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Foreword

This translation has been made based on the original Japanese Industrial Standard established by the Minister of Land, Infrastructure and Transport through deliberations at the Japanese Industrial Standards Committee.

This Standard has been made based on **ISO/DIS 16000-4:2001** *Indoor air—Part 4: Determination of formaldehyde—Diffusive sampling method* for the purpose of making it easier to compare this Standard with International Standard; to prepare Japanese Industrial Standard conforming with International Standard; and to propose a draft of an International Standard which is based on Japanese Industrial Standard.

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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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Indoor air—Determination of formaldehyde —Diffusive sampling method

Introduction This Japanese Industrial Standard has been prepared based on the first edition of **ISO/DIS 16000-4** *Indoor air—Part 4 : Determination of formaldehyde—Diffusive sampling method* published in 2001 with some modifications of the technical contents.

The portions given sidelines or dotted underlines are the matters in which the contents of the original International Standard have been modified. A list of modifications with the explanations is given in Annex 3 (informative).

1 Scope This Standard specifies a passive sampler ⁽¹⁾/solvent desorption/high performance liquid chromatography (HPLC) method for the determination of formaldehyde in indoor air.

Note (1) Both terms, “diffusive sampler” and “passive sampler”, may be used in English, however, “パッシブサンプラ (PASSIBU SANPURA)” (passive sampler) is adopted hereafter in this Standard.

The test method is applicable to the measurement of formaldehyde over the range from 0.001 mg/m³ to 1.0 mg/m³ for a sampling period of between 24 h and 72 h. For sampling periods of 24 h, the applicable concentration range is 0.003 mg/m³ to 1.0 mg/m³, and for 72 h it is 0.001 mg/m³ to 0.33 mg/m³. The method is suitable for measurements in atmospheres of up to 80 % relative humidity and for monitoring at air velocities as low as 0.02 m/s.

Remarks : Samplers whose measurement sensitivity and precision are assured may apply to the short-term (less than 24 h) sampling (hereafter referred to as “short-term sampling”).

Potential interferences, including those due to the presence of other carbonyl compounds, shall be eliminated by the chromatographic step in the method. The sampling method gives a time-weighted average result.

In this Standard, reagents (DNPH-formaldehyde derivatives) and samplers to be used are presupposed as own works, however, those commercially available may be used in the case where the quality and performance are confirmed.

Remarks : The International Standard corresponding to this Standard is as follows.

In addition, 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**.

ISO/DIS 16000-4 : 2001 *Indoor air—Part 4 : Determination of formaldehyde—Diffusive sampling method* (MOD)

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 A 1961 *Indoor air—Sampling strategy for formaldehyde*

Remarks : ISO/DIS 16000-2 *Indoor air—Part 2 : Sampling strategy for formaldehyde* is identical with the said standard.

JIS A 1962 *Indoor air—Determination of formaldehyde and other carbonyl compounds—Active sampling method*

Remarks : ISO 16000-3 *Indoor air —Part 3 : Determination of formaldehyde and other carbonyl compounds—Active sampling method* is identical with the said standard.

JIS K 8180 *Hydrochloric acid*

JIS K 8295 *Glycerol*

JIS K 8480 *2,4-Dinitrophenylhydrazine*

JIS K 8872 *Formaldehyde solution*

JIS K 9005 *Phosphoric acid*

JIS Q 17025 *General requirements for the competence of testing and calibration laboratories*

Remarks : ISO/IEC 17025 *General requirements for the competence of testing and calibration laboratories* is identical with the said standard.

JIS Z 9900 *Quality management and quality assurance standards Part 1 : Guidelines for selection and use*

Remarks : ISO 9000-1 *Quality management and quality assurance standards—part 1 : Guidelines for selection and use* is identical with the said standard.

prEN 13528-2 *Ambient air quality—Diffusive samplers for the determination of gas and vapours—Requirements and test methods—Part 2 : Specific requirements and test methods*

3 Principle The passive sampler is exposed to air for a defined time period. The rate of sampling depends on the diffusion coefficient of formaldehyde, and is inversely proportional to the diffusion length of the passive sampler and proportional to the cross-sectional area of the opening of the monitor. This rate is known as the passive uptake rate of the sampler, and has been determined by prior calibration in a standard

atmosphere.

