

#1

## **Ordinance of Offensive Odor Control Law (abstract)**

**Cabinet order No.207 of 1972**

**Note: amended by Cabinet Order 322 of 1995**

**and Cabinet Order 406 of 1998**

**(Specified offensive odor substances)**

### **Article 1**

Substances as described in the ordinance of the Cabinet Order in Paragraph 1, Article 2 of the Offensive Odor Control Law (hereinafter referred to as simply the "Law") shall be the substances listed below.

- 1 Ammonia
- 2 Methyl mercaptan
- 3 Hydrogen sulfide
- 4 Methyl sulfide
- 5 Methyl di-sulfide
- 6 Tri-methyl amine
- 7 Acetaldehyde
- 8 Propionaldehyde
- 9 n-Buthylaldehyde
- 10 iso-Buthylaldehyde
- 11 n-Valericaldehyde
- 12 iso-Valericaldehyde
- 13 iso-Buthylalcohol
- 14 Ethylacetate
- 15 Methyl-iso-buthylketone
- 16 Toluene
- 17 Stylene
- 18 Xylene
- 19 Propionic acid
- 20 n-Butyric acid
- 21 n-Valeric acid
- 22 iso-Valeric acid

## **(Delegation of Administration)**

### **Article 2**

The administration of the recommendation that is stipulated in Paragraph 1, Article 8 of the Law, the administration of the order that is stipulated in Paragraph 2, Article 8 of the Law, the administration of the measurement that is stipulated in Paragraph 1, Article 11 of the Law and the administration of the report acceptance and the inspection that is stipulated in Paragraph 1, Article 18 of the Law that are included in the administration within the authority of the prefectural governors authorized under the Law shall be delegated to the mayors of municipalities (except mayors of municipalities that are stipulated in the following paragraph).

2□ The administration that is stipulated in the previous paragraph and the administration to specify the regulation area that is included in the administration within the authority of prefectural governors authorized under the Law, the administration to establish the regulation standards, the administration to hear opinions that is stipulated in Paragraph 2, Article 5, the administration relating to public announcements that is stipulated in Article 6 in the Law and the administration for cooperation that is stipulated in Paragraph 1, Article 19 shall be delegated to the mayors of municipalities that are stipulated in Law of Local self-government (No.67 of 1947) and to the mayors of kernel municipalities that are stipulated in the Law.

#2

## **Regulation of the Ordinance of Offensive Odor Control Law**

**Ordinance of the Prime Minister's Office No.39 of 1972**

**Amended by the ordinance of the Prime Minister's Office No.49 of 1976,**

**the ordinance of the Prime Minister's Office No.50 of 1989,**

**the ordinance of the Prime Minister's Office No.34 of 1993,**

**the ordinance of the Prime Minister's Office No.23 of 1994,**

**the ordinance of the Prime Minister's Office No.42 of 1995**

**the ordinance of the Prime Minister's Office No.62 of 1997.**

**and the ordinance of the Prime Minister's Office No.10 of 1999**

### **Chapter 1 Regulations**

#### **(Calculation of odor index)**

##### **Article 1**

The odor index for gases as stipulated in Paragraph 2, Article 2 of the Offensive Odor Control Law (hereinafter referred to as the "Law") shall be calculated according to the methods devised in the ordinance of the Chief Secretary of the Ministry of Environment, as a multiple of the dilution (hereinafter referred to "odor concentration") in cases where the gas has been diluted until an offensive odor is no longer detectable to the human sense of smell and by multiplying ten to the logarithm of odor concentration.

\*"The Chief Secretary of the Ministry of Environment" = Recommendation No.63 of 1995  
(Calculation method for odor index)

#### **(Range of regulation standard for concentration of the specified odor substances at the boundary of the site)**

##### **Article 2**

The range in the stipulation of the ordinance of the Prime Minister's Office in Subparagraph 1, Paragraph 1, Article 4 of the Law shall be listed in the right column of Attached Table No.1 according to the type of the specified odor substances stipulated by the ordinance of paragraph 1, Article 2 of the Law (hereinafter referred as "the specified odor substances").

#### **(Definition of regulation standard for the flow rate or concentration of the specified odor substances at the point of emission from facilities)**

##### **Article 3**

The methods in the stipulation of the ordinance of the Prime Minister's Office in Subparagraph 2, Paragraph 1, Article 4 of the Law shall be the methods that calculate each flow rate per specified odor substance (except Methyl mercaptan, Methyl sulfide, Methyl di-sulfide, Acetaldehyde, Styrene, Propionic acid, n-Butyric acid, n-Valeric acid and iso-Valeric acid).

where  $q$ ,  $He$  and  $Cm$  are as follows;

$$q = 0.108 \times He^2 \cdot Cm$$

$q$  : flow rate (unit : cubic meter per hour converted into condition of zero degree Celsius and 1 atm.)

$He$  : height of emission point corrected using method stipulated in following paragraph (unit : meter)

$Cm$  : value that is specified as regulation standard of Subparagraph 1, Paragraph 1, Article 4 of the Law (unit : parts per million)

This formula shall not be applied in cases where the height of the emission point is less than 5 meters.

2□ The height of the emission point shall be corrected using the following equations;

$$He = Ho + 0.65(Hm + Ht)$$

$$Hm = \frac{0.795\sqrt{Q \cdot V}}{1 + \frac{2.58}{V}}$$

$$Ht = 2.01 \times 10^{-3} \cdot Q \cdot (T - 288) \cdot \left( 2.30 \log J + \frac{1}{J} - 1 \right)$$

$$J = \frac{1}{\sqrt{Q \cdot V}} \left( 1460 - 296 \times \frac{V}{T - 288} \right) + 1$$

where  $He$ ,  $Ho$ ,  $Q$ ,  $V$  and  $T$  are as follows;

$He$  : corrected height of the emission point (unit : meter)

$Ho$  : height of the emission point (unit : meter)

$Q$  : flow rate of the emission gas at 15 Celsius (unit : cubic meter per second)

$V$  : velocity of the emission gas (unit : meter per second)

$T$  : temperature of the emission gas (unit : absolute temperature)

**(Definition of regulation standard for the concentration of the specified odor substances in the water)**

#### **Article 4**

The methods in the stipulation of the ordinance of the Prime Minister's Office in Subparagraph 3, Paragraph 1, Article 4 of the Law shall be the methods that calculate each concentration in the water per specified odor substance (except Ammonia, Tri-methyl amine, Acetaldehyde, Propionaldehyde, n-Buthylaldehyde, iso-Buthylaldehyde, n-Valericaldehyde, iso-Valericaldehyde, iso-Buthylalcohol, Ethylacetate, Methyl-iso-buthylketone, Toluene, Styrene, Xylene, Propionic acid, n-Butyric acid, n-Valeric acid and iso-Valeric acid).

$$C_{Lm} = k \times C_m$$

where CLm, k and Cm are as follows;

CLm : concentration in the water (unit : milligrams per liter)

K : value listed in the fourth column of the attached table 2, per effluent pursuant from the place of the business to the outside of the site listed in the third column of the said attached table, for type of the offensive odor substances in the second column of the said attached table (unit : milligrams per liter)

Cm : value that is specified as regulation standard of Subparagraph 1, Paragraph 1, Article 4 of the Law (unit : parts per million)

#### **(Measurement method for the specified odor substances)**

#### **Article 5**

The specified odor substances shall be measured using the method as defined by the Chief Secretary of Ministry of Environment, in cases of applying regulation standard in Paragraph 1, Abstract 4 of Law.

\* "Definition" of the Chief Secretary = the Recommendation No.9 of 1972

#### **(Range of regulation standard for the odor index at the boundary of the site)**

#### **Article 6**

The range in the stipulation of the ordinance of the Prime Minister's Office in Subparagraph 1, Paragraph 2, Article 4 of the Law shall be valued from ten to twenty for odor index of the air.

#### **Article 6-2**

The method used in the stipulation of the ordinance of the Prime Minister's Office in Subparagraph 2, Paragraph 2, Article 4 of the Law shall be the method that is defined in the following subparagraphs for the height of the emission point of the said paragraph. In cases of defining the regulation standard in Subparagraph 2, Paragraph 2 of the article for odor index of

emission gas, the value shall be equal to or less than the value of the regulation standard in Subparagraph 1, Paragraph 2 of the article

1 □ Facilities where practical height of the emission point exceeds 15 meters

The method to calculate the value of the odor intensity (the value that is calculated by the method specified by the Chief Secretary of Ministry of Environment based on the odor index and flow rate) with equation defined by i).

i) The value of the odor intensity shall be calculated using the following equation;

$$q_i = \frac{60 \times 10^4}{F_{\max}}$$
$$A = \frac{L}{10} - 0.2255$$

where  $CI_t$  and  $E_{\max}$  are as follows;

$CI_t$  : Odor intensity of the emission gas (unit : cubic meter converted to condition of 0 degree Celsius and 1 atm.)

$E_{\max}$  : Maximum of  $F(x)$  (the odor concentration on ground surface at wind downstream distance  $x$  (unit : meter) from emission point) that is calculated by the equation of the attached table 3. In cases where the value that is calculated as maximum value of  $F(x)$  exceeds the value that is one divided by flow rate of gas (unit : cubic meter converted to condition of 0 degree Celsius and 1 atm.), the value shall be one divided by flow rate of gas.

$L$  : The value that is stipulated as the regulation standard in Subparagraph 1, Paragraph 2, Article 4 of the Law.

ii) The value of  $E_{\max}$  shall be calculated in the conditions for the following cases;

(1) In cases where the initial height of the emission point, which is calculated by the method in the following paragraph, equals or exceeds 2.5 times the height of the largest surrounding building (The highest building located in the site of the place of business (structure as stipulated in Paragraph 1, Article 2 of Building Standard Law (Law 201 of 1950) and creation that is stipulated in Paragraph 3, Article 138 of the Ordinance of Building Standard Law (Cabinet Order 338 of 1950)), a part and whole of the building is included in the area within a distance of ten times the height of said building. Hereinafter referred as the same.) (hereinafter referred to "the height of the largest surrounding building"), the maximum in the section where the distance toward downstream of the wind exceeds shortest distance from the emission point to the boundary of the site.

(2) In cases where the initial height of the emission point that is calculated by the method in the following paragraph is less than 2.5 times of the height of the largest surrounding building, the maximum in the section where the distance x toward downstream of the wind equals to or exceeds R specified in the following provisory clause. The value R shall be the lesser value of the shortest distance from the emission point to the boundary of the site or the shortest distance from the largest surrounding building to the boundary of the site that is calculated by method specified by the Chief Secretary of Ministry of Environment.

2□ Facilities where practical height of the emission point is lower than 15 meters

The method used to calculate the odor index of the gas is the following equation;

$$I = 10 \times \log C$$

$$C = K \times H_b^2 \times 10^B$$

$$B = \frac{L}{10}$$

where I, K, H<sub>b</sub> and L are as follows;

I : the odor index of the gas

K : the value listed in the right column for the diameter of the emission outlet listed in the left column in the following table. In cases of non-circular emission outlet, the diameter of the emission outlet is calculated as the diameter from the sectional area of the outlet.

The diameter of the outlet less than 0.6 meters	0.69
The diameter of the outlet equals or exceeds 0.6 meter but less than 0.9 meters	0.20
The diameter of the outlet equals or exceeds 0.9 meters	0.10

H<sub>b</sub> : the height of the largest surrounding building (unit : meter). In cases where the calculated value is less than 10, or equals or exceeds 10 and exceeds height of 1.5 times of practical height (unit : meter) of the emission outlet, the height calculated by the equation listed in the third column for the value listed in the first column and the practical height of the emission outlet.

less than 10	equal to or greater than 6.7 meters	10 meters
	less than 6.7 meters	1.5 times of practical height of emission outlet
equal to or greater than 10 and equal to or greater than 1.5 times of		1.5 times of practical height of emission outlet

practical height (unit : meter) of emission outlet		
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L : the value of regulation standard in stipulation of the Subparagraph 1, Paragraph 2, Article 4 of the Law

2□ The initial height of the emission point shall be calculated by the following equation. In cases where the calculated value exceeds the practical height of the emission point, the initial emission height shall be the practical height of the emission point (unit : meter).

where  $H_i$ ,  $H_o$ ,  $V$  and  $D$  are as follows;

$$H_i = H_o + 2(V - 1.5)D$$

$H_i$  : the initial height of emission point (unit : meter)

$H_o$  : the practical height of emission point (unit : meter)

$V$  : the velocity of emission gas (unit : meter per second)

$D$  : the diameter of emission outlet (unit : meter). In cases of non-circular emission outlet, diameter of the emission outlet is calculated as the diameter from the sectional area of the outlet.

**(Announcement)**

**Article 7**

Announcements, as stipulated in of the Article 6 of the Law, shall be made through the public announcement by the prefecture or the city that is stipulated in Paragraph 2, Article 2 of the Ordinance of Offensive Odor Control Law (Cabinet order No.207 of 1972).

**(Identification of inspection)**

**Article 8**

The format of the identification in the Paragraph 2, Article 18 of the Law shall be the Format No.1.

**Chapter 2**

**Delegation of Measurement**

**(Persons who can appropriately undertake measurement)**

**Article 9**

A person as stipulated in the Ordinance of the Prime Minister's Office shall be stipulated in the paragraphs below for the cases listed.

1□ Delegation of measurement of the concentration of the specified odor substances



A person that is registered to carry out measurements of air (including gas emitted to the air) or the concentration of the substances by prefecture as stipulated in the Measurement Law (Law No.51 of 1992) and country or prefecture in the stipulation of the provisory clause of the article.

2□ Delegation of measurement of the odor index and odor intensity (hereinafter referred to "odor index and so on")

Country or local public organizations and odor judges (A person who has received license of the odor judge in the Paragraph 1, Article 12 for business of measurement of odor index and so on. Hereinafter referred to in the same manner.) and legal persons whose employee in charge of measurement of odor index and so on is the odor judge.

### **(Process of Delegation)**

#### **Article 10**

The Delegation of the measurement of odor index and so on shall be conducted by preparing a contract, including the following items. However, in cases of delegation to the country or local public organization, it shall not be applied.

1□ The delegator can ask for report presentation from the trustee if required and the trustee must reply.

2□ The delegator can cancel the contract in cases where the trustee is not eligible as a person stipulated in paragraph 2 of the previous article or is found to be illegally involved in delegated measurement.

