# PATTYS Volume II, Part F INDUSTRIAL HYGIENE and TOXICOLOGY

TOXICOLOGY/With Cumulative Indexes

4th Edition

# INDUSTRIAL HYGIENE FACETS



ENGINEERING



**PHYSICS** 



**CHEMISTRY** 



MEDICINE

Edited by

George D. Clayton & Florence E. Clayton

# PATTY'S INDUSTRIAL HYGIENE AND TOXICOLOGY

# **Fourth Edition**

Volume I, Parts A and B GENERAL PRINCIPLES

**Volume II, Parts A, B, C, D, E, and F TOXICOLOGY** 

# **Third Edition**

Volume III, Parts A and B THEORY AND RATIONALE OF INDUSTRIAL HYGIENE PRACTICE This text is printed on acid-free paper.

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Volume II of this series is dedicated to Paul D. Halley, past president of the American Industrial Hygiene Association, former Director of Environmental Health Services for AMOCO, (Industrial Hygiene, Safety and Toxicology), and Editor-in-Chief for eight years of the *AIHA Journal*, who, after retirement from the latter position, initiated contacts for the fourth revision of this volume, but was forced to relinquish its editorship because of illness.

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# **Preface**

This is the sixth and last book of the fourth revision of Volume II on *Toxicology* in the Patty series. It has been a tremendous undertaking, with more than three years spent in its development.

Approximately 6,000 chemicals are either discussed or indexed in these six books. Forty-five individuals, either singly or with co-authors, in addition to two panels from the Chemical Manufacturers Association, namely the "Glycol Ethers Panel, Toxicological Research Group," and the "Nitrosamines Panel"—all have spent thousands of hours in preparation of this fourth revision of Volume II. Several authors have expressed the opinion that this probably would be the last revision of the series in this format. With the proliferation of computer communication, the use of the printed word will be diminished. There are those who even have gone so far as to predict that the printed word will become obsolete or rare!

This sixth book contains three chapters new to the series, four revised chapters, and two complete indexes, both subject and chemical, covering all six books.

During the past 18 years we have edited Volumes I and II of this series, producing the third and fourth revisions, and have overseen the expansion from one-book volumes to two- and six-book volumes, respectively. It is now time to pass on the responsibility to another generation. Our relationship with the publisher, John Wiley & Sons, Inc., has been exemplary; they have been most supportive in the expansion of this series. Our thanks to the authors of this volume and to all authors who have participated in these revisions with the objective of continuing the prestigious reputation of this series. We applied their dedication, their expertise and their willingness to generously share their knowledge with their peers. It has been a great pleasure, as well as gratifying, to work with them.

GEORGE D. CLAYTON FLORENCE E. CLAYTON

# **USEFUL EQUIVALENTS AND CONVERSION FACTORS**

To convert degrees Celsius to degrees Fahrenheit:  $^{\circ}$ C (9/5) + 32 =  $^{\circ}$ F  $^{\circ}$ To convert degrees Fahrenheit to degrees Celsius: (5/9) ( $^{\circ}$ F - 32) =  $^{\circ}$ C

To convert mg/liter to ppm (by volume): mg/liter (24,450/mol. wt.) = ppm

Atmospheric contamination: 1 mg/liter  $\approx 1$  oz/1000 cu ft (approx) For gases or vapors in air at 25°C and 760 mm Hg pressure:

