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Indoor air—Sampling and analysis of volatile organic compounds by solvent desorption/capillary gas chromatography—Pumped sampling

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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 in accordance with the Industrial Standardization Law.

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.

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In the event of any doubts arising as to the contents, the original JIS is to be the final authority.

Contents

Indoor air—Sampling and analysis of volatile organic compounds by solvent desorption/capillary gas chromatography —Pumped sampling

1 Scope This Japanese Industrial Standard indicates the general guideline relating to the pumped sampling and analysis of volatile organic compounds (VOC) in air. This Standard is applied to the indoor air.

This Standard is applied to the wide range of VOC including hydrocarbons, halogenated hydrocarbons, esters, glycol ethers, ketones and alcohols. For the measurements of these VOC, it is recommended to use samplers of which scopes are respectively different. For the compounds with low boiling point, only a part of them can be collected, therefore only a qualitative evaluation is possible. And semi-volatile compounds are wholly adsorbed in adsorbent, however, only a part of them can be recovered.

For the adsorbent, coconut shell activated carbon is generally used besides many adsorbents(1), and for the measurement of VOC, it is recommended to use adsorbents of which scopes are respectively different.

This Standard can be applied to the measurement of VOC of individual organic compound of which concentration range is from 1 $\mu g/m^3$ to 1×10^6 $\mu g/m^3$.

The upper limit of available range is determined according to the adsorption capacity of sampler and gas chromatograph column to be used and the linear range of detector or the sample split ratio of analytical equipment to be used.

The lower limit of available range depends on the noise level of detector and the blank level due to analytical system, sampler and the interference of impurities from desorption solvent.

This Standard presupposes that test performers themselves prepare and make samplers, however, samplers on the market may be used when the quality and performance are confirmed. When samplers on the market are used, for clause **8** and **9.2**, it is required to operate according to the instructions manual of the sampler to be used as referring to the concerned provisions.

Note (1) It is known that the adsorbents indicated in the list of Annex 3 and other International Standards shows the same characteristics as those indicated in this Standard. The adsorbent and its product identified by the brand name are manufactured by a single manufactures, however, they are available from many different suppliers. This information is shown for the user's convenience, however, it is not to recommend especially the product with name given in this Standard. The other products, when the same performance is indicated, may be used.

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 1960 *Indoor air—General aspects of sampling strategy*

Remarks : **ISO/DIS 16000-1** *Indoor air—General aspects of sampling strategy* is equivalent to the said standard.

JIS A 1964 *Indoor air—Sampling strategy for volatile organic compounds (VOCs)*

Remarks : **ISO/CD 16000-5** *Indoor air—Part 5: Sampling strategy for volatile organic compounds (VOCs)* is equivalent to the said standard.

3 Definitions For the purposes of this Standard, the following definitions apply.

a) **breakthrough volume**(2) volume of air passed through a sampler until the concentration of eluted compound has reached to 5 % of the concentration of injected sample

Note (2) The breakthrough volume of the analyte component differs depending on the class of adsorbent.

Remarks : See [1].

b) **retention volume** volume of carrier gas which has flowed until the peak top of small amount of organic gas component eluted from a sampler appears after a sampler is connected to gas chromatograph

c) **Safe Sample Volume (SSV)** maximum sampling volume of a sampler to be used

Volume of sampling air which is equal to 70 % of breakthrough volume or 50 % of retention volume.

4 Principle The sample air is sucked into the sampler as measuring its volume. One class or some classes of adsorbents suitable to the analyte components are selected. The volatile organic compounds (VOC) are collected in the sampler by selecting appropriate adsorbents and removed from air current. The component held in each sampler is eluted and analyzed with using inert carrier gas by the gas chromatograph with flame ionization detector or other appropriate detector.

5 Reagents and equipment For the reagents, only the analytical grade reagents shall be used.

5.1 Volatile organic compounds (VOC) For the calibration standard, the one containing the VOC mixed reference material with wide boiling points is recommended.

5.2 Solvent For the solvent (desorption solvent and dilution solvent), carbon disulfide is generally used, however, other solvent may be used corresponding to the analyte component. The blank value of the analyte component contained in solvent should be not more than the lower limit value of determination.

5.3 Calibration standard The calibration standard shall be prepared in accordance with any one of the following methods every definite period and used after the composition change is checked. When the composition change is recognized, the preparation period shall be shortened.

