.
- 5) **Phenol reference solution ($\text{C}_6\text{H}_5\text{OH}$ 1 mg/ml)** Dissolve 1.00 g of phenol specified in **JIS K 8798** in water, transfer to a 1 000-ml volumetric flask and add water to the mark. Store this solution in a dark place at 0 °C to 10 °C.
- 6) **Phenol reference solution ($\text{C}_6\text{H}_5\text{OH}$ 10 $\mu\text{g/ml}$)** Place 10 ml of phenol reference solution ($\text{C}_6\text{H}_5\text{OH}$ 1 mg/ml) in a 1 000-ml volumetric flask, and add water to the mark. Prepare this solution immediately before use.

b) **Apparatus** The following apparatus shall be used.

- 1) **Photometer** Spectrophotometer or photoelectric photometer

c) **Procedure** The test procedure shall be as follows.

- 1) Place a suitable volume (containing 50 μg to 500 μg as $\text{C}_6\text{H}_5\text{OH}$) of the sample which has or has not been pretreated (distilled) in **28.1.1** in a 100-ml measuring cylinder (with a stopper), and add water to the 100-ml mark. If the total volume of distillate obtained in the procedure in NOTE 2 and NOTE 3 was 50 ml, transfer a suitable volume (containing 25 μg to 250 μg as $\text{C}_6\text{H}_5\text{OH}$) of the sample to a

50-ml measuring cylinder (with a stopper) and add water to the 50 ml mark. In the case of the procedure using a 50-ml measuring cylinder (with a stopper), the volumes of reagents specified in **2)** and **3)** shall be halved, and blank test specified in **4)** shall be performed with 50 ml of water.

- 2) Then, add 3 ml of ammonium chloride-ammonia buffer solution (pH 10), shake to mix, and adjust the pH to 10 ± 0.2 .
 - 3) Add 2 ml of 4-aminoantipyrine solution (20 g/L), shake to mix, add 2 ml of potassium hexacyanoferrate (III) solution, and after sufficiently shaking to mix, allow to stand for about 3 min.
 - 4) Separately, as a blank test, carry out the procedures in **2)** and **3)** using 100 ml of water.
 - 5) Using the blank test solution as a contrast solution, measure the absorbance at the wavelength near 510 nm.
 - 6) By reference to the working curve, determine the amount equivalent to phenol, and calculate the concentration of phenols (C_6H_5OH mg/L) in the sample.
- d) **Working curve** The working curve shall be prepared as follows.
- 1) Place a series of aliquots in stepwise increment ranging from 5 ml to 50 ml of phenol reference solution (C_6H_5OH 10 $\mu g/ml$) in as many 100-ml measuring cylinders (with a stopper), and add water to each of these to the 100-ml mark. If the sample volume before coloration in **c) 1)** was 50 ml, place a series of aliquots in stepwise increment ranging from 2.5 ml to 25 ml of phenol reference solution (C_6H_5OH 10 $\mu g/ml$) in as many 50-ml measuring cylinders (with a stopper), and add water to each of these to the 50-ml mark.
 - 2) Carry out the procedures in **2)** to **5)** of **c)**, and plot the relation curve between the amount of phenol and the absorbance.

28.1.2.2 Solvent extraction method If the color of antipyrine dye generated in the solution is too faint, extraction with chloroform and methyl benzoate is performed, and the absorbance of the organic layer is measured. This procedure does not apply to the distillate described in NOTE 2 and NOTE 3.

a) **Reagents** The following reagents shall be used.

- 1) **Water**, as specified in **28.1.1 a) 1)**.
- 2) **Ammonium chloride-ammonia buffer solution (pH 10)**, in accordance with **28.1.2.1 a) 2)**.
- 3) **Potassium hexacyanoferrate (III) solution**, as specified in **28.1.2.1 a) 3)**.
- 4) **4-Aminoantipyrine solution (20 g/L)**, as specified in **28.1.2.1 a) 4)**.
- 5) **Phenol reference solution (C_6H_5OH 1 $\mu g/ml$)** Place 50 ml of phenol reference solution (C_6H_5OH 10 $\mu g/ml$) specified in **28.1.2.1 a) 6)** in a 500-ml volumetric flask, and add water to the mark. Prepare this solution immediately before use.
- 6) **Chloroform**, specified in **JIS K 8322**.

- 7) **Methyl benzoate**
 - 8) **Sodium sulfate**, specified in **JIS K 8987**.
 - b) **Implement and apparatus** The following implement and apparatus shall be used.
 - 1) **Photometer** Spectrophotometer or photoelectric photometer
 - 2) **Separatory funnel**, of 200-ml capacity.
 - c) **Procedure** The test procedure shall be as follows.
 - 1) Transfer the whole volume of the colored solution obtained in **28.1.2.1 c) 3)** to a 200-ml separatory funnel, add 10 ml of the chloroform or methyl benzoate, and after shaking vigorously for about 1 min to 2 min, allow to stand. This procedure does not apply in the case where the sample volume of 50 ml has been used in the procedure in **28.1.2.1 c) 1)**.
 - 2) Separate the chloroform layer or the methyl benzoate layer, and dehydrate it either by filtrating it through a dry filter paper or by transferring into a beaker and adding about 1 g of sodium sulfate.
 - 3) Separately, for a blank test, carry out the procedures in **2)** and **3)** of **28.1.2.1 c)**, and then those in **1)** and **2)** using 100 ml of water.
 - 4) Using the chloroform layer or methyl benzoate layer prepared in the blank test as a contrast solution, measure the absorbance of the chloroform layer or methyl benzoate layer obtained in **2)** at the wavelength near 460 nm for the former and 465 nm for the latter.
 - 5) By reference to the working curve, determine the amount equivalent to phenol, and calculate the concentration of phenols (C_6H_5OH mg/L) in the sample.
 - d) **Working curve** The working curve shall be prepared as follows.
 - 1) Place a series of aliquots in stepwise increment ranging from 2.5 ml to 50 ml of phenol reference solution (C_6H_5OH 1 $\mu g/ml$) in as many 100-ml measuring cylinders (with a stopper), and add water to each of these to the 100-ml mark.
 - 2) Carry out the procedures in **2)** and **3)** of **28.1.2.1 c)**, and **1)** to **4)** of **c)** to plot the relation curve between the amount of phenol and the absorbance.
- NOTE 4 If 500 ml of sample has been used in the procedure in **28.1.1 c)**, the determination may be performed according to the following.
- 1) Transfer 500 ml of the distillate obtained in pretreatment into a 1 000-ml separatory funnel, and add 10 ml of ammonium chloride-ammonia buffer solution (pH 10) and shake to mix to adjust the pH to 10 ± 0.2 .
 - 2) Add 3 ml of 4-aminoantipyrine solution (20 g/L) and 3 ml of potassium hexacyanoferrate (III) solution, and shake to mix well. After allowing to stand for about 3 min, add 20 ml of chloroform and shake vigorously for about 1 min to mix.

- 3) Separate the chloroform layer, and dehydrate it either by filtering through a dry filter paper or transferring to a beaker and adding about 1 g of sodium sulfate.
- 4) Separately, as a blank test, carry out the procedures in **1)** to **3)** using 500 ml of water.
- 5) Using the chloroform layer obtained in the blank test as a contrast solution, measure the absorbance of the chloroform layer in **3)** at a wavelength near 460 nm.
- 6) By reference to the working curve, determine the amount equivalent to phenol, and calculate the concentration of phenols ($\text{C}_6\text{H}_5\text{OH}$ mg/L) in the sample. For construction of working curve, place a series of aliquots of phenol reference solution ($\text{C}_6\text{H}_5\text{OH}$ 1 $\mu\text{g/ml}$) ranging from 2.5 ml to 50 ml in as many 1 000 ml separatory funnels, dilute each of these with water to make 500 ml, and perform the same operation as done on the sample.

28.1.2.3 Solid-phase extraction method The antipyrine dye generated in the solution is collected in the hydrophobic solid-phase column. After elution with acetonitrile, absorbance of the acetonitrile layer is measured and the amount of phenols determined.

a) **Reagents** The following reagents shall be used.

- 1) **Water**, as specified in **28.1.1 a) 1)**.
- 2) **Ammonium chloride-ammonia buffer solution (pH 10)**, prepared in accordance with **28.1.2.1 a) 2)**.
- 3) **Potassium hexacyanoferrate (III) solution**, prepared in accordance with **28.1.2.1 a) 3)**.
- 4) **4-Aminoantipyrine solution (20 g/L)**, prepared in accordance with **28.1.2.1 a) 4)**.
- 5) **Phenol reference solution ($\text{C}_6\text{H}_5\text{OH}$ 1 $\mu\text{g/ml}$)**, prepared in accordance with **28.1.2.2 a) 5)**.
- 6) **Phenol reference solution ($\text{C}_6\text{H}_5\text{OH}$ 0.1 $\mu\text{g/ml}$)** Place 5 ml of phenol reference solution ($\text{C}_6\text{H}_5\text{OH}$ 10 $\mu\text{g/ml}$) specified in **28.1.2.1 a) 6)** in a 500-ml volumetric flask, and add water to the mark. Prepare this solution immediately before use.
- 7) **Acetonitrile**, specified in **JIS K 8032**.

b) **Implement and apparatus** The following implement and apparatus shall be used.

- 1) **Photometer** Spectrophotometer or photoelectric photometer
- 2) **Solid-phase column** Commercial divinylbenzene copolymer packed column or an ODS column

c) **Procedure** The test procedure shall be as follows.

- 1) Place a suitable volume (containing 0.2 µg to 15 µg as C₆H₅OH) of the sample which has or has not been pretreated in **28.1.1** in a 50-ml measuring cylinder (with a stopper), and add water to the 50-ml mark.
 - 2) Add 1.5 ml of ammonium chloride-ammonia buffer solution (pH 10), shake to mix, and adjust the pH to 10 ± 0.2.
 - 3) Add 1 ml of 4-aminoantipyrine solution (20 g/L), shake to mix, and after adding 1 ml of potassium hexacyanoferrate (III) solution, shake to mix well and leave to stand for about 10 min to allow formation of antipyrine dye.
 - 4) Wash and condition the hydrophobic column by flowing through it 10 ml of acetonitrile and 10 ml of water, and then pass the coloring solution in **3)** at the rate of 10 ml/min.
 - 5) Dry the column by aerating it for about 5 min.
 - 6) Flow 5 ml of acetonitrile through the column to elute antipyrin dye.
 - 7) Separately, as a blank test, perform the procedures in **2)** to **6)** using 50 ml of water.
 - 8) Using the acetonitrile eluate obtained in the blank test as a contrast solution, measure the absorbance of the acetonitrile eluate in **6)** near the wavelength of 475 nm.
 - 9) By reference to the working curve, determine the amount equivalent to phenol, and calculate the concentration of phenols (C₆H₅OH mg/L) in the sample.
- d) **Working curve** The working curve shall be prepared as follows.
- 1) Place a series of aliquots of phenol reference solution (C₆H₅OH 0.1 µg/ml) or phenol reference solution (C₆H₅OH 1 µg/ml) in stepwise increments so that the amount of phenol is 0.2 µg to 15 µg in as many 50-ml measuring cylinders (with stoppers), and add water to each to the 50-ml mark.
 - 2) Perform the procedures in **2)** to **8)** of **c)** to prepare a relation curve between the amount of phenol and the absorbance.

NOTE 5 Recovery rate of phenol should be checked beforehand by performing the procedures of **28.1.1 c)**, and **28.1.2.1 c)**, **28.1.2.2 c)** or **28.1.2.3 c)** using phenol reference solution (C₆H₅OH 10 µg/ml).

28.1.3 Flow analysis method Phenols in sample are determined by the CFA method in which distillation and coloration are performed based on the same principle as described in **28.1.1** and **28.1.2.1**, or the FIA method in which the distillate obtained in pretreatment (distillation) in **28.1.1** is coloured based on the same principle as described in **28.1.2.1**. With certain types of phenols, the generated antipyrine dye may fade away with time in an aqueous phase. Therefore, verify prior to performing the flow analysis that the set of conditions given in **JIS K 0170-5**, such as concentration of reagents and flow rate, are consistent with the conditions for the analysis performed according to **28.1.2.1**.

Determination range: C₆H₅OH: 0.01 mg/L to 1 mg/L, Repeatability: 10 % max.

The test procedure or other related matters shall be referred to in **JIS K 0170-5**, except that the method in **6.3.2** of the said standard shall be applied to the distillate obtained in pretreatment (distillation) specified in **28.1.1**, and the method in **6.3.4** and **6.3.5** of the said standard shall not be used.

31.2.1 a)

Replace “ 6) **Potassium hexacyanoferrate (III) solution**, in accordance with **28.1.2 a) 3).**” by “6) **Potassium hexacyanoferrate (III) solution**, in accordance with **28.1.2.1 a) 3).**”

32.3 b) 2)

Replace “**JIS B 7411-1**” by “**JIS B 7414**”.

32.4 b) 3)

Replace “**JIS B 7411-1**” by “**JIS B 7414**”.

Clause 33

Replace the entire clause by the following:

33 Residual chlorine Residual chlorine refers to both hypochlorous acid which is produced when chlorinating agent is dissolved in water, and chloroamine which is formed by reaction of this hypochlorous acid and ammonia. The former is called free residual chlorine and the latter, combined residual chlorine, and they are collectively called residual chlorine.

For the determination of residual chlorine, in the case of samples with low concentration of residual chlorine, the *o*-tolidine colorimetry, the diethyl-*p*-phenylenediammonium (DPD) colorimetry or the diethyl-*p*-phenylenediammonium (DPD) absorptiometry is applied, and in the case of samples with relatively high concentration of residual chlorine, the iodometry is applied.

