Odor as an Aid to Chemical Safety: Odor Thresholds Compared with Threshold Limit Values and Volatilities for 214 Industrial Chemicals in Air and Water Dilution

John E. Amoore†
Olfacto-Labs, PO Box 757, El Cerrito, California 94530, USA

Earl Hautala
Western Regional Research Center, US Department of Agriculture, Agricultural Research Service, Berkeley, California 94710, USA

Key words: odor threshold; threshold limit value; volatility; solubility; distribution ratio; chemical safety.

The body of information in this paper is directed to specialists in industrial health and safety, and air and water pollution, who need quantitative data on the odor thresholds of potentially hazardous chemical vapors and gases. The literature, largely unorganized, has been reviewed for 214 compounds and condensed into tables based on consistent units. Data on the volatility, solubility, ionization and water–air distribution ratio at 25 °C are included. From the currently recommended threshold limit value (TLV), a safe dilution factor and an odor safety factor are calculated for each compound. The equivalent data are presented for both air and water dilutions of the chemicals. Available data are summarized on the variability of odor sensitivities in the population, and the increased odor concentrations that are required to elicit responses from persons whose attention is distracted, or who are sleeping. This information is reduced to calibration charts that may be used to estimate the relative detectability, warning potential and rousing capacity of the odorous vapors. Each compound has been assigned a letter classification, from A to E, to indicate the margin of safety, if any, that may be afforded by the odor of the compound as a warning that its threshold limit value is being exceeded.

INTRODUCTION

The human sense of smell, although not as acute as that of some other mammals and certain insects, can be a valuable source of information about chemicals in the environment. The nose is exceedingly sensitive to certain repulsive-smelling compounds, produced in trace amounts by pathogenic or putrifying bacteria and molds, such as methyl mercaptan, trimethylamine, 1-pyrroline and isovaleric acid. Although these chemicals themselves are generally harmless to man in the concentrations occurring naturally in air, water or food, heightened odor sensitivities to them may have developed from the protection offered against dangerous or fatal infection or food poisoning.

With the advent of the industrial revolution, persons have been exposed to diverse chemicals, many of which are commonly found in workplace settings at concentrations much higher than occur naturally. Some of these pose an inherent risk to health at certain concentrations. In recognition of this potential hazard, the American Conference of Governmental Industrial Hygienists (ACGIH) publishes an annual listing of Threshold Limit Values (TLV).[1] (TLV® is a registered trademark of ACGIH, whom we thank for permission to use the TLV designation in this paper.) The TLV used in this paper is the time-weighted average value. Based on the best available industrial health data, it is defined as the time-weighted average concentration for a normal 8-h work-day and a 40-h work-week, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.

The actual concentrations of specific chemicals in the working environment can be sampled and analyzed by various chemical and instrumental means, to determine whether the TLV is being exceeded. The necessary equipment, however, is often expensive, cumbersome and slow, and requires professional skills to operate and interpret. Nevertheless, there is a little-considered alternative, the human nose, that could serve as a first-line warning system for hazardous concentrations of many chemical vapors. The nose is perfectly placed to sample the inspired air, monitors rapidly and continuously, and may even exceed the sensitivity of the best instruments. It is, however, at best only semi-quantitative, and it requires calibration to determine its sensitivity to those chemicals that are of importance in industrial practice. In this regard, it is necessary to evaluate the increased concentration of a compound that may be required to alert the average person to the presence of an odor, while engaged in another activity which requires attention. The typical variability of the population for odor sensitivity and responsiveness should also be taken into consideration.

METHODS

Literature search for basic data

A search was conducted for the olfactory and physiochemical characteristics of all volatile compounds and gases listed

† Author to whom correspondence should be addressed.

CCC-0260-437X/83/0003-0272$09.50

in the *Threshold Limit Values*[1] for 1982. The first objective was to find literature values for the odor-detection thresholds, measured by dilution in either air or water. Dilution of odorants in air can be achieved either dynamically, by adding a calibrated flow of odorant vapor to an air-stream, or statically, by dispersing a known amount of odorant in a vessel or chamber. In the water-dilution procedure, the odorant is prepared as a series of aqueous dilutions in closed, partially filled vessels from which the head-space vapors can be sniffed. Previous reviews include those of Laffort,[2] Patte *et al.*,[3] van Gemert and Nettenbreijer,[4] van Gemert,[5] Fazzalari[6] and the ACGIH *Documentation of Threshold Limit Values*.[7]

In practically every case, we consulted the original articles, so as to minimize errors of transcription, calculation or duplication. Nearly all of the odor thresholds and references are available in the recent comprehensive compilations by van Gemert.[4,5] If an author gave only a recognition threshold, this was accepted, because recognition of an odor requires on average only about three times the detection threshold concentration.[8]

If, for any compound, an odor threshold could be located, then a further search was conducted for relevant physical data. The molecular weights, liquid densities and ionization constants (of acids and bases) for these common compounds can be found in laboratory handbooks. The vapor pressures at 25 °C were usually interpolated by linear regression computations from the tables of Stull.[9] Solubilities in water at 25 °C were often interpolated graphically from data collected by Seidell and co-workers.[10,11] More current information is given in Verschueren's handbook.[12] Certain missing data on vapor pressures, solubilities, ionization constants, and also occasionally data on the air-water partition coefficient, were found in Beilstein's *Handbuch*[13] and its four supplements. A few solubilities were estimated by extrapolation of homologous series or by comparison with isomers.

The air-water partition coefficient describes the relative distribution of a chemical in this two-phase system. Quantitatively, it is the ratio of the concentrations of the chemical in air and water (both expressed as g l^{-1}) at equilibrium. For compounds of finite water solubility, the coefficient

Table 1. Literature odor thresholds for *n*-butyl alcohol[a]

Water-dilution threshold		Air-dilution threshold		
Original data	g l^{-1}	Original data	g l^{-1}	First reference
		1 μg/l	1.00×10^{-6}	Passy, 1892
		0.565×10^{-8} mol l^{-1}	4.18×10^{-7}	Backman, 1917
		0.000223 mg/l	2.23×10^{-7}	Jung, 1936
		$Act_{25} = 6 \times 10^{-6}$	1.61×10^{-7}	Gavaudan, 1948
		$Act_{37} = 7.0 \times 10^{-4}$	4.09×10^{-5}	Mullins, 1955
0.005% (v/v)	4.03×10^{-2}		1.45×10^{-5}	Moncrieff, 1957
		15 ppm (v/v)	4.56×10^{-5}	Scherberger, 1958
1 mg/l	1.00×10^{-3}		3.60×10^{-7}	Nazarenko, 1962
1.00 ppm (w/v)	1.00×10^{-3}		3.60×10^{-7}	Rosen, 1962
2.5 ppm (v/v)	2.01×10^{-3}		7.24×10^{-7}	Baker, 1963
		$Act_{25} = 5 \times 10^{-5}$	1.40×10^{-6}	Gavaudan, 1966
		33 mg/m^3	3.30×10^{-5}	May, 1966
0.50 ppm (v/v)	4.02×10^{-4}		1.45×10^{-7}	Flath, 1967
		1.10×10^{13} mol/cc	1.34×10^{-6}	Dravnieks, 1968
		1.2 mg/m^3	1.20×10^{-6}	Khachaturyan, 1969
		0.013 mg/l	1.30×10^{-5}	Corbitt, 1971
		$-\log_{10}$ M/l = 7.91	9.12×10^{-7}	Laffort, 1973
		0.30 ppm (v/v)	9.11×10^{-7}	Hellman, 1974
		3.16 ppm (v/v)	9.60×10^{-6}	Moskowitz, 1974
		62 ppm (v/v)	1.88×10^{-4}	Moskowitz, 1974
2.0 mg/kg	2.00×10^{-3}		7.20×10^{-7}	de Grunt, 1975
3.6×10^{-4} M/l	2.67×10^{-2}		9.61×10^{-6}	Hertz, 1975
2.77 ppm (w/v)	2.77×10^{-3}		9.97×10^{-7}	Lillard, 1975
		0.0231 mmHg	9.23×10^{-5}	Piggott, 1975
		0.390 ppm (v/v)	1.18×10^{-6}	Dravnieks, 1976
		2.8×10^{-1} ppm (v/v)	8.50×10^{-7}	Williams, 1977
6.5×10^{-3} g/l	6.50×10^{-3}		2.34×10^{-6}	Amoore, 1978
		3.5 ppm (v/v)	1.06×10^{-5}	Laing, 1978
		$\log_2$ ppb = 10.42	4.15×10^{-6}	Punter, 1980

Geometric mean, air-dilution threshold = 2.54×10^{-6} g l^{-1} ($N = 29$)
= 2.54 mg m^{-3}
= 0.835 ppm (v/v)
Standard deviation = $x/\div 7.14$; Standard error = $x/\div 1.44$

[a] MW = 74.1 g; D_{25} 0.806 g ml^{-1}; VP_{25} = 6.99 mmHg; S_{25} = 73.0 g l^{-1}; air-water partition coefficient at 25 °C = 3.6×10^{-4} (expt.), 3.61×10^{-4} (calc.).

Table 2(a) Air-dilution odor threshold data on 214 industrial chemicals. The numerical data are mostly rounded off to two significant figures. Note that ppm on this half of Table 2 are in v/v units ($\mu l\, l^{-1}$) for the gaseous chemical in air dilution. See Methods for further explanation of each column. TLVs are reproduced from Ref. 1 (1982) with permission from ACGIH

Substance	1 Threshold limit value (ppm; v/v)	2 Volatility at 25 °C (ppm; v/v)	3 Air odor threshold (ppm; v/v)	4 Standard error (x/÷)	5 Safe dilution factor	6 Odor safety factor	7 Odor safety class
Acetaldehyde	100	g	0.050	1.7	10 000	2000	A
Acetic acid	10	20 000	0.48	1.5	2000	21	C
Acetic anhydride	5	6700	0.13	1.1	1300	39	B
Acetone	750	290 000	13	1.6	390	57	B
Acetonitrile	40	120 000	170	2.8	3000	0.23	D
Acetylene	140 000[i]	g	620	2.8	7	230	B
Acrolein	0.1	360 000	0.16	1.5	3 600 000	0.61	D
Acrylic acid	10	5800	0.094	–	580	110	B
Acrylonitrile	2	140 000	17	2.4	72 000	0.12	E
Allyl alcohol	2	33 000	1.1	1.3	16 000	1.8	C
Allyl chloride	1	480 000	1.2	2.5	480 000	0.84	D
Ammonia	25	g	5.2	2.0	40 000	4.8	C
n-Amyl acetate	100	5200	0.054	2.1	52	1800	A
sec-Amyl acetate	125	9200	0.0020	–	74	61 000	A
Aniline	2	630	1.1	1.6	310	1.9	C
Arsine	0.05	g	0.50	–	20 000 000	0.10	E
Benzene	10	120 000	12	1.6	12 000	0.85	D
Benzyl chloride	1	1600	0.044	1.1	1600	23	C
Biphenyl	0.2	11	0.00083	–	56	240	B
Bromine	0.1	270 000	0.051	2.2	2 700 000	2.0	C
Bromoform	0.5	8000	1.3	2.3	16 000	0.39	D
1,3-Butadiene	1000	g	1.6	2.5	1000	640	A
Butane	800	g	2700	1.4	1300	0.29	D
2-Butoxyethanol	25	1300	0.10	–	52	250	B
n-Butyl acetate	150	16 000	0.39	2.5	110	390	B
n-Butyl acrylate	10	7100	0.035	5.3	720	290	B
n-Butyl alcohol	50	9200	0.83	1.4	180	60	B
sec-Butyl alcohol	100	23 000	2.6	2.0	230	38	B
tert-Butyl alcohol	100	55 000	47	2.6	550	2.1	C
n-Butylamine	5	93 000	1.8	2.5	19 000	2.7	C
n-Butyl lactate	5	590	7.0	–	120	0.71	D
n-butyl mercaptan	0.5	~49 000	0.00097	1.4	97 000	510	B
p-tert-Butyltoluene	10	850	5.0	–	85	2.0	C
Camphor	2	450	0.27	1.9	230	7.3	C
Carbon dioxide	5000	g	74 000	1.5	200	0.067	E
Carbon disulfide	10	470 000	0.11	1.9	47 000	92	B
Carbon monoxide	50	g	100 000	10	20 000	0.00050	E
Carbon tetrachloride	5	140 000	96	1.8	29 000	0.052	E
Chlorine	1	g	0.31	1.8	1 000 000	3.2	C
Chlorine dioxide	0.1	g	9.4	1.6	10 000 000	0.011	E
α-Chloroacetophenone	0.05	9.9	0.035	1.1	200	1.4	C
Chlorobenzene	75	15 000	0.68	1.6	200	110	B
Chlorobromomethane	200	190 000	400	–	940	0.50	D
Chloroform	10	250 000	85	1.7	25 000	0.12	E
Chloropicrin	0.1	34 000	0.78	1.4	340 000	0.13	E
β-Chloroprene	10	290 000	15	7.9	29 000	0.68	D
o-Chlorotoluene	50	4700	0.32	1.5	94	150	B
m-Cresol	5	180	0.00028	2.4	36	17 000	A
trans-Crotonaldehyde	2	~41 000	0.12	1.1	20 000	17	C
Cumene	50	5900	0.088	2.9	120	570	A

