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Testing method for alkyl phenols in
industrial water and wastewater

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Foreword

This translation has been made based on the original Japanese Industrial Standard revised by the Minister of Economy, Trade and Industry through deliberations at the Japanese Industrial Standards Committee as the result of proposal for revision of Japanese Industrial Standard submitted by Japan Industrial Water Association (JIWA)/Japanese Standards Association (JSA) with the draft being attached, based on the provision of Article 12 Clause 1 of the Industrial Standardization Law applicable to the case of revision by the provision of Article 14.

Consequently **JIS K 0450-20-10:2002** is replaced with this Standard.

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JIS K 0450 consists of the following parts.

JIS K 0450-10-10 *Testing method for bisphenol A in industrial water and waste water*

JIS K 0450-20-10 *Testing method for alkyl phenols in industrial water and wastewater*

JIS K 0450-30-10 *Testing method for phthalic acid esters in industrial water and wastewater*

JIS K 0450-40-10 *Testing method for hexanedioic acid bis(2-ethylhexyl) ester in industrial water and wastewater*

JIS K 0450-50-10 *Testing method for benzophenone in industrial water and wastewater*

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Testing method for alkyl phenols in industrial water and wastewater

1 Scope This Japanese Industrial Standard specifies the testing method for substances of table 1 among alkyl phenols in industrial water and wastewater.

Table 1 Analyte list

Chemical Abstracts name	Common name	CAS No.	Molecular formula
4-(1,1-dimethylethyl) phenol	4- <i>t</i> -butylphenol	98-54-4	C ₁₀ H ₁₄ O
4-pentylphenol	4- <i>n</i> -pentylphenol	14938-35-3	C ₁₁ H ₁₆ O
4-hexylphenol	4- <i>n</i> -hexylphenol	2446-69-7	C ₁₂ H ₁₈ O
4-heptylphenol	4- <i>n</i> -heptylphenol	1987-50-4	C ₁₃ H ₂₀ O
4-(1,1,3,3-tetramethylbutyl) phenol	4- <i>t</i> -octylphenol	140-66-9	C ₁₄ H ₂₂ O
4-octylphenol	4- <i>n</i> -octylphenol	1806-26-4	C ₁₄ H ₂₂ O
Nonylphenol *	Nonylphenol	104-40-5 25154-52-3	C ₁₅ H ₂₄ O

Note * Nonylphenol here refers to, for the most part, the substance in which the 4-position (*p*-position) of phenol is substituted by nonane [CH₃(CH₂)₇CH₃] (4-nonylphenol), however, it also includes the substance in which the 2-position (*o*-position) or 3-position (*m*-position) is substituted and the isomer whose carbon number is 9 (the sum of carbon number of a normal chain and a side chain).

2 Normative references The standards listed in attached table 1 contain provisions which, through reference in this text, constitute provisions of this part of **JIS K 0450**. The most recent editions of these standards (including amendments) shall be applied.

3 Common matters Common matters shall be as follows.

- General rules** The general matters common to chemical analysis shall be in accordance with **JIS K 0050**.
- Terms and definitions** For the purposes of this part of **JIS K 0450**, the definitions given in **JIS K 0101**, **JIS K 0102**, **JIS K 0211** and **JIS K 0215** apply.
- Gas chromatography/mass spectrometry method** The general matters common to gas chromatography/mass spectrometry shall be in accordance with **JIS K 0123**.
- Name of compound** For the name of compound, the nomenclature of compounds [based on the nomenclature of organic chemistry of International Union of Pure and Applied Chemistry (IUPAC)] established by the Chemical Society of Japan shall be used, and the common name thereof shall be suffixed in parentheses.
- Water** The water to be used in this part of **JIS K 0450** shall be A1 to A4 water specified in **JIS K 0557**.

f) Reagents

- 1) The reagents, which are specified in **JIS** and do not hinder the test, shall be used. When there are no specifications in **JIS**, those which do not hinder the test shall be used.
- 2) The concentration of standard solution shall be expressed in mg/ml, µg/ml or ng/ml.
- 3) The concentration of the mixed solution of A and B shall be expressed by C(a+b). This expression indicates that A and B are mixed in the rate of *a* ml and *b* ml.
- 4) The concentration indicated in parentheses behind the name of standard solution means that it is a correct concentration.
- 5) The designations of reagents shall basically conform to the nomenclature of compounds established by the Chemical Society of Japan based on the nomenclature of inorganic chemistry and the nomenclature of organic chemistry of the International Union of Pure and Applied Chemistry (IUPAC) and the designations of **JIS** reagents.
- 6) The standard substances or the approved standard substances of which the traceability is secured to a maximum extent shall be used for the reagents for the preparation of standard solution. When they are not available, those of which purity and uncertainty are clarified shall be used⁽¹⁾. In this part of **JIS K 0450**, they are described as “standard products”. Some of them may include the resembling compounds as impurities, so those which do not hinder the test shall be used.

