GUIDELINES ON ODOUR POLLUTION & ITS CONTROL

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CENTRAL POLLUTION CONTROL BOARD
Ministry of Environment & Forests,
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Table -1
Details of Offensive Odorous Compounds Emitted from Industries

Sl. No.	Compound/ Odorant	Formula	Molecular Weight	Volatility at 25°C in ppm	Odour Detection Threshold in ppm (v/v)	Offensive Odour Description
1.	**Inorganic Compounds**					
	▪ Ammonia	NH_3	17	Gas	17	Pungent, Irritating
	▪ Chlorine	Cl_2	71	Gas	0.080	Pungent, Suffocation
	▪ Hydrogen Sulphide	H_2S	34	Gas	0.00047	Rotten eggs
	▪ Ozone	O_3	48	Gas	0.5	Pungent, irritating
	▪ Sulphur dioxide	SO_2	64	Gas	2.7	Pungent, irritating
2.	**Acids**					
	▪ Acetic Acid	CH_3COOH	60	Gas	1.0	Vinegar
	▪ Butyric Acid	$CH_3CH_2CH_2COOH$	88	Gas	0.12	Rancid butter
	▪ Propionic Acid	CH_3CH_2COOH	74	Gas	0.028	---
3.	**Alcohols**					
	▪ Amyl alcohol	$C_5H_{11}OH$	88	Gas	---	---
	▪ Butyl alcohol	$CH_3(CH_2)_3OH$	74	Gas	0.10	---
4.	**Aldehydes & Ketones**					
	▪ Formaldehyde	$HCHO$	30	Gas		Acrid
	▪ Acetaldehyde	CH_3CHO	44	Gas	0.067	Fruit
	▪ Butylaldehyde	C_3H_7CHO	72			Rancid
	▪ Acetone	CH_3COCH_3	58			Fruit
5.	**Amines**					
	▪ Methyl amine	CH_3NH_2	31	Gas	4.7	Putrid, Fishy
	▪ Dimethyl amine	$(CH_3)_2NH$	45	Gas	0.34	Putrid, Fishy
	▪ Trimethyl amine	$(CH_3)_3N$	59	Gas	0.0004	Putrid, Fishy
	▪ Ethyl amine	$C_2H_5NH_2$	45	Gas	0.27	Ammoniacal
	▪ Diethyl amine	$(C_2H_5)_2NH$	73		0.020	Fishy
	▪ Di-isopropyl amine	$(C_3H_7)_2NH_2$	101		0.13	Fishy
	▪ Dibutyl amine	$(C_4H_9)_2NH$	129	8,000	0.016	Fishy
	▪ n butyl amine	$CH_3(CH_2)_3NH_2$	73	93,000	0.080	Sour, ammonia
6.	**Mercaptans**					
	▪ Allyl mercaptan	CH_2CHCH_2SH	74	---	0.0015	Disagreeable, garlic
	▪ Amyl mercaptan	$CH_3(CH_2)_4SH$	104	---	0.0003	Unpleasant, Putrid
	▪ Benzyl mercaptan	$C_6H_5CH_2SH$	124	---	0.0002	Unpleasant, strong
	▪ Ethyl mercaptan	C_2H_5SH	62	710,000	0.0003	Decayed Cabbage
	▪ Methyl mercaptan	CH_3SH	48	Gas	0.0005	Rotten Cabbage
	▪ Phenyl mercaptan	C_6H_5SH	110	2,000	0.0003	Putrid, garlic
	▪ Propyl mercaptan	C_3H_7SH	76	2,20,000	0.0005	Unpleasant
7.	**Sulphides**					
	▪ Diethyl sulphide	$(C_2H_5)_2S$	106		0.02	Ether
	▪ Dimethyl sulphide	$(CH_3)_2S$	62	830,000	0.001	Decayed Cabbage
	▪ Dimethyl disulphide	$(CH_3)_2S_2$	94		0.0076	Putrid
	▪ Diphenyl sulphide	$(C_6H_5)_2S$	186	100	0.0001	Unpleasant
8.	**Organic Heterocycles**					
	▪ Indole	$C_6H_4(CH)_2NH$	117	360	0.0001	Faecal, nauseating
	▪ Pyridine	C_5H_5N	79	27,000	0.0001	Pungent, irritating
	▪ Skatole	C_9H_8N	131	200	0.001	Fecal, nauseating
	▪ Thiocresol	$CH_3C_6H_4SH$	124	---	0.0001	Rancid

Measurement of Odor Threshold by Triangle Odor Bag Method

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Keywords

Odor threshold , Triangle odor bag method , Reproducibility

Abstract

The detection thresholds of odor substances analyzed in field investigations were measured by the triangle 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 (1500ppm). 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 triangle 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 triangle odor bag method. In the triangle 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 (Figure 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.
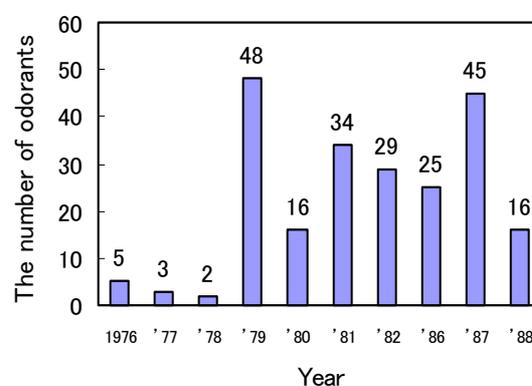

Figure 1　Carried-out year and the measured number of substances

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

Table1　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	10	～　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.

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.

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 triangle odor bag method. Then, the threshold determined by the triangle 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.
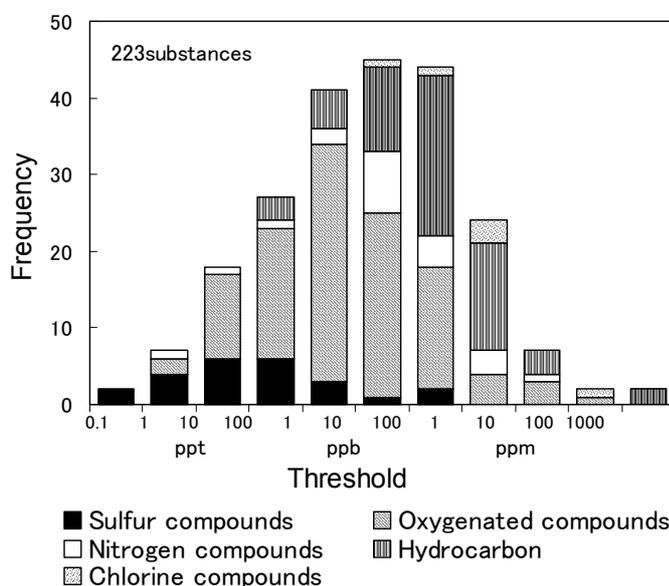