This test shall be performed immediately after sampling.

The diethyl-*p*-phenylenediammonium (DPD) colorimetry described in this clause is in consistency with the second edition of **ISO 7393-2** published in 2017 and the iodometry, with the second edition of **ISO 7393-3** published in 1990.

NOTE: The corresponding International Standards relevant to this test method are as follows.

The symbols which denote the degree of correspondence in the contents between the corresponding International Standards and **JIS** are IDT (identical), MOD (modified), and NEQ (not equivalent) according to **ISO/IEC Guide 21-1**.

ISO 7393-2:2017 *Water quality—Determination of free chlorine and total chlorine—Part 2: Colorimetric method using N,N-diethyl-1,4-phenylenediamine, for routine control purposes* (MOD)

ISO 7393-3:1990 *Water quality—Determination of free chlorine and total chlorine—Part 3: Iodometric titration method for the determination of total chlorine* (MOD)

33.1 *o*-Tolidine colorimetry The 3,3'-dimethylbenzidine (*o*-tolidine) solution is added to the sample to react it with the residual chlorine in the sample. The yellow color developed by this reaction is compared with the reference color solution of residual chlorine in order to determine the residual chlorine. Distinction among residual chlorine, free residual chlorine, and combined residual chlorine can be made by treatment with sodium arsenite solution.

Determination range: Cl 0.01 mg/L to 2.0 mg/L, Repeatability: 5 % to 10 %

a) **Reagents** The following reagents shall be used.

- 1) **Water**, of A3 specified in **JIS K 0557** ⁽¹⁾.
- 2) ***o*-Tolidine solution** Dissolve 0.14 g of 3,3'-dimethylbenzidine dichloride (*o*-tolidine dihydrochloride) in 50 ml of water, and add this to 50 ml of hydrochloric acid (3+7) (prepared using hydrochloric acid specified in **JIS K 8180**) while stirring. Preserve this solution in a colored bottle. Do not use this solution after a lapse of 6 months or longer from preparation.
- 3) **Phosphate buffer solution (pH 6.5)** Heat disodium hydrogenphosphate specified in **JIS K 9020** at 110 °C for about 2 h, and allow to cool in a desiccator. Dissolve 22.86 g of this and 46.14 g of potassium dihydrogen phosphate specified in **JIS K 9007** in water to make 1 L. If precipitate has formed, separate it by filtration. Take 200 ml of this solution and add water to make 1 L.
- 4) **Potassium chromate-potassium dichromate solution** Dissolve 3.63 g of potassium chromate specified in **JIS K 8312** and 1.21 g of potassium dichromate specified in **JIS K 8517** in phosphate buffer solution (pH 6.5). Transfer it into a 1 000-ml volumetric flask, and add phosphate buffer solution (pH 6.5) to the mark.
- 5) **Residual chlorine reference color solution** Depending on the corresponding concentration of residual chlorine (Cl mg/L), place potassium chromate-potassium dichromate solution and phosphate buffer solution (pH 6.5) in a 100-ml color comparison tube in the ratio as shown in table 33.1, and mix. Preserve this solution in a dark place, and do not use when precipitate has formed in it.
- 6) **Sodium arsenite solution (5 g/L)** Dissolve 0.5 g of sodium metaarsenite in water to make 100 ml.

Note ⁽¹⁾ Check prior to test that the water to be used for this test is free from residual chlorine or does not consume chlorine according to the method described in NOTE 3.

b) **Implements** The following implements shall be used.

- 1) **Color comparison tube**, of 100 ml, flat-bottomed type with the mark of 100 ml drawn at the height of (200 ± 1.5) mm from the bottom.
- 2) **Stand for color comparison tubes**, for 100 ml tubes and provided with a milky plate at the bottom and on the side.

Table 33.1 Residual chlorine reference color solution (for liquid layer 200 mm)

Residual chlorine Cl mg/L	Potassium chromate-potassium dichromate solution ml	Phosphate buffer solution pH6.5 ml	Residual chlorine Cl mg/L	Potassium chromate-potassium dichromate solution ml	Phosphate buffer solution pH6.5 ml
0.01	0.18	99.82	0.70	7.48	92.52
0.02	0.28	99.72	0.80	8.54	91.46
0.05	0.61	99.39	0.90	9.60	90.40
0.07	0.82	99.18	1.00	10.66	89.34
0.10	1.13	98.87	1.10	12.22	87.78
0.15	1.66	98.34	1.20	13.35	86.65
0.20	2.19	97.81	1.30	14.48	85.52
0.25	2.72	97.28	1.40	15.60	84.40
0.30	3.25	96.75	1.50	16.75	83.25
0.35	3.78	96.22	1.60	17.84	82.16
0.40	4.31	95.69	1.70	18.97	81.03
0.45	4.84	95.16	1.80	20.09	79.91
0.50	5.37	94.63	1.90	21.22	78.78
0.60	6.42	93.58	2.00	22.34	77.66

c) **Procedure** The test procedure shall be as follows.

- 1) Place 5 ml of *o*-tolidine solution in a color comparison tube, add a suitable volume of sample ⁽²⁾ (containing 0.2 mg or less of residual chlorine), add water up to the mark of 100 ml, stopper quickly and shake to mix.
- 2) Allow to stand for 5 min ⁽³⁾ in a dark place.
- 3) Compare, by observing from above, this solution against residual chlorine reference color solutions and record the residual chlorine concentration *a* (Cl mg/L) of the matching reference color solution.
- 4) Take 5 ml of *o*-tolidine solution in another color comparison tube, add the same volume of the sample as used in 1), stopper quickly and shake to mix.
- 5) Within 5 s, add 5 ml of sodium arsenite solution (5 g/L), and shake to mix. Further add water up to the mark of 100 ml and shake to mix.
- 6) Compare this solution against residual chlorine reference color solutions and record the residual chlorine concentration *b* (Cl mg/L) of the matching reference color solution.
- 7) For a blank test, place 5 ml of sodium arsenite solution (5 g/L) in a 100-ml color comparison tube, add the same volume of the sample as used in 1), and shake to mix.
- 8) Add 5 ml of *o*-tolidine solution, shake to mix, and after adding water up to the mark of 100 ml, shake to mix.
- 9) Within 5 s, compare this solution against the residual chlorine reference color solutions and record the residual chlorine concentration *c*₁ (Cl mg/L) of the matching reference color solution.

- 10) After allowing to stand in a dark place for 5 min, compare this solution against the residual chlorine reference color solutions and record the residual chlorine concentration c_2 (Cl mg/L) of the matching the reference solution.
- 11) Calculate the concentration of residual chlorine, free residual chlorine, and combined residual chlorine according to the following formulas:

$$A = (a - c_2) \times \frac{100}{V}$$

$$B = (b - c_1) \times \frac{100}{V}$$

$$C = A - B$$

where,

- A : concentration of residual chlorine (Cl mg/L)
- a : concentration of residual chlorine obtained in **3)** (Cl mg/L)
- c_2 : concentration of residual chlorine obtained in **10)** (Cl mg/L)
- V : volume of sample (ml)
- B : concentration of free residual chlorine (Cl mg/L)
- b : concentration of residual chlorine obtained in **6)** (Cl mg/L)
- c_1 : concentration of residual chlorine obtained in **9)** (Cl mg/L)
- C : concentration of combined residual chlorine (Cl mg/L)

Notes ⁽²⁾ Alkaline sample shall be neutralized to a pH of about 7 by adding hydrochloric acid (1+5) and measuring with a pH meter. The pH value during coloring procedure should be always 1.3 or less.

⁽³⁾ For combined residual chlorine, this procedure requires 6 min at 0 °C, 3 min at 20 °C, and 2 min and 30 s at 25 °C, before maximum coloring is attained.

NOTES 1 If a blank test is not performed, presence of 0.3 mg/L or more of iron, 10 µg/L or more of manganese, or 0.3 mg/L or more of nitrite ion will interfere. To prevent the interference by iron and manganese, add to the sample 3 ml of 1,2-cyclohexanediaminetetraacetate solution (10 g/L) (prepared by dissolving 1.05 g of *trans*-1,2-cyclohexanediaminetetraacetate monohydrate in water to make 100 ml) per 100 ml of sample.

2 When using a commercially available residual chlorine measuring instrument, confirm that it is free from errors by comparing it with residual chlorine reference color solutions prior to use.

3 Confirm that the water to be used for this test contains no residual chlorine or consumes no chlorine according to either of the following procedures.

- 1) **Confirmation of absence of residual chlorine** Place approximately 45 ml of water [a) 1)] in a 50-ml color comparison tube, add approximately 0.5 g of potassium iodide specified in **JIS K 8913** and shake to mix. After a lapse of approximately 1 min, add 2 ml of phosphate buffer solution (pH 6.5) [prepared in accordance with **33.2 a) 4)**] and 0.5 g of DPD diluted powder [in accordance with **33.2 a) 3)**], shake to mix, and check that the solution develops no color. Alternatively, perform the procedures in 1) and 2) of **33.1 c)** to check that no color development occurs.
- 2) **Confirmation of no consumption of chlorine** Place approximately 45 ml of water [a) 1)] in a 50-ml color comparison tube, add one or two drops of sodium hypochlorite solution (effective chlorine 0.1 g/L) [prepared by diluting sodium hypochlorite solution (effective chlorine 10 g/L) in **42.2 a) 4)** 100 times], shake to mix, and allow to stand for approximately 2 min. Then, carry out the procedure of the phosphate buffer solution (pH 6.5) given in 1) and subsequent procedures to confirm that the solution colors.

33.2 Diethyl-*p*-phenylenediammonium (DPD) colorimetry Sample is combined with sulfuric acid *N,N*-diethyl-*p*-phenylenediammonium (DPD) in a color comparison tube. Reaction of residual chlorine in the sample with DPD causes the solution to develop a pink to pinkish red color, which is then compared against the residual chlorine reference color solutions to determine the amount of residual chlorine.

Determination range: Cl 0.05 mg/L to 2 mg/L, Repeatability: 5 % to 10 %

a) **Reagents** The following reagents shall be used.

- 1) **Water**, as specified in **33.1 a) 1)**.
- 2) **Potassium iodide**, as specified in **JIS K 8913**.
- 3) **DPD diluted powder** Grind 1.0 g of sulfuric acid *N,N*-diethyl-*p*-phenylenediammonium (*N,N*-diethyl-*p*-phenylenediamine sulfate) in an agate mortar. Add to this 24 g of sodium sulfate specified in **JIS K 8987**, mix well, transfer to a colored glass bottle, and preserve at 0 °C to 10 °C in a dark place away from moisture. Do not use colored chemicals.
- 4) **Phosphate buffer solution (pH 6.5)** Take 100 ml of potassium dihydrogen phosphate solution (0.2 mol/L) (prepared by dissolving 27.2 g of potassium dihydrogen phosphate specified in **JIS K 9007** in water to make 1 L), add sodium hydroxide solution (0.2 mol/L) (prepared by dissolving 8 g of sodium hydroxide specified in **JIS K 8576** in water to make 1 L) using a pH meter until the pH is 6.5, and add 0.13 g of *trans*-1,2-cyclohexanediaminetetraacetate monohydrate to dissolve it.
- 5) **C.I. Acid Red 265 solution** Heat C.I. Acid Red 265 [disodium 1-(4-methylbenzenesulfonamide)-7-(2-methylphenylazo)-8-hydroxy-3,6-naphthalenedisulfonate] at 105 °C to 110 °C for 3 h to 4 h, and allow to cool in a desiccator. Weigh 0.329 g of this to the nearest 1 mg, dissolve in a small volume of water, transfer into a 1 000-ml volumetric flask, and add water to the mark. Transfer 50 ml of this

solution to a 500-ml volumetric flask, and add water to the mark. Preserve at 0 °C to 10 °C in a dark place. Do not use this solution after a lapse of 6 months or longer from preparation.

- 6) **DPD residual chlorine reference color solution** Take C.I. Acid Red 265 solution into a 50-ml volumetric flask by reference to table 33.2, and add water to the mark. Transfer each solution into a 50-ml color comparison tube. Stopper tightly and preserve at 0 °C to 10 °C in a dark place. Do not use this solution after a lapse of 6 months or longer from preparation.

Table 33.2 DPD residual chlorine reference color solution (in 50 ml)

Residual chlorine Cl mg/L	C.I. Acid Red 265 solution ml
0.05	0.5
0.1	1.0
0.2	2.0
0.3	3.0
0.4	4.0
0.5	5.0
0.6	6.0
0.7	7.0
0.8	8.0
0.9	9.0
1.0	10.0
1.2	12.0
1.4	14.0
1.6	16.0
1.8	18.0
2.0	20.0

- b) **Implements** The following implements shall be used.

- 1) **Color comparison tube**, of 50 ml, flat-bottomed type with the mark of 50 ml drawn at the height of (150 ± 1) mm from the bottom.
- 2) **Stand for color comparison tubes**, for 50 ml tube and provided with a milky plate at the bottom and on the side.

- c) **Procedure** The test procedure shall be as follows.

- 1) Place 2.5 ml of phosphate buffer solution (pH 6.5) in a 50-ml color comparison tube and add 0.5 g of DPD diluted powder. Then, add a suitable volume (containing 0.1 mg or less of residual chlorine) of sample ⁽⁴⁾ to it, and add water to the mark.
- 2) After stoppering, shake well to mix, and within 1 min ⁽⁵⁾, observe the coloring of the solution from sideways to compare it with DPD residual chlorine reference color solutions. Obtain the concentration of residual chlorine (Cl mg/L) corresponding to the matching DPD residual chlorine reference color solution, and taking this as free residual chlorine, calculate the concentration of free residual chlorine (Cl mg/L) in the sample.

