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Methods for determination of formaldehyde in flue gas

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Foreword

This translation has been made based on the original Japanese Industrial Standard revised by the Minister of Economy, Trade and Industry through deliberations at the Japanese Industrial Standards Committee, as the result of proposal for revision of Japanese Industrial Standard submitted by The Japan Society for Analytical Chemistry (JSAC)/Japanese Standards Association (JSA) with the draft being attached, based on the provision of Article 12 Clause 1 of the Industrial Standardization Law applicable to the case of revision by the provision of Article 14. Consequently **JIS K 0303 : 1993** is replaced with this Standard.

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Methods for determination of formaldehyde in flue gas

1 Scope This Japanese Industrial Standard specifies the methods of analyzing formaldehyde in flue gas.

In this Standard, the flue gas means the gas exhausted in a flue, chimney, or duct (hereafter referred to as “duct”) in cases where such process is carried out as manufacturing of resin or the like, burning of methanol, other chemical reactions or the working process using or generating formaldehyde, or the gas exhausted to the exhaust pipe or the like of internal combustion engine.

2 Normative references Standards listed in attached table 1 contain provisions which, through reference in this Standard, constitute provisions of this Standard. The most recent editions of the standards (including amendments) shall be applied.

3 Common matters The common matters shall be as follows:

- a) **General rule** The general matters in common to chemical analysis shall be in accordance with **JIS K 0050**.
- b) **Definitions** For the purposes of this Standard, the definitions given in **JIS K 0211** or **JIS K 0215** apply.
- c) **Sampling of flue gas** The general matters in common to sampling of flue gas shall be in accordance with **JIS K 0095**.
- d) **Reagents and water** The general matters in common to reagents and water shall be in accordance with **JIS K 8005** and **JIS K 0557**.
- e) **Absorptiometry** The general matters in common to absorptiometry shall be in accordance with **JIS K 0115**.
- f) **Gas chromatography** The general matters in common to gas chromatography shall be in accordance with **JIS K 0114**.
- g) **High performance liquid chromatography** The general matters in common to high performance liquid chromatography shall be in accordance with **JIS K 0124**.

4 Classification of analytical methods and outline The classification of analytical methods and outline shall be in accordance with table 1.

Table 1 Classification of analytical methods and outline

Classification of analytical methods (Abbreviation)	Outline of analytical method			Matters that require attention on application
	Summary	Sampling	Range of determination ⁽¹⁾ vol ppm (mg/m ³)	
4-amino-3-hydrazino-5-mercapto-1,2,4-triazol absorptiometry (AHMT absorptiometry)	After collecting formaldehyde in sample gas into boric acid solution, alkalize it, add AHMT to colour it and measure its absorbance.	[Collection in absorption bottle] Absorption solution: boric acid solution (5 g/L) Absorption volume: 40 ml × 2 bottles Standard sampling volume: 2 L to 20 L	0.4 to 75 (0.5 to 100)	According to 6.1.1
2,4-dinitrophenyl-hydrazine collection—gas chromatography (DNPH-GC method)	After collecting formaldehyde in sample gas into DNPH solution, extract it by chloroform or the like, and separate to determine it by gas chromatograph.	[Collection in absorption bottle] Absorption solution: DNPH hydrochloric acid solution (2 g/L) Absorption volume: 40 ml Standard sampling volume: 2 L to 10 L	0.4 to 56 (0.5 to 75)	According to 6.2.1
	After collecting formaldehyde in sample gas in the cartridge packed with collector impregnated with DNPH solution, elute with acetonitrile, and then dissolve it again by chloroform and separate to determine it by gas chromatograph.	[Collection in cartridge] Standard sampling volume: 2 L to 10 L	0.4 to 45 (0.5 to 60)	According to 6.3.1
2,4-dinitrophenyl-hydrazine collection—high performance liquid chromatography (DNPH-HPLC method)	After collecting formaldehyde in sample gas in DNPH solution, extract it by chloroform and the like, dissolve it again in acetonitrile and separate to determine it by high performance liquid chromatograph.	[Collection in absorption bottle] Absorption solution: DNPH hydrochloric acid solution (2 g/L) Absorption volume: 40 ml Standard sampling volume: 2 L to 10 L	0.2 to 56 (0.3 to 75)	According to 6.2.1
	After collecting formaldehyde in sample gas in the cartridge packed with collector impregnated with DNPH solution, elute with acetonitrile and separate to determine it by high performance liquid chromatograph.	[Collection in cartridge] Standard sampling volume: 2 L to 10 L	0.2 to 45 (0.3 to 60)	According to 6.5.1

