DETERMINATION OF THE EMISSION OF VOLATILE ORGANIC COMPOUNDS AND ALDEHYDES BY BUILDING PRODUCTS – SMALL CHAMBER METHOD

1 SCOPE

This Standard specifies a general laboratory test method for determination of emission rate of chemical substances emitted from building products into the air, by the use of chamber method.

This measurement procedure is applicable to building products such as boards, wallpapers and floor materials, adhesives, paints and coating materials, and heat insulating materials. This standard aims at volatile organic compounds (VOCs), aldehydes as target chemical substances.

2 PRINCIPLE

The principle of this test is to determine the area specific emission factor of target chemical substances emitted from building products, to be tested by obtaining the emission test chamber concentration, passing air flow rate and surface area of the test specimen, performed in a chamber.

The area specific emission factor of target chemical substance at time, t, is calculated as specified in clause 12, by passing air through the chamber at constant temperature, relative humidity and air flow rate, and with knowledge of the emission test chamber concentration and air flow rate from the outlet air.

3 REAGENTS

3.1 2,4-Dinitrophenylhydrazine Recrystallized at least twice with acetonitrile for ultraviolet absorption measurement or high performance liquid chromatography before use.

3.2 Acetonitrile For ultraviolet absorption measurement or high performance liquid chromatography.

3.3 Water For high performance liquid chromatography (distilled water)

3.4 Perchloric acid 60%(wt/wt), 1.51 kg/L

3.5 Hydrochloric acid 36.5% to 38% (wt/wt), 1.19 kg/L

3.6 Formaldehyde 37% solution (wt/wt)

3.7 Aldehydes and ketones High purity, used for the preparation of DNPH derivative standards (optional)

3.8 Ethanol or methanol Equivalent to that of high performance liquid chromatography.

3.9 Nitrogen High purity grade [at least 99.999% (wt/wt)]

3.10 Activated carbon Granular

3.11 Helium High purity grade [at least 99.999% (wt/wt)]

3.12 Preparation of reagents and cartridges

3.12.1 Purification of 2,4-dinitrophenylhydrazine

Formaldehyde contamination of the DNPH reagent is a frequently encountered problem. The DNPH

shall be purified by multiple recrystallizations in acetonitrile for ultraviolet absorption measurement or high-performance liquid chromatography. Recrystallization is accomplished, at 40°C to 60°C, by slow evaporation of the solvent to maximize crystal size. Impurity levels of carbonyl compounds in the DNPH are determined prior to use by HPLC and should be less than 0.15 µg per cartridge and per individual compound.

Prepare a supersaturated solution of DNPH by boiling excess DNPH in 200 ml of acetonitrile for approximately 1 h. After 1 h, remove and transfer the supernatant to a covered beaker on a hot plate and allow gradual cooling to 40°C to 60°C. Maintain the solution at this temperature (40°C) until 95 % volume fraction of solvent has evaporated. Decant the solution to waste and rinse the remaining crystals twice with three times their apparent volume of acetonitrile. Transfer the crystals to another clean beaker, add 200 ml of acetonitrile, heat to boiling, and again let crystals grow slowly at 40°C to 60°C until 95 % volume fraction of the solvent has evaporated. Repeat the rinsing process as described above. Take an aliquot of the second rinse, dilute ten times with acetonitrile, acidify with 1 ml of perchloric acid (3.8 mol/L) per 100 ml of DNPH solution.

An acceptable impurity level is not exceeding 0.025 µg/ml of formaldehyde hydrazone in recrystallized DNPH reagent or not exceeding 0.02 % (wt/wt) mass fraction of the DNPH. If the impurity level is not acceptable for the intended sampling application, repeat recrystallization.

Transfer the purified crystals to an all-glass reagent bottle, add 200 ml of acetonitrile, stopper, shake gently, and let stand overnight.

Analyze the supernatant by HPLC according to 10.2.4. If the impurity level is not satisfactory, pipette off the solution to waste, then add 25 ml of acetonitrile to the purified crystals. Repeat rinsing with 20 ml portions of acetonitrile until a satisfactorily low impurity level in the supernatant is confirmed by HPLC analysis.

If the impurity level is satisfactory, add another 25 ml of acetonitrile, stopper, and shake the reagent bottle, then set aside. The saturated solution above the purified crystals is the stock DNPH reagent. Maintain only a minimum volume of saturated solution adequate for day-to-day operation. This will minimize waste of purified reagent.

It is necessary to re-rinse the crystals to decrease the level of impurity for applications requiring more stringent purity specifications. Use clean pipettes when removing saturated DNPH stock solution for any analytical applications. Do not pour the stock solution from the reagent bottle.

3.12.2 Preparation of DNPH-formaldehyde derivative:

To a portion of the recrystallized DNPH add sufficient HCl (2 mol/L) to obtain an approximately saturated solution. Add to this solution formaldehyde in molar excess of the DNPH. Filter the DNPH-formaldehyde precipitate, wash it with hydrochloric acid (2 mol/L) and water, and allow it to dry in air.

Check the purity of the DNPH-formaldehyde derivative by melting point determination (165 °C to 166 °C) or HPLC analysis. If the impurity level is not acceptable, recrystallize the derivative in ethanol.

Repeat the purity check and recrystallization as necessary until an acceptable level of purity [for example, 99 % (wt/wt)] is achieved.

The DNPH-formaldehyde derivative should be stored in a refrigerator (4 °C) and protection from light. It should be stable for at least six months. Storage under nitro- gen or argon further prolongs the lifetime of the derivative.

Melting points of DNPH derivatives of several carbonyl compounds are given in Annex B.

DNPH derivatives of formaldehyde and other carbonyls suitable for use as standards are commercially available both in the form of pure crystals and as individual or mixed stock solutions in acetonitrile.

3.12.3 Preparation of DNPH-formaldehyde standards

Prepare a standard stock solution of the DNPH-formaldehyde derivative by dissolving accurately weighed amounts in acetonitrile. Prepare a working calibration standard mix from the standard stock solution. The concentration of the DNPH-formaldehyde derivative in the standard mix solutions should be adjusted to reflect the range of concentrations expected in real samples.

Individual stock solutions of approximately 100 mg/L can be prepared by dissolving 10 mg of the solid derivative in 100 ml of acetonitrile. The individual solution is used to prepare calibration standards containing the derivative of interest at concentrations of 0.5 µg/ml to 20 µg/ml, that spans the concentration of interest.

Store all standard solutions in tightly capped containers in a refrigerator and protected from light. Allow them to equilibrate to room temperature before use. They should be replaced after four weeks.

3.13 Preparation of cartridges

3.13.1 General This procedure shall be performed in an atmosphere with a very low aldehyde background. All glassware and plasticware shall be thoroughly cleaned and rinsed with deionized water and aldehyde-free acetonitrile. Contact of reagents with laboratory air shall be minimized. Polyethylene gloves shall be worn when handling the cartridges.

DNPH coating solution Pipette 30 ml of saturated DNPH stock solution into a 1000 ml volumetric flask, then add 500 ml acetonitrile. Acidify with 1.0 ml of concentrated hydrochloric acid.

The atmosphere above the acidified solution should preferably be filtered through a DNPH-coated silica gel cartridge, to minimize contamination from laboratory air. Shake solution, then make up to volume with acetonitrile. Stopper the flask, invert, and shake several times until the solution is homogeneous. Transfer the acidified solution to a reagent bottle equipped with a positive-displacement dispenser of capacity in the O ml to 10 ml range.

Prime the dispenser and slowly dispense 10 ml to 20 ml to waste. Dispense an aliquot solution to a sample vial and check the impurity level of the acidified solution by HPLC according to 13.2.1 The impurity level should be 0.025 µg/ml or under of formaldehyde concentration.

3.13.2 Coating of silica gel cartridges Open the cartridge package, connect the short end to a 10 ml syringe, and place it in the syringe rack as illustrated in figures 1 a) and b). Using a positive-displacement and repetitive-dispensing pipette, add 10 ml of acetonitrile to each of the syringes. Let liquid drain to waste by gravity.

Remove any air bubbles that may be trapped between the syringe and the silica cartridge by displacing them with the acetonitrile in the syringe.