### **Chapter 3**

#### **Odor judge**

##### **Clause 1**

##### **Responsibilities**

##### **Article 11**

The odor judge shall carry out strictly the measurement of odor index and shall not act illegally.

##### **Clause 2**

##### **License of Odor judge**

### **(License of Odor judge)**

#### **Article 12**

The license of odor judge (hereinafter referred to "license") shall be issued to the person who has passed the odor judge examination of the Article 18 and smell inspection of the Article 21 by the Chief Secretary of the Ministry of Environment.

2□ The license is effective for 5 years.

3□ The Chief Secretary of the Ministry of Environment shall not issue the license to the person who falls under one of following paragraphs.

□1□ a person whose license has been canceled and one year has not passed since the day of the cancellation.

□2□ a person who was made to pay a penalty and two years has not passed since the day of termination of the execution or expiration of the effect.

### **(Application of the license)**

#### **Article 13**

A person to whom a license is given in accordance with the stipulation of Paragraph 1 of the previous article is to submit the following materials together with the application form in No.2 to the Chief Secretary of the Ministry of Environment.

□1□ a copy or abstract of his/her census register

□2□ a copy of certificate of the odor judge examination in Article 18

□3□ a copy of certificate of the smell inspection in Article 21

### **(License renewal)**

#### **Article 14**

A person who requires renewal of the effective term of their license (hereinafter referred to as "License renewal") shall receive the smell inspection of the Article 21 and submit the application of the form given in No.3 and a copy of the certificate of the smell inspection to the Chief Secretary of the Ministry of Environment within 6 months before the date of expiration. However, in cases where inspection and submission have not been completed within the date of the expiration due to unavoidable situations such as disaster and illness, the license shall be renewed by submitting material stating the situation and the application and the copy of certificate within one month from the date of termination of the situation.

### **(Reissue of the License)**

#### **Article 15**

The licensee can apply for reissue of the license to the Chief Secretary of the Ministry of

Environment in case of breakage, contamination or loss of license.

2□ The application of the previous paragraph shall be conducted by submitting application of form given in No.4.

□□ The applicant shall submit the license in case of breakage or contamination as per Paragraph 1.

□□ In case of discovery of the original license after reissue of license, licensee has to return original license to the Chief Secretary of the Ministry of Environment within 5 days from the date of discovery.

### **(Rewriting of license)**

#### **Article 16**

Licensee can apply for rewriting of the license by submitting the license with a copy or abstract of his/her census register in cases where the contents of the license have changed.

2□ The application shall be conducted with application of form as given in No.5.

### **(Cancellation of issued license)**

#### **Article 17**

The Chief Secretary of the Ministry of Environment shall cancel the issued license in cases where the odor judge is recognized to be illegal in his measurement of odor index and so on, or to commit a claim in stipulation of the Law.

2□ In case of cancellation of the issued license, the odor judge must return the license to the Chief Secretary of the Ministry of Environment within 5 days from the date of cancellation.

3□ In cases of the licensee dying or going missing, the person in charge of the death or missing report in stipulation of Law of Census (Law No.224 of 1947) has to return the license to the Chief Secretary of the Ministry of Environment within one month.

### **Clause 3**

#### **Odor judge examination**

### **(Odor judge examination)**

#### **Article 18**

Odor judge examination (hereinafter referred to as "examination") shall test the knowledge required to measure the odor index and so on.

2□ The examination is held by the Chief Secretary of the Ministry of Environment.

3□ The Chief Secretary of the Ministry of Environment shall announce the date and place of the examination and the terms, and the address to which to submit the application in a government

report in advance

- 4  The subjects of the examination are as follows:
- 1  General smell function
  - 2  Offensive odor administration
  - 3  General measurement of offensive odor
  - 4  General analysis and statistics
  - 5  Practical measurement of odor index and so on
- 5  The applicant shall be aged over 18 years old.

**(Application)**

**Article 19**

Applicant shall submit application as given in format No.6, proof of age and photo (taken 6 months before application, front view shot of the face without hat, size 6 cm x 4 cm, with the date when the photo was taken and name written on the back surface of the photo) to the Chief Secretary of the Ministry of Environment.

**(Certificate)**

**Article 20**

The Chief Secretary of the Ministry of Environment shall issue certificates to the persons who pass the examination.

**Clause 4**

**Smell inspection**

**Article 21**

The smell inspection (hereinafter referred to "inspection") shall be a test of eligibility of the smell for odor index measurement.

- 2  The stipulations in Paragraph 2, 3 and 5 of Article 18, Article 19 and previous article shall be applied to the inspection. In this case, "format No.6" in Article 19 shall be read as "format No.7".

**Clause 5**

**Designated organizations**

**(Designated organization)**

**Article 22**

The Chief Secretary of the Ministry of Environment can delegate designated

administrations (Administrations of the license (except administrations of cancellation of issued license in stipulation of the Paragraph 1, Article 17) and examination and inspection. Hereinafter referred to in the same manner.) to the designated organization (hereinafter referred to "designated organization"). However, in cases of delegation of the designated administration to the designated organization, no designated administration is conducted by the Chief Secretary of the Ministry of Environment.

2□ The Chief Secretary of the Ministry of Environment shall specify the execution manner of the designated administration for the designated organization.

3□ The designated organization can delegate a part of the administration of the inspection in the stipulations of Paragraph 1 according to the standard that is specified at the permission of the Chief Secretary of the Ministry of Environment.

4□ Description of "the Chief Secretary of the Ministry of Environment" shall be read as "the designated organization in stipulation of Paragraph 1, Article 22" for application of stipulation of Article 12 through 16, Paragraph3 Article 17, Article 19 (including application in Paragraph 2 of the previous article) and Article 20 (including application in Paragraph 2 of the previous article), in cases where the designated organization conducts the designated administration.

### **(Applying designation)**

#### **Article 23**

Designation of designated organization shall be conducted on application by applicant who conducts the designated administration.

2□ The applicant in the previous paragraph shall submit application of format No.8 with the following materials:

- i) the article of association, contribution and a transcript of register
- ii) the list of directors and their curriculum vitae
- iii) the inventory of property and balance sheet at the end of fiscal year just before the fiscal year that the date of application is included.
- iv) the business plan and balance sheet of the budget of the fiscal year that the date of application is included and materials that describe the business and financial plan from the next fiscal year of the year that the date of application is included to the fiscal year that the date after 5 years from the date of application is included.
- v) the material that describes the organization of the administration for designated administration
- vi) the material that is a proof of achievement of designation standard in the stipulation of next article.

3□ The materials that are listed in Subparagraph 4 of the previous paragraph shall describe the business related to designated administration separate from items related to other business.

**(Standard of designation)**

**Article 24**

The Chief Secretary of the Ministry of Environment can only designate a designated organization in cases where no organization is designated and application of Paragraph 1 of the previous article is recognized to satisfy the following requirements.

- i) Plans for officer, facility, process of designated administration and other items shall be reasonable for proper management of the designated administration.
- ii) Financial and technical basis and administrative ability shall be established to realize the plan properly for designated administration.

2□ The Chief Secretary of the Ministry of Environment must not designate a designated organization in cases where the application in Paragraph 1 of the previous article falls under one of the following:

- i) The applicant is not a legal person as established in stipulation of Article 34 of the Civil Law (Law No.89 of 1896).
- ii) The applicant is not likely to conduct the designated administration fairly, due to business that is not related to the designated administration.
- iii) The applicant is a person who was condemned to a penalty and two years have not passed since the day of termination of the execution or expiration of the effect.
- iv) The applicant is a person whose designation was cancelled and two years have not passed since the day of cancellation.
- v) Director who falls under the Subparagraph 3 is included in the organization of the applicant.

**(Attached article of designation)**

**Article 25**

Designation of Paragraph 1, Article 22 shall be applied to the expiration date or to the required conditions for items listed below:

- i) Selection or dismissal of director of the designated organization
- ii) Selection or dismissal of test committee (person who conducts the judgement on knowledge of

licensee among the administrations of examination by the designated organization) and inspection committee (persons who conduct the judgement of knowledge of licensee among the administrations of examination by the designated organization).

- iii) Preparation or renewal of regulations for designated administration.
- iv) Report to the Chief Secretary of the Ministry of Environment on results of examination and inspection.
- v) Cancel of designation.
- vi) Items required for designated administration, which are not listed in previous subparagraphs.

**(Announcement of designation)**

**Article 26**

The Chief Secretary of the Ministry of Environment shall announce the following items on the public announcement in case of designation in Paragraph 1, Article 22.

- i) Name of the designated organization, address and name of representatives
- ii) Term for designated administration by designated organization
- iii) The date of designation

**Clause 6 Handling fee**

**Article 27**

The persons listed in the following subparagraphs shall pay the said amount of handling fee, stipulated in the following subparagraph, to the country (the designated organization in cases where the designated administration is conducted by the designated organization in stipulation of Paragraph 1, Article 22)

- i) Issue of license, renewal of license, re-issue of license or rewrite of license 4,000 yen
- ii) Application of examination 18,000 yen
- iii) Application of inspection 8,000 yen

2□ Handling fee that is paid to the designated organization shall be the income of the designated organization.

**Supplemental provision**

**The ordinance is effective from the date of enforcement (1972 May 31).**

**Supplemental provision (the Ordinance of Prime Minister's Office No.23 of 1994)**

- i) The ordinance is effective from the date 1995 April 1.
- ii) For methyl mercaptane, the permitted limit of the concentration in the water of less than 0.002 mg per liter that is calculated by the method in stipulation of Article 3 of the modified Ordinance of Offensive Odor Control Law is maintained at 0.002 mg per liter for while.

**Supplemental provision (the Ordinance of Prime Minister's Office No.42 of 1995)**

i) The ordinance is effective from the date of enforcement of the law for modification of the Offensive Odor Control Law. However, the stipulation of Article 23 of the modified ordinance of Offensive Odor Control Law (hereinafter referred to "Partly modified Ordinance of Offensive Odor Control Law") is effective from the date of the official announcement.

ii) In the period when the ordinance of the Prime Minister's Office, as stipulated in Subparagraph 3, Paragraph 2, Article 4 of the Law, is enforced, for definition of regulation standard in stipulation of Paragraph 2, Article 4 of the Law that is read in stipulation of Article 3 of supplemental provision of the Law for partly modified Offensive Odor Control Law, the regulation standard of Subparagraph 1, Paragraph 2, Article 4 instead of the regulation standard of Subparagraph 1, Paragraph 1 of the article, and the regulation standard of Subparagraph 2, Paragraph 2 of the article instead of Subparagraph 2, Paragraph 2 of the article instead of the regulation standard of Subparagraph 1, Paragraph 1 of the article shall be defined.

**Attached Table 1 (related to Article 1)**

1	Ammonia	Concentration in the air equals or is greater than one 1 part per million and equals or is less than 5 parts per million
2	Methyl mercaptan	Concentration in the air equals or is greater than one 0.002 part per million and equals or is less than 0.01 part per million
3	Hydrogen sulfide	Concentration in the air equals or is greater than one 0.02 part per million and equals or is less than 0.2 part per million
4	Methyl sulfide	Concentration in the air equals or is greater than one 0.01 part per million and equals or is less than 0.2 part per million
5	Methyl di-sulfide	Concentration in the air equals or is greater than one 0.009 part per million and equals or is less than 0.1 part per million
6	Tri-methyl amine	Concentration in the air equals or is greater than one 0.005 part per million and equals or is less than 0.07 part per million
7	Acetaldehyde	Concentration in the air equals or is greater than one 0.05 part per million and equals or is less than 0.5 part per million
8	Propionaldehyde	Concentration in the air equals or is greater than one 0.05 part per million and equals or is less than 0.5 part per million
9	n-Buthylaldehyde	Concentration in the air equals or is greater than one 0.009 part per million and equals or is less than 0.08 part per million
10	Iso-Buthylaldehyde	Concentration in the air equals or is greater than one 0.02 part per million and equals or is less than 0.2 part per million
11	n-Valericaldehyde	Concentration in the air equals or is greater than one 0.009 part per million and equals or is less than 0.05 part per million



12	Iso-Valeraldehyde	Concentration in the air equals or is greater than one 0.003 part per million and equals or is less than 0.01 part per million
13	iso-Buthylalcohol	Concentration in the air equals or is greater than one 0.9 part per million and equals or is less than 20 part per million
14	Ethylacetate	Concentration in the air equals or is greater than one 3 part per million and equals or is less than 20 part per million
15	Methyl-iso-buthylketone	Concentration in the air equals or is greater than one 1 part per million and equals or is less than 6 part per million
16	Toluene	Concentration in the air equals or is greater than one 10 part per million and equals or is less than 60 part per million
17	Stylene	Concentration in the air equals or is greater than one 0.4 part per million and equals or is less than 2 part per million
18	Xylene	Concentration in the air equals or is greater than one 1 part per million and equals or is less than 5 part per million
19	Propionic acid	Concentration in the air equals or is greater than one 0.03 part per million and equals or is less than 0.2 part per million
20	n-Butyric acid	Concentration in the air equals or is greater than one 0.001 part per million and equals or is less than 0.006 part per million
21	n-Valeric acid	Concentration in the air equals or is greater than one 0.0009 part per million and equals or is less than 0.004 part per million
22	iso-Valeric acid	Concentration in the air equals or is greater than one 0.001 part per million and equals or is less than 0.01 part per million

**Attached table 2 (related to Article 3)**

1	Methyl mercaptan	Equals or is less than one 0.001 cubic meter second	16
		Greater than one 0.001 cubic meter second equals or is less than one 0.001 cubic meter second	3.4
		Greater than one 0.1 cubic meter second	0.71
2	Hydrogen sulfide	Equals or is less than one 0.001 cubic meter second	5.6
		Greater than one 0.001 cubic meter second equals or is less than one 0.001 cubic meter second	1.2
		Greater than one 0.1 cubic meter second	0.26
3	Methyl sulfide	Equals or is less than one 0.001 cubic meter second	32
		Greater than one 0.001 cubic meter second equals or is less than one 0.001 cubic meter second	6.9
		Greater than one 0.1 cubic meter second	1.4
4	Methyl di-sulfide	Equals or is less than one 0.001 cubic meter second	63
		Greater than one 0.001 cubic meter second equals or is less than one 0.001 cubic meter second	14

		Greater than one 0.1 cubic meter second	2.9
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**Attached table 3 (related to Article 6-2)**

$$F(X) = \frac{1}{3.14\sigma_y\sigma_z} \exp\left[-He(X)^2 / (2\sigma_z^2)\right]$$

**Note:**

where x,  $\sigma_y$ ,  $\sigma_z$  and He(x) are as follows;

x : distance toward downstream of wind from emission point (unit : meter)

$\sigma_y$  : horizontal diffusion width of emitted gas related to the distance toward downstream of wind from emission point that is calculated by the method defined by the Chief Secretary of the Ministry of Environment with consideration of effect of the largest surrounding building (unit : meter)

$\sigma_z$  : vertical diffusion width of emitted gas related to the distance toward downstream of wind from emission point that is calculated by the method defined by the Chief Secretary of the Ministry of Environment with consideration of effect of the largest surrounding building (unit : meter)

He(x) : height of central axis of gas flow that is calculated by the following equation for the distance toward downstream of wind (unit : meter). However, 0 meter in case where the summation of Hi and  $\Delta Hd$  is lower than 0.5 multiplied height of the largest surrounding building.

where Hi,  $\Delta H$  and  $\Delta Hd$  are as follows;

Hi : initial emission height that is calculated by the method listed in Paragraph 2 (unit: meter)

$\Delta H$  : increased height of center axe of gas flow that is calculated by the method that defined by the Chief Secretary of the Ministry of Environment for the distance toward downstream of wind. (unit : meter)

$\Delta Hd$  : lowered distance of center axe of gas flow by effect of the largest surrounding building that is calculated by the equation listed in the right column for range of initial emission height listed in the left column in the following table (unit : meter)

Hi is less than Hb.	-1.5H <sub>b</sub>
Hi equals to or is greater than Hb and less than 2.5 times of Hb.	Hi-2.5H <sub>b</sub>
Hi equals to or is greater than 2.5 times of Hb.	0

In the table,  $H_i$  shall be the initial emission height that is calculated by method listed in Paragraph 2 (unit : meter) and  $H_b$  shall be height of the largest surrounding building (unit : meter).

