

## 【 Reference 3 】

**Odor measurement in Japan**

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## ABSTRACT

The triangular odor bag method, the most popular olfactory sensory test in Japan, was first developed in 1972, and introduced into the Offensive Odor Control Law in 1995. This is an air dilution method in which “odor index” is measured. In recent years, the necessity of developing quality control system for olfactometry and standardization of measurement procedure for the promotion of nationwide spread of olfactometry has been recognized. This paper presents about the measurement procedure of the triangular odor bag method, establishment of quality control framework for olfactometry, including selection of a reference odor, development of reference odor preparation technique, interlaboratory comparison of olfactometry, and key elements of quality control manual. Nationwide comparison of olfactometry in 2002 and 2003 is also discussed.

## 1. INTRODUCTION

The Offensive Odor Control Law enacted in 1971, regulated “specific offensive odor substances” arising from the activities at factories or other businesses at the beginning. According to the Law, the concentrations of these substances should be measured by gas chromatography or other instruments. There, however, have been many cases in which odor complaints cannot be adequately evaluated by those instrumental measurements. A considerable number of complaints has been observed in which, for example, none of the designated substances is not detected or the concentrations of the specific offensive odor substances fall below the regulation standards.

To deal with these problems, various investigations on olfactometry have been carried out, mainly by local governments. The triangular odor bag method, the most popular olfactory sensory test in Japan, was first developed by Tokyo metropolitan government in 1972.<sup>1)2)</sup> This is an air dilution method in which “odor index” (logarithm of odor concentration, multiplied by ten) is measured. Following these advances of olfactometry, the Japan Ministry of the Environment investigated the possible use of the triangular odor bag method. Subsequently, the Offensive Odor Control Law was amended in 1995 and the regulatory method by means of olfactometry (the triangular odor bag method) was newly adopted. The regulation by means of

olfactometry is to be applied to the cases in which odor complaints cannot be adequately evaluated by the instrumental measurements of the specific offensive odor substances.

In this paper, measurement procedure of the triangular odor bag method is briefly explained, and the establishment of quality control framework for olfactometry is discussed. Nationwide comparison of olfactometry, which was carried out in order to evaluate proficiency of olfactometry laboratories in Japan, is also mentioned.

## **2. TRIANGULAR ODOR BAG METHOD**

The triangular odor bag method was notified in 1995 (Notification No. 63 of the Ministry of the Environment, 1995) as follows:

### 1) Panel

A panel should consist of six or more members. They are required to have passed the screening test of using five kinds of standard odor.<sup>3)</sup>

### 2) Sampling

Samples are taken at smoke stacks or boundary lines of the site. Polyester bags or vacuum bottles are used as containers.

### 3) Apparatus

An apparatus necessary for practicing judgment is as follows:

- a) A pump for supplying odorless air into odor bags.
- b) A gadget for feeding odorless air which consists of a column packed with activated carbon and multi-way piping.
- c) Glass syringes for injecting odorous air into odor bags.
- d) Polyester odor bags, with a piece of glass tube fixed at the corner, with a capacity of 3 liters.
- e) Nose cones.
- f) Silicone rubber stoppers.

### 4) Procedure for ambient air

Measurements for samples taken at boundary lines are made as follows:

- a) Three odor bags numbered from 1 to 3 per panel member are prepared.
- b) These odor bags are filled with odorless air passed through the activated carbon column, and plugged up with silicone rubber stoppers.
- c) Odorous air is injected into one of three odor bags until a given dilution ratio is obtained.
- d) Each member of the panel removes the stopper and sniffs by bringing the odor bag close to one's nose. After sniffing three odor bags, one should choose only one odor bag which is likely to contain odorous air out of three bags, and write down the number of the bag one chose.

