【 Reference 2 】

Measurement of Odor Threshold by Triangular Odor Bag Method

Measurement of Odor Threshold by Triangular Odor Bag Method

Yoshio Nagata
Japan Environmental Sanitation Center

Abstract

The detection thresholds of odor substances analyzed in field investigations were measured by the triangular odor bag method[1). The number of substances used for the experiment is 223. The experiment was carried out from 1976 to 1988.

As the results of the experiments, the odor thresholds were distributed over the concentration of large range depending on the odor substances. Isoamyl mercaptane exhibited the lowest threshold (0.77ppt), and propane exhibited the highest threshold (1500 ppm). The distribution of thresholds expresses the normal distribution. Sulfur compounds with the exception of sulfur dioxide and carbon disulfide have the comparatively low threshold. It is showed the tendency that threshold becomes low as the increase of molecular weight in a certain range of molecular weight.

When the dispersion of odor thresholds for the same substance was shown at the ratio of the highest to the lowest odor threshold tested, the dispersion of odor thresholds was about 5 at the maximum. The thresholds of 223 substances measured by our laboratory were considered to be the average values with small bias comparatively.

1. Introduction

The thresholds were needed also in the evaluation based on instrumental measuring method, and also in the evaluation based on olfactory measuring method in odor studies. On that occasion, the data of the threshold by the foreign researcher, for example, Leonardos et al. (53 substances)[2)] or Hellman et al. (101substances)[3)], has greatly been made reference in Japan. But, the thresholds of substances that aren't reported to these literatures are also needed. And, a threshold may vary considerably in the difference of measuring method to the same material. Therefore, the need to measure thresholds individually is arising. The detection thresholds of 223 substances detected in various odor sources were measured in our laboratory by the triangular odor bag method[4)].

2. Odorants and experimental method

2.1 Preparation of primary odor sample

The standard gas such as the sulfurous acid gas taken from the standard gas bomb was injected in polyester bag filled with nitrogen gas using gastightsyringe. In case the reagent was liquid, the primary odor sample was prepared by vaporizing, after it was injected in polyester bag filled with nitrogen gas with microsyringe. And in case the reagent was a solid like Skatole, the sublimation gas was collected in the bag. The odor samples were left for 2 hours or more in order to stabilize their gas concentration.

2.2 Concentration measurement of primary odor sample

Ammonia was measured by indophenol method, diosmin, skatole, indole were measured by gas chromatography-mass spectrometry. Other odorants were measured by gas chromatography (FID, FPD, FTD). In case of the standard gas such as sulfur dioxide, the concentration displayed on the bomb were used.

2.3 Measurement of odor concentration , and odor panel

The odor concentration was measured by the triangular odor bag method. In the triangular odor bag method, the threshold is obtained by detecting the difference from odor-free background. Therefore, the odor thresholds reported are nearly equal to the detection threshold. The measurement of the threshold was carried out in 12 years from 1976 to 1988 (Fgure 1). An odor panel consists of 6 panelists. All panelists have passed the panel screening test by T&T olfactometer. Their ages are 50-year-old from 20-year-old. Some panelists changed in these 12 years. However, four persons (woman) among 6 panelists are the panelists from the first time. All panelists are trained.

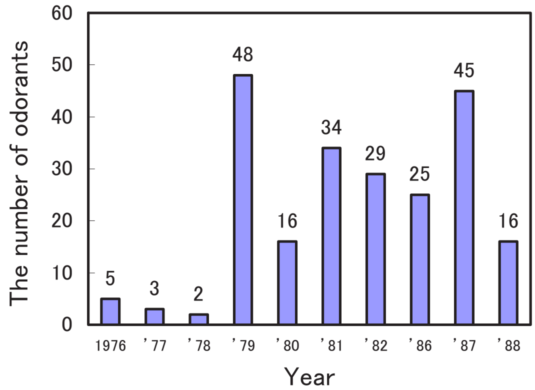


Figure1 Carried-out year and the measured number of substances

2.4 Calculation of threshold value

In this examination, the value which divided the concentration of the primary odor sample by the odor concentration as a principle was determined as the detection threshold (ppm,v/v).

detection threshold (ppm,v/v) =
the concentration of primary odor sample / odor concentration

As shown in Table 1, about the odorants such as amines, fatty acids, skatole and indole, since the dilution error was large compared with other substances, their thresholds were corrected by their recovery rate. About the odorants of which the thresholds were measured repeatedly, the geometric mean of each observed value was taken as the threshold of the odorant.