Table 1 (concluded)

Classification of analytical methods (Abbreviation)	Outline of analytical method			Matters that require attention on application
	Summary	Sampling	Range of determination ⁽¹⁾ vol ppm (mg/m ³)	
4-amino-3-hydrazino-5-mercapto-1,2,4-triazol absorption—automated analysis method (AHMT automated analysis method)	Carry out periodically the automatic analysis of formaldehyde in sample gas with using the automatic measuring apparatus of AHMT absorptiometry.	[Collection in absorption bottle] Absorption solution: potassium hydroxide solution (0.12 mol/L) Absorption volume: 40 ml Standard sampling volume: 25 L	0 to 20 (0 to 27)	According to 6.6.1

Note ⁽¹⁾ The range of determination is the value given when, in case of absorptiometry, sample gas is taken by 20 L for low concentration side and by 2 L for high concentration side, and in the case of gas chromatography and high performance liquid chromatography, sample gas is taken by 10 L for low concentration side and by 2 L for high concentration side individually.

Moreover, the value in AHMT automated analysis shall be the one indicating range.

- Remarks 1 There is the detecting tube method for the simplified measuring method of formaldehyde concentration in flue gas. The sample gas of approximately 100 ml is sucked in a detecting tube, reacted with the reagent in the tube and the formaldehyde concentration is obtained from the coloured length of reagent. The range of determination varies depending on the type of tube and the sucked volume, and 20 vol ppm to 1 500 vol ppm when 100 ml is sucked. When the moisture in flue gas is condensed, formaldehyde is dissolved in the condensed water and it gives a negative error, and the existence of other aldehydes in flue gas gives a positive error. It is usable for setting up a standard of formaldehyde concentration or the self-control of concentration.
- 2 In addition to the methods in table 1, this Standard specifies 4,5-dihydroxy-2,7-naphthalene disulfonic acid absorptiometry (chromotropic acid absorptiometry) in annex (normative).
- 3 The vol ppm and mg/m³ as shown in this Standard mean the volume concentration and mass concentration under the standard condition (0 °C, 101.325 kPa).

5 Taking method of sample gas

5.1 Case of 4-amino-3-hydrazino-5-mercapto-1,2,4-triazol absorptiometry

5.1.1 Taking of sample gas The taking position of sample gas to be used for analysis shall be the point where the representative gas can be taken, and the sample gas shall be taken usually at least 2 times, which are in adjacent interval of time, at the same taking position, and they shall be used for analysis respectively.

5.1.2 Reagents and preparation of reagent solution

5.1.2.1 Reagents The reagents shall be as follows:

- a) **Water**, class A2 specified in **JIS K 0557**.
- b) **Boric acid**, specified in **JIS K 8863**.

5.1.2.2 Preparation of reagent solution

- a) **Absorption solution (5 gH₃BO₃/L)** Dissolve 5 g of boric acid in water to make 1 L in total. Prepare this solution when used.

5.1.3 Apparatus

5.1.3.1 Absorption bottle For the absorption bottle, the absorption bottle (100 ml in capacity) as shown in figure 1 shall be used with connecting two bottles.

5.1.3.2 Apparatus for sampling gas The apparatus shall be constructed as shown in figure 2 and be provided with the following requirements.

- a) For the gas sampling tube (B), glass tube, quartz glass tube, polytetrafluoroethylene tube and the like, which is not attached by or does not absorb such corrosive gas as formaldehyde, etc. in flue gas.
- b) For the purpose of preventing the sample gas from being mingled with dust, etc., stuff with suitable media⁽²⁾ at the top of the gas sampling tube or an adequate position.
- c) For the purpose of preventing the moisture in the sample gas from condensation, the portion between the gas sampling tube and the stop cock (P₁) shall be constructed to be heated⁽³⁾.