Figure 2   Distribution of thresholds for compounds

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.
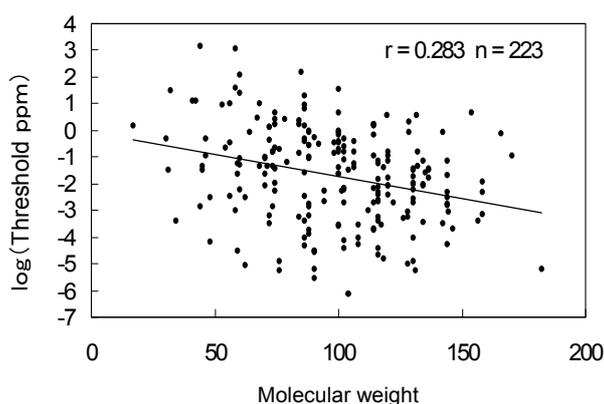

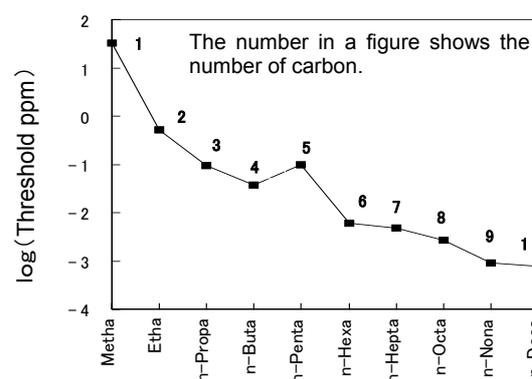*Figure 3　Relation between threshold and molecular weight*

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).
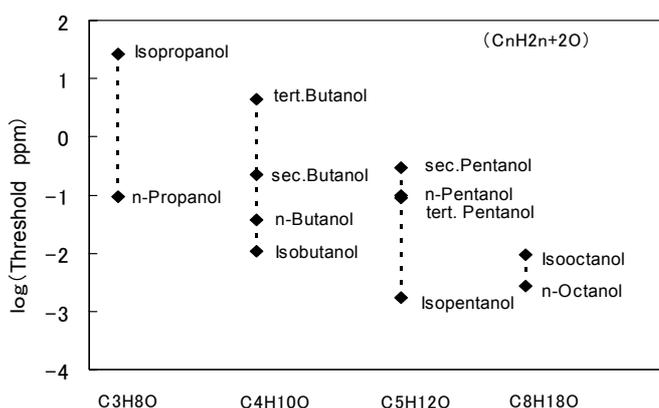

Figure 5　Thresholds of Aliphatic alcohols (Between isomers)

Table 2 Odor thresholds measured by the triangle 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		

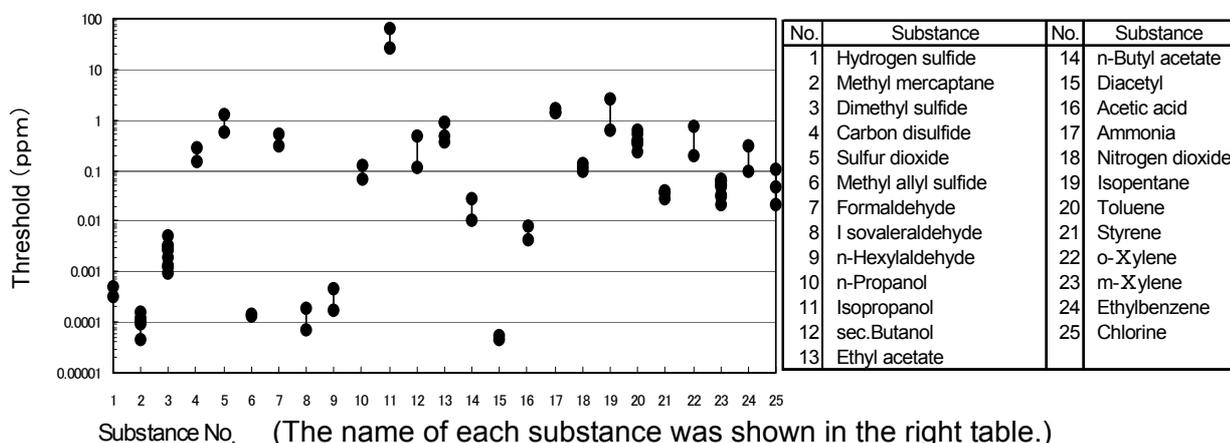Substance No.   (The name of each substance was shown in the right table.)

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 triangle 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 triangle 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.

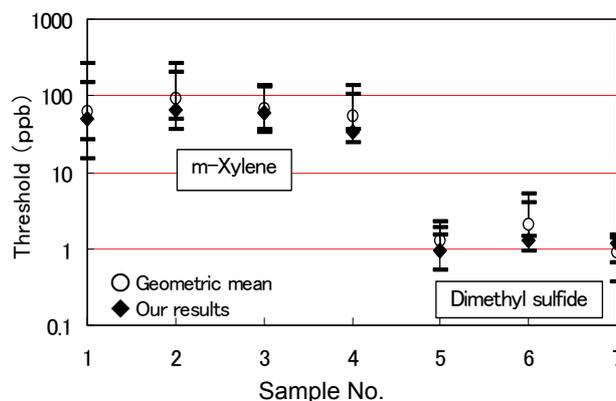The dispersion of the measure- ment results was shown the ratio of highest to

Figure 8   Results of inter-laboratory test by 5 laboratories

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 thre shold	Geometoric mean	
			Every sample	Every substance
1	m-Xylene	18	61 ppb	67 ppb
2		7.4	92 ppb	
3		4.2	67 ppb	
4		5.6	53 ppb	
5	Dimethyl sulfide	4.3	1.3 ppb	1.3 ppb
6		5.6	2.0 ppb	
7		4.2	0.9 ppb	

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 triangle odor bag method. A total of 137 odor laboratories in Japan participated in the test. In the test, the threshold of ethyl acetate was measured7). 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 ppb8). We had reported that the threshold of n-butanol measured by the triangle 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 triangle odor bag method anew.

References

1) Iwasaki,Y. and Ishiguro,T. : Measurement of odor by triangle odor bag method（Ⅰ） : 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 triangle 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

Where health-based standards or guideline values exist for specific substances, these should be compared to the benchmark value as calculated above. The more stringent should be used as a benchmark. The odour thresholds for many substances are very low therefore it will be unusual for the odour exposure benchmark to be numerically higher than other pollution control limits.

Other standards or guideline values

Use of odour threshold values

The odour threshold value is the concentration at which an odorous substance becomes detectable to 50% of a test panel. The exposure concentration at which the odour (i) will be recognisable, and (ii) exposure is likely to lead to reasonable cause for annoyance, will be different multiples of the odour threshold. The emission rate at source which is equivalent to the odour threshold at sensitive receptors can be calculated by using an atmospheric dispersion model.

The actual emission in mg m^{-3} of odorous substance can be converted to odour units and compared with the odour exposure acceptability criteria described in Appendix 6 (refer to Figure A5.1, above).