Note ⁽¹⁾ The purity of nonylphenol varies according to the content of isomer whose carbon number is 9 as well as that of 4-nonylphenol.

- 7) Care shall be taken of the room pollution, the inhalation and adherence to human body due to reagents and waste liquids. For handling reagents and wastewater, care shall be sufficiently taken to ensure that the related laws and regulations shall be observed.

g) Glasswares The common matters of glasswares shall be as follows.

- 1) Unless otherwise specified, the glasswares specified in **JIS R 3503** and **JIS R 3505** shall be used. However, for the cock parts of the separatory funnel and the like, those made of tetrafluoroethylene resin may be used. When heating operation is accompanied, the borosilicate glass-1 specified in **JIS R 3503** shall be used.

For the desiccant to be used in desiccator, unless otherwise specified, silica gel⁽²⁾ shall be used.

Note ⁽²⁾ The desiccant of Type A Class 1 silica gel for packing specified in **JIS Z 0701** shall be used.

- 2) The glasswares to be used in the test shall be washed with water of **5.1.1 a)** before using, and furthermore washed with acetone (of the quality of concentration 300 or more, specified in **JIS K 8040**), and acetone shall be volatilized by leaving it as it is. Afterward, they shall be heated about at 200 °C about for 2 h and be allowed to cool in a pollution-free place.

- h) **Working curve** For the preparation of working curve, the determination range shown in the test method shall be divided into four stages to six stages, and the standard solution shall be taken so that the amount of alkyl phenols on introduction to the gas chromatograph mass spectrometer shall coincide with the respective amount. The working curve shall be prepared within the determination range.

4 Sample

4.1 Sampling

4.1.1 Sample container For the sample container, a 1 000 ml glass bottle with ground stopper⁽³⁾ shall be used.

Note ⁽³⁾ A screw cap (with a tetrafluoroethylene resin packing) may be used instead of a ground stopper.

4.1.2 Sampling operation The sampling operation shall be as follows.

- a) **Sampling of surface water** In accordance with 4.1.1 or 4.1.2 of JIS K 0094.
- b) **Sampling of water at each depth** In accordance with 4.1.4 of JIS K 0094.
- c) **Sampling from piping apparatus** In accordance with 4.3 of JIS K 0094.

4.2 Handling of sample The test shall be carried out immediately after sampling. When it is unable, it shall be preserved at a dark place of 0 °C to 10 °C and be tested as quickly as possible. When it is preserved in a cool place, it shall be made so as not to be frozen.

5 Pretreatment of sample For the pretreatment of sample, the solvent extraction method or the solid phase extraction method shall be applied. For the sample containing suspended matters, the solid phase extraction method may influence extraction and therefore, care shall be taken.

When plenty of suspended matters are contained in the sample, carry out operations of NOTE 1 of 5.1.3.

5.1 Solvent extraction method Adjust the pH value to about 3 by adding hydrochloric acid to the sample, add sodium chloride, and add deuteride shown in table 2 as the internal standard material. Then, extract analyte by dichloromethane, dehydrate and concentrate, and make it a defined quantity by adding phenanthrene-*d*₁₀⁽⁴⁾.

Note ⁽⁴⁾ In accordance with 3 f) 7).

Table 2 List of deuteride of analyte

No.	Deuteride of analyte
1	4-(1,1-dimethylethyl) phenol [4- <i>t</i> -butylphenol]- <i>d</i> ₄
2	4-pentylphenol [4- <i>n</i> -pentylphenol]- <i>d</i> ₄
3	4-hexylphenol [4- <i>n</i> -hexylphenol]- <i>d</i> ₄
4	4-heptylphenol [4- <i>n</i> -heptylphenol]- <i>d</i> ₄
5	4-(1,1,3,3-tetramethylbutyl) phenol [4- <i>t</i> -octylphenol]- <i>d</i> ₄
6	4-octylphenol [4- <i>n</i> -octylphenol]- <i>d</i> ₄
7	4-nonylphenol [4- <i>n</i> -nonylphenol]- <i>d</i> ₄

5.1.1 Reagents The reagents shall be as follows.

- a) **Water** Of A4 (or A3) in **3 e)** shall be used⁽⁵⁾ for the preparation of reagents, operations and the blank test.