Table 2(b) Water-dilution odor threshold data on the same 214 chemicals. Note that ppm on this half of Table 2 are in w/v units (mg l^{-1}) for the chemical in aqueous solution. The numerical values in Table 2 are almost invariably compiled, averaged, re-calculated or extrapolated from the literature, and are *not* new experimental determinations

	8	9	10	11	12	13	14	
							Number of thresholds performed	
Substance	Water TLV equivalent (ppm; w/v)	Solubility at 25°C (ppm; w/v)	Water odor threshold (ppm; w/v)	Molecular weight (g)	Density at 20–25°C (g ml^{-1})	Water–air distribution ratio (w/v)	air	water
Acetaldehyde	67	∞	0.034	44	0.79_{16}	370	6	3
Acetic acid (A/4.7)	2000	∞	97	60	1.05	82 000	14	4
Acetic anhydride	d	d	d	102	1.08	d	2	–
Acetone	1100	∞	20	58	0.79	620	20	8
Acetonitrile	70	∞	300	41	0.78	1000	3	–
Acetylene	(150)	1000	(0.67)	26	g	1.0	2	–
Acrolein	0.066	200 000	0.11	56	0.84	290	7	1
Acrylic acid (A/4.3)		∞		72	1.05		1	–
Acrylonitrile	1.1	73 000	9.1	53	0.80	240	2	2
Allyl alcohol	26	∞	14	58	0.85	5600	4	–
Allyl chloride	(0.0075)	3600_{20}	(0.0089)	76	0.94	2.4	2	–
Ammonia (B/9.2)	7.1	280 000	1.5	17	g	400	11	2
n-Amyl acetate	68	1800_{20}	0.037	130	0.88	130	5	4
sec-Amyl acetate	110	1700	0.0017	130	0.87	160	–	1
Aniline (B/4.6)	120	37 000	65	93	1.02	16 000	9	1
Arsine	(0.000035)	670	(0.00035)	78	g	0.22	1	–
Benzene	(0.15)	1800	(0.17)	78	0.88	4.6	19	4
Benzyl chloride	0.28	460_{30}	0.012	127	1.10	55	2	–
Biphenyl	0.12	6.7	0.00050	154	s	95	–	1
Bromine	0.012	33 000	0.0063	160	3.12	19	4	–
Bromoform	0.20	3100	0.51	253	2.89	38	4	1
1,3-Butadiene	(0.88)	850	(0.0014)	54	g	0.40	6	–
Butane	(0.051)	61	(0.17)	58	g	0.027	4	–
2-Butoxyethanol		∞		118	0.90		1	–
n-Butyl acetate	65	6800	0.17	116	0.88	91	9	3
n-Butyl acrylate	2.2	1600_{20}	0.0078	128	0.90	43	2	1
n-Butyl alcohol	420	73 000	7.1	74	0.81	2800	20	9
sec-Butyl alcohol	730	200 000	19	74	0.81	2400	5	1
tert-Butyl alcohol	620	∞	290	74	0.78	2000	4	1
n-Butylamine (B/10.6)	17	∞	6.2	73	0.73	1100	3	2
n-Butyl lactate	370	42 000	520	146	0.98	12 000	1	–
n-Butyl mercaptan (A/10.8)	(0.0061)	600_{20}	(0.000012)	90	0.84	3.3	6	–
p-tert-Butyltoluene	(0.064)	~5.5	(0.032)	148	0.86	1.1	1	–
Camphor	7.5	1700_{20}	1.0	152	s	600	9	3
Carbon dioxide (A/6.4)	(7.5)	1400	(110)	44	g	0.83	2	–
Carbon disulfide	(0.036)	1700	(0.00039)	76	1.26	1.2	6	–
Carbon monoxide	(0.0013)	26	(2.7)	28	g	0.023	2	–
Carbon tetrachloride	(0.027)	770	(0.52)	154	1.59	0.85	10	1
Chlorine	(0.0065)	6300	(0.0020)	71	g	2.2	7	–
Chlorine dioxide (A)	0.0071	$87\,000_{15}$	0.67	67	g	26	1	1
α-Chloroacetophenone	d	d	d	155	s	d	2	–
Chlorobenzene	5.5	1100	0.050	113	1.10	16	6	2
Chlorobromomethane	17	~16 000	34	129	1.93	16	1	–
Chloroform	(0.28)	7100	(2.4)	119	1.48	5.7	14	1
Chloropicrin	(0.0048)	1600	(0.037)	164	1.65	7.1	1	1
β-Chloroprene	(0.016)	480_{20}	(0.024)	88	0.96	0.45	2	1
o-Chlorotoluene	(1.1)	100_{30}	(0.0069)	127	1.08	4.1	1	1
m-Cresol (A/10.1)	640	23 000	0.037	108	1.03	29 000	3	3
trans-Crotonaldehyde	7.2	$150\,000_{20}$	0.42	70	0.85	1200	1	1
Cumene	(0.45)	53	(0.00080)	120	0.86	1.8	6	1

Table 2(a)—*Continued*

Substance	1 Threshold limit value (ppm; v/v)	2 Volatility at 25°C (ppm; v/v)	3 Air odor threshold (ppm; v/v)	4 Standard error (×/÷)	5 Safe dilution factor	6 Odor safety factor	7 Odor safety class
Cyclohexane	300	130 000	25	2.8	430	12	C
Cyclohexanol	50	2000	0.15	2.1	39	340	B
Cyclohexanone	25	6000	0.88	2.2	240	28	B
Cyclohexene	300	99 000	0.18	–	330	1600	A
Cyclohexylamine	10	15 000	2.6	–	1500	3.8	C
Cyclopentadiene	75	~560 000	1.9	–	7500	40	B
Decaborane	0.05	~110	0.060	–	2300	0.83	D
Diacetone alcohol	50	1600	0.28	–	33	180	B
Diborane	0.1	g	2.5	–	10 000 000	0.040	E
o-Dichlorobenzene	50	1800	0.30	4.2	37	160	B
p-Dichlorobenzene	75	1200	0.18	4.1	17	420	B
trans-1,2-Dichloroethylene	200	420 000	17	16	2100	12	C
β,β'-Dichloroethyl ether	5	1500	0.049	–	290	100	B
Dicyclopentadiene	5	3600	0.0057	1.9	720	870	A
Diethanolamine	3	78	0.27	–	26	11	C
Diethylamine	10	310 000	0.13	2.9	31 000	77	B
Diethylaminoethanol	10	2900	0.011	–	290	910	A
Diethyl ketone	200	22 000	2.0	2.1	110	97	B
Diisobutyl ketone	25	3300	0.11	–	130	230	B
Diisopropylamine	5	110 000	1.8	3.9	21 000	2.7	C
N-Dimethylacetamide	10	2600	47	–	260	0.21	D
Dimethylamine	10	g	0.34	3.1	100 000	29	B
N-Dimethylaniline	5	1000	0.013	3.8	200	400	B
N-Dimethylformamide	10	3100	2.2	46	310	4.6	C
1,1-Dimethylhydrazine	0.5	210 000	1.7	5.5	410 000	0.30	D
1,4-Dioxane	25	52 000	24	2.4	1000	1.1	C
Epichlorhydrin	2	21 000	0.93	12	11 000	2.1	C
Ethane	140 000[i]	g	120 000	5.9	7	1.2	C
Ethanolamine	3	780	2.6	–	260	1.2	C
2-Ethoxyethanol	5[n]	7100	2.7	9.0	1400	1.8	C
2-Ethoxyethyl acetate	5[n]	2700	0.056	–	530	89	B
Ethyl acetate	400	120 000	3.9	1.8	300	100	B
Ethyl acrylate	5	50 000	0.0012	4.1	10 000	4000	A
Ethyl alcohol	1000	75 000	84	1.8	75	12	C
Ethylamine	10	g	0.95	2.6	100 000	11	C
Ethyl *n*-amyl ketone	25	3600	6.0	–	140	4.2	C
Ethyl benzene	100	13 000	2.3	2.7	130	44	B
Ethyl bromide	200	610 000	3.1	–	3100	64	B
Ethyl chloride	1000	g	4.2	–	1000	240	B
Ethylene	140 000[i]	g	290	2.6	7	490	B
Ethylenediamine	10	16 000	1.0	–	1600	10	C
Ethylene dichloride	10	110 000	88	2.1	11 000	0.11	E
Ethylene oxide	1[n]	g	430	1.6	1 000 000	0.0023	E
Ethylenimine	0.5	260 000	1.5	1.3	520 000	0.32	D
Ethyl ether	400	700 000	8.9	3.3	1800	45	B
Ethyl formate	100	320 000	31	1.6	3200	3.3	C
Ethylidene norbornene	5		0.014	1.4		350	B
Ethyl mercaptan	0.5	710 000	0.00076	2.0	1 400 000	650	A
N-Ethylmorpholine	5	11 000	1.4	18	2100	3.5	C
Ethyl silicate	10	3000	17	4.9	300	0.57	D
Fluorine	1	g	0.14	–	1 000 000	7.3	C
Formaldehyde	1[n]	g	0.83	2.3	1 000 000	1.2	C
Formic acid	5	57 000	49	1.9	11 000	0.10	E
Furfural	2	2100	0.078	1.7	1000	25	C
Furfuryl alcohol	10	810	8.0	–	81	1.2	C