Table 1 Dilution error of the odor bag

Substance	Primary odor (ppm)	Dilution multiple	Recovery rate %
Hydrogen sulfide	20	10 ～ 300	102
Methyl mercaptane	10	10 ～ 300	93
Dimethyl sulfide	80	10 ～ 300	100
n -Hexane	600	10 ～ 1000	98
Toluene	900	10 ～ 1000	94
n-Nonane	800	10 ～ 1000	93
o,m,p - Xylene	23	10 ～ 1000	99
Styrene	22	10 ～ 1000	105
Ammonia	1100	10 ～ 1000	95
Trimethylamine	5.0	30 ～ 3000	50
〃	5.0	30 ～ 3000	93*
〃	0.02	30	13
Propionaldehyde	6.7	100 ～ 300	82
Isobutylaldehyde	6.6	100 ～ 300	82
n-Valeraldehyde	4.6	100 ～ 300	83
n-Butyric acid	0.3	10 ～ 30	40
Isobutyric acid	83	1000 ～ 3000	35
Isovaleric acid	0.5	10 ～ 30	39
Indole	1.8	30 ～ 100	6.5
Skatole	1.7	30 ～ 3000	13

* The injector made from a plastic was used.
The glass injector was used in the result of others.

3. Result of threshold measurement

The thresholds of 223 odorants measured in the experiment are shown in the Table 2. The thresholds in the wide range of about 2 billion times to 1500ppm (propane) from 0.77ppt (Isoamyl mercaptane) were observed.

3.1 Comparison with the measurement results of odor intensity by the odorless chamber method

About 53 offensive odor substances, the relation between odor intensity (6-points scale) and the concentration of odor substance was observed in our laboratory[5]. The odorless chamber of 4 m^3 was used for the experiment. As for 51 of 53 substances, the threshold of each substance was determined also by the triangular odor bag method. Then, the threshold determined by the triangular odor bag method was substituted for the relational expression between the concentration of odorant and odor intensity, and the threshold was converted into odor intensity. As the calculated results, the average value of the odor intensity equivalent of each substance was almost scale 1 of odor intensity. Scale 1 of odor intensity corresponded to the detection threshold. Both the measuring methods are based on the air dilution method, and the thresholds observed by both methods agreed in many substances approximately.

3.2 Distribution of thresholds for chemical compounds

The histogram of Figure 2 shows the distribution of the thresholds of compounds, such as sulfur compounds and oxygenated compounds, etc. The distribution of thresholds expresses the normal distribution. As shown in this figure, the thresholds are distributed in a wide range of concentration depending on the odor substances and compounds. The top of the distribution of the threshold was 10ppt～1ppb as for the sulfur compounds, 1ppb～10ppb as for the oxygenated compounds, 10ppb～100ppb as for the nitrogen compounds, 100ppb～1ppm as for the hydrocarbon and 1ppm～10ppm as for the chlorine compounds. Sulfur compounds with the exception of sulfur dioxide and carbon disulfide have the comparatively low threshold.

