

JIS

JAPANESE INDUSTRIAL STANDARD

Pyridine Bases (Pyridine · Picoline · Quinoline)

Ⓔ JIS K 2438—1990

Translated and Published

by

Japanese Standards Association

In the event of any doubt arising,
the original Standard in Japanese is to be final authority.



JAPANESE INDUSTRIAL STANDARD

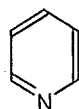
J I S

Pyridine Bases

K 2438-1990

(Pyridine • Picoline • Quinoline)

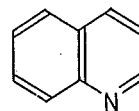
FW = 79.10



FW = 93.13

 C_6H_7N

FW = 129.16

1. Scope

This Japanese Industrial Standard specifies industrial pyridine, picoline and quinoline (hereafter referred to as the "pyridine bases").

- Remarks 1. The units and numerical values given in { } in this Standard are based on the traditional units and are currently the criteria in force.
2. Since pyridine bases have strong stimulus to the skin, eye, etc. and an offensive odor and further, are inflammable explosive materials, precaution shall be taken enough for treatment.

2. Classification

The classification shall be as given in Table 1.

Table 1. Classification

Classification	Main component
Pure pyridine	Pyridine
α -Picoline	Picoline
High boiling point picoline	
Fractionated quinoline	Quinoline

3. Quality

The quality of pyridine bases, when subjected to the tests specified in 4., shall conform to the requirements specified in Table 2.

Applicable Standards and Reference Standards: See pages 31 and 32.

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Table 2. Quality

Classification Item	Pure pyridine	α -Picoline	High boiling point picoline	Fractionated quinoline
Density (20°C) g/cm ³	0.980 to 0.988	0.940 to 0.948	0.940 to 0.955	1.086 to 1.096
Specific gravity (15/4°C)	0.985 to 0.993	0.945 to 0.953	0.945 to 0.960	1.090 to 1.100
Moisture content %	0.5 max.			
Pyridine %	99 min.	—	—	—
α -Picoline %	—	98 min.	—	—
Quinoline %	—	—	—	95 min.
Distillation test (for dehydrated sample)	—	—	Distillate amount at 140 to 145°C is 95 v/v % min.	—
Color	No. 20 max. of Hazen standard colorimetric solution	Colorless to light brown	Colorless to light yellow	Light brown to brown

Remark: Either density or specific gravity shall be applied.

4. Testing Methods

4.1 General Matters General matters common to the tests shall be in accordance with JIS K 0050 and, in addition, shall be as follows.

4.1.1 The % indicating the concentration of a reagent and a solution means, unless otherwise specified, mass percentage.

4.1.2 When a scale is read by the surface of a solution, the scale shall be read out by the upper or lower fringe of the solution having risen by surface tension according to the following classification.

(1) For a Hydrometer The upper fringe

(2) For a Measuring Cylinder or Others The lower fringe

4.1.3 For the hydrometer and thermometer, those which have been preliminarily calibrated shall be used.

Remark: All those which are described simply by solution and are not especially described by solvent, mean aqueous solution.

4.2 Sampling and Preparation of Sample

4.2.1 Sampling A sample is sampled in accordance with JIS K 2420, which shall be taken as a representative sample. However, in the case of sampling from a storage tank, when the contents have become thoroughly

uniform, the sample which is once sampled at one position may be taken as the representative sample.

Further, since pyridine bases have hygroscopicity and a coloring property, a shaded sealed container shall be used for a sample container.

4.2.2 Preparation of Sample A representative sample without dehydration which is sufficiently mixed as it is by shaking shall be used for a test.

4.2.3 Preparation of Dehydrated Sample Take about 300 ml a sample into a 500 ml glass interchangeable ground joint Erlenmeyer flask, add about 100 g potassium hydroxide specified in JIS K 8574, and stopper it. Then, heat at 50 to 60°C, after sufficiently shaking for 5 min min. keeping at almost a same temperature, allow to stand still for 30 min and further, repeat the same operation three times. Thereafter, take the supernatant, and take it as the dehydrated sample.

4.3 Method for Measurement of Density The method for measurement of density shall be in accordance with either of the following methods.

4.3.1 The First Method Measure specific gravity (15/4°C) in accordance with 4.4, and calculate density at 20°C from the following formula.

$$D = (d - 5 \times k) \times 0.99997$$

where, D : density (20°C) (g/cm³)

d : specific gravity (15/4°C)

k : specific gravity - temperature correction coefficient (°C⁻¹)

A value ⁽¹⁾ of k shall be as follows.