5.3.1 Reference solution addition method This method is to add the concentration-known reference solution to an unused sampler and to prepare a calibration curve by desorption and analysis of that. The concentration level of calibration curve can be prepared by changing the amount of addition. The procedure shall be as follows.

a) **Solution containing approximately 100 μg/ml of each liquid component** Weight approximately 10 mg of objective substance precisely in order from lower volatile substance and put in a 100 ml volumetric flask. Make it 100 ml with solvent, stopper and shake to mix.

b) **Solution containing approximately 10 μg/ml of each liquid component** Pour 50 ml of dilution solvent in a 100 ml volumetric flask. Add 10 ml of solution in **a**). Make it 100 ml with dilution solvent, stopper and shake to mix.

c) **Reference solution added sampler** Inject the reference solution into an unused sampler to prepare the reference solution addition sampler. Fix the sampler to an appropriate apparatus (figure 1), and inject 1 μl to 5μl of the solution of **a**) or **b**) passed through a septum as purging (3) inert gas. After elapsing of an appropriate time, detach the sampler and close hermetically.

Note (3) The purge condition shall be studied corresponding to the solvent to be used.

Remarks : The above-mentioned preparation concentration of reference solution for calibration curve is an example, and it is required to study the range of preparation concentration according to the concentration of sample to be analyzed.

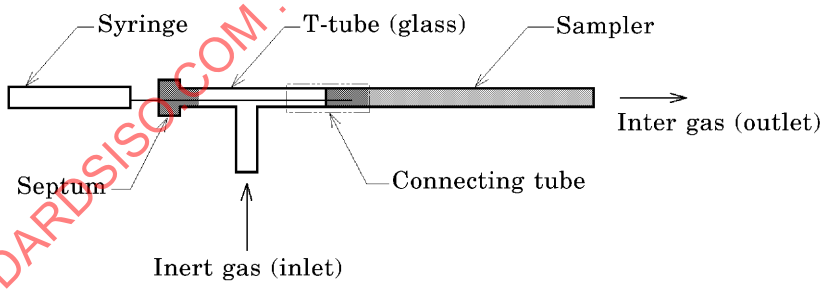

Figure 1 Example of reference solution adding apparatus

5.3.2 Introduction method of reference solution This method is that the different concentration levels of reference solutions are respectively prepared and the calibration curve is prepared by introducing those directly to gas chromatograph and analyzing, and can be used when the desorption efficiency of sampler to be used is confirmed to be not less than 80 %. The procedure shall be as follows.

a) Prepare the appropriate concentration of calibration standard solution by applying either **a**) or **b**) in **5.3.1** corresponding to the concentration of the analyte component.

b) Dilute the calibration standard solution with using solvent, and prepare the appropriate concentration sequence (for example, five stages).

c) Take the calibration standard solution sequence in a vial for analysis, respectively.

5.4 Adsorbent For the class of adsorbent, those mentioned in Annex 3 are such examples. The samplers filled by manufacturer are on the market and available. The blank value of adsorbent per the amount offered to sampling (for example, 300 mg) shall not exceed 10 % of the level to be usually measured.

Moreover, there are the articles of lower desorption efficiency depending on the analyte component, therefore it is required to grasp the characteristics to be used beforehand.

6 Apparatus The usual implements and apparatus for laboratory shall be used.

6.1 Sampler For example, a glass tube of 3 mm to 4 mm in outside diameter filled with approximately 300 mg of adsorbent.

6.2 Syringe A 10 μl precision liquid syringe capable of reading down to 0.1 μl.

6.3 Pump for sampling The pump, which corresponds to the conditions of **EN 1232** [2] or is equivalent thereto, is recommended.

6.4 Connecting tube It shall be a plastics or rubber tube of approximately 90 cm in length which has the diameter to fit closely to pump and sampler or sampler holder (if used). The connection part of sampler and connecting tube should be tightened with a clip.

There is the possibility to produce contamination and the adsorption of VOC contained in sample, therefore these connecting implements shall not be used at the upper stream of sampler.

6.5 Soap film flowmeter or other pump calibrating implement The flowmeter shall be calibrated in accordance with the traceable method to the primary standard (4).

Note (4) When the uncalibrated integrating flowmeter is used for calibrating the flowrate of pump, several tens % of systematic error may appear in some cases.

6.6 Gas chromatograph It shall be the gas chromatograph with flame ionization detector, photoionization detector, mass spectrometer or other appropriate detector which is capable of detecting 0.5 ng of toluene at least with S/N ratio of 5:1.

For the gas chromatograph, the capillary column capable of separating each the analyte component from other components shall be used.

7 Calibration of pump The pump shall be calibrated by using the exclusive meter calibrated adequately under such condition that the sampler is connected similarly to the actual sampling. One end of the calibrated meter shall be under the condition of atmospheric pressure for ensuring the adequate operation.