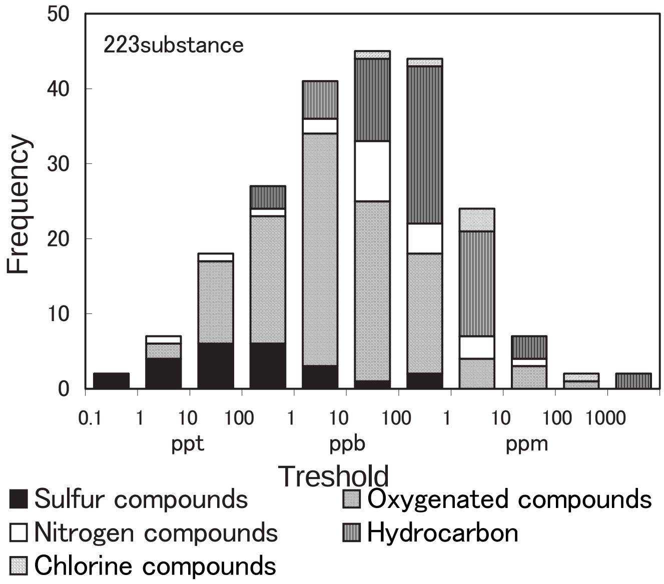


Figure 2 Distribution of thresholds for compounds

3.3 Relation between threshold and Molecular Weight

Although a clear tendency is not recognized on the whole, there is the tendency that the threshold decreases as the increase of molecular weight in the range to 120-130 as molecular weight (Figure 3).

Further that tendency becomes clear when it is observed in the homologous series.
In most case of homologous series in the chemical compounds such as alcohol (Figure 4), aldehyde, mercaptan, ketone and hydrocarbon, it is showed the tendency that threshold becomes low as the increase of molecular weight in a certain range of molecular weight.

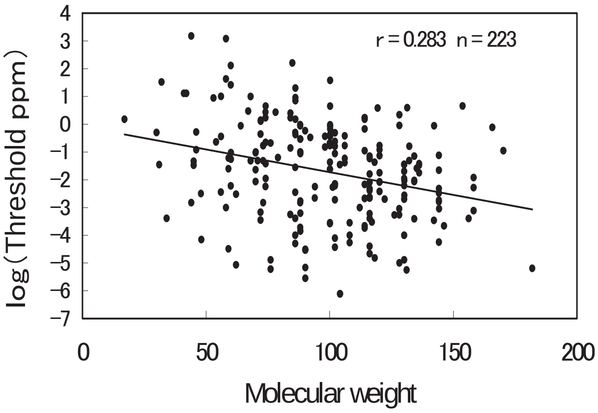


Figure 3 Relation between threshold and Molecular weight

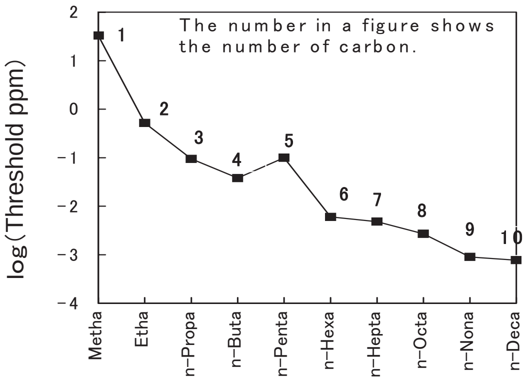


Figure 4 Thresholds of Aliphatic alcohols (Homologous series)

3.4 Difference of the threshold between isomers

It is further found that a great difference in the thresholds between isomers. When the functional group is different such as aldehyde and ketone, fatty acid and ester, it is not rare that the thresholds are different about 10000 times between isomers. Moreover, the thresholds may be different even between position isomerism more than 100 times (Figure 5).

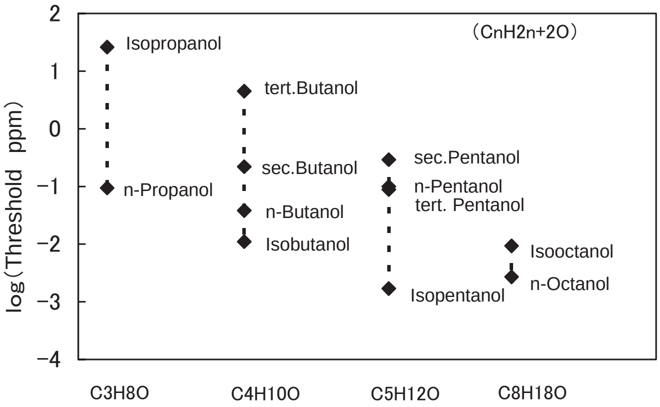


Figure 5 Thresholds of Aliphatic alcohols (Between isomers)