Table 2(b)—*Continued*

Substance	8 Water TLV equivalent (ppm; w/v)	9 Solubility at 25 °C (ppm; w/v)	10 Water odor threshold (ppm; w/v)	11 Molecular weight (g)	12 Density at 20-25 °C (g ml^{-1})	13 Water–air distribution ratio (w/v)	14 Number of thresholds performed: air	14 Number of thresholds performed: water
Cyclohexane	(0.13)	55	(0.011)	84	0.78	0.12	6	–
Cyclohexanol	940	36 000	2.8	100	0.95	4600	3	2
Cyclohexanone	240	~54 000	8.3	98	0.95	2400	8	2
Cyclohexene	(0.65)	210	(0.00039)	82	0.81	0.64	1	–
Cyclohexylamine (B/10.6)	94	∞	25	99	0.87	2300	–	1
Cyclopentadiene	(0.24)	~1800	(0.0060)	66	0.80	1.2	1	–
Decaborane				122	s		1	–
Diacetone alcohol		∞	64	116	0.94		1	2
Diborane	d	d	d	28	g	d	1	–
O-Dichlorobenzene	3.9	140	0.024	147	1.30	13	3	2
p-Dichlorobenzene	4.7	79	0.011	147	s	10	2	3
trans-1,2-Dichloroethylene	(3.0)	6300	(0.26)	97	1.26	3.8	2	–
β,β′-Dichloroethyl ether	36	11 000	0.36	143	1.21	1200	–	1
Dicyclopentadiene				132	s		2	–
Diethanolamine (B/8.9)	240 000	∞	22 000	105	1.10	19 000 000	1	–
Diethylamine (B/11.0)	36	∞	0.47	73	0.71	1200	6	1
Diethylaminoethanol (B/8.8)		∞		117	0.88		1	–
Diethyl ketone	450	48 000	4.7	86	0.81	640	3	–
Diisobutyl ketone	3.3	430	0.014	142	0.81	23	1	–
Diisopropylamine (B/11.0)	3.5		1.3	101	0.72	~170	2	1
N-Dimethylacetamide		∞		87	0.94		1	–
Dimethylamine (B/10.7)	8.6	550 000	0.29	45	g	460	6	2
N-Dimethylaniline (B/5.2)	9.9	2000	0.025	121	0.96	400	3	–
N-Dimethylformamide		∞	50	73	0.94		2	1
1,1-Dimethylhydrazine (B/7.2)		∞		60	0.79		2	–
1,4-Dioxane	240	∞	230	88	1.03	2700	7	1
Epichlorhydrin	6.4	65 000	3.0	92	1.18	840	2	–
Ethane	(8.8)	60	(7.5)	30	g	0.051	2	–
Ethanolamine (B/9.5)	23 000	∞	20 000	61	1.02	3 100 000	1	–
2-Ethoxyethanol		∞	190	90	0.93		2	1
2-Ethoxyethyl acetate	450	$200\,000_{20}$	5.0	132	0.97	16 000	1	–
Ethyl acetate	270	73 000	2.6	88	0.90	180	8	4
Ethyl acrylate	1.5	15 000	0.00038	100	0.92	74	2	1
Ethyl alcohol	9000	∞	760	46	0.79	4800	13	5
Ethylamine (B/10.7)	45	∞_{16}	4.3	45	0.69_{15}	2400	3	3
Ethyl *n*-amyl ketone	10	~1500	2.5	128	0.83	80	1	–
Ethyl benzene	(1.3)	160	(0.029)	106	0.87	2.9	2	3
Ethyl bromide	(2.9)	9000	(0.046)	109	1.43	3.3	1	–
Ethyl chloride	(4.7)	4700	(0.019)	64	g	1.8	1	–
Ethylene	(19)	130	(0.039)	28	g	0.12	4	1
Ethylenediamine (B/10.0)		∞	16 000	60	0.90		1	1
Ethylene dichloride	0.80	8600	7.0	99	1.26	20	8	2
Ethylene oxide	0.33	$270\,000_{20}$	140	44	g	180	2	–
Ethylenimine (B/8.0)	d	∞d	170d	43	0.83	d	2	1
Ethyl ether	34	56 000	0.75	74	0.71	28	7	–
Ethyl formate	35	100 000	11	74	0.92	120	1	1
Ethylidene norbornene				120			2	–
Ethyl mercaptan (A/10.5)	(0.0049)	7000	(0.0000075)	62	0.83	3.9	12	1
N-Ethylmorpholine (B/)		∞		115	0.90		2	–
Ethyl silicate	d	d	d	208	0.93	d	2	–
Fluorine	d	d	d	38	g	d	1	–
Formaldehyde	0.73	550 000	0.60	30	g	590	9	4
Formic acid (A/3.7)	170	∞	1700	46	1.22	18 000	4	5
Furfural	89	86 000	3.5	96	1.16	11 000	2	3
Furfuryl alcohol	d	∞d	d	98	1.13	d	1	–

Table 2(a)—*Continued*

Substance	1 Threshold limit value (ppm; v/v)	2 Volatility at 25 °C (ppm; v/v)	3 Air odor threshold (ppm; v/v)	4 Standard error ($x/\div$)	5 Safe dilution factor	6 Odor safety factor	7 Odor safety class
Halothane	50[n]	390 000	33	–	7900	1.5	C
Heptane	400	60 000	150	1.7	150	2.7	C
Hexachlorocyclopentadiene	0.01	78	0.030	5.1	7800	0.34	D
Hexachloroethane	10	770	0.15	–	77	64	B
Hexane	50	200 000	130	2.0	4000	0.37	D
Hexylene glycol	25	100	50	–	4.0	0.50	D
Hydrazine	0.1	18 000	3.7	1.1	180 000	0.027	E
Hydrogen bromide	3	g	2.0	–	330 000	1.5	C
Hydrogen chloride	5	g	0.77	2.2	200 000	6.5	C
Hydrogen cyanide	10	970 000	0.58	1.9	97 000	17	C
Hydrogen fluoride	3	g	0.042	1.2	330 000	71	B
Hydrogen selenide	0.05	g	0.30	–	20 000 000	0.17	E
Hydrogen sulfide	10	g	0.0081	1.5	100 000	1200	A
Indene	10	2200	0.015	3.9	220	690	A
Iodoform	0.6	~49	0.0050	1.8	81	120	B
Isoamyl acetate	100	7100	0.025	1.6	71	3900	A
Isoamyl alcohol	100	4300	0.042	1.3	43	2300	A
Isobutyl acetate	150	26 000	0.64	1.8	170	230	B
Isobutyl alcohol	50	16 000	1.6	2.0	330	30	B
Isophorone	5	450	0.20	–	89	25	C
Isopropyl acetate	250	79 000	2.7	2.9	320	93	B
Isopropyl alcohol	400	57 000	22	1.8	140	18	C
Isopropylamine	5	740 000	1.2	2.8	150 000	4.1	C
Isopropyl ether	250	210 000	0.017	–	850	15 000	A
Maleic anhydride	0.25	~170	0.32	–	670	0.77	D
Mesityl oxide	15	13 000	0.45	26	850	33	B
2-Methoxyethanol	5[n]	16 000	2.3	26	3200	2.1	C
Methyl acetate	200	270 000	4.6	3.5	1400	44	B
Methyl acrylate	10	110 000	0.0048	–	11 000	2100	A
Methyl acrylonitrile	1	88 000	7.0	–	88 000	0.14	E
Methyl alcohol	200	160 000	100	2.0	800	2.0	C
Methylamine	10	g	3.2	4.6	100 000	3.1	C
Methyl *n*-amyl ketone	50	2000	0.35	2.1	40	140	B
N-Methylaniline	0.5	640	1.7	–	1300	0.29	D
Methyl *n*-butyl ketone	5	5000	0.076	–	1000	66	B
Methyl chloroform	350	160 000	120	2.8	470	2.8	C
Methyl 2-cyanoacrylate	2	~530	2.2	–	260	0.91	D
Methylcyclohexane	400	61 000	630	–	150	0.63	D
cis-3-Methylcyclohexanol	50	710	500	–	14	0.10	E
Methylene chloride	100	550 000	250	1.2	5500	0.40	D
Methyl ethyl ketone	200	130 000	5.4	1.9	660	37	B
Methyl formate	100	760 000	600	2.9	7600	0.17	E
Methyl hydrazine	0.2	65 000	1.7	–	330 000	0.12	E
Methyl isoamyl ketone	50	4800	0.012	–	96	4200	A
Methyl isobutyl carbinol	25	7800	0.070	–	310	360	B
Methyl isobutyl ketone	50	9500	0.68	2.3	190	73	B
Methyl isocyanate	0.02	630 000	2.1	–	32 000 000	0.0094	E
Methyl isopropyl ketone	200	39 000	1.9	2.3	200	100	B
Methyl mercaptan	0.5	g	0.0016	2.0	2 000 000	300	B
Methyl methacrylate	100	52 000	0.083	1.9	520	1200	A
Methyl *n*-propyl ketone	200	21 000	11	2.2	110	18	C
α-Methyl styrene	50	3800	0.29	4.0	76	170	B
Morpholine	20	13 000	0.01	–	670	2000	A
Naphthalene	10	120	0.084	1.9	12	120	B
Nickel carbonyl	0.05	520 000	0.30	3.3	10 000 000	0.17	E