#3

## **Measurement method of Specified Offensive Odor Substances**

**Announcement of Ministry of Environment No.9 of 1972**

**Amended by Announcement of Ministry of Environment No.49 of 1976,**

**Announcement of Ministry of Environment No.7 of 1984,**

**Announcement of Ministry of Environment No.47 of 1989, Announcement of Ministry of**

**Environment No.72 of 1993**

**and Announcement of Ministry of Environment No.4 of 1996.**

The measurement method of Specified Offensive Odor Substances stipulated in the Article 5 of the Ordinance of the Offensive Odor Control Law (the ordinance of the Prime Minister's Office No.39 of 1972) is enforced as of May 31, 1972.

The measurement methods of Specified Offensive Odor Substances stipulated in the Article 5 of the Ordinance of the Offensive Odor Control Law are listed in the following subparagraphs;

- i) Ammonia: The method listed in Attached 1
- ii) Methyl mercaptan, Hydrogen sulfide, Methyl sulfide and Methyl di-sulfide: The method listed in Attached 2
- iii) Tri-methyl amine: The method listed in Attached 3
- iv) Acetaldehyde, Propionaldehyde, n-Buthylaldehyde, iso-Buthylaldehyde, n-Valericaldehyde and iso-Valericaldehyde: The method listed in Attached 4
- v) iso-Buthylalcohol: The method listed in Attached 5
- vi) Ethylacetate, Methyl-iso-buthylketone: The method listed in Attached 6
- vii) Toluene, Styrene and Xylene: The method listed in Attached 7
- viii) Propionic acid, n-Butyric acid, n-Valeric acid and iso-Valeric acid: The method listed in Attached 8

### **Attached Table 1**

#### **Measurement method of Ammonia**

##### **1 Reagent**

Reagent shall be prepared in the following manner:

##### **(1) Collecting solution**

Five grams of boric acid is dissolved in water and diluted to 1 liter.

##### **(2) Phenol sodium penta-cyanonitrosyl ion (III) acid solution**

5 grams of phenol and 25 mg of sodium penta-syanonitrosyl ion (III) acid with 12 hydrates are dissolved in water and diluted to 500 ml (the solution must be stored in a cold, dark

place. Solution older than 1 month should not be used.).

(3) Sodium hypochloride solution

Sodium hypochloride solution (effective chlorine 3 to 10 %) 60/C ml (where C is the concentration of the effective chlorine in the sodium hypochloride weighed at preparation.), 10 g of sodium hydroxide and 35.8 g of disodium hydrogen phosphate with two hydrates are dissolved in the water and diluted to 1 liter (this solution shall be prepared on usage).

(4) Standard ammonia solution

Sodium sulfate, desiccated at 130 degree Celsius, is dissolved in water and diluted to 1 liter and then diluted 50 times by the collection solution (1 ml of this solution contains ammonium ion corresponding to 2 micro liter of ammonia (0 degree Celsius and 1 atm.)).

## 2 Equipment

The equipment used is listed as follows:

(1) Sampling equipment

It is configured as shown in attached drawing and the following conditions shall be satisfied:

- i) Absorption bottle, volume 200 ml, equipped with half-melted glass filtration spare (note 1), and containing 20 ml of collection solution. Two bottles can be connected in a series.
- ii) Suction pump able to draw air at 10 liters per minute with absorption bottle connected.
- iii) Gas meter able to measure a flow rate of 5 to 15 liters per minute.

(2) Optical intensity meter

Spectral meter or opto-electric meter

(note 1) fine filter shall be used to avoid bottle receiving negative pressure.

## 3. Measurement process

Concentration measurement is performed according to the following process:

(1) Sample collection

Sample is collected in the collecting solution by air suction for 5 minutes at flow rate of 10 liters per minute.

(2) Preparation of sample solution for analysis

After collection is completed in the two suction bottles, the collecting solution is poured into a 50 ml scaled flask, then the bottles are washed with the collected solution and then cleansing fluid is added to the collecting solution. 10 ml of this solution is then placed in a capped tube for analysis of the sample solution.

(3) Measurement of optical absorption

Five milliliters of phenol and sodium penta-cyano nitrosyl ion (III) acid is added to the analyzing sample solution, and after mixing, 5 ml of sodium hypochlorite solution is added. After one hour of keeping the liquid temperature at 25 to 30 degrees Celsius, optical absorption is measured at the wavelength of 640 nm. Reference solution is the collecting solution processed in the same manner as the analyzing sample.

(4) Calibration curve

Zero to 40 ml of standard ammonia solutions are sampled sequentially, and are diluted to 50 ml with collecting solution, then 10 ml of the solution is placed in the capped tube. The solution is processed in the same manner as the optical absorption for analyzing solution and a calibration curve is drawn.

(5) Calculating concentration

Through the calibration curve in (4), the amount of ammonia in the analyzed sample solution is sought (0 degree Celsius and 1 atm.) and, using the following equation, the density of its air is calculated.

$$C = \frac{5A}{V \times \frac{273}{273+t} \times \frac{P}{101.3}}$$

Where C is the concentration of ammonia in the air (unit : ppm), A is quantity of the ammonia in the analyzing sample solution (unit : micro liter), V is the gas volume measured by the gas meter (unit : liter), t is temperature at gas meter (unit : degree Celsius) and P is the atmospheric pressure at the sampling (unit : kPa).

**Remarks**

1. In the operation of 3-(1), a lower flow rate is permitted in cases where a constant flow rate of 10 liter per minute is not achievable owing to a clogged filtration sphere or to unavoidable reasons, but the sensitivity is still high enough to conduct proper analysis.

2. In cases of low water content in the sample and no sorption effect, sample gas may be collected through operation of 1-3-(2)-i) of the attached table 2 by using the equipment shown in 1-2-(1)-i) and (2) (note 2) of the attached table 2. The sample gas collected in the sampling bag shall be collected as soon as possible through operation of 1-3-(1) (note 3) by using the sampling equipment shown in 1-3-(1) (note 3).

(note 2) The inner volume of the sampling bag shall be approximately 50 liter.

(note 3) Lower flow rate is permitted in case where the constant flow rate of 10 liter per minute is not easily achieved.

3. Terminology and other items in this measurement method that are not defined, shall follow the definition of Japan Industrial Standard (JIS).

#### **Second) Flow rate measurement at the gas emission point**

The flow rate at the gas emission point is calculated by multiplying gas quantity measured by method of JIS Z8808 to the ammonia concentration in the exhaust gas measured by method of JIS K0099.

#### **Remark**

Terminology and other items in this measurement method that are not defined, shall follow the definition of Japan Industrial Standard.

#### **Attached drawing**

- A Suction bottle
- B Suction pump
- C Gas meter

#### **Attached Table 2**

#### **Measurement method of Methyl mercaptan, Hydrogen sulfide, Methyl sulfide and Methyl di-sulfide**

#### **First) Concentration measurement at the border of the site**

##### **1 Reagent**

The calibration gas for measurement of Methyl mercaptan, Hydrogen sulfide, Methyl sulfide and Methyl di-sulfide is prepared before use by permeation tube method or equivalent method, or method listed below. Calibration gas bottle for preparation is shown in the figure 1, is

made of borosilicate glass, contains a piece of fluoride resin, and the volume is known. Before use, bottle shall be washed with 10N-phosphoric acid and water, and be desiccated and substituted air by nitrogen.

(1) Calibration gas of Methyl mercaptan

One milliliter of gaseous Methyl mercaptan is collected with a gas syringe, and is injected through silicon rubber cap of calibration gas bottle. Leave longer than 10 minutes after mixing.

(2) Calibration gas of Hydrogen sulfide

One milliliter of gaseous Hydrogen sulfide is collected with a gas syringe, and is injected through silicon rubber cap of calibration gas bottle. Leave longer than 10 minutes after mixing.

(3) Methyl sulfide

Three micro liters of Methyl sulfide is collected with a micro-syringe, and is injected through silicon rubber cap of calibration gas bottle. To be vaporized and leave longer than 10 minutes after mixing.

(4) Methyl di-sulfide

Three micro liters of Methyl di-sulfide is collected with a micro-syringe, and is injected through silicon rubber cap of calibration gas bottle. To be vaporized and leave longer than 10 minutes after mixing.

## 2 Equipment and apparatus

Equipment and apparatus are listed as follows;

(1) Gas sampler

One of the equipment shown below

- i) Sampler pump with air suction power of over 10 liter per minute and the gas through portion is changeable.
- ii) Sampler with configuration shown in fig.2 (note 1)(note 2)
- iii) Air tight gas sampling suction bottle of volume larger than 5 liter that is shown in fig. 3 and the sampling bag is connected inside the bottle.

(2) Sampling bag

Made of poly-vinyl fluoride film, polyester (compound name : poly-ethylene telephthalate) film or equivalent on the storage performance, and the volume is larger than 5 liter. (note 3)



### (3) Condenser tube

The configuration shown in fig. 4 and the following condition is satisfied.

- i) The tube is made of borosilicate glass or fluoride resin and the inner diameter of 4 mm.
- ii) The tube is washed with phosphoric acid (1+4) and water, and is desiccated, then the same type of gas chromatograph filler as used for the analysis or equivalent is filled in the tube.
- iii) Aluminum foil is placed on the outside of the tube. It is isolated with glass fiber tape. Thermocouple is attached to measure the temperature. Nickel-chrome wire with glass fiber tube is turned on the same spacing, and fixed with glass fiber tape.

### (4) Gas chromatograph analysis equipment

The configuration shown in fig. 5 and the following condition is satisfied.

- i) The gas chromatograph includes flame optical detector.
- ii) Carrier gas path is changed at the sample inlet and is connected to contamination trap and condenser tube.
- iii) The molecular sieve 5A or the equivalent is filled in contamination trap and is cooled by coolant of liquid oxygen or equivalent.
- iv) The column is made of glass or fluoride resin and the inner diameter of 3 mm and length of 3 to 5 meters. Inner side is washed with phosphoric acid (1+4) and water, and desiccated.
- v) The white diatomaceous earth holder of the filler is washed with acid. The filler is processed by dimethyl-dichloro silane and coated 25% with beta, beta'-oxy-di-propyionitril. Or equivalent filler is used for the purpose.
- vi) Temperature at the sample inlet shall be 130 degrees Celsius.
- vii) Temperature at the column chamber shall be 70 degrees Celsius.
- viii) Nitrogen is employed for carrier gas of flow of 40-50 ml per minute.

(note 1) Suction case shall be made of transparent resin and is air tight structure.

(note 2) Suction pump shall be with air suction power of over 10 liter per minute

(note 3) The thickness more than 35 micro meters shall be used owing to concentration change of the sample in thinner bag.

## **3 Measurement process**

Concentration measurement is performed in following process;

### (1) Blank test

Sample condenser tube is heated for approximately 10 minutes at 70 degrees Celsius with nitrogen flow. An analysis routine is performed on item (4) to verify no peak in the holding time of the subject component.

## (2) Gas sampling

According to the type of gas sampling equipment, one of the following methods is employed for gas collection to the sampling bag.

i) In case of 2-(1)-i), sampling pump and the sampling bag is connected with silicon rubber tube, 5 liter of sample gas is collected in the sampling bag for 6 to 30 seconds. (note 4)

ii) In case of 2-(1)-ii), the sampling bag is installed in the suction case, and is connected to the fluoride resin valve. After verifying the fluoride resin valve and suction valve are opened, the suction pump connected to the suction valve is stated to operate. Approximately 5 liter of sample gas is collected in the sampling bag by depressurizing the suction case. Flow rate is adjusted by suction valve and flow rate adjustment of suction pump. The collection is performed for 6 to 30 seconds at constant flow rate.

iii) In case of 2-(1)-iii), the following process is used. Open two valves of the suction bottle. Evacuate glass container by evacuation pump at the valve that is not connected to the bag (hereinafter referred as "valve A"). The evacuation pump is stopped when the sampling bag in the bottle is filled with air. Then close the valve A and connect evacuation pump to the valve that is connected to the bag (hereinafter referred as "valve B"). The air in the sampling bag is fully evacuated and the valve B is closed. Finally, by opening valve B, sample gas is introduced into the sampling bag in duration longer than 6 seconds.

## (3) Sample condensing

As shown in fig.6, subject component in the sampling bag is collected in the sample condenser tube for constant quantity of sample by connecting sampling bag to sample condenser tube that is cooled with coolant such as liquid oxygen.

## (4) Gas chromatograph analysis

As shown in fig.5, the sample condenser tube with trapped subject component, that is cooled with coolant such as liquid oxygen, is connected to the gas chromatograph analyzer. Then, flow carrier gas through the sample condenser tube, and verify the stability of the flow rate and the detector sensitivity. Raise the temperature of the condenser tube to 70 degrees Celsius in approximately two minutes. Introduce subject component to the gas chromatograph.