8 Sampling The sampler (or a combination of samplers) suitable for the analyte component or mixture shall be selected.

The sampler is connected to a pump with using a connector of plastics or rubber tube. When some different adsorbents are used, the sampler containing stronger adsorbent is connected at the nearest position to the pump.

The adequate position of sampling is selected and the sampler is fixed. The selection for sampling position is described in **JIS A 1960** and **JIS A 1964**.

Information : The contents in this clause is equivalent to **ISO/DIS 16000-1**:2001 and **ISO/CD 16000-5**:2002.

The pump is started and adjusted at an adequate flowrate. The sampling time is set and adjusted in the range between 10 min and 24 h according to the measurement concentration, and the flowrate is set and adjusted in the range between 10 ml/min and 1 000 ml/min according to the class of adsorbent so that the total amount of sampling does not exceed Safety Sampling Volume (hereafter referred to as "SSV").

Most carbon series adsorbents are not influenced by the temperature and flowrate to breakthrough volume, but reduced by a high concentration of VOC vapour or a high relative humidity. The values of presumed retention volume and SSV obtained from experiments are shown in table 1 to table 4.

When the SSV of compound is not present in the list of table 1 to table 4, that shall be presumed. In other cases, SSV shall be confirmed by means of experiment.

When pump is started, the time, temperature, flowrate or the value of recorder, and if necessary, atmospheric pressure shall be recorded. When sampling is completed, the flowrate or the indication of recorder should be read, and the pump is stopped, and if necessary, the time and atmospheric pressure should be recorded.

The both ends of sampler are tightly stoppered by using adequate caps (of plastics, etc.) The attaching to sampler of identifying label is recommended. When the label is directly attached to sampler, the using of paint and marker containing solvent or adhesive type label shall be avoided.

When the sampler are not analyzed within 8 h, they are placed in a clean, uncoated, hermetic container made of metal or glass and stored under clean environment. When results are expressed with the concentration converted to the conditions of specific temperature and pressure, the temperature and value of barometer are recorded during sampling as appropriate (**10.1**)

For the travel blank, the sampler same as that used for sampling is used, and that is treated by the same procedure as the sampler used for sampling except sampling and it shall be identified to be the travel blank.

9 Procedures

9.1 Precautions on safety This Standard does not purport to address all the safety problems with its use. The users of this Standard shall establish appropriate safety and health practices and to determine the applicability of the regulatory limitations prior to the use.

9.2 Desorption and analysis Take out the adsorbent from the sampler to a vial for analysis, stopper after adding of solvent, shake to mix it sometimes until bubbles have not appeared, and then take it as the test solution. The solvent is made to add the appropriate amount to the amount of adsorbent, for example, 1 ml to 2 ml of carbon disulfide is the appropriate amount to 300 mg of coconut shell activated carbon.

Set the analytical condition of gas chromatograph for VOC. The various types of columns for gas chromatograph can be used. The column selection, in many cases, depends on what type of interfering component is present. For the general example, there is the column of molten silica with thicker film thickness (1 μm to 5 μm) which is 0.22 mm in inside diameter, 50 m in length and in which polydimethyl cyloxane or 7 % cyanopropyl / 7 % phenyl / 86 % methylcyloxane is taken as the stationary phase. For these columns, the initial holding time shall be made 10 min at 50 °C and the temperature program to heat up from 50 °C to 250 °C at the rate of 5 °C/min is the general set conditions.

The peak can not be identified only by the correspondence of retention time in single column.

9.3 Calibration curve Analyze the extract according to **9.2** of each reference solution added sampler (**5.3.1**) prepared for calibration curve or the reference solution (**5.3.2**) according to gas chromatograh.

Prepare the calibration curve so that the lograrithm of mass of the analyte component obtained is plotted on abscissa and the logarithm(5) of peak area of the analyte component is plotted on ordinate.

Note (5) When the range of calibration is within the single digits, it is not required to take logarithm.

9.4 Measurement of sample concentration Analyze the sample and sample blank according to **9.2**. Obtain peak area and read the mass of the analyte component in the extracted sample from the calibration curve.

9.5 Measurement of desorption efficiency Obtain the desorption efficiency so that the peak area or height on chromatograph of reference solution added sample is compared with the peak area or height measured by injecting directly the reference solution in gas chromatograph. The value of the peak area or height according to the reference sampler divided by the peak area or height at the time of injecting directly the reference solution is taken as desorption efficiency.