Table 2(b)—*Continued*

Substance	8 Water TLV equivalent (ppm; w/v)	9 Solubility at 25°C (ppm; w/v)	10 Water odor threshold (ppm; w/v)	11 Molecular weight (g)	12 Density at 20–25°C (g ml^{-1})	13 Water-air distribution ratio (w/v)	14 Number of thresholds performed: air	14 Number of thresholds performed: water
Halothane	(0.44)	3400	(0.29)	197	1.87	1.1	1	–
Heptane	(0.020)	2.9	(0.0073)	100	0.68	0.012	4	–
Hexachlorocyclopentadiene	0.0026	20	0.0077	273	1.70	23	1	1
Hexachloroethane	(0.65)	50	(0.010)	237	s	6.7	–	1
Hexane	(0.0024)	9.5	(0.0064)	86	0.66	0.014	2	–
Hexylene glycol		∞		118	0.92		1	–
Hydrazine (B/8.5)		∞	160	32	1.01		2	1
Hydrogen bromide (A)	d	1 200 000	d	81	g	d	1	–
Hydrogen chloride (A)	d	500 000	d	36	g	d	6	–
Hydrogen cyanide (A/9.2)	3.0	∞	0.17	27	0.70	270	2	3
Hydrogen fluoride (A/3.2)	d	∞_{19}	d	20	0.96	d	2	–
Hydrogen selenide (A/3.9)	(0.00035)	6800	(0.0021)	81	g	2.1	1	–
Hydrogen sulfide (A/7.0)	(0.036)	3500	(0.000029)	34	g	2.6	25	1
Indene	(0.18)	~40	(0.00026)	116	1.01	3.7	1	1
Iodoform	1.3	110	0.011	394	s	130	3	–
Isoamyl acetate	66	1400	0.017	130	0.87	120	8	3
Isoamyl alcohol	630	26 000	0.27	88	0.80	1700	5	3
Isobutyl acetate	34	5900	0.15	116	0.87	48	3	1
Isobutyl alcohol	310	89 000	10	74	0.80	2100	7	5
Isophorone	140	12 000	5.4	138	0.92	4800	1	–
Isopropyl acetate	97	30 000	1.0	102	0.87	92	4	–
Isopropyl alcohol	3000	∞	160	60	0.78	3000	12	4
Isopropylamine (B/10.5)	20	∞	4.9	59	0.69	~1700	2	1
Isopropyl ether	12	10 000	0.00080	102	0.73	11	1	–
Maleic anhydride	d	d	d	98	s	d	1	–
Mesityl oxide	35	29 000	1.0	98	0.85	570	2	–
2-Methoxyethanol		∞		76	0.97		2	–
Methyl acetate	130	220 000	3.0	74	0.93	210	5	–
Methyl acrylate	4.5	49 000	0.0021	86	0.95	130	1	–
Methyl acrylonitrile	0.29	25 000	2.1	67	0.80	110	1	–
Methyl alcohol	1500	∞	740	32	0.79	5600	13	4
Methylamine (B/10.6)	7.4	550 000	2.4	31	g	580	2	3
Methyl *n*-amyl ketone	40	4300	0.28	114	0.81	170	2	2
N-Methylaniline (B/4.8)	5.3	6700_{30}	18	107	0.99	2400	1	–
Methyl *n*-butyl ketone	17	16 000	0.25	100	0.81	800	1	–
Methyl chloroform	(2.8)	1300	(0.97)	133	1.34	1.4	3	–
Methyl 2-cyanoacrylate				111	1.11		1	–
Methylcyclohexane	(0.092)	14	(0.15)	98	0.77	0.057	1	–
cis-3-Methylcyclohexanol	660	9300	6600	114	0.91	2800	1	–
Methylene chloride	3.6	19 000	9.1	85	1.34	10	4	1
Methyl ethyl ketone	310	210 000	8.4	72	0.80	530	8	1
Methyl formate	25	170 000	150	60	0.97	100	3	–
Methyl hydrazine (B/7.9)		∞		46	0.87		1	–
Methyl isoamyl ketone	56	5400	0.013	114	0.81	240	1	–
Methyl isobutyl carbinol	53	16 000	0.15	102	0.81	510	1	–
Methyl isobutyl ketone	94	18 000	1.3	100	0.80	460	5	–
Methyl isocyanate	d	d	d	57	0.96	d	1	–
Methyl isopropyl ketone	320	60 000	3.1	86	0.80	460	1	1
Methyl mercaptan (A/10.7)	(0.0075)	~14 000	(0.000024)	48	g	7.6	8	2
Methyl methacrylate	30	15 000	0.025	100	0.94	73	4	1
Methyl *n*-propyl ketone	270	54 000	15	86	0.81	380	2	1
α-Methyl styrene	7.4	560	0.043	118	0.91	31	3	1
Morpholine (B/8.7)		∞		87	1.00		1	–
Naphthalene	2.5	30	0.021	128	s	47	6	4
Nickel carbonyl	(0.000012)	130	(0.000072)	171	1.32	0.035	3	–

Table 2(a)—*Continued*

Substance	1 Threshold limit value (ppm; v/v)	2 Volatility at 25°C (ppm; v/v)	3 Air odor threshold (ppm; v/v)	4 Standard error (x/÷)	5 Safe dilution factor	6 Odor safety factor	7 Odor safety class
Nitrobenzene	1	360	0.018	1.7	360	56	B
Nitroethane	100	27 000	2.1	–	270	46	B
Nitrogen dioxide	3	g	0.39	2.6	330 000	7.8	C
Nitromethane	100	47 000	3.5	–	470	29	B
1-Nitropropane	25	13 000	11	4.2	520	2.3	C
2-Nitropropane	10[n]	22 000	70	2.2	2200	0.14	E
m-Nitrotoluene	2	~280	0.045	–	140	45	B
Nonane	200	6000	47	4.1	30	4.3	C
Octane	300	18 000	48	3.2	61	6.3	C
Osmium tetroxide	0.0002	12 000	0.0019	–	61 000 000	0.10	E
Oxygen difluoride	0.05	g	0.10	–	20 000 000	0.50	D
Ozone	0.1	g	0.045	1.9	10 000 000	2.2	C
Pentaborane	0.005	270 000	0.96	–	54 000 000	0.0052	E
Pentane	600	670 000	400	1.9	1100	1.5	C
Perchloroethylene	50	25 000	27	1.8	490	1.8	C
Phenol	5	460	0.040	1.5	92	130	B
Phenyl ether	1	29	0.0012	3.7	29	800	A
Phenyl mercaptan	0.5	2000	0.00094	4.4	4100	530	B
Phosgene	0.1	g	0.90	1.7	10 000 000	0.11	E
Phosphine	0.3	g	0.51	2.5	3 300 000	0.58	D
Phthalic anhydride	1	0.67	0.053	–	0.7	19	C
Propane	140 000[i]	g	16 000	1.3	7	8.8	C
Propionic acid	10	5400	0.16	1.8	540	61	B
n-Propyl acetate	200	43 000	0.67	4.1	220	300	B
n-Propyl alcohol	200	26 000	2.6	1.7	130	78	B
Propylene	140 000[i]	g	76	3.0	7	1800	A
Propylene dichloride	75	69 000	0.25	–	920	300	B
Propylene glycol 1-methyl ether	100	16 000	10	–	160	10	C
Propylene oxide	20	700 000	44	4.5	35 000	0.45	D
n-Propyl nitrate	25	30 000	50	–	1200	0.50	D
Pyridine	5	27 000	0.17	1.4	5300	30	B
Quinone	0.1	130	0.084	3.0	1300	1.2	C
Styrene	50	9600	0.32	2.0	190	160	B
Sulfur dioxide	2	g	1.1	1.3	500 000	1.7	C
1,1,2,2-Tetrachloroethane	5	8400	1.5	2.1	1700	3.4	C
Tetrahydrofuran	200	230 000	2.0	5.4	1100	99	B
Toluene	100	37 000	2.9	1.6	370	34	B
Toluene-2,4-diisocyanate	0.005[n]	~21	0.17	2.9	4200	0.030	E
o-Toluidine	2	330	0.25	4.1	170	8.0	C
1,2,4-Trichlorobenzene	5	570	1.4	2.1	110	3.6	C
Trichloroethylene	50	99 000	28	1.7	2000	1.8	C
Trichlorofluoromethane	1000	g	5.0	–	1000	200	B
1,1,2-Trichloro-1,2,2-trifluoroethane	1000	430 000	45	–	430	22	C
Triethylamine	10[n]	93 000	0.48	2.1	9300	21	C
Trimethylamine	10[n]	g	0.00044	1.4	100 000	23 000	A
1,3,5-Trimethylbenzene	25	3600	0.55	1.9	150	45	B
Trimethyl phosphite	2	34 000	0.00010	–	17 000	20 000	A
n-Valeraldehyde	50	21 000	0.028	2.5	420	1800	A
Vinyl acetate	10	140 000	0.50	1.6	14 000	20	C
Vinyl chloride	5	g	3000	3.7	200 000	0.0017	E
Vinylidene chloride	5[n]	790 000	190	3.7	160 000	0.027	E
Vinyl toluene	50	2400	10	–	48	5.0	C
m-Xylene	100	11 000	1.1	2.1	110	92	B
2,4-Xylidine	2	190	0.056	–	97	36	B

Table 2(b)—*Continued*

Substance	8 Water TLV equivalent (ppm; w/v)	9 Solubility at 25°C (ppm; w/v)	10 Water odor threshold (ppm; w/v)	11 Molecular weight (g)	12 Density at 20–25°C (g ml^{-1})	13 Water–air distribution ratio (w/v)	14 Number of thresholds performed: air	14 Number of thresholds performed: water
Nitrobenzene	6.0	2100	0.11	123	1.20	1200	13	2
Nitroethane (A/8.4)	100	27 000	2.2	75	1.05	330	—	1
Nitrogen dioxide (A)	d	d	d	46	g	d	6	—
Nitromethane (A/10.2)	260	110 000	9.1	61	1.13	1000	—	1
1-Nitropropane (A/~8)	29	15 000	12	89	1.00	310	2	1
2-Nitropropane (A/7.7)	7.6	16 000	53	89	0.98	210	1	1
m-Nitrotoluene	3.6	500_{30}	0.080	137	1.16	320	1	—
Nonane	(0.0056)	~0.17	(0.0013)	128	0.72	0.0054	2	—
Octane	(0.011)	0.66	(0.0017)	114	0.70	0.0077	2	—
Osmium tetroxide (A/12.0)	0.0012	69 000	0.012	254	s	580	1	—
Oxygen difluoride	(0.0000054)d	100_{20}d	(0.000011)d	54	g	0.049d	1	—
Ozone	(0.00064)	6100	(0.00028)	48	g	3.2	6	—
Pentaborane	d	d	d	63	0.63	d	1	—
Pentane	(0.033)	38	(0.022)	72	0.62	0.019	3	—
Perchloroethylene	(0.31)	150	(0.17)	166	1.61	0.90	3	1
Phenol (A/10.0)	1000	85 000	7.9	94	s	52 000	16	6
Phenyl ether	150	4300	0.18	170	1.07	21 000	2	3
Phenyl mercaptan (A/6.5)	0.15	610	0.00028	110	1.08	66	2	2
Phosgene	d	d	d	99	g	d	6	—
Phosphine	(0.00011)	370_{17}	(0.00020)	34	g	0.27	6	—
Phthalic anhydride	d	d	d	148	s	d	1	—
Propane	(9.0)	62	(1.0)	44	g	0.036	2	—
Propionic acid (A/4.9)	1700	∞	28	74	1.00	56 000	11	2
n-Propyl acetate	92	$19\,000_{20}$	0.31	102	0.89	110	4	—
n-Propyl alcohol	1800	∞	23	60	0.80	3600	12	5
Propylene	(50)	350	(0.028)	42	g	0.21	3	1
Propylene dichloride	(3.0)	2800	(0.010)	113	1.16	8.8	1	—
Propylene glycol 1-methyl ether				90	0.92		1	—
Propylene oxide	14	370 000	31	58	0.83	300	2	—
n-Propyl nitrate	7.4	8800_{20}	15	105	1.05	69	1	—
Pyridine (B/5.2)	28	∞	0.95	79	0.98	1700	15	10
Quinone	11	14 000	9.3	108	s	25 000	2	1
Styrene	(1.7)	320	(0.011)	104	0.90	7.8	10	3
Sulfur dioxide (A/1.9)	0.19	88 000	0.11	64	g	37	13	—
1,1,2,2-Tetrachloroethane	1.7	2900	0.50	168	1.60	50	3	1
Tetrahydrofuran		∞		72	0.89		3	—
Toluene	(1.4)	540	(0.042)	92	0.86	3.8	18	2
Toluene-2,4-diisocyanate	d	d	d	174	1.22	d	4	—
o-Toluidine (B/4.4)	91	15 000	11	107	1.00	10 000	3	1
1,2,4-Trichlorobenzene	(0.23)	~26	(0.064)	181	1.45	6.1	1	1
Trichloroethylene	(0.55)	1100	(0.31)	131	1.46	2.1	7	1
Trichlorofluoromethane				137	1.49		1	—
1,1,2-Trichloro-1,2,2-trifluoroethane				187	1.56		1	—
Triethylamine (B/10.9)	8.8	71 000	0.42	101	0.73	210	4	1
Trimethylamine (B/9.7)	4.5	$410\,000_{19}$	0.00020	59	g	190	3	1
1,3,5-Trimethylbenzene	(0.67)	97	(0.015)	120	0.86	5.4	6	3
Trimethyl phosphite	d	d	d	124	1.05	d	1	—
n-Valeraldehyde	29	12 000	0.017	86	0.81	170	1	3
Vinyl acetate	1.8	$25\,000_{20}$	0.088	86	0.93	50	4	1
Vinyl chloride	(0.0057)	1100	(3.4)	62	g	0.44	3	—
Vinylidene chloride	(0.041)	6400	(1.5)	97	1.22	2.0	2	—
Vinyl toluene	(2.1)	~100	(0.42)	118	0.90	8.7	1	—
m-Xylene	(1.6)	170	(0.017)	106	0.86	3.7	8	2
2,4-Xylidine (B/4.9)	66	6400	1.8	121	0.97	6600	1	—

at 25 °C can be calculated[14] from the vapor pressure and the solubility at 25 °C. The coefficients for some of the compounds that are infinitely soluble in water at 25 °C were calculated from tabulated activity data[15] or measured experimentally.[14]

The results for *n*-butyl alcohol, which has provided the most plentiful odor-threshold data, are given in Table 1 as a demonstration of data reduction. The original threshold data, in a variety of concentration units, were converted[2] into common units of g l^{-1}. Any water dilution thresholds were further converted to the equivalent air dilution threshold, through multiplication by the air-water partition coefficient.[14] The relationship between odor-intensity sensation and odorant concentration is exponential.[16] Therefore, in order to preserve the normal distributions of olfactory-threshold measurements, all chemical concentrations of odorants were calculated on a logarithmic scale. Hence the geometric mean of all 29 odor thresholds, expressed in air dilution, was computed (by converting to the logarithms, finding their arithmetic mean, and taking its antilogarithm).[2] The mean air dilution threshold, in g l^{-1}, was finally converted to mg m^{-3}, and to ppm by volume.