Table 2 Odor thresholds measured by the triangular odor bag method (ppm,v/v)

Substance	Odor Threshold	Substance	Odor Threshold
Formaldehyde	0.50	Hydrogen sulfide	0.00041
Acetaldehyde	0.0015	Dimethyl sulfide	0.0030
Propionaldehyde	0.0010	Methyl allyl sulfide	0.00014
n-Butylaldehyde	0.00067	Diethyl sulfide	0.000033
Isobutylaldehyde	0.00035	Allyl sulfide	0.00022
n-Valeraldehyde	0.00041	Carbon disulfide	0.21
I sovaleraldehyde	0.00010	Dimethyl disulfide	0.0022
n-Hexylaldehyde	0.00028	Diethyl disulfide	0 0020
n-Heptylaldehyde	0.00018	Diallyl disulfide	0.00022
n-Octylaldehyde	0.000010	Methyl mercaptane	0.000070
n-Nonylaldehyde	0.00034	Ethyl mercaptane	0.0000087
n-Decylaldehyde	0.00040	n-Propyl mercaptane	0.000013
Acrolein	0.0036	Isopropyl mercaptane	0.0000060
Methacrolein	0.0085	n-Butyl mercaptane	0.0000028
Crotonaldehyde	0.023	Isobutyl mercaptane	0.0000068
Methanol	33	sec. Butyl mercaptane	0.000030
Ethanol	0.52	tert. Butyl mercaptane	0.000029
n-Propanol	0.094	n-Amyl mercaptane	0.00000078
I sopropanol	26	Isoamyl mercaptane	0.00000077
n-Butanol	0.038	n-Hexyl mercaptane	0.000015
I sobutanol	0.011	Thiophene	0.00056
sec.Butanol	0.22	Tetrahydrothiophene	0.00062
tert.Butanol	4.5	Nitrogen dioxide	0.12
n-Pentanol	0.10	Ammonia	1.5
Isopentanol	0.0017	Methylamine	0.035
sec.Pentanol	0.29	Ethylamine	0.046
tert. Pentanol	0.088	n-Propylamine	0.061
n-Hexanol	0.0060	Isopropylamine	0.025
n-Heptanol	0.0048	n-Butylamine	0.17
n-Octanol	0.0027	Isobutylamine	0.0015
Isooctanol	0.0093	sec. Butylamine	0.17
n-Nonanol	0.00090	tert. Butylamine	0.17
n-Decanol	0.00077	Dimethylamine	0.033
2-Ethoxyethanol	0.58	Diethylamine	0.048
2-n-Buthoxyethanol	0.043	Trimethylamine	0.000032
1-Butoxy-2-propanol	0.16	Triethylamine	0.0054
Phenol	0.0056	Acetonitrile	13
o-Cresol	0.00028	Acrylonitrile	8.8
m-Cresol	0.00010	Methacrylonitrile	3.0
p-Cresol	0.000054	Pyridine	0.063
Geosmin	0.0000065	Indole	0.00030
Acetic acid	0.0060	Skatole	0.0000056
Propionic acid	0.0057	Ethyl-o-toluidine	0.026
n-Butyric acid	0.00019	Propane	1500
Isobutyric acid	0.0015	n-Butane	1200
n-Valeric acid	0.000037	n-Pentane	1.4
Isovaleric acid	0.000078	Isopentane	1.3
n-Hexanoic acid	0.00060	n -Hexane	1.5
Isohexanoic acid	0.00040	2-Methylpentane	7.0
Sulfur dioxide	0.87	3-Methylpentane	8.9
Carbonyl sulfide	0.055	2, 2-Dimethylbutane	20

Table 2 Odor thresholds measured by the triangle odor bag method (ppm,v/v) *(continued)*

