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**Testing methods for water quality by flow
analysis—Part 9: Cyanide compounds**

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Foreword

This translation has been made based on the original Japanese Industrial Standard established by the Minister of Economy, Trade and Industry through deliberations at the Japanese Industrial Standards Committee according to the proposal for establishment of Japanese Industrial Standard submitted by Japan Environmental Measurement and Chemical Analysis (JEMCA)/Japanese Standards Association (JSA) with the draft being attached, based on the provision of Article 12 Clause 1 of the Industrial Standardization Law.

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JIS K 0170 series consists of the following 9 parts under the general title

“Testing methods for water quality by flow analysis”:

Part 1: Ammonium nitrogen

Part 2: Nitrite nitrogen and nitrate nitrogen

Part 3: Total nitrogen

Part 4: Orthophosphate and total phosphorus

Part 5: Phenol index

Part 6: Fluoride

Part 7: Chromium (VI)

Part 8: Anionic surfactants

Part 9: Cyanide compounds

Testing methods for water quality by flow analysis—

Part 9: Cyanide compounds

Introduction

This Japanese Industrial Standard has been prepared based on the first edition of ISO 14403 published in 2002, with some of the technical contents modified so as to make them applicable to apparatuses, etc. used in Japan.

The portions with continuous sidelines or dotted underlines are the matters in which the contents of the corresponding International Standard have been modified. A list of modifications with explanations is given in Annex JA.

1 Scope

This Standard specifies the method for determination of cyanide compounds contained in industrial water, industrial wastewater, etc. by using the flow analysis by the 4-pyridine carboxylic acid•dimethyl barbituric acid absorption spectrophotometry or 4-pyridine carboxylic acid•pyrazolone absorption spectrophotometry. The method is also applicable to surface water, ground water, seepage water, etc.

It dose not apply to samples with much suspended matter.

NOTE: The International Standard corresponding to this Standard and the symbol of degree of correspondence are as follows.

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

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

WARNING The reagents shall be handled with utmost attention, ensuring compliance with the relevant laws, ordinances, regulations and the like.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this Standard. The most recent editions of the standards (including amendments) indicated below shall be applied.

JIS K 0050 *General rules for chemical analysis*

JIS K 0094 *Sampling methods for industrial water and industrial wastewater*

JIS K 0101 *Testing methods for industrial water*

JIS K 0102 *Testing methods for industrial wastewater*

JIS K 0115	<i>General rules for molecular absorptiometric analysis</i>
JIS K 0126	<i>General rules for flow analysis</i>
JIS K 0211	<i>Technical terms for analytical chemistry (General part)</i>
JIS K 0215	<i>Technical terms for analytical chemistry (Analytical instrument part)</i>
JIS K 0557	<i>Water used for industrial water and wastewater analysis</i>
JIS K 8180	<i>Hydrochloric acid (Reagent)</i>
JIS K 8283	<i>Citric acid monohydrate (Reagent)</i>
JIS K 8295	<i>Glycerol (Reagent)</i>
JIS K 8318	<i>Sodium para-toluenesulfonchloramide trihydrate (Reagent)</i>
JIS K 8443	<i>Potassium cyanide (Reagent)</i>
JIS K 8500	<i>N,N-Dimethylformamide (Reagent)</i>
JIS K 8576	<i>Sodium hydroxide (Reagent)</i>
JIS K 8801	<i>Potassium hexacyanoferrate (III) (Reagent)</i>
JIS K 8809	<i>Potassium hydrogen phthalate (Reagent)</i>
JIS K 8953	<i>Zinc sulfate heptahydrate (Reagent)</i>
JIS K 9001	<i>Potassium thiocyanate (Reagent)</i>
JIS K 9005	<i>Phosphoric acid (Reagent)</i>
JIS K 9007	<i>Potassium dihydrogen phosphate (Reagent)</i>
JIS K 9020	<i>Disodium hydrogenphosphate (Reagent)</i>
JIS K 9548	<i>3-Methyl-1-phenyl-5-pyrazolone (Reagent)</i>
JIS R 3503	<i>Glass apparatus for chemical analysis</i>
JIS R 3505	<i>Volumetric glassware</i>

3 Terms and definitions

For the purpose of this Standard, the terms and definitions given in JIS K 0101, JIS K 0102, JIS K 0115, JIS K 0126, JIS K 0211 and JIS K 0215 and the following apply.

3.1 cyanide compounds

the generic term for cyanide ion, cyano complex, etc. in water

The cyanide compounds producing hydrogen cyanide depend on the condition of pre-treatment, therefore the total cyanide and the free cyanide are separately measured. The total cyanide is the sum of those cyanide compounds which become cyanide ions by ultraviolet irradiation•distillation (pH 3.8) or heating distillation (pH 2.0 or under), and the free cyanide is the sum of those cyanide compounds which are cyanide ions or become cyanide ions by heating distillation (pH 3.8 or pH 5.5 under the presence of zinc acetate), gas diffusion (pH 3.8) or aeration method (pH 5.0).