Explanation of Table 2 (odor thresholds)

Column 1. Threshold limit values (TLV) adopted by ACGIH, 1982.[1] The superscript n indicates that the TLV used is the value proposed in the 1982 Notice of Intended Changes. The superscript i indicates an inert gas (simple asphyxiant) for which no TLV is assigned by ACGIH, merely a requirement that the oxygen content of the air not be reduced below 18%. This would be expected to occur if the asphyxiant reaches 14%, or 140 000 ppm, which is in effect the TLV for inert gases.

Column 2. The volatility in ppm (v/v) is given by the literature vapor pressure (in mmHg at 25 °C) multiplied by 1316 (1 000 000 ppm per 760 mmHg). ~ indicates approximate value obtained by extrapolating the linear regression from vapor pressures recorded at substantially higher temperatures. g, gaseous at 25 °C.

Column 3. Air-dilution odor thresholds are geometric averages of all available literature data, omitting extreme points and duplicate quotations. Odor thresholds originally measured in water dilution were converted to the equivalent air dilution, as illustrated in Table 1 for *n*-butyl alcohol.

Column 4. When two or more acceptable literature thresholds were located, the standard error of their mean was calculated. The standard error is the standard deviation divided by the square root of the number of literature thresholds. This factor is applicable to the data in columns 3, 6 and 10. The smaller the standard error, the greater the confidence that may be placed in the accuracy of the mean threshold value. (It should be borne in mind, however, that a small standard error, based on only two thresholds, could itself be the result of a fairly probable coincidence.)

Column 5. Safe dilution factor, for the saturated vapor at 25 °C, is the volatility divided by the threshold limit value (column 2 divided by column 1). For substances that are less than infinitely soluble in water, the same safe dilution factor applies to the saturated solution at 25 °C (column 9).

Column 6. Odor safety factor is the threshold limit value divided by the odor threshold (column 1 divided by column 3). This factor may be interpreted quantitatively by reference to Fig. 2, in terms of what percentage of attentive persons can detect the TLV concentration, and what percentage of distracted persons will perceive a warning of the TLV concentration.

Column 7. The scale of odor safety classes is explained in Table 3. Class A substances provide the strongest odorous warning of their presence at threshold limit value concentrations, whereas class E substances are practically odorless at the TLV concentration.

Table 3. Odor safety classification

Class	Odor safety factor	Interpretation
A	>550	More than 90% of distracted persons perceive warning of TLV concentration in the air
B	26–550	50–90% of distracted persons perceive warning of TLV
C	1–26	Less than 50% of distracted persons perceive warning of TLV
D	0.18–1	10–50% of attentive persons can detect TLV concentration in the air
E	<0.18	Less than 10% of attentive persons can detect the TLV

Column 8. Water TLV equivalent is the concentration of the substance in water, which will generate the air TLV concentration in the headspace of a stoppered flask or other closed system. It is calculated from column 1 by multiplying by the distribution ratio in column 13, then dividing by 24 400 (volume in ml of one gram molecule of vapor at 25 °C) and multiplying by the molecular weight. Solutions with values in parentheses lack enough persistence for reference purposes, due to an unfavorably low water-air distribution ratio (<10) in column 13; d, decomposes in water.

Column 9. Solubility in ppm (w/v) is the literature solubility (expressed as g l^{-1} of saturated solution at 25°C) multiplied by 1000. ~indicates uncertain or extrapolated values. Temperatures other than 25 °C are indicated by subscripts.

Columns 10. Water-dilution odor threshold is the concentration of the substance in water which will generate the air odor threshold concentration in the headspace of a stoppered flask. It is calculated from column 3 by multiplying by the distribution ratio in column 13, then dividing by 24 400 and multiplying by the molecular weight. Values in parentheses have the same meaning as in column 8.

Column 11. The molecular weight (MW, rounded off to the nearest whole number expressed in grams) can be used to convert the air concentrations in ppm (v/v) (columns 1, 2 and 3) into mg m^{-3}. Multiply by MW and divide by 24.4 (volume in liters of one gram molecule of vapor at 25 °C).

Column 12. The density (D, at 20-25 °C) is needed when measuring out liquid odorants by volume to prepare water or air dilutions:

$$1 \text{ ppm (w/v)} = 1 \text{ mg} \quad [\text{or } (1/D)\ \mu\text{l}) \text{ per liter of water}$$

$$1 \text{ ppm (v/v)} = \frac{\text{MW}}{24.4} \text{ mg} \left(\text{or } \frac{\text{MW}}{24.4 \times D}\ \mu\text{l} \right) \text{ per cubic meter of air}$$

g, gaseous at 20 °C; s, solid at 20 °C.

Column 13. The water-air distribution ratio is the reciprocal of the air-water partition coefficient. Where experimental values are unavailable in the literature, which is usually the case, the ratio has been calculated from data in columns 9, 2 and 11, or from other approaches mentioned earlier. An estimate of the water-air distribution ratio is given by dividing the solubility (column 9) by the volatility (column 2), then multiplying by 24 400 and dividing by the molecular weight (column 11).

Column 14. The numbers indicate how many original literature odor thresholds were included in calculating the average threshold in column 3 and the standard error in column 4. On the left is the number of air-dilution thresholds, and on the right the number measured in water dilution.

Ionizable odorants (weak acids and bases) are indicated in Table 2(b) by appending to the compound name the symbol A for acid and B for base, followed by the acid dissociation constant pK_a. Data given for such compounds in columns 8, 9, 10 and 13 are accurate only for solutions in which the odorant is practically un-ionized and hence potentially volatile. That is, the pH of the solution should be less than two pH units lower than the pK_a for an acid, or should be more than two pH units higher than the pK_a for a base. The odorant volatilities at pH values outside of these limits can be estimated by calculating the concentration of the un-ionized species using the Henderson-Hasselbalch equation.[16] For demonstration purposes, it will suffice to make solutions of the acids in 0.01 N H_2SO_4, and the bases in 0.01 N NaOH.

The data in Table 2 are incomplete for some physical properties of 25 compounds, because no literature values could be located, and no justifiable estimates could be made. The missing data are mostly water solubilities or water-air distribution ratios, which in turn preclude estimates of TLV equivalents in water and water-dilution odor thresholds. If the reader is aware of values for the missing data, or knows of more accurate measurements or estimates of the recorded data, the authors would be grateful for the information. Odor threshold data on TLV-listed compounds not included in Table 2 would also be welcome.

Variance of human responsiveness to odors

When the individual olfactory detection thresholds for a given compound are determined on a sample of the human population, the data typically generate a (log)normal or Gaussian distribution.[17] For this result, it is necessary to use a logarithmic scale for the odorant concentration, such as a binary or decadic dilution series. The quantitative interpretation of a Gaussian curve is facilitated by re-plotting the data on probability graph paper. The resulting probit approximates a straight line if the distribution of sensitivities in the population is in fact normal. Literature data on the percentages of persons responding to odorants when they were attentive,[18] distracted,[19] or asleep[20] were replotted as probits in Figs 1, 2 and 3.

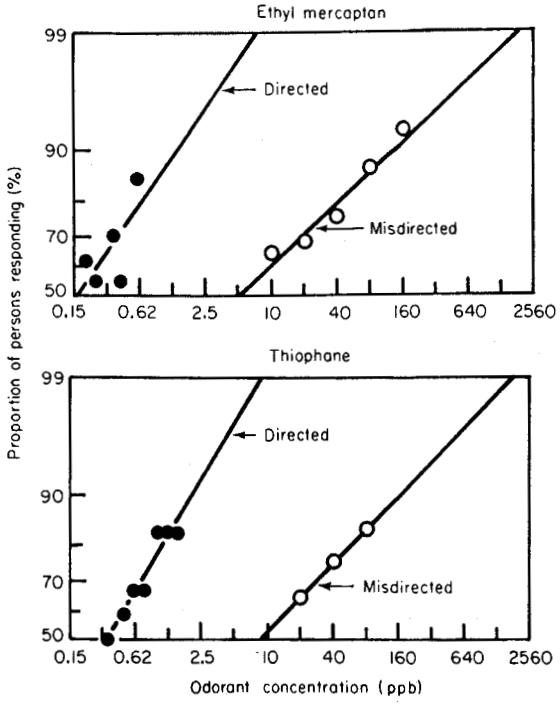

Figure 1. Tests of responsiveness of persons to fuel gas odorants. The data were taken from the report by Whisman *et al.*,[19] Figs 12 and 13, and Table 28, then re-plotted on log/probit coordinates. In the misdirected tests, the attention of the subjects was deliberately channeled to other matters. Note that the concentration units in this Figure are ppb (v/v).

Some chemicals, but not all, besides having a true odor, also cause immediate irritation in the nose, eyes or throat. The sensation of stinging, prickling or burning, conveyed by the trigeminal or 5th cranial nerve, is quite distinct from the smell sensation carried by the olfactory or 1st cranial nerve.[21] Irritation usually requires a higher chemical concentration than odor, and trained normal subjects can readily report the distinct irritation threshold.[22] Another approach is to use subjects who have suffered a chronic loss of their olfactory nerve function, but still retain an active trigeminal nerve sensitivity.[23]

Explanation of Table 4 (irritant thresholds)

Column 1. In this Table, each odor threshold was derived from the same source which reported the irritation threshold; hence the odor threshold in Table 4 may differ from that given for the same compound in Table 2(a), column 3, which may be an average of several literature values.

Columns 2 and 3. Irritation thresholds are the lowest concentrations that cause immediate stinging or burning sensations in the nose, or stinging or lacrimation of the eye.