Substance	Odor Threshold	Substance	Odor Threshold
2, 3-Dimethylbutane	0.42	Ethyl acetate	0.87
n-Heptane	0.67	n-Propyl acetate	0.24
2-Methylhexane	0.42	Isopropyl acetate	0.16
3-Methylhexane	0.84	n-Butyl acetate	0.016
3-Ethylpentane	0.37	Isobutyl acetate	0.0080
2, 2-Dimethylpentane	38	sec.Butyl acetate	0.0024
2, 3-Dimethylpentane	4.5	tert.Butyl acetate	0.071
2, 4-Dimethylpentane	0.94	n-Hexyl acetate	0.0018
n-Octane	1.7	Methyl propionate	0.098
2-Methylheptane	0.11	Ethyl propionate	0.0070
3-Methylheptane	1.5	n-Propyl propionate	0.058
4-Methylheptane	1.7	Isopropyl propionate	0.0041
2, 2, 4-Trimethylpentane	0.67	n-Butyl propionate	0.036
n-Nonane	2.2	Isobutyl propionate	0.020
2, 2, 5-Trimethylhexane	0.90	Methyl n-butyrate	0.0071
n-Undecane	0.87	Methyl isobutyrate	0.0019
n-Decane	0.62	Ethyl n-butyrate	0.000040
n-Dodecane	0.11	Ethyl isobutyrate	0.000022
Propylene	13	n-Propy n-butyrate	0.011
1-Butene	0.36	Isopropyl n-butyrate	0.0062
Isobutene	10	n-propyl isobutyrate	0.0020
1-Pentene	0.10	Isopropyl isobutyrate	0.035
1-Hexene	0.14	n-Butyl n-butyrate	0.0048
1-Heptene	0.37	Isobutyl n-butyrate	0.0016
1-Octene	0.0010	n-Butyl isobutyrate	0.022
1-Nonene	0.00054	Isobutyl isobutyrate	0.075
1,3-Butadiene	0.23	Methyl n-valerate	0.0022
Isoprene	0.048	Methyl isovalerate	0.0022
Benzene	2.7	Ethyl n-valerate	0.00011
Toluene	0.33	Ethyl isovalerate	0.000013
Styrene	0.035	n-Propyl n-valerate	0.0033
Ethylbenzene	0.17	n-Propyl isovalerate	0.000056
o-Xylene	0.38	n-Butyl isovalerate	0.012
m-Xylene	0.041	Isobutyl isovalerate	0.0052
p-Xylene	0.058	Methyl acryrate	0.0035
n-Propylbenzene	0.0038	Ethyl acryrate	0.00026
Isopropylbenzene	0.0084	n-Butyl acryrate	0.00055
1, 2, 4-Trimethylbenzen	0.12	Isobutyl acryrate	0.00090
1, 3, 5-Trimethylbenzen	0.17	Methyl methacryrate	0.21
o-Ethyltoluene	0.074	2-Ethoxyethyl acetate	0.049
m-Ethyltoluene	0.018	Acetone	42
p-Ethyltoluene	0.0083	Methyl ethyl ketone	0.44
o-Diethylbenzene	0.0094	Methyl n-propyl ketone	0.028
m-Diethylbenzene	0.070	Methyl isopropyl ketone	0.50
p-Diethylbenzene	0.00039	Methyl n-butyl ketone	0.024
n-Butylbenzene	0.0085	Methyl isobutyl ketone	0.17
1, 2, 3, 4-Tetramethylbenzen	0.011	Methyl sec.butyl ketone	0.024
1, 2, 3, 4-Tetrahydronaphthalene	0.0093	Methyl tert.butyl ketone	0.043
α-Pinene	0.018	Methyl n-amyl ketone	0.0068
β-Pinene	0.033	Methyl isoamyl ketone	0.0021
Limonene	0.038	Diacetyl	0.000050
Methylcyclopentane	1.7	Ozone	0.0032
Cyclohexane	2.5	Furane	9.9
Methylcyclohexane	0.15	2, 5-Dihydrofurane	0.093
Methyl formate	130	Chlorine	0.049
Ethyl formate	2.7	Dichloromethane	160
n-Propyl formate	0.96	Chloroform	3.8
Isopropyl formate	0.29	Trichloroethylene	3.9
n-Butyl formate	0.087	Carbon tetrachloride	4.6
Isobutyl formate	0.49	Tetrachloroethylene	0.77
Mthyl acetate	1.7		