## (5) Calibration curve

Perform the same operation as item (4) for samples of calibration gases of methyl mercaptan, hydrogen sulfide, methyl sulfide and methyl di-sulfide, or diluted sample with calibration gas bottle, that are injected to the sample condenser tube that is cooled with coolant

such as liquid oxygen. The calibration curve is plotted according to the peak height of the chromatogram.

(6) Calculating concentration

The concentration in the air is calculated by following equation by using quantity of methyl mercaptan, hydrogen sulfide, methyl sulfide or methyl di-sulfide in the air (0 degree Celsius and 1 atm.) in the condenser tube.

$$C = \frac{A}{V \times \frac{273}{273+t} \times \frac{P}{101.3}}$$

where C is the concentration of the subject component in the air (unit : ppm), A is quantity of the subject component in the condenser tube (unit : micro liter), V is the gas volume collected in the condenser tube (unit : liter), t is temperature at sample condensing (unit : degree Celsius) and P is the atmospheric pressure at the sample condensing (unit : kPa).

(note 4) Sample gas path of the sampling pump and silicon rubber tubes connecting between the sampling pump and the sampling bag shall be replaced after usage.

**Remark**

1 Flow ratio mixing method may be used as equivalent method of permeation method (a method that a teflon tube containing liquid gas is placed in constant temperature chamber, the low concentration gas is continuously produced by diluting liquid gas passed through the tube wall with dilution gas) for calibration gas preparation.

2 Coolant for cooling condenser tube and trap tube equivalent to the liquid oxygen shall be liquid argon or material that is verified to equal to or to be higher performance of capture efficiency for sample condenser tube than liquid oxygen.

3 In case of poor peak separation of gas chromatograph, optimum separation condition may be adopted such as a temperature raising of 4 degrees Celsius per minutes in the temperature range of column from 40 to 70 degrees Celsius.

4 In case where the separate quantitative analysis is enable, capillary column may be used.

5 Terminology and other items in this measurement method that are not defined, shall follow the definition of Japan Industrial Standard.

## **Second) Flow rate measurement at the gas emission point**

The flow rate at the gas emission point is calculated by multiplying gas quantity measured by method of JIS Z8808 to the hydrogen sulfide concentration in the exhaust gas measured by following method.

### **1 Reagent**

The same as shown in the First-1.

### **2 Equipment and apparatus**

Equipment and apparatus are listed as follows;

(1) Gas sampler and sampling bag

The same as shown in the First-2-(1)-i, ii) and (2).

(2) Condenser tube

The same as defined in the First-2-(3).

(3) Gas chromatograph analysis equipment

The same as defined in the First-2-(4).

### **3 Measurement process**

Concentration measurement is performed in following process;

(1) Gas sampling

The same operation as defined in the First-3-(2)-i) and ii).

(2) Gas chromatograph analysis

i) A part of the sample gas collected within 12 hours is taken with the gas syringe and directly injected to the sample inlet of the gas chromatograph analysis equipment.

ii) In case where the result of procedure i) exceeds the upper detecting limit, following procedure is used. An exactly known volume of the sample gas is taken with the gas syringe, and is diluted by method of calibration bottle of the First-1, the gas chromatograph analysis is performed in the manner the same as i).

iii) In case where the result of procedure i) does not reach to the lower detecting limit, perform the same operation as the First-3-(2) and (3).

(3) Calibration curve

Perform the same operation as item (2) for sample of calibration gas of hydrogen sulfide, that is diluted sequentially. The calibration curve is plotted according to the peak height of the chromatogram.

(4) Calculating concentration

i) In case of (2)-i) or ii), the concentration in the air is calculated by the equation of the First-3-(6) by using quantity of hydrogen sulfide in the air (0 degree Celsius and 1 atm.) from the calibration curve of (3). Here, C is the concentration of the hydrogen sulfide in the exhaust gas (unit : ppm), A is quantity of the hydrogen sulfide (unit : micro liter), V is the gas volume collected (unit : liter), t is temperature of exhaust gas (unit : degree Celsius) and P is the pressure of exhaust gas (unit : kPa).

ii) In case of (2)-iii), the same procedure defined in the First-3-(6).

**Remark**

Terminology and other items in this measurement method that are not defined, shall follow the definition of Japan Industrial Standard.

**Fig. 1 Calibration gas bottle**

- A Silicon rubber cap
- B Piece of fluoride resin

**Fig. 2 Gas sampling equipment**

- A Sampling tube
- B Valve made of fluoride resin
- C Sampling bag
- D Suction case
- E Suction valve
- F Suction pump

**Fig. 3 Gas sampling equipment**

- A Valve made of fluoride resin
- B Valve made of fluoride resin
- C Cramp
- D Sampling bag
- E Gas sampling suction bottle

**Fig. 4 Condenser tube**

- A Silicon rubber cap
- B Capillary tube

- C Syringe needle made of stainless steel
- D Quartz glass wool

**Fig. 5 Gas chromatograph analyzer**

- Main body of gas chromatograph
- A Nitrogen bottle
- B Flow meter
- C Flow adjust valve
- D Contamination trap
- E three direction valve
- F Condenser tube
- G Sample inlet
- H Column
- I Detector
- J Bypass

**Fig. 6 Condensing method**

- or
- A Sampling bag
- B Condenser tube
- C Fluoride resin tube
- D Suction pump
- E Gas meter
- F Syringe

**Third) Concentration measurement in the water**

**1 Reagent**

Reagent shall be prepared in the manner listed below.

- (1) Hydrochloric acid (0.1 mol/liter)
- (2) Calibration gas

The same as defined in the First-1.

**2 Equipment and apparatus**

Equipment and apparatus are listed as follows;

- (1) Sampling bottle

Glass bottle with teflon packing cap or capped glass bottle, volume from 500 ml to 1 liter.

(2) Whole pipet

Made of glass and volume of 50 ml.

(3) pH meter

(4) Liquid syringe

Made of resin and with suitable volume (1-5 ml).

(5) Vial

Volume of 100 ml (for injection purpose) and air tight with rubber cap.

(6) Teflon film (Quad-fluoro ethylene resin film)

Quad-fluoro ethylene resin film with thickness of 0.05mm, with the size that prevents the rubber cap to touch to the sample in case of inserting between rubber cap and vial. (note 5)

(7) Aluminum cap

Fixing vial and rubber cap.

(8) Aluminum cap fixing tool

Aluminum cap is deformed to fix the cap to the vial.

(9) Constant temperature water chamber

Maintain water temperature at 30 degrees Celsius plus or minus 0.2 degree.

(10) Micro syringe (for gas use)

With suitable volume from 20 to 1000 micro liter (note 6).

(11) Gas chromatograph analysis equipment

The same as defined in the First-2-(4)

(note 5) Teflon film is not required in case of using vial rubber cap with performance equivalent to using teflon film.

(note 6) Clean with nitrogen and verify no peak appears at position of subject component.

### **3 Measurement process**

Concentration measurement is performed in following process;

(1) Blank test

Pour 50 ml of water into a vial. Perform analysis in the procedure (3). Verify no peak appears in the holding time of the subject component.

(2) Water sampling

Collecting the sample water into the sampling bottle, fill with water avoiding bubble formation and seal with cap (note 7).

(3) Head space test

- i) Taking 50 ml of sample water to glass container (note 8), find the required hydrochloric acid quantity to adjust pH value of 3.0 to 4.0.
- ii) Another 50 ml of sample water is taken to the vial with whole pipet (note 9).
- iii) Inject the hydrochloric acid of the quantity that is found in i) quietly in the vial (note 10).
- iv) Place the teflon film on vial. Seal the vial with rubber cap. Place aluminum cap on the rubber cap, fix the vial and rubber cap with aluminum cap deformed by the aluminum cap fixing tool.
- v) Vibrate the vial up and down by hand for approximately 30 seconds.
- vi) Install the vial in the constant temperature water chamber of 30 degrees Celsius for 30 minutes.
- vii) The constant volume (0.2 to 1 ml) of gas from the vial is taken with micro syringe through vial. Directly inject to gas chromatograph inlet for analysis.
- viii) Measure the pH value of the solution left in the vial by removing rubber cap of the vial. In case of pH value out of the range of 3.0-4.0, the measurement is decided to be ineffective and repeat the operation from i) to vii).

#### (4) Calibration curve

Perform the same operation as item (4) for samples of calibration gases of methyl mercaptan, hydrogen sulfide, methyl sulfide and methyl di-sulfide, or diluted sample with calibration gas bottle, that are diluted sequentially and injected to the inlet of the gas chromatograph inlet. The calibration curve is plotted according to the peak height of the chromatogram.

#### (5) Calculating concentration

The concentration in the water is calculated by following equation by using quantity of methyl mercaptan, hydrogen sulfide, methyl sulfide or methyl di-sulfide in the vapor phase by the calibration curve of (4).

$$C_L = \frac{V_L + b \cdot V_g}{a \cdot V_L} \cdot C_h$$

$$a = \frac{T_R}{T} \cdot K_H$$

$$b = \frac{K_H \cdot P \cdot M_A \cdot 10^{-3}}{R \cdot T}$$

where CL is the concentration of the subject component in the water (unit : mg/liter), Ch is the concentration of the subject component in the vapor phase (unit : ppm), VL is volume of the



liquid (unit : liter),  $V_g$  is volume of the liquid (unit : liter, "full volume"- "liquid volume"),  $T_a$  is the room temperature at the time of sample injected to the vial (unit : K),  $K_H$  is a equivalent value of Henry's constant (unit : liter/kg, shown in the following table),  $M_A$  is molecular weight (unit : g/mol, shown in the following table),  $T$  is the temperature of the chamber (unit : K),  $P$  is the atmospheric pressure (unit : kPa),  $R$  is the gas constant (8.31 kPa liter/mol K).

Material	$\square_{\square}$	$\square_{\square}$
Methyl mercaptan	83.1	48.11
Hydrogen sulfide	322	34.08
Methyl sulfide	38.0	62.14
Methyl di-sulfide	18.4	94.20

(note 7) Store at dark place of temperature of 0 to 5 degrees Celsius. As the subject component is easily vaporized, the analysis shall be performed as soon as possible.

(note 8) The sampling bottle shall be sealed immediately to store back to the dark place of temperature of 0 to 5 degrees Celsius.

(note 9) Whole pipets and vials shall be cooled at temperature of 0 to 5 degrees Celsius.

(note 10) Teflon film and vial rubber cap are placed on the vial, then insert the syringe.

### Remark

Terminology and other items in this measurement method that are not defined, shall follow the definition of Japan Industrial Standard.

### Attached Table 3

#### Measurement method of Tri-methyl amine

#### First) Concentration measurement at the border of the site

##### 1 Reagent

Reagent shall be prepared in the manner listed below.

##### (1) Reagent decomposition

500 grams of potassium hydroxide is dissolved in water and diluted to 1 liter.

##### (2) Standard solution of Tri-methyl amine

Solution that is diluted tri-methyl amine solution (20-40%) by 20 times with water. The concentration of the tri-methyl amine is measured by titration with 0.1N-hydrochloric acid, employing an indication reagent of 0.1% ethyl alcohol solution of bromocresol green and 0.1% ethyl alcohol solution of methylred, with volume ratio of five to one.

##### (3) Ethyl alcohol

No peak shall appear in the holding time of tri-methyl amine, when it is injected in gas chromatograph.

(4) Collecting solution

Sulfuric acid diluted with water by 360 times.

## 2 Equipment and apparatus

Equipment and apparatus are listed as follows;

(1) Sampler and sampling bag

The equipment defined in the First-2-(1) in the attached table 1.

(2) Condenser tube

The configuration shown in fig. 2 and the following condition is satisfied.

- i) The tube is made of borosilicate glass and the inner diameter of 4 mm.
- ii) The tube is washed with potassium hydroxide (100 g/liter) and water, and is desiccated, then the same type of gas chromatograph filler as used for the analysis or equivalent is filled in the tube.

- iii) Aluminum foil is placed on the outside of the tube. It is isolated with glass fiber tape. Thermocouple is attached to measure the temperature. Nickel-chrome wire with glass fiber tube is turned on the same spacing, and fixed with glass fiber tape.

(3) Sample decomposition and condenser equipment

- i) The molecular sieve 5A or the equivalent is filled in contamination trap and is cooled by coolant of liquid oxygen or equivalent.
- ii) Twenty milliliter of Decomposition reagent is poured in the decomposition bottle, and the air is substituted by nitrogen.
- iii) In case where the condenser tube is clogged with water in short time, the desiccated tube filled with potassium hydroxide is connected to the decomposition bottle.

(4) Gas chromatograph analysis equipment

The configuration shown in fig. 5 and the following condition is satisfied.

- i) The gas chromatograph includes hydrogen flame ion detector.
- ii) Carrier gas path is changed at the sample inlet and is connected to contamination trap and condenser tube.
- iii) The molecular sieve 5A or the equivalent is filled in contamination trap and is cooled by coolant of liquid oxygen or equivalent.
- iv) The column is made of glass or fluoride resin and the inner diameter of 3 mm and length of 3 to 5 meters. Inner side is washed with potassium hydroxide and water, and desiccated.
- v) The white diatomaceous earth holder of the filler with particle diameter of 180-250 micrometer is coated with 15% of di-glycerol, 15% of tetra-ethylene pentamine and 2% of potassium

hydroxide. Or equivalent filler is used for the purpose.

- vi) Temperature at the sample inlet shall be 130 degrees Celsius.
- vii) Temperature at the column chamber shall be 70 degrees Celsius.
- viii) Nitrogen is employed for carrier gas of flow of 40-50 ml per minute.

### **3 Measurement process**

Concentration measurement is performed in following process;

#### (1) Blank test

Sample condenser tube is heated for approximately 10 minutes at 70 degrees Celsius with nitrogen flow. An analysis routine is performed on item (4) to verify no peak in the holding time of the subject component.

#### (2) Sampling

The same operation defined in the First-3-(1) of the attached table 1.

#### (3) Sample decomposition and condensing

- i) After collection is finished, collecting solution in two collection bottles and that is washed inside the bottled is pour into 50 ml scaled flask, and then add collection solution to the volume of 50 ml.
- ii) A constant quantity of the sample solution is taken with a syringe. It is injected to the decomposition bottle of the sample decomposition and condensing equipment of 2-(3) through silicon rubber cap. Tri-methyl amine generated by nitrogen flow of 2-3 liter at 0.2-0.3 liter per minute is collected in the sample condenser tube that is cooled with coolant such as liquid oxygen. In the case, blank test is conducted to verify the interfering component by heating sample condenser tube at 70 degrees Celsius with nitrogen flow.