- e) The test is carried out three times per each panel member for the same dilution ratio.
- f) Replies made by the panel members are collected and compiled. The rate of correct answer 1.00 is assigned to a correct reply, 0.00 to a wrong reply, and 0.33 to a reply “I cannot identify.”
- g) The mean rate of correct answer for all replies is calculated. If the mean is 0.58 or more, the next session in which the sample is diluted ten times further is carried out. If the mean is less than 0.58, a series of the test ends.
- h) Odor index of the sample is calculated by Equation (1).

$$Y=10\log \{M \cdot 10^{(r_1-0.58)/(r_1-r_0)}\} \quad (1)$$

In Equation (1),

Y=odor index.

M=the maximum odor dilution ratio when the mean rate of correct answer is 0.58 or more.

r<sub>1</sub>=the mean rate of correct answer when odor dilution ratio is M.

r<sub>0</sub>=the mean rate of correct answer when odor dilution ratio is 10M.

The starting dilution ratio of this method is ordinarily fixed at ten. When the rate of correct answer at the dilution ratio ten is less than 0.58, the odor index should be “below ten.” In this method, odor index value less than ten cannot be measured, since it is difficult to get sample dilution ratio less than ten.

#### 5) Procedure for source air

Measurements for samples taken at smoke stacks or other gas emission facilities are made as follows:

Steps a)-d) are identical to those of the procedure for measurement at boundary lines.

- e) Replies made by the panel members are collected and compiled. If one made a correct reply, one should participate in the next session in which the sample is diluted three times further, and repeat the above steps a)-d). If one made a wrong reply or could not identify the odor, one should end a series of the test. The test should be continued until all panel members make wrong replies.

- f) Odor index of the sample is derived from the following steps:

First, the odor threshold value (logarithm) of each panel member is calculated by Equation (2).

$$X_i=(\log M_{1i}+\log M_{0i})/2 \quad (2)$$

In Equation (2),

$X_i$ =odor threshold value (logarithm) of a panel member.

$M_{1i}$ =the maximum odor dilution ratio when the panel member made a correct reply.

$M_{0i}$ =odor dilution ratio when the panel member made a wrong reply or could not identify the odor.

Then, among these odor threshold values of the panel members, the maximum and the minimum are removed and the mean of the rest ( $X$ ) is calculated. Finally, the odor index is obtained by Equation (3).

$$Y=10X \quad (3)$$

### 3. QUALITY CONTROL FRAMEWORK FOR OLFACTOMETRY

In recent years, the necessity of developing quality control system for olfactometry and standardization of measurement procedure for the promotion of nationwide spread of olfactometry in municipalities has been recognized.

#### 3.1 Reference odor for olfactometry

Reference odor is necessary in order to conduct interlaboratory comparison of olfactometry as well as routine verification of measurement results in each olfactometry laboratory. Four odorous compounds (*i.e.*, *n*-butanol, ethyl acetate, *m*-xylene, and dimethyl sulfide) were proposed for reference odor. In Europe, *n*-butanol is defined to be a reference odor in CEN standard EN 13725: 2003.<sup>4)</sup> Ethyl acetate is one of “specific offensive odor substances” designated in the Offensive Odor Control Law, and *m*-xylene and dimethyl sulfide are compounds used as reference odors in previous interlaboratory comparison in Japan. Reference odor for olfactometry should fulfill the following requirements:

- Odor sample should be prepared easily and accurately.
- Odor sample should remain stable for a period of the measurement.
- Odor threshold values of panelists should not vary widely.
- Odor quality should be easily recognized.
- Low health and psychological effect on operators and panelists should be ensured.

Considering all these things, ethyl acetate was selected as a reference odor for olfactometry in Japan. Although *n*-butanol is designated as a reference odor in CEN EN 13725, it was not selected because there is less measurement data for *n*-butanol in Japan and ethyl acetate has the advantages in sample preparation and data accumulation.