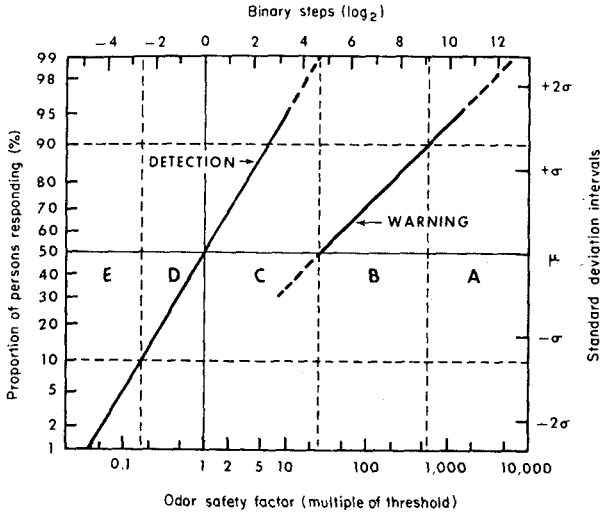

Figure 2. A practical guide to the quantitative interpretation of odor safety factors. The coordinates are log/probit, so care is required in interpolating between marked intervals. The sloping lines indicate the percentages of the population expected to respond to various fractions or multiples of the mean detection threshold concentration (1.0 on the *x* axis). The detection line represents the performance of fully attentive persons under good laboratory conditions. The warning line shows what may be expected for distracted persons under factory or field conditions. The warning line is based on the results of Whisman *et al.*[19] for the gas odorants ethyl mercaptan and thiophane.

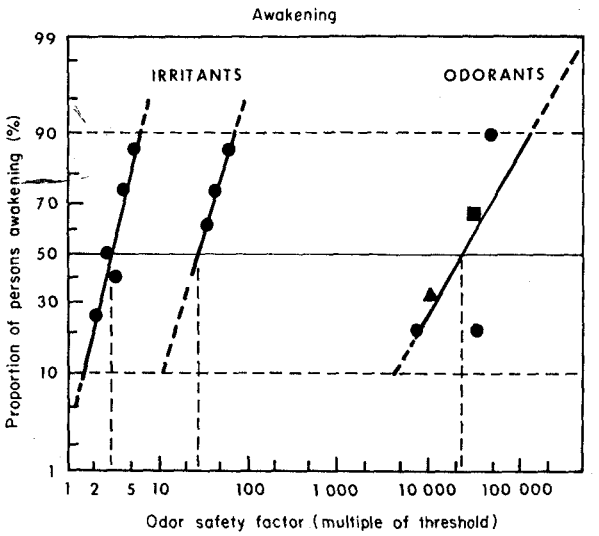

Figure 3. An illustration of the efficacy of certain vapors in awakening sleeping persons. The data were taken from the work of Fieldner *et al.*,[20] Tables 8, 12 and 14, then plotted on log/probit coordinates. The irritants were allyl alcohol on the left, and crotonaldehyde on the right. The odorants were ethyl mercaptan (●), phenyl ether (▲) and isoamyl acetate (■). The concentrations in this Figure are stated as multiples of the odor thresholds reported by Fieldner *et al.*[20]

In four compounds, designated by superscript a, they are the lowest concentrations that could be distinguished from pure air by a general anosmic, i.e. by a person who has no olfactory nerve sensation, but whose trigeminal nerve sensitivity is intact.

Column 4. The lower of the nose and eye thresholds (if both are available) was used for calculating this ratio of irritation and odor thresholds.

Column 5. The irritation hazard factor is obtained by dividing the nose or eye irritation threshold (whichever is lower, columns 2 or 3) by the threshold limit value from Table 2(a), column 1. This datum indicates by what multiple the TLV is exceeded, if eye or nose irritation can be detected.

Column 6. References in italics indicate that thresholds were obtained using water dilutions.

RESULTS AND DISCUSSION

Literature search for odor thresholds

The ACGIH compilation includes approximately 350 appreciably volatile compounds for which time-weighted average threshold limit values have been adopted or pro-

Table 4. Irritant threshold concentrations of ten industrial chemicals. See Methods for further explanation of each column

Substance	1 Odor threshold (ppm; v/v)	2 Irritation thresholds: Nose (ppm; v/v)	3 Irritation thresholds: Eye (ppm; v/v)	4 Ratio of irritation and odor thresholds	5 Irritation hazard factor	6 Reference
Acetaldehyde	0.066	2200	11 000	33 000	22	22
Acetic acid	0.16	160[a]		1000	16	*23*
Acrolein	1.8	11	12	6.1	110	22
Allyl alcohol	1.4	30	59	21	15	22
Benzyl chloride	0.040	35	8.0	200	8.0	22
α-Chloroacetophenone	0.040	0.034	0.022	0.55	0.44	22
trans-Crotonaldehyde	0.11	14	19	130	7.0	22
Formic acid	130	1100[a]		8.5	220	*23*
Propionic acid	0.24	370[a]		1500	37	*23*
Pyridine	0.71	700[a]		990	140	*27*

[a] Detection threshold for a general anosmic.

posed.[1] Among these, there are 214 compounds for which we were able to locate at least one literature value for the olfactory detection or recognition threshold, measured in air or water dilution. The data are widely scattered in the literature, and there is little conformity in the choice of units for expressing the results. For example, the 29 reported thresholds for *n*-butyl alcohol (Table 1) were gathered from the works of 26 principal authors, who used 18 different systems of concentration units in publishing their data, in 24 journals. Furthermore, no two of these 29 thresholds were measured by precisely the same experimental method.

The lack of standardization, taken in conjunction with the inconsistent purity of the chemical samples and the variability of human sensitivity, is responsible for the rather wide range of threshold concentrations usually found in the literature for a given compound. As indicated at the foot of Table 1, the mean threshold for *n*-butyl alcohol is 0.835 ppm. (In this compilation, the data were collected and calculated to three significant figures, then rounded off to two significant figures for the Tables.) The threshold concentrations having been calculated as logarithms, statistical deviations and errors from the geometric mean should be stated in the form of factors (rather than the differences used with ordinary arithmetic means). The standard deviation of the logarithms of the observed thresholds was ± 0.854 $\log_{10}$ units, for which the antilog yields a factor of $\times/\div 7.14$. Taking into account all 29 literature values (i.e. dividing by $\sqrt{29}$), this reduces to a standard error of ± 0.159 $\log_{10}$ units, corresponding to a factor of $\times/\div 1.44$. This indicates that there is approximately a 68% probability ($\pm 1\sigma$ or SD) that the true threshold for *n*-butyl alcohol lies between $(0.835/1.44) = 0.58$ ppm and $(0.835 \times 1.44) = 1.20$ ppm. There is a 96% probability ($\pm 2\sigma$) that it lies between $(0.58/1.44) = 0.40$ ppm and $(1.20 \times 1.44) = 1.73$ ppm. Olfactory thresholds could, if necessary, be obtained with greater consistency and smaller standard errors, by determining conversion factors between different experimental methods,[2,3,14] or by redetermining the thresholds by using a standardized procedure with careful minimization of known sources of error.

In the literature, we found for these 214 compounds a total of 1054 acceptable thresholds. Some thresholds had to be rejected on the grounds that they had been measured without consideration of substantial ionization, unfavorable partition coefficients, likely impurities or the inapplicability of Raoult's law. A few remaining extreme points were discarded because they diverged more than 100-fold from the nearest of two or more other thresholds for the same compound.[24] For 152 of the compounds, we found two or more acceptable thresholds. We calculated the mean threshold and its standard deviation for each compound. The average of the individual standard deviations for all these 152 multiple threshold compounds was a factor of $\times/\div 7.0$. The remaining 62 compounds each yielded only one usable threshold, so no standard error could be calculated, which accounts for the dashes in column 4 of Table 2(a). The uncertainty in a given olfactory threshold measurement should be independent of whether the compound has been reported several times in the literature, or only once. As a rough guide, we may assume the same average standard error factor of $\times/\div 7.0$ for these single-threshold compounds.

Safe dilution factors for saturated vapors

The procedure of expressing threshold limit values, volatilities and odor thresholds all in the same units (ppm; v/v) brings to light certain relationships that are not apparent when miscellaneous units are used. Nearly all of the compounds in Table 2(a) have volatilities at 25 °C which exceed, sometimes by an enormous factor, their threshold limit values. Accordingly, a sniff, from the headspace of a bottle or drum, or from a confined space containing a spill, of almost any of these substances, inevitably exceeds the TLV. The safe dilution factor in column 5 indicates the minimum number of volumes of uncontaminated air that would be required to dilute, to the safe level, one volume of air that has been saturated by exposure to the named compound (assuming perfect mixing). Plant location, layout, ventilation, chimneys and emergency procedures should be designed with the realization of the safe dilution factor in mind, at least for compounds for which dilution ventilation is an allowable method of control. Any increase in temperature of the chemical above 25 °C increases the required safe dilution factor, in proportion to the vapor pressure.

A majority of these compounds are not completely miscible with water. Nevertheless, a saturated solution of any volatile compound is theoretically capable of saturating the headspace to the same concentration as the pure compound could achieve. Whether or not it will do so in a finite time depends upon the water-air distribution ratio, the relative volumes of air and water, and the degree of agitation. To err on the safe side, it would be prudent to use the same safe dilution factor in calculating the number of volumes of clean water which would be needed to dilute one volume of a saturated aqueous solution of the compound before discharge to a sewer, lagoon or river, where this is permitted.

Odor safety factors as chemical safeguards

When the threshold limit value is substantially higher than the odor threshold, the intrinsic odor of the compound usually, but not invariably, provides an indication of its presence, at a concentration level low enough that no harm is likely to the human observer. Conversely, if the odor threshold is much higher than the TLV, then anybody detecting the odor of the compound has a warning that a safe vapor concentration has already been exceeded. The exposed worker would be well advised to request a professional evaluation and perhaps instrumental assessment of the situation. It should be determined whether the applicable TLV criterion (time-weighted average, short-term exposure limit or ceiling value)[1] is likely to be exceeded in the particular working regime, and if so, what the health significance may be.

The potential warning power of a given chemical is conveniently expressed by the odor safety factor (column 6 of Table 2(a)), which is simply the TLV divided by the odor threshold. Any chemical with an odor safety factor less than 1.0 carries the risk that hazardous concentrations will not be detected by odor. Conversely, an odor safety factor greater than 1.0 bears the promise that a hazardous concentration could be perceived by smell. Nevertheless, the question of whether or not a hazardous concentra-

tion will actually be smelt, is quite complex, and depends upon a variety of circumstances. (A very few people, roughly 1 in 500, have no true sense of smell at all;[25] the existence of anosmic persons, while of some practical importance, is omitted from our discussion.)

The average odor threshold has not been sufficiently rigorously evaluated for all these compounds, many of which possess measured or implied standard errors as large as seven-fold. This is not, in principle, an insurmountable problem, because 63 compounds in Table 2(a), column 4, already have thresholds evaluated with standard errors less than two-fold. Equal, or better, accuracy could readily be attained by new experimental measurements on the deficient compounds.

The ability of members of the population to detect a given odor is strongly influenced by the innate variability of different persons' olfactory powers, their prior experience with that odor, and by the degree of attention they accord to the matter. The thresholds listed in column 3 of Table 2(a) represent the most favorable conditions for testing. The subjects were well aware that these were tests of their sense of smell, they were attentive and they were trying their best to detect the presence of the odor. Even so, the odor-detecting ability of different people varies over quite a wide range. The compilation of individual sensitivities to a given compound typically yields a Gaussian or bell-shaped curve,[17] provided that a logarithmic concentration scale is employed. For this normal distribution, the standard deviation is a measure of the spread of odor sensitivity in the population. We have evaluated this standard deviation with seven odorants: isobutyl isobutyrate, isovaleric acid, 1-pyrroline, trimethylamine, isobutyraldehyde, androst-16-en-3-one and pentadecalactone, each tested with 18–443 normal observers. The average standard deviation was ± 1.97 binary steps, which may be rounded off at two binary steps.[18] The standard deviation indicates that 68% of people tested, on the average, will have a personal threshold that lies within the range from one-fourth of the mean, to four times the mean, threshold of the population.