#### (4) Gas chromatograph analysis

As shown in fig.4, the sample condenser tube with trapped subject component that is cooled with coolant such as liquid oxygen, is connected to the gas chromatograph analyzer. Then, flow carrier gas through the sample condenser tube, and verify the stability of the flow rate and the detector sensitivity. Raise the temperature of the condenser tube to 70 degrees Celsius in approximately two minutes. Introduce subject component to the gas chromatograph.

#### (5) Calibration curve

Tri-methyl amine standard solution that is diluted sequentially with ethyl alcohol or water is injected to the inlet of the gas chromatograph inlet. The calibration curve is plotted according to the peak area of the chromatogram.

(6) Calculating concentration

The concentration in the air is calculated by following equation by using quantity of the tri-methyl amine (0 degree Celsius and 1 atm.) in the liquid separated from the analyzing sample solution by the calibration curve of (5).

$$C = \frac{22.4 A}{59,000V \times \frac{273}{273+t} \times \frac{P}{101.3}}$$
$$A = \frac{50}{V} \times m$$

where C is the concentration of the tri-methyl amine in the air (unit : ppm), A is quantity of the tri-methyl amine in the sample solution for analysis (unit : ng), V is the gas volume measured by gas meter (unit : liter), t is temperature at gas meter (unit : degree Celsius), P is the atmospheric pressure at the sampling (unit : kPa), m is the quantity of the tri-methyl amine from the calibration curve and V is the volume of the solution taken from the sample solution for analysis (unit : ml).

**Remark**

1 The concentration of the tri-methyl amine is calculated by following equation;

$$C = \frac{a \times 59.11 \times 0.1}{20}$$

where C is the concentration of the tri-methyl amine (g/liter) and a is the assumption (ml) of hydrochloric acid (0.1 mol/liter).

2 Indication reagent is prepared by mixing 50 ml of bromocresol green solution and 10 ml of methylred solution, that are respectively dissolved 100 mg of bromocresol green and methylred and to dilute to 100ml with ethyl alcohol.

3 In case of low content of water in the sample and no sorption effect, sample gas may be collected through operation of 1-3-(2)-i) of the attached table 2 by using the equipment shown in 1-2-(1)-i) and (2) (note 2) of the attached table 2. The sample gas collected in the sampling bag shall be collected as soon as possible through operation of 1-3-(1) (note 3) by using the sampling equipment shown in 1-3-(1) (note 3). Flow rate lower than 10 liter/minute is permitted.

(note 1) The inner volume of the sampling bag shall be approximately 50 liter.

4 In case where the separate quantitative analysis is enable, capillary column may be used.

5 Terminology and other items in this measurement method that are not defined, shall follow the definition of Japan Industrial Standard.

**Second) Flow rate measurement at the gas emission point**

The flow rate at the gas emission point is calculated by multiplying gas quantity measured by method of JIS Z8808 to the tri-methyl amine concentration in the exhaust gas measured by method listed in the First.

**Fig. 1 Condenser tube**

- A Silicon rubber cap
- B Capillary tube
- C Syringe needle made of stainless steel
- D Quartz glass wool

**Fig. 2 Sample decomposition and condenser equipment**

- A Nitrogen bottle
- B Flow adjust valve
- C Contamination trap
- D Decomposition bottle
- E Desiccater
- F Filter
- G Condenser tube

**Fig. 3 Gas chromatograph analyzer**

- Main body of gas chromatograph
- A Nitrogen bottle
- B Flow meter
- C Flow adjust valve
- D Contamination trap
- E three direction valve
- F Condenser tube
- G Sample inlet
- H Column
- I Detector
- J Bypass

#### **Attached Table 4**

### **Measurement method of Acetaldehyde, Propionaldehyde, n-Butylaldehyde, iso-Butylaldehyde, n-Valeraldehyde and iso-Valeraldehyde**

#### **First) Concentration measurement at the border of the site - Gas chromatograph method**

##### **1 Reagent**

Reagent shall be prepared in the manner listed below.

(1) Acetnitril (extract)

In case of injection into gas chromatograph, no peak appears in the holding time of acetoaldehyde-2,4-dinitro phenyl hydrazone, propion aldehyde-2,4-dinitro phenyl hydrazone, n-buthyl aldehyde-2,4-dinitro phenyl hydrazone, n-valeric aldehyde-2,4-dinitro phenyl hydrazone and iso-valeric aldehyde-2,4-dinitro phenyl hydrazone (hereinafter referred to "aldehydes-2,4-dinitro phenyl hydrazone").

(2) Sodium sulfate

Five grams of sodium sulfate with particle diameter of 150-250 micro meter is heated for four hours at 450 degrees Celsius, and 5 ml of acetnitril is added. After being filtered, 5 ml of acetnitril is repeatedly added. After being filtered, the filtered solution is vaporized to concetrate to 50 micro liter and to solved into 1 ml of ethyl acetate. In case of injection into gas chromatograph, no peak appears in the holding time of aldehydes-2,4-dinitro phenyl hydrazone.

(3) Ethyl acetate

In case of injection into gas chromatograph, no peak appears in the holding time of aldehydes-2,4-dinitro phenyl hydrazone.

(4) Ethyl alcohol

In case of injection into gas chromatograph, no peak appears in the holding time of aldehydes-2,4-dinitro phenyl hydrazone.

(5) 2,4-dinitro phenyl hydrazine

Recrystallized with solution of acetnitril and water mixed in the volume ratio of 1 to 3.

(6) Sample collection reagent

Particle octa-desil-siryl silica gel with particle diameter of 35-105 micrometer or equivalent.

(7) Cathion exchange resin

Hydrophilic porous vinyl polymer with particle diameter of 40-100 micrometer or equivalent.

(8) Inner standard solution

Ten milligrams of di-phenyl amine dissolved in ethyl acetate and diluted to 100 ml.

(9) Standard solution of aldehydes

One gram of 2,4-dinitro phenyl hydrazine and conc.-sulfuric acid is dissolved in 5 ml of ethyl alcohol for aldehyde listed in column 1 of the following table. The aldehydes listed in column 2 is dissolved in the 5 ml of ethyl alcohol is added to the solution. Suction filtration is made for crystallized material, and it is washed with water and ethyl alcohol, and is desiccated. The crystal that is crystallized in the ethyl alcohol of the quantity listed in column 3 is dissolved in ethyl acetate (each of them is the standard solution containing 10 mg of aldehyde listed in column 1).

Column 1	Column 2 □□□□	Column 3 □□□□
Acetaldehyde	220	50.9
Propionaldehyde	290	41.0
n-Buthylaldehyde	360	35.0
iso-Buthylaldehyde	360	35.0
n-Valericaldehyde	430	30.9
iso-Valericaldehyde	430	30.9

## 2 Equipment and apparatus

Equipment and apparatus are listed as follows;

(1) Gas sampler and sampling bag

The same as the first-2-(1)-i) and (2) (note 1) of the attached table 2.

(2) Sample collection equipment

The configuration shown in fig. 1 and the following condition is satisfied.

i) Condenser tube

(i) Shape shown in fig. 2, made of resin and inner diameter of 10 mm and length of 45 mm, and capable of cap for both ends.

(ii) The coating of the sample collection reagent is washed by acetonitrile. The 0.5 mg of reagent that is dried with pressurized or suction nitrogen, is dipped in the 2 ml of ethyl alcohol solution containing 1 mg of 2,4-dinitro phenyl hydrazine and 5 mg of phosphoric acid. After eliminating ethyl alcohol solution, the reagent is dried with pressurized or suction nitrogen. Then being dried in the desiccator for 12 hours and dried by nitrogen flow of 50-100 ml per minute. Or the equivalent coating method shall be employed.

(iii) Filling sample collection reagent coated in (ii) to the tube and the glass wool or equivalent is used to clog the both ends to avoid filler lost from the tube.

- ii) Sampler pump with air suction power of over 1 liter per minute.
- iii) Gas meter is able to measure the flow rate range of 0-1 liter/min.

(3) Cathion exchange resin tube

i) Shape shown in fig. 3, made of resin and inner diameter of 10 mm and length of 60 mm, and capable of cap for both ends.

(ii) The cathion exchange resin of 0.1 g is washed sequentially by 6 ml of water, sodium chloride (1 mol/liter), water, hydrochloric acid (1 mol/liter), water, ethyl alcohol, acetnitril, or equivalent.

(iii) 0.1 g of cathion exchange resin prepared in ii) is filled in the tube and the glass wool or equivalent is used to clog the both ends to avoid resin lost from the tube.

(4) Gas chromatograph analysis equipment

The configuration shown in fig. 4 and the following condition is satisfied.

i) Alkaline thermal ionization detector is equipped with the gas chromatograph or equivalent.

ii) The column is a capillary column made of melted quartz, and inner diameter of 0.2 mm and the length of 25 meter, methyl silicone is coated with the thickness of 0.1 micrometer or equivalent.

iii) The temperature of the sample inlet shall be 250 degrees Celsius.

iv) The column chamber shall be set to the optimum separation condition of the subject component. (For example, maintaining for 1 minute on 50 degrees Celsius, raising temperature from 50 degrees Celsius to 200 degrees Celsius at 25 degrees Celsius per minute for 6 minutes, and raise temperature to 250 degrees at 3 degrees Celsius per minute)

v) The nitrogen or helium is used for carrier gas or make up gas of flow rate of 20-3-ml/minute.

vi) The structure is able to contain the 1 micro liter of the test liquid in the column.

(note 1) Inner volume of the sampling bag shall be 50 liter.

### 3 Measurement process

Concentration measurement is performed in following process;

(1) Blank test

As shown in fig. 5, the sample collection tube and the cathion exchange resin tube are connected, 6 ml of the solved liquid drips to the cap type tube (with scale) naturally or in the flow rate of 1 ml/minute. Dehydrate the liquid by adding small amount of sodium sulfate, and



vaporized acetnitril to 50 micro liter (1 drip) by blowing with nitrogen from top of the tube. The acetnitril is dissolved by adding 1 ml of ethyl acetate, and add 80 micro liter of inner standard solution to make test liquid. Then performing gas chromatograph in the sequence (4) to verify no peak appeared in the holding time of aldehydes-2,4-dinitro phenyl hydrazone.

(2) Gas sampling

Sample gas is collected in the sampling bag in the operation of the First-3-(2) of the attached table 2.

(3) Sample collection

As soon as the sample gas is collected, remove the caps at both end of the collection tube. Then, the tube is connected to the sampling bag as shown in fig. 1. The sample is collected in the bag by absorbing 30 liter at flow rate of 1 liter/minute. (note 2)

(4) Gas chromatograph analysis

The sample collection tube with collected sample is treated in the same manner as (1) (note 3), 1 micro liter of sample is taken with micro syringe to inject from the inlet of the gas chromatograph. In case where the peak is separated for stereoisomer of aldehydes-2,4-dinitro phenyl hydrazone on the chromatogram, the peak area of the subject component is summation of peak area.

(5) Calibration curve

Standard solutions of the aldehydes are diluted sequentially with ethyl acetate. One micro liter of diluted standard solution that is prepared by adding 80 micro liter of inner standard solution with 1 ml of diluted solution is injected to the inlet of the gas chromatograph inlet. By taking ratio ( $A_x/A_s$ ) of the peak area ( $A_x$ ) of chromatogram of aldehydes-2,4-dinitro phenyl hydrazone and the peak area ( $A_s$ ) of chromatogram of di-phenyl amine as the vertical axe, and ratio ( $M_x/M_s$ ) of injection quantity of aldehydes ( $M_x$ ) and injection quantity of di-phenyl amine ( $M_s$ ) as the horizontal axe, the calibration curve is plotted in the range of linear relation.

(6) Calculating concentration

The concentration in the air is calculated by following equation by using quantity of the acetaldehyde, propionaldehyde, n-buthylaldehyde, iso-buthylaldehyde, n-valericaldehyde and iso-Valericaldehyde (0 degree Celsius and 1 atm.) in the liquid separated from the analyzing sample solution by the calibration curve of (5) (note 4).

$$C = \frac{22.4A}{MV \times \frac{273}{273+t} \times \frac{P}{101.3}}$$

where C is the concentration of the subject component in the air (unit : ppm), A is quantity of the subject component in the sample solution for analysis (unit : ng), V is the gas volume measured by gas meter (unit : liter), t is temperature at gas meter (unit : degree Celsius), P is the atmospheric pressure at the sampling (unit : kPa).

(note 2) Caps shall be applied to both end of the sample collection tube. It shall be covered from the light storage or transportation.

(note 3) Sample collection tube shall be solved by solution as soon as possible.

(note 4) For the quantity (A) of the subject component in the test solution of the sample, the chromatogram is recorded in the same condition by mixing uniformly to control the added quantity of the di-phenyl amine in the range of the calibration curve and by adjusting the volume of test solution in order to control the peak area of the di-phenyl amine to be approximately the same as calibration curve plot. The quantity of the subject component (A) is calculated from the added quantity of di-phenyl amine, by calculating ratio of (A'x/A's) of the peak area of the subject component (A'x) and the peak area of the di-phenyl amine (A's) from the chromatogram and by obtaining ratio of (A/M's) of the quantity of the subject component (A) and the quantity of the di-phenyl amine (M's) from the calibration curve.

### Remark

Terminology and other items in this measurement method that are not defined, shall follow the definition of Japan Industrial Standard.

### Fig. 1 Gas sampling equipment

- A Sampling bag
- B Sampling tube
- C Suction pump
- D Gas meter

### Fig. 2 Collecting tube

- Transportation and storage
- A Sample collection reagent
- B Quartz glass wool
- C Resin cap
- Aluminum foil

**Fig. 3 Cathion exchange resin tube**

- A Cathion exchange resin
- B Quartz glass wool
- C Resin cap
- Aluminum foil

**Fig. 4 Gas chromatograph analyzer**

- Main body of gas chromatograph
- A Nitrogen bottle
- B Flow meter
- C Flow adjust valve
- D Sample inlet
- E Column
- F Detector

**Fig. 5 Solving operation**

- A Syringe
- B Collecting tube
- C Cathion exchange resin
- D Capped test tube

**Second) Concentration measurement at the border of the site - Gas chromatograph mass analysis method**

**1 Reagent**

Reagent shall be prepared in the manner listed below.