Set the repetitive dispenser, containing the acidified DNPH coating solution, to dispense 7 ml into the cartridges. Once the effluent flow at the outlet of the cartridge has stopped, dispense 7 ml of the coating reagent into each of the syringes. Let the coating reagent drain by gravity through the cartridge until flow at the other end of the cartridge stops. Wipe away the excess liquid at the outlet of each of the cartridges with clean tissue paper.

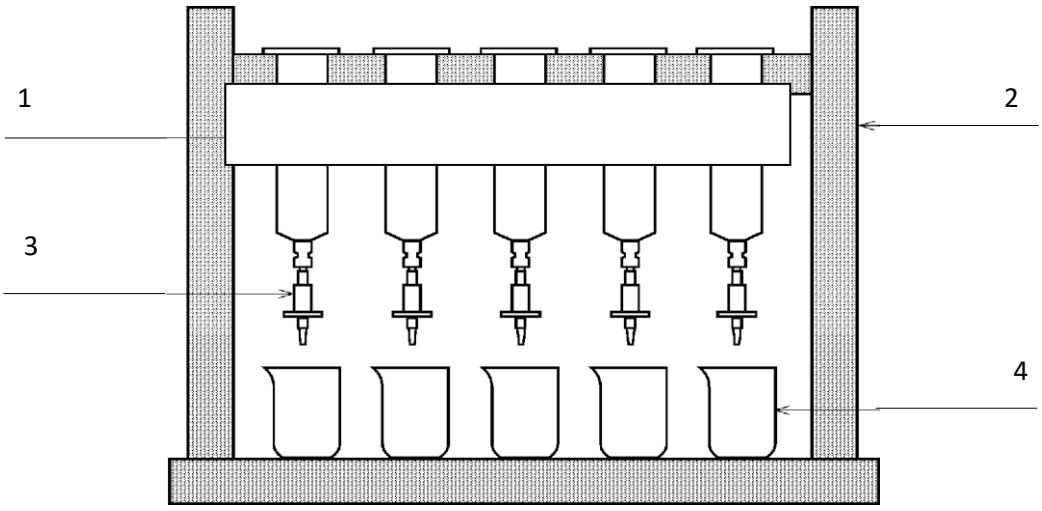
Assemble a drying manifold as shown in figure 1 b). This contains a previously pre· pared DNPH-coated cartridge at each of the exit ports (for example, scrubber or "guard cartridges"). These scrubbers serve to remove traces of formaldehyde that may be pre- sent in the nitrogen gas supply. They can be

prepared by drying a few of the newly coated cartridges in accordance with the instructions below and sacrificing these few to ensure the purity of the rest.

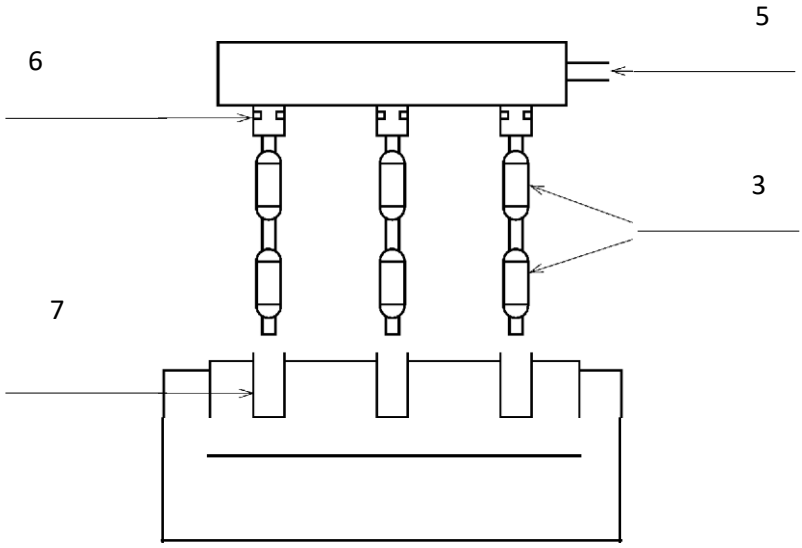
Insert cartridge connectors (flared at both ends, 0.64 cm by 2.5 cm outside diameter TFE-fluorocarbon tubing with inside diameter slightly smaller than the outside diameter of the cartridge port) onto the long end of the scrubber cartridges.

Remove the cartridges from the syringes and connect the short ends of the cartridges to the open end of the cartridge connectors already attached to the scrubber cartridges.

Pass nitrogen through each of the cartridges at about 300 ml/min to 400 ml/min. Rinse the exterior surfaces and outlet end of the cartridges with acetonitrile using a Pasteur pipette.



a) Rack for coating cartridges



b) Rack for drying DNPH coated cartridges

Designation

1. 10 ml glass syringes 2. Test tube rack 3. Cartridges 4. Waste beakers

5. N2 gas stream 6. Syringe fitting 7. Waste vials

Figure 1 Syringe rack for coating and drying sample cartridges

After 15 min, stop the flow of nitrogen, wipe the cartridge exterior free of rinse acetonitrile and remove the dried cartridges. Plug both ends of the coated cartridge with standard polypropylene male syringe plugs and place the plugged cartridge in a borosilicate glass culture tube with polypropylene screw caps.

Put a serial number and a lot number label on each of the individual cartridge glass storage containers and refrigerate the prepared lot until use.

Sampling cartridges have been found to be stable for at least six months when stored at 4 °C in the absence of light.

4 APPARATUS

4.1 General

Equipment used to perform an emission test of target chemical substances emitted from building products shall be as follows.

Chamber

Sealing materials for specimen

Clean air supply

Temperature control and humidification system

Integrating flowmeter

Air sampling device

Oven

Analyzer

4.2 Chamber

An outline of chamber system is shown in figure 2. The outlet air and inlet air shall not be circulated.

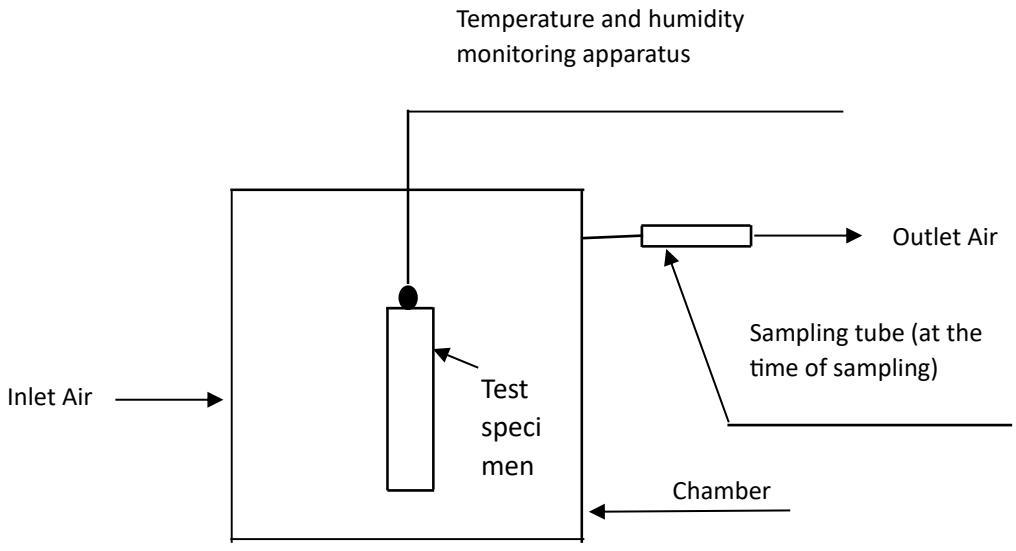


Figure 2 Outline of chamber

4.3 Shape

The chamber shall be designed to ensure proper mixing of inside air. In principle, any components mounted on the chamber shall be detachable for washing and heat- treatment.

The part of chamber coming into contact with the emitted target chemical substances shall be made of stainless steel or glass, with a volume of 20 L (±5 %) to 1000 L (±5 %). Mixing devices, e.g. fan, and sealing materials of the chamber shall be low emitting and low adsorbing materials which do not contribute to the emission test chamber background concentration.