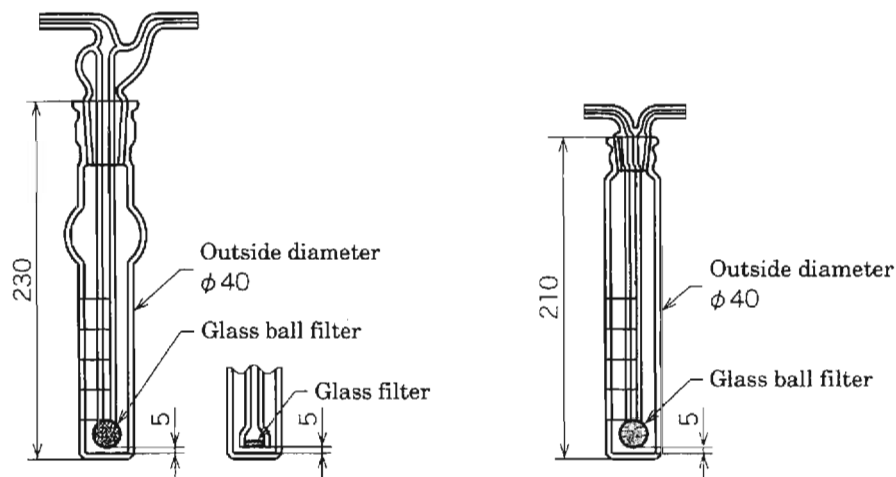
For the connecting part between those, a ground joint tube, silicone rubber tube or polytetrafluoroethylene tube and the like shall be used.

- d) The apparatus shall be assembled so as not to generate gas leakage at the connecting of each part in it.

Notes ⁽²⁾ The material in quality, which does not produce the chemical reaction with the component in flue gas, for example, silica wool or non-alkali glass wool shall be used.

- ⁽³⁾ The piping shall be as short as possible, and when the moisture is possibly condensed, the portion between the gas sampling tube (B) and the stop cock (P₁) shall be heated at 100 °C to 110 °C.

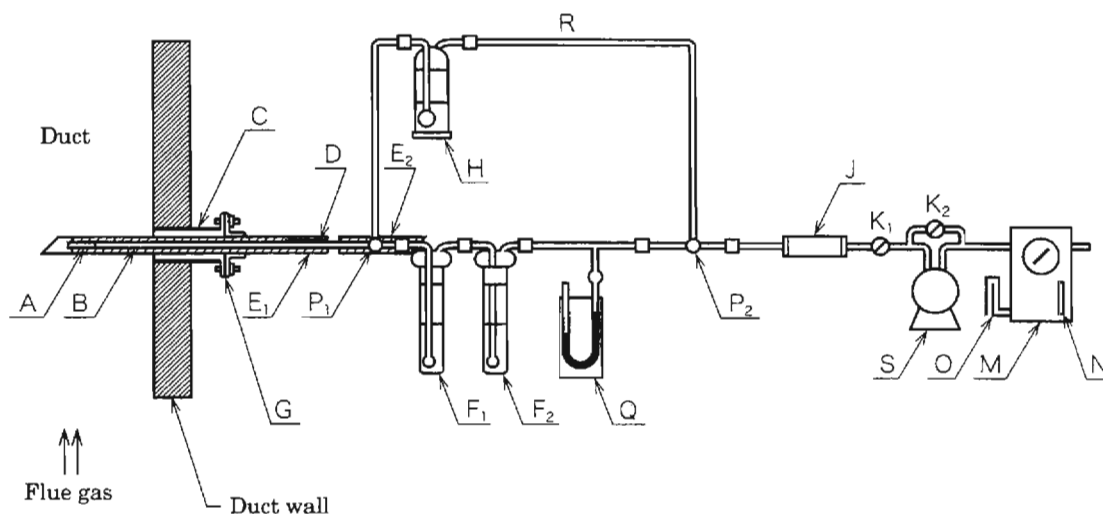
Unit: mm



Glass ball filter: maximum pore diameter 40 μm to 120 μm (No. 1 to No. 2)

Glass filter: maximum pore diameter 60 μm

Figure 1 An example of absorption bottle (100 ml)



- | | |
|---|--|
| A : Filter media | K ₁ , K ₂ : Cock for flow rate adjusting |
| B : Gas sampling tube | M : Wet type gas metre or dry type gas metre |
| C : Sampling hole | N : Thermometer |
| D : Thermometer | O : Manometer |
| E ₁ , E ₂ : Heater, ribbon heater | P ₁ , P ₂ : Three way stop cock for switching of flow path |
| F ₁ , F ₂ : Absorbing bottle, cartridge collector | Q : Mercury manometer |
| G : Flange | R : Bypass |
| H : Washing bottle (contained with 40 ml of absorption solution) | S : Suction pump |
| J : Drying tube | |

Figure 2 An example of gas sampling apparatus

Remarks : When the sample gas is taken from other place than duct, the sampling method shall be adequately changed. When, for example, the emission gas is taken from an internal combustion engine, the apparatus in figure 2 is recommended for the sampling at steady operation, however, when including transient operation, it is required that a dilution device by air is put between a gas-generating source and the sampling apparatus. An example of concept diagram shall be as shown in figure 3. When the constant volume sampling apparatus is directly used, the sample gas shall be taken at the rear step of mixing part of the apparatus and at the front step of heat exchanger. When a dilution tunnel is used together, the sample gas shall be taken at down stream side of 10 times tunnel diameter from the mixing part.