10 Calculation

10.1 Mass concentration of the analyte component Calculate the concentration of the analyte component in sample air according to the following formula.

$$c_m = \frac{m_F - m_B}{V \times D} \times 1\,000 \quad \text{..... (1)}$$

where, c_m : mass concentration of the analyte component in sample air (μg/m³)

m_F : mass of the analyte component in sampler sampled (μg)

m_B : mass of the analyte component in blank sampler (μg)

V : amount of sampling (L)

D : desorption efficiency

Remarks 1 When the units of m_F and m_B are expressed in mg, the unit of concentration c_m obtained as the result is mg/m^3.

2 The concentration in the case of expressing the converted concentration to the specific conditions (for example 101.3 kPa at 25 °C) shall be in accordance with the following formula.

$$c_c = c_m \times \frac{101.3}{P} \times \frac{T + 273}{298} \quad \cdots\cdots (2)$$

where, c_c : concentration of the analyte component in sample air, converted to the specific conditions (μg/m^3)

P : actual pressure of sample air (kPa)

T : actual temperature of sample air (°C)

10.2 Volume concentration of the analyte component Calculate the volume concentration of the analyte component in air according to the following formula (ppb).

$$c_v = c_m \times \frac{24.5}{M} \times \frac{101.3}{P} \times \frac{T + 273}{298} \quad \cdots\cdots (3)$$

where, c_V : volume concentration of the analyte component during sampling (ppb)

24.5 : molar volume at the time of 10.1.3 kPa at 25 °C

M : molecular weight of analyte component

11 Interference The organic component, to which the retention time of the analyte component is close, has the possibility to be interference in gas chromatographic analysis. The interference is restrained to a minimum by the selection of adequate column of gas chromatograph and setting of conditions.

When activated carbon is used as an adsorbent, the adsorption of moisture is considered under the condition of high humidity, therefore when the relative humidity at sampling place is not less than 60 %, the dehumidifying tube filled with magnesium perchlorate, etc. should be used.

Ozone and nitrogen oxide have the possibility so as to react with the analyte component, therefore when it is supposed that a plenty of these components are contained in sample air, the amount of sampling is made to be reduced as far as possible.

12 Analytical characteristics It is required to grasp the analytical characteristics (total uncertainty, precision, storage stability, blank level) when tested according to the procedure in this Standard.

13 Test report The following items shall be at least added in the test report.

a) Clear identification of sample contents

b) This Standard referred to or other supplementary standards

c) Sampling place and period, and amount of air sucked

d) Atmospheric pressure and temperature, if necessary

e) Test results

f) Special affairs observed during measurement

g) Operations which are not included in this Standard or standards referred to, or operations regarded as optional

14 Quality control The adequate level of quality control should be carried out [3].

It is allowed that the peak area of travel blank is not more than 10 % of the usual value of the analyte component. It is recommended that the storage conditions are controlled by the comparison with operation blank (6).

Note (6) It is that being extracted and analyzed for an unused sampler.

Table 1 Presumed retention volume and Safety Sampling Volume (SSV) of Charcoal (300 mg) at 20 °C

Organic compound	Boiling point °C	Vapor pressure kPa (25 °C)	Retention volume L	SSV L	SSV/g L/g
Propane	–42	—	10	5	15
Butane	–0.5	—	900	450	600
Pentane	35	56	2.7×10^4	1.3×10^4	4.3×10^4
Hexane	69	16	1.5×10^6	7.5×10^5	2.5×10^6
Benzene	80	10.1	3.4×10^5	1.7×10^5	5.6×10^5

Table 2 Presumed retention volume and Safety Sampling Volume (SSV) of Carbotrap (525 mg) at 20 °C

Organic compound	Boiling point °C	Vapor pressure kPa (25 °C)	Retention volume L	SSV L	SSV/g L/g
Hexane	69	16	83	42	80
Heptane	98	3.6	470	240	450
Octane	125	1.9	7.9×10^3	3.9×10^3	7.5×10^3
Nonane	151	—	7.4×10^4	3.7×10^4	7.0×10^4
Decane	174	—	1.7×10^{11}	8.6×10^{10}	1.6×10^{11}
Benzene	80	—	120	61	120
Toluene	111	—	680	340	650
Xylene	138 to 144	0.67 to 0.87	4.5×10^4	2.2×10^4	4.3×10^4
Ethyl benzene	136	0.93	2.1×10^4	1.1×10^4	2.0×10^4
Trichloro ethylene	87	2.7	8.4	4.2	8.00
Tetrachloro ethylene	121	1.87	42	21	40.0
p-Dichloro benzene	174	0.085	540	270	510

Table 3 Presumed retention volume and Safety Sampling Volume (SSV) of Carboxene 569 (300 mg) at 20 °C