To convert ppm to mg/liter: ppm (mol. wt./24,450) = mg/liter

For solutes in water: 1 mg/liter  $\approx$  1 ppm (by weight)

```
1 \text{ kilometer} = 0.6214 \text{ mile}
                                                           1 \text{ gram} = 15.43 \text{ grains}
1 \text{ meter} = 3.281 \text{ feet}
                                                           1 pound = 453.59 grams
1 \text{ centimeter} = 0.3937 \text{ inch}
                                                           1 ounce (avoir.) = 28.35 grams
1 micrometer = 1/25.4000 inch = 40 microinches
                                                           1 gram mole of a perfect gas \approx 24.45 liters (at
     = 10,000 Angstrom units
                                                                25°C and 760 mm Hg barometric pressure)
1 \text{ foot} = 30.48 \text{ centimeters}
                                                           1 atmosphere = 14.7 pounds per square inch
1 \text{ inch} = 25.40 \text{ millimeters}
                                                           1 foot of water pressure = 0.4335 pound per
1 square kilometer = 0.3861 square mile (U.S.)
                                                                square inch
1 square foot = 0.0929 square meter
                                                           1 inch of mercury pressure = 0.4912 pound per
1 square inch = 6.452 square centimeters
                                                                square inch
1 square mile (U.S.) = 2,589,998 square meters
                                                           1 dyne per square centimeter = 0.0021 pound
     = 640 acres
                                                                per square foot
1 \text{ acre} = 43,560 \text{ square feet} = 4047 \text{ square}
                                                           1 gram-calorie = 0.00397 Btu
    meters
                                                           1 \text{ Btu} = 778 \text{ foot-pounds}
1 cubic meter = 35.315 cubic feet
                                                           1 Btu per minute = 12.96 foot-pounds per
1 cubic centimeter = 0.0610 cubic inch
                                                                second
1 cubic foot = 28.32 liters = 0.0283 cubic meter
                                                           1 \text{ hp} = 0.707 \text{ Btu per second} = 550 \text{ foot-pounds}
     = 7.481 gallons (U.S.)
                                                                per second
1 cubic inch = 16.39 cubic centimeters
                                                           1 centimeter per second = 1.97 feet per minute
1 U.S. gallon = 3.7853 liters = 231 cubic inches
                                                                = 0.0224 mile per hour
     = 0.13368 cubic foot
                                                           1 footcandle = 1 lumen incident per square foot
1 liter = 0.9081 quart (dry), 1.057 quarts (U.S.,
                                                                = 10.764 lumens incident per square meter
    liquid)
                                                           1 grain per cubic foot = 2.29 grams per cubic
1 cubic foot of water = 62.43 pounds (4°C)
                                                                meter
1 U.S. gallon of water = 8.345 pounds (4°C)
                                                           1 milligram per cubic meter = 0.000437 grain per
1 \text{ kilogram} = 2.205 \text{ pounds}
                                                               cubic foot
```

# CONVERSION TABLE FOR GASES AND VAPORS<sup>a</sup>

(Milligrams per liter to parts per million, and vice versa; 25°C and 760 mm Hg barometric pressure)

Molec- ular Weight	1 mg/liter ppm	l ppm mg/liter	Molec- ular Weight	1 mg/liter ppm	1 ppm mg/liter	Molec- ular Weight	l mg/liter ppm	1 ppm mg/liter
1	24,450	0.0000409	39	627	0.001595	77	318	0.00315
2	12,230	0.0000818	40	611	0.001636	78	313	0.00319
3	8,150	0.0001227	41	596	0.001677	79	309	0.00323
4	6,113	0.0001636	42	582	0.001718	80	306	0.00327
5	4,890	0.0002045	43	569	0.001759	81	302	0.00331
6	4,075	0.0002454	44	556	0.001800	82	298	0.00335
7	3,493	0.0002863	45	543	0.001840	83	295	0.00339
8	3,056	0.000327	46	532	0.001881	84	291	0.00344
9	2,717	0.000368	47	520	0.001922	85	288	0.00348
10	2,445	0.000409	48	509	0.001963	86	284	0.00352
11	2,223	0.000450	49	499	0.002004	87	281	0.00356
12	2,038	0.000491	50	489	0.002045	88	278	0.00360
13	1,881	0.000532	51	479	0.002086	89	275	0.00364
14	1,746	0.000573	52	470	0.002127	90	272	0.00368
15	1,630	0.000614	53	461	0.002168	91	269	0.00372
16	1,528	0.000654	54	453	0.002209	92	266	0.00376
17	1,438	0.000695	55	445	0.002250	93	263	0.00380
18	1,358	0.000736	56	437	0.002290	94	260	0.00384
19	1,287	0.000777	57	429	0.002331	95	257	0.00389
20	1,223	0.000818	58	422	0.002372	96	255	0.00393
21	1,164	0.000859	59	414	0.002413	97	252	0.00397
22	1,111	0.000900	60	408	0.002554	98	249.5	0.00401
23	1,063	0.000941	61	401	0.002495	99	247.0	0.00405
24	1,019	0.000982	62	394	0.00254	100	244.5	0.00409
25	978	0.001022	63	388	0.00258	101	242.1	0.00413
26	940	0.001063	64	382	0.00262	102	239.7	0.00417
27	906	0.001104	65	376	0.00266	103	237.4	0.00421
28	873	0.001145	66	370	0.00270	104	235.1	0.00425
29	843	0.001186	67	365	0.00274	105	232.9	0.00429
30	815	0.001227	68	360	0.00278	106	230.7	0.00434
31	789	0.001268	69	354	0.00282	107	228.5	0.00438
32	764	0.001309	70	349	0.00286	108	226.4	0.00442
33	741	0.001350	71	344	0.00290	109	224.3	0.00446
34	719	0.001391	72	340	0.00294	110	222.3	0.00450
35	699	0.001432	73	335	0.00299	111	220.3	0.00454
36	679	0.001472	74	330	0.00303	112	218.3	0.00458
37	661	0.001513	75	326	0.00307	113	216.4	0.00462
38	643	0.001554	76	322	0.00311	114	214.5	0.00466