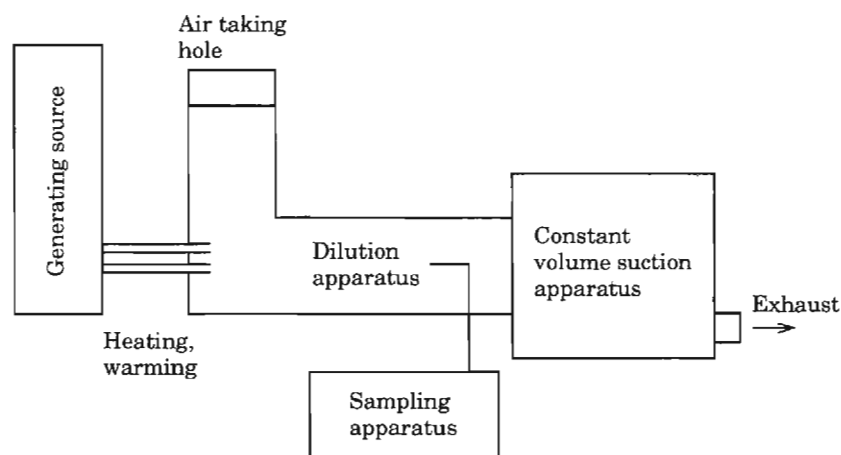


Figure 3 Sampling apparatus of sample gas exhausted from internal combustion engine (concept diagram) (example)

5.1.4 Sampling operation The operation shall be as follows. The symbols of apparatus as shown herein shall be in accordance with figure 2.

- a) Pour respectively 40 ml of absorption solution of 5.1.2.2 a) into the absorption bottles (100 ml in capacity) (F_1 , F_2).
- b) Turn the switching cock of flow path (P_1) to bypass side (direction of cock, $\oplus$) and the switching cock (P_2) to suction cock side (direction of cock, $\oplus$), and then operate a suction pump (S), which has been regulated beforehand at 1 L/min to 2 L/min in flow rate, and replace the inside of piping between the gas sampling tube (B) and the switching cock (P_1) with the sample gas.

Remarks 1 When the distance between the gas sampling tube (B) and the absorption bottle is short, no leakage is found in the inside of apparatus and the flow rate can be constantly regulated, it is not required to equip the bypass (R) between P_1 and P_2 in figure 2.

- 2 When no leakage in the sampling apparatus can be confirmed by other means, it is not required to equip the mercury manometer (Q) in figure 2.

- c) Stop the suction pump (S), and turn the switching cocks of flow path (P_1 , P_2) to the absorption bottles (F_1 , F_2) side (direction of both cocks, $\oplus$). Next, read the value (V_1) indicated on gas metre (M) to the nearest 0.01 L.
- d) Operate the suction pump (S) and pass the sample gas through the absorption bottles (F_1 , F_2)⁽⁴⁾. In this case, regulate the cocks (K_1 , K_2) for adjusting flow rate to approximately 1 L/min⁽⁵⁾.
- e) Measure the temperature of gas and gauge pressure by using the thermometer (N) and manometer (O) of gas metre (M). Measure, also, the atmospheric pressure.
- f) Take approximately 20 L⁽⁶⁾ of the sample gas, stop the suction pump (S) and shut the switching cocks of flow path (P_1 , P_2) (direction of cock, $\oplus$, $\oplus$ respectively). Read the value (V_2) of gas metre to the nearest 0.01 L.
- g) As occasion demands, measure the moisture in sample gas according to clause 6 of JIS Z 8808.

Notes (4) When the gas to be sampled shows comparatively high temperature and the absorption solution is likely warmed, the absorption bottle is kept to place in a cooling vessel.

(5) When it is obvious beforehand that formaldehyde is completely collected in the absorption solution, it would be allowed to increase flow rate up to 1.5 L/min.

(6) It may be suitably increased or decreased depending on the concentration of formaldehyde. However, it shall be about 90 L at most.