(1) N,N-dimethyl formamide

In case of injecting a few micro litter of solution diluted to one tenth concentration with water into gas chromatograph mass analyzer, no peak appears in the holding time of subject component.

(2) Standard solution of aldehydes

Hundred micro liters of aldehyde is dissolved in water or N,N-dimethyl formamide to dilute to 100 ml for type of aldehyde listed in column 1 of the following table. (one micro liter of each solution correspond to the quantity listed in the column 2 (o degree Celsius and 1 atm.) as a gaseous aldehyde listed in the column 1. For acetaldehyde, the containing rate shall be multiplied.)

Column 1	Column 2 (unit : micro liter)
Acetaldehyde	0.311
Propionaldehyde	0.311
n-Buthylaldehyde	0.249
iso-Buthylaldehyde	0.247
n-Valericaldehyde	0.211
iso-Valericaldehyde	0.204

(3) Porous polymer beads

Polymer beads that absorb hydrocarbons of carbon number greater than 6, release the absorbed component at 200 degrees Celsius, are made of para-phenylene oxide, are in particle diameter range of 180-250 micro meter and are durable at 350 degrees Celsius.

(4) Porous silica beads

Silica beads that absorb hydrocarbons, release the absorbed component at 200 degrees Celsius, is in particle diameter range of 100-300 micro meter and surface area is 10 m<sup>2</sup>/g.

(5) Activated carbon

Particle diameter range of 180-250 micro meter

**2 Equipment and apparatus**

Equipment and apparatus are listed as follows;

(1) Gas sampler and sampling bag

The same as the first-2-(1)-i) and (2) of the attached table 2.

(2) Sample collection equipment

The configuration shown in fig. 6 and the following condition is satisfied.

i) Collecting tube

(i) Shape shown in fig. 7, made of borosilicate glass and inner diameter of 5 mm and length of 18 cm, and capable of attaching syringe needle at the one end of the tube.

(ii) After washing the inside of the tube with acetone and being desiccated, 0.2 g of porous polymer beads, 0.2 g of porous silica beads and 0.2 g of activated carbon or equivalent are filled as filler. The glass wool is used to clog the both ends to avoid filler lost from the tube.

(iii) The both end of the tube shall be closed with fluoride resin cap and silicon rubber cap.

ii) Sampler pump with air suction power of over 1 liter per minute.

iii) Gas meter is able to measure the flow rate range of 0-1 liter/min.

### (3) Condenser tube

The configuration shown in fig. 8 and the following condition is satisfied.

i) The tube is made of borosilicate glass or fluoride resin and the inner diameter of 4 mm.

ii) After washing the inside the tube with water and desiccated, the white diatomaceous earth with particle diameter of 180-250 micro meter, holder of the filler is washed with acid and processed by dimethyl-dichloro silane or equivalent is used as filler.

iii) Aluminum foil is placed on the outside of the tube. It is isolated with glass fiber tape. Thermocouple is attached to measure the temperature. Nickel-chrome wire with glass fiber tube is turned on the same spacing, and fixed with glass fiber tape.

### (4) Gas chromatograph analysis equipment

The configuration shown in fig. 4 and the following condition is satisfied.

i) The gas chromatograph includes detector of electron impact ionization (EI method) and selective ion detection (SIM method) or equivalent chromatograph measurement shall be enabled.

ii) Carrier gas path is changed at the sample inlet and is connected to contamination trap and condenser tube.

iii) The column is a capillary column made of melted quartz, and inner diameter of 0.5 mm and the length of 50 meter, methyl silicone is coated with the thickness of 5 micrometer or equivalent.

iv) The temperature of the sample inlet shall be 150 degrees Celsius.

v) The column chamber shall be set to the optimum separation condition of the subject component. (For example, raising temperature from 30 degrees Celsius to 100 degrees Celsius at 5 degrees Celsius per minute)

v) The helium is used for carrier gas of flow rate of 10 ml/minute.

## **3 Measurement process**

Concentration measurement is performed in following process;

### (1) Blank test

Sample collecting tube is heated at 200 degrees Celsius with nitrogen or helium flow of 50 ml/min from the activated carbon side, and this condition is kept for approximately 6 hours. An

analysis routine is performed on item (4) to verify no peak in the holding time of the subject component.

(2) Gas sampling

Sample gas is collected in the sampling bag by the operation of the First-3-(2) in the attached table 2.

(3) Sample collection

As soon as the sample gas is collected, remove the caps made of fluoride resin and silicon rubber at both end of the collection tube. Then, the tube is connected to the sampling bag. The sample is collected in the bag at flow rate of 1 liter/minute from the porous polymer beads. (note 5)

(4) Gas chromatograph analysis

As shown in fig. 10, the sample condenser tube that is cooled with coolant such as liquid oxygen, is connected to the gas collection tube. By heating the sample collecting tube to 150 degrees Celsius, and this condition is kept for 5 minutes, with nitrogen or helium flow of 50 ml/min, the subject component is moved to the condenser tube. As shown in fig. 9, the condenser tube with subject component is connected to the chromatograph analyzer. Then, flow carrier gas through the sample condenser tube, raise the temperature of the condenser tube to 150 degrees Celsius in short time. Introduce subject component to the gas chromatograph. (note 6)

(5) Calibration curve

The calibration curve is plotted according to the peak area of the chromatogram of the selective ion detection method on the same operation (4), by injecting a few micro liter of aldehydes standard solution from the porous polymer beads side at room temperature.

(6) Calculating concentration

The concentration in the air is calculated by following equation by using quantity of the acetaldehyde, propionaldehyde, n-buthylaldehyde, iso-buthylaldehyde, n-valericaldehyde and iso-Valericaldehyde (0 degree Celsius and 1 atm.) in the liquid separated from the analyzing sample solution by the calibration curve of (5).

$$C = \frac{A}{V \times \frac{273}{273+t} \times \frac{P}{101.3}}$$

where C is the concentration of the subject component in the air (unit : ppm), A is quantity of the subject component in the sample solution for analysis (unit : ng), V is the gas

volume measured by gas meter (unit : liter),  $t$  is temperature at gas meter (unit : degree Celsius),  $P$  is the atmospheric pressure at the sampling (unit : kPa).

(note 5) Caps shall be applied to both end of the sample collection tube. It shall be covered from the light storage or transportation. The sample collecting tube is refrigerated as soon as possible.

(note 6) Ions of mass number 44 is monitored for acetaldehyde, n-buthylaldehyde, n-valericaldehyde and iso-Valericaldehyde, ions of mass number 58 or 29 is monitored for propionaldehyde and ions of mass number 72 is monitored for iso-buthylaldehyde

#### **Remark**

Terminology and other items in this measurement method that are not defined, shall follow the definition of Japan Industrial Standard.

#### **Third) Flow rate measurement at the gas emission point**

The flow rate at the gas emission point is calculated by multiplying gas quantity measured by method of JIS Z8808 to the concentration of acetaldehyde, propionaldehyde, n-buthylaldehyde, iso-buthylaldehyde, n-valericaldehyde and iso-Valericaldehyde in the exhaust gas measured by method listed in the First and Second. In case of using the method listed in the First, two collecting tubes in series are used and flow rate shall be adjusted.

#### **Remark**

Terminology and other items in this measurement method that are not defined, shall follow the definition of Japan Industrial Standard.

#### **Fig. 6 Sampling equipment**

- A Sampling bag
- B Sampling tube
- C Suction pump
- D Gas meter

#### **Fig. 7 Collecting tube**

- Analyzing
- Direction of heated degas
- Direction of sample collection

- A Silicon rubber cap
- B Quartz glass wool
- C Activated carbon
- D Porous silica beads
- E Porous polymer beads
- F Syringe needle made of stainless steel

Transportation and storage

Aluminum foil

- A Fluoride resin cap
- B Quartz glass wool
- C Activated carbon
- D Porous silica beads
- E Porous polymer beads

**Fig. 8 Condenser tube**

- A Silicon rubber cap
- B Capillary tube
- C Syringe needle made of stainless steel
- D Quartz glass wool

**Fig. 9 Gas chromatograph mass analyzer**

Main body of gas chromatograph mass analyzer

- A Nitrogen bottle
- B Flow meter
- C Flow adjust valve
- D Sample inlet
- E Column
- F Gas chromatograph mass analyzer
- G Condenser tube
- H Three direction valve
- J Bypass

**Fig. 10 Condensing operation**

- A Nitrogen bottle
- B Flow meter



- C Flow adjust valve
- D Liquid oxygen
- E Sample collecting tube
- F Furnace of sample collecting tube
- G Condenser tube

#### **Attached Table 5**

Measurement method of iso-Buthylalcohol

#### **First) Concentration measurement at the border of the site**

##### **1 Reagent**

Reagent shall be prepared in the manner listed below.

(1) n-penthan

No peak shall appear in the holding time of iso-buthylalcohol, when it is injected in gas chromatograph.

(2) Standard solution of iso-buthylalcohol

The standard solution of iso-buthylalcohol is prepared by dissolving iso-buthylalcohol in n-pentane and to dilute to 100 ml.

##### **2 Equipment and apparatus**

Equipment and apparatus are listed as follows;

(1) Gas sampler and sampling bag

The same as the First-2-(1) and (2) in the attached table 2.

(2) Condenser tube

The configuration shown in fig. 1 and the following condition is satisfied.

- i) The tube is made of borosilicate glass or fluoride resin and the inner diameter of 4 mm.
- ii) After washing the inside the tube with acetone and water and desiccated, the white diatomaceous earth with particle diameter of 180-250 micro meter, holder of the filler is washed with acid and processed by dimethyl-dichloro silane or equivalent is used as filler.
- iii) Aluminum foil is placed on the outside of the tube. It is isolated with glass fiber tape. Thermocouple is attached to measure the temperature. Nickel-chrome wire with glass fiber tube is turned on the same spacing, and fixed with glass fiber tape.

(3) Gas chromatograph analysis equipment

The configuration shown in fig. 2 and the following condition is satisfied.

- i) The gas chromatograph includes hydrogen flame ion detector.
- ii) Carrier gas path is changed at the sample inlet and is connected to contamination trap and condenser tube.
- iii) The column is made of glass and the inner diameter of 3 mm and length of 3 meters. Inner side is washed with acetone and water, and desiccated.
- ) The white diatomaceous earth holder of the filler with particle diameter of 180-250 micro meter is coated with 25% of poly-ethylene glycol. Or equivalent filler is used for the purpose.
- v) Temperature at the sample inlet shall be 180 degrees Celsius.
- vi) The column chamber shall be set to the optimum separation condition of the subject component. (For example, raising temperature from 30 degrees Celsius to 120 degrees Celsius at 5 degrees Celsius per minute)
- vii) Nitrogen is employed for carrier gas of flow of 40-50 ml per minute.

### **3 Measurement process**

Concentration measurement is performed in following process;

#### **(1) Blank test**

Sample condenser tube is heated for approximately 10 minutes at 200 degrees Celsius with nitrogen flow. An analysis routine is performed on item (4) to verify no peak in the holding time of the iso-buthylalcohol.

#### **(2) Gas sampling**

Gas is collected in the sampling bag by the operation of the first-3-(2) of the attached table 2.

#### **(3) Sample condensing**

As shown in fig. 3, the iso-buthylalcohol in the sampling bag is collected in the sample condenser tube for constant quantity of sample by connecting sampling bag to sample condenser tube that is cooled with coolant such as liquid oxygen.

#### **(4) Gas chromatograph analysis**

As shown in fig. 2, the sample condenser tube with trapped the iso-buthylalcohol, that is cooled with coolant such as liquid oxygen, is connected to the gas chromatograph analyzer. Then, flow carrier gas through the sample condenser tube, and verify the stability of the flow rate and the detector sensitivity. Raise the temperature of the condenser tube to 200 degrees Celsius in

approximately two minutes. Introduce the iso-buthylalcohol to the gas chromatograph.

(5) Calibration curve

The calibration curve is plotted according to the peak area of the chromatogram on the same operation (4), by injecting a few micro liter of iso-buthylalcohol standard solution that is sequentially diluted with n-pentane.

(6) Calculating concentration

The concentration in the air is calculated by following equation by using quantity of the

$$C = \frac{22.4A}{74V \times \frac{273}{273+t} \times \frac{P}{101.3}}$$

iso-buthylalcohol (0 degree Celsius and 1 atm.) collected in the condenser tube by the calibration curve of (5).

where C is the concentration of the iso-buthylalcohol in the air (unit : ppm), A is quantity of the iso-buthylalcohol in the condenser tube (unit : micro gram), V is the gas volume collected in condenser tube (unit : liter), t is temperature at the sample condensing (unit : degree Celsius), P is the atmospheric pressure at the sample condensing (unit : kPa).

**Remark**

- 1 In case where the qualitative analysis is enabled, a part of the sampled gas is taken in the gas syringe, and may be directly injected to sample inlet.
- 2 In case where no interfering substances exists and the separate quantitative analysis is enable, capillary column may be used with ethyl acetate, methyl-iso-buthylketone, and toluene, styrene and xylene.
- 3 For the calibration curve, iso-buthyl alcohol calibration gas may be used in the same manner as the First-1 of the attached table 2. (4 micro liter of iso-buthyl alcohol corresponds to 0.969 ml of gas(0 degree Celsius and 1 atm.))
- 4 Terminology and other items in this measurement method that are not defined, shall follow the definition of Japan Industrial Standard.

**Second) Flow rate measurement at the gas emission point**

The flow rate at the gas emission point is calculated by multiplying gas quantity measured by method of JIS Z8808 to the iso-buthyl alcohol concentration in the exhaust gas measured by method of listed in the First.

**Remark**

- 1 In case where the qualitative analysis is enabled, a part of the sampled gas is taken in the gas syringe, and may be directly injected to sample inlet.
- 2 In case where no interfering substances exists and the separate quantitative analysis is enable, capillary column may be used with ethyl acetate, methyl-iso-buthylketone, and toluene and xylene.
- 3 Terminology and other items in this measurement method that are not defined, shall follow the definition of Japan Industrial Standard.