The formaldehyde vapour migrates into the sampler by diffusion and is collected on a collector which has been coated with 2,4-dinitrophenylhydrazine (DNPH) and phosphoric acid.

A stable hydrazone is formed which can be desorbed by acetonitrile and the solution analysed by means of a high performance liquid chromatograph (HPLC) equipped with an ultraviolet (UV) absorbance detector. The passive sampler may also be used for personal sampling, for which purpose it is attached to the clothing of the person being monitored.

4 Reagents

4.1 Reagents For the analysis, only the grade-known reagents shall be used. Acetonitrile and water shall be those for high performance liquid chromatograph. The following reagents shall be required.

- a) 2,4-dinitrophenylhydrazine : specified in **JIS K 8480**, and recrystallized at least twice with acetonitrile for measurement of UV absorbance or high performance liquid chromatograph
- b) Acetonitrile : being equivalent to that for measurement of UV absorbance or high performance liquid chromatograph (each solvent shall be tested before use)
- c) Water : being equivalent to that for high performance liquid chromatograph (distilled water)
- d) Concentrated hydrochloric acid : 36.5 % to 38 % (wt/wt) and 1.19 kg/L is density of guaranteed reagent specified in **JIS K 8180**
- e) Formaldehyde : 37 % solution (wt/wt) specified in **JIS K 8872**
- f) Ethanol : being equivalent to that for high performance liquid chromatograph
- g) Methanol : being equivalent to that for high performance liquid chromatograph
- h) Phosphoric acid : 85 % (wt/wt) and 1.69 kg/L in density of guaranteed reagent specified in **JIS K 9005**
- i) Glycerin : 99 % (wt/wt) and 1.26 kg/L in density of that specified in **JIS K 8295**

4.2 Formaldehyde hydrazone (DNPH-formaldehyde derivative) preparation Weigh 2 g of 2,4-dinitrophenylhydrazine and place in a 500 ml flask. Add 10 ml of concentrated hydrochloric acid with stirring. Dissolve the yellow precipitate formed in 200 ml of ethanol of 95 %.

Filter the solution to remove undissolved hydrazine hydrochloride (DNPH-HCl). To the filtered solution add 0.8 ml of formaldehyde of 37 %. Collect by filtration the yellowish precipitate formed, and wash with 5 ml of cold ethanol. Recrystallize the precipitate twice from hot ethanol and allow to dry in air. Check the purity of the DNPH-formaldehyde derivative by melting-point determination (166 °C).

Remarks : The quality-confirmed formaldehyde hydrazones which are commercially available may be used.

Warning 2,4-dinitrophenylhydrazine is explosive in the dry state. Handle with extreme care. It is also toxic (LD50, rat = 654 mg/kg), has been shown to be mutagenic in some tests, and is irritating to the eyes and skin.

4.3 DNPH-formaldehyde calibration standards preparation Accurately weigh about 10 mg of DNPH-formaldehyde derivative, place in a 100 ml volumetric flask, and fill to the 100 ml mark with acetonitrile.

Shake the flask until the crystals are dissolved. Prepare a minimum of five calibration standards in the range 1 µg/ml to 140 µg/ml (equivalent to 0.14 µg/ml to 20 µg/ml formaldehyde) by dilution of aliquots of the DNPH-formaldehyde solution with acetonitrile.

4.4 DNPH coating solution preparation Weigh 900 mg of DNPH hydrochloride that has been recrystallized twice from 4 M of HCl into a flask. Add 1.7 ml of 85 % phosphoric acid, 5 ml of 20 % glycerin in ethanol, and 180 ml of acetonitrile.

Remarks : This Standard specifies the preparation method for the coated filter or coated silica gel used in the sampler, however, the samplers, in which a coated filter or a coated silica gel is built in, are commercially available and have the advantage of more uniform manufacture and potentially lower blank levels.

4.5 Coated filter or coated silica gel (granular) preparation

4.5.1 Coated filter preparation The size of the coated filter depends on the construction of the passive sampler. For example, for a sampler requiring a 20 mm × 45 mm filter, add 0.5 ml of DNPH coating solution dropwise to the filter using a pipette.