Quality Objectives

Some of the substances for which air quality objectives exist are odorous:

For example:

- sulphur dioxide
- benzene
- butadiene

Emission limits set in sector specific guidance notes

- volatile organic compounds (VOCs)
- ammonia
- hydrogen sulphide

World Health Organisation guideline values

The World Health Organisation provide exposure guideline values for a limited range of substances as 24-hour average concentrations, (see Reference 21). These were derived with the aim of providing a basis for protecting the public from the adverse effects of air pollution.

For a few of these substances which exhibit malodorous properties at concentrations below that at which toxic effects occur, guideline values have been established for avoidance of substantial annoyance. Again these relate to single species, rather than compounds present in mixtures.

Table A5.1: Guideline values based on sensory effects or annoyance reactions,

(averaging time of 30 minutes.)

Odorous substance	Detection threshold	Recognition threshold	WHO Guideline value set to protect against "substantial annoyance"
Carbon disulphide in viscose emissions			20µg m^{-3}
Hydrogen sulphide	0.2 - 2.0µg m^{-3}	0.6 - 6.0µg m^{-3}	7µg m^{-3}
Styrene	70µg m^{-3}	210 – 280µg m^{-3}	70µg m^{-3}
Tetrachloroethylene	8mg m^{-3}	24 - 32mg m^{-3}	8mg m^{-3}
Toluene	1mg m^{-3}	10mg m^{-3}	1mg m^{-3}

Derivations of Occupational Exposure Limits (OELs)

In general terms occupational exposure limits (OELs) are not really suitable for determining a level of annoyance – they are derived from health-related data and the transposition of these limits from workplace to community is not straightforward.

"Substantial annoyance" does not appear to have been defined.

APPENDIX 8 – TESTING PROTOCOL

An assessment may involve walking along a route selected according to the above factors, or to the conditions found upon arrival. Alternatively points may be fixed in order to evaluate the changing situation over a period of some weeks or months, or may vary from test to test according to local conditions. The latter may be of use in identifying worst case conditions.
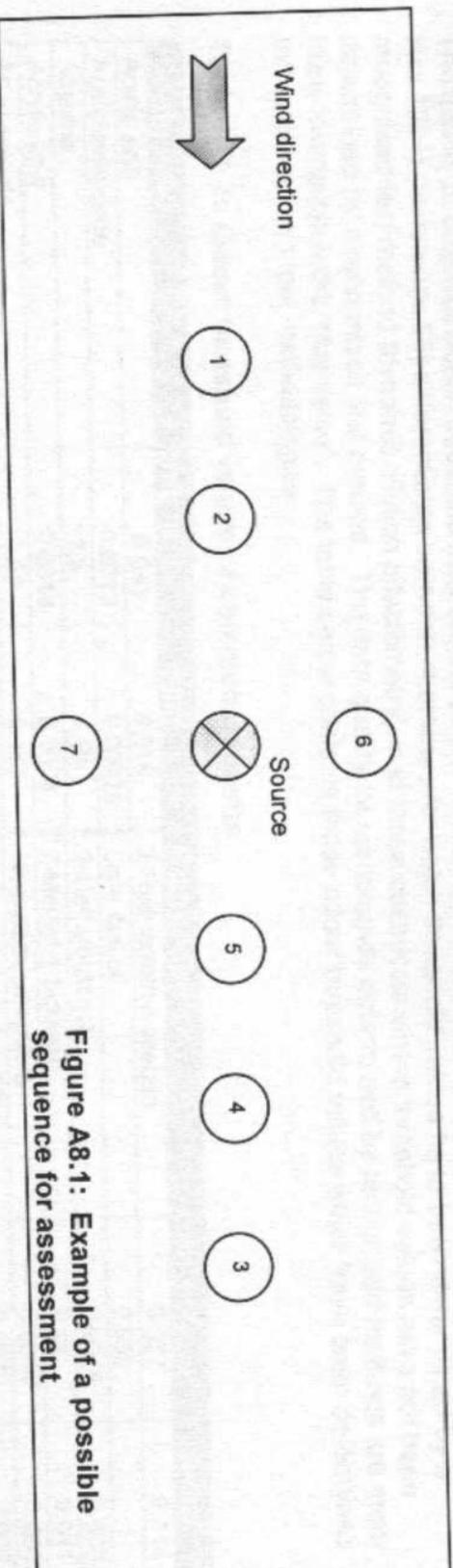

Figure A8.1: Example of a possible sequence for assessment

Data collection and recording

Parameters of interest are:

- detectability / Intensity
- extent & persistence
- sensitivity of the location where the assessment is being made with regard to receptors, and
- offensiveness

A note should also be made of any external activities such as agricultural practices that could be either the source, a contributor to, or a confounding factor in a particular odour event.

The categories of intensity, extent and sensitivity are:

DETECTABILITY / INTENSITY

1. No detectable odour
2. Faint odour (barely detectable, need to stand still and inhale facing into the wind)
3. Moderate odour (odour easily detected while walking & breathing normally)
4. Strong odour
5. Very strong odour (possibly causing nausea)

EXTENT & PERSISTENCE (assuming odour detectable, if not then 0)

1. Local & transient (only detected on installation or at installation boundary during brief periods when wind drops or blows)
2. Transient as above, but detected away from installation boundary
3. Persistent, but fairly localised
4. Persistent and pervasive up to 50m from plant or installation boundary
5. Persistent and widespread (odour detected >50 m from installation boundary)

SENSITIVITY OF LOCATION WHERE ODOUR DETECTED (assuming detectable, if not then 0)

1. Remote (no housing, commercial/industrial premises or public area within 500m)
2. Low sensitivity (no housing, etc. within 100m of area affected by odour)
3. Moderate sensitivity (housing, etc. within 100m of area affected by odour)
4. High sensitivity (housing, etc. within area affected by odour)
5. Extra sensitive (complaints arising from residents within area affected by odour)

OFFENSIVENESS:

The assessment of the offensiveness of odour is necessarily based upon the subjective sensory olfactory response of an observer. Determination of offensiveness depends upon intensity in addition to character, frequency of exposure and persistence (see below).

The determination of whether the odour is "offensive" should be made on the basis that episodes of odour exposure in the locality could be frequent and persistent. The determining officer may be exposed for a few minutes only but the determination needs to take into account the likely long-term response of nearby receptors who may be

Odour - H4 Part 1

Odour threshold values

The quality of odour detection threshold data can be poor. *"Odour measurement and control - an update"* (Woodfield and Hall 1994) (Reference 26) differentiates between chemicals for which threshold values have been determined by a recognised test method (dynamic dilution olfactometry), and those chemicals where threshold values have not been determined by a recognised test method. The data quality for compounds determined by recognised methods are more likely to approach the "true value". The table below contains those odour threshold values which have been determined using recognised test methodologies.