Chambers of capacity from several **L** to and excluding 20 L may be used for tests of adhesives, paints and coating materials, if they are confirmed to correlate with chambers of capacity 20 **L** or more.

4.4 Air tightness

The chamber shall be kept airtight to avoid air change with uncontrolled external air. The pressure in the chamber shall be positive against the laboratory atmosphere pressure, and the inside of the chamber shall be kept airtight.

With the inside kept airtight, the chamber can avoid any influence from the laboratory environment.

4.5 Air supply and mixing facilities

The chamber shall have facilities (e.g. electronic mass flow controller) capable of continuously controlling the air flow rate at a fixed value. The requirements shall be in accordance with 7.5 and 8.4.

4.6 Seal of test specimen

When measuring the chemical substances emitted only from the surface of test specimen, seal the edges and the underside of the test specimen with materials like aluminum foil.

4.7 Clean air supply

Air to be supplied in the chamber shall be as clean as possible, therefore clean air supply or clean air of gas cylinder shall be used to prevent increase in background concentration.

4.8 Temperature control and humidification system

The control of temperature shall be carried out either by placing the chamber in the laboratory environment controlled to the required temperature such as thermostat or by maintaining the inside of the chamber at required temperature. In principle, the relative humidity shall be controlled by maintaining the required relative humidity of supply air. Temperature and relative humidity shall be monitored continuously and independently of the system for controlling the temperature and humidity.

In addition, precautions shall be taken to avoid condensation of moisture or spray of water in the chamber.

4.9 Integrating flowmeter

The air flow rate shall be accurately measured within the emission test chamber by setting an integrating flowmeter which is set on the chamber outlet. Alternatively, other equipment of performance at least equivalent thereto may be used.

4.10 Air sampling procedure

For the sampling of air, the exhaust air at the chamber outlet shall be used. When a multiport sampling manifold is used, the air shall be sampled directly from the chamber outlet. If a duct and a tube are to be used, they shall be as short as possible, and maintained at the same temperature as the chamber.

The duct and tube shall be made of materials of minimal adsorption, e.g. polytetrafluoroethylene. If the air flow rate at the time of air sampling is smaller than the air flow rate of the chamber, the air flow

rate shall be held constant using a sampling manifold, etc. The exhaust air from the chamber shall be discharged from the laboratory environment.

4.11 Oven

The oven shall be used to volatilize target chemical substances adhered within the chamber.

4.12 Analyzer

VOC shall be analyzed by gas chromatograph using FID detector (GC/FID) or by gas chromatograph using mass spectrometer (GC/MS). For the analysis of aldehydes, high performance liquid chromatograph (HPLC) shall be used.

HPLC system consists of a mobile phase reservoir; a high-pressure pump; an injection valve (automatic sampler with a 25 µl or other convenient loop volume) ; a C18 reverse phase (RP) column (length : 25 cm, inside diameter : 4.6 mm, particle size : 5 µm) ; a UV detector or diode array detector operating at 360 nm; and a data system or strip chart recorder.

The DNPH-formaldehyde derivative is determined using isocratic reverse phase HPLC, equipped with an ultraviolet (UV) absorption detector operated at 360 nm. A blank cartridge is likewise desorbed and analyzed. Formaldehyde and other carbonyl compounds in the sample are identified and quantified by comparison of their retention times and peak heights or peak areas with those of standard solutions.

4.12.1 Syringes and pipettes

4.12.1.1 **HPLC Injection syringes** with capacity at least four times the loop volume.

4.12.1.2 **Syringes** Of volume 10 ml, used to prepare DNPH-coated cartridges (poly-propylene syringes are adequate).

4.12.1.3 **Syringe fittings and plugs** To connect cartridges to the sampling system and to cap prepared cartridges.

4.12.1.4 **Pipettes** Positive-displacement, repetitive-dispensing, with capacities in the 0 ml to 10 ml range.

5 Test conditions

5.1 General

Test shall be performed under the test conditions specified in 5.2 to 5.5**,** and at the pressure close to the atmospheric pressure.

5.2 Temperature and relative humidity

Temperature in the chamber shall be 28 °C and relative humidity shall be 50 % given in JIS Z 8703. The performances of the chamber shall be controlled within the following range of conditions.

- Temperature 28 °C ± 1 °C
- Relative humidity (50 ± 5) %

Alternative temperature and humidity conditions should be used according to the test purpose, in order to confirm the temperature humidity dependence.

Initial variance can be observed in the chamber environment when loading a test specimen, because of the differences of temperature and relative humidity between the laboratory environment and the chamber. These variances shall be recorded. The ranges of temperature and relative humidity

indicate variance by change with time. The distribution of temperature and relative humidity in the chamber shall be minimized.

5.3 Supply air quality and background concentration

The quality of supply air and background concentrations shall be low enough not to interfere with the emission determinations.

The pure water used for humidification shall not contain interfering target chemical substances.

5.4 Mass transfer coefficient

The mass transfer coefficient over the surface of the test specimen in the chamber should be about 9 m/h to 18 m/h, by converting it into water vapor.

When a fan is set in order to stir the contents of the chamber, forced convection field shall not be of mass transfer coefficient 18 m/h or over.

NOTE 1 The volume of the mass transfer coefficient sometimes influences the emission factor for evaporative controlled emission. The emission factor depends on the substrate to be used.

NOTE 2 The mass transfer coefficients of about 9 m/h to 18 m/h correspond ap- proximately to air velocities of about 0.1 m/s to 0.3 m/s over the surface of the test specimen.

5.5 Area specific air flow rate and air change rate

At steady state, the emission test chamber concentration depends on the area specific air flow rate which is selected as a parameter in designing the emission test conditions. The standard air change rate shall be 0.5 ± 0.05 times/h.

For the evaporative controlled building products such as adhesives and coatings (e.g wet adhesives and coatings), appropriate measurement can be carried out by increasing air change rate or decreasing the product loading factor. The air change rate, n and the product loading factor, L shall be kept on the same conditions, when comparing results obtain from different chambers.

NOTE 1 Air change rate, n, and product loading factor, L, can influence the emission factor.

NOTE 2 For target substances which considerably adsorb to building product itself (e.g. formaldehyde), the measurement results of emission factor can be compared only when the results are common in the rate of the product loading factor to the air change rate (L/n, n/L values).

6. Verification of the test conditions

6.1 Monitoring of the test conditions

Temperature, relative humidity and air flow rate shall be monitored and recorded continuously with the following accuracies.

For the temperature and relative humidity, the outlet air may be measured.

- Temperature ± 0.5 °C
- Relative humidity ± 5 %
- Air change rate ± 10 %

6.2 Air tightness of chamber

The air tightness of chamber shall be regularly checked with a minimum frequency of every 12 months, or by pressure drop measurement, by comparison of simultaneous measurement of flow rates at the inlet and the outlet or by measurement of tracer gas dilution.

6.3 Air change rate in chamber

An integrating flowmeter is set at the chamber outlet, and the air change rate, n, is obtained by calculating the measured air flow rate Q divided by the chamber volume, V.

The variance of the set value of air change rate shall be minimized. The air change rate shall be regularly checked with a minimum frequency of 12 months, by using the tracer gas procedure.

When the test is carried out on the outlet by using integrating flowmeter, one should be aware that the back pressure introduced by the instrument can lower the flow rate through the chamber.

6.4 Coefficient of air change performance in chamber

The test to determine the coefficient of air change performance in the chamber shall be carried out by placing the test specimen or the inert substrate (e.g. glass plate or stainless steel sheet) of the same size as the test specimen in the test chamber. The co· efficient of air change performance shall be calculated as follows.

a) Step-up method: After the tracer gas is adequately mixed with the supply air at constant concentration and flow, the time course of concentration in the chamber outlet shall be measured. The coefficient of air change performance η in the chamber is calculated from the temporal change by the nominal time constant, τn, divided by the mean age $< \tau >$. The coefficient of air change performance should be at least 90 %.

b) Step-down method: The age of the air at the chamber outlet shall agree with the mean age. Alternatively, the tracer gas concentration at the chamber outlet may be measured by supplying clean air after thoroughly mixing tracer gas in the chamber by using a fan or other devices. The coefficient of air change performance is calculated from the temporal change of concentration.

