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**Testing method for phthalic acid
esters in industrial water and
wastewater**

ICS 13.060.50; 83.040.30

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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 0450-30-10:2002** is replaced with this Standard.

Attention is drawn to the possibility that some parts of this Standard may conflict with a patent right, application for a patent after opening to the public, utility model right or application for registration of utility model after opening to the public which have technical properties. The relevant Minister and the Japanese Industrial Standards Committee are not responsible for identifying the patent right, application for a patent after opening to the public, utility model right or application for registration of utility model after opening to the public which have the said technical properties.

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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Contents

	Page
1 Scope.....	1
2 Normative references	1
3 Common matters	1
4 Sample.....	3
4.1 Sampling	3
4.2 Handling of sample	3
5 Pretreatment of sample	3
5.1 Solvent extraction method	3
5.2 Solid phase extraction method	6
6 Gas chromatography/mass spectrometry	9
6.1 Reagents	9
6.2 Implements and apparatus	11
6.3 Operation	12
6.4 Working curve	13
7 Expression of result	14
Annex 1 (normative) Confirmation method for quality of water used for test	16
Annex 2 (normative) Column chromatographic separation method by using activated magnesium silicate	18
Annex 3 (normative) Calculation method for concentration by using sensitivity coefficient	22
Annex 4 (informative) Confirmation method for lower limit value in determination range of apparatus	23

Testing method for phthalic acid esters in industrial water and wastewater

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

NOTE : In this test, since the contamination coming from reagents, organic solvents and apparatus and the contamination coming from operations and air have serious influences on the results, special care shall be taken. Therefore, it is necessary to minimize reagents, the amount of contact with air and the contacting time.

Table 1 Analyte list

Chemical Abstracts name	Common name	CAS No.	Molecular formula
1,2-benzenedicarboxylic acid diethyl ester	diethyl phthalate	84-66-2	C ₁₂ H ₁₄ O ₄
1,2-benzenedicarboxylic acid dipropyl ester	dipropyl phthalate	131-16-8	C ₁₄ H ₁₈ O ₄
1,2-benzenedicarboxylic acid dibutyl ester	dibutyl phthalate	84-74-2	C ₁₆ H ₂₂ O ₄
1,2-benzenedicarboxylic acid dipentyl ester	dipentyl phthalate	131-18-0	C ₁₈ H ₂₆ O ₄
1,2-benzenedicarboxylic acid dihexyl ester	dihexyl phthalate	84-75-3	C ₂₀ H ₃₀ O ₄
1,2-benzenedicarboxylic acid bis (2-ethylhexyl) ester	di-2-ethylhexyl phthalate	117-81-7	C ₂₄ H ₃₈ O ₄
1,2-benzenedicarboxylic acid dicyclohexyl ester	dicyclohexyl phthalate	84-61-7	C ₂₀ H ₂₆ O ₄
1,2-benzenedicarboxylic acid butylphenylmethyl ester	butylbenzyl phthalate	85-68-7	C ₁₉ H ₂₀ O ₄

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.

e) **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. 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.
- 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 relate 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⁽¹⁾ shall be used.

Note ⁽¹⁾ 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 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 at about 200 °C or higher about for 2 h and be allowed to cool at 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 phthalic acid esters 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⁽²⁾ shall be used.

Note ⁽²⁾ 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 at 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 the extraction, therefore care shall be taken.

5.1 Solvent extraction method Add deuteride shown in table 2 as the internal standard material and sodium chloride. Then, add hexane, and after shaking and extracting, concentrate it to a fixed quantity, and dehydrate.

Table 2 List of deuteride of analyte

No.	Deuteride of analyte
1	1,2-benzenedicarboxylic acid diethyl ester [diethyl phthalate]- <i>d</i> ₄
2	1,2-benzenedicarboxylic acid dipropyl ester [dipropyl phthalate]- <i>d</i> ₄
3	1,2-benzenedicarboxylic acid dibutyl ester [dibutyl phthalate]- <i>d</i> ₄
4	1,2-benzenedicarboxylic acid dipentyl ester [dipentyl phthalate]- <i>d</i> ₄
5	1,2-benzenedicarboxylic acid dihexyl ester [dihexyl phthalate]- <i>d</i> ₄
6	1,2-benzenedicarboxylic acid bis (2-ethylhexyl) ester [di-2-ethylhexyl phthalate]- <i>d</i> ₄
7	1,2-benzenedicarboxylic acid dicyclohexyl ester [dicyclohexyl phthalate]- <i>d</i> ₄
8	1,2-benzenedicarboxylic acid butylphenylmethyl ester [butylbenzyl phthalate]- <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⁽³⁾ for the preparation of reagents, operations and the blank test.

Note ⁽³⁾ 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 phthalic acid esters or does not influence the test. When the purification is additionally required, treat by the method according to NOTE 6 in clause 4 of **JIS K 0557** or treat the water of A4 or A3 by activated carbon and the like.

In the case of using an activated carbon cartridge, the cartridge made of stainless steel or tetrafluoroethylene resin shall be used.

When storing, the material of storage tank shall be tetrafluoroethylene resin, and the activated carbon cartridge shall be placed in the inlet in contact with air.

- b) **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.
- c) **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.

Information : Sodium sulfate for the test of phthalic acid esters is on the market.