Dry the coated filters on a glass surface in an oven at 85 °C for 15 min. For other filter sizes, adjust the volume of coating solution accordingly.

Remarks : Blank coated filters prepared and stored according to this Standard should contain less than 0.7 µg of DNPH-formaldehyde derivative per filter of dimension 20 mm × 20 mm (equivalent to 0.1 µg of formaldehyde).

4.5.2 Coated silica gel (granular) preparation Pour 75 ml of acetonitrile, 0.9 ml of 85 % phosphoric acid and 450 mg of purified DNPH (2,4-dinitrophenylhydrazine : specified in JIS K 8480 and recrystallized at least twice with acetonitrile for UV absorbance measurement or high performance liquid chromatograph) in a 1 L flask, carry out ultrasonic dispersion for 5 minutes and dissolve DNPH. Then, add 60 g of silica gel and 250 ml of acetonitrile in the above-mentioned flask, carry out ultrasonic dispersion for 5 minutes and disperse uniformly DNPH into silica gel. Next, transfer the above-mentioned solution into a 1 L eggplant type flask and set it to an evaporator. Carry out desolvation and dry under conditions of 40 °C to 50 °C in temperature and reduced pressure (0.08 MPa to 0.09 MPa). Transfer the coated silica gel into a light resistant bottle, furthermore put it in a bag of aluminium laminated, and after deairing, carry out heat-sealing. Then, keep it in a refrigerator (not more than 5 °C). A se-

quence of procedure should be carried out in the atmosphere of nitrogen.

Remarks 1 The cleaning method for silica gel to be used shall be as follows :

Put 60 g of silica gel (105 μm to 210 μm in particle size, 350 cm^2/g to 450 cm^2/g in surface area) and 250 ml of acetonitrile in a 500 ml beaker and carry out ultrasonic cleaning for 15 minutes as covering with a sheet of aluminium foil. Then carry out filtration under reduced pressure in the atmosphere of nitrogen. Afterwards, pour 100 ml of acetonitrile in a funnel and carry out cleaning. Carry out filtration under reduced pressure again. Repeat this procedure three times and complete the cleaning. Put the cleaned silica gel in a light resistant bottle seal, then store it.

2 The blank value of coated silica gel which has been prepared and stored according to this Standard should be not more than 0.7 μg of DNPH-formaldehyde derivative (0.1 μg as the amount of formaldehyde) per 250 mg.

5 Apparatus Ordinary laboratory apparatus shall be as follows :

5.1 Passive sampler Commercially available or laboratory constructed devices may be used provided that they meet the performance requirements.

The passive sampler shall have the opening exposed to the air and an appropriate diffusion length.

Remarks : A badge type sampler and a tube type sampler are supposed in this Standard, however, the sampling cartridge used for pumped sampling may be used in some cases. For the badge type sampler, various shapes of samplers (rectangular, round) exist. The tube type sampler is a porous tube filled with the collector (coated silica gel).

The passive sampling rate shall be independent of air concentration between 0.001 mg/m^3 and 0.33 mg/m^3 for 72 h and 0.003 mg/m^3 and 1.0 mg/m^3 for 24 h. Humidity shall have no effect on sampling rate up to 80 % relative humidity and the sampling rate shall not be significantly influenced by ambient air velocities as low as 0.02 m/s.

Remarks : In the case of applying to a short-time sampling, it shall be required to confirm diffusion uptake rate, sensitivity of measurement, precision and the like.

The sampler may require a stand or clip for positioning during sampling. When not in use, keep the sampler in a protective airtight container with a protective coated filter.

Guidance on the design and performance test procedures for a passive sampler is given in **prEN 13528-2**. This requires the generation of standard atmospheres in order to determine the diffusive uptake rate of the sampler under different conditions of temperature, humidity, air velocity, exposure time and gas concentration appropriate to the intended use of the sampler.

Examples of studies of the performance of a passive sampler for the measurement of formaldehyde in air are given in the Bibliography.

5.2 High performance liquid chromatograph HPLC consists of one or two solvent pumps, solvent reservoir(s), a solvent mixer, a reverse-phase column, a column oven, a pump controller and data-handling system. The column shall be linked to a UV detector able to monitor at a wavelength of 345 nm to 360 nm.