The coefficient of air change performance, the nominal time constant and the mean age obtained in a) and b) can be expressed by formulae (1) to (4), respectively.

Coefficient of air change performance $\eta = \tau_n / < \tau >$ ---------- 1)

Nominal time constant $\tau_n = V/Q$ ----------2)

Step up method $< \tau > = Q/V \int_0^\infty t\,(1- \rho_e\,(t) / \rho_s\,)\,dt$ ----------3)

Step down method $< \tau > = Q/V \int_0^\infty t\,\rho_e\,(t) / \rho\,(0)\,.dt$ ----------4)

6.5 Recovery and sink effects

The recovery of target chemical substances can be determined using standard gas of target component or gas of a known concentration emitted with permeation tube, etc. The concentrations generated shall be of similar magnitude to those expected during the emission tests of building products.

Two or more chambers may be connected in series.

The chamber performance shall ensure a mean recovery of not less than 80 % for toluene and n-dodecane. The recovery of other target chemical substances shall be also recorded. Dehumidified air shall be used in determining the recovery of hydrophilic target chemical substances.

Sink effects, leaks or poor calibration can cause difficulties to meet the minimum accuracy required for tests. Sink and adsorption characteristics are very much dependent on the type of chemical substances emitted. Additional recovery tests using target chemical substances with different molecular weight and polarity can be

used to increase understanding of these effects. The mean recovery shall be calculated from the ratio of outlet concentration to inlet concentration at the chamber.

7 Chamber Preparation

Before starting the test, the chamber shall be demounted and washed. After washed with water, it is heated in an oven to volatilize any remaining chemical substance. If the chamber cannot be placed in an oven, it is allowed to heat the inside of the chamber. After the heat treatment, the chamber shall be cooled enough for the measurement.

8 Preparation of test specimen

The preparation of test specimens shall be as follows.

Apply a uniform coating of the sample over the surface of a stainless steel or glass plate under the standard condition (23 ± 2.0)°C, in principle. The coating amount of sample shall be (300 ± 15) g/m^2. If the test specimen cannot be prepared under standard condition, the temperature of the site where preparation has been performed shall be recorded in the test report. The temperature of the site shall not exceed 28°C. The application of sample shall be performed as quickly as possible by using means such as a brush or a notched-margin trowel. The preparation of the test specimen shall not take longer than 5 min. The stainless-steel plate or glass plate to be used for preparation of the test specimen shall be rinsed in advance with an ion-exchanged water and then dried overnight at 200°C or higher (preferably 280°C or higher) before use. For starch adhesives for wallpaper fabrication and those for fixtures, the coating amount of sample shall be (180 ± 10) g/m^2 based on the standard coating amount of 130 g/m^2 to 180 g/m^2, and in view of curing and retention of form of the adhesive.

The coating area of the sample shall be determined based on a relationship with the product loading factor specified as 0.4 m^2/m^3 to 2.2 m^2/m^3.

The test specimens shall be prepared in as clean an environment as possible so that specimens are free from influence by emission from other specimens or sorption of chemical pollutant.

8.1 Curing of test specimens

For test specimens prepared from samples, the curing period of 60 min ± 10 min to 24 h ± 3 h under standard conditions of 23 °C ± 2.0 °C shall be secured. The curing period shall be sufficient for the VOC emission to have stabilized, and for the adhesive to have hardened enough so that it does not run down from the test specimen or so that it can retain its form. The curing of test specimen shall be performed in as clean an environment as possible so that specimens is free from influence by emission from other specimens and sorption of chemical pollutant. Where curing under the standard condition cannot be ensured, the temperature of the site where curing has been performed shall be recorded in the test report. If curing has been performed under fluctuating temperature, the range of temperature, i.e., the difference between maximum and minimum temperatures shall be recorded. The temperature of the site shall not exceed 28 °C. The curing environment of the test specimen shall be in a draft, for example, where the wind velocity is maintained constant at 0.3 m/s which allows the specimen free contact with air, so that there is no influence from any possible VOC emission source.

9 Test methods

9.1 Background concentration and travel blank

An air sample of the chamber background is taken after one-day ventilation of an empty chamber before the start of a new emission test, to quantify any background concentration of volatile organic compounds from the empty chamber. Travel blank shall be analyzed every time air is sampled.

Travel blank shall be low enough not to interfere with the emission determinations. The background concentration of TVOC shall be 20 µg/m3 or less. The background concentration of each target component, however, shall be 2 µg/m3 or less.

9.2 Test specimen location in the chamber

The test specimen shall be positioned in the center of the chamber to ensure that the air flow is evenly distributed over the emitting surface of the test specimen.

9.3 Time for measurements of chamber air concentration

After starting the test according to 9.3.1, air sampling shall be started at predefined sampling times in accordance with 11.4.

9.3.1 Emission test

Check the integrating air flow rate through the chamber and the air tightness and carry out air sampling. Verify that the outlet air flow rate during air sampling is equal to the inlet airflow minus the air flow at the time of air sampling.

Air samples shall be taken after 1, 3, 7, 14 ± 1 and 28 ± 2 days, in principle, after the test start. Air sampling may be carried out at additional time.

NOTE 1 The test durations may be selected depending on the purpose of the test.

NOTE 2 If decay studies are required, air samples can be taken after 28 days or longer after the test start.

NOTE 3 If the test chamber concentrations become lower than the quantification limit, the test may be completed.

9.3.2 Storage of test specimen

The test specimen shall be stored under the same conditions as in measurement, when removed from the chamber in long-term testing. The removed test specimens can be exposed to air freely, but they should be kept in a safe place to minimize contamination by other test specimens or the place where stored. In principle, the test specimens should be returned to the chamber at least 72 h prior to air sampling. Preservation of test specimens in temperature over 28 °C shall be avoided.

9.4 Air sampling

As sampling tubes, Tenax-TA® 1> or others shall be used for sampling VOC, and DNPH cartridge shall be used for sampling aldehydes. In 8 h or longer after supplying the chamber with clean air, the temperature and relative humidity shall be confirmed to be at steady state. Then a sampling tube shall be connected to the chamber and the outlet concentration in the chamber after one day as well as the travel blank shall be measured.

After that, the outlet concentration in the chamber and travel blank shall be measured at each given time.

If the concentration in the chamber is hardly predictable, two sampling tubes shall be connected to confirm there is no breakthrough in a series. Presence or absence of breakthrough shall be judged by formula (5). The absence of breakthrough can be confirmed when the calculated value is 95 % or over, because it means that target chemical adsorbed only in the primary sampling tube.

9.4.1 Sampling tube

Packed with silica gel and coated with DNPH and also available commercially. For example, the cartridge shall contain a minimum quantity of 350 mg of silica gel coated with a minimum DNPH loading of 0.29 % mass fraction. The ratio of the silica gel bed diameter to bed length shall not exceed 1 : 1. The capacity of the cartridge for formaldehyde shall be at least 75 μg and the collection efficiency at least 95 % at a sampling rate of 1.5 L/min. Sampling cartridges with very low blank levels and high performance are commercially available.

$(\rho 1 / (\rho 1 + \rho 2)) \geq 95\ (\%)$ ---------- (5)

where, p_1 : concentration of tubing upstream of air ($\mu g/m^3$)

p_2 : concentration of tubing downstream of air ($\mu g/m3$)

Note 1 "Tenax-TA®" is a commercially available product, given in this Standard for the convenience of users. Equivalent products may be used if they are proved to give the same results.

10 Analysis method

10.1 Analysis of aldehydes

The DNPH derivatives of carbonyl compound in a DNPH cartridge is dissolved and desorbed using acetonitrile.

10.1.1 Sample preparation

Return the samples to the laboratory in a suitable external container with 2 cm to 5 cm of granular charcoal and store them in a refrigerator until analysis. Alternatively, the samples may also be stored alone in their individual containers. The time between sampling and analysis should not exceed two weeks.

10.1.2 Sample desorption

Connect the sample tube to a clean syringe.