- 3) Upon finishing the procedure in **2)**, add about 0.5 g of potassium iodide, stopper and shake to dissolve it. Allow to stand for about 2 min, and compare the coloring of the solution, similarly to **2)**, with the residual chlorine reference color solutions. Obtain the concentration of residual chlorine (Cl mg/L) corresponding to the matching residual chlorine reference color solution, and calculate the concentration of residual chlorine in the sample.
- 4) The concentration of combined residual chlorine (Cl mg/L) shall be calculated according to the following formula.

Concentration of combined residual chlorine (Cl mg/L) = residual chlorine (Cl mg/L) – free residual chlorine (Cl mg/L)

- Notes ⁽⁴⁾ When a sample has strong acidity or alkalinity, its pH should be adjusted to about 6.5 by using sodium carbonate solution (50 g/L) (prepared using the sodium carbonate specified in **JIS K 8625**) or hydrochloric acid (1+11) [prepared in accordance with **21 a) 2)**].
- ⁽⁵⁾ It includes the time for agitating. Sodium sulfate in DPD diluted powder need not be completely dissolved.

NOTES 4 When using a commercially available residual chlorine measuring instrument or glass color standard scale, check before use that it is free from errors by comparison with DPD residual chlorine reference color solutions.

- 5 The correction for interference caused by manganese oxide in the sample is as follows.
 - 1) Take 100 ml of the sample, add 1 ml of sodium metaarsenite solution (2 g/L) (prepared by using sodium metaarsenite) or thioacetamide (ethanethioamide) solution (2.5 g/L), and shake to mix.
 - 2) Carry out the procedures given in **1)** and **2)** of **c)** by using this solution, and obtain the concentration of residual chlorine from the color development caused by manganese oxide.
 - 3) Using the value obtained, correct the concentration of free residual chlorine and the concentration of residual chlorine.
- 6 Chlorine (IV) dioxide is included in the value of residual chlorine and free residual chlorine.
- 7 The oxidation of DPD is caused not only by chlorine compounds, but also by other oxidizers, such as bromine, iodine, bromoamines, iodoamines, ozone, hydrogen peroxide, chromate, manganese oxide, nitrite, iron (III) ion, and copper ion. In this method, however, up to 2 mg/L of copper ion, 3 mg/L of iron (II) ion, 4 mg/L of aluminium and 4 mg/L of nitrite ion will make no interference.
- 8 If the sample is sea water, some microalgae contained in it may react with DPD and develop color. To prevent this from occurring, filter the sample naturally or under pressure through a filter medium such as glass fibre or organic polymer (with pore diameter of 100 µm or smaller), and use an adequate volume of the filtrate for the procedure from **c) 1)** on.

The filter medium and implements used for filtration should be washed with the sample prior to use to prevent the loss of residual chlorine at the liquid-contact surface, and should also be verified not to change the concentration of residual chlorine.

NOTE 9 After the operation in c) 1), the sample should be protected from sunlight since exposure to sunlight may advance the color development.

33.3 Iodometry Iodine isolated by the reaction between residual chlorine and potassium iodide is titrated with sodium thiosulfate solution. Based on the results of the titration, the residual chlorine is determined. If the oxidizing substance which isolates iodine coexists in the sample, this also is determined as residual chlorine.

Determination range: Cl 0.1 mg min.

a) **Reagents** The following reagents shall be used.

- 1) **Water**, as specified in 33.1 a) 1).
- 2) **Potassium iodide**, as specified in 33.2 a) 2).
- 3) **Acetic acid (1+1)**, prepared by using the acetic acid specified in JIS K 8355.
- 4) **Starch solution (10 g/L)**, in accordance with 19 a) 5).
- 5) **10 mmol/L sodium thiosulfate solution**, in accordance with 19 a) 9).

b) **Procedure** The test procedure shall be as follows.

- 1) Place a suitable a volume (containing 0.1 mg to 7 mg as Cl) of sample ⁽²⁾ in a 500-ml Erlenmeyer flask with a ground stopper, add water to make about 300 ml, and add 1 g of potassium iodide and 5 ml of acetic acid (1+1).
- 2) Stopper the flask and shake to mix, and allow to stand in a dark place for about 5 min.
- 3) Titrate isolated iodine with 10 mmol/L sodium thiosulfate solution. When the yellow color of the solution has become faint, add 1 ml of starch solution (10 g/L) as an indicator and continue the titration until the blue color of iodo-starch disappears.
- 4) Perform a blank test by carrying out the procedures in 1) to 3) using 100 ml of water.
- 5) Calculate the concentration of residual chlorine (Cl mg/L) in the sample according to the following formula:

$$A = (a - b) \times f \times \frac{1000}{V} \times 0.3545$$

where,

A : concentration of residual chlorine (Cl mg/L)

a : volume of 10 mmol/L sodium thiosulfate solution required for titration (ml)

b : volume of 10 mmol/L sodium thiosulfate solution required for blank test (ml)

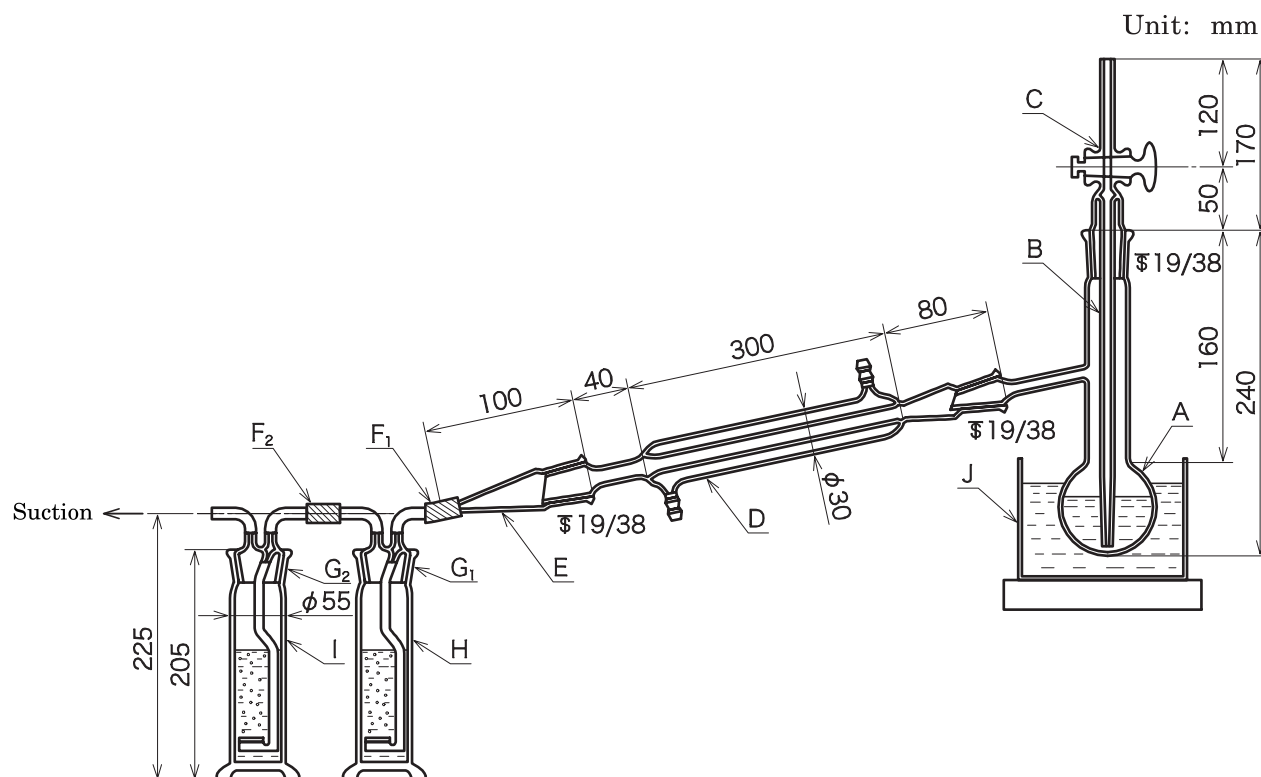
f : factor of 10 mmol/L sodium thiosulfate solution

V : volume of sample (ml)

0.354 5 : mass of residual chlorine corresponding to 1 ml of
10 mmol/L sodium thiosulfate solution (mg)

NOTE 10 When the test is difficult due to severe coloring or turbidity of the sample, separation of residual chlorine may be performed before measurement according to the following procedure.

- 1) Place a suitable volume (containing 2 mg or more as Cl) of the sample in a 200-ml distillation flask shown in figure 33.1, add sulfuric acid (1+15) to adjust the pH to 0.9 to 1.0, add water to make about 80 ml, and connect the flask to a distillation apparatus.
- 2) Add 20 ml of 10 mmol/L sodium thiosulfate solution in a gas washing bottle (H) and 5 ml of the same solution in a gas washing bottle (I), and add water to each to make total 50 ml. Further, add to each of them 4 ml of acetate buffer solution (pH 3.5) [dissolve 240 g of sodium acetate trihydrate specified in **JIS K 8371** in about 300 ml of water, add 460 ml of acetic acid, and add water to make 1 L] and 0.1 g of potassium iodide, and shake to mix.
- 3) Place the distillation flask in a thermostatic bath (J) at 40 °C, and aerate gently for about 40 min. Transfer the solution in the gas washing bottles into a 300-ml Erlenmeyer flask, wash the inside of the bottles with water, and join the washings to the above solution. Add to this 10 ml of iodine solution (dissolve 12 g of potassium iodide specified in **JIS K 8913** in a small volume of water, add 4 g of iodine specified in **JIS K 8920** to dissolve, and add water to make total 1 L).
- 4) Titrate excess iodine with 10 mmol/L sodium thiosulfate solution, and when the solution turns faint yellow, add 1 ml of starch solution (10 g/L) as an indicator, and continue the titration until the blue color of iodo-starch disappears.
- 5) For a blank test, place 25 ml of 10 mmol/L sodium thiosulfate solution in a 300-ml Erlenmeyer flask, and add 8 ml of acetate buffer solution (pH 3.5), 0.2 g of potassium iodide and about 120 ml of water, and shake to mix. Add to this 10 ml of iodine solution, and titrate it, similarly to the case of the sample, with 10 mmol/L sodium thiosulfate solution. Calculate the concentration of residual chlorine (Cl mg/L) in the sample according to the formula in **b) 5**).



- A : Distillation flask (with interchangeable ground branch)
200 ml
- B : Center tube (inside diameter at tip is about 1 mm)
- C : One-way cock
- D : Liebig condenser with interchangeable ground joint
(200 mm to 300 mm)
- E : Adapter with interchangeable ground joint

- F₁, F₂ : Rubber tube
- G₁, G₂ : Interchangeable ground joint
- H, I : Gas washing bottle with interchangeable ground filter plate (250 ml)
- J : Thermostatic bath

Figure 33.1 Example of distillation apparatus (with interchangeable ground joint)

33.4 Diethyl-*p*-phenylenediammonium (DPD) absorptiometry Sulfuric acid *N,N*-diethyl-*p*-phenylenediammonium (DPD) is added to the sample and the absorbance of the pink to pinkish red color developed by the reaction of DPD with residual chlorine in the sample is measured at the wavelength near 510 nm (or 555 nm) to determine residual chlorine.

Determination range: Cl 2.5 µg to 150 µg, Repeatability: 5 % to 10 %

a) **Reagents** The following reagents shall be used.

- 1) **Water**, as specified in 33.1 a) 1).
- 2) **Diluted water** Add approximately 3 ml of chlorine water (concentration: approximately 50 mg/L) to 1 L of water, allow to stand for 1 h, and then boil or expose to ultraviolet ray irradiation to remove residual chlorine.
- 3) **Potassium iodide**, in accordance with 33.2 a) 2).
- 4) **DPD diluted powder**, in accordance with 33.2 a) 3).

- 5) **Phosphate buffer solution (pH 6.5)**, in accordance with **33.2 a) 4)**.
- 6) **0.1 mol/L sodium thiosulfate solution**, in accordance with **19 a) 8)**.
- 7) **10 mmol/L sodium thiosulfate solution**, in accordance with **19 a) 9)**. Use the factor calculated for 0.1 mol/L sodium thiosulfate solution given in **19 a) 8)**. This solution shall not be used after a lapse of 12 h or longer from preparation.
- 8) **Starch solution (10 g/L)**, in accordance with **19 a) 5)**.
- 9) **Chlorine reference solution** The preparation of chlorine water, the measurement of effective chlorine concentration and the preparation of chlorine reference solution shall be as follows.

The effective chlorine concentration of the chlorine reference solution shall be measured before each use.