5.2 Case of 2,4-dinitrophenylhydrazine collection—gas chromatography (collection in absorption bottle) and 2,4-dinitrophenylhydrazine collection—high performance liquid chromatography (collection in absorption bottle)

5.2.1 Sampling gas Follow 5.1.1.

5.2.2 Reagents and preparation of reagent solution

5.2.2.1 Regents The reagents shall be as follows:

- a) **Hexane**, specified in JIS K 8848. Concentrate 10 ml of it approximately to 1 ml, inject 5 μ l of it into a gas chromatograph or a high performance liquid chromatograph, and it shall not give a peak in the retention time of formaldehyde • 2,4-dinitrophenylhydrazine.
- b) **2,4-dinitrophenylhydrazine**, specified in JIS K 8480. In this reagent, the equal volume of water is contained for safety. After breaking the seal, care shall be taken so as not to dry, and stock it.
- c) **Hydrochloric acid**, specified in JIS K 8180.

5.2.2.2 Preparation of reagent solution

- a) **Absorption solution (approximately 1 gDNPH/L)** Pour 1 L of hydrochloric acid (2 mol/L) in a container which is able to close up tightly, take 2,4-dinitrophenylhydrazine (DNPH) on filter paper, add 2 g of it in which the moisture is removed by the filter paper, expel the air in the container with nitrogen and then dissolve it. After leaving it as being closed tightly for approximately half day as it is, and filter it through a glass filter (G3). Take 200 ml of filtrate into a separating funnel of 1 000 ml, add 200 ml of hexane, shake to mix them vigorously for 5 min, after leaving it quietly as it is, transfer the water phase into another separating funnel, carry out the similar washings operation with adding 200 ml of hexane again, and then separate⁽⁷⁾ the water phase and throw away the organic phase. Carry out the similar washing operation on the residual filtrate. Transfer the solution after washing quickly into a brown coloured hard-quality bottle which has been washed with hydrochloric acid and hexane, and store it in a cool and dark place after stoppering tightly⁽⁸⁾.

Notes (7) Take 40 ml of this solution and carry out a blank test. If the content of formaldehyde · 2,4-dinitrophenylhydrazone exceeds 0.4 µg, further repeat the washing operation with hexane, and confirm that the value is not more than this value.

- (8) Storing in a cool and dark place after stoppering tightly may give effectiveness to the solution for approximately 2 weeks, however, it is recommended to carry out this washing operation when it is to be used.

5.2.3 Apparatus

5.2.3.1 **Absorption bottle** Follow 5.1.3.1.

5.2.3.2 **Gas sampling apparatus** Follow 5.1.3.2.

5.2.4 **Sampling operation** The operation shall be as follows:

- a) Pour 40 ml of absorption solution in 5.2.2.2 a) into the absorption bottles (100 ml in capacity) (F₁, F₂) respectively.
- b) Successively, carry out the operation from 5.1.4. The sampling amount of gas shall be approximately 2 L to 10 L.

5.3 Case of 2,4-dinitrophenylhydrazine collection—gas chromatography (collection in cartridge) and 2,4-dinitrophenylhydrazine collection—high performance liquid chromatography (collection in cartridge)

5.3.1 **Sampling of gas** Follow 5.1.1.

5.3.2 **Reagents, gas and preparation of sample solution**

5.3.2.1 **Reagents** The reagents shall be as follows:

- a) Acetonitrile, specified in **JIS K 8032**. Condensate 10 ml of it to approximately 1 ml, inject 5 µl of it into a gas chromatograph or a high performance liquid chromatograph and it shall not give a peak in the retention time of formaldehyde · 2,4-dinitrophenylhydrazone.

- b) **2,4-dinitrophenylhydrazine**, specified in **JIS K 8480**.
- c) **Hydrochloric acid**, specified in **JIS K 8180**.
- d) **Nitrogen**, grade 2 of high purity of nitrogen specified in **JIS K 1107**.

5.3.2.2 Preparation of reagent solution

- a) **2,4-dinitrophenylhydrazine (DNPH) solution** Take the reagent on the market of 2,4-dinitrophenylhydrazine on filter paper and remove the moisture with the filter paper. Dissolve approximately 5 g of it in acetonitrile at 60 °C, after heating and filtering it, carry out recrystallization by cooling it gradually as passing nitrogen. Dissolve 1 g of this recrystallized DNPH in 100 ml of acetonitrile to take it as the stock solution, pour it into a brown bottle and store it in a cool and dark place after stoppering tightly. It is usable approximately for 2 weeks. Just before using, dilute 25 ml of this stock solution to 1 L with acetonitrile and prepare DNPH solution by adding 1 ml of hydrochloric acid⁽⁹⁾.