The liquid flow during desorption should be in the same direction as the air flow during sampling, to prevent insoluble particulates from getting into the eluate. Reverse desorption may be performed if the eluate is filtered prior to HPLC analysis. A filtered blank extract shall be analyzed with each batch of samples to confirm that no contamination is being introduced by the filter.

Place the tube/syringe in the syringe rack. Desorb the DNPH derivatives of the carbonyls and the unreacted DNPH from the tube (gravity feed) by passing 5 ml of acetonitrile from the syringe through the tube to a graduated test tube or to a 5 ml volumetric flask. Other volumes of acetonitrile may be appropriate, depending on the sampling tube used.

Dilute to the 5 ml mark with acetonitrile. Label the flask with sample identification.

Pipette an aliquot into a sample vial with a fluorocarbon-lined septum. Analyze the aliquot for the carbonyl derivatives by HPLC. As a backup, a second aliquot may be taken and stored under refrigeration until the results of the analysis of the first aliquot are complete and validated. The second aliquot can be used for confirmatory analysis, if necessary.

For glass sealed DNPH sampling tubes that contain two sorbent beds, uncap the end of the tube closest to the second sorbent layer (exit end). Carefully remove the spring and plug of glass wool holding the sorbent layer in place. Empty the sorbent into a clean 4 ml glass vial with a fluorocarbon-lined septum or cap. Mark this as the back-up sampling section. Carefully remove the next plug of glass wool and empty the remaining sorbent into another 4 ml vial. Mark this as the primary sampling section. To each vial, carefully pipette 3 ml acetonitrile into each vial, cap the vials and let stand for 30 min with occasional agitation.

10.1.3 HPLC calibration

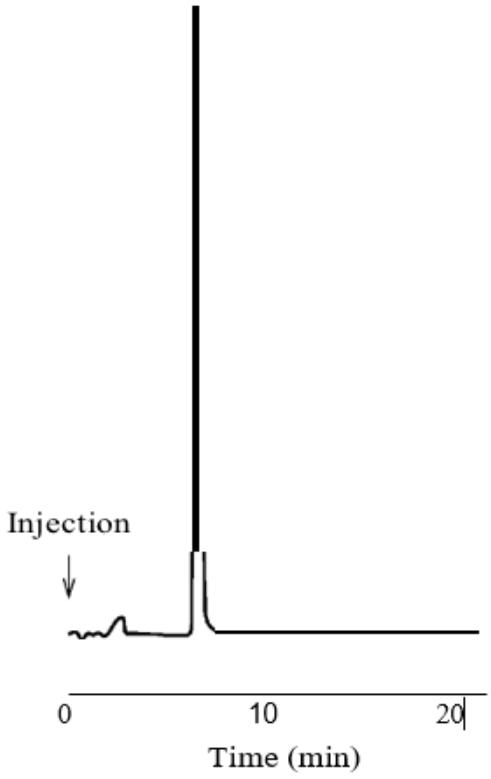
Prepare calibration standards in acetonitrile from the DNPH-formaldehyde derivative (see 3.12.2). Individual stock solutions of 100 mg/L are prepared by dissolving 10 mg of solid derivative in 100 ml of mobile phase.

Analyze each calibration standard (at least five levels) twice and tabulate area response against mass injected (or, more conveniently, versus the DNPH-formaldehyde injected, for a fixed loop volume; see figures 4 and 5). Perform all calibration runs as described for sample analysis in 9.3.4. To avoid carryover effects, start with the lower concentration.

Using the UV detector or the diode array detector, a linear response range of ap- proximately 0.05 µg/ml to 20 µg/ml should be achieved for 25 µl injection volumes. The results can be used to prepare a calibration curve, as illustrated in figure 5. Linear response is indicated where a correlation coefficient of at least 0.999 for a linear least-squares fit of the data (concentration versus area response) is obtained. The retention times for each analyte should agree within 2 %.

Once linear response has been documented, an intermediate concentration standard near the anticipated levels of each component, but at least ten times the detection limit, should be chosen for daily calibration. The day-to-day response for the various components should be within 10 % for analyte concentrations of 1 µg/ml or

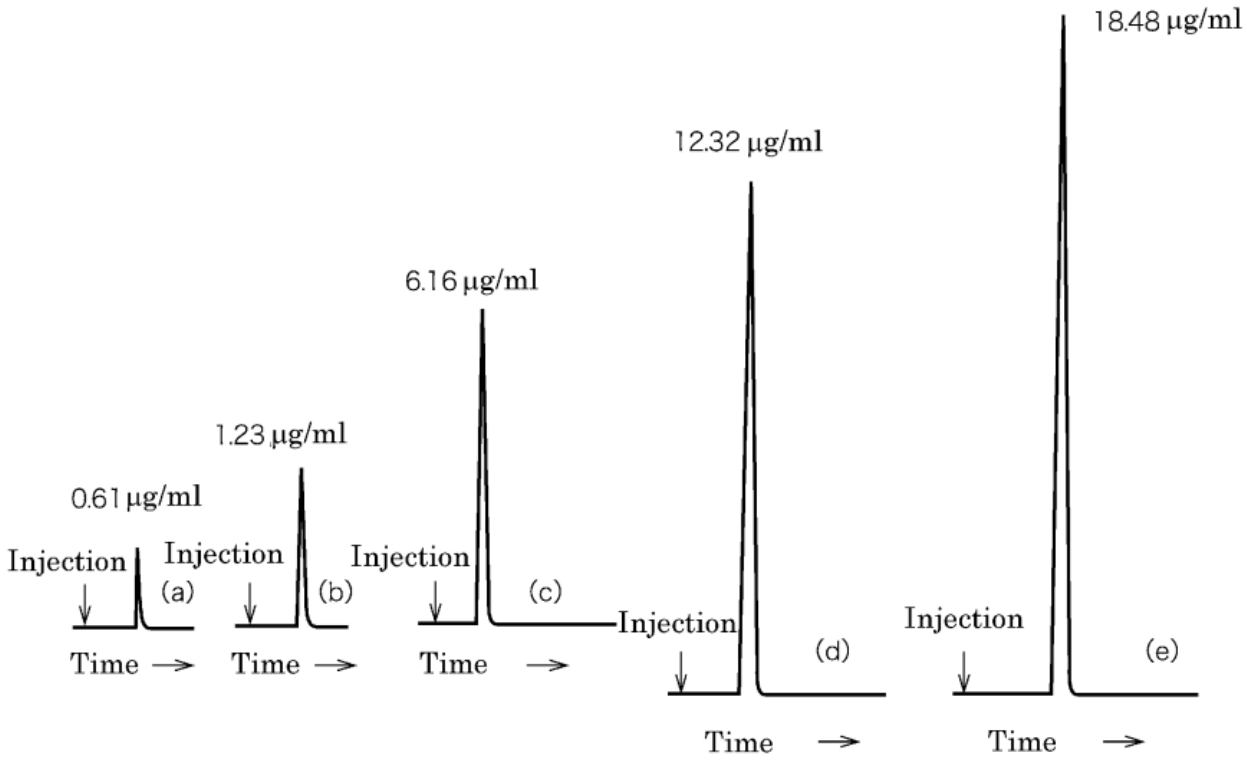
greater, and below 20 % for analyte concentrations near 0.5 µg/ml. If greater variability is observed, re-calibration may be required or a new calibration curve shall be developed from fresh standards.



