JAPANESE INDUSTRIAL STANDARD

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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
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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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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 pretreatment 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.

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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, ∝g/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, ∝g/ml, ng/ml, g/L, mg/L or ∝g/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 ∝g/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.

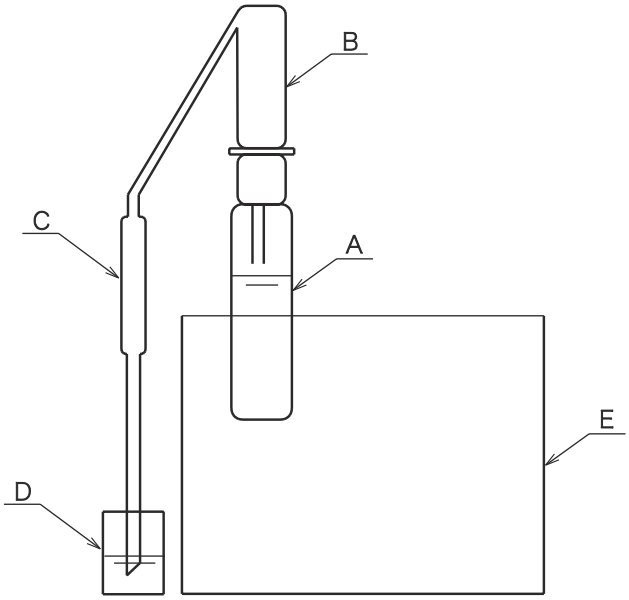
If using a 200-ml distillation flask, the volumes of sample, copper (II) sulfate solution, receiver, and distillate shall all be double the volumes for a standard procedure.

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-3*H*-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 (C_6H_5OH), 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 C_6H_5OH 50 ∝g to 500 ∝g,
Repeatability: 3 % to 10 %

Solvent extraction method C_6H_5OH 2.5 ∝g to 50 ∝g,
Repeatability: 3 % to 10 %

Solid-phase extraction method C_6H_5OH 0.2 ∝g to 15 ∝g,
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 (C_6H_5OH 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 (C_6H_5OH 10 ∝g/ml)** Place 10 ml of phenol reference solution (C_6H_5OH 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 ∝g to 500 ∝g as C_6H_5OH) 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 ∝g to 250 ∝g as C_6H_5OH) of the sample to a