- 9.1) **Preparation of chlorine water** Dissolve sodium hypochlorite solution [effective chlorine 7 % to 12 % (mass percentage)] in water. The chlorine water may be prepared by other methods.
- 9.2) **Measurement of effective chlorine concentration**
 - 9.2.1) Place 100 ml of the chlorine water prepared in **9.1)** in a 200-ml Erlenmeyer flask with a ground stopper and add 1 g of potassium iodide and 5 ml of acetic acid (1+1) (prepared by using acetic acid specified in **JIS K 8355)**.
 - 9.2.2) Shake to mix after stoppering and leave to stand in a dark place for 5 min.
 - 9.2.3) Titrate the isolated iodine with 0.1 mol/L sodium thiosulfate solution. After the yellow color of the solution has become faint, add 1 ml of starch solution (10 g/L) as an indicator and continue the titration until the blue color that has developed vanishes.
 - 9.2.4) Calculate the concentration of effective chlorine (Cl mg/L) contained in chlorine water according to the following formula:

$$C = a \times f_1 \times \frac{1\,000}{V} \times 3.545$$

where,

C : concentration of effective chlorine (Cl mg/L)

a : volume of 0.1 mol/L sodium thiosulfate solution required for titration (ml)

f_1 : factor of 0.1 mol/L sodium thiosulfate solution

V : volume of chlorine water used in **9.2.1)** (ml)

3.545: mass of chlorine corresponding to 1 ml of 0.1 mol/L sodium thiosulfate solution (mg)

- 9.3) **Chlorine reference solution (Cl 50 µg/ml)** Place, in a 500-ml volumetric flask, the chlorine water of which the concentration of effective chlorine has been determined in **9.2)** so as to be equivalent to 25 mg of chlorine and add the diluted water to the mark. The standardization of correct concentration shall be as follows:

Take 100 ml of this solution and carry out the procedures of **9.2.1** to **9.2.3**. For the titration, 10 mmol/L sodium thiosulfate solution shall be used. Calculate the accurate concentration of chlorine reference solution (Cl 50 µg/ml) according to the following formula:

$$C = a \times f_1 \times \frac{1\,000}{V} \times 0.354\,5$$

where, C : concentration of effective chlorine (Cl mg/L)
 a : volume of 10 mmol/L sodium thiosulfate solution required for titration (ml)
 f_1 : factor of 10 mmol/L sodium thiosulfate solution
 V : volume of chlorine reference solution used for titration (Cl 0.05 mg/ml) (ml)
0.354 5: mass of chlorine corresponding to 1 ml of 10 mmol/L sodium thiosulfate solution (mg)

9.4) **Chlorine reference solution (Cl 5 µg/ml)** Place 20 ml of chlorine reference solution (Cl 50 µg/ml) in a 200-ml volumetric flask and add the diluted water to the mark. Prepare this solution immediately before use.

b) **Apparatus** The following apparatus shall be used.

1) **Photometer** Spectrophotometer or photoelectric photometer

c) **Procedure** The test procedure shall be as follows.

- 1) Carry out the procedure in **33.2 c) 1)** using an adequate volume of sample ⁽⁴⁾.
- 2) Stopper, shake well to mix, take a part of this solution in an absorption cell within 1 min ⁽⁵⁾, and measure the absorbance at a wavelength near 510 nm (or 555 nm) by using water as a contrast solution.
- 3) Obtain the amount of chlorine (Cl µg) from the working curve and by regarding this as free residual chlorine, calculate the concentration of free residual chlorine (Cl mg/L) in sample.
- 4) Then, add approximately 0.5 g of potassium iodide to the remaining solution of **2)**, stopper and dissolve by shaking. After leaving to stand for approximately 2 min, take a part of this solution in an absorption cell and measure the absorbance at a wavelength near 510 nm (or 555 nm) using water as the contrast solution.
- 5) Determine the amount of chlorine (Cl µg) with reference to the working curve and by regarding this as the residual chlorine, calculate the concentration of residual chlorine (Cl mg/L) in sample.
- 6) Calculate the concentration of combined residual chlorine (Cl mg/L) according to **33.2 c) 4)**.

d) **Working curve** The working curve shall be prepared as follows.

- 1) Perform the procedures in **1)** and **2)** of **c)** using 0.5 ml to 30 ml of chlorine reference solution (Cl 5 µg/ml) to measure the absorbance, and plot the relation curve between the amount of chlorine (Cl) and the absorbance.

NOTES 11 See NOTE 8.

12 See NOTE 9.

Clause 34

Replace the entire clause by the following:

34 Fluorine compound Fluorine compound is a generic term for fluoride ion, metal fluoride, and so on, and is expressed in terms of fluoride ion. For the determination of fluoride ion, the lanthanum-alizarin complexone absorptiometry, ion-selective electrode method, ion chromatography or the flow analysis by lanthanum-alizarin complexone coloring is applied.

The distillation procedure described in this clause is in consistency with the first edition of **ISO 10359-2** published in 1994, the ion-selective electrode method, in consistency with the first edition of **ISO 10359-1** published in 1992, and the ion chromatography, in consistency with the second edition of **ISO 10304-1** published in 2007.

NOTE: The corresponding International Standards relevant to this test method are as follows.

The symbols which denote the degree of correspondence in the contents between the corresponding International Standards and **JIS** are IDT (identical), MOD (modified), and NEQ (not equivalent) according to **ISO/IEC Guide 21-1**.

ISO 10359-1:1992 *Water quality—Determination of fluoride—Part 1: Electrochemical probe method for potable and lightly polluted water* (MOD)

ISO 10359-2:1994 *Water quality—Determination of fluoride—Part 2: Determination of inorganically bound total fluoride after digestion and distillation* (MOD)

ISO 10304-1:2007 *Water quality—Determination of dissolved anions by liquid chromatography of ions—Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate* (MOD)

34.1 Lanthanum-alizarin complexone absorptiometry Fluorine compound is distilled and separated, and the complex of lanthanum (III) and alizarin complexone are added, which react with fluoride ion and generate a blue colored compound complex. The absorbance of this blue colored compound complex is measured and fluoride ion is determined. The fluorine compound is expressed in terms of the determined concentration of fluoride ion.

34.1.1 Pretreatment (distillation method) Fluorine compounds are separated as fluoride ion by steam distillation.

a) **Reagents** The following reagents shall be used.

- 1) **Perchloric acid** Heat the perchloric acid specified in **JIS K 8223** until white fumes form, and allow to cool.
- 2) **Sulfuric acid** Heat the sulfuric acid specified in **JIS K 8951** until white fumes form, and allow to cool.
- 3) **Phosphoric acid**, specified in **JIS K 9005**.

- 4) **Sodium hydroxide solution (100 g/L)**, in accordance with **28.2.1 a) 3)**.
- 5) **Silicon dioxide**, specified in **JIS K 8885** ⁽¹⁾.
- 6) **Phenolphthalein solution (5 g/L)**, in accordance with NOTE 2 to clause **15**.

Note ⁽¹⁾ Employ that of crystalline, with the particle size approximately 100 μm to 150 μm . When quality is unknown, heat it in a platinum crucible at 1 150 °C or higher for about 1 h and allow to cool in a desiccator prior to use. In this case, using 50 ml of fluoride ion reference solution (F^- 2 $\mu\text{g/ml}$), check the recovery rate by carrying out the procedures in **2)** to **5)** of **c)** and **1)** to **5)** of **34.1.2 c)**.

b) **Apparatus** The following apparatus shall be used.

- 1) **Distillation apparatus**, as exemplified in figure 34.1.

c) **Distillation** Distillation shall be carried out as follows.

The distillation procedure described in NOTE 1 may be used if proven to achieve a recovery rate of 80 % to 120 % by testing a sample to which a definite volume of fluoride ion reference solution has been added.

- 1) Place a suitable volume (containing 30 μg or more as F^-) of sample in a porcelain basin or a beaker, add two or three drops of phenolphthalein solution (5 g/L), add drops of sodium hydroxide solution (100 g/L) to make the solution weak alkaline, and heat it to concentrate to about 30 ml.

For the test of dissolved fluorine compounds, use the sample filtered in **3.2**.

- 2) Wash it into a distillation flask shown in figure 34.1 with about 10 ml of water. Add about 1 g of silicon dioxide, 1 ml of phosphoric acid, and 40 ml of perchloric acid or 30 ml of sulfuric acid and add boiling chips (2 mm to 3 mm in grain size). Pour 20 ml of water ⁽²⁾ into a 250-ml volumetric flask to be used as a receiver, and keep the tip of the back-flow stopper under water.
- 3) Heat the distillation flask with direct flame, and when the temperature of the liquid in the distillation flask has reached about 140 °C, start to pass the steam.
- 4) Adjusting the distillation temperature to 145 °C $\pm$ 5 °C and distilling rate to 3 ml/min to 5 ml/min, perform distillation until about 220 ml of distillate has been collected in the receiver.
- 5) Disconnect the condenser and back-flow stopper, wash the inner pipe of the condenser and inside and outside surfaces of the back-flow stopper with a small amount of water. Put the washings in the receiver, and add water up to the mark.

Note ⁽²⁾ When the sample contains a large amount of halogenide other than fluoride ion, add four to five drops of sodium hydroxide solution (40 g/L) [prepared in accordance with **21 a) 3)**] and two or three drops of phenolphthalein solution (5 g/L). If necessary, add drops of sodium hydroxide solution (40 g/L) to the solution in the receiver so that the faint red color of the solution is maintained throughout the distillation.

In this case, upon completion of distillation, drip sulfuric acid (1+35) [prepared in accordance with **30.1.1 a) 2)**] until faint red color disappears, and then carry out the procedure in **5)**.

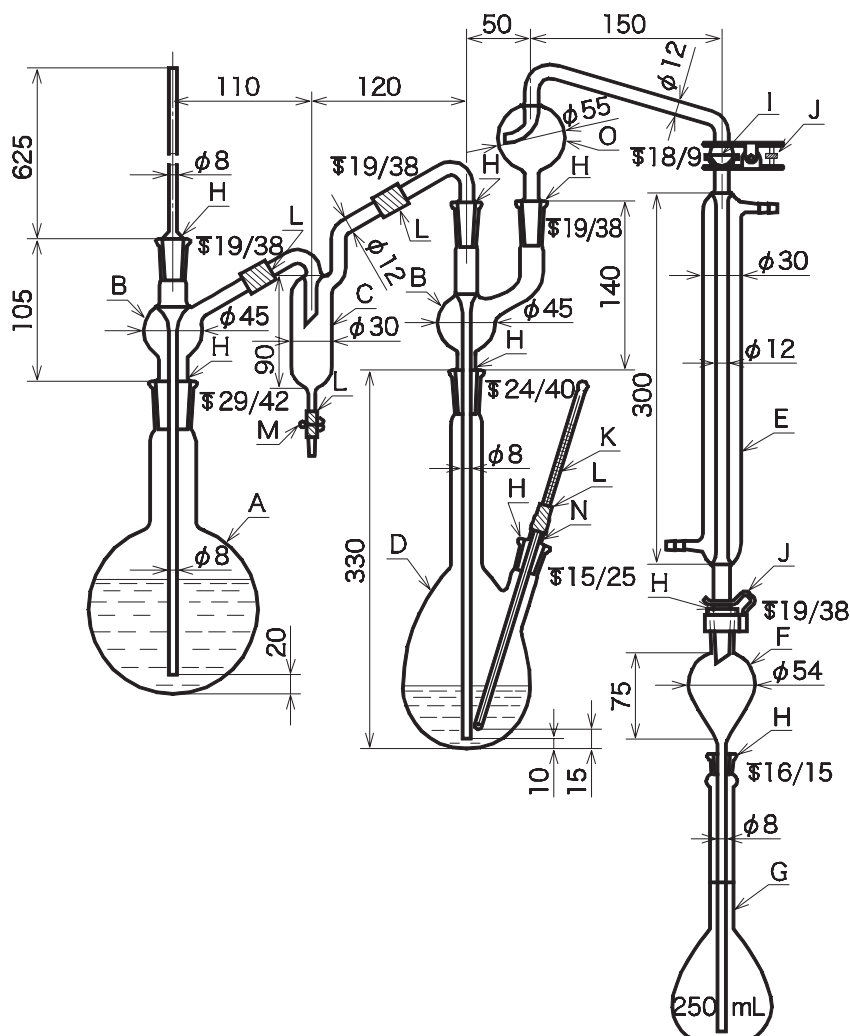
NOTE 1 The distillation procedure using a small distillation apparatus is as follows. An example of a small distillation apparatus is shown in figure 34.2. The distillate obtained by this procedure is not applicable for the method specified in **34.2**.

- 1) Place a suitable volume (containing 30 μg or more as F^- , or 10 μg or more in the case of performing flow analysis after distillation) of sample in a porcelain basin or a beaker, add two or three drops of phenolphthalein solution (5 g/L), add drops of sodium hydroxide solution (100 g/L) to make the solution weak alkaline, and heat it to concentrate to about 5 ml to 10 ml.
- 2) Wash this concentrated sample into a distillation vessel shown in figure 34.2 with a small amount of water and make up the volume to 10 ml to 15 ml. Gently add about 0.25 g of silicon dioxide, 0.5 ml of phosphoric acid and 12 ml of perchloric acid or 0.5 ml of phosphoric acid and 8 ml of sulfuric acid. Set a distillation tube and a condenser to the distillation vessel. If perchloric acid has been added, add 20 ml of water, several drops of sodium hydroxide solution and phenolphthalein solution to a 100 ml graduated receiver with a stopper and maintain the tip of the condenser under water.

If sulfuric acid has been added, use a 50 ml graduated receiver with a stopper and 5 ml of water instead. Drop sodium hydroxide solution in the solution in the receiver as necessary to maintain the faint red color of the solution throughout the distillation.