CONVERSION TABLE FOR GASES AND VAPORS (Continued)
(Milligrams per liter to parts per million, and vice versa; 25°C and 760 mm Hg barometric pressure)

Molec-	1	1	Molec-	1	1	Molec-	1	4
ular Wojaht	mg/liter	1 ppm	ular Waiaht	mg/liter	1 ppm	ular	mg/liter	1 ppm
Weight	ppm	mg/liter	Weight	ppm	mg/liter	Weight	ppm	mg/liter
115	212.6	0.00470	153	159.8	0.00626	191	128.0	0.00781
116	210.8	0.00474	154	158.8	0.00630	192	127.3	0.00785
117	209.0	0.00479	155	157.7	0.00634	193	126.7	0.00789
118	207.2	0.00483	156	156.7	0.00638	194	126.0	0.00793
119	205.5	0.00487	157	155.7	0.00642	195	125.4	0.00798
120	203.8	0.00491	158	154.7	0.00646	196	124.7	0.00802
121	202.1	0.00495	159	153.7	0.00650	197	124.1	0.00806
122	200.4	0.00499	160	152.8	0.00654	198	123.5	0.00810
123	198.8	0.00503	161	151.9	0.00658	199	122.9	0.00814
124	197.2	0.00507	162	150.9	0.00663	200	122.3	0.00818
125	195.6	0.00511	163	150.0	0.00667	201	121.6	0.00822
126	194.0	0.00515	164	149.1	0.00671	202	121.0	0.00826
127	192.5	0.00519	165	148.2	0.00675	203	120.4	0.00830
128	191.0	0.00524	166	147.3	0.00679	204	119.9	0.00834
129	189.5	0.00528	167	146.4	0.00683	205	119.3	0.00838
130	188.1	0.00532	168	145.5	0.00687	206	118.7	0.00843
131	186.6	0.00536	169	144.7	0.00691	207	118.1	0.00847
132	185.2	0.00540	170	143.8	0.00695	208	117.5	0.00851
133	183.8	0.00544	171	143.0	0.00699	209	117.0	0.00855
134	182.5	0.00548	172	142.2	0.00703	210	116.4	0.00859
135	181.1	0.00552	173	141.3	0.00708	211	115.9	0.00863
136	179.8	0.00556	174	140.5	0.00712	212	115.3	0.00867
137	178.5	0.00560	175	139.7	0.00716	213	114.8	0.00871
138	177.2	0.00564	176	138.9	0.00720	214	114.3	0.00875
139	175.9	0.00569	177	138.1	0.00724	215	113.7	0.00879
140	174.6	0.00573	178	137.4	0.00728	216	113.2	0.00883
141	173.4	0.00577	179	136.6	0.00732	217	112.7	0.00888
142	172.2	0.00581	180	135.8	0.00736	218	112.2	0.00892
143	171.0	0.00585	181	135.1	0.00740	219	111.6	0.00896
144	169.8	0.00589	182	134.3	0.00744	220	111.1	0.00900
145	168.6	0.00593	183	133.6	0.00748	221	110.6	0.00904
146	167.5	0.00597	184	132.9	0.00753	222	110.1	0.00908
147	166.3	0.00601	185	132.2	0.00757	223	109.6	0.00912
148	165.2	0.00605	186	131.5	0.00761	224	109.2	0.00916
149	164.1	0.00609	187	130.7	0.00765	225	108.7	0.00920
150	163.0	0.00613	188	130.1	0.00769	226	108.2	0.00924
151	161.9	0.00618	189	129.4	0.00773	227	107.7	0.00928
152	160.9	0.00622	190	128.7	0.00777	228	107.2	0.00933