- d) **Acetone** Of 300 or more in concentration specified in **JIS K 8040**⁽⁴⁾.

Note ⁽⁴⁾ Before using, carry out the operation in accordance with **5.1.3 c)** 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 phthalic acid esters or does not influence the test. Open the same lot immediately before using, which has been examined that it does not hinder the measurement, and use it. If 24 h or longer elapse after opening, newly use the sealed one.

- e) **Hexane** Of 300 or more in concentration specified in **JIS K 8825**⁽⁵⁾.

Note ⁽⁵⁾ Before using, carry out the operation in accordance with **5.1.3 c)** by using 2.5 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 phthalic acid esters or does not influence the test. Open the same lot immediately before using, which has been examined that it does not hinder the measurement, and use it. If 24 h or longer elapse after opening, newly use the sealed one.

- f) **Individual deuteride standard solution (1 mg/ml-acetone)** Take 0.100 g of the standard product of individual deuteride shown in table 2 in 100 ml volumetric flasks respectively, and add acetone up to the marked line⁽⁶⁾ ⁽⁷⁾ ⁽⁸⁾.

Notes ⁽⁶⁾ Preserve it at a dark place of 5 °C or lower.

⁽⁷⁾ When contamination is observed, prepare them again.

(⁸) When preparing the working curve, each deuteride standard solution shall be prepared using hexane.

- g) **Deuteride mixture internal standard solution (10 µg/ml–acetone for each)**
Take 1 ml of individual deuteride standard solution (1 mg/ml–acetone) respectively prepared in f) in a 100 ml volumetric flask and add acetone up to the marked line(⁶) (⁷) (⁸).
- h) **Nitrogen** Nitrogen Class 2, specified in **JIS K 1107**.

5.1.2 Implements The implements shall be as follows. The washing procedure of glass apparatus to be used shall be in accordance with g) 2) of clause 3.

- a) **Graduated test tube with ground stopper** Of 10 ml to 20 ml, transparently ground having the graduation at 1 ml.
- b) **Microsyringe** Of 10 µl to 200 µl, or an automatic injecting apparatus.
- c) **Volumetric flask** Of 100 ml, transparently ground.
- d) **Shaker** Capable of shaking horizontally.

5.1.3 Operation The operation shall be as follows.

- a) Take 95 ml of sample taken in 4.1.2 in a 100 ml volumetric flask, add 10 µl of deuteride mixture internal standard solution (10 µg/ml–acetone for each) with a microsyringe and add 15 g of sodium chloride(⁹). Successively, add 2.5 ml of hexane(¹⁰), stopper and mix the sample and hexane. Keep this volumetric flask laterally on the shaker, shake(¹¹) (¹²) horizontally for about 10 min, and leave it as it is. Turn the volumetric flask over twice or three times, shake again(¹¹) (¹²) horizontally for about 10 min using a shaker, and leave it as it is.

Notes (⁹) Take care so as not to make it stick to the ground part of volumetric flask. A funnel should be used.

- (¹⁰) When plenty of suspended matters is contained in the sample, 0.1 ml to 0.5 ml of acetone should be added.
- (¹¹) Since the shaking time required for extraction is greatly influenced by the shape of volumetric flask and the shaking speed, confirm the optimum condition in the recovery test or the like beforehand.
- (¹²) The shaking extraction by a rotor using a magnetic stirrer may be carried out.

The shaking time is greatly influenced by the shape of volumetric flask and the rotation speed of magnetic stirrer, and the shaking for 1 h or longer may be required in some cases. Confirm the optimum condition in the recovery test or the like beforehand.

When the shaking time becomes longer, a magnetic stirrer generates heat and it may influence the extraction of analyte, so make the heat from the magnetic stirrer not to transfer to the volumetric flask.

- b) Transfer the separated hexane layer(¹³) into a graduated test tube with a ground stopper with a Pasteur pipette or a glass capillary tube paying attention so as not to make water come into as much as possible(¹⁴).

Notes ⁽¹³⁾ When the hexane layer develops emulsion, centrifuge at 20 000 m/s² to 30 000 m/s² (2 000 g to 3 000 g) for about 10 min to separate the hexane layer.

⁽¹⁴⁾ When plenty of interfering substance coexists in the sample, successively carry out the column chromatographic separation operation of Annex 2 (normative).

c) Concentrate until it becomes about 1 ml by spraying nitrogen gently at a room temperature⁽¹⁵⁾.

Note ⁽¹⁵⁾ 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.

d) Add about 0.3 g of sodium sulfate to this concentrated solution and take this solution as the solution for measurement.

e) For the blank test, take 95 ml of water in a 100 ml volumetric flask instead of the sample, carry out operations of **a)** to **d)** and take this as the solution for blank test.

5.2 Solid phase extraction method Add deuteride shown in table 2 as the internal standard material to the sample, make adsorb the analyte to the solid phase by passing the sample by the pressurization method⁽¹⁶⁾ or the depressurization method⁽¹⁷⁾ with a solid phase column or a solid phase disc, afterwards elute it with ethyl acetate and concentrate it at about 40 °C.

Notes ⁽¹⁶⁾ 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.

⁽¹⁷⁾ The method such that the sample is fed so that the bottom side of solid phase column is made to 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 is able to be treated by using a simple apparatus at the same time, and the like. In this method, take care so as not to be contaminated from air.