HPLC operating conditions

Column	C 18 reverse phase
Mobile phase	60 % acetonitrile/40 % water
Detector	ultraviolet, at 360 nm
Flowrate	1 ml/min
Retention time	approx. 7 min (formaldehyde)
Sample injection volume :	25 Ll

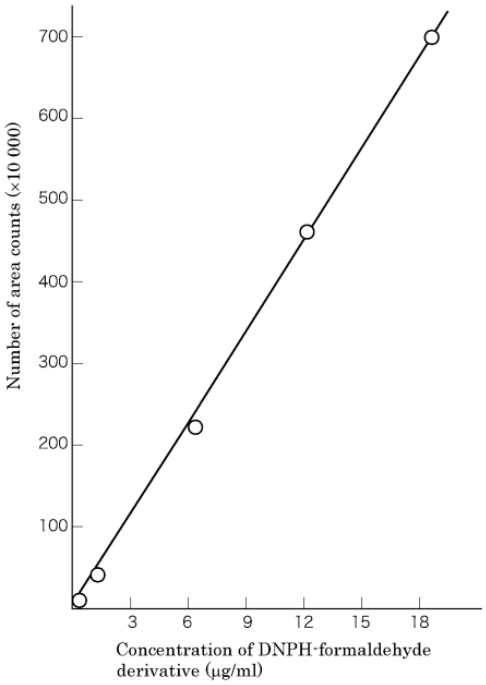
Figure 3 Example of chromatogram of DNPH-formaldehyde derivative



HPLC operating conditions
Column : C 18 reverse phase
Mobile phase : 60 % acetonitrile/40 % water
Detector : ultraviolet, at 360 nm
Flowrate : 1 ml/min
Retention time : approx. 7 min (formaldehyde)
Sample injection volume : 25 µl

Concentration	Number of area counts
0.61 µg/ml	226 541
1.23 µg/ml	452 166
6.16 µg/ml	2 257 271
12.32 µg/ml	4 711 408
18.48 µg/ml	6 953 812

Figure 4 Examples of HPLC chromatograms of varying concentrations of DNPH-formaldehyde derivative



HPLC operating conditions
Correlation coefficient : 0.999 9
Column : C 18 reverse phase
Mobile phase : 60 % acetonitrile/40 % water
Detector : ultraviolet, at 360 nm
Flowrate : 1 ml/min
Retention time : approx. 7 min (formaldehyde)
Sample injection volume : 25 µl

Figure 5 Example calibration curve for formaldehyde

10.2.4 HPLC analysis for formaldehyde

Assemble the HPLC system and calibrate as described in 10.2.3. Typical operating parameters are as follows.

Column — C 18 (length : 25 cm, inside diameter : 4.6 mm, or equivalent), A column thermostat bath should be installed.

Mobile phase — 60 % acetonitrile/40 % water (vol/vol), isocratic

Detector — Ultraviolet, operating at 360 nm

Flowrate — 1.0 ml/min

Retention time 7 min for formaldehyde with one C 18 column, 13 min for formaldehyde with two C 18 columns

Sample injection volume 25 µl

Before each analysis, check the detector baseline to ensure stable conditions.

Prepare the HPLC mobile phase by mixing 600 ml of acetonitrile and 400 ml of water or set the parameters on the gradient elution HPLC appropriately. Filter this mixture through a 0.22 µm polyester membrane filter in an all-glass and fluorocarbon suction filtration apparatus. Degas the filtered mobile phase by purging with helium for 10 min to 15 min (100 ml/min) or by heating to 60 °C for 5 min to 10 min in an Erlen meyer flask covered with a watch glass. The ultrasonic method, the online method with reduced pressure membrane, and the like may be used for other degas method. The constant back pressure restrictor (350 kPa) or short length (15 cm to 30 cm) of 0.25 mm inside diameter fluorocarbon tubing should be placed after the detector to eliminate further mobile phase out gassing.

Place the mobile phase in the HPLC solvent reservoir and set the pump at a flowrate of 1.0 ml/min. Allow it to pump for 20 min to 30 min before the first analysis. Switch the detector on at least 30 min before the first analysis. Display the detector output on a strip chart recorder or similar output device.

For manual injection systems, draw at least 100 µl of the sample into a clean HPLC injection syringe. Fill the HPLC loop (load position of valve) by addition of excess sample via the syringe. Turn the valve to the inject position to start the run. Activate the data system simultaneously with the injection and mark the point of injection on the strip chart recorder. After approximately 1 min, return the injection valve to the load position and rinse or flush the syringe and valve with acetonitrile/water mixture in preparation for the next sample analysis. Do not syringe solvent through the HPLC loop while the valve is in the inject position.

After elution of the DNPH-formaldehyde derivative (see figure 3), terminate data acquisition and calculate the component concentrations as described in clause 10. After a stable baseline is achieved, the system can be used for further sample analysis as described above.

NOTE : After several cartridge analyses, buildup on the column (if indicated, e.g. by increasing pressure from run to run at a given flow and solvent composition) may be removed by flushing with several column volumes of 100 % acetonitrile. The same protection can be achieved if precolumn are used.

If the concentration of analyte exceeds the linear range of the instrument, the sample should be diluted with mobile phase, or a smaller volume injected into the HPLC. If the retention time found in earlier runs is not duplicated (± 10 %), the acetonitrile/ water ratio may be increased or decreased to obtain the correct elution time. If the elution time is too long, increase the ratio; if it is too short, decrease the ratio. If a solvent change is necessary, always recalibrate before running samples (see 10.2.3).

NOTE: The chromatographic conditions described here have been optimized for the detection of formaldehyde. Analysts are advised to experiment with their HPLC system to optimize chromatographic conditions for their particular analytical needs. HPLC systems with automated injection and start of data acquisition may also be used.

11. Calculations

The total mass of analyte (DNPH derivative) for each sample is calculated by the following equation.

$m_d = m_s - m_b$

where, m_d: the corrected mass of DNPH derivative extracted from the cartridge (mg)

m_s: the uncorrected mass of the sample cartridge

$= A_s \text{ X } (C_{std} / A_{std}) \text{ X } V_s \text{ X } d_s$ ---------- (6)

m_b: the analyte mass, in micrograms, on the blank cartridge

$= A_b \text{ X } (C_{std} / A_{std}) \text{ X } V_b \text{ X } d_b$ ---------- (7)

Where A_s : the number of area counts, eluate from sample cartridge

A_b : the number of area counts, eluate from blank cartridge

A_{std}: the number of area counts, standard

C_{std}: the concentration of analyte in the daily calibration standard (mg/ml)

V_s: the total volume of the sample cartridge eluate (ml)

V_b: the total volume of the blank cartridge eluate (ml)

d_s: the dilution factor for the sample cartridge eluate

= 1, if sample was not rediluted

$= V_d / V_a$, if sample was rediluted to bring the detector response within linear range

V_d: the redilute volume (ml)

V_a: the aliquot used for redilution (ml)

d_b: the dilution factor for the blank cartridge eluate = 1.0

The concentration of the carbonyl compound in the original sample is calculated by the following equation.

$C_A = m_d \text{ x } (M_c/M_{der}) \text{ x } 1000 / V_m$ ---------- (8)

Where, C_A: the concentration of carbonyl compound in the original sample (ng/L)

V_m: the total air sample volume under indoor conditions (L)

M_e: the molecular mass of carbonyl compound (for formaldehyde = 30)

M_{der}: the molecular mass of the DNPH derivative (for formaldehyde = 210)

NOTE: The use of ppb or ppm is deprecated in ISO. However, for the convenience of certain users, the following information is provided.

To convert carbonyl compound concentration to ppm (10^{-6}) use the following equation.

$C_A = C_{As}$ x (mg/L) x 24.4 / M_c ---------- (9)

Where, C_A: (volume fraction in 10^{-6}) = the concentration of carbonyl compound, in ppm by volume

C_{As}: the concentration of carbonyl compound, in the original sample, calculated using the air volume corrected to 25°C and 101.3 kPa (V_s) (mg/L)

24.4: the ideal gas volume corrected to 25 °C (ml/mmol)

The corrected air volume at 25°C and 101.3 kPa is calculated from the following equation

$V_s = V_m X (P_A/101.3) X (298/ 273 + T_A)$

Where, V_s : the total sample volume at 25°C and 101.3 kPa (L)

P_A: the average indoor pressure (kPa)

T_A: the average indoor temperature (°C)

It is desired to obtain a concentration result in terms of ppm at standard conditions (25°C and 101.3 kPa) to compare with standard stated in these terms, the volume sampled should not be corrected for temperature and pressure.

12 Calculation of emission factor and expression of results

The area specific emission factor q_A at a given time, t, from the start of measurement after placing the test specimen in the chamber can be expressed by formula (10). The length specific emission factor q_l, mass specific emission factor q_m, volume specific emission factor q_v and unit specific emission factor q_u can be expressed by formulae (11) to (14), respectively. Emission factor can be expressed in integral value and can be rounded off.