Organic compound	Boiling point °C	Vapor pressure kPa (25 °C)	Retention volume L	SSV L	SSV/g L/g
Butane	–0.5	—	15	7.5	25
Pentane	35	56	120	60	200
Hexane	69	16	1.6×10^3	780	2.6×10^3
Heptane	151	98	6.6×10^3	3.3×10^3	1.1×10^4
Toluene	111	—	1.6×10^3	810	2.7×10^3
Xylene	138 to 144	0.67 to 0.87	4.5×10^3	2.3×10^3	7.5×10^3
Ethyl benzene	136	0.93	1.5×10^3	750	2.5×10^3

Table 4 Presumed retention volume and Safety Sampling Volume (SSV) of Carbosieve SIII (300 mg) at 20 °C

Organic compound	Boiling point °C	Vapor pressure kPa (25 °C)	Retention volume L	SSV L	SSV/g L/g
Propane	–42	—	5.1	2.6	8.5
Butane	–0.5	—	76	38	63
Pentane	35	56	360	180	600
Hexane	69	16	3.0×10^3	1.5×10^3	5.0×10^3
Heptane	151	98	6.0×10^3	3.0×10^3	1.0×10^4

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[2] EN1232:1993, *Workplace atmospheres—Pumps for personal sampling of chemical agents-Requirements and test methods.*

[3] UK Health and Safety Executive. *Methods for the Determination of Hazardous Substances. Analytical quality in workplace air monitoring.* MDHS 71. HSE: (1991) London.

Related standards

ISO 6141:1984 *Gas analysis—Calibration gas mixtures—Certificate of mixture preparation*

ISO 6145-1:1986 *Gas analysis—Preparation of calibration gas mixtures—Dynamic volumetric methods—Part 1: Methods of calibration*

ISO 6145-3:1986 *Gas analysis—Preparation of calibration gas mixtures—Dynamic volumetric methods—Part 3: Periodic injections into a flowing gas stream*

ISO 6145-4:1986 *Gas analysis—Preparation of calibration gas mixtures—Dynamic volumetric methods—Part 4: Continuous injection method*

ISO 6145-5:1986 *Gas analysis—Preparation of calibration gas mixtures—Dynamic volumetric methods—Part 5: Capillary gas devices*

ISO 6145-6:1986 *Gas analysis—Preparation of calibration gas mixtures—Dynamic volumetric methods—Part 6: Sonic orifices*

ISO 6349:1979 *Gas analysis—Preparation of calibration gas mixtures—Permeation method*

Annex 1 (informative)
Measurement of breakthrough volume

This Annex (informative) is to supplement the matters related to the text and not to constitute the provisions of this Standard.

1 Dynamic standard gas The dynamic standard gas is prepared by using the concentration-known substance. The adequate preparation methods for standard gas are described in **ISO 6141**, **ISO 6145** and **ISO 6349**. The production temperature of concentration is the general temperature presumed at the time of using sampler.

2 Apparatus usual implements for laboratory and those as shown in the following

2.1 Sampler those as same as **6.1** of the text, however, a back-up collecting tube is not used

2.2 Flowmeter those as of 20 ml/min to 200 ml/min in the range of measurement

2.3 Detector flame ionization detector (FID)

3 Measurement Assemble a series of sampling apparatus composed of the preparation device of dynamic standard gas to produce the analyte component of the concentration corresponding to twice of adequate exposure limit(**1**), a sampler (**2.1**), a flowmeter (**2.2**) and a detector (**2.3**).

Let a definite and known flow rate in the range between 20 ml/min to 200 ml/min of gas flow into the sampling apparatus. Set the flow rate at the adequate range to the sampling flow rate presumed. Record the starting time of flow of gas. When the outflow of VOC component starts, the response is visible in the detector. Continue the measurement until the response of detector has reached to equilibrium (equivalent to the inlet concentration) or the response of main component or total component of VOC has been confirmed. Obtain the time when it has reached to 5 % of equilibrium value.

Usually, the dead volume of sampling apparatus becomes comparatively smaller than the breakthrough volume. In other cases, obtain repeatedly the dead volume by attaching an empty pipe (a pipe without filling of adsorbent) to the sampling apparatus, and correct the results by corresponding to it.

Carry out repeatedly the above-mentioned test with the relative humidity of gas flow being humidified approximately at 80 %, and confirm the influence of moisture to breakthrough volume. Dilute and humidify the primary gas flow so that the produced concentration becomes five times (volume ratio of 1:4) by using the fresh water vapour of 100 % in relative humidity. The water for humidifying shall not be contaminated by VOC.