4. Precision and accuracy of the measurement results of the threshold

4.1 Reproducibility-within-laboratory (The result measured by our laboratory)

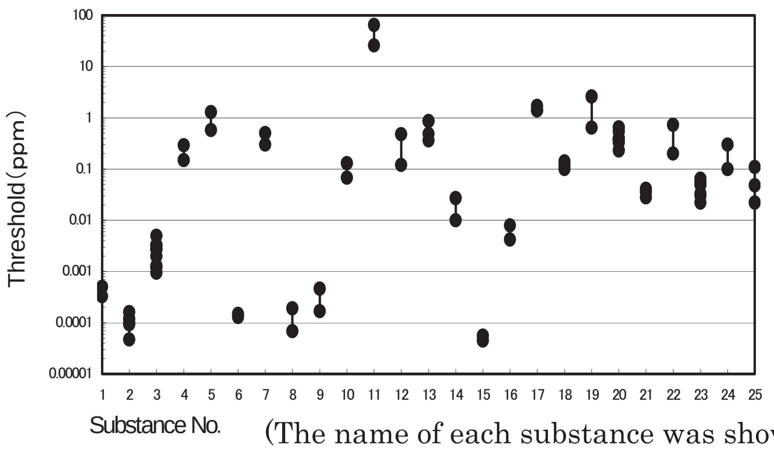
It was thought that the odor thresholds would vary because of the difference in the measuring method and the attribute of odor panel, etc.

The measurement of the threshold of each odor substance was carried out on separate days. The measuring instruments used on each test were the same. 4 persons in panel member of 6 persons are same during the measurement period. About some substances, the measurements of the threshold have carried out after ten years or more have passed since the first measurement. Though the measurements for many of prepared substances were carried out only once. But the measurements were carried out twice or more per substance about 25 substances of 223 substances.

Figure 6 shows that variation of odor thresholds for repeated tests on the same substances. The sensory tests were carried out on separate days. And, the dispersion of odor thresholds for the same substance was shown at the ratio of the highest to the lowest odor threshold tested, and it was shown in Table 3. Though the number of repetitions is different with substance from 2 times to 9 times, the dispersion of odor thresholds was about 5 at the maximum.

Table 3 Variation of thresholds on the same substances

The number of times of measurement	The number of substances	Ratio of the highest to the lowest threshold
2	16	1．2～4．0
3	3	1．2～5．0
4	2	1．5，2．4
5	1	2．6
7	1	3．0
9	2	3．0、5．2



No.	Substance	No.	Substance
1	Hydrogen sulfide	14	n-Butyl acetate
2	Methyl mercaptane	15	Diacetyl
3	Dimethyl sulfide	16	Acetic acid
4	Carbon disulfide	17	Ammonia
5	Sulfur dioxide	18	Nitrogen dioxide
6	Methyl allyl sulfide	19	Isopentane
7	Formaldehyde	20	Toluene
8	I sovaleraldehyde	21	Styrene
9	n-Hexylaldehyde	22	o-Xylene
10	n-Propanol	23	m-Xylene
11	Isopropanol	24	Ethylbenzene
12	sec.Butanol	25	Chlorine
13	Ethyl acetate		

(The name of each substance was shown in the right table.)

Figure 6 Result of repeated tests on the same substances by trained panel.