The effect of distracted attention

In connection with testing the efficacy of certain odorants as warning agents for fuel gas, Whisman *et al.*[19] conducted a thorough study of the influence of various degrees of distraction on the responsiveness of people to these well-known warning odors. Their 'directed' test corresponds with usual laboratory conditions, in which the attention of the subject is purposely focused on the sole objective of detecting an odor. In the 'semi-directed' test, the subjects were asked to report on visual, tactile, aural and nasal stimuli in the test room. In the 'undirected' test, the subjects were given no indication of the object of the exercise. In the 'misdirected' test, the attention of the participants was deliberately distracted by asking each to try to read some print in a dim light and to judge the temperature of the room. All except the directed tests were performed with inexperienced subjects recruited by a mobile laboratory arriving unannounced at shopping centers, and each volunteer was used for one test only at one odorant concentration.

Whisman *et al.* found that the responsiveness of the subjects to a given concentration of odorant was substantially decreased in the semidirected, undirected and misdirected tests, compared with their performance in the directed test mode. The misdirected test was probably the most difficult set of conditions imposed upon the subjects. In our opinion, the misdirected test is the most appropriate of the available models for evaluating the effects of conditions encountered in industrial practice. A factory worker would not be familiar with odor-threshold testing techniques, but would hopefully be aware that chemical vapors may be hazardous, and might know that a distinct smell indicates the presence of appreciable vapor in the air. On the other hand, the worker is likely to be concentrating on following instructions, reading charts, controlling equipment and generally trying to get the work done. Such a degree of mental distraction, as Whisman *et al.* showed, is ample to divert attention away from any but the most obvious of odors.

In Fig. 1, the results of Whisman *et al.*[19] for their directed and misdirected test modes are presented in $\log_2$/probit coordinates, which have the advantage of exhibiting an approximately linear relationship between olfactory stimulus and response. Each data point in the directed tests was obtained from 22 subjects, and in the misdirected tests from over 100 subjects. The data points were fitted by a logarithmic transformation linear regression, from which the slope and 50% response intercept were obtained. The directed test threshold for ethyl mercaptan, at which 50% of the subjects would respond, was found by extrapolation to be 0.17 ppb. In the misdirected test situation, however, the 50% response threshold was at 4.8 ppb, or 28 times higher. Furthermore, the slope of the regression line is shallower, so that disproportionately higher concentrations are required to elicit a response from 90% of the participants. The results for thiophane (tetrahydrothiophen) are virtually superimposable upon those for ethyl mercaptan, except that about double the concentration of odorant is needed to achieve a given level of response. That is, 0.35 ppb for detection threshold and 8.7 ppb for misdirected threshold, or 24 times higher.

The good agreement between the results for ethyl mercaptan and for thiophane encourages us to generalize the data, so as to provide a practical guide for interpreting threshold ratios and odor safety factors (Fig. 2). This graph is set in log/probit coordinates. Since neither the logarithmic nor the probit scales go to zero, the origin of the graph is considered to be the intersection of threshold multiple 1.0 on the x axis, with 50% persons responding on the y axis. This, by definition, is the average detection threshold, measured under laboratory conditions, i.e. a directed test. The logarithmic binary step concentration scale and the standard deviation intervals are also entered in Fig. 2. It was previously demonstrated[18] that the sensitivities of people to various odorants exhibit standard deviations close to 2.0 binary steps. Hence, the detection line in Fig. 2 is based on this generalization, and constructed by drawing a line with a slope of 2.0 binary steps per standard deviation unit, through the origin of the graph. The detection line is shown as a broken line above 95% response, because there are some indications that a small percentage of the population has specific anosmias to one or more of the sulfurous odorants.[17] Such persons, while they may perceive most other odors normally, are found to have an innate lower sensitivity or 'odor blindness' to the typical gas odorants.

The warning line in Fig. 2 is based on the average of the misdirected data for both ethyl mercaptan and thiophane. It was constructed as follows. The results for ethyl mercaptan and for thiophane (Fig. 1) showed that the ratios of the 50%-detection thresholds in the misdirected and directed test protocols were 28.3 and 24.5, respectively. Their geometric mean is 26.3, which was rounded off to 26 for the threshold multiple. In Fig. 2, the warning line is drawn to intersect the 50% response level at the threshold multiple value of 26-fold. The slope of the warning line was likewise determined by averaging the slopes of the regression lines for the misdirected tests in Fig. 1. The averaged warning line has a slope of 3.5 binary steps per standard deviation unit.

Therefore, in order to be perceived by 50% of distracted subjects, the concentration of gas odorant had to be raised to 26 times the concentration that could be detected by 50% of attentive subjects in laboratory test conditions. This illustration lends emphasis to the compelling conclusion of Whisman *et al.*[19] that there is a substantial difference between the level of odorant that *can* be detected, and the level that *will* be detected, in a given set of circumstances. The available data do not permit extrapolation of the warning line in Fig. 2 below the 50% response level.

Odor safety classification of chemicals

Figure 2 represents a provisional synthesis of the best available data. The slope of the detection line appears quite soundly established, and to be applicable to many chemicals. For those uncommon chemicals that exhibit a pronounced and frequently occurring specific anosmia among members of the population,[26] the curve is expected to flatten at higher response percentages. The slope and intercept of the warning line, however, are based on only two, quite closely related, fuel gas odorants. Intuitively, we feel that the results for ethyl mercaptan and thiophane represent a relatively favorable case, because, thanks to the public awareness developed by the suppliers of household and bottled gas, it is a widely known fact that the 'smell of gas' is an indication of danger. In other words, gas odorants may have a better chance of penetrating the consciousness of a distracted person than many other odors that are not mentally associated with harmful consequences.

Until more data become available, we propose that the relationships in Fig. 2 can be used to set up a provisional classification of the 214 chemicals, according to the level of safety indicated by their odors. For this purpose, we are adopting the 10%, 50% and 90% response levels as practical guides. According to Fig. 2, the obvious benchmarks are the detection threshold at which 50% of people can perceive the odor, and the higher warning threshold at which 50% of people will notice the odor even when they are distracted. Secondary criteria are provided by the concentrations at which 10% of attentive people can detect the odor, and the other extreme where 90% of distracted people get a warning of the odor. These four borderlines are indicated by vertical lines in Fig. 2.

Our tentative odor safety classification is presented in Table 3. At their threshold limit value concentration, class A compounds will be perceived by 90% of distracted persons. To achieve this rating, the odor safety factor must be at least 550; i.e. the threshold limit value for the compound is more than 550 times higher than its odor threshold. At the other extreme, class E compounds at their TLV concentration can be detected by less than 10% of attentive persons. In this category, the odor safety factor is below 0.18. The quantitative ranges for the intermediate B, C and D classifications are as indicated in Table 3. The zones of odor safety factor for the five classes are also labeled on Fig. 2. The odor safety class of each of the 214 compounds, for which adequate data are available, are entered in column 7 of Table 2(a). Class A compounds provide the strongest odorous warning of their presence at the TLV level, whereas class E compounds are practically undetectable by odor at their TLV concentration.

The effect of sleeping

Although it is not considered relevant to most workplace situations, the power of an odorant to waken a sleeping person is significant where industrial products can escape into a residential area. This is an obvious risk with household gas, and the question was included in a study by Fieldner *et al.*[20] Their data for several odorants are displayed in $\log_{10}$/probit coordinates in Fig. 3. They tested three compounds (ethyl mercaptan, phenyl ether and isoamyl acetate) which can be regarded as more or less purely olfactory stimulants, i.e. they have little or no irritating power for the trigeminal nerve. Each data point in Fig. 3 was calculated from the results of tests with three to eight sleepers. The points were then fitted by linear regression. The performances of these three odorants seem fairly concordant, and imply that an odorant concentration about 20 000 times the normal detection threshold is required to awaken 50% of soundly sleeping persons. That is more than 700 times stronger a stimulus than suffices to serve as a warning for wakeful, but misdirected, observers (Fig. 2). If this result were applicable to all odorants, it would mean that virtually none of the 214 compounds examined in Table 2(a) would awaken the average person, without exceeding the TLV.

There is, however, a complicating factor. Some odorants, besides stimulating the olfactory nerve, also irritate the trigeminal nerve. Two examples are included on the left side of Fig. 3. These substances were far more effective in waking the sleepers. A 50% response was obtained at 27 times the odor threshold of crotonaldehyde, and at only three times the odor threshold of allyl alcohol. From the comments of those that woke up, it is obvious that the irritation was the determining factor. It is an interesting observation that the trigeminal nerve has some sort of a 'hot line' directly into the subconscious, that is denied to the olfactory nerve.

Some data on irritant thresholds

Trained normal observers can report distinct concentration levels at which a vapor produces nasal or eye irritation, quite apart from its odor. Katz and Talbert[22] tabulated considerable data, from which we have selected those compounds that are on the ACGIH list (Table 4). We have also added a few compounds from our own work, in which nasal irritation thresholds were obtained from an anosmic person lacking the ability to perceive true odors as opposed to irritants. The ratio of the irritation and odor

thresholds for these compounds ranges from 33 000 for acetaldehyde, to less than unity for α-chloroacetophenone. Where this ratio is relatively small, it seems very likely that irritation would become an important factor in determining the intercept and slope of the warning line in Fig. 2.

If irritation of the trigeminal nerve can wake a sleeping person so effectively, it seems very likely also to be able to preempt the attention of a distracted person. No quantitative treatment of this factor is possible at present, because irritant thresholds are available for so few of the compounds on the TLV list, and no tests have been reported on perception of irritants by distracted persons. It may, however, be worth noting the irritation hazard factor in column 5 of Table 4. These figures indicate the degree to which the TLV is being exceeded, if there is appreciable eye or nose irritation for an attentive subject.

Threshold in water dilution

Many of the odor thresholds found in our literature survey had been measured by sniff-tests from the head-space above aqueous dilutions. Theoretically, the air-dilution threshold and the water-dilution threshold are simply related by the air-water partition coefficient of the odorant, provided the concentrations are measured in equivalent weight per volume units. This expectation has been borne out in comparisons made for *n*-butyl alcohol, pyridine and isovaleric acid,[14] and has been further supported by the data for many compounds listed in Table 2(b). For example, the data for *n*-butyl alcohol in Table 1 exhibit, for the reported olfactory thresholds, more than a 1000-fold range, yet the group means of the 20 air thresholds and the nine water thresholds differ by a factor of only about three-fold, and this is not considered significant ($P > 0.1$). Odor thresholds measured in air and water dilutions are generally concordant, unless the water–air distribution ratio is less than approximately ten. In that case, the reported water-dilution threshold concentration is liable to be too high, due to substantial evaporative loss of odorant from the solution during the course of conducting the odor threshold tests.