Note ⁽⁹⁾ Recrystallization shall be carried out with using the minimum quantity as required for obtaining 1 g of the recrystallized. When the recrystallized is left, it shall be placed in a silicagel desiccator and stored at cool and dark place.

5.3.3 Apparatus

5.3.3.1 Collecting cartridge The silicagel cartridge for pretreatment on the market [a cylinder of approximately 10 mm in inside diameter and approximately 30 mm in length packed with 0.7 g of silicagel (approximately 150 µm in particle diameter)] shall be treated as follows and used. Wash by letting approximately 10 ml of acetonitrile flow and dry by passing nitrogen. After impregnating DNPH by letting 10 ml of DNPH solution flow, remove excess DNPH by passing nitrogen and dry the cartridge in a vacuum desiccator. After preparing, store it in a refrigerator with stoppering tightly. The formaldehyde collecting cartridge on the market (DNPH-aldehyde sampler) may be used⁽¹⁰⁾.

Note ⁽¹⁰⁾ The collecting cartridge shall be usually disposable and shall not be renewed. The blank test for collecting cartridge shall be carried out every lot.

5.3.3.2 Gas sampling apparatus The apparatus shall be in accordance with 5.1.3.2. However, instead of the absorption bottles (F₁, F₂) in figure 2, the collecting cartridge in 5.3.3.1 shall be equipped⁽¹¹⁾ and heated at the degree (70 °C to 80 °C) so that the condensation of moisture, degeneration of reagent and deformation of material quality of cartridge are not produced.

Note ⁽¹¹⁾ For the purpose of not exceeding the breakthrough capacity of formaldehyde in the collecting cartridge at collecting time, when the concentration of formaldehyde is high, the connected couple collecting cartridge shall be used or the gas sampling volume and the suction flow rate at sampling time shall be adjusted. No producing of breakthrough of the cartridge after collected shall be confirmed by the fact that the pale yellow colour of cartridge before collecting is left from the rear end by not less than 10 %.

5.3.4 Sampling operation The operation shall be carried out according to the procedure from 5.1.4 b) onward. However the flow rate of sample gas shall be 0.5 L/min to 1 L/min and the gas sampling volume of sample gas shall be approximately 2 L to 10 L.

5.4 Gas sampling volume The gas sampling volume under the standard condition (0 °C, 101.325 kPa) shall be calculated as dry gas volume (V_{SD}) or wet gas volume (V_{SW}) according to the following formulae.

a) Case of obtaining by dry gas volume

- 1) When a wet gas metre is used

$$V_{SD} = V \times \frac{273.15}{273.15 + t} \times \frac{P_a + P_m - P_v}{101.325} + 22.41(a + b)$$

- 2) When a dry gas metre is used

$$V_{SD} = V \times \frac{273.15}{273.15 + t} \times \frac{P_a + P_m}{101.325} + 22.41(a + b)$$

b) Case of obtaining by wet gas volume

- 1) When a wet gas metre is used

$$V_{SW} = V \times \frac{273.15}{273.15 + t} \times \frac{P_a + P_m - P_v}{101.325} + 22.41(a + b + c)$$

- 2) When a dry gas metre is used

$$V_{SW} = V \times \frac{273.15}{273.15 + t} \times \frac{P_a + P_m}{101.325} + 22.41(a + b + c)$$

where, V_{SD} : dry gas volume (L)

V_{SW} : wet gas volume (L)

V : gas volume measured by gas metre (L)
[$V_2 - V_1$ in the operation of 5.1.4 c) to d)]

t : temperature at gas metre (°C)

P_a : atmospheric pressure (kPa)

P_m : gauge pressure at gas metre (kPa)⁽¹²⁾

P_v : saturation steam pressure at t °C (kPa) (see attached table 2)

$a^{(12)}$: target gas for analysis collected by absorption solution or collecting cartridge (mol)

$b^{(12)}$: other gas than target gas for analysis collected by absorption solution or collecting cartridge (mol)

$c^{(12)}$: volume of moisture obtained by clause 6 of JIS Z 8808 (mol)

273.15: absolute temperature corresponding to 0 °C (K)

101.32: pressure corresponding to 1 atmospheric pressure (kPa)