4.2 Reproducibility-within-laboratory (the results of the practices in the Environment training center where these are carried out once a year)

We have held the training session of the sensory test method for inexperienced person once a year since 1983. The thresholds of hydrogen sulfide, m-xylene and ethyl acetate were measured during the practical training. The measurements were carried out in the same place every year. The measuring instruments used on each test were also the same. Operators and panel members are untrained persons and are changed every year. The results are shown in Table 4 and Figure 7.

When the results by the untrained panel were compared with the results by the trained panel, the significant difference was not recognized on mean value and dispersion of the thresholds[6]. The untrained panel members are considered to have got used to the sensory test through the panel screening test and the preliminary practice of the triangular odor bag method before the measurement of the thresholds.

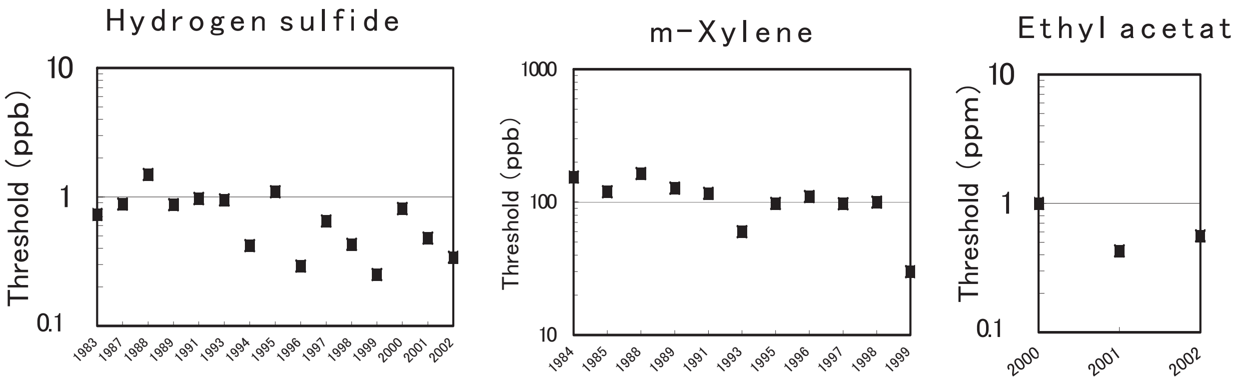


Figure 7 Result of odor thresholds on the same substances (Untrained persons carried out the measurements once per year.)

Table 4 Variation of odor thresholds on the same substances (from Figure 7)

Substance	carried-out year	The number of panelist	The number of times of measurement	Ratio of the highest to the lowest threshold	Geometric mean
Hydrogen sulfide	1983 ～2002	6 ～ 16	15	6.0	0.63 ppb
m-Xylene	1984 ～1999	6 ～ 16	11	5.5	99 ppb
Ethyl acetate	2000 ～2002	11 ～ 12	3	3.2	0.62 ppm

4.3 Reproducibility by inter-laboratory test

In 1985, inter-laboratory comparison test by the triangular odor bag method was carried out. 5 odor laboratories including our laboratory participated in the test. The results are shown in Figure 8 and Table 5. m-Xylene and dimethyl sulfide were chosen as the reference materials for sensory test. The sample no.1,2,3,4 are m-xylene of which the concentration differs, and the sample no.5,6,7 are dimethyl sulfide of which the concentration differs.