The air-dilution thresholds in column 3 of Table 2(a) are based on a pool of all available data from both air- and water-dilution measurements, omitting water thresholds for compounds with unfavorable water–air distribution ratios. The water dilution thresholds in column 10 of Table 2(b) were generally calculated from the data in column 3 of Table 2(a), by applying the water–air distribution ratio. In this way, we have been able to calculate water-dilution thresholds for many compounds for which only air-dilution threshold data were previously available. By applying the same distribution ratio, the water equivalent concentrations were also calculated for the TLV, and are listed in column 8 of Table 2(b). With odorants that are ionizable (acids and bases), these calculations are strictly valid only within specified pH limits, as explained in the Methods section.

We felt that it would be informative to provide the theoretical water threshold and TLV data, even for compounds with distribution ratios of less than ten. The equilibrium air concentration can develop and persist in conditions of high liquid-vapor volume ratio and low vapor loss, such as a closed vessel or a sewer. TLV and threshold data for odorants with distribution ratios less than ten are in parentheses in Table 2(b). This is to indicate that those solutions lack enough persistence to serve as reliable standards in setting up water dilution sniff-tests for training or testing personnel.

CONCLUSION

The interpretation of these data in any particular safety or pollution problem will depend markedly on the individual circumstances. The threshold data in the Tables and Figures are based on averages for samples of the population, presumably in good health. Individuals can differ quite markedly from the population average in their smell sensitivity, due to any of a variety of innate, chronic or acute physiological conditions.[23, 28, 29] Likewise, the time-weighted average threshold limit values are for workers, who by the mere fact of being able to work evidently represent a generally healthy segment of the population.

Continuing exposure to an odor usually results in a gradual diminution or even disappearance of the smell sensation. This phenomenon is known as olfactory adaptation or smell fatigue.[30] If the adaptation has not been too severe or too prolonged, sensitivity can often be restored by stepping aside for a few moments to an uncontaminated atmosphere, if available. Unfortunately, workers chronically exposed to a strong odor can develop a desensitization which persists up to two weeks or more after their departure from the contaminated atmosphere. In such cases, it should be the responsibility of supervisors and inspectors to note the odor and take appropriate action.

Hydrogen sulfide and perhaps other dangerous gases can very quickly lose their characteristic odor at high concentrations. At levels of H_2S above 100 ppm (over 10 000 times the average detection threshold), the sense of smell is rapidly abolished, so that potentially lethal concentrations may not be detected by odor at all.[31] Certain commercial diffusible odor masking or suppressing agents may reduce the perceptibility of odors, without removing the chemical source. The use of such agents might interfere with the capability of the nose to provide a warning at the expected concentration level.

There are many potential applications of these data in chemical safety and in air- and water-pollution control, some of which have been mentioned previously. In addition, we believe that the data might find some less apparent uses: Table 2 is also a guide to what data are in the literature on odor thresholds, on TLV-listed substances, is unavailable, unconfirmed or erratic. Readily prepared water dilutions could be used to test the individual smell thresholds of workers to the chemicals they handle. A water TLV dilution of an odorant could be prepared to demonstrate quickly to workers the practical experience of its TLV concentration. The general experimental procedures for preparing and testing aqueous solutions of odorants have been described.[32] These concepts could improve the reliability of odor breakthough as an indication of when to change the organic vapor cartridge in a respirator. The feasibility might be considered of using class A or B compounds as warning odorants to be added to class D or E substances, or to pesticides. The water–air distribution ratios could also be a guide to the possible success of water-scrubbing as a means of removing vapors from effluent gases.

The TLVs used in Table 2 and discussed in this paper are those recommended by the ACGIH in its 1982 listing.[1] The values are re-published annually, and are subject to revision, usually with two years notice of intended changes. The US Government Occupational Safety and Health Administration (OHSA) and many State Administrations have established their own lists of permitted exposures. While the values adopted are often based on the ACGIH recommendations, they may not coincide with current ACGIH TLVs, and quite different standards may be set for certain compounds. Some foreign governments issue guidelines with independently derived limits. If the applicable exposure limit for a particular compound is different from the TLV cited in Table 2, column 1, it will be necessary to adjust the values in columns 5, 6 and 8 by the appropriate ratio, and perhaps reassign the odor safety class (column 7). Values in Table 4, column 5 may also have to be altered.

Every chemical that can be detected by smell exhibits a property that can be turned to advantage as an aid in maintaining safe operating conditions. It must be recognized that background odors, odor fatigue, preoccupation and individual insensitivity may combine to reduce the margin, if any, between odor detection and safe operating conditions. No odor safety factor is large enough to justify condoning the presence of a fleeting odor, let alone a persistent stench, unless professional assurance has been obtained that the working conditions are safe.

The first detectable odor should be a sure signal that something abnormal has happened somewhere. It may be the last warning. During chemical operations, when an odor is detected, the source should be located and the concentration determined. Then effective steps can be taken to prevent the escape of vapor, and restore a neutral and healthful odor background. Even in the unnatural environment of the industrial workplace, our sense of smell has much to offer as a natural safety warning system.

Acknowledgements

We are very grateful to Dr R. G. Buttery for measuring the air–water partition coefficients of some infinitely soluble compounds by gas chromatography, and to Mr C. J. Thompson for an advance copy of his manuscript with Whisman *et al.* on the responsiveness of people to gas odorants.[19] We thank Mr W. D. Kelly, Executive Secretary of the American Conference of Governmental Industrial Hygienists, Inc., for permission to use the TLV data from Ref. 1 in Table 2(a).

The preparation of this paper was supported in part with funding provided under Service Order No. 34 016, from the Hazard Evaluation System and Information Service, Department of Health Services–Department of Industrial Relations, State of California. This report has been reviewed by the staff of the Hazard Evaluation System and Information Service Section, Department of Health Services–Department of Industrial Relations, State of California, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Hazard Evaluation System and Information Service Section, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Reference to a company and/or product in this publication is only for purposes of information and does not imply approval or recommendation for the product by the US Department of Agriculture to the exclusion of others which may also be suitable.

REFERENCES

1. *Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment*, American Conference of Governmental Industrial Hygienists, Cincinnati (1982).
2. P. Laffort, Essai de standardisation des seuils olfactifs humains pour 192 corps purs. *Arch. Sci. Physiol.* **17**, 75–105 (1963).
3. F. Patte, M. Etcheto and P. Laffort, Selected and standardized values of suprathreshold odor intensities for 110 substances. *Chem. Sens. Flavor* **1**, 283–305 (1975).
4. L. J. van Gemert and A. H. Nettenbreijer, *Compilation of Odour Threshold Values in Air and Water*, Central Institute for Nutrition and Food Research, Zeist (1977).
5. L. J. van Gemert, *Compilation of Odour Threshold Values in Air, Supplement III*, Central Institute for Nutrition and Food Research, Zeist (1980).
6. F. A. Fazzalari, *Compilation of Odor and Taste Threshold Values Data*, American Society for Testing and Materials, Philadelphia (1978).
7. *Documentation of the Threshold Limit Values*, 3rd edn, 4th printing, American Conference of Governmental Industrial Hygienists, Cincinnati (1977).
8. T. M. Hellman and F. H. Small, Characterization of the odor properties of 101 petrochemicals using sensory methods. *J. Air Poll. Control. Assoc.* **24**, 979–982 (1974).
9. D. R. Stull, Vapor pressure of pure substances. *Ind. Eng. Chem.* **39**, 517–550 (1947).
10. A. Seidell, *Solubilities of Organic Compounds*, 3rd edn, Vol. 2, D. Van Nostrand, New York (1941).
11. A. Seidell and W. F. Linke, *Solubilities of Inorganic and Organic Compounds*, Suppl. to 3rd edn, D. Van Nostrand, New York (1952).
12. K. Verschueren, *Handbook of Environmental Data on Organic Chemicals*, Van Nostrand Reinhold, New York (1977).
13. *Beilstein's Handbuch der organischen Chemie*, 4th edn and Supplements 1–4, Julius Springer, Berlin (1918 ff.).
14. J. E. Amoore, and R. G. Buttery, Partition coefficients and comparative olfactometry. *Chem. Sens. Flavor* **3**, 57–71 (1978).
15. G. J. Pierotti, C. H. Deal and E. L. Derr, Activity coefficients and molecular structure. *Ind. Eng. Chem.* **51**, 95–102 (1959).
16. J. E. Amoore, Odor theory and odor classification. In *Fragrance Chemistry*, ed. by E. T. Theimer, pp. 27–76. Academic Press, New York (1982).
17. J. E. Amoore, Odor blindness as a problem in odorization. *Am. Gas Assoc. Oper. Sect. Proc., Distribution Conf.* pp. 242–247 (1968).
18. J. E. Amoore, P. Pelosi and L. J. Forrester, Specific anosmias to 5α-androst-16-en-3-one and ω-pentadecalactone: the urinous and musky primary odors. *Chem. Sens. Flavor* **2**, 401–425 (1977).
19. M. L. Whisman, J. W. Goetzinger, F. O. Cotton, D. W. Brinkman and C. J. Thompson, *A New Look at Odorization Levels for Propane Gas*, Bartlesville Energy Research Center, Bartelsville, OK (1977).
20. A. C. Fieldner, R. R. Sayers, W. P. Yant, S. H. Katz, J. B. Shohan and R. D. Leitch, *Warning Agents for Fuel Gases*, U.S. Dept. of Commerce, Bureau of Mines, Monograph 4 (1931).
21. R. I. Henkin, The definition of primary and accessory areas of olfaction as the basis for a classification of decreased olfactory acuity. In *Olfaction and Taste II*, ed. by T. Hayashi, pp. 235–252. Pergamon Press, Oxford (1967).
22. S. H. Katz and E. J. Talbert, Intensities of odors and irritating effects of warning agents for inflammable and poisonous gases. U.S. Dept. of Commerce, Bureau of Mines, Technical Paper 480 (1930).
23. J. E. Amoore, D. Venstrom and A. R. Davis, Measurement of specific anosmia. *Percept. Motor Skills* **26**, 143–164 (1968).
24. V. C. Allison and S. H. Katz, An investigation of stenches and odors for industrial purposes. *Ind. Eng. Chem.* **11**, 336–338 (1919).
25. P. M. Patterson and B. A. Lauder, The incidence and probable inheritance of smell-blindness. *J. Heredity* **39**, 295–297 (1948).
26. J. E. Amoore, Specific anosmia and the concept of primary odors. *Chem. Sens. Flavor* **2**, 267–281 (1977).

27. A. H. Sherman, J. E. Amoore and V. Weigel, The pyridine scale for clinical measurement of olfactory threshold: a quantitative reevaluation. *Otolaryngol. Head Neck Surg.* **87**, 717–733 (1979).
28. R. A. Schneider, The sense of smell in man – its physiologic basis. *New Engl. J. Med.* **277**, 299–303 (1967).
29. R. L. Doty, A review of olfactory dysfunctions in man. *Am. J. Otolaryngol.* **1**, 57–79 (1979).
30. G. T. Pryor, G. Steinmetz and H. Stone, Changes in absolute detection threshold and in subjective intensity of supra-threshold stimuli during olfactory adaptation and recovery. *Percept. Psychophys.* **8**, 331–335 (1970).
31. *Occupational Exposure to Hydrogen Sulfide: Criteria for a Recommended Standard*, National Institute for Occupational Safety and Health, Washington DC (1977).
32. J. E. Amoore, Directions for preparing aqueous solutions of primary odorants to diagnose eight types of specific anosmia. *Chem. Sens. Flavor* **4**, 153–161 (1979).

Received 17 August 1982; accepted (revised) 15 February 1983