Table A10.3: Odour threshold values of common odorants

Compound	mg m⁻³	ppm
Acetic acid	0.043	0.016
Acetic anhydride	0.0013	0.00029
Acetone	13.9	4.58
Acrylic acid	0.0013	0.0004
Amyl acetate	0.95	0.163
iso Amyl acetate	0.022	0.0038
Benzene	32.5	8.65
1,3-Butadiene	1.1	0.455
1-Butanol	0.09	0.03
2-Butanol	3.3	1
2-Butanone (MEK)	0.87	0.27
Butoxybutane	0.03	0.005
2-Butoxyethanol	0.0051	0.00097
2-Butoxyethyl acetate	0.045	0.0063
Butoxypropanol	0.191	0.0324
Butyl acetate	0.047	0.0066
2-(2-Butoxyethoxy)ethanol	0.0092	0.0013
2,2-butoxyethoxyethyl acetate	0.015	0.0016
Carbon tetrachloride	280	40.73
Carbon sulphide	0.0275	0.0102
m-Cresol	0.0013	0.0003
o-Cresol	0.0028	0.0005
p-Cresol	0.0029	0.0006
Cyclohexane	315	83.8
Cyclohexanone	0.083	0.019
Dichloromethane	3.42	0.912
Diesel	0.06	
Dimethyl adipate	7.101	0.913
Dimethyl glutarate	1.212	0.169
Dimethyl succinate	0.992	0.152
1,4-Dioxane	30.6	7.78
1,3-Dioxolane	56.3	17.02
Diphenylmethane	0.41	0.55
Ethoxypropanol	0.161	0.035
Ethoxypropyl acetate	0.0052	0.0008
Ethyl acetate	2.41	0.61
Ethyl alcohol	0.28	0.136
2-Ethyl-1-butanol	0.07	0.015
2-Ethyl-1-hexanol	0.5	0.086
2-Ethylhexyl acrylate	0.6	0.073
2-Furaldehyde	0.25	0.058
1-Hexanol	0.005	0.0011
Hydrogen sulphide	0.00076	0.0005

Compound	mg m⁻³	ppm
2-Hydroxyethyl acetate	0.527	0.114
Light fuel oil	0.053	
3-Methylbutanal	0.0016	0.0004
2-Methyl-1-butanol	0.16	0.041
Methyldithiomethane	0.0011	0.00026
Methyl 5-ethyl pyridine	0.032	0.006
Methyl methacrylate	0.38	0.085
3-Methoxybutyl acetate	0.044	0.007
1-Methoxypropan-2-ol	0.0122	0.003
1-Methoxy-2-propylacetate	0.0075	0.0014
2-Methyl pentaldehyde	0.096	0.021
2-Methyl-1-pentanol	0.09	0.02
4-Methyl-2-pentanone (MIBK)	0.54	0.121
2-Methyl-2-propanol	71	21.46
α-Methyl styrene	0.021	0.003
1-Nitropropane	28.2	7.09
2-Octene	0.33	0.066
1-Octene	0.5	0.1
2-Octyne	0.03	0.006
2,4-Pentanedione	0.045	0.01
1-Pentanol	0.02	0.0051
Petroleum naptha	0.2	
Phenyl ether	0.0021	0.0003
2-Picoline	0.014	0.0034
Propanal	0.014	0.0054
2-Propanol	1.185	0.442
2-Propen-1-ol	1.2	0.47
iso Propylamine	0.158	0.06
Propylbenzene	0.048	0.009
Propylene-n-butylether	0.206	0.01
Propyl ether	0.024	0.0053
Styrene	0.16	0.0344
1,1,2,2-Tetrachloroethane	1.6	0.21
Toluene	0.644	0.16
Trichloroethylene	8	1.36
Trimethylamine	0.0026	0.001
Xylene (mixed)	0.078	0.016
2,3 Xylenol	0.0037	0.0007
2,4 Xylenol	0.064	0.0117

Other sources of threshold values

Compilation of odour threshold values in air and water, Central Institute for Nutrition and Food Research, TNO, Netherlands, June 1997. Editors: van Gembert L J; Nettenbrejer A H.

Compilation of odour and taste threshold values data, American Society for Testing and Materials, ASTM Data Series DS 48A. Editor: Fazzalari F A.

The documents listed above contain odour threshold values for a much wider range of substances. The fact that a document is listed does not necessarily mean that the values given are consistent with other documents and it is advisable to cross-check values with more than one source as there can be considerable variation. This list is not exhaustive and other published values exist.

Converting mg m³ to odour units using odour threshold values

Chemical analysis of a sample taken at source can be used to determine a mass emission or compliance with an emission limit. The emission can be modelled to give a predicted ground level concentration at receptors.

To allow the impact of a source to be considered in terms of odour concentration, the data can be converted to odour units by using odour threshold values as given overleaf. This can be only reliably be applied to single compounds. It does not work well with mixtures (ie by adding the relative contributions of each to the total mixture) as it does not take synergistic or additive effects into account.

The odour concentration of a mixture can be estimated by:

$$D = C_a / T_a$$

D   is the odour concentration of a mixture (dimensionless, odour units ou_E m^{-3})

C_a is the chemical concentration of compound (a) in mg m^{-3}

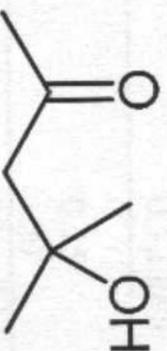T_a is the published odour threshold value of compound (a) in mg m^{-3}

However, there can be large uncertainties in the:
- quality of threshold data;
- quality of chemical data.

Monument Chemical

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A Division of Monument Chemical

Technical Data & Safety Bulletin

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Diacetone Alcohol (DAA)

PRODUCT OVERVIEW

Diacetone Alcohol (DAA) is a clear, colorless liquid is widely used as an industrial and consumer based solvent.

DAA exposure is possible in both industrial and consumer applications. Occupational exposure limits have been established to control the allowable amount of exposure in workplace settings.

Consumer exposure, generally infrequent and short in duration, is also highly dependent upon the conditions under which Diacetone Alcohol is used. See Health Information.

Diacetone Alcohol does not cause adverse health or environmental effects at levels typically found in the workplace or in the environment.

OTHER NAMES

CAS 123-42-2   DAA
4-Hydroxy-4-methylpentan-2-one   2-Pentanone, 4-hydroxy-4-methyl-
4-Hydroxy-2-keto-4-methylpentane 4-Hydroxy-4-methyl-2-pentanone

TYPICAL PROPERTIES

Property	Value
Molecular Weight	116.2 g/mol
Empirical Formula	$C_6H_{12}O_2$
Appearance	Colorless Liquid
Boiling Point @ 760mm Hg	168°C (334°F)
Freezing Point	-43°C (-45.4°F)
Flash Point – Closed Cup	60°C (140°F)
Autoignition Temperature	620°C
Density @ 20°C	0.938 kg/L
Vapor Pressure @ 20°C	0.12 kPa
Evaporation Rate (n-butyl acetate =1) (ether = 1)	0.15 150
Solubility in Water @ 20°C	Miscible
Surface Tension @ 20°C	30 mN/m
Refractive Index @ 20°C	1.421
Viscosity @ 20°C	2.9 mPa·s
Lower Explosive Limit	1.8 v/v%
Upper Explosive Limit	6.9 v/v%
Conductivity @ 20°C	20 µS/m
Dielectric Constant @ 20°C	18.2
Specific Heat @ 20°C	1.9 kJ/kg/°C
Heat of Vaporization @ Tboil	377 kJ/kg
Heat of Combustion (net) @ 25°C	28500 kJ/kg
Odor Threshold	0.27 ppm

Note: The properties reported above are typical physical properties. Haltermann in no way guarantees that the product from any particular lot will conform exactly to the given values.