**Fig. 1 Condenser tube**

- A Silicon rubber cap
- B Capillary tube
- C Syringe needle made of stainless steel
- D Quartz glass wool

**Fig. 2 Gas chromatograph analyzer**

- Main body of gas chromatograph
- A Nitrogen bottle
- B Flow meter
- C Flow adjust valve
- D Sample inlet
- E Column
- F Detector
- H three direction valve
- G Condenser tube
- I Bypass

**Fig. 3 Condensing method**

- or
- A Sampling bag
- B Condenser tube
- C Fluoride resin tube
- D Suction pump
- E Gas meter
- F Syringe

## Attached Table 6

### Measurement method of Ethylacetate and Methyl-iso-buthylketone

#### First) Concentration measurement at the border of the site - low temperature condensing

##### 1 Reagent

Reagent shall be prepared in the manner listed below.

##### (1) n-penthan

No peak shall appear in the holding time of iso-buthylalcohol, when it is injected in gas chromatograph.

##### (2) Standard solution of ethylacetate and methyl-iso-buthylketone

The standard solutions of ethylacetate and methyl-iso-buthylketone are prepared by dissolving 1 g of ethylacetate and methyl-iso-buthylketone in n-pentane and to dilute to 100 ml.

##### 2 Equipment and apparatus

Equipment and apparatus the same as the First-2 of the attached table 5. The white diatomaceous earth with particle diameter of 180-250 micro meter, holder of the filler is washed with acid and processed by dimethyl-dichloro silane and coated 25% with Uconoil 50LB550X or equivalent is used as filler. The column temperature shall be 90 degrees Celsius.

##### 3 Measurement process

Concentration measurement is performed in the process defined in the First-3-(1) through (5) in the attached table 5 ("iso-buthyl alcohol" is treated as "ethylacetate and methyl-iso-buthylketone") and the calculation methods for concentration are shown as follows;

Calculating concentration

The concentration in the air is calculated by following equation by using quantity of the ethylacetate and methyl-iso-buthylketone (0 degree Celsius and 1 atm.) collected in the condenser tube by the calibration curve.

$$C = \frac{22.4A}{MV \times \frac{273}{273+t} \times \frac{P}{101.3}}$$

where C is the concentration of the subject component in the air (unit : ppm), A is quantity of the subject component in the condenser tube (unit : micro gram), V is the gas volume collected in condenser tube (unit : liter), t is temperature at the sample condensing (unit : degree Celsius), P is the atmospheric pressure at the sample condensing (unit : kPa).

## **Remark**

- 1 In case where the qualitative analysis is enabled, a part of the sampled gas is taken in the gas syringe, and may be directly injected to sample inlet.
- 2 In case where no interfering substances exists and the separate quantitative analysis is enable, capillary column may be used with iso-buthyl alcohol, toluene, styrene and xylene.
- 3 For the calibration curve, iso-buthyl alcohol calibration gas may be used in the same manner as the First-1 of the attached table 2. (4 micro liter of ethylacetate corresponds to 0.969 ml of gas (0 degree Celsius and 1 atm.) and 6 micro liter of methyl-iso-buthylketone corresponds to 1.07 ml of gas (0 degree Celsius and 1 atm.))
- 4 Terminology and other items in this measurement method that are not defined, shall follow the definition of Japan Industrial Standard.

## **Second) Concentration measurement at the border of the site - room temperature absorbing**

### **1 Reagent**

Reagent shall be prepared in the manner listed below.

- (1) Standard solution of ethylacetate and methyl-iso-buthylketone

The same as the First-1.

- (2) Porous polymer beads

The same as the Second-1-(3) in the attached table 4.

### **2 Equipment and apparatus**

Equipment and apparatus are listed as follows;

- (1) Gas sampler and sampling bag

The same as the Second-2-(1) and (2) in the attached table 4.

- (2) Sample collection equipment

The same as the Second-2-(2) in the attached table 4. However, the 0.6 gram of porous polymer beads shall be filled in the sample collection tube.

- (3) Gas chromatograph analysis equipment

The same as the First-2. However, the collecting tube can be heated in the heating furnace by connecting a collecting tube equipped a syringe needle to the gas chromatograph instead of condenser tube.

### **3 Measurement process**

Concentration measurement is performed in following process;

(1) Blank test

Sample condenser tube is heated at 230 degrees Celsius with nitrogen flow. An analysis routine is performed on item (4) to verify no peak in the holding time of the subject component.

(2) Gas sampling

Gas is collected in the sampling bag by the operation of the first-3-(2) of the attached table 2.

(3) Sample condensing

As soon as the sample gas is collected, remove the caps made of fluoride resin and silicon rubber at both end of the collection tube. Then, the tube is connected to the sampling bag as shown in fig. 1. The subject component is collected in the collection tube at constant quantity of flow.

(4) Gas chromatograph analysis

The sample condenser tube with trapped the subject component is connected to the gas chromatograph analyzer. Then, flow carrier gas through the sample condenser tube, and verify the stability of the flow rate and the detector sensitivity. Raise the temperature of the condenser tube to 200 degrees Celsius in approximately one minute. Introduce the subject component to the gas chromatograph.

(5) Calibration curve

The calibration curve is plotted according to the peak area of the chromatogram on the same operation (4), by injecting a few micro liter of ethylacetate and methyl-iso-buthylketone standard solution that is sequentially diluted with n-pentane.

(6) Calculating concentration

The concentration of subject component in the air is calculated by method of the First-3 with the calibration curve of (5). "Condenser tube" is treated as "sample collecting tube" and "sample condensing" as "sample collecting".

**Remark**

1 In case where the qualitative analysis is enabled, a part of the sampled gas is taken in the gas syringe, and may be directly injected to sample inlet.

2 In case where no interfering substances exists and the separate quantitative analysis is

enable, capillary column may be used with toluene, styrene and xylene.

3 For the calibration curve, subject component calibration gas may be used in the same manner as the First-1 of the attached table 2. (4 micro liter of ethylacetate corresponds to 0.969 ml of gas (0 degree Celsius and 1 atm.) and 6 micro liter of methyl-iso-butylketone corresponds to 1.07 ml of gas (0 degree Celsius and 1 atm.))

4 Terminology and other items in this measurement method that are not defined, shall follow the definition of Japan Industrial Standard.

### **Third) Flow rate measurement at the gas emission point**

The flow rate at the gas emission point is calculated by multiplying gas quantity measured by method of JIS Z8808 to the ethylacetate and methyl-iso-butylketone concentrations in the exhaust gas measured by method of listed in the First.

### **Remark**

1 In case where the qualitative analysis is enabled, a part of the sampled gas is taken in the gas syringe, and may be directly injected to sample inlet.

2 In case where no interfering substances exists and the separate quantitative analysis is enable, capillary column may be used with ethyl acetate, iso-butyl alcohol, toluene and xylene.

3 Terminology and other items in this measurement method that are not defined, shall follow the definition of Japan Industrial Standard.

### **Fig. 1 Gas sampling equipment**

- A Sampling bag
- B Sampling tube
- C Suction pump
- D Gas meter

### **Attached Table 7**

#### **Measurement method of Toluene, Styrene and Xylene**

#### **First) Concentration measurement at the border of the site - low temperature condensing**

##### **1 Reagent**

Reagent shall be prepared in the manner listed below.

(1) n-penthan

No peak shall appear in the holding time of iso-butylalcohol,



when it is injected in gas chromatograph.

(2) Standard solution of toluene, styrene and xylene

The standard solutions of toluene, styrene and xylene are prepared by dissolving 1 g of isomers (o-, m- and p-) of toluene, styrene and xylene in n-pentane and to dilute to 100 ml.

## 2 Equipment and apparatus

Equipment and apparatus the same as the First-2 of the attached table 5. The white diatomaceous earth with particle diameter of 180-250 micro meter, holder of the filler is washed with acid and processed by dimethyl-dichloro silane and coated 5% with SP-1200 and 1.75% with Benton 34 or equivalent is used as filler. The column temperature shall be 40-100 degrees Celsius.

## 3 Measurement process

Concentration measurement is performed in the process defined in the First-3-(1) through (5) in the attached table 5 ("iso-buthyl alcohol" is treated as "toluene, styrene and xylene") and the calculation method for concentration is shown as follows;

### Calculating concentration

The concentration in the air is calculated by following equation by using quantity of the toluene, styrene and xylene (0 degree Celsius and 1 atm.) collected in the condenser tube by the calibration curve. For xylene, the summation of the concentration of all the isomers is considered to be the concentration of the xylene.

$$C = \frac{22.4A}{MV \times \frac{273}{273+t} \times \frac{P}{101.3}}$$

where C is the concentration of the subject component in the air (unit : ppm), A is quantity of the subject component in the condenser tube (unit : micro gram), V is the gas volume collected in condenser tube (unit : liter), t is temperature at the sample condensing (unit : degree Celsius), P is the atmospheric pressure at the sample condensing (unit : kPa).

### Remark

- 1 In case where the qualitative analysis is enabled, a part of the sampled gas is taken in the gas syringe, and may be directly injected to sample inlet.
- 2 In case where no interfering substances exists and the separate quantitative analysis is enable, capillary column may be used with iso-buthyl alcohol, ethylacetate and methyl-iso-buthylketone.
- 3 For the calibration curve, subject component calibration gas may be used in the same

manner as the First-1 of the attached table 2. (5 micro liter of toluene corresponds to 1.06 ml of gas (0 degree Celsius and 1 atm.), 5 micro liter of styrene corresponds to 0.975 ml of gas (0 degree Celsius and 1 atm.), 5 micro liter of o-xylene corresponds to 0.928 ml of gas (0 degree Celsius and 1 atm.), 5 micro liter of m-xylene corresponds to 0.916 ml of gas (0 degree Celsius and 1 atm.) and 5 micro liter of p-xylene corresponds to 0.908 ml of gas (0 degree Celsius and 1 atm.))

4 Terminology and other items in this measurement method that are not defined, shall follow the definition of Japan Industrial Standard.

## **Second) Concentration measurement at the border of the site - room temperature absorbing**

### **1 Reagent**

Reagent shall be prepared in the manner listed below.

(1) Standard solution of toluene, styrene and xylene

The same as the First-1.

(2) Porous polymer beads

The same as the Second-1-(3) in the attached table 4.

### **2 Equipment and apparatus**

The same as the Second-2 in the attached table 6.

### **3 Measurement process**

Measurement of the concentration is the same as the Second-3-(1) through (5) in the attached table 6. "ethylacetate and methyl-iso-butylketone" is treated as "toluene, styrene and xylene". The concentration is calculated by method of the First-3. "Condenser tube" is treated as "sample collecting tube" and "sample condensing" as "sample collecting".

### **Remark**

1 In case where the qualitative analysis is enabled, a part of the sampled gas is taken in the gas syringe, and may be directly injected to sample inlet.

2 In case where no interfering substances exists and the separate quantitative analysis is enable, capillary column may be used with iso-butyl alcohol, ethylacetate and methyl-iso-butylketone.

3 For the calibration curve, subject component calibration gas may be used in the same manner as the First-1 of the attached table 2. (5 micro liter of toluene corresponds to 1.06 ml of gas (0 degree Celsius and 1 atm.), 5 micro liter of styrene corresponds to 0.975 ml of gas (0 degree

Celsius and 1 atm.), 5 micro liter of o-xylene corresponds to 0.928 ml of gas (0 degree Celsius and 1 atm.), 5 micro liter of m-xylene corresponds to 0.916 ml of gas (0 degree Celsius and 1 atm.) and 5 micro liter of p-xylene corresponds to 0.908 ml of gas (0 degree Celsius and 1 atm.))

4 Terminology and other items in this measurement method that are not defined, shall follow the definition of Japan Industrial Standard.

### **Third) Flow rate measurement at the gas emission point**

The flow rate at the gas emission point is calculated by multiplying gas quantity measured by method of JIS Z8808 to the toluene, styrene or xylene concentration in the exhaust gas measured by method of listed in the First and the second.

### **Remark**

1 In case where the qualitative analysis is enabled, a part of the sampled gas is taken in the gas syringe, and may be directly injected to sample inlet.

2 In case where no interfering substances exists and the separate quantitative analysis is enable, capillary column may be used with iso-buthyl alcohol, ethylacetate and methyl-iso-buthylketone.

3 Terminology and other items in this measurement method that are not defined, shall follow the definition of Japan Industrial Standard.

### **Attached Table 8**

#### **Measurement method of Propionic acid, n-Butyric acid, n-Valeric acid and iso-Valeric acid**

### **First) Concentration measurement at the border of the site**

#### **1 Reagent**

Reagent shall be prepared in the manner listed below.

#### **(1) Formic acid**

No peak shall appear in the holding time of subject component, when it is injected in gas chromatograph.

#### **(2) Standard solution of propionic acid**

The standard solutions of propionic acid are prepared by dissolving 1.0 ml of propionic acid and to dilute to 100 ml. (1 micro liter of this solution corresponds to 3.02 micro liter of gaseous propionic acid (0 degree Celsius and 1 atm.))

(3) Standard solution of n-butyric acid

The standard solutions of n-butyric acid are prepared by dissolving 1.0 ml of n-butyric acid and to dilute to 100 ml. (1 micro liter of this solution corresponds to 2.43 micro liter of gaseous n-butyric acid (0 degree Celsius and 1 atm.))

(4) Standard solution of n-valeric acid

The standard solutions of n-valeric acid are prepared by dissolving 1.0 ml of n-valeric acid and to dilute to 100 ml. (1 micro liter of this solution corresponds to 2.06 micro liter of gaseous n-valeric acid (0 degree Celsius and 1 atm.))

(5) Standard solution of iso-valeric acid

The standard solutions of iso-valeric acid are prepared by dissolving 1.0 ml of iso-valeric acid and to dilute to 100 ml. (1 micro liter of this solution corresponds to 2.04 micro liter of gaseous iso-valeric acid (0 degree Celsius and 1 atm.))

## 2 Equipment and apparatus

Equipment and apparatus are listed as follows;

(1) Sampling equipment

The configuration is shown in fig. 1 and the following condition is satisfied.

i) Collecting tube

(i) The tube is made of borosilicate glass and the inner diameter of 7-8 mm and the length of 10 cm, syringe needle can be connected at one end of the tube as shown in fig. 2.

(ii) The tube is washed with phosphoric acid (1+4) and water, and is desiccated, then the 3 g of filler is filled in the tube, and quartz glass wool is used to clog the both ends to avoid filler lost from the tube.

(iii) The glass beads with particle diameter of 500-1180 micro meter are washed with hydrochloric acid (1+3) and water, then desiccated and coated 1% of strontium hydroxide. Coating is made by strontium hydroxide of 1 % weight of glass beads that is dissolved with small amount of water, is mixed with glass beads on the ceramic dish and quickly dried or equivalent.

