Ⅱ　Odor Measurement Review

1. Policy Frameworks and Role of Measurement

The History of Odor Measurement in Japan and Triangle Odor Bag Method

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Abstract
An outline of the history of odor measurement methods in Japan is mentioned in this paper. The syringe method was widely used about 30 years ago. This method, however, had the several disadvantages.
In order to eliminate these disadvantages, the syringe was replaced by a plastic bag (polyester film) with a 3 liter volume and any preconception of the panel was removed by adopting a triangle test. This new method (Triangle Odor Bag Method) was published for the first 1972 by the author. The outline, procedure and precision of this method were printed in this paper.

1. History of odor measurement in Japan

For odor measurement, there have been instrumental methods which use instruments such as gas chromatograph to determine the odorous gas concentration in ppm and olfactory sensory methods which use the human sense of smell.
The results of the olfactory sensory methods are represented by odor intensity, allowable limit (or acceptability), and odor concentration. Particularly, the last one has widely been used in Japan and foreign countries such as the European countries and the United State of America with high reliability.
Odor concentration is indicated by the dilution ratio, that is, pure air volume required to dilute odorous air to an odor threshold point (odor free point).
In Japan, the A.S.T.M. syringe method[1)] that was published in 1960 by N.A.Huey[2)], had been widely used as a means of measuring odor concentrations until about 30 years ago. This method, however, had the following several disadvantages .
(1) Small volume of syringe (100ml).
(2) Adsorption of odor on syringe surface.
(3) Long preparation time of highly diluted sample.
(4) Occurrence of unnatural feeling when sniffing odor from the syringe into nose.
(5) Influence of preconception of panel members.

Our data obtained by the A.S.T.M. syringe method at that time was very scattered.
In order to eliminate these disadvantages, the syringe was replaced by a plastic bag (polyester film) with a 3 liter volume and any preconception of the panel was removed by adopting a triangle test.
This new method (Triangle Odor Bag Method) was published for the first time at the

annual meeting of the Japan Society for Atmospheric Environment in 1972 by the author. The details (sampling, procedure, calculation, etc.) of this method will be explained later.

Next, I will explain the odor measurement methods, except for the Triangle Odor Bag Method. From the late 1970s, we imported the Scentometer[3) from The Barnebey-Cheney Company located in the United States of America and investigated the credibility of this method such as dilution accuracy, repeatability and so on. As a result, the Scentometer was scarcely fit for use.

In the early 1970s, some institutions in Japan made a respective Olfactometer similar to that used in European countries. Some instruments adopted the 2-step dilution method and some equipment adopted a triangle test.

In 1973, a certain Japanese company placed the Olfactometer on the market. However, adsorption loss of odors on the inner surface of the gas line of the olfactometer in those days could not be disregarded. For this reason, the production of the olfactometer was stopped after the several years.

We investigated the accuracy and availability of the various odor measurement method mentioned above from 1970 to 1990.

After 1974, in Japan, many local governments such as Tokyo, Saitama, Niigata, Yamaguchi and so on adopted the Triangle Odor Bag Method[4)5)] for the measurement method for local odor regulations or ordinances. The national government adopted this method for the Odor Control Law in 1997.

Now, the production of the bags has reached one million bags per year in Japan. The sample number measured by the Triangle Odor Bag Method may be over 10,000 samples.

2. Triangle odor bad method

2.1 Introduction

The A.S.T.M. syringe method had widely been used as a means of measuring odor concentration in Japan, as already mentioned. The syringe method was very easy for measurements at the sources of offensive odor, and there were many examples of this type of measurement till 1975 in Japan.

However, because of the unreliability of obtaining reproducible concentration values, it has been considered that the syringe method is useful only for a rough estimation of odor and not for precise administrative regulation. This paper presents a new Triangle Odor Bag Method which is almost completed after many investigations.

In order to eliminate the disadvantages mentioned above, a 3 liter plastic bag is used instead of the 100 ml syringe. The diluted sample is prepared in the bag by filling it with odor free air and injecting a certain amount of odor sample（primary odor）into it. In this way, the use of the odor bag eliminates (1), (2) and (3) described in a previous paper. (4) is eliminated by breathing odor in the bag using a nose cone.