### 3.2 Preparation of reference odor

Easy-to-operate and cost-effective technique for reference odor preparation is necessary to be employed in nationwide municipalities and olfactometry laboratories. On the assumption that reference odor sample with odor concentration of two to three thousand is appropriate to be used in quality control process, the concentration of ethyl acetate is calculated to be around 2000 ppm in consideration of odor threshold of 0.87 ppm.<sup>5)6)</sup>

Four preparation methods for reference odor (*i.e.*, steel cylinder method, standard gas generator method, odor bag/vacuum bottle method, and handy gas cylinder method) were proposed. Steel cylinder containing ethyl acetate of 2010 ppm was specially ordered. In odor bag/vacuum bottle method, an odor bag or a glass vacuum bottle is employed to vaporize ethyl acetate reagent. These four preparation methods were verified at three olfactometry laboratories and confirmed to be applicable to quality control processes.

### 3.3 Interlaboratory comparison of olfactometry

In 2000 and 2001, interlaboratory comparison of olfactometry was carried out in order to collect basic data for the establishment of quality control procedure and the determination of quality control criteria for the triangular odor bag method.

#### 3.3.1 Methods

In 2000, interlaboratory comparison was conducted by using measurement method for samples taken at smoke stacks. A total of seven olfactometry laboratories in Japan participated in the test. A three-liter-capacity sampling bag filled with ethyl acetate of around 2000 ppm was delivered to each laboratory four times. Odor index of each sample was measured according to the official procedure of the triangular odor bag method. The tests were conducted six times over four days (*i.e.*, three times for the second sample and only once for other three samples). Steel cylinder method was used to prepare reference odor, *i.e.*, ethyl acetate of 2010 ppm. Gas concentration of each sample was analyzed with GC-FID just before the delivery.

In 2001, interlaboratory comparison was carried out by using measurement method for samples taken at boundary lines. A sampling bag with the capacity of 20 liters filled with ethyl acetate of around 50 ppm was delivered to each laboratory four times. Steel cylinder method was used to prepare reference odor, *i.e.*, ethyl acetate of 50.9 ppm.

Other measurement conditions were identical to those in 2000.

### 3.3.2 Results

Mean values, repeatability standard deviations, and reproducibility standard deviations of detection thresholds were calculated from the results according to JIS Z 8402-2: 1999<sup>7)</sup>, which is Japanese version of ISO 5725-2: 1994 as shown in **Table 1**. In practice, logarithms of detection thresholds were used for the calculation of these values. Statistical data depicted in **Table 1** can be used to determine quality control criteria for the triangular odor bag method.

Table 1. Mean values ( $m$ ), repeatability standard deviations ( $s_r$ ), and reproducibility standard deviations ( $s_R$ ) of logarithms of detection thresholds obtained from interlaboratory comparison in 2000 and 2001.

Measurement method (Year)	$m$	$s_r$	$s_R$
For ambient air (2001)	-0.10	0.13	0.24
For source air (2000)	-0.26	0.17	0.22

### 3.4 Quality control manual

On the bases of foregoing discussions about reference odor and interlaboratory comparison, quality control manual for laboratory use was published in 2002. **Figure 1** shows quality control framework for olfactometry in a laboratory. The fundamental topics in the manual are as follows:

- Establishment of quality control system and organization in a laboratory
- Education and training of staff concerned
- Documentation of measurement processes
- Preparation of standard operating procedures (SOPs)
- Evaluation and report of measurement results
- Regular internal quality checks using reference odor
- Occasional proficiency tests using certified reference odor

On the basis of collaborative assessment experiment, accepted reference value, repeatability, and reproducibility of reference odor are obtained. Then individual olfactometry laboratory is able to carry out regular quality checks and compare the results with these values.