$q_A = (\rho_t X Q) / A = (\rho_t X nV) / A = \rho_t X k_Q = \rho_t X n / L$ ---------- (10)

$q_l = (\rho_t X Q) / l$ ----------(11)

$q_m = (\rho_t X Q) / m$ ----------(12)

$q_v = (\rho_t X Q) / v$ ----------(13)

$q_u = (\rho_t X Q) / u$ ----------(14)

NOTE 1 For certain purposes, emission factor q can be calculated from time con- centration profiles, or by applying the decay model from concentration time data.

NOTE 2 The concentrationp1 can be calculated after subtracting the travel blank from the total mass of chemical substances sampled at the chamber outlet.

13 Performance characteristics

The performance characteristics should include as a minimum, the estimation of uncertainty components from the following resource-

Sampling: Flow rate

Time Temperature Pressure

Sampling efficiency

Sampling validity: Measurement method and stability

Blank stability

Desorption efficiency:

Calibration: Standard substances

Unevenness of calibration curve

Analysis: Repeatability

Contaminated level of blank sampler

Environmental influences: Temperature at sampling

Humidity at sampling

Interfering substance

Field repeatability

Thermal control of chamber: Air exchange rate

Preparation of test specimen

The accuracy and repeatability of the measuring method are important factors, which shall be determined to evaluate the results and the suitability of the method for the intended purposes. The accuracy of the VOC measurement method can be determined if atmospheres of known level ($\mu g/m^3$ level) can be reliably produced. This is relatively difficult and therefore most researchers only determine the repeatability of their measuring method by repeated sampling from a constant (concentration) atmosphere.

NOTE : In material emission testing, interlaboratory comparisons have been organized to assess the agreement among laboratories undertaking tests to characterize the emission of VOCs from indoor materials and products.

14 Test report

The test report shall include the following information, in principle.

a) **Test laboratory**

1) Name and address of the laboratory

2) Name of the responsible person

b) **Sample description**

1) Type of product (and brand name if appropriate)

2) Sample selection process (e.g. random)

3) Product history (e.g. date of production, batch number, date of arrival to the test laboratory, date and time of unpacking and of test specimen preparation)

c) **Results** emission factor of target chemical substances (VOCs, aldehydes) and/or TVOC at a given time from the test start.

d) **Data analysis**

1) Describe the method used to derive specific emission factor qA from measured emission test chamber concentration (specify mathematical models or formulae used), if any

2) Describe the transformable formula when test conditions of temperature and relative humidity are changed.

e) **Test conditions**

1) Chamber conditions (temperature, relative humidity, air change rate, mass transfer coefficient)

2) Test specimen area and product loading factor

3) With or without sealing

4) Sampling of emitted target chemical substances (e.g. sampling tube used, volume sampled, sampling period and number of air sampling after introduction into the chamber)

f) **Devices** Information of equipment and procedure (e.g. chamber, seal material, seal box, clean air supply, temperature control and humidification system, integrating flowmeter, oven, air sampling devices, analyser)

g) **Quality assurance and quality control**
The quality assurance and quality control shall be as specified in Annex A, and as follows.

1) Background concentration and travel blank of target chemical substances

2) Recovery data to evaluate sink effect of target chemical substances

3) Number of measurements

4) In the case of duplicate sampling, results of individual analyses

5) Accuracy of temperature, relative humidity and air change rate

6) Quality assurance report

Annex

Example of chamber (20 L)

20 L chamber

20 L chamber is convenient for transporting, demounting, cleaning, settling and heat treatment. This chamber is composed of a main chamber, an air control unit, and others.

Apparatus

Composition of 20 L chamber system is shown in Figure IS.1

When the emission factor of VOCs, aldehydes are measured with 20 L chamber, the following apparatuses should be mainly used.

a. 20 L chamber
b. Seal box
c. Clean air supply (or cylinder)
d. Temperature control and humidification system (thermostatic bath, chamber, mixer)
e. Flow rate control apparatus
f. Temperature and humidity recorder
g. Integrating flowmeter
h. Air sampling device
i. Oven

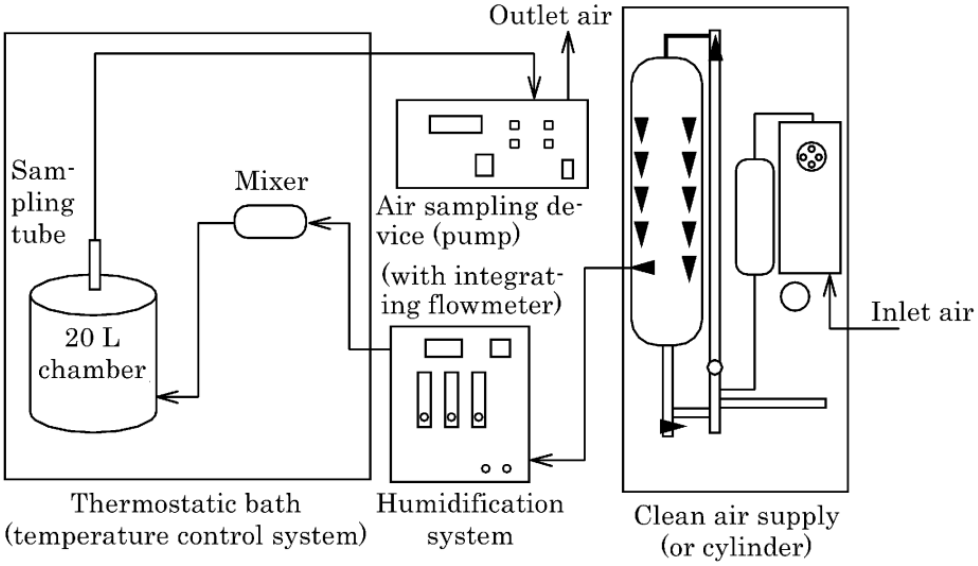
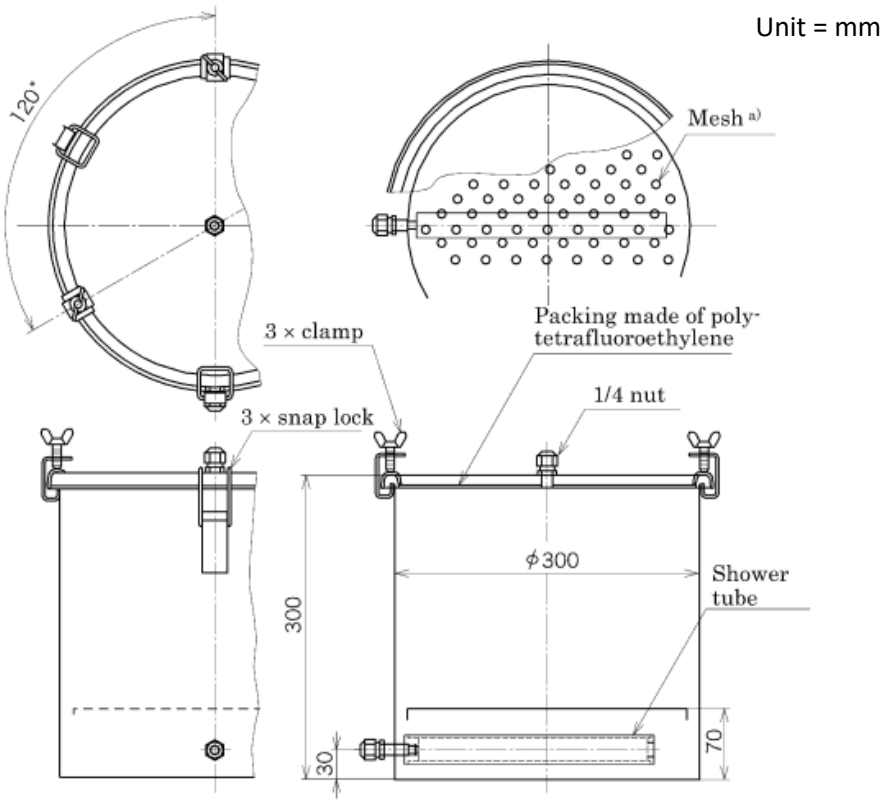


Figure IS.1 Composition of 20L chamber system

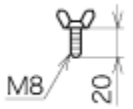
a. 20 L chamber

Main chamber is made of stainless steel (SUS304) to minimize contamination caused by the system itself and the adsorption of contaminant. The chamber is made cylindrical to minimize leak from the joint and to reduce the weld.