Class	k
Pure pyridine	0.001 01
α -Picoline	0.000 93
High boiling point picoline	0.000 91
Fractionated quinoline	0.000 76

0.99997: density of water at 4°C (g/cm³)

Note ⁽¹⁾ The value of k does not contain temperature correction of a hydrometer itself. Though the temperature correction value of the hydrometer of specific gravity (15/4°C) is given by $0.000\ 025 \times d \times (15 - t)$, since this correction value is very small, it may be ignored. Herein, t is measuring temperature (°C).

4.3.2 The Second Method Obtain density of a sample at 20°C in accordance with 4.3 Oscillating Type Density Meter Method of JIS K 2249. However, in the case where measuring temperature is except 20°C, calculate density (20°C) from the following formula.

$$D_{20} = D_t + k \times (t - 20)$$

where, D_{20} : density (20°C) (g/cm³)

D_t : measuring density at t °C (g/cm³)

k : density - temperature correction coefficient (g/cm³°C)

The value of k shall be as follows.

Class	k
Pure pyridine	0.001 01
α -Picoline	0.000 93
High boiling point picoline	0.000 91
Fractionated quinoline	0.000 76

t : measuring temperature of D_t (°C)

4.4 Method for Measurement of Specific Gravity

4.4.1 Summary Use a hydrometer, measure the specific gravity of a sample, and obtain specific gravity (15/4°C) by using specific gravity - temperature corrective coefficient.

4.4.2 Apparatus The apparatus shall be as follows.

- (1) Cylinder A glass cylinder with a spout of about 40 mm in inside diameter and about 350 mm in height.
- (2) Hydrometer A large type 19 pieces set (0.001 in subdivided scale) of No. 5 to 7 specified in JIS B 7525.
- (3) Thermometer A bar thermometer of which a scale is marked each 1°C from 0°C to 100°C, or that at least equivalent in accuracy.

4.4.3 Operation Carry out the operation as follows.

- (1) Take a sample into a cylinder, quietly float a hydrometer and allow to stand still as it is for about 10 min.
- (2) Sink the hydrometer by about two scales. When the hydrometer stands still by releasing one's hand, read out its scale (2).
- (3) Remove the hydrometer, and immediately put a thermometer. After stirring, make the indication position of the thermometer appear slightly above the surface of solution, read out the indication, and takes it as the temperature of the sample at the time of measuring.

- (4) Take the amount of the sample, when the hydrometer is put in, so as to make the distance between its lower end and the bottom of the cylinder not less than 15 mm, and perform the measurement at 10 to 20°C.

Note (2) The operation of sinking the hydrometer into solution by about two scales is performed in order to make a meniscus at the neck of the hydrometer clear. In the case where the meniscus is not clear, the hydrometer shall be washed.

Further, when the neck is sunk into the solution by two scales or over at the time of measuring, adhering solution increases to that extent and the mass of the hydrometer is increased. Then, precaution shall be taken therefor.

4.4.4 Calculation Calculate specific gravity from the following formula.

$$d = d_1 + k(t - 15)$$

where, d : specific gravity (15/4°C)

d_1 : measured specific gravity

k : specific gravity - temperature correction coefficient (°C⁻¹)

A value of k (1) shall be as described in the value of k of 4.3.1.

t : measured temperature (°C)

4.5 Method for Determination of Moisture Moisture shall be determined in accordance with either of volumetric titration method or coulometric titration method according to Karl Fischer's method. General matters common to this test shall be in accordance with JIS K 0068.

4.5.1 Volumetric Titration Method

- (1) Summary The volumetric titration method is a measuring method in which the quantitative reaction of Karl Fischer's reagent having iodine, sulfur dioxide, pyridine or base instead thereof, and organic solvent such as methanol, chloroform, etc. as components with water is utilized.

- (2) Apparatus The apparatus shall be as follows.

(2.1) Sampling Apparatus

(a) Syringe

Injection Cylinder lock type, 1 to 10 ml

Injection Needle lock type, 1 mm in outside diameter, 50 to 70 mm in length

- (b) Pipette 2 to 20 ml
- (c) Rubber Stopper Silicon rubber stopper of round style, diameter 13 to 15 mm, thickness 5 to 7 mm
- (2.2) Chemical Balance A chemical balance capable of weighing to the nearest 0.1 mg.