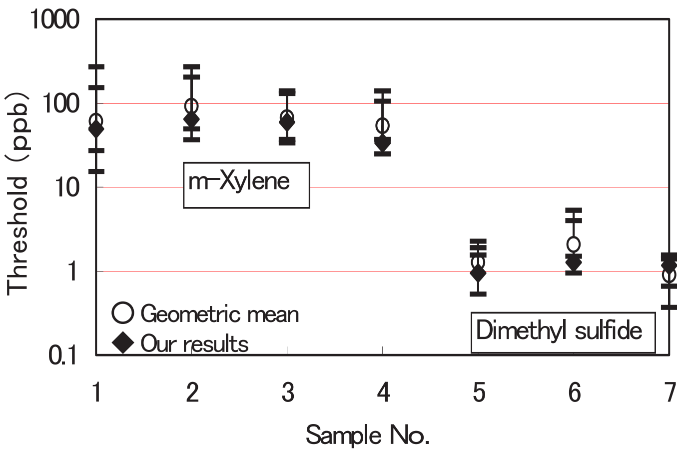


Figure 8 Results of inter-laboratory test by 5 laboratories

The dispersion of the measure- ment results was shown the ratio of highest to lowest odor threshold measured by each laboratory. The dispersion of the thresholds between 5 laboratories was as large as 18 in the sample no.1 that was measured first. And, the dispersion of other 6 samples was less than 8. When the measurement results of 2 laboratories which have a few measurement experience are removed, the dispersions are less than 5 every sample.

Table 5 Dispersion of thresholds measured by 5 laboratories on the same substances (from Figure 8)

Sample	Substance	Ratio of the highest to the lowest threshold	Geometoric mean	
			Every sample	Every substance
1	m-Xylene	18	61ppb	67ppb
2		7.4	92ppb	
3		4.2	67ppb	
4		5.6	53ppb	
5	Dimethyl sulfide	4.3	1.3ppb	1.3ppb
6		5.6	2.0ppb	
7		4.2	0.9ppb	

4.4 Accuracy of the thresholds measured by our laboratory

1) In 2002, the inter-laboratory test was carried out in order to raise the accuracy of the triangular odor bag method. A total of 137 odor laboratories in Japan participated in the test. In the test, the threshold of ethyl acetate was measured[7]. As the result measured by 137 laboratories, the mean value of the threshold of ethyl acetate was 0.89 ppm. The threshold of ethyl acetate measured by our laboratory－0.87 ppm (the measured value in 1979) is almost the same as this value.
2) As shown in Figure 8, in the inter-laboratory test by 5 laboratories, the threshold measured by our laboratory is 0.6 times to 1.3 times of the geometric mean, almost near the average value.
3) In Europe, the dynamic olfactometry has been standardized as the measuring method of odor concentration, and it has been reported that the threshold of n-butanol measured by this method was approximately 40 ppb[8]. We had reported that the threshold of n-butanol measured by the triangular odor bag method was 38 ppb (the measured value in 1980). Although measuring method is different, both of results are almost the same.

From these results, the thresholds of 223 substances measured by our laboratory are considered to be the average values with small bias comparatively.

5. Conclusion

Although the threshold values shown in this report were reported 15 years ago, but the remarkable differences from the reported values are not seen in the latest remeasurement results. So, I was sure of the practicality of the triangular odor bag method anew.

References

1) Iwasaki,Y. and Ishiguro,T. : Measurement of odor by triangular odor bag method ( ) : Japan Society Atmospheric Environment ,(1978),13(6),pp.34-39
2) Leonardos,G.,D.,Kendall and N.Barnard : Odor threshold determination of 53 odorant chemicals,J.of APCA.,(1969),19(2),pp.91-95
3) Hellman,T.M.and F.H.Small : Characterization of the odor properties of 101 petrochemicals using sensory method,J.of APCA.,(1974),24(10),pp.979-982
4) Nagata,Y. and Takeuchi,N. : Measurement of odor threshold by triangular odor bag method, Bulletin of Japan Environmental Sanitation Center,(1990),17,pp.77-89

5) Nagata,Y. and Takeuchi,N. : Relationship between concentration of odorants and odor intensity , Bulletin of Japan Environmental Sanitation Center,(1980),7,pp.75-86
6) Nagata,Y. and Takeuchi,N. : A report on sensory measurement of odor in exercise at National Environmental Training Institute , Bulletin of Japan Environmental Sanitation Center,(1996),23,pp.67-79
7) Fukuyama,Jyoji : Evaluation of a cross-check examination result, Odor Research and Engineering Association of Japan, (2003), pp.37-49
8) Ishikawa,Y. and Nishida,K. (translation) : A Review of 20 years of standardization of odor concentration measurement by dynamic olfactometry in europe, Journal of odor research and engineering, (2000) ,31(3),pp.6-13