(iv) The both end of the tube shall be closed with fluoride resin cap and silicon rubber cap.

ii) Sampler pump with air suction power of over 5 liter per minute.

iii) Gas meter is able to measure the flow rate range of 0-10 liter/min.

(2) Gas chromatograph analysis equipment

The configuration shown in fig. 3 and the following condition is satisfied.

- i) The gas chromatograph includes hydrogen flame ion detector.
- ii) Carrier gas path is changed at the sample inlet and is connected to contamination trap and condenser tube.
- iii) The column is made of glass and the inner diameter of 3 mm and length of 3 to 5 meters. Inner side is washed with phosphoric acid and water, and desiccated.
- iv) The carbon black holder with particle diameter of 180-250 micrometers, that is coated with 0.3% of FFAP and 0.3% of phosphoric acid is used as filler. Or equivalent filler is used for the purpose.
- v) Temperature at the sample inlet shall be 230 degrees Celsius.
- vi) Temperature at the column chamber shall be controllable in the range of 80-200 degrees Celsius.
- vii) Nitrogen is employed for carrier gas of flow of 40-50 ml per minute.

### **3 Measurement process**

Concentration measurement is performed in following process;

#### **(1) Blank test**

Sample collecting tube is heated at 300 degrees Celsius for 10 minutes. Connect the collection tube to the gas chromatograph. With nitrogen flow of 50 ml/min, 20 micro liter of 5 % formic acid is injected to verify no peak appeared in the holding time of the subject component.

#### **(2) Sample collection**

By removing the caps made of fluoride resin and silicon rubber at both end of the collection tube. The sample is collected in the tube at flow rate of 5 liter/minute for 5 minutes.

#### **(3) Gas chromatograph analysis**

A syringe needle is connected to the gas collection tube. By heating the sample collecting tube to 180 degrees Celsius with nitrogen flow of 50 ml/min. As shown in fig. 9, the collecting tube is connected to the chromatograph analyzer, after cooling to room temperature. Then, flow carrier gas through the sample condenser tube, and verify the stability of the flow rate and the detector sensitivity. Raise the temperature of the collecting tube to 180 degrees Celsius in approximately 1 minute. Introduce subject component to the gas chromatograph. The column temperature is raised from 80 to 200 degrees Celsius in 10 minutes.

#### **(4) Calibration curve**

The calibration curve is plotted according to the peak area of the chromatogram on the same operation (3), by injecting a few micro liter of propionic acid, n-butyric acid, n-valeric acid

and iso-valeric acid standard solutions diluted in sequence.

(5) Calculating concentration

The concentration in the air is calculated by following equation by using quantity of the propionic acid, n-butyric acid, n-valeric acid and iso-valeric acid from the calibration curve of (4).

where C is the concentration of the subject component in the air (unit : ppm), A is

$$C = \frac{A}{V \times \frac{273}{273+t} \times \frac{P}{101.3}}$$

quantity of the subject component in the sample collecting tube (unit : micro gram), V is the gas volume measured by gas meter (unit : liter), t is temperature at gas meter (unit : degree Celsius), P is the atmospheric pressure at the gas sampling (unit : kPa).

**Remark**

1 In case of low content of water in the sample and no sorption effect, sample gas may be collected through operation of the First-3-(2)-i) of the attached table 2 by using the equipment shown in the First-2-(1)-i) and (2) (note 1) of the attached table 2. The sample gas collected in the sampling bag shall be collected as soon as possible through operation of 1-3-(2) by using the sampling equipment shown in 2-(1).

(note 1) The inner volume of the sampling bag shall be approximately 50 liter.

2 Terminology and other items in this measurement method that are not defined, shall follow the definition of Japan Industrial Standard.

**Fig. 1 Gas sampling equipment**

- A Collecting tube
- B Suction pump
- C Gas meter

**Fig. 2 Gas sampling equipment**

- A Silicon rubber cap
- B Quartz glass wool
- C Alkaline beads
- D Cap made of fluoride resin
- E Syringe needle made of stainless steel

**Fig. 3 Gas chromatograph analyzer**

Main body of gas chromatograph

A Nitrogen bottle

B Flow meter

C Flow adjust valve

D three direction valve

E Collection tube

F Furnace for collection tube

G Sample inlet

H Column

I Detector

J Bypass

#4

## **Calculation method of odor index and odor intensity**

**Announcement of Ministry of Environment No.63 of 1995**

**Amended by Announcement of Ministry of Environment No.7 of 1996**

**And Announcement of Ministry of Environment No.18 of 1999**

In stipulation of ordinance of Offensive Odor Control Law (the ordinance of Prime Minister's Office No.39 of 1972) Article 1, calculation method of odor index is defined as follows and this is applied from April 1 1996. The test method of the odor judgement with smell function (Announcement of Ministry of Environment No.92 of 1992) shall be ineffective on March 31 1996.

The calculation method of odor index and the odor intensity in stipulation of ordinance of Offensive Odor Control Law Article is shown in the attached table.

### **Attached table**

#### **Calculation method of odor index and odor intensity**

##### **First) Panel**

Panel (a person who judges the odor with smell function) shall a person who is recognized to have normal smell function by selection method 2 with the standard odor liquid.

##### 1 Standard odor liquid

Following 5 types of liquids are used;

Beta-phenyl ethyl alcohol	$10^{-4.0}$
Methyl cycro pentenolon	$10^{-4.5}$
iso-Valeric acid	$10^{-5.0}$
gamma-Undecaracton	$10^{-4.5}$
Scatol	$10^{-5.0}$

Note : the right column represent ratio of weight to non-smell flow paraffin.

##### 2 Selection method of panel

(1)Five sheets of test paper (length of 14 cm, width of 7 cm, hereinafter referred to "odor paper") expressed number 1 through 5 are prepared. One centimeter of any edge of the odor paper is dipped into the standard odor liquid (one type only) for two sheets of odor paper and similarly dipped into non-smell flow paraffin.



(2) Five sheets of odor paper are given to examinee (age over 18), examinee choose two of five sheets according to smell function.

(3) Processes of (1) and (2) are conducted for 5 types of standard odor liquid, the examinee who made correct response is recognized person with normal smell function.

(4) Above experiment is conducted in the period less than 5 years (3 years for age over 40) to confirm examinee's smell function.

### **Second)Equipment and apparatus**

Equipment and apparatus are as follows;

#### 1 Sampling equipment

(1) Sampling equipment for environmental sample

It shall be one of equipment listed in i) through iv).

i) Air tight glass sampling bottle with fluoride resin valve and ground glass part of 10 liter capacity.

ii) An equipment with sampling bag in the sampling suction bottle with following condition.

(i) Gas sampler is visible for sampling bag and air tight of 10 liter capacity.

(ii) Sampling bag is made of non-smell and low odor absorbing polyester (compound name : poly-ethylene terephtharate) film or equivalent of 10 liter capacity with suitable shape for gas sampling injector.

iii) Equipment that can deliver sample to the sampling bag through sampler pump that satisfies following requirement.

(i) Suction pump shall be able to air at 20 liter/minute, and made of non-smell material and low odor absorption is required.

(ii) Sampling bag shall be made of material 2-1-i)-(i) and capacity of 10 liter.

iv) An equipment in which the sampling bag is equipped inside the suction case with suction pump and the following requirement shall be satisfied.

(i) The sampling bag inside of the suction case is visible and is with air tight structure.

(ii) Sampler pump with air suction power of over 10 liter per minute and the gas through portion is changeable.

(iii) Sampling bag shall be made of material 2-1-i)-(i) and capacity of 10 liters.

## (2) Outlet sampler

An equipment that can collect sample in sampler bag through sampler pump or an equipment with sampler bag connected inside the suction case that the suction pump is mounted and that satisfy following requirement.

- (i) Sampler pump with air suction power of over 4 liter per minute and is made of non-smell material and low odor absorption is required.
- (ii) The sampling bag inside of the suction case is visible and is with air tight structure.
- (iii) Suction pump with air suction power of over 4 liter per minute.
- (iv) Sampling bag shall be made of material 2-1-i)-(i) and capacity of 3-20 liters.
- (v) Heat resistive sampler tube on outlet shall be used for high temperature gas. Gas washer bottle of capacity of 25ml shall be used for condensed water trap in case of highly moist sample.

## 2. Judge test equipment and apparatus

### (i) Air injection pump

Capable of air supply of 30 liter/min.

### (ii) Non-smell air supply apparatus

Smell of supplied air and air injection pump is deodorized in case of injecting non-smell air to odor bag.

### (iii) Injector

It is made of glass. Gas tight syringe shall be used for capacity less than 1 ml. Injector made of resin with similar air tightness as glass injector or gas tight syringe, or the injector made of low odor absorption and non-smell material can be used.

### (iv) Odor bag

It is made of non-smell and polyester film of low odor absorption and low transmission with capacity of 3 liter or equivalent, attached glass tube of inner diameter 10 mm and length 6cm.

### (v) Nose pad

Non-smell material and structure of direct nose covering and connected to the outlet of the odor bag.

### (vi) Silicon rubber cap

Seals outlet of the odor bag.

## Remark

Tubes used for apparatus connect which the sample passes through shall be made off

poly-fluoride vinyl of low odor absorption capability.

### **Third) Measurement method**

Measurement shall be conducted as follows. In case of measurement by panel, the measurement shall be managed by a person who is recognized to have proper smell function and to be the expert of the odor index measurement.

#### 1 Sampling and flow rate measurement

##### (1) Environment sample

According to type of sampling equipment, sample is introduced to sampling container or sampling bag by one of following methods.

- i) A method of sampling by opening a valve of sampling container depressurized below 1.3 kPa for 6 to 30 seconds, in case of equipment listed in 2-1-(1)-(i)
- ii) A method of sampling a quantity of sample corresponding to sampling bag by using sampling bottle for 6 to 30 seconds in case of equipment listed in 2n 2-1-(1)-(ii)
- iii) A method if bay calculate sample for 6 to 30 seconds in case of equipment listed in 2-1(1)-(iii).

##### (2) Outlet sample

A method of collecting 3 to 10 liter sample for one to 3 minutes in case of equipment listed in 2-1-(2).

##### (3) Flow rate measurement

Gas flow rate at the emission point of the gas (unit : cubic meter per second at 0 degree Celsius and 1 atm.) is a value that measured by method specified in JIS Z8808 and by using unit of flow per second.

#### 2 Judgement test

##### (1) When to perform judgment test

Judgement test (A test made by panel to judge existence of odor in odor bag. Hereinafter referred in the same manner.) shall be conducted as soon as possible on the day of sampling or the next day.

##### (2) Number of panel

More than 6 panels who are previously selected by 1-(2) are employed for the test.

##### (3) Place to perform judgment test

The test is performed in a place where the ventilation or window is equipped and no odor shall be existed and the panels can relax in the facility.

(4) Procedure of the judgment test

i) Environmental sample

Sample is prepared in one of three odor bags filled with non smell air and sealed with silicon rubber, by introducing sampling gas with injector and diluted to the dilution ratio for the first test (Hereinafter referred to "First dilution ratio") (note 1). Prepared odor bag (hereinafter referred to "smell odor bag") and two odor bag with non-smell air (hereinafter referred to "non-smell odor bag") are given to the panel. Panel selects on odor bag that he/she suspects that odor substance is injected. (It is called "selecting operation". Hereinafter referred in the same manner.) The selecting operation is repeated three times by each panel.

For selecting operation performed by each panel, correct answer point, 1.00 is given to the panel in case of selecting smell odor bag, 0.00 is given to the panel in case of selecting non-smell odor bag and 0.33 is given in case where selection is disabled. The summation of correct answer points is divided by number of selection made by panels. The average correct point is less than 0.58, the judgement test is finished. In case where the average correct point equals to or is greater than 0.58, the dilution ratio is set 10 times greater than original value and perform the same operation above, then the judgment test is finished.

(note 1) The first dilution ratio shall normally be 10. However, in case where the average correct answer point can be estimated to equal to or be greater than 0.58, the first dilution ratio is decided to value greater than 10 for the value of average correct point to be lower than 0.58.

ii) Emission point sample

Selecting operation is conducted by each panel for one smell odor bag and two non-smell odor bag that are prepared at the first dilution ratio (note 2) in the same manner as 3-2-4-i). In this selecting operation, the test is finished for the panel who selected non-smell odor bag or could not select. The test is further performed by using sample diluted by three times for the panel who selected smell odor bag, then the test is finished in case where the panel selects non-smell odor bag or is unable to select.

(note 2) The first dilution ratio shall be the value that the panel is able to make decision of existence of odor and to avoid the effect of exhausted smell function.

3 Calculation of odor index

(1) Environment sample

The odor index is calculated by following equation;

However in case where the average correct answer point for the first dilution ratio is 0.58, the value of the odor index is indicated the value less than  $10\log M$ . In case where the value Y has fractional number less than 1, the odor index is rounded value of Y.

where Y is odor index, M is the first dilution ratio, r1 is the average correct answer point

$$Y = 10 \log \left( M \times 10^{\frac{r_1 - 0.58}{r_1 - r_0}} \right)$$

and r0 is the average correct answer for the first dilution ratio multiplied by 10.

(2) Emission point sample

i) Threshold of each panel is calculated for the dilution ratio of the sample odor by following equation.

$$X_1 = \frac{\log M_{11} + \log M_{01}}{2}$$

where X1 is a threshold of a panel for the dilution ratio of sample odor, M1i is the maximum of the dilution ratio for odor bag in case where the panel selects the smell odor bag, M0i is the dilution ratio for odor bag in case where the panel selects the non-smell odor bag or could not select the bag.

ii) After eliminating minimum and maximum of calculated Xi for panel, all the values except eliminated values were added and the summation is divide by number that is two less than number of panels.

iii) Calculation made by using following equation. However, in case where the value Y has fraction number less than 1, the odor index is rounded value of Y.

$$Y = 10X$$

where Y is the odor index and X is the value that is calculated by ii) shown above.

4 Calculation method of odor intensity

(1) Odor concentration of the sample odor is calculated by the following equation;

$$C = 10^{\frac{Y}{10}}$$

where Y is the odor index that is calculated by method of previous paragraph.

(2) Odor concentration of the sample odor is calculated by the following equation;

$$q_d = 60 \times C \times Q_0$$

where  $q_d$  is odor intensity (unit : cubic meter per second at 0 degree Celsius and 1 atm.),  
 $C$  is the value calculated in (1) and  $Q_0$  is flow rate of the exhaust gas (unit : cubic meter per second  
at 0 degree Celsius and 1 atm.).