CONVERSION TABLE FOR GASES AND VAPORS (Continued)
(Milligrams per liter to parts per million, and vice versa; 25°C and 760 mm Hg barometric pressure)

Molec- ular Weight	l mg/liter ppm	1 ppm mg/liter	Molec- ular Weight	1 mg/liter ppm	l ppm mg/liter	Molec- ular Weight	l mg/liter ppm	1 ppm mg/liter
229	106.8	0.00937	253	96.6	0.01035	277	88.3	0.01133
230	106.3	0.00941	254	96.3	0.01039	278	87.9	0.01137
231	105.8	0.00945	255	95.9	0.01043	279	87.6	0.01141
232	105.4	0.00949	256	95.5	0.01047	280	87.3	0.01145
233	104.9	0.00953	257	95.1	0.01051	281	87.0	0.01149
234	104.5	0.00957	258	94.8	0.01055	282	86.7	0.01153
235	104.0	0.00961	259	94.4	0.01059	283	86.4	0.01157
236	103.6	0.00965	260	94.0	0.01063	284	86.1	0.01162
237	103.2	0.00969	261	93.7	0.01067	285	85.8	0.01166
238	102.7	0.00973	262	93.3	0.01072	286	85.5	0.01170
239	102.3	0.00978	263	93.0	0.01076	287	85.2	0.01174
240	101.9	0.00982	264	92.6	0.01080	288	84.9	0.01178
241	101.5	0.00986	265	92.3	0.01084	289	84.6	0.01182
242	101.0	0.00990	266	91.9	0.01088	290	84.3	0.01186
243	100.6	0.00994	267	91.6	0.01092	291	84.0	0.01190
244	100.2	0.00998	268	91.2	0.01096	292	83.7	0.01194
245	99.8	0.01002	269	90.9	0.01100	293	83.4	0.01198
246	99.4	0.01006	270	90.6	0.01104	294	83.2	0.01202
247	99.0	0.01010	271	90.2	0.01108	295	82.9	0.01207
248	98.6	0.01014	272	89.9	0.01112	296	82.6	0.01211
249	98.2	0.01018	273	89.6	0.01117	297	82.3	0.01215
250	97.8	0.01022	274	89.2	0.01121	298	82.0	0.01219
251	97.4	0.01027	275	88.9	0.01125	299	81.8	0.01223
252	97.0	0.01031	276	88.6	0.01129	300	81.5	0.01227

<sup>&</sup>lt;sup>a</sup> A. C. Fieldner, S. H. Katz, and S. P. Kinney, "Gas Masks for Gases Met in Fighting Fires," U.S. Bureau of Mines, Technical Paper No. 248, 1921.

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 Table 39.1 Physical and Chemical Properties of Sulfur Chemicals