For elimination of (5), we adopted the triangle method, that is , each panel chooses one bag having odor out of 3 bags in order to obtain more objective results.

2.2 Panel

The sensory method is done using the human nose. It is very important to investigate the scattering of the human olfactory sense results. We used the 5 standard dilution liquids that were developed by Takagi et al. in about 1972. These standard odorants are called “the T&T olfactometer”. These standard odorants are now on the market.
We have investigated the data scatters of the olfactory sense for about 1,000 Japanese. The following results were obtained.

(1) The number of dysosmia, who are unsuitable as panel members, was about 5% of the total study subjects and the ratio increased with age.
(2) The mean threshold difference between the sexes depended on the quality of the odor.
(3) It is evident with age that the olfactory sensitivity to isovaleric acid declines at the rate of 30% per 10 years, which corresponds to a 50% loss of sensitivity in 20 years. Based on the condition of health, the slightly poorer group achieved a lower threshold than the ordinary group.
(4) As a result of analyzing the accuracy of the measured values from the olfactory thresholds of normal subjects, the probability between ±10% of the population mean was about 91% in case of 4 panel members.
When the panel members is 6, it was about 95%.

2.3 Panel screening test

The panel screening test is done using standard 5 odorants. The concentration of the odorants is as follows (dilution liquid is odor-free liquid paraffin).

β—phenyl ethyl archole	$10^{-4.0}$ w/w
methyl cyclo pentenorone	$10^{-4.5}$ w/w
isovaleric acid	$10^{-5.0}$ w/w
γ—undecaractone	$10^{-4.5}$ w/w
Skatole	$10^{-5.0}$ w/w

(1) The 5-2 method is adopted as the procedure for the panel screening test.
(2) 5 odor-free papers (size: 14cm × 7mm) are prepared. We soak the top 1 cm of 2 papers in a standard odorant liquid. The remaining 3 papers are soaked in the odor-free liquid paraffin using the same method.
The subjects sniff the 5 papers, and report the 2 papers that contains the odor
(3) Each subject is tested for the 5 standard odorants using the same above mentioned method.
(4) The subject whose answers are all correct for the 5 standard odorants is passed in the panel screening test.

2.4 Instruments

2.4.1 Sampling instruments

(1) For sampling of odorous flue gas

① Pump
Diaphragm pump
Exhaust capacity is greater than 5 liters/min.

② Sampling bags
Polyester bags or polyvinyl fluoride bags
The capacity of this bag is about 15 liters.

(2) For sampling of odorous ambient air

① Pump
Fan-type pump in general. Exhaust capacity is greater than 20 liters/min.

② Sampling bags
Polyester bags or polyvinyl fluoride bags
The capacity of this bag is about 15 liters

2.4.2 Instruments for olfactory sensory test

(1) Pump to send odor-free air
Diaphragm pump or non-oil pump
Exhaust capacity is greater than 30 liters/min.

(2) Syringe
Glass syringe with volume of 5 to 200 ml and PS gas syringe of 1 ml or less in volume

(3) Odor bag
Polyester bag with glass pipe （outer diameter of 12 mm and length of 6 cm）and labeled No.1 to 3

(4) Nose cone
It is made of hard polyvinyl chloride, nose shaped cover and connected to the glass pipe of the odor bag.

(5) Odor-free air supply equipment
Holder with activate carbon

2.5 Sampling

2.5.1 Method for sampling of odorous flue gas

(1) Sampling time is 1-3 minutes.

(2) We must use an odor-free pump such as a diaphragm pump, for the direct sampling method.

(3) Sampling volume is about 10 liters. Material of sampling bag is usually polyester. （refer to Fig.1）

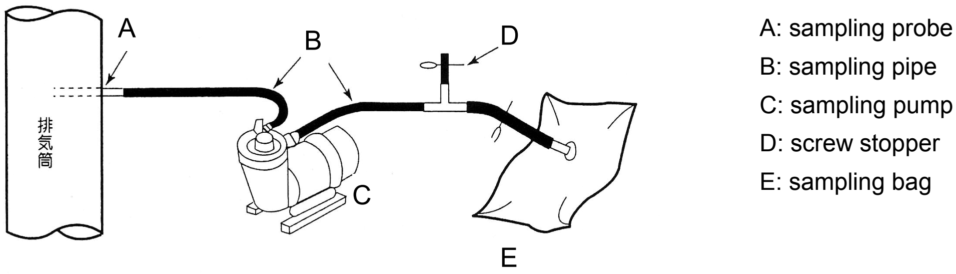

Fig.1 Sampling of odorous flue gas

(4) When moisture of flue gas is at a very high level, it is better to have a drain trap between the sampling probe and sampling bag for the purpose of avoiding condensation in the sampling bag.