Note ⁽⁵⁾ Use the water immediately after purified. If required, carry out the operation of Annex 1 (normative) before using, and confirm that the peak is not found at the position corresponding to the retention time of alkyl phenols. When the purification is additionally required, treat by the method according to Remarks 6 in clause 4 of **JIS K 0557** or treat the water of A4 or A3 by activated carbon and the like.

- b) **Hydrochloric acid (1 mol/L)** Prepare by using the hydrochloric acid specified in **JIS K 8180**.
- c) **Sodium chloride** Heat the sodium chloride specified in **JIS K 8150** at about 600 °C for about 60 min, and then allow it to cool in a desiccator.
- d) **Sodium sulfate** Heat the sodium sulfate specified in **JIS K 8987** at about 600 °C for about 60 min, and then allow it to cool in a desiccator.
- e) **Acetone** Of 300 or more in concentration specified in **JIS K 8040**⁽⁶⁾.

Note ⁽⁶⁾ Before using, carry out the operation of **5.1.3 d)** and **e)** [provided that the addition of phenanthrene-*d*₁₀ internal standard solution (1 µg/ml) is not carried out] by using 10 ml, carry out the operation of **6.3 c)** by using this solution and confirm that the peak is not found at the position corresponding to the retention time of individual analyte.

After breaking the seal, preserve it in a pollution-free place.

- f) **Dichloromethane** Of 300 or more in concentration specified in **JIS K 8117**⁽⁷⁾.

Note ⁽⁷⁾ Before using, carry out the operation of **5.1.3 d)** and **e)** [provided that the addition of phenanthrene-*d*₁₀ internal standard solution (1 µg/ml) is not carried out] by using 100 ml, carry out the operation of **6.3 c)** by using this solution and confirm that the peak is not found at the position corresponding to the retention time of individual analyte.

- g) **Individual deuteride internal standard solution (1 mg/ml-acetone)** Take 0.100 g of the standard product of individual deuteride shown in table 2, transfer

it into a 100 ml volumetric flask containing 5 ml to 10 ml of acetone respectively, and add acetone up to the marked line⁽⁸⁾.

Note ⁽⁸⁾ Preserve it in a dark place of 5 °C or lower.

- h) **Deuteride mixture internal standard solution (10 µg/ml–acetone for each)**
Take 1 ml of individual deuteride internal standard solution (1 mg/ml–acetone) respectively prepared in **g**), transfer it into a 100 ml volumetric flask containing 5 ml to 10 ml of acetone and add acetone up to the marked line⁽⁸⁾.
- i) **Deuteride mixture internal standard solution (1 µg/ml–acetone for each)**
Take 1 ml of deuteride mixture internal standard solution (10 µg/ml–acetone for each), transfer it into a 10 ml volumetric flask containing about 2 ml of acetone and add acetone up to the marked line⁽⁸⁾.
- j) **Phenanthrene-*d*₁₀ internal standard solution (10 µg/ml)** Take 0.100 g of the standard product of phenanthrene-*d*₁₀ (C₁₄H₁₀-*d*₁₀), transfer it into a 100 ml volumetric flask containing 5 ml to 10 ml of dichloromethane and add dichloromethane up to the marked line⁽⁸⁾.
- k) **Phenanthrene-*d*₁₀ internal standard solution (1 µg/ml)** Take 1 ml of phenanthrene-*d*₁₀ internal standard solution (10 µg/ml) to a 10 ml volumetric flask and add dichloromethane up to the marked line⁽⁸⁾.
- l) **Nitrogen** Nitrogen Class 2, specified in **JIS K 1107**.