PRODUCT USES

The principal end uses of Diacetone Alcohol are in industrial coatings, household cleaners, inks, paints, paint removers, paint thinners, pharmaceutical preparations, sealants, primer and pesticides.

DAA is used as a chemical intermediate in the preparation of Methyl Isobutyl Ketone and Hexylene Glycol.

Human exposure will be both in occupational atmospheres and from use of consumer products containing Diacetone Alcohol.

HEALTH INFORMATION

Diacetone Alcohol has a low order of acute toxicity.

Vapor concentrations of 100 ppm for 15 minutes are irritating to the eyes, nose and throat. The ACGIH and OSHA has established a 50 ppm exposure limit.

The acute oral LD_{50} is between approximately 4000 mg/kg.

Moderate skin irritation occurred by application of 500 mg of pure Diacetone Alcohol.

There are no known sensitization or cancer hazards.

POTENTIAL FOR EXPOSURE

There is a potential for occupational and consumer exposure through inhalation and skin contact although exposures through inhalation are expected to be low due to the low vapor pressure.

Based on the uses for Diacetone Alcohol the public could be exposed through:

- **Workplace exposure** – This refers to potential exposure to DAA in a manufacturing facility or through evaporation in various industrial applications. Generally, exposure to DAA of personnel in manufacturing facilities is relatively low because of the low volatility and because the process, storage and handling operations are enclosed. The US Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) to DAA vapors is 50 parts per million (ppm) per an 8-hour work day.

- **Consumer use of products containing DAA** – This category of exposure is highly variable depending on the products used and the conditions under which they are used. Exposure of the majority of consumers is through its use in cleaners, paints and inks. Exposure to aerosols is possible as a result of industrial spraying with paints containing Diacetone Alcohol. Indirect exposures via the environment (e.g. ingestion of surface water contaminated with Diacetone Alcohol) are also possible.

- **Environmental releases** – Diacetone Alcohol can enter the environment as emissions from its manufacture and use as a solvent. It biodegrades within 14 days.

Chemical manufacturers are committed to operating in an environmentally responsible manner everywhere business is done. Efforts are guided by in-depth scientific understanding of the environmental impact of operations, as well as the social and economic needs of the communities. Industrial spills or releases are rare; however a spill may pose a significant flammability issue.

REGULATORY STATUS

Refer to the JHL Material Safety Data sheet for more specific information.

Diacetone Alcohol is not subject to the reporting requirement of CERCLA.

Diacetone Alcohol is not SARA Section 313 chemical.

Diacetone Alcohol is on the U.S. TSCA list and is included in the EEC's EINECS, Canadian DSL, Australian and Japanese chemical inventories.

STORAGE AND HANDLING

General industry practice is to store Diacetone Alcohol in carbon steel vessels, however stainless steel is preferred.

Diacetone Alcohol should be stored only in tightly closed, properly vented containers away from heat, sparks, open flame or strong oxidizing agents.

Handle empty containers carefully. Combustible residue remains after emptying.

Provided proper storage and handling precautions are taken, expect Diacetone Alcohol to be technically stable for at least 12 months. Color may increase overtime depending on storage conditions.

Undue exposure or spillage should be strictly avoided as a matter of good practice. Refer to the Material Safety Data Sheet for more specific information.

ADDITIONAL INFORMATION

Johann Haltermann Ltd. Diacetone Alcohol MSDS
OECD SIDS Assessment for Diacetone Alcohol

Product Code: 40747
Effective Date: 10/1/2012
Revision: 1

ACUTE TOXICITY SUMMARY

VINYL CHLORIDE

(chloroethene; chloroethylene; vinyl chloride monomer; VC; VCM)

CAS Registry Number: 75-01-4

I.   Acute Toxicity Summary (for a 1-hour exposure)

Inhalation reference exposure level	**180,000 µg/m³**
Critical effect(s)	mild headache and dryness of eyes and nose in healthy human volunteers
Hazard Index target(s)	Eyes; Nervous System; Respiratory System

II.   Physical and Chemical Properties (HSDB, 1994 except as noted)

Description	colorless gas
Molecular formula	C_2H_3Cl
Molecular weight	62.5
Density	2.56 g/L @ 25°C
Boiling point	-13°C
Melting point	-153.8°C
Vapor pressure	2,660 mm Hg @ 25°C
Flashpoint	-77.8°C (open cup) (ACGIH, 1991)
Explosive limits	4 to 22% by volume in air (ACGIH, 1991)
Solubility	soluble in alcohol, ethyl ether, carbon tetrachloride, benzene
Odor threshold	3,000 ppm (Amoore and Hautala, 1983)
Odor description	sweet (AIHA, 1989)
Metabolites	chloroethylene oxide, chloroacetic acid (Antweiler, 1976)
Conversion factor	1 ppm = 2.56 mg/m³ @ 25°C

III. Major Uses or Sources

The chief use of vinyl chloride (VC) is in the production of polyvinyl chloride (PVC) resins used for plastic piping and conduit (IARC, 1979). It is also used in the manufacture of methyl chloroform. Vinyl chloride was used as a propellant until 1974 when this use was banned due to its demonstrated carcinogenicity. The main toxicological concern for vinyl chloride is from exposure to the monomer rather than the polymerized forms (i.e., PVC). Thermal decomposition of VC produces hydrogen chloride, carbon monoxide, and traces of phosgene (ACGIH, 1991).

IV.   Acute Toxicity to Humans

The primary acute physiological effect of VC inhalation is CNS depression (Holmberg, 1984). Anesthesia may occur at high concentrations (7,000 - 10,000 ppm) for short durations in both animals and humans (Purchase et al., 1987).

In two accidental human poisonings, workers became incapacitated when exposed to high concentrations of VC gas (Anon., 1953). Following removal from exposure, one of the workers experienced tightness of the chest, nausea, abdominal pain, and headache. Before VC's relationship with certain forms of cancer was established, workers in at least one polyvinyl chloride manufacturing facility reportedly inhaled VC fumes for its euphoric effect, sometimes to the point of unconsciousness (Klein, 1976). Danziger (1960) reported a worker death associated with exposure to high concentrations of VC. Autopsy revealed cyanosis, local burns of the conjunctiva and cornea, congestion of internal organs (especially lung and kidneys), and failure of blood to clot.

Suciu et al. (1975) reported that factory workers exposed to high concentrations of VC experienced euphoria, giddiness, somnolence and, in some cases, narcosis. Yearly average concentrations reported at this factory were between 98 and 2,298 mg/m^3 (38 to 898 ppm).

Two male volunteers exposed to 25,000 ppm (64,000 mg/m^3) VC for 3 minutes reported the odor as pleasant, but became dizzy and disoriented to the space and size of surrounding objects. The men also reported a burning sensation on the soles of their feet (Patty et al., 1930).