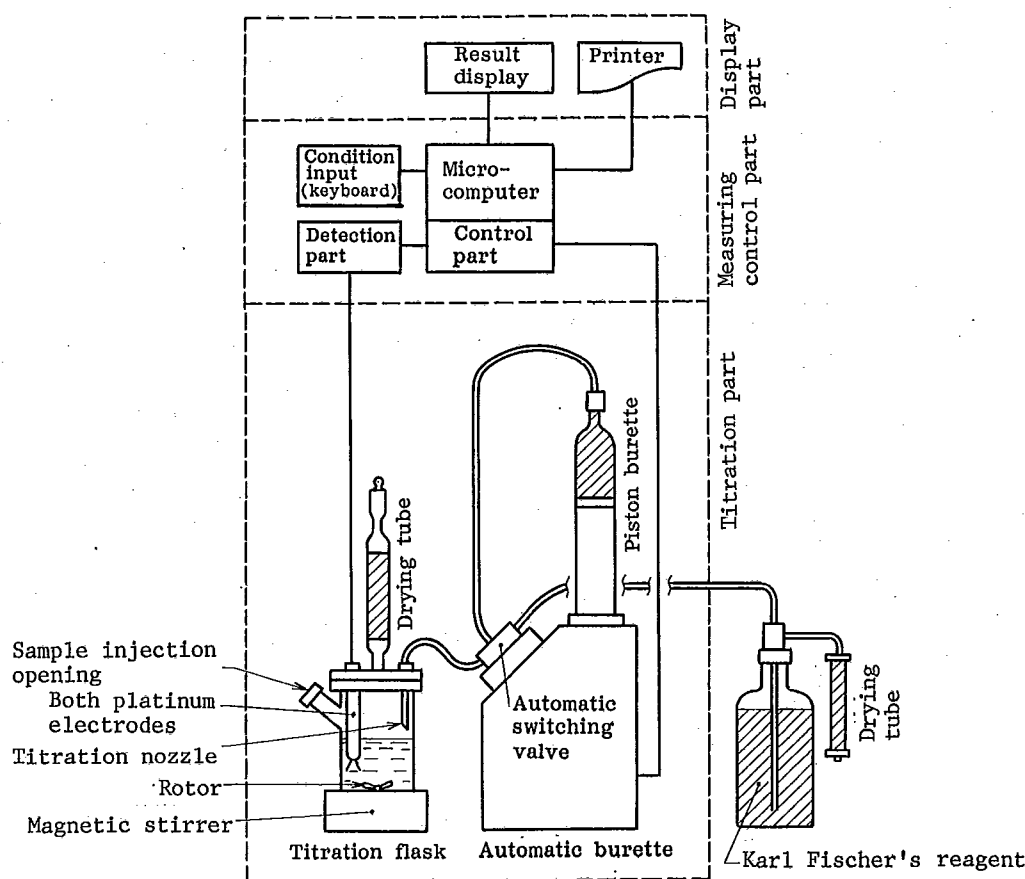
Remark: It is convenient to use a chemical balance which is connected to an automatic titration apparatus with an appropriate connection tool and to which mass can be automatically inputted.

- (2.3) Automatic Volumetric Titration Apparatus An automatic volumetric titration apparatus is composed of a titration part consisting of a titration flask and an automatic burette, a measuring control part having a titration control function with a micro-computer, a data processing function, and an end point detecting function, and a display part.

The joint part of glassware shall be ground-in, which is prevented from absorbing humidity in the open air by applying grease (neither reacted on nor dissolved in Karl Fischer's reagent).

A constitutional example is given in Fig. 1.

Fig. 1. Constitutional Example of Automatic Volumetric Titration Apparatus



- (2.4) Titration Flask A titration flask shall be an about 100 to 250 ml capacity glass flat bottom flask equipped with a sample injection opening, both platinum electrodes, a titration nozzle, and a drying tube containing drying agent such as silica gel or the like, which is placed on a magnetic stirrer capable of controlling suitably a stirring speed.

The sample injection opening is so constructed that a stainless steel or ethylene tetrafluoride resin stopper can be ground-in to be jointed thereto.

- (2.5) Both Platinum Electrodes Polarization is caused by making a weak current (a.c. or d.c.) flow to both platinum electrodes immersed in titrant. Iodine becomes slightly excess by titration with Karl Fischer's reagent, and the polarization is depolarized. Both platinum electrodes capable of detecting electrically the depolarization of said polarization as an end point.
- (2.6) Automatic Burette An automatic burette is a 10 ml or 20 ml capacity piston burette with an automatic switching valve, of which the minimum discharge amount with a pulse motor is 0.01 to 0.02 ml.
- (2.7) Drying Desiccator A drying desiccator containing drying agent such as silica gel or the like.
- (2.8) Desiccator for Regulation of Moisture A desiccator for regulation of moisture containing sodium bromide specified in JIS K 8514 plus about 10 % water.