- The indirect method has the advantage of avoiding odor contamination in the sampling pump, but sampling is very difficult when the pressure of the inner duct is very low.
- Sampling must be done on the sensory test day or on the previous day.

2.5.2 Method for sampling of odorous ambient air

(1) Sampling time is 6-30 sec.
(2) We must use odor-free pump such as a fan-type pump. The capacity of the sampling pump must be over 30 L/min.
(3) Volume of sampling bag is about 15 liters,
(4) Sampling volume is at least 10 liters.
(5) Material of sampling bag is usually polyethylene terephthalate.
(6) The sampling is carried out when the odor is strong. Method of the sampling is shown in Fig.2. Odor is sampled in a bag after 1 to 2 exchange of the odor between the outside air and inside of the bag.

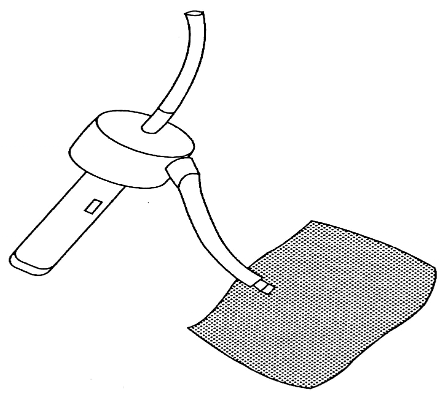

Fig.2 Sampling of odorous ambient air

2.6 Sensory test

2.6.1 Abstract

One bag is the odor bag into which a certain amount of the primary odor is injected and the two other bags are filled with only odor-free air.

Panel tests to determine the odor concentration are carried out by means of dilution, that is, the test is started with a concentration that the panel can easily recognize the odor, and the dilution ratio is successively diluted approximately 3 times in any step of dilution when the answer of the panelist is correct. It is continued until an incorrect answer occurs.

In this way, panels can easily distinguish the odor sample and avoid the risk of coincidence with the concentration ascending method. The dilution of approximately 3 times is adopted because of the distinguishable limit of the human olfactory and convenience in the preparation of diluted sample.

Usually the maximum dilution ratio of the correct answer has been taken for each panel to determine the threshold concentration, but in the present method, the mean maximum dilution ratio coupled with the correct answer and minimum dilution ratio coupled with incorrect answer is used to represent the concentration.

For the final presentation of the result using the present method and not the mean of the threshold concentrations for 6 panels, but the mean of the threshold concentrations for 4 out of 6 panel test results which excludes the maximum and minimum values is taken. This is to avoid the influence of an anomalous threshold value due to panelists who are ill on the test day or make a mistake in writing down the number of dilutions. These mistakes are possible even if they have a normal olfactory.

An odor scale, which is the logarithm of the odor concentration is introduced to indicate similar scale to the human sense. The odor scale corresponds to decibels in sound level.

The screening of a panel is performed based of the conception of J. Amoore, that is, the screening is not for the selection of the ones having an excellent olfactory sense but for ones who have an average olfactory sense, provided that those having an abnormal sense are excluded.

2.6.2 Panel member

A panel consists of over 6 panelists. It is necessary for each panelist to be over 18 years old. All panelist need to pass the panel screening test.

2.6.3 Procedure

(1) Fill 3 odor bags with odor-free air until the bags are almost full and closed with silicone rubber stoppers. Beforehand, completely exchange the remaining air in the bag with odor-free air.

(2) Inject primary odor taken from a sampling bag into one of the odor bags through its label. Its injection volume should meet the required concentration.

(3) The other 2 bags are filled only with odor free air, holes are marked on the labels of the bags by the syringe needle, and the bags are delivered together with an odor-filled bag to a panelist.