Compound	CAS #	Emp. Formula	Mol. Wt.	W/V Conversion (mg/m³ to 1 ppm)	Density
Mercaptan					
Methyl	74-93-1	CH₄S	48.11	1.96	0.8665
Ethyl	75-08-1	C <sub>2</sub> H <sub>6</sub> S	62.13	2.54	0.8391
Propyl	107-03-9	$C_3H_8S$	76.17	3.12	0.8411
Isopropyl	75-33-2	$C_3H_8S$	76.17	3.12	0.8143
n-Butyl	109-79-5	$C_4H_{10}S$	90.19	3.69	0.8337
Isobutyl	513-44-0	$C_4H_{10}S$	90.19	3.69	0.8363
s-Butyl	513-53-1	$C_4H_{10}S$	90.19	3.69	0.8299
t-Butyl	75-66-1	$C_4H_{10}S$	90.19	3.69	0.79 - 0.82
n-Amyl	110-66-7	$C_5H_{12}S$	104.22	4.26	0.8421
s-Amyl	2084-19-7	$C_5H_{12}S$	104.22	4.26	0.8327
Isoamyl	541-31-1	$C_5H_{12}S$	104.22	4.26	0.8410
t-Amyl	1679-09-0	$C_5H_{12}S$	104.22	4.26	0.831
n-Hexyl	111-31-9	$C_6H_{14}S$	118.24	4.84	0.8424
n-Heptyl	1639-09-4	$C_7H_{16}S$	132.27	5.41	0.8427
n-Octyl	111-88-6	$C_8H_{18}S$	146.30	5.98	0.8433
s-Octyl	25265-79-6	$C_8H_{18}S$	146.30	5.98	0.8366
t-Octyl	141-59-3	$C_8H_{18}S$	146.30	5.98	0.848
n-Nonyl	1455-21-6	$C_9H_{18}S$	160.32	6.56	0.040
t-Nonyl	25360-10-5	$C_9H_{20}S$	161.21	6.59	0.855 sp gr
n-Decyl	143-10-2	$C_{10}H_{20}S$	174.35	7.13	0.8443
Undecyl	5332-52-5	$C_{10}H_{24}S$	188.37	7.69	0.0443
n-Dodecyl	112-55-0	$C_{12}H_{26}S$	202.41	8.28	0.8450
t-Dodecyl	25103-58-6	$C_{12}H_{26}S$	202.41	8.28	0.85
Triisobutyl	25103-58-6	C <sub>12</sub> 11 <sub>26</sub> 3	200.10	8.18	0.8649
n-Tetradecyl	2079-95-0	$C_{14}H_{30}S$	230	0.10	0.8398
n-Hexadecyl	2917-26-2		258.22	10.57	0.0390
n-Octadecyl	2885-00-9	$C_{16}H_{34}S$	286.57	11.72	0.8475
Cyclohexyl	1569-69-3	$C_{18}H_{38}S$ $C_6H_{11}SH$	116.24	4.75	0.97824
Phenyl	108-98-5		110.24	4.73	
Benzyl	100-53-8	C <sub>6</sub> H <sub>6</sub> S C <sub>7</sub> H <sub>8</sub> S	124.20	5.08	1.0766
Ethylenedi-	540-63-6		94.20	3.84	1.058
Allyl	870-23-5	$C_2H_6S_2$	94.20 74	3.84	1.123
		C <sub>3</sub> H <sub>6</sub> S			0.9259 (sp gr
3-Chloropropyl	17481-19-5 594-42-3	C <sub>3</sub> H <sub>7</sub> ClS	110	7.60	0.1264 (sp gr
Perchloromethyl	28679-10-9	CCl₄S	185.88 176	7.60	1.7 (sp gr)
Ethylcyclohexanedithiol		$C_8H_{16}S_2$			1.06 (sp gr)
Vinylcyclohexenedimercaptan	37241-32-0	$C_8H_{16}S_2$	176		1.050
d-Limomene dimercaptan	4802-20-4	$C_{10}H_{20}S_2$	204	2 10	1.025 (sp gr)
Mercaptoethanol	60-24-2	C <sub>2</sub> H <sub>6</sub> OS	78.13	3.19	1.1143
Dimercaprol Dithiothroital	59-52-9	C <sub>3</sub> H <sub>8</sub> OS <sub>2</sub>	124.21	5.07	1.2463
Dithiothreitol	3483-12-3	$C_4H_{10}O_2S_2$	154.24	6.30	0.0402
Methyl sulfide	75-18-3	C <sub>2</sub> H <sub>6</sub> S	62.13	2.54	0.8483
Ethyl sulfide	352-93-2	$C_4H_{10}S$	90.19	3.68	0.8362
Butyl sulfide	544-40-1	$C_8H_{18}S$	146.30	5.97	0.886
Methyl disulfide	624-92-0	$C_2H_6S_2$	94.2	3.84	1.0625
Thiophene	110-02-1	C <sub>4</sub> H <sub>4</sub> S	84.14	3.43	1.0649
Tetrahydrothiophene	111-01-0	C <sub>4</sub> H <sub>8</sub> S	88.18	3.60	0.9987
Benzothiazole	95-16-9	C <sub>7</sub> H <sub>5</sub> NS	135.19	5.52	1.2460
Mercaptobenzothiazole	149-30-4	$C_7H_5NS_2$	167.25	6.83	1.42