In a controlled exposure, 6 adult volunteers (3 male, 3 female) were exposed to varying concentrations up to 20,000 ppm (51,200 mg/m^3) of VC via an oral-nasal mask (Lester et al., 1963). The 5 minute exposures took place twice each day and were separated by 6-hour periods for 3 successive days. No CNS effects were reported at 4,000 ppm (10,240 mg/m^3). Exposure to 12,000 ppm (30,720 mg/m^3) resulted in complaints of dizziness and reeling in 2 subjects. A clear dose-response was observed in this study, but statistical comparisons were not made by the authors.

In a chamber exposure, human volunteers were exposed to 59, 261, 491, or 493 ppm VC for up to 7.5 hours (excluding a 0.5-hour lunch period) (Baretta et al., 1969). The subjects exposed to either 59 or 261 ppm VC reported no untoward effects. However, 2 of 7 subjects exposed to 491 ppm for 3.5 hours and 2 of 4 subjects exposed to 493 ppm for 7.5 hours reported mild headache and dryness of eyes and nose.

Vinyl chloride is known to cause "vinyl chloride disease" upon repeated exposures in workers. This multisystem disorder consists of Raynaud's phenomenon, acro-osteolysis, thrombocytopenia, splenomegaly, portal fibrosis, and hepatic and pulmonary dysfunction (IARC, 1979). This disease is likely an immune complex disorder from the adsorption of VC or a metabolite onto tissue proteins and is unlikely to occur following single acute exposure (Ward et al., 1976).

Differences in genetic susceptibility to hepatotoxicity of vinyl chloride have been described (Huang *et al.*, 1997). Vinyl chloride is metabolized by cytochrome P450 2E1 (CYP2E1) to form the toxic electrophilic metabolites, chloroethylene oxide and chloroacetaldehyde. These metabolites are detoxified by glutathione S-transferases (GSTs). A total of 251 workers from polyvinyl chloride plants were categorized into high or low exposure groups based on air exposure monitoring. Serum alanine aminotransferase (ALT) was used as an indicator of liver function. CYP2E1, GST theta, and GST mu were determined by polymerase chain reaction (PCR) and restriction fragment length polymorphism (RFLP) on peripheral white blood cell DNA. For the low vinyl chloride exposure group, positive GST theta (odds ratio = 3.8, 95% CI 1.2-14.5) but not CYP2E1 was associated with abnormal ALT levels in serum. For the high exposure group, a c2c2 CYP2E1 genotype was associated with an increased risk of abnormal ALT (odds ratio = 5.4, 95% CI 0.7-35.1), while a positive GST theta was associated with significantly reduced risk of abnormal ALT (odds ratio = 0.3, 95% CI 0.1-0.9).

Predisposing Conditions for Vinyl Chloride Toxicity

Medical: Inherited cytochrome P450 and glutathione S-transferase alleles may affect individual susceptibility (Huang *et al.*, 1997).

Chemical: Inducers of hepatic cytochrome-P450 enzymes, such as phenobarbital, potentiate the hepatotoxic effects of inhaled VC in rats (IARC, 1979; Jaeger *et al.*, 1974; Kappus *et al.*, 1975). Liver damage was measured by the release of alanine alpha-ketoglutarate, SGOT, and SGPT enzymes.

Ethanol co-administration with VC resulted in greater toxicity to pregnant mice, rats, or rabbits than exposure to VC alone (John *et al.*, 1981).

V.   Acute Toxicity to Laboratory Animals

A lethality study was carried out by Prodan *et al.* (1975) in which mice, rats, guinea pigs, and rabbits were exposed to VC for 2 hours. Deaths were due to respiratory failure. Animals that were still alive at the end of exposure recovered quickly following removal from the gas. However, no post-exposure observation period was included in the study to investigate possible delayed mortality. Table 1 below shows the LC_{50}, MLE_{05} (maximum likelihood estimate expected to produce a response rate of 5%), BC_{05} and BC_{01} (benchmark concentration at the 95% lower confidence interval of the 5% and 1% lethality level, respectively) as determined by log normal probit analysis (Crump, 1984; Crump and Howe, 1983).

Table 1. Animal lethality benchmark concentration estimates from Prodan et al. (1975) for 2-hour vinyl chloride exposure

Species	LC_{50} (mg/m³ x 10³)	MLE_{05} (mg/m³ x 10³)	BC_{05} (mg/m³ x 10³)	BC_{01} (mg/m³ x 10³)
mouse	299	253	246	227
rat[1]	(394)	(329)	(292)	(260)
guinea pig	591	527	453	410
rabbit	600	545	466	424

[1] Log normal probit analysis indicates the data points for rats resulted in an unacceptable fit.

Exposure of rats, mice and guinea pigs to 100,000 ppm VC (5 animals/species) resulted in increased motor activity at 10 minutes but progressed to muscular incoordination, unsteady gait and pronounced tremor in all species 15 minutes into the exposure (Mastromatteo et al., 1960). Rats and mice became unconscious at 25 minutes while guinea pigs remained conscious during the entire 30 minute exposure period. At 200,000 and 300,000 ppm VC, rats and mice exhibited muscular incoordination at 2 and 1 minutes, respectively, following initiation of exposure. Guinea pigs were slightly more tolerant of the CNS depressant effects at these concentrations. Deaths in mice, rats and guinea pigs occurred at 200,000 ppm and above, 300,000 ppm and 400,000 ppm, respectively.

Exposure to 5,000 and 10,000 ppm vinyl chloride for 8 hours did not produce signs of CNS depression in guinea pigs (Patty et al., 1930). Inhalation of 25,000 ppm (64,000 mg/m³) (sample size unspecified) resulted in motor ataxia and unsteadiness by 5 minutes, deep narcosis without convulsions or twitching by 90 minutes, and death by respiratory paralysis by 6 hours. Gross pathological changes included congestion and edema in the lungs, and hyperemia in the liver and kidneys. Guinea pigs exposed to 100,000 ppm developed complete loss of coordination and incomplete narcosis 2 minutes into exposure.

Lester et al. (1963) showed that rats exposed to 50,000 ppm (128,000 mg/m³) VC for 2 hours exhibited moderate intoxication with loss of the righting reflex. Loss of the corneal reflex was apparent following a 2-hour exposure to 100,000 ppm (256,000 mg/m³). Exposure of these rats to 100,000 ppm (256,000 mg/m³) for two 8-hour periods resulted in mortality from a "pneumonic process."

Tatrai and Ungvary (1981) exposed mice, rats and rabbits to 1,500 ppm VC for up to 24 hours. Rats and rabbits were unaffected, but 90% of mice died following 12 hours of exposure and 100% of mice died following 24 hours of exposure. Pathological examination of mice revealed hemorrhages and vasodilatation in the lungs, suggestive of pulmonary edema.

Dermal exposure of monkeys to gaseous VC indicated that absorption of VC across the intact skin is very limited (Hefner et al., 1975).

Rhesus monkeys eliminate VC at approximately half the rate of mice and rats (Buchter et al., 1980). Rodents may therefore be less sensitive than primates to systemic VC toxicity.