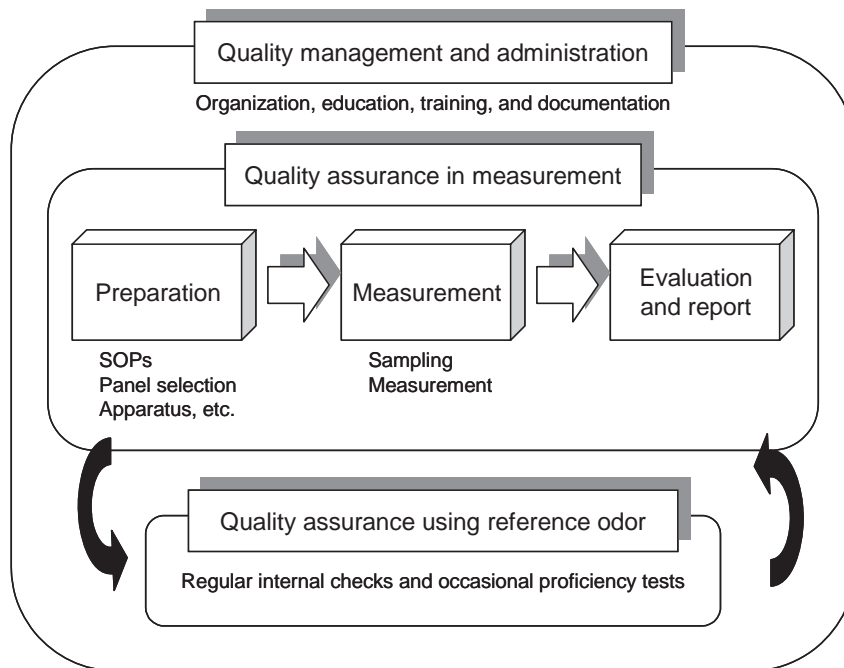


Figure 1. Quality control framework for olfactometry.

#### 4. NATIONWIDE COMPARISON OF OLFACTOMETRY

In 2002 and 2003, nationwide comparison of olfactometry was carried out in order to evaluate proficiency of olfactometry laboratories in Japan.

##### 4.1 Methods

In 2002, nationwide comparison of olfactometry was conducted by using measurement method for samples taken at smoke stacks. A total of 137 olfactometry laboratories in Japan participated in the test. A handy gas cylinder filled with ethyl acetate of around 2000 ppm was delivered to each laboratory. Odor index of the sample was measured only once in each laboratory according to the official procedure of the triangular odor bag method.

In 2003, a total of 120 olfactometry laboratories in Japan participated in the test. A handy gas cylinder filled with odor mixture of ethyl acetate (2000 ppm) and *m*-xylene (94 ppm) was delivered to each laboratory. Odor index of the sample was measured three times within one day in each laboratory according to the official procedure of the triangular odor bag method.



## 4.2 Results and discussion

A distribution of odor index obtained from 137 olfactometry laboratories in 2002 is depicted in **Figure 2**. The mean value and standard deviation were 34 and 3.3, respectively. Theoretical odor index of the sample is calculated from the concentration of ethyl acetate filled in the handy gas cylinder (2000 ppm) and the detection threshold of ethyl acetate shown in **Table 1** (antilog of  $-0.26=0.56$  ppm) as follows:

$$10\log (2000/0.56)=35.5 \quad (4)$$

A permitted limit of odor index of the sample is calculated to be  $35.5 - 3.5$  from the mean value and standard deviation in **Table 1**. Among 137 laboratories, 94 laboratories (69%) lay within this limit. It is desirable for olfactometry laboratories which lay out of this limit to specify the problems and improve the measurement methods.