4 Common matters

4.1 General

The general matters common to the chemical analyses shall be in accordance with JIS K 0050. The general requirements relating to the flow analysis shall be in accordance with JIS K 0126.

4.2 Water

The water used in this Standard shall be the water of A3 or A4 specified in JIS K 0557.

4.3 Reagents

The reagents to be used shall be those specified in Japanese Industrial Standards and shall not be such that they impair the measurement. In the case of using reagents not specified in Japanese Industrial Standards, those reagents shall not be such that they impair the measurement. The reagent blank shall be periodically checked.

NOTE: The concentration indicated in parentheses at the rear of the designation of a reagent solution, except when it is a reference solution, is an approximate concentration.

4.4 Glassware

The glassware to be used, unless otherwise specified, shall be in accordance with JIS R 3503 and JIS R 3505.

5 Sample

5.1 Sampling

The sampling, sample container, water sampler and sampling operation shall be in accordance with JIS K 0094. For the sample container, a polyethylene bottle with ground-in stopper or a glass bottle with ground-in stopper shall be used.

A polypropylene bottle with ground-in stopper, a polystyrene bottle with ground-in stopper or a polycarbonate bottle with ground-in stopper, which is chemically inert may be used.

5.2 Handling of sample

The test shall be carried out immediately after sampling. When this is not practicable, the sample shall be preserved according to 3.3 b) 5) of JIS K 0102 and tested as soon as possible.

6 Measurement of total cyanide

6.1 Principle

In the flow, sample is distilled by ultraviolet irradiation under the acidity of citric acid at pH 3.8 or is distilled by heating under the acidity of phosphoric acid at pH 2 so that cyanide compounds in the sample are decomposed and distilled as hydrogen cyanide. After this is mixed with the buffer solution of which the pH has been adjusted, it

is mixed with chloramine T solution and made to cyanide chloride. Next, it is mixed with 4-pyridine carboxylic acid • dimethyl barbituric acid solution or 4-pyridine carboxylic acid • pyrazolone solution, and the absorbance of the resultant blue compound is measured at a wavelength of 600 nm to 640 nm to determine the total cyanide.

Range of determination CN^- : 0.01 mg/L to 1 mg/L

NOTE: Though it differs depending on the apparatus and measuring conditions, repeatability of this method, expressed by relative standard deviation (%), is not more than 10 %.

6.2 Interferences

When salts in sample exceed 10 g/L in concentration, they may be precipitated by distillation. In this case, therefore, the sample shall be diluted prior to measurement.

When oxidizing substances such as residual chloride or reducing substances such as sulfide are contained in a sample, they shall be removed according to 3.3 b) 5) of JIS K 0102 prior to measurement.

6.3 Classification of measuring methods and reagents and apparatus

6.3.1 Classification of measuring methods

Classification of measuring methods shall be in accordance with table 1.

Table 1 Classification of measuring methods

Classification of measuring method	Clause					
	Reagent and preparation of reagent solution	Apparatus	Measuring operation	Calculation of concentration	Expression of results	Test report
CFA method of ultra-violet irradiation • distillation (pH 3.8)—4-pyridine carboxylic acid • dimethyl barbituric acid colouring	6.3.2.1	6.3.2.2	6.4	6.5	8	9
CFA method of heating • distillation (pH 2 or under)—4-pyridine carboxylic acid • pyrazolone colouring	6.3.3.1	6.3.3.2				
NOTE: CFA means continuous flow analysis.						

6.3.2 CFA method of ultraviolet irradiation • distillation (pH 3.8)—4-pyridine carboxylic acid • dimethyl barbituric acid colouring

6.3.2.1 Preparation of reagents and reagent solutions

6.3.2.1.1 Reagents

The reagents shall be as follows.

- a) **Hydrochloric acid**, specified in JIS K 8180.
- b) **Sodium hydroxide**, specified in JIS K 8576.
- c) **Polyoxyethylene dodecyl ether**
- d) **Citric acid monohydrate**, specified in JIS K 8283.
- e) **Potassium hydrogen phthalate**, specified in JIS K 8809.
- f) **Sodium para-toluenesulfonchloramide trihydrate**, specified in JIS K 8318.
- g) **1,3-Dimethyl barbituric acid**
- h) **4-Pyridine carboxylic acid**
- i) **Potassium cyanide**, specified in JIS K 8443.

6.3.2.1.2 Preparation of reagent solutions

The reagent solutions shall be prepared as follows.