VI.   Reproductive or Developmental Toxicity

In a review of the epidemiological data, Hemminki and Vineis (1985) concluded that there was inadequate evidence of increased teratogenesis in humans exposed to VC.

Animal studies have also failed to show significant association between VC exposure and teratogenesis. In rats, exposure to VC at a concentration of 1,500 ppm (3,840 mg/m³) for 24 hours/day during all three trimesters of pregnancy did not result in an increased incidence of birth defects (13-28 rats per group) (Ungvary et al., 1978). Pharmacokinetic studies showed that VC crossed the placental barrier of these rats, and was present in fetal blood.

John et al. (1981) showed that exposure of pregnant mice, rats or rabbits to 500 ppm (1,280 mg/m³) VC for 7 hours/day during organogenesis did not result in teratogenicity or embryotoxicity. Inhalation of 2,500 ppm (6,400 mg/m³) caused slight ossification changes in the offspring and maternal mortality in the mice. Co-administration of 15% ethanol in drinking water resulted in maternal toxicity, but no elevation in fetal effects above that seen for ethanol exposure alone.

Male mice exposed to 30,000 ppm (76,800 mg/m³) VC 6 hours/day for 5 days were mated to control females, with no resultant increase in spontaneous abortions (Purchase, 1975). However, Bi et al. (1985) showed that inhalation exposure of male rats to 100 ppm VC for 6 hours/day, 6 days/week for 3 months resulted in significant damage to seminiferous tubules compared to controls (p < 0.05).

VII.   Derivation of Acute Reference Exposure Level and Other Severity Levels
(for a 1-hour exposure)

Reference Exposure Level (protective against mild adverse effects):   180,000 µg/m³

Study	Baretta et al., 1969
Study population	4-8 healthy human volunteers
Exposure method	(1) 7.5 hour exposures to 261 ppm VC
	(2) 3.5 hour exposures to 491 ppm VC
	(3) 7.5 hour exposures to 493 ppm VC
Critical effects	subjective reports of mild headaches and dryness of eyes and nose (groups 2 and 3); no effects reported by group 1
LOAEL	3.5 to 7.5 hour exposure to 491 or 493 ppm
NOAEL	7.5 hour exposure to 261 ppm
Exposure duration	7.5 hours
Equivalent 1 hour concentration	715 ppm (C² * 1 hr = [261 ppm]²* 7.5 hrs)

LOAEL uncertainty factor   1

Interspecies uncertainty factor   1

Intraspecies uncertainty factor   10

Cumulative uncertainty factor   10

Reference Exposure Level   72 ppm (180 mg/m³, 180,000 µg/m³)

Level Protective Against Severe Adverse Effects

Exposure of guinea pigs to 10,000 ppm VC for 8 hours did not produce signs of CNS depression (Patty *et al.*, 1930). Exposure to 25,000 ppm produced motor ataxia and unsteadiness within 5 minutes and unconsciousness in 90 minutes. Exposure to 100,000 ppm produced motor ataxia within 2 minutes in guinea pigs (Patty *et al.*, 1930) and motor ataxia with a pronounced tremor within 15 minutes in rats and mice (Mastromatteo *et al.*, 1960). Higher concentrations of VC (200,000 and 300,000 ppm) reduced the onset of CNS depression to 1 to 2 minutes following initiation of exposure (Mastromatteo *et al.*, 1960).

Based on the results of Patty *et al.* (1930), the NOAEL for motor ataxia, or muscular incoordination, in guinea pigs was 10,000 ppm for 8-hour exposure. The LOAEL was 25,000 ppm, which resulted in motor ataxia within 5 minutes and unconsciousness in 90 minutes. The NOAEL was adjusted to a 1-hour exposure by the formula $C^n \times T = K$ (where "n" = 2), which resulted in a concentration of 28,282 ppm VC. Applying uncertainty factors of 10 each to account for interspecies differences and increased susceptibility of sensitive human individuals results in a final value of 280 ppm (720 mg/m³) VC for a level protective against serious adverse effects.

Level Protective Against Life-threatening Effects

Log-normal analysis of lethality data for mice, guinea pigs, and rabbits (Prodan *et al.*, 1975) yielded BC_{05} estimates of 246,000, 453,000, and 466,000 mg/m³, respectively. Mastromatteo *et al.* (1960) reported 30-minute no-observed-lethality levels of 100,000, 300,000, and 400,000 ppm, respectively, for mice, rats and guinea pigs.

The study by Prodan *et al.* (1975) provides data from which to derive an estimate for VC using the benchmark concentration approach. The BC_{05} of the most sensitive species, the mouse, was adjusted to a 1-hour equivalent exposure using the equation $C^n \times T = K$, where "n" = 2. Uncertainty factors of 3 and 10 were applied to the adjusted BC_{05} of 348,000 mg/m³ (136,000 ppm) to account for interspecies differences and increased susceptibility of sensitive human individuals, respectively. The resultant level protective against life-threatening effects is thus 4,500 ppm (12,000 mg/m³).

VIII. References

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Odour guidance 2010

natural
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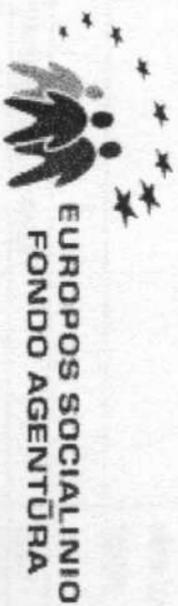SCOTTISH GOVERNMENT