- (3) Reagents The reagents shall be as follows.

- (3.1) Karl Fischer's Reagent A Karl Fischer's reagent of which potency is about 3 mgH₂O/ml by preliminarily standardizing it in accordance with (4) (4.1).

Remark: This reagent is reserved in a cold dark place by putting in a sealed container. In preparing it is prepared in accordance with 2.1 (2) (d) of JIS K 0068. However, in the case where it is prepared, it shall be standardized after not less than 24 h have elapsed.

Further, since the potency varies as time elapse, it is standardized each service.

Informative Reference: Karl Fischer's reagent on the market may be used.

- (3.2) Sodium Tartrate Recrystallize from the solution of sodium tartrate specified in JIS K 8540, remove moisture stuck to the crystal, put into a desiccator for regulation of moisture, and keep at 10 to 30°C for 48 h or longer. Sodium tartrate obtained thus.

- (3.3) Solvent Methanol for Karl Fischer's Titration Take 1000 ml methanol specified in JIS K 8891 into a titration flask, add 5 g magnesium powder specified in JIS K 8876, attach a moisture absorbing tube containing calcium chloride specified in JIS K 8125 and a reflux condenser to the upper end of the titration flask, and gently heat. When required, add 0.5 g iodine specified in JIS K 8920, and promote the reaction.

After generation of gas has been stopped, connect a collection bottle equipped with a condenser and the above-mentioned moisture absorbing tube to the upper part of the titration flask, distillate methanol, and seal to be reserved.

Further, allow moisture in 1 ml this product to be 0.2 mg or under.

Informative Reference: Solvent for Karl Fischer's titration on the market having methanol as a main component may be used.

- (4) Operation Carry out the operation as follows.

- (4.1) Standardization of Karl Fischer's Reagent Take 50 ml methanol into a titration flask, and add Karl Fischer's reagent accurately thereto to the end point of titration. Then, quickly add about 50 mg water to this solution by weighing to the nearest 0.1 mg, or otherwise add about 150 mg sodium tartrate thereto by weighing to the nearest 0.1 mg, and immediately titrate with Karl Fischer's reagent to the end point sufficiently stirring them.

Calculate the mass (mg) (potency) of water corresponding to 1 ml Karl Fischer's reagent from the following formula.

In the case where water is used $F = \frac{W}{a}$

In the case where sodium tartrate is used $F = \frac{Z \times \frac{36.0}{230.1}}{a}$

where, F : potency (mg H₂O/ml)

W : mass of water (mg)

Z : mass of sodium tartrate (mg)

a : volume of Karl Fischer's reagent used for titration (ml)

- (4.2) Sampling Carry out the sampling by using either of a syringe or a pipette.

(4.2.1) In the Case Where Syringe Is Used

- (a) Preliminarily wash an injection cylinder and an injection needle. After drying, reserve in a desiccator.
- (b) Take the injection cylinder and the injection needle out from the desiccator, connect, and quickly insert the top of the injection needle into a rubber stopper.
- (c) After temperature of a sample in a sealed container has reached room temperature, make uniform by shaking the sample, and open the stopper of the sealed container.
- (d) Remove the rubber stopper of the syringe. After pushing a piston sufficiently down, quickly sample in accordance with Table 3, and immediately insert the injection needle into the rubber stopper. At that time, even though some bubbles remain in the injection cylinder, there is no trouble.

Table 3. Sampling Amount

Expected moisture	Under 0.1 %	0.1 to 0.5 %	0.5 to 1 %
Sampling amount	10 to 20 ml	5 to 10 ml	2 ml

- (e) After ending the operation of (d), immediately weigh the mass of all the syringe to the nearest 0.1 mg.

Remark: When a syringe is necessarily washed together with a sample, move a piston up and down while an injection needle is immersed into the sample, and complete the operation from washing together to sampling as short as possible.

(4.2.2) In the Case Where Pipette Is Used

- (a) Preliminarily wash a pipette to be dried.
- (b) After the temperature of a sample in a sealed container has reached room temperature, mix the sample by shaking. After making uniform, open the stopper of the sealed container.
- (c) Quickly sample the amount determined according to Table 1 of the sample, and conform to the mark.

Remark: In order to obtain mass from the volume of the sample, use density at a temperature at the time of sampling, and calculate from the following formula.

$$\text{Mass of sample (g)} = \text{density (g/ml)} \times \text{volume of sample (ml)}$$