(4) The panel sniffs the air in the bags with his or her nose which is connected to glass pipes and lists the number of the bag from which he or she senses an odor.(refer to Fig.3)

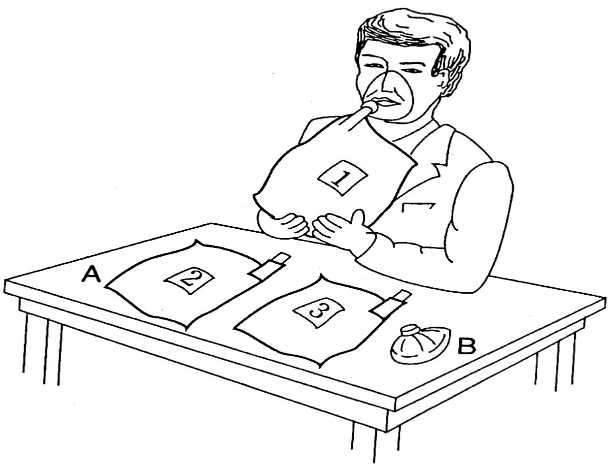

Fig.3　Triangle Odor Bag Method

(5) When his or her answer is correct, the same procedure is carried out at the next stage in which the odor is diluted approximately 3 times. This procedure is continued until the panel gives an incorrect answer and then test by the panel is finished.

2.7　Calculation

2.7.1　For the emission point sample

(1) Threshold values are calculated for each panelist using the following formula (For example, Panelist A).

$Xa = (\log a1 + \log a2) / 2$
Xa : threshold value for panelist A
a1 : correct maximum dilution ratio
a2 : incorrect minimum dilution ratio

(2) Mean of the threshold values calculated for each panelist in (1) excluding minimum and maximum values is taken as the threshold value for a group of all the panelists.
(3) The odor concentration is calculated by converting the threshold value obtained in (2) as follows:

$Y = 10^X$
X : threshold value for a group of all panels
Y : odor concentration

(4) Introduce order index（Z）as follows.

$$Z = 10 \log Y = 10X$$

2.7.2 For an environmental sample (site borderline sample)

As for a sample collected on the site borderline, the selected operations mentioned above are carried out three times for each panel at the dilution rate of 10 as a rule. We calculated the average correct answer rate as follows.
The scores ”correct answer = 1.00”, ”incorrect answer = 0.00” and “unknown = 0.33” to various results, and the average correct answer rate is obtained for all the answers. When the average correct answer rate falls below 0.58, the sensory test will stop, and the final odor index of the sample is below 10.
When the average correct answer rate becomes greater than 0.58 with the initial dilution rate, the same operation will be repeated at the second operation (dilution rate = 10 × initial dilution rate).
The final odor index of the odor sample is calculated using the following equation.

$$Y = 10 \log \{M \times 10^{(R1-0.58)/(R1-R0)}\}$$

where
Y : odor index
M : the dilution rate 10 at a rule
R1: average correct answer rate obtained from the first operation
R2: average correct answer rate obtained from the second operation
(dilution rate = 100 as a rule)

3. Precision

3.1 Volume error of the odor bags

The size of the odor bag（25cm × 25cm） is specified as a volume of approximately 3 liters when filled with the odor-free air. The variation in the volume of the odor bags was measured. Table I shows the variation when ten operators separately prepared 12 bags filled with odor-free air. The measurement is taken as follows. At first the air in the bag is pumped out by a diaphragm pump through a syringe needle which is inserted through a silicone rubber stopper and the air volume in the bags is measured with an authorized wet-type gas meter.

The errors in the volume in comparison with the specified volume of 3 liters are as follows. For 7 operators out of 10, the errors for all of the 12 bags are within ±150 ml (5% of 3,000ml) and for the remaining 3 operators, one of their measurements was more then 150ml, that is, +170ml, +152ml and -219 ml . Regarding the operator to operator variation, the maximum average for one operator is 3,108 ml and the minimum is 2,929 ml. Based on our opinion, the allowable error for this kind olfactory testing is about 10%, so that the above results are within the limit both personally and interpersonally.