5.1.2 Implements The implements shall be as follows.

- a) **Separatory funnel** Of 2 000 ml
- b) **Graduated test tube with ground stopper** Of 10 ml to 20 ml having the graduation at 0.5 ml and 1 ml
- c) **Erlenmeyer flask with ground stopper** Of 100 ml to 500 ml
- d) **Concentrator** Rotary evaporator or Kuderna-Danish concentrator⁽⁹⁾
Note ⁽⁹⁾ Those without capillary.
- e) **Flask for concentrator** An egg-plant type flask when a rotary evaporator is used, and a concentrating flask with concentration tube when a Kuderna-Danish concentrator is used. The flask shall be the one of 200 ml to 300 ml with interchangeable ground joint and be capable of connecting with a concentrator.
- f) **Shaker**

5.1.3 Operation The operation shall be as follows.

- a) Take an adequate amount (for example, 1 L) of sample⁽¹⁰⁾ taken in **4.1.2** in a separatory funnel, adjust the pH at about 3 by adding hydrochloric acid (1 mol/L), and add 30 g of sodium chloride per 1 L of liquid amount⁽¹¹⁾. Successively, add 1 ml of deuteride mixture internal standard solution (1 µg/ml–acetone for each), add 50 ml of dichloromethane, shake to mix it by using a shaker for about 10 min, and leave it as it is.

Notes ⁽¹⁰⁾ When plenty of suspended matters are contained in the sample, carry out operations of NOTE 1.

⁽¹¹⁾ When the sample is sea water, do not add sodium chloride.

- b) Transfer the dichloromethane layer into an Erlenmeyer flask with ground stopper. Add 50 ml of dichloromethane per 1 L of liquid amount in the water layer of separatory funnel, shake to mix it by using a shaker for about 10 min, and leave it as it is. Join the dichloromethane layer obtained together to the previous Erlenmeyer flask with ground stopper.
- c) Add 20 g to 30 g⁽¹²⁾ of sodium sulfate in 100 ml of dichloromethane solution in the Erlenmeyer flask with ground stopper, shake to mix it lightly, leave it for about 10 min as it is, and dehydrate it⁽¹³⁾. Filter it by using the filter paper of Class 5 A (or Class 5 B)⁽¹⁴⁾ and receive the filtrate in a flask for concentrator. Wash the Erlenmeyer flask with ground stopper in which the dichloromethane solution had been contained twice or thrice by using a small amount of dichloromethane. Furthermore, wash the previous filter paper and sodium sulfate on filter paper with this washings and join the washings together to the flask for concentrator.

Notes ⁽¹²⁾ When emulsion is produced, it is required to add it more excessively.

⁽¹³⁾ In addition, for the dehydration operation, there is a method that the dichloromethane solution is preserved in a dark place at -20 °C and separated by freezing water. This method should be used when the concentration operation is not carried out on that day.

⁽¹⁴⁾ The filter paper shall be washed with dichloromethane preliminarily.

- d) Concentrate the dichloromethane solution by using a concentrator as heating it in a water bath at about 40 °C⁽¹⁵⁾ until it becomes about 5 ml.

Note ⁽¹⁵⁾ When a rotary evaporator is used, concentrate it in a water bath at about 40 °C under reducing pressure, and take care so as not to be exsiccated. When a Kuderna-Danish concentrator is used, concentrate it by heating at 75 °C or lower under atmospheric pressure, not the reducing pressure system. After completing the concentration, detach the Snyder column attached to the concentration part from the apparatus, wash it by adding a small amount of dichloromethane from the upper part of Snyder column and allow it to cool as the Snyder column is attached as it is.

- e) Transfer this concentrated solution into a graduated test tube with ground stopper. Wash the flask for concentrator used for concentration with 2 ml to 3 ml of dichloromethane and join its washings together in the graduated test tube with ground stopper. Successively, add 1 ml of phenanthrene-*d*₁₀ internal standard solution (1 µg/ml), concentrate it until it becomes about 1 ml by spraying nitrogen gently as heating it in a water bath at about 40 °C⁽¹⁶⁾ ⁽¹⁷⁾ ⁽¹⁸⁾, and take this as the solution for measurement.

Notes ⁽¹⁶⁾ When the operation of **6.3** is not carried out immediately, preserve this concentrated solution in a dark place at -20 °C.

⁽¹⁷⁾ When the interfering substance coexists, carry out the operation of Annex 2 (normative).

- (¹⁸) In the operation of spraying nitrogen, take care so that the concentrated solution does not scatter. Regulate the flow rate of nitrogen to the degree that the moving of the surface of concentrated solution is barely visible. When it is exsiccated, the analyte may be volatilized by spraying nitrogen in some cases. Therefore, care shall be taken.
- f) For the blank test, take the same amount of water as the sample in a separatory funnel instead of the sample, and carry out operations of **a)** to **e)**. Take this as the solution for blank test.

NOTE 1 When plenty of suspended matters are contained in the sample, carry out the following operations and successively carry out operations on and after the addition of sodium chloride of **5.1.3 a)**.