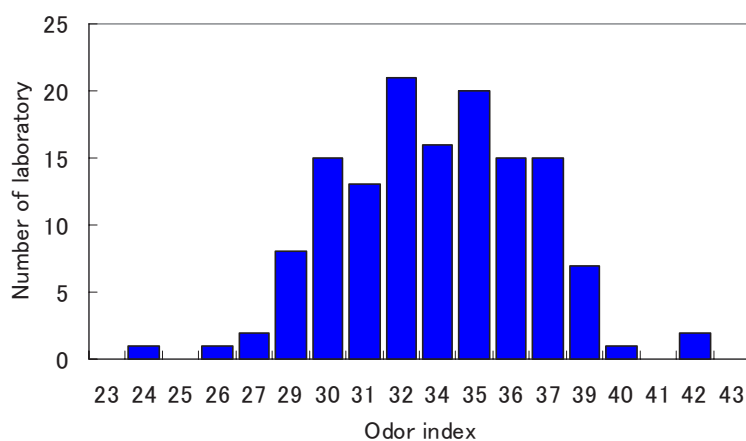


Figure 2. A distribution of odor index obtained from 137 laboratories in nationwide comparison in 2002.

**Table 2** indicates the comparison of mean values and standard deviations among member categories of the Japan Association on Odor Environment (JAOE) in 2002. The standard deviation obtained from accredited corporate members of JAOE was calculated to be the minimum and that obtained from non-members the maximum. These results imply the effectiveness of accreditation system of JAOE.

Table 2. The number of laboratories ( $n$ ), mean values ( $m$ ), and standard deviations ( $s$ ) of odor index obtained from each member category of JAOE in nationwide comparison in 2002.

Member category	$n$	$m$	$s$
Accredited corporate member of JAOE	46	34	2.6
Corporate member of JAOE	43	33	3.4
Non-member of JAOE	48	34	3.7

A distribution of mean odor index obtained from 120 olfactometry laboratories in 2003 is depicted in **Figure 3**. The mean value and standard deviation were 35 and 2.6, respectively.

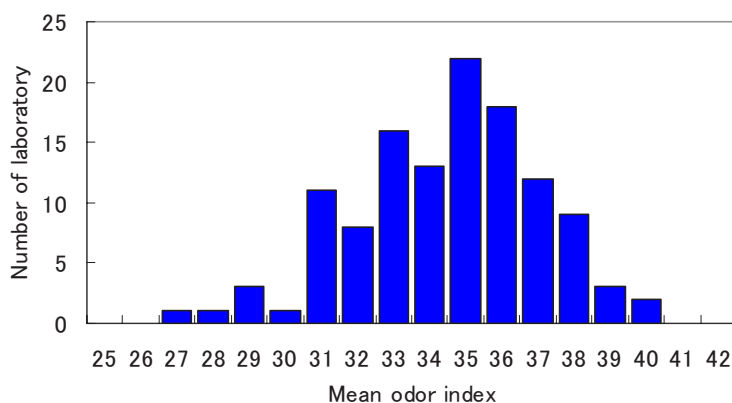


Figure 3. A distribution of odor index obtained from 120 laboratories in nationwide comparison in 2003.

The comparison of mean values, repeatability standard deviations, and reproducibility standard deviations among member categories of the JAOE in 2003 is shown in **Table 3**. Repeatability and reproducibility standard deviations obtained from accredited corporate members of JAOE were calculated to be the minimum.

Table 3. The number of laboratories ( $n$ ), mean values ( $m$ ), repeatability standard deviations ( $s_r$ ), and reproducibility standard deviations ( $s_R$ ) of odor index obtained from each member category of JAOE in nationwide comparison in 2003.

Member category	$n$	$m$	$s_r$	$s_R$
Accredited corporate member of JAOE	41	34	1.1	2.2
Corporate member of JAOE	34	34	1.1	3.1
Non-member of JAOE	45	35	1.3	2.4

## 5. CONCLUSIONS

In this paper, measurement procedure of the triangular odor bag method was briefly explained and the establishment of quality control framework for olfactometry was mentioned. Nationwide comparison of olfactometry, which was carried out in order to evaluate proficiency of olfactometry laboratories in Japan, was also discussed. In the future, interlaboratory comparison with different reference odor should be necessary to confirm reliability of measurement results. Moreover, presentation of the standard deviations of odor index calculated from the results, independent of the investigated material or unknown mixture and of the method applied, will enable the comparison of olfactometry all over the world.

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