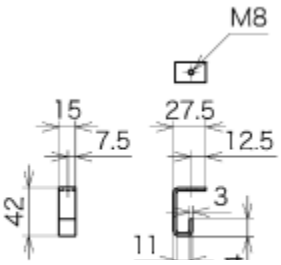
The packing is sealed with low emitting and low absorbing frame made of or coated with polytetrafluoroethylene. The components in the chamber are made of stainless steel and are demountable therefore suited for washing and heat treatment. Fresh air is supplied to the chamber through a shower tube which is designed to mix the air thoroughly. An example of details for 20 L chamber is shown in Figure IS.2.



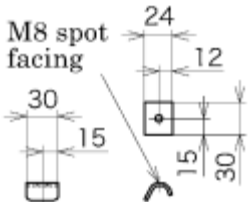
a) 20 L chamber (container)



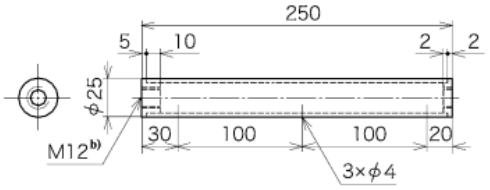
b) M8 butterfly nut



c) Clamp



d) Press plate for clamp



e) Shower tube

Figure IS.2 Example of details of 20 L chamber

b. Seal box

When setting the sample in the chamber, employ a seal box to seal the back and cut ends of the test specimen, so that chemical substances can be emitted only from the surface.

Seal box can hold a constant surface area of the test specimen according to the product loading factor. In the case of 20 L chamber, the product loading factor comes to 2.2 m^2/m^3 if two sets of the seal box shown in Figure IS.3 are used. Insert polytetrafluoroethylene frame in a gap between a test specimen and the stainless-steel body and fix the test specimen with screws from the back.

This method is useful to minimize the emission of chemical substances at the time of setting, because the body can be set up quickly, using only eight fasteners for fixing the cover of seal box and four screws for fixing a test specimen. An example of the composition of seal box is shown in Figure JA.3 and an example of the cross-section of a seal box is shown in Figure IS.4.

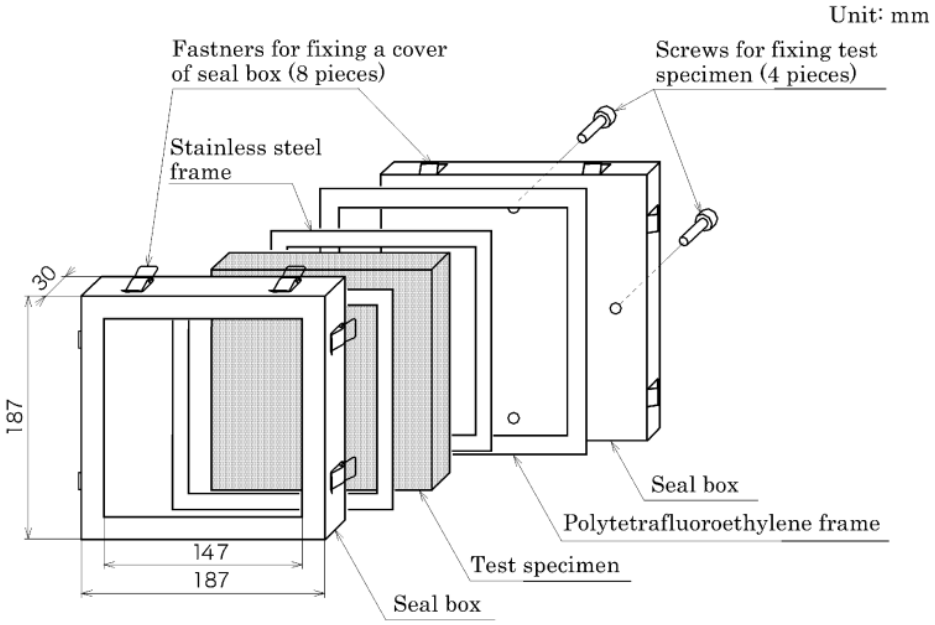


Figure IS.3 The composition of seal box (example)

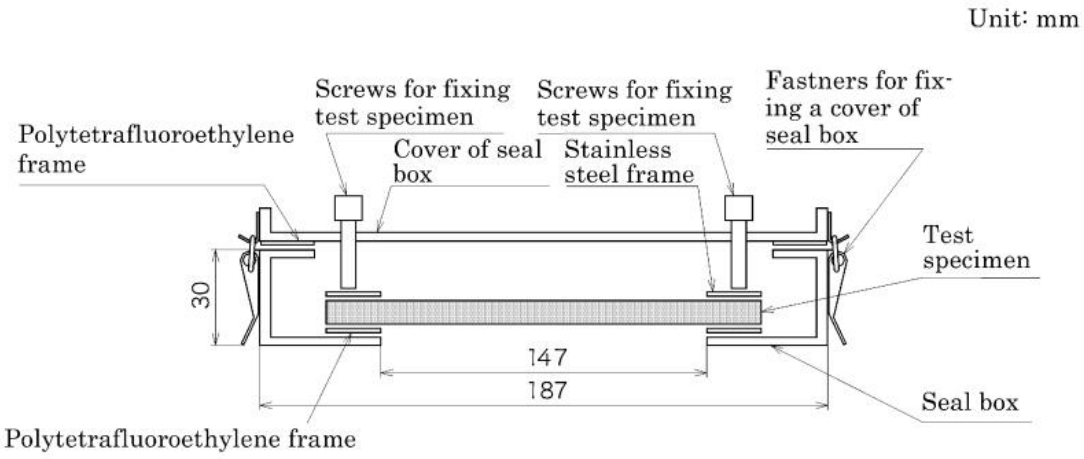


Figure IS.4 The cross section of seal-box

c. Clean air supply

The clean air supply should be in accordance with 4.7.

d. Temperature control and humidification system

The temperature of 20 L chamber should be controlled by installing the chamber body into a thermostatic bath controlled to the required temperature. The relative humidity and the flow rate of ventilated air should be controlled with an air control unit.

Divide the ventilation air, which is dehumidified and purified with the clean air supply, into two lines with the air control unit, introduce one of them into a tank filled with distilled water and bubble it to humidify. Wet air and dried air are joined in one line and sent to the mixer. After mixing, air is sent to the chamber.

e. Flow rate control apparatus

The pump for air control unit should be the pump employed in a clean room, which can suck in and out at the same time (vacuum pump). Air sucked out is divided to two lines, and their flow rates are to be measured.

The chamber should be ventilated at a specified air change rate until sampling is carried out. The emission factor is calculated on the supposition of perfect mixing.

During ventilating, suck the air inside the chamber with a pump of the air control unit. The flow rate can be controlled by a digital-indicated flowmeter placed in front of the pump. In sampling, use an external sampling pump. Fresh air is supplied to the chamber through a shower tube which is designed to mix the air thoroughly.

f. Temperature and humidity recorder

Temperature/humidity sensor and pressure gauge can be installed on a mixer, and and their data can be outputted if necessary. In the case of 20 L chamber, take values obtained with a temperature and humidity measuring apparatus as a temperature and humidity inside the chamber, and monitor them continuously.

g. Integrating flowmeter

The integrating flowmeter should be in accordance with **4.9.**

h. Air sampling device

The air sampling device (pump) should be in accordance with **4.10.**

i. Oven

The oven should be in accordance with **4.11.**

References

1. **JIS A 1901: 2015**
2. **JIS A 1902-2:2015**
3. **JIS A 1962 : 2005**
4. **JIS A 1965 : 2007**
5. **JIS K 0124 : 2011**