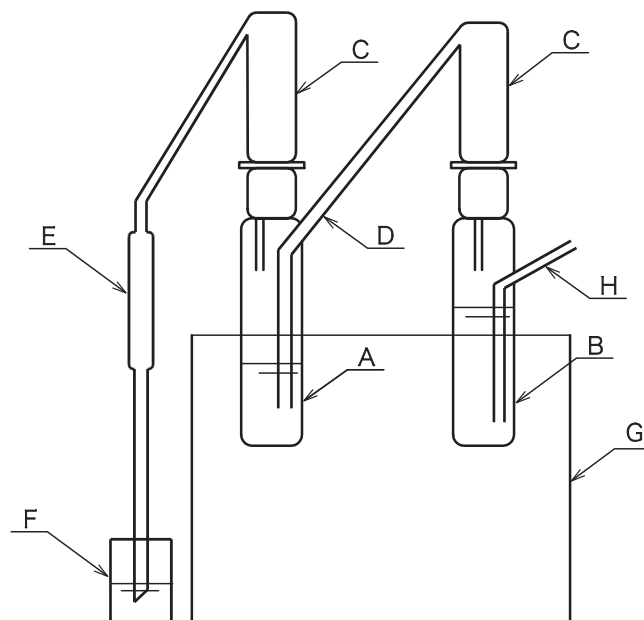
- 3) Install the distillation vessel and steam generating container in the heating equipment heated at 170 °C to 210 °C beforehand (optimum temperature differs depending on the apparatus), and pass air in the steam generation container at 0.1 L/min to 0.5 L/min to provide a stable supply of steam inside the distillation vessel.
- 4) Adjusting the distilling rate to 1.0 ml/min to 1.6 ml/min, perform distillation until about 70 ml of distillate, or about 45 ml of distillate in the case of using sulfuric acid, has been collected in the receiver.
- 5) After the distillation, disconnect the condenser and other devices, wash the inner pipe of the condenser with a small volume of water. Put the washings in the receiver, and add water to make the total volume 100 ml, or 50 ml in the case of using sulfuric acid.

Unit: mm



- | | |
|--|--|
| A : Steam generating flask 1 000 ml | I : Interchangeable spherically ground joint |
| B : Connecting and introducing tube | J : Fixing spring |
| C : Trap | K : Thermometer 200 °C |
| D : Distillation flask 500 ml | L : Rubber tube |
| E : Liebig condenser 300 mm | M : Pinch cock |
| F : Back-flow stopper (approx. 50 ml) | N : Stopper for inserting thermometer |
| G : Receiver (250-ml volumetric flask) | O : Trap sphere (Kjeldahl type) |
| H : Interchangeable ground joint | |

Figure 34.1 Example of distillation apparatus



- A : Distillation vessel (made of heat-resistant glass, 50 ml to 80 ml in capacity)
 B : Steam generating container (50 ml to 80 ml in capacity)
 C : Distillation tube (capable of gas-liquid separation)
 D : Connecting tube (capable of supplying steam into the distillation vessel)
 E : Condenser
 F : Receiver (e.g. 50-ml measuring cylinder with a stopper).
 G : Heating equipment (capable of controlling to 170 °C to 210 °C)
 H : Air introduction port

Figure 34.2 Example of small distillation apparatus

34.1.2 Determination method by lanthanum-alizarin complexone colouring

The fluoride ion in the distillate obtained in 34.1.1 is determined by the lanthanum-alizarin complexone absorptiometry. This method is hardly influenced by anion but susceptible to interference by cation, in particular, aluminium, cadmium, cobalt, iron, nickel, beryllium, lead, etc. To counter this interference, distillation is performed prior to analysis to separate fluoride ion.

Determination range: F^- 4 µg to 50 µg, Repeatability: 3 % to 10 %

a) **Reagents** The following reagents shall be used.

1) **Lanthanum-alizarin complexone solution** ⁽³⁾, prepared as follows:

- Dissolve 0.192 g of alizarin complexone (1,2-dihydroxyanthraquinon-3-ilmethylamin-*N,N*-diacetate dihydrate) in the mixture of 4 ml of ammonia solution (1+10) (prepared by using ammonia solution specified in **JIS K 8085**) and 4 ml of ammonium acetate solution (200 g/L) (prepared by using ammonium acetate specified in **JIS K 8359**).
- Add this solution, while stirring, to the sodium acetate solution (prepared by dissolving 41 g of sodium acetate trihydrate specified in **JIS K 8371** in 400 ml of water, and adding 24 ml of acetic acid specified in **JIS K 8355**).

— To this solution, add, while stirring, 400 ml of acetone specified in **JIS K 8034** gradually, further add lanthanum solution [prepared by heating to dissolve 0.163 g of lanthanum (III) oxide in 10 ml of hydrochloric acid (1+5) (prepared by using hydrochloric acid specified in **JIS K 8180**)], and stir. After allowing it to cool, adjust the pH to about 4.7 with acetic acid or ammonia solution specified in **JIS K 8085** using a pH meter, and add water to make 1 L.

2) **Fluoride ion reference solution (F^- 100 mg/L)** Place sodium fluoride of reference material for volumetric analysis specified in **JIS K 8005** in a platinum dish, heat at 500 °C for about 1 h, and allow it to cool in a desiccator. Take 0.221 g of NaF (100 %), and dissolve it in a small amount of water. Transfer it into a 1 000-ml volumetric flask, and add water to the mark. Store this solution in a polyethylene bottle.

3) **Fluoride ion reference solution (F^- 2 µg/ml)** Place 10 ml of fluoride ion reference solution (F^- 100 mg/L) in a 500-ml volumetric flask, and add water to the mark. Store in a polyethylene bottle and use within 1 month of preparation.

Note ⁽³⁾ A commercially available solution may be used. If using Alfusone, dissolve 2.5 g of it in water to make 50 ml. Prepare immediately before use.

Information: The name of the product, Alfusone (trade name), is given for the convenience of users of this Standard and does not constitute an endorsement of a particular product.

b) **Apparatus** The following apparatus shall be used.

1) **Photometer** Spectrophotometer or photoelectric photometer

c) **Determination** The following procedure shall be used.

- 1) Transfer a suitable volume (containing 4 µg to 50 µg as F^-), but not more than 30 ml, of the distillate obtained as a result of distillation according to **34.1.1 c)** to a 50-ml volumetric flask.
- 2) Add 20 ml of lanthanum-alizarin complexone solution ⁽⁴⁾, add water to the mark, shake to mix, and leave to stand for about 1 h.
- 3) Separately, place 30 ml of water in a 50-ml volumetric flask, and carry out the procedure in **2)**.
- 4) Transfer a part of the solution obtained in **2)** into an absorption cell, and measure the absorbance near the wavelength of 620 nm by using the solution obtained in **3)** as a contrast solution.
- 5) Determine the amount of fluoride ion by reference to the working curve, and calculate the concentration of fluoride ion (F^- mg/L) in the sample.

Note ⁽⁴⁾ When using the Alfusone solution prepared as described in Note ⁽³⁾, add 5 ml of it and 10 ml of acetone specified in **JIS K 8034** to the solution in **1)**, and then add water to the mark.

d) **Working curve** The working curve shall be prepared as follows.

- 1) Place a series of aliquots in stepwise increment ranging from 2 ml to 25 ml of the fluoride ion reference solution (F^- 2 µg/ml) in as many 50-ml volumetric flasks.

- 2) Perform the procedures in 2) to 4) of c) to measure the absorbance, and prepare a relation curve between the amount of fluoride ion (F^-) and the absorbance.

34.2 Ion-selective electrode method Fluorine compound is distilled and separated in pretreatment. With addition of buffer solution (control solution of total ionic strength), the pH is adjusted to 5.2 ± 0.2 and the electric potential is measured by using the fluoride ion-selective electrode as an indicator electrode to determine fluoride ion. This procedure does not apply to the distillate described in NOTE 1.

NOTE 2 When determining the dissolved fluoride ion in a clean sample not containing interfering substance, the sample may be filtered instead of being distilled, and analyzed according to the procedure in NOTE 3. It should be noted, however, that by this method, both dissolved fluoride ion and complex ion which easily becomes fluoride ion are determined. Further, this pretreatment method is not applicable to contaminated drainage.

Determination range: F^- 0.1 mg/L to 100 mg/L, Repeatability: 5 % to 20 %

a) **Reagents** The following reagents shall be used.

- 1) **Buffer solution (pH 5.2)** Dissolve 58 g of sodium chloride specified in **JIS K 8150** and 1 g of diammonium hydrogen citrate specified in **JIS K 8284** in 500 ml of water, add 50 ml of acetic acid specified in **JIS K 8355**, add drops of sodium hydroxide solution (200 g/L) (prepared by using sodium hydroxide specified in **JIS K 8576**) to adjust its pH to 5.2 using a pH meter, and add water to make 1 L.
- 2) **Fluoride ion reference solution (F^- 100 mg/L)**, in accordance with **34.1.2 a) 2)**. Store in a plastic bottle and use within 1 month of preparation.
- 3) **Fluoride ion reference solution (F^- 10 mg/L)** Place 20 ml of fluoride ion reference solution (F^- 100 mg/L) in a 200-ml volumetric flask, and add water to the mark. Prepare this solution immediately before use.
- 4) **Fluoride ion reference solution (F^- 1 mg/L)** Place 20 ml of fluoride ion reference solution (F^- 10 mg/L) in a 200-ml volumetric flask, and add water to the mark. Prepare this solution immediately before use.
- 5) **Fluoride ion reference solution (F^- 0.1 mg/L)** Place 20 ml of fluoride ion reference solution (F^- 1 mg/L) in a 200-ml volumetric flask, and add water to the mark. Prepare this solution immediately before use.

b) **Implements and apparatus** The following implements and apparatus shall be used.

- 1) **Potentiometer**, capable of resolving the potential differences of 0.1 mV or smaller. High input resistance potentiometer (e.g. digital pH-mV meter, pH-mV meter with magnifying span, potentiometer for ion-selective electrode).
- 2) **Indicator electrode** Fluoride ion-selective electrode, of which the electromotive force response using the reference solution is not less than 55 mV per decade change in fluoride ion concentration at 25 °C ⁽⁵⁾.
- 3) **Reference electrode** Silver/silver chloride electrode ⁽⁶⁾
- 4) **Measuring container**, of capacity 100 ml, made of polypropylene, and fitted with a thermostatted jacket.

- 5) **Thermostatic bath**, capable of supplying water to the jacket of measuring container at the temperature of $25\text{ }^{\circ}\text{C} \pm 0.2\text{ }^{\circ}\text{C}$.
- 6) **Magnetic stirrer**, with a polytetrafluoroethylene (PTFE)-coated stirring bar.

Notes ⁽⁵⁾ An electrode shall be submerged in fluoride ion reference solution (F^- 0.1 mg/L) until the instrument reading has stabilized, immediately before use. It should be noted that impairment on the sensitive membrane of an indicator electrode can cause lessening of the gradient (potential inclination) of the working curve and can also reduce the response speed. The contamination on the sensitive membrane of an indicator electrode, which may reduce the response speed, shall be wiped off with absorbent cotton or a soft paper moistened with ethanol (95), then washed away with water.

- ⁽⁶⁾ Choose the reference electrode with small resistance. The most typically used are single-junction sleeve type and ceramics type electrodes which reduce the liquid-liquid junction potential. Being small in resistance, a sleeve type electrode would be the optimum choice, but it should be adequately tightened for effective use; overtightening will result in larger resistance, and loose tightening will allow excessive discharge of the liquid. If using ceramics type electrode, one intended for an ion-selective electrode should be selected among other products that may have larger resistance. A ceramics type electrode may have larger resistance when it is dry or contaminated, and due attention should be paid. These electrodes shall have been dipped in the same solution as their internal liquids. When potassium chloride solution (saturated) is used for the internal liquid of the reference electrode, be aware of the possibility that drop in the solution temperature can cause the precipitate of crystal of potassium chloride to be formed, which will then adhere to the electrode and result in larger resistance.

- c) **Working curve** The working curve shall be prepared as follows.

Depending on the concentration to be measured, however, reference solutions covering other concentration range than below may be required.

- 1) Place 100 ml of fluoride ion reference solution (F^- 0.1 mg/L) in a measuring container and add 10 ml of buffer solution (pH 5.2) ⁽⁷⁾.
- 2) Send water from the thermostatic bath and maintain the solution in this measuring container at $25\text{ }^{\circ}\text{C} \pm 0.5\text{ }^{\circ}\text{C}$.
- 3) Submerge and fix an indicator electrode and a reference electrode, put in a stirring bar and vigorously agitate ⁽⁹⁾ using a magnetic stirrer ⁽⁸⁾, but with care not to allow bubbles to reach the electrodes.
- 4) Check the temperature of the solution and measure the potential with a potentiometer ⁽¹⁰⁾.
- 5) Place 100 ml of fluoride ion reference solution (F^- 1 mg/L), fluoride ion reference solution (F^- 10 mg/L) and fluoride ion reference solution (F^- 100 mg/L) in three separate measuring containers and add 10 ml of buffer solution (pH 5.2) to each ⁽⁷⁾.

- 6) Carry out the procedures of **2)** to **4)** and measure the potential of respective fluoride ion reference solutions ⁽¹¹⁾ ⁽¹²⁾.
- 7) Plot the logarithm of the concentration of fluoride ion on abscissa and the potential on ordinate to create a relation curve between the concentration of fluoride ion (mg/L) and the potential ⁽¹¹⁾.

Notes ⁽⁷⁾ This addition of buffer solution (pH 5.2) is for the purpose of adjusting the pH to 5.2 ± 0.2 and making its ionic strength constant.

- ⁽⁸⁾ A magnetic stirrer, if used for an extended period of time, may generate heat and affect the temperature of the solution; the solution temperature should be carefully monitored during use of a magnetic stirrer.
- ⁽⁹⁾ Unstable indication of a potentiometer owing to the stirring rate often results from the increase in the resistance of the reference electrode.