SEPA
Scottish Environment
Protection Agency

Table A1.5 Additional odour threshold values of common odorants

Compound	mg m⁻³	ppm	Compound	mg m⁻³	ppm
Acetic acid	0.043	0.016	2-Hydroxyethyl acetate	0.527	0.114
Acetic anhydride	0.0013	0.00029	Light fuel oil	0.053	Acetone
13.9	4.58	3-	Methylbutanal	0.0016	0.0004
Acrylic acid	0.0013	0.0004	2-Methyl-1-butanol	0.16	0.041
Amyl acetate	0.95	0.163	Methyldithiomethane	0.0011	0.00026
iso Amyl acetate	0.022	0.0038	2-Methyl 5-ethyl pyridine	0.032	0.006
Benzene	32.5	8.65	Methyl methacrylate	0.38	0.085
1,3-Butadiene	1.1	0.455	3-Methoxybutyl acetate	0.044	0.007
1-Butanol	0.09	0.03	1-Methoxypropan-2-ol	0.0122	0.003
2-Butanol	3.3	1	2-Methoxy-2-propylacetate	0.0075	0.0014
2-Butanone (MEK)	0.87	0.27	2-Methyl-1-pentanol	0.096	0.021
Butoxybutane	0.03	0.005	2-Methyl pentaldehyde	0.09	0.02
2-Butoxyethanol	0.0051	0.00097	4-Methyl-2-pentanone (MIBK)	0.54	0.121
2-Butoxyethyl acetate	0.045	0.0063	2-Methyl-2-propanol	71	21.46
Butoxypropanol	0.191	0.0324	α-Methyl styrene	0.021	0.003
Butyl acetate	0.047	0.0066	1-Nitropropane	0.0021	0.0003
2-(2-Butoxyethoxy)ethanol	0.0092	0.0013	1-Octene	28.2	7.09
2,2-butoxyethoxyethyl acetate	0.015	0.0016	2-Octene	0.33	0.066
Carbon tetrachloride	280	40.73	2-Octyne	0.5	0.1
Carbon sulphide	0.0275	0.0102	2,4-Pentanedione	0.03	0.006
m-Cresol	0.0013	0.0003	1-Pentanol	0.045	0.01
o-Cresol	0.0028	0.0005	Petroleum naptha	0.2	
p-Cresol	0.0029	0.0006	Phenyl ether	0.0021	0.0003
Cyclohexane	315	83.8	2-Picoline	0.014	0.0034
Cyclohexanone	0.083	0.019	Propanal	0.014	0.0054
Dichloromethane	3.42	0.912	2-Propanol	1.185	0.442
Diesel	0.06		2-Propen-1-ol	1.2	0.47
Dimethyl adipate	7.101	0.913	iso Propylamine	0.158	0.06
Dimethyl glutarate	1.212	0.169	Propylbenzene	0.048	0.009
Dimethyl succinate	0.992	0.152	Propylene-n-butylether	0.206	0.01
1,4-Dioxane	30.6	7.78	Propyl ether	0.024	0.0053
1,3-Dioxolane	56.3	17.02	Styrene	0.16	0.0344
Diphenylmethane	0.41	0.55	1,1,2-Tetrachloroethane	1.6	0.21
Ethoxypropanol	0.161	0.035	Toluene	0.644	0.16
Ethoxypropyl acetate	0.0052	0.0008	Trichloroethylene	8	1.36
Ethyl acetate	2.41	0.61	Trimethylamine	0.0026	0.001
Ethyl alcohol	0.28	0.136	Xylene (mixed)	0.078	0.016
2-Ethyl-1-butanol	0.07	0.015	2,3 Xylenol	0.0037	0.0007
2-Ethyl-1-hexanol	0.5	0.086	2,4 Xylenol	0.064	0.0117
2-Ethylhexyl acrylate	0.6	0.073			
2-Furaldehyde	0.25	0.058			
1-Hexanol	0.005	0.0011			
Hydrogen sulphide	0.00076	0.0005			

Kvapų valdymo metodinės rekomendacijos

Metodinės rekomendacijos parengtos įgyvendinant 2007–2013 m. Žmogiškųjų išteklių plėtros veiksmų programos 4 prioriteto „Administracinių gebėjimų stiprinimas ir viešojo administravimo efektyvumo didinimas" įgyvendinimo priemonės VP1-4.3-VRM-02-V „Viešųjų politikų reformų skatinimas" projektą „Gyvenamosios aplinkos sveikatos rizikos veiksnių valdymo tobulinimas"

VILNIAUS GEDIMINO
TECHNIKOS UNIVERSITETAS

Valstybinė visuomenės sveikatos priežiūros tarnyba
prie Sveikatos apsaugos ministerijos

Vilnius, 2012

1.2 lentelė. Kvapo slenksčio vertę turintys cheminiai junginiai (Duomenys, surinkti Aplinkos ministerijos nustatyta tvarka, pildant ataskaitos formą Nr. 2 – Atmosfera)

Teršalo pavadinimas	Kvapo slenkstis, ppm	Teršalo pavadinimas	Kvapo slenkstis, ppm
1	2	1	2
trimetilbenzenas	2,4	etilo eteris (dietilo eteris)	2,29
1,3 – butadienas (divinilas)	0,455	fenolis	0,011
2-etoksietanolis (etilceliozolvas, etilenglikolio etilo esteris)	6,5	fluoro vandenilis	0,042
2-metoksietanolis (metilceliozolvas)	0,11	formaldehidas (skruzdžių aldehidas)	0,871
acetaldehidas (acto aldehidas)	0,186	ftalio anhidridas	0,052
akrilo rūgštis (etilenkarboninė rūgštis)	0,4	furfurolas (2-formilfuranas)	0,078
akrilo nitrilas	16,6	heksametilen-1,6-diizocianatas	0,001
akroleinas (2-propenalis, akrilo aldehidas)	0,174	izobutanolis (izobutilo alkoholis, 2-metilpropanolis)	0,832
amoniakas	5,75	izobutilacetatas (acto rūgšties izobutilo esteris)	0,479
azoto dioksidas	0,186	izopropanolis (izopropilo alkoholis, dimetilkarbinolis)	0,44
azoto rūgštis	0,267	izopropilbenzenas (kumolas)	0,024
benzilo alkoholis (fenilkarbinolis)	5,55	izopropilbenzeno hidroperoksidas (kumolo hidroperoksidas)	0,005
butanolis (butilo alkoholis)	0,03	kaprolaktamas	0,064
butanonas (metiletilketonas)	5,0	metanolis (metilo alkoholis)	141
butilacetatas	0,007	metilacetatas	6,17
butilakrilatas (akrilo rūgšties butilo esteris)	0,03	metilakrilatas	0,263
butilceliozolvas (etilenglikolio monoizobutilo eteris, butilglikolis)	0,001	metilpentanas	65-248
chloras	0,05	metil-tret-butilo-esteris (2-metoksi-2-metilpropanas)	0,053
chlorbenzenas	0,741	monoetanolaminas	2,59
chloro vandenilis (druskos rūgštis)	0,77	naftalinas	0,015
chloroprenas	14,9	ozonas	0,051
cikloheksanas	83,3	pentanolis (amilo alkoholis)	0,1-0,3
cikloheksanonas	0,019	piridinas	0,117
diacetonas (diacetono alkoholis)	0,891	propilenas	17
dietanolaminas (2,2'-dioksietilaminas, 2,2'-imidoetanolis)	0,025	propanalis (propiono aldehidas)	0,145
difenilmetandiizocianatas	0,4	sieros dioksidas	0,708
dimetilaminas	0,081	sieros vandenilis (vandenilio sulfidas)	0,0005
dimetiletanolaminas	0,045	skruzdžių rūgštis (metano rūgštis)	28,2
dimetilo eteris	0,3-9,0	terpentinas	100-200
epichlorhidrinas (3-chlor-1,2-epoksipropanas)	0,934	tetrachloretilenas (perchloretilenas)	6,17
etanolaminas	2,59	tetrahidrofuranas (TGF,oksolanas)	3,8
etilacetatas	0,61	toluilendiizocianatas	0,17
etilacetonas	1,55	toluenas	0,16
etilakrilatas (akrilo rūgšties etilo esteris)	0,0009	trichloretilenas	1,36
etilbenzenas	2,3	trichlormetanas (chloroformas, chladonas 20)	11,7
etilenglikolis (etandiolis)	60,3 mg/m³	trikrezolis	0,00005-0,0079
etileno dioksidas (dioksanas)	7,78	vinilacetatas	0,603
etileno oksidas	851	vinilo chloridas	0,253