Table 1　Fluctuation in the volume of the odor bag

Operator	A	B	C	D	E	F	G	H	I	J
N	12	12	12	12	12	12	12	12	12	12
Min	2966	3067	3038	2875	2870	2897	2954	2924	2978	2981
Max	3170	3152	3145	3003	2983	3030	3056	3048	3117	3017
Ave	3108	3103	3100	2938	2929	2986	2999	2996	3059	2961
S.D.	50	23	31	31	32	43	33	33	41	59

3.2　Diffusion speed of odor in the odor bags

For preparing the odor bag, the primary odor sample is injected through the label as mentioned before. We examined the diffusion speed of the odorants in the bag using the following experiment. The odor bag was filled with odor-free air and then an odorous gas sample of 3 ml was injected into it. 1 ml of the sample at a corner of the bag（2 cm away from the corner）is periodical sampled with a syringe and the concentration of the odorants determined by gas-chromatography.

The final concentrations are 70 ppm for CH4, 0.4 ppm for CH3SSCH3, 7 ppm for C6H4CH3, and 4 ppm for CH3COC2H5.

Fig.4 shows the diffusion speed of the odorants versus time.

The vertical axis indicates the ratio of the concentration of the odorants in the air sampled at the corner of the bag to that after they have completely diffused. The figure shows that all the gases completely diffused within one minute.

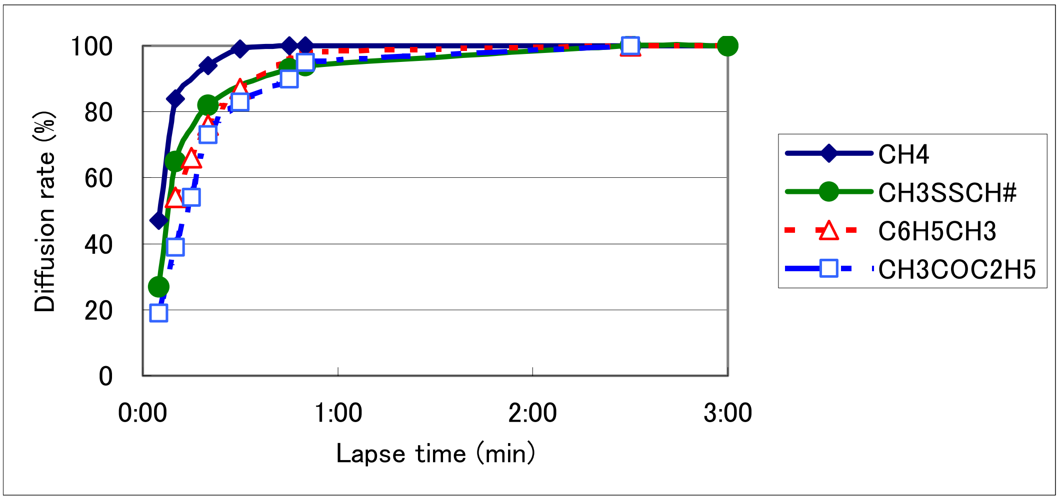

Fig.4　Diffusion rate of odorants in the odor bag

3.3　Stability of sample gases in the sampling bag

To examine the stabilities of odorous sample gases, we used typical offensive odorants and field sample gases. We investigated the relationship between the odor concentration and the time required since the sample gases added to the sampling bag. Six panelists examined the odors on all of the days. The odor samples were dry exhaust odor from a fishmeal plant, indoor air of chocolate manufacturing plant and exhaust gas from incinerator of sewage sludge cake, and drying exhaust air from gravure printing industry. As shown in Fig.5, the measured results remain unchanged for several days after the samplings.