It is recommended that the stirring rate be controlled to approximately 180 min^{-1} to 200 min^{-1} .

- ⁽¹⁰⁾ When the liquid temperature is 10°C to 30°C , the response time of fluoride ion-selective electrode is about 1 min in the case of the fluoride ion concentration of 0.1 mg/L, and about 30 s in the case of 1 mg/L or more.

When the potential of the cell does not change by more than 0.5 mV in 5 min, switch off the magnetic stirrer. Record the value obtained after at least 15 s.

- ⁽¹¹⁾ Potential discrepancy between fluoride ion reference solution (F^- 1 mg/L) and fluoride ion reference solution (F^- 100 mg/L) falls in the range of 110 mV to 120 mV (25°C) and the working curve shows linearity between fluoride ion concentrations F^- 0.1 mg/L and 100 mg/L.
- ⁽¹²⁾ Before the next measurement is started, rinse the stirring bar, electrode and so on with the next solution to be measured. Start the measurement with the lowest concentration, and then proceed in the order of increasing concentration. After measuring a sample of high concentration, perform the procedures in Note ⁽⁵⁾ before going on to the next measurement.

d) **Procedure** The test procedure shall be as follows.

- 1) Place 100 ml of the distillate obtained by the distillation in **34.1.1 c)** in a measuring container, and add 10 ml of buffer solution (pH 5.2) ⁽⁷⁾.
- 2) Carry out the procedures in **2)** to **4)** of **c)** ⁽¹²⁾, determine the concentration of fluoride ion by reference to the working curve, and calculate the concentration of fluoride ion (F^- mg/L) in the sample.

NOTE 3 When the filtration is carried out instead of distillation, filter the sample according to **3.2**. Place 25 ml of the buffer solution (pH 5.2) (TISAB) in a measuring container and add 25 ml of filtered sample. Then carry out the procedure of **d) 2)**. The working curve is prepared according to the same procedure.

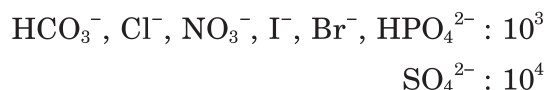
Buffer solution (pH 5.2) (TISAB) Add 58 g of sodium chloride specified in **JIS K 8150** and 57 ml of acetic acid specified in **JIS K 8355** in a 1 000-ml beaker containing 500 ml of water. Stir until it is dissolved.

Add 150 ml of sodium hydroxide solution (5 mol/L) (prepared by using sodium hydroxide specified in **JIS K 8576**) and 4 g of *trans*-1,2-cyclohexanediaminetetraacetate monohydrate and stir until all of the solid matter is dissolved. Then adjust the pH to 5.2 with sodium hydroxide solution (5 mol/L) by using a pH meter.

NOTES 4 In the case of an ion densitometer, carry out the procedure in **2)** and **3)** of **c)** using fluoride ion reference solution (F^- 1 mg/L) and fluoride ion reference solution (F^- 100 mg/L) to control the reading on the ion densitometer to 1 mg/L and 100 mg/L. Furthermore, confirm the reading on the ion densitometer using fluoride ion reference solution (F^- 0.1 mg/L) and fluoride ion reference solution (F^- 10 mg/L).

5 In ion-selective electrode method, since it only detects fluoride ion, distillation operation is required to change all fluorine compounds into fluoride ion before measurement.

The permissible limits of main coexisting substances are shown by the maximum ratio of concentration as follows:



Though hydroxide ion, aluminium ion and iron (III) ion all interfere with the measurement, since they are removed by distillation-separation procedure, interference by them do not occur.

6 **Potentiometric titration by fluoride ion-selective electrode** Place 100 ml of the distillate obtained by the distillation operation in **34.1.1 c)** in a beaker. While measuring the electric potential according to the procedures in **2)** to **4)** of **c)**, titrate it with $\frac{1}{300}$ mol/L to $\frac{1}{30}$ mol/L lanthanum (III) nitrate solution, and plot the titration curve. Find the end point, and calculate the amount of fluoride ion. One milliliter of $\frac{1}{30}$ mol/L lanthanum (III) nitrate solution is equivalent to 1.899 mg of fluoride ion F^- .

34.3 Ion chromatography After filtration of a sample, fluoride ion in the sample is determined according to ion chromatography. This test shall be carried out immediately after sampling. When this is impracticable, the sample shall be stored in a dark place at 0 °C to 10 °C, and tested as soon as possible. This method is applicable to clean samples, and determines dissolved fluoride ion and complex ion which easily becomes fluoride ion.

NOTE 7 Samples containing interfering substance shall be treated with the distillation operation in **34.1.1 c)** before analysis. Samples containing much halide shall also be treated with the distillation operation according to **34.1.1 c)** before analysis, but ignoring the second paragraph in Note (2), and using pH test paper in place of phenolphthalein solution (5 g/L) for determining alkalinity of the distillate.

When the distillation operation is carried out, the fluorine compound in the sample is determined.

For the procedure or other related matters, see **35.3**.

34.4 Flow analysis Fluorine compound in a sample is determined by the flow analysis where the sample is colored using the principle as used in the analysis method specified in **34.1.2**.

Determination range: F^- 0.08 mg/L to 10 mg/L, Repeatability: 10 % max.

For the procedure or other related matters of the flow analysis, see **JIS K 0170-6**. When applying the method in **6.3.2** of **JIS K 0170-6**, the distillation operation in **34.1.1 c)** shall be performed before analysis. In the case of using Alfusone as a coloring reagent, hydrochloric acid (1+11) [specified in **21 a) 2)**] may be used for neutralization of the distillate obtained after distillation procedure.

NOTE 8 When a sample containing an excessive amount of interfering substances, halide or hydrogen halide is analyzed by the method in **6.3.3** of **JIS K 0170-6**, determine the recovery rate by comparing the increment of the instrument reading in analysis of a sample mixed with a definite amount of fluoride ion against the instrument reading in analysis of a working curve reference solution containing the same amount of fluoride ion, check that the determined recovery rate is in the range of 80 % to 120 %, and correct the analysis value of the sample by the recovery rate. When the recovery rate is outside this range, this method is not applicable.

Clause 35

Delete “NOTE 4 See NOTE 3 to clause **34.**”

Clause 35

Replace “Note ⁽⁵⁾ See Note ⁽¹³⁾ to clause **34.**” by “Note ⁽⁵⁾ See Note ⁽⁵⁾ to clause **34.**”

Clause 35

Replace “Note ⁽⁶⁾ See Note ⁽¹⁴⁾ to clause **34.**” by “Note ⁽⁶⁾ See Note ⁽⁶⁾ to clause **34.**”

Clause 35

Replace “Note ⁽⁹⁾ See Note ⁽¹⁵⁾ to clause **34.**” by “Note ⁽⁹⁾ See Note ⁽⁸⁾ to clause **34.**”

Clause 35

Replace “Note ⁽¹⁰⁾ See Note ⁽¹⁶⁾ to clause **34.**” by “Note ⁽¹⁰⁾ See Note ⁽⁹⁾ to clause **34.**”

Clause 35

Replace “Note ⁽¹¹⁾ See Note ⁽¹⁷⁾ to clause **34.**” by “Note ⁽¹¹⁾ See Note ⁽¹⁰⁾ to clause **34.**”

Clause 35

Replace “Note ⁽¹³⁾ See Note ⁽¹⁹⁾ to clause **34.**” by “Note ⁽¹³⁾ See Note ⁽¹²⁾ to clause **34.**”

Clause 35

Replace “NOTE 5” by “NOTE 4”.

Clause 35

Replace “NOTE 6” by “NOTE 5”.

Clause 35

Replace “NOTE 7” by “NOTE 6”.

35.3 a) 2)

Replace “NOTE 8” by “NOTE 7”.

35.3 a) 3)

Replace “NOTE 8” by “NOTE 7”.

Clause 35

Replace “Note ⁽²¹⁾ See NOTE 8.” by “Note ⁽²¹⁾ See NOTE 7.”

Clause 35

Replace “NOTE 8” by “NOTE 7”.

35.3 c) 1)

Replace “Filtrate the sample in accordance with **3.2.**” by “Filtrate the sample using a filter with 0.45 µm or smaller pore diameter.”

Clause 35

Replace “NOTE 9” by “NOTE 8”.

Clause 35

Replace “NOTE 10” by “NOTE 9”.

Clause 35

In NOTE 10, replace “NOTE 8” by “NOTE 7”.

Clause 35

Replace “NOTE 11” by “NOTE 10”.

Clause 38

Replace the entire clause by the following:

38 Cyanide compound Cyanide compound is a generic term for cyanide ion, cyano complex, and so on in water, and is grouped into cyanide ion and total cyanide.

Cyanide compound is changed into cyanide ion by pretreatment. For the determination of cyanide compound, the pyridine-pyrazolone absorptiometry, 4-pyridinecarboxylic acid-pyrazolone absorptiometry, ion-selective electrode method or the flow analysis by 4-pyridinecarboxylic acid-pyrazolone coloring is applied.

Since cyanide compounds easily change, the test shall be carried out immediately after sampling. When immediate testing is infeasible, the sample shall be stored in accordance with **3.3**, and tested as soon as possible.

The flow analysis in this clause is in consistency with the first edition of **ISO 14403** published in 2002.

NOTE: The corresponding International Standard relevant to this test method is as follows.

The symbols which denote the degree of correspondence in the contents between the corresponding International Standard and **JIS** are IDT (identical), MOD (modified), and NEQ (not equivalent) according to **ISO/IEC Guide 21-1**.

ISO 14403:2002 *Water quality—Determination of total cyanide and free cyanide by continuous flow analysis* (MOD)

38.1 Pretreatment Sample is made slightly acidic, and then either aerated or distilled by heating to liberate hydrogen cyanide. The generated hydrogen cyanide is collected.

38.1.1 Cyanide By this pretreatment, hydrogen cyanide liberates nearly completely from cyanide ion and from the cyano complex of zinc, cadmium, etc. of which the formation constant is small, and partly from the cyano complex of such as nickel and copper. No hydrogen cyanide liberates from cyano complex of iron (II) and iron (III).

38.1.1.1 Aeration (hydrogen cyanide that issues at pH 5.0) Adjust the pH of the sample to 5.0, aerate at the rate of about 1.2 L/min while keeping it at 40 °C in a thermostatic water bath, and collect the liberated hydrogen cyanide in sodium hydroxide solution.

a) **Reagents** The following reagents shall be used.

- 1) **Acetic acid (1+1)**, prepared using the acetic acid specified in **JIS K 8355**.
- 2) **Acetic acid (1+49)**, prepared by using the acetic acid specified in **JIS K 8355**.
- 3) **Sodium hydroxide solution (200 g/L)** Dissolve 20 g of sodium hydroxide specified in **JIS K 8576** in water to make 100 ml.
- 4) **Sodium hydroxide solution (20 g/L)**, prepared by diluting the sodium hydroxide solution (200 g/L) 10 times with water.

b) **Apparatus** The following apparatus shall be used.

- 1) **Aeration apparatus**, as exemplified in figure 38.1.

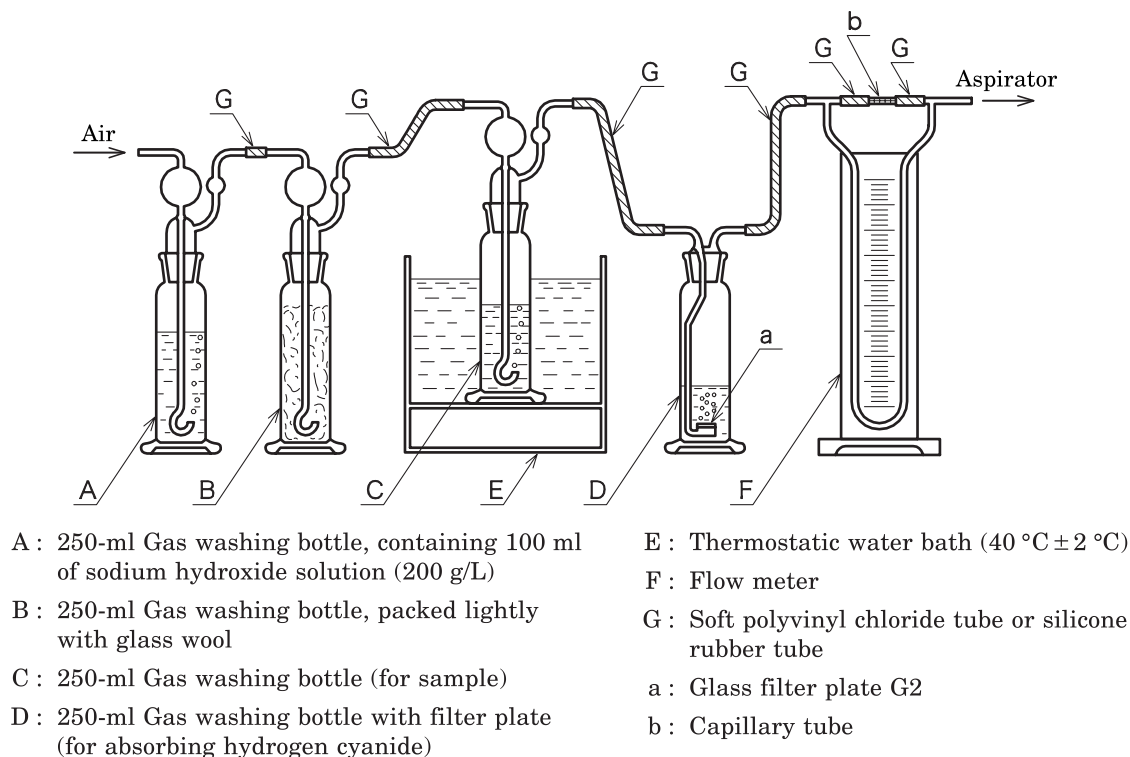


Figure 38.1 Example of aeration apparatus

c) **Aerating operation** The aerating operation shall be carried out as follows.