- 1) Shake to mix the sample taken in **4.1.2**, disperse the suspended matters uniformly and take the adequate amount of it. Then, carry out suction filtration by using the glass fibre filter paper whose hole diameter is 1 μm washed with acetone [use the filter (separate type) in **14.1** of **JIS K 0102**].
- 2) Transfer the whole suspended matters on the glass fibre filter paper together with the glass fibre filter paper into a beaker, add about 10 ml of acetone and carry out the eluting operation twice or thrice by using a ultrasonic cleaner. Join the eluate together, carry out the concentration under reduced pressure by using a concentrator and make it about 5 ml.
- 3) Transfer the filtrate of **1)** and the concentrated solution of **2)** into a separatory funnel, adjust the pH at about 3 by adding hydrochloric acid (1 mol/L), and successively carry out operations on and after the addition of sodium chloride of **5.1.3 a)**.

5.2 Solid phase extraction method Adjust the pH at about 3.5 by adding hydrochloric acid to the sample, add deuteride shown in table 2 as the internal standard material, adsorb the analyte by passing water by the pressurization method(¹⁹) or the depressurization method(²⁰) with a solid phase column or a solid phase disc, afterwards elute it with dichloromethane, concentrate it at about 40 °C and make it a defined quantity by adding phenanthrene-*d*₁₀(⁴).

Notes (¹⁹) The method such that the sample is fed to a solid phase column under the pressurized condition.

The apparatus shall consist of a regulation part and a pump part. The regulation part controls the time of passing sample and the flow rate of water flow. For the pump part, there are the method using a syringe and the method using a peristaltic pump. For the syringe, the tube made of tetrafluoroethylene resin shall be used. For the peristaltic pump, the tube for pump suitable to the solvent to be used shall be used.

(²⁰) The method such that the sample is fed so that the bottom side of solid phase column is made to be the depressurized condition.

The apparatus shall consist of a piping part for suction and a vacuum pump or an aspirator.

It is difficult in this method to keep the flow rate at constant rate due to the dispersion in liquid-flow resistance of solid phase, the suspended matters in the sample and the like, however there are advantages that plenty of samples are able to be treated by using a simple apparatus at the same time, and the like.

5.2.1 Reagents The reagents shall be as follows.

- a) **Water** In accordance with **5.1.1 a)**.
- b) **Hydrochloric acid (1 mol/L)** In accordance with **5.1.1 b)**.
- c) **Acetone** In accordance with **5.1.1 e)**.
- d) **Dichloromethane** In accordance with **5.1.1 f)**⁽²¹⁾.

Note ⁽²¹⁾ Methyl acetate specified in **JIS K 8382** may be used. In this case, concentrate 10 ml using the concentrator [in accordance with **5.1.2 d)**] by the concentration operation of **5.1.3 e)** [provided that the addition of phenanthrene-*d*₁₀ internal standard solution (1 µg/ml) is not carried out] to about 1 ml before using. Carry out the operation of **6.3 c)** by using this solution and confirm that the peak is not found at the position corresponding to the retention time of individual analyte.

After breaking the seal, preserve it in a pollution-free place.

- e) **Deuteride mixture internal standard solution (1 µg/ml–acetone for each)**
In accordance with **5.1.1 i)**.
- f) **Phenanthrene-*d*₁₀ internal standard solution (1 µg/ml)** In accordance with **5.1.1 k)**.
- g) **Nitrogen** In accordance with **5.1.1 l)**.

5.2.2 Implements The implements shall be as follows.

- a) **Graduated test tube with ground stopper** In accordance with **5.1.2 b)**.
- b) **Solid phase column** The cartridge of 10 mm in inside diameter and 30 mm to 50 mm in length. The column packing shall be the silica gel bonded chemically with reversed phase compound or the one filled with synthetic adsorbent. The synthetic adsorbent shall be porous styrene-divinylbenzene copolymer or the one having the same performance as it. Before using, wash it by passing about 10 ml of acetone and next about 10 ml of water.

NOTE 2 For the solid phase, there is a disc type on the market, and it may be used. In this case, confirm the flow rate of sample and the required amount of eluting solvent beforehand.

Information : For the solid phase column or the solid phase disc, the following is available on the market.

Sep-Pak PS-2, OasisTMHLB, InertSep RP-1, Aquisis PLS-3, Excelpak SPE-ENV/124 cartridge type, Empore disk SDB-RPS, and the like.