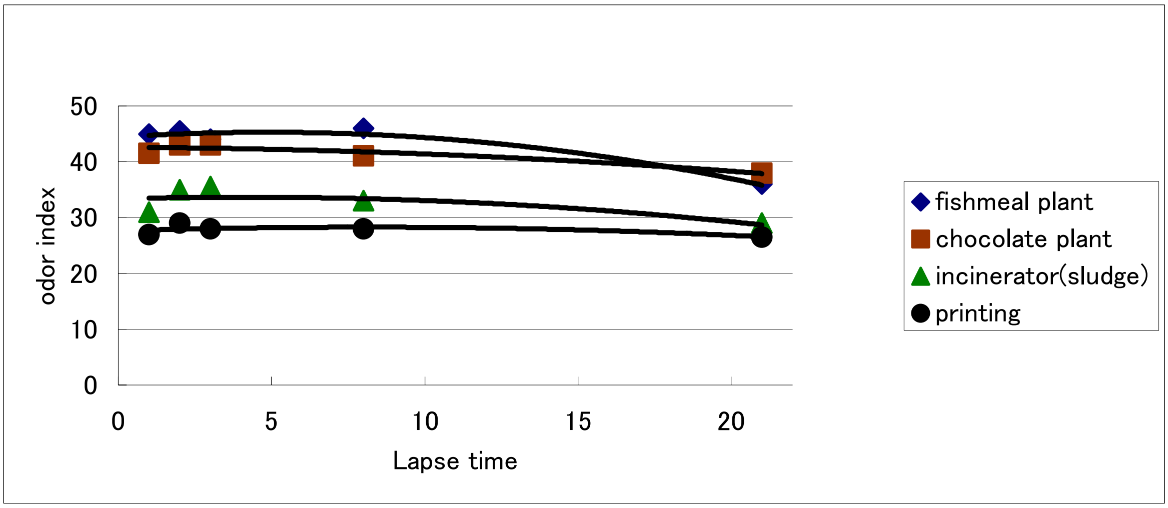

Fig.5 Stability of odors in the sampling bag

3.4 Influence of panel on precision of odor measurement

Panel selection and their number have a strong influence on the precision of the odor measurement. Abnormal olfactory persons are to be excluded by panel screening test, but it is not expected that all of them are excluded through the panel screening test indicated in 2.3). Sometimes it is also probable that some one gets ill on the test day. To exclude these problems, the Triangle Odor Bag Method adopted the mean of calculation method averaging with removal of the maximum data and minimum data.
Thus it might be mentioned that the influence from any olfactory abnormality is almost totally excluded.
It is natural that increasing of the number of panel members would increase the reproducibility of the measurement results.

4. Measurement Results by Triangle Odor Bag Method

The measurement results taken at the odor sources by the Triangle Odor Bag Method are shown in Table 2. The odor concentrations of the exhaust gas from the offset printing were higher than that of the exhaust gas from gravure printing. This result corresponds to actual complaints near the odor sources.
As for metal printing, the odor intensity depends on the quality of the ink used. The measured printing factories had odor control instruments of the activated carbon type or catalytic combustion system. The concentrations at the printing factories were measured upstream of the odor control apparatus.
The results for the dried exhaust air of the fish meal plant showed a high odor concentration of 31,000. This value was reasonable considering the severe trouble caused by this type of industry.
The sludge cake incinerator of the vertical multistage incineration type was exhausted directly without going through a high temperature combustor. For this reason, the odor concentration for this type was at a very high level.

The results for boilers showed that the odor concentration of the exhaust gas depended on the type of fuel used. For city gas or kerosene, the odor concentrations were very low, but the concentration was rather high for heavy oils A and C.

Table 2 Measured results of odor concentrations at the odor source

Type of industry	Sampling point	Odor concentration	Odor index
printing (gravure)	drier outlet	410 ～ 1700	26 ～ 32
〃 (off-set)	〃	9700 ～ 41000	40 ～ 46
〃 (metal)	〃	1700 ～ 31000	32 ～ 45
fish meal	〃	31000	45
Food (chocolate)	roaster outlet	41000	46
〃 (〃)	kneading room	13000	41
〃 (curry)	mixing room	1300	31
〃 (chewing gum)	mixing room	23000	44
Incinerator (refuse)	stack inlet	1300 ～ 1700	31 ～ 32
〃 (sludge cake)	〃	970 ～ 3100	30 ～ 35
boiler (city gas)	〃	97 ～ 310	20 ～ 25
〃 (kerosene)	〃	97 ～ 310	20 ～ 25
〃 (heavy oil A)	〃	550	27
〃 (heavy oil C)	〃	4100	36
〃 (waste wood)	〃	1300	31

Odor index = 10 × log(odor concentration)

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