- 1) Set up the aerating apparatus as shown in figure 38.1, and place 40 ml of water and 20 ml of sodium hydroxide solution (20 g/L) in the gas washing bottle with a filter plate (D), for absorbing hydrogen cyanide.
- 2) Place 100 ml or a suitable volume of sample in a 300-ml beaker, and add dropwise either acetic acid (1+1) and acetic acid (1+49) or sodium hydroxide solution (20 g/L) until the pH is 5.0 ± 0.2 using a pH meter, and note the added volume. The sample volume shall be the optimum volume determined according to the determination range of a specific analysis method given in **38.2** to **38.4**, and shall not exceed 100 ml.
- 3) Place the same volume of sample as used in **2**) in a gas washing bottle (C), add water to make 100 ml, and then add the noted volume in **2**) of either acetic acid (1+1) and acetic acid (1+49) or sodium hydroxide solution (20 g/L). Connect the bottle as shown in figure 38.1. In cases where the sample contains oxidizing substances such as oils and fats and residual chlorine, or reducing substances such as sulfide, remove these prior to analysis according to the methods shown in NOTES 1 to 3.
- 4) Maintain the thermostatic water bath at $40\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$, and aerate for 1 h at the rate of about 1.2 L/min.
- 5) After aeration, transfer the sodium hydroxide solution (absorbing liquid) kept in the gas washing bottle with a filter plate (D) into a 100-ml volumetric flask. Wash the gas washing bottle with a filter plate (D) with water, join the washings to the flask, and add water to the mark.

- NOTES 1 When the sample contains a large amount of oils and fats, adjust its pH to 6 to 7 by adding acetic acid or sodium hydroxide, and transfer it into a separatory funnel. Add hexane or chloroform of about 2 % of the sample in volume percentage, shake gently, allow to stand until oils and fats are separated, and then carry out the procedure in **38.1.1.1**.
- 2 When the sample contains oxidizing substances such as residual chlorine, reduce them by adding L(+)-ascorbic acid solution (100 g/L) [prepared by dissolving 10 g of L(+)-ascorbic acid specified in **JIS K 9502** in water to make 100 ml].
- 3 When sample contains sulfide, add previously 2 ml of zinc acetate solution (100 g/L) [prepared in accordance with **38.1.1.2 a) 4**]. One milliliter of zinc acetate solution (100 g/L) corresponds to about 14 mg of sulfide ion.

38.1.1.2 Thermal distillation method (hydrogen cyanide that issues at pH 5.5 under existence of zinc acetate) Zinc acetate is added to the sample, and the pH is adjusted to 5.5. The sample is then distilled by heating and the liberated hydrogen cyanide is caught in sodium hydroxide solution.

a) **Reagents** The following reagents shall be used.

- 1) **Acetic acid (1+1)**, in accordance with **38.1.1.1 a) 1**).
- 2) **Acetic acid (1+49)**, in accordance with **38.1.1.1 a) 2**).
- 3) **Sodium hydroxide solution (20 g/L)**, in accordance with **38.1.1.1 a) 4**).
- 4) **Zinc acetate solution (100 g/L)**, prepared by dissolving 12 g of zinc acetate dihydrate specified in **JIS K 8356** in water to make 100 ml.

b) **Apparatus** The following apparatus shall be used.

- 1) **Distillation apparatus**, as exemplified in figure 38.2.

Unit: mm

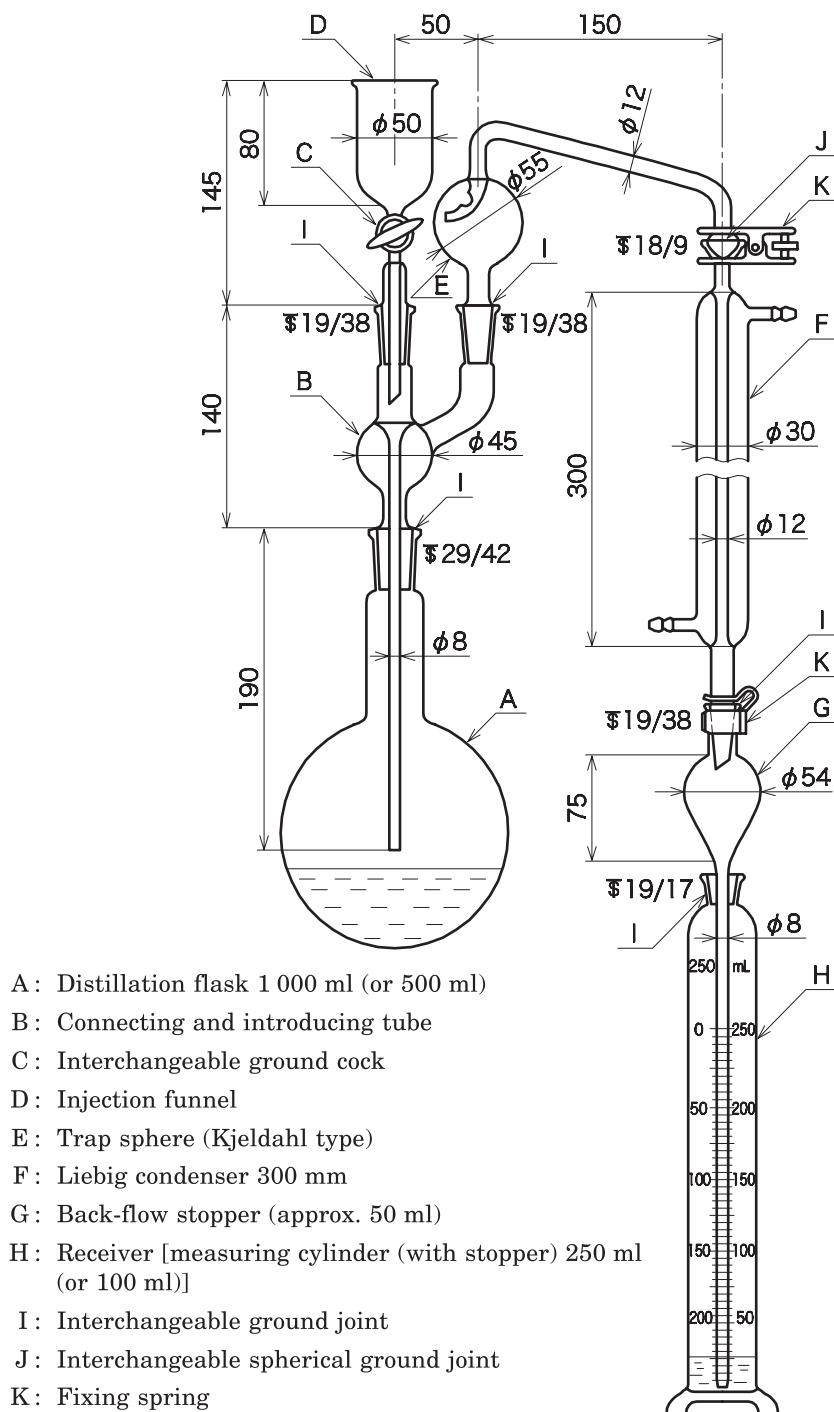


Figure 38.2 Example of distillation apparatus

c) **Distillation** Distillation shall be carried out as follows.

- 1) Place 500 ml or a suitable volume of the sample in a 1 000-ml beaker, add dropwise acetic acid (1+1) to adjust the pH to about 7 using a pH meter. Determine the volume of acetic acid required for this neutralization. The suitable sample volume shall be the optimum volume determined according to the determination range of a specific analysis method among those given in 38.2 to 38.4, and shall not exceed 500 ml.

- 2) Add 20 ml of zinc acetate solution (100 g/L), and again add dropwise acetic acid (1+49) and adjust the pH to 5.5 using a pH meter. Note the volume of acetic acid (1+49) required for this operation.
- 3) Place the same volume of sample as used in 1) in a 1 000-ml distillation flask, dilute with water to make 500 ml, and add boiling chips (grain size 2 mm to 3 mm).
- 4) Add acetic acid (1+1) obtained in 1), and mount the distillation flask on the distillation apparatus as shown in figure 38.2.
- 5) Employ a 250-ml measuring cylinder (with a stopper) for the receiver of the distillation apparatus. Place in it 20 ml of sodium hydroxide solution (20 g/L), and connect the receiver as shown in figure 38.2.
- 6) Then, add 20 ml of zinc acetate solution (100 g/L) through the injection funnel, and add the volume of acetic acid (1+49) noted in 2).
- 7) Heat the distillation flask, and while controlling the distilling rate to 2 ml/min to 3 ml/min and ensuring it never exceeds 3 ml/min, distil until about 230 ml of distillate has been collected in the receiver. During this operation, adjust the height of the 250-ml measuring cylinder (with a stopper) so that the tip of the back-flow stopper is always about 15 mm below the liquid surface in the receiver.
- 8) Disconnect the condenser and back-flow stopper, wash the inside tube of the condenser and both the inner and outer surfaces of the back-flow stopper with a small volume of water, put the washings in the receiver, and add water up to the mark of 250 ml.

NOTES 4 When the sample contains a large amount of oils and fats, follow the procedures shown in NOTE 1.

5 When the sample contains oxidizing substances such as residual chlorine, follow the procedures shown in NOTE 2.

6 When the sample contains reducing substances such as sulfide, remove them by oxidizing the distillate obtained by the procedures in 1) to 7) of c) as described below, and then performing distillation again.

- Put back the distillate collected in a receiver by the distillation procedure and washings into a distillation flask, add two or three drops of phenolphthalein solution (5 g/L) [prepared in accordance with NOTE 2 to clause 15] as an indicator, neutralize with acetic acid (1+1), and then add about 30 ml of nitric acid (50 mmol/L) (prepared by dissolving 3.8 ml of nitric acid specified in **JIS K 8541** in water to make 1 L).
- Add dropwise the potassium permanganate solution (3 g/L) (prepared by using potassium permanganate specified in **JIS K 8247**), and at the point where either the permanganate develops a faint red color or manganese (IV) oxide gives brown turbidity, add excessively 1 ml of the solution, and add water to make about 300 ml.

- Mount the distillation flask on the distillation apparatus as shown in figure 38.2. Connect the receiver, which shall be a 100-ml measuring cylinder (with a stopper) containing 20 ml of sodium hydroxide solution (20 g/L), to the apparatus as shown in figure 38.2.
- Heat the distillation flask, and while controlling the distilling rate to 2 ml/min to 3 ml/min, perform distillation until about 90 ml of distillate has been collected in the receiver. Disconnect the condenser and back-flow stopper, wash the inside tube of the condenser and both the inner and outer surfaces of the back-flow stopper with a small volume of water, put the washings in the receiver, and add water to the mark of 100 ml.

38.1.2 Total cyanide (hydrogen cyanide that issues at pH 2 or less) After the pH of the sample is brought to 2 or lower with the addition of phosphoric acid, the sample is subjected to thermal distillation using disodium dihydrogen ethylenediamine tetraacetate. The hydrogen cyanide liberated by this distillation is caught in the sodium hydroxide solution.

NOTE 7 All cyanide ion and almost all cyanide in cyano complex will distill out by the pretreatment. If distillation is performed under the presence of oxidizing substances, thiocyanic acid, 2-propenenitril (acrylonitrile), etc. are decomposed, causing generation of hydrogen cyanide. To avoid this, reduction of oxidizing substances should be performed before analysis.

a) **Reagents** The following reagents shall be used.

- 1) **Phenolphthalein solution (5 g/L)**, in accordance with NOTE 2 to clause 15.
- 2) **Sodium hydroxide solution (20 g/L)**, in accordance with 38.1.1.1 a) 4).
- 3) **Sodium hydroxide solution (40 g/L)**, in accordance with 21 a) 3).
- 4) **Ammonium amidosulfate solution (100 g/L)** Dissolve 10 g of ammonium amidosulfate specified in **JIS K 8588** in water to make 100 ml.
- 5) **EDTA solution** Dissolve 10 g of disodium dihydrogen ethylenediamine tetraacetate dihydrate specified in **JIS K 8107** in water, add five to seven drops of sodium hydroxide solution (20 g/L) to make it slightly alkaline, and add water to make 100 ml.
- 6) **Phosphoric acid**, specified in **JIS K 9005**.

b) **Apparatus** The following apparatus shall be used.

- 1) **Distillation apparatus**, as exemplified in figure 38.2.

c) **Distillation** Distillation shall be carried out as follows.

The distillation procedure described in NOTE 11 may be used if proven to achieve a recovery rate of 80 % to 120 % by testing a sample to which a definite volume of cyanide ion reference solution has been added.

- 1) Place 50 ml of sample in a 500-ml distillation flask, and add water to make about 250 ml, and add boiling chips (grain size 2 mm to 3 mm). Add one drop of phenolphthalein solution (5 g/L) as an indicator.