- a) **Hydrochloric acid (1 mol/L)** Take 10 ml of hydrochloric acid, and add water to make 120 ml.
- b) **Sodium hydroxide solution (2.5 mol/L)** Dissolve 100 g of sodium hydroxide in water to make 1 000 ml.
- c) **Sodium hydroxide solution (1 mol/L)** Dissolve 40 g of sodium hydroxide in water to make 1 000 ml.
- d) **Sodium hydroxide solution (0.01 mol/L)** Take 10 ml of sodium hydroxide solution (1 mol/L) and add water to make 1 000 ml.
- e) **Polyoxyethylene dodecyl ether solution** Dissolve 30 g of polyoxyethylene dodecyl ether in 100 ml of water.
- f) **Buffer solution for distillation (pH 3.8)** Dissolve 50 g of citric acid monohydrate in 350 ml of water, then add 120 ml of sodium hydroxide solution (2.5 mol/L). Adjust the pH to 3.8 with hydrochloric acid (1 mol/L) or sodium hydroxide solution (1 mol/L), then add water to make 500 ml.
- g) **Buffer solution for colouring (pH 5.2)** Dissolve 2.3 g of sodium hydroxide and 20.5 g of potassium hydrogen phthalate in 500 ml of water and add water to make approximately 975 ml. Adjust the pH to 5.2 with hydrochloric acid (1 mol/L) or sodium hydroxide solution (1 mol/L), then after adding water to make 1 000 ml, add 1 ml of polyoxyethylene dodecyl ether solution.
- h) **Chloramine T solution** Add water to 2.0 g of sodium para-toluenesulfonchloramide trihydrate to make 1 000 ml.
- i) **Colouring solution (pH 5.2)** Add 7.0 g of sodium hydroxide to 500 ml of water to dissolve, then add 16.8 g of 1,3-dimethyl barbituric acid and 13.6 g of 4-pyridine carboxylic acid to dissolve and add water to make approximately 975 ml. Adjust the pH to 5.2 with hydrochloric acid (1 mol/L) or sodium hydroxide solution (1 mol/L), then add water to make 1 000 ml.

Heat this solution to about 30 °C for accelerating dissolution and stir it by means of a stirrer for about 1 hour. When insoluble matter is present, filter it through a Class 5B filter paper.

- j) **Sampler rinsing solution** Add 2 ml of polyoxyethylene dodecyl ether solution to 1 000 ml of water.
- k) **Cyanide ion reference solution (CN^- : 100 mg/L)** Dissolve 250 mg of potassium cyanide in sodium hydroxide solution (0.01 mol/L), transfer it into a 1 000 ml volumetric flask and make up to the mark with sodium hydroxide solution (0.01 mol/L).

The standardization of the concentration of this solution shall be in accordance with 38.2 a) 7) of JIS K 0102.

- l) **Cyanide ion reference solution (CN^- : 10 mg/L)** Take 10 ml of cyanide ion reference solution (CN^- : 100 mg/L) in a 100 ml volumetric flask and make up to the mark with sodium hydroxide solution (0.01 mol/L). Prepare this solution freshly before use.
- m) **Cyanide ion reference solution (CN^- : 1 mg/L)** Take 10 ml of cyanide ion reference solution (CN^- : 10 mg/L) in a 100 ml volumetric flask and make up to the mark with sodium hydroxide solution (0.01 mol/L). Prepare this solution freshly before use.

6.3.2.2 Apparatus

In general, the system comprises the following components (see figure 1).

- a) **Liquid sending part** A low pulsation pump shall be used.
- b) **Sample introduction part**, with good reproducibility for the sample introduction.
- c) **Ultraviolet decomposition apparatus**

The combination of UV lamp and coil shall be in accordance with either 1) or 2) below.

- 1) The apparatus shall be composed of a UV lamp with the maximum wavelength at 351 nm (45 nm or under in bandwidth, 8 W to 12 W in output) and a coil of quartz glass or a coil of fluoride resin (PTFE). The coil shall be about 4 ml in capacity, 1 mm or under in thickness and 1 mm to 2 mm in internal diameter.
- 2) The apparatus shall be composed of a UV lamp (8 W to 12 W in output) with the maximum wavelength at $312 \text{ nm} \pm 5 \text{ nm}$ and a coil of borosilicate glass. The coil shall be about 14 ml in capacity, 1 mm or under in thickness and 2 mm in internal diameter.

NOTE: The light of 290 nm or under in wavelength radiated from a UV lamp can decompose thiocyanide ion to cyanide ion, and therefore should not be used.

- d) **Distillation apparatus**, composed of a heater and a distillation unit, and capable of setting the heating temperature at 125 °C.