Remarks : It is known that an octadecylsilane column (5 µm in particle size, 150 mm in length, 4.6 mm in inside diameter) with using of a mobile phase of methanol/water = 70/30 or acetonitrile/water = 60/40 can provide sufficient resolution of the DNPH-formaldehyde and possible interfering compound.

Either a gradient method or an isocratic method may be employed. It is recommended that a DNPH-formaldehyde derivative of 0.21 µg/ml in concentration (0.03 µg/ml as formaldehyde concentration) is detectable by using the concerned apparatus and procedure.

6 Sampling Immediately before sampling, the passive sampler is removed from its protective bag or other suitable airtight container.

For area monitoring, the sampler shall be located in accordance with guidance given in JIS A 1961.

Information : The measurement method specified in JIS A 1961 is equivalent to that in ISO/DIS 16000-2.

The sampler shall be located at least 1 m from the walls of the room at height of 0.75 m to 1.5 m above the floor.

Areas of the room strongly influenced by local ventilation, such as near windows and doors, and areas near known sources of formaldehyde, such as uncoated particleboard, should be avoided unless these are of specific interest for the study.

When used for personal sampling, the sampler should be mounted on the lapel or other unobstructed part of the subject's clothing.

Once the sampler has been sited, begin the sampling period by opening the closure window of the sampler. Record the time and date of opening the sampler.

After the exposure has been finished, close the cover, etc. of the sampler and put in a protective airtight container together with the DNPH coated filter, if necessary, wrapped by metallic screen.

This DNPH coated filter adsorbs the formaldehyde in air in the container, therefore it can prevent contamination from the sample. The date and time of completion of sampling shall be recorded.

Remarks : The storage of the sampler after sampling shall follow the storing method of products on the market. In the case of the sampler of own work, it is recommended that an protective airtight container is pre-

pared including the preparation of DNPH coated filter to prevent contamination.

Prepare sample blanks (travel blanks) by using samplers identical to those used for sampling, and subject them to the same handling procedure as the exposed samplers except they shall not be exposed.

Alternatively, the sampler design may incorporate an unexposed portion of the coated filter that can serve as the blank. Return blank samples and exposed samplers to the laboratory for analysis.

Remarks : During active sampling of ambient air under particular atmospheric conditions, it has been reported that ozone can result in negative interference by reaction with DNPH and DNPH-formaldehyde derivative. This interference has not been observed with the passive sampler. Further information about this possible interference is described in JIS A 1962.

Information : The contents specified in JIS A 1962 are equivalent to that in ISO 16000-3.

7 Procedure

7.1 Desorption and sample preparation

7.1.1 Coated filter Desorption of the DNPH-formaldehyde derivative from the coated filter is carried out in a clean atmosphere. Remove the coated filter from the sampler with forceps.

If the sampler includes an integral blank coated filter, separate it from the exposed section of the filter by cutting. For example, for a filter that is 20 mm × 45 mm, cut it into sample and blank sections, place each filter section in a 4 ml glass vial.

Desorption is achieved by pipetting 3 ml of acetonitrile into each vial followed by agitation for 1 min. Remove the coated filter from the vial, then seal it.

If necessary, the extract may be filtered before HPLC analysis. For filters of other dimensions, the desorption procedure can be varied but it shall be shown to be at least 95 % efficient for desorbing DNPH-formaldehyde derivative. The DNPH-formaldehyde solution should be analysed within 3 days.

7.1.2 Coated silica gel (granular) The desorption of DNPH-formaldehyde derivative from coated silica gel (granular) shall be carried out in a clean atmosphere. For example, connect an injection tube (5 ml to 10 ml) to the sampler, and place it on a syringe rack. Pour 5 ml of acetonitrile into the injection tube and make it drop naturally (by gravity) or make it push to flow gently by the injection tube. Extract the DNPH derivative with unreacted DNPH into a test tube with graduation or a volumetric flask, and then adjust it at the marked line with using acetonitrile. Carry out the same procedure for the travel blank. If necessary, the extract may be filtered before HPLC analysis.

7.2 Calibration Analyse each calibration standard prepared according to 4.3 by in-