- 2) If the sample is alkaline, make it mildly acidic by adding phosphoric acid drop by drop until the red color of the solution disappears.
- 3) Then, add 1 ml ⁽¹⁾ of ammonium amidosulfate solution (100 g/L).
- 4) Mount the distillation flask as shown in figure 38.2. Connect, as a receiver, a 100-ml measuring cylinder (with a stopper) containing 20 ml of sodium hydroxide solution (20 g/L) to the apparatus as shown in figure 38.2.
- 5) Add 10 ml of phosphoric acid from an injection funnel into the distillation flask, then add 10 ml of EDTA solution. Wash the injection funnel with a small volume of water, and join the washings to the flask.
- 6) After allowing the solution to stand for a few minutes, heat the distillation flask, and while controlling the distilling rate to 2 ml/min to 3 ml/min, perform distillation until about 90 ml of distillate has been collected in the receiver. Ensure that the distilling rate never exceeds 3 ml/min. During this operation, adjust the height of the 100-ml measuring cylinder (with a stopper) so that the tip of the back-flow stopper is always about 15 mm below the liquid surface in the receiver.
- 7) Disconnect the condenser and back-flow stopper, wash the inside tube of the condenser and both the inside and outside surfaces of the back-flow stopper with a small volume of water, put the washings in the receiver, and add water up to the mark of 100 ml.

Note ⁽¹⁾ Ammonium amidosulfate solution (100 g/L) is added in order to eliminate the interference by nitrite ion in the sample. Without this addition, nitrite ion would react with EDTA during thermal distillation and produce hydrogen cyanide. One milliliter of ammonium amidosulfate solution (100 g/L) corresponds to about 40 mg of nitrite ion. When 40 mg or more of nitrite ion coexists, the added volume shall be increased accordingly.

Some special kinds of samples may contain substances other than nitrite ion that react with EDTA and produce hydrogen cyanide, of which the interference cannot be removed by addition of ammonium amidosulfate solution (100 g/L). Where relevance of the added EDTA is suspected, the procedures in 1) to 7) shall be carried out without addition of the EDTA solution.

It should be noted that there are other organic substances may react similarly to EDTA.

- NOTES 8 For removing oils and fats, carry out the procedure shown in NOTE 1.
- 9 When the sample contains oxidizing substance like residual chlorine, carry out the procedure shown in NOTE 2.
 - 10 When the sample contains reducing substance like sulfide, carry out the distillation for total cyanide, and treat the distillate according to NOTE 6.
 - 11 The distillation procedure in the case of using a small distillation apparatus as shown in figure 28.1 is as follows.

- 1) Place 25 ml of sample in a distillation vessel, and add water to make about 50 ml, and add boiling chips (grain size 2 mm to 3 mm). Add one drop of phenolphthalein solution (5 g/L) as an indicator, and add phosphoric acid drop by drop until the red colour of the solution disappears. Then add 0.5 ml (*) of ammonium amidosulfate solution (100 g/L).
- 2) Add 2 ml each of phosphoric acid and EDTA solution through the upper opening of the distillation vessel, and set a distillation tube and condenser to the distillation vessel. Mount this assembly to the heating equipment. Employ a 50-ml measuring cylinder (with a stopper) for the receiver of the distillation apparatus. Place in it 5 ml of sodium hydroxide solution (40 g/L).
- 3) At a distilling rate of 0.3 ml/min to 0.7 ml/min, perform distillation until about 30 ml of distillate has been collected in the receiver.
Ensure that throughout the operation, the tip of the back-flow stopper connected to the condenser is kept under water.
- 4) Disconnect the condenser, wash its inner wall with a small volume of water, put the washings in the receiver, and add water up to the mark of 50 ml.

Note (*) See Note (1).

38.2 Pyridine-pyrazolone absorptiometry A part of cyanide ion solution obtained as a result of the pretreatment performed according to **38.1** is taken and neutralized with acetic acid, and turned to cyanogen chloride with addition of chloramine T solution. The pyridine-pyrazolone solution is added to this, and the absorbance of the blue color produced as a result is measured to determine cyanide ion.

Determination range: CN^- 0.5 μg to 9 μg , Repeatability: 2 % to 10 %

a) **Reagents** The following reagents shall be used.

- 1) **Acetic acid (1+8)**, prepared by using the acetic acid specified in **JIS K 8355**.
- 2) **Phenolphthalein solution (5 g/L)**, in accordance with NOTE 2 to clause 15.
- 3) **Phosphate buffer solution (pH 6.8)** Dissolve 17.0 g of potassium dihydrogen phosphate specified in **JIS K 9007** and 17.8 g of disodium hydrogenphosphate specified in **JIS K 9020** in water to make 500 ml.
- 4) **Chloramine T solution (10 g/L)** Dissolve 0.62 g of sodium *p*-toluenesulfon-chloramide trihydrate (chloramine T) specified in **JIS K 8318** in water to make 50 ml. Prepare this solution immediately before use.
- 5) **Pyridine-pyrazolone solution** Dissolve 0.25 g of 3-methyl-1-phenyl-5-pyrazolone specified in **JIS K 9548** in 20 ml of pyridine specified in **JIS K 8777**. In this, dissolve 20 mg of bis(3-methyl-1-phenyl-5-pyrazolone) specified in **JIS K 9545**, and add 100 ml of water and mix. If stored at a temperature 10 °C or lower, this solution can be used for 1 week since its preparation.
- 6) **0.1 mol/L silver nitrate solution** Dissolve 17 g of silver nitrate specified in **JIS K 8550** in water to make 1 L. Store in a colored glass bottle.

Standardization The standardization shall be performed as follows.

- Heat sodium chloride of reference material for volumetric analysis specified in **JIS K 8005** at 600 °C for about 1 h, and allow it to cool in a desiccator. Weigh 1.17 g of NaCl (100 %) to the nearest 1 mg, dissolve it in a small volume of water, transfer it into a 200-ml volumetric flask, and add water to the mark.
- Take 20 ml of this solution, and add water to make about 50 ml. Add 5 ml of dextrin solution [prepared in accordance with **35.1 a) 4)**] and three or four drops of sodium dichlorofluorescein solution (2 g/L) [prepared in accordance with **35.1 a) 3)**] as an indicator, and titrate it with 0.1 mol/L silver nitrate solution until the end point has been reached where the solution loses yellowish green fluorescence and turns faintly red. Calculate the factor (*f*) of 0.1 mol/L silver nitrate solution according to the following formula:

$$f = a \times \frac{b}{100} \times \frac{20}{200} \times \frac{1}{x \times 0.005\,844}$$

where,

a : amount of sodium chloride (g)

b : purity of sodium chloride (%)

x : volume of 0.1 mol/L silver nitrate solution required for titration (ml)

0.005 844 : mass of sodium chloride corresponding to 1 ml of 0.1 mol/L silver nitrate solution (g)

- 7) **Cyanide ion reference solution (CN⁻ 1 mg/ml)** Dissolve 0.63 g of potassium cyanide specified in **JIS K 8443** in a small volume of water, add 2.5 ml of sodium hydroxide solution (20 g/L), and add water to make 250 ml. Prepare this solution immediately before use. Its concentration shall be determined according to the following.

Take 100 ml of this solution, add 0.5 ml, as an indicator, of acetone solution (0.2 g/L) of 5-(4-dimethylaminobenzylidene) rhodanine [prepared by dissolving 20 mg of 5-(4-dimethylaminobenzylidene) rhodanine specified in **JIS K 8495** in 100 ml of acetone specified in **JIS K 8034**], and titrate it with 0.1 mol/L silver nitrate solution until the end point has been reached where the color of the solution has turned from yellow to red. Calculate the concentration of cyanide ion reference solution (CN⁻ mg/ml) according to the following formula:

$$C = a \times f \times 5.204 \times \frac{1}{100}$$

where,

C : concentration of cyanide ion reference solution (CN⁻ mg/ml)

a : volume of 0.1 mol/L silver nitrate solution required for titration (ml)

f : factor of 0.1 mol/L silver nitrate solution

5.204 : mass of cyanide ion corresponding to 1 ml of 0.1 mol/L silver nitrate solution (mg)

- 8) **Cyanide ion reference solution (CN^- 1 $\mu\text{g}/\text{ml}$)** Place 10 ml of cyanide ion reference solution (CN^- 1 mg/ml) in a 1 000-ml volumetric flask, add 100 ml of sodium hydroxide solution (20 g/L), and add water to the mark. Take 10 ml of this in a 100-ml volumetric flask, and add water to the mark. Prepare this solution immediately before use. The concentration of this solution shall be calculated from the concentration of cyanide ion reference solution (CN^- 1 mg/ml).
- b) **Apparatus** The following apparatus shall be used.
- 1) **Photometer** Spectrophotometer or photoelectric photometer
- c) **Procedure** The test procedure shall be as follows.
- 1) Place a 10 ml portion (containing 0.5 μg to 9 μg as CN^-) of cyanide ion solution obtained by the pretreatment according to **38.1** in a 50-ml volumetric flask.
 - 2) Add one drop of phenolphthalein solution (5 g/L) as an indicator, and add dropwise acetic acid (1+8) while gently shaking until the red color of the solution fades away.
 - 3) Add 10 ml of phosphate buffer solution (pH 6.8) to make the pH 6.8, stopper tightly and gently shake.
 - 4) Add 0.25 ml of chloramine T solution (10 g/L) to this, immediately stopper tightly, gently shake, and allow to stand for about 5 min.
 - 5) Add 15 ml of pyridine-pyrazolone solution, add water to the mark, and after stoppering tightly, gently shake.
 - 6) Submerge this in a water bath at about 25 °C for about 30 min, and observe as the solution turns faint red, violet, and then stable blue.
 - 7) Transfer a part of the solution to an absorption cell, and measure the absorbance at a wavelength near 620 nm.
 - 8) For a blank test, place 10 ml of water in a 50-ml volumetric flask, carry out the procedures in **3)** to **7)** to measure the absorbance, and correct the measured absorbance of the sample.
 - 9) Determine the amount of cyanide ion by reference to the working curve, and calculate the concentration of cyanide ion (CN^- mg/L) in the sample.
- d) **Working curve** The working curve shall be prepared as follows.
- 1) Place a series of aliquots in stepwise increment ranging from 0.5 ml to 9 ml of the cyanide ion reference solution (CN^- 1 $\mu\text{g}/\text{ml}$) in as many 50-ml volumetric flasks and add water to each of these solutions to make about 10 ml.
 - 2) Carry out the procedures in **2)** to **8)** of **c)**, and plot the relation curve between the amount of cyanide ion (CN^-) and the absorbance.

38.3 4-Pyridinecarboxylic acid-pyrazolone absorptiometry A part of cyanide ion solution obtained as a result of pretreatment performed according to **38.1** is taken and neutralized with acetic acid, and turned to cyanogen chloride with addition of chloramine T solution. The 4-pyridinecarboxylic acid-pyrazolone solution is added to

this, and the absorbance of the blue color generated as a result is measured to determine cyanide ion.

Determination range: CN^- 0.5 μg to 9 μg , Repeatability: 2 % to 10 %

a) **Reagents** The following reagents shall be used.

- 1) **Acetic acid (1+8)**, in accordance with **38.2 a) 1)**.
- 2) **Phenolphthalein solution (5 g/L)**, in accordance with NOTE 2 to clause **15**.
- 3) **Phosphate buffer solution (pH 7.2)** Dissolve 17.8 g of disodium hydrogen-phosphate specified in **JIS K 9020** in about 300 ml of water, add potassium dihydrogen phosphate solution (200 g/L) (prepared by using potassium dihydrogen phosphate specified in **JIS K 9007**) until the pH is 7.2, and add water to make 500 ml.
- 4) **Chloramine T solution (10 g/L)**, in accordance with **38.2 a) 4)**.
- 5) **4-Pyridinecarboxylic acid-pyrazolone solution** Dissolve 0.3 g of 3-methyl-1-phenyl-5-pyrazolone specified in **JIS K 9548** in 20 ml of *N,N*-dimethylformamide specified in **JIS K 8500**. Separately, dissolve 1.5 g of 4-pyridinecarboxylic acid in about 20 ml of sodium hydroxide solution (40 g/L) [prepared in accordance with **21 a) 3)**], and add dropwise hydrochloric acid (1+10) (prepared using hydrochloric acid specified in **JIS K 8180**) until the pH is about 7. Instead of this solution, the solution obtained by dissolving 1.8 g of sodium 4-pyridine carboxylate in about 50 ml of water may be used. Put together the pyrazolone solution and the 4-pyridinecarboxylic acid solution, and add water to make 100 ml. Store this solution in a dark place at 10 °C or lower and do not use after a lapse of 20 days or more.
- 6) **Cyanide ion reference solution (CN^- 1 $\mu\text{g/ml}$)**, in accordance with **38.2 a) 8)**.

b) **Apparatus** The following apparatus shall be used.

- 1) **Photometer** Spectrophotometer or photoelectric photometer

c) **Procedure** The test procedure shall be as follows.

- 1) Place a 10 ml portion (containing 0.5 μg to 9 μg as CN^-) of cyanide ion solution obtained by the pretreatment according to **38.1** in a 50-ml volumetric flask.
- 2) Add one drop of phenolphthalein solution (5 g/L) as an indicator, add dropwise acetic acid (1+8) while shaking gently to make neutral, and add 10 ml of phosphate buffer solution (pH 7.2) to make the pH 7 to 8.
- 3) Add 0.5 ml of chloramine T solution (10 g/L), and allow to stand in a water bath at about 25 °C for about 5 min.
- 4) Add 10 ml of 4-pyridinecarboxylic acid-pyrazolone solution, and add water to the mark. Stopper tightly, gently shake, and allow to stand in a water bath at about 25 °C for about 30 min.
- 5) Within 1 h of coloration, transfer a part of the solution to an absorption cell, and measure the absorbance at a wavelength near 638 nm.