Vapor Pressure (mm Hg)	Vapor Density (Air = 1)	Odor Threshold	Solubility w/al/et	<sup>а</sup> М.Р. (°С)	B.P. (°C)	Flash Pt. (°F)
1520 (79°F)	1.66	2 ppb	d/v/v	- 123	5.95	<0
442 (68°F)	2.14	0.1 ppb	d/s/s	- 144.4	35.0	-55
155 (77°F)	>1	0.0016 ppm	d/s/s	-113.3	67.8	-5
454 (100°F)	2.62		d/s/s	-130.54	52.56	-30
83 (100°F)	3.1	0.0001-0.001 ppm	d/v/v	-115.67	98.46	38
		0.84 ppb			85-95	15
205 (100000	3.11	promoting .	d/v/v	-165	84.7	- 10
305 (100°F)	3.1	0.08 ppb	d/v/v	-0.5	63.7-64.2	- 15
13.8 (77°F)	3.59	0.8 ppb	i/v/v	-75.7	126.6 (460 mm Hg)	65
52		0.0003	/s/	- 169	112.9	
	1.6	0.0083 ppm	i/s/	-110.8	116-118	
	1.6		., ,	0.1	95–119	30
			i/v/v	-81	149-151	
1.2 (100°F)	>1		i/v/v i/v/	-43 40.2	177	154 155
1.2 (100 1)	- 1		/s/	-49.2	199.1	156–175
	5.0		i/—/—		186.4 154–166	100
	2.10		1//		134-100	109
1.2 (78°F)	>1		i/—/—		188-196	147
. ,			i/s/s	-26	240.6	147
				20	210.0	
2.5 (77°F)	>1		i/s/s	<b>-7</b>	267-278	190-262
<0.1 (75°F)	6.98		i//	-7.5	230-247	230
					68-86 (5 mm Hg)	
				6.5	176–180	
0.1			i/d/s	18 - 20	123-128	275
10)			i/d/s	24-26	188	
10	4.0	0.0000	i/s/s		158.66	110-120
2.0 (77°F)		0.00025 ppm	i/s/s	-14.8	168.7	132
4 () (729F2)		0.031 ppm	i/v/v		194–95	158
4.0 (73°F)	>1	0.0015	i/s/s	-41.2	146	122
		0.0015 ppm	i/s/s		67-68	
65 (158°F)	6.414	0.001 ppm	:/ /-		142-152	
<0.1 (70°F)	>1	0.001 ppiii	i/—/s i/—/—		147-148	0.50
(,,,,	- 1		i/d/s		290	250
			1/4/5		97-99	
					(1.25 mm Hg)	
					157-158	
					140 (40)	
					Subl.	
15 (25°C)		0.001 ppm		-98.27		
					92.1	
28.6 (25°C)				-79.7	185-185.5	
					109.7	
				-38.25	84.16	
				-96.16	121.12	
					231	
				180.2		

<sup>&</sup>quot;Solubility in water/alcohol/ether: s = soluble; i = insoluble; v = very soluble; d = decomposes.

# 1.2 Uses and Applications

Industrial uses of organic sulfur compounds include intermediates in chemical synthesis, gas odorants ( $C_1$  to  $C_4$  mercaptans), chelating or complexing agents, catalysts, solvents, and accelerators or components of synthetic rubber products. The sulfonates are used in the production of anionic detergents, surfactants, and wetting agents and in some cases as lubricant additives.

### 1.3 Environmental Occurrence

Sulfur-containing materials are widespread in the environment and are essential for survival of mammalian and submammalian species. Bacterial decomposition of vegetative matter contributes significantly to the atmospheric content of organic sulfur compounds, along with their release from, and occurrence in, natural gases and oil deposits.

# 1.4 Industrial Hygiene Monitoring

Atmospheric monitoring of sulfur compounds is somewhat limited by the ability of analytic methods to distinguish between individual compounds. Although validated methods exist for hydrogen sulfide, carbon disulfide, methyl and ethyl mercaptans, butyl mercaptan, mercaptobenzothiazole, and tetrahydrothiophene, large air samples are needed to facilitate detection and identification of other sulfurcontaining compounds, especially in mixtures containing several related materials.

### 1.5 Animal Metabolism and Excretion

Methyl and ethyl mercaptans can be utilized as sources of sulfur or carbon fragments in mammalian biosynthetic pathways. Excretion of excess amounts of these compounds occurs either as unchanged material through the lungs or as the sulfate metabolite sulfate through sulfone and/or sulfoxide intermediates. Incorporation of higher mercaptan homologues into biosynthetic pathways does not occur, although similar hepatic oxidative biotransformations result in the excretion of sulfides, sulfates, and other oxidized materials of intermediate oxidation state.

Methyl and ethyl sulfides can be excreted unchanged through the lungs but are also readily metabolized. Methyl sulfide is a product of the reductive metabolism of dimethyl sulfoxide.

## 2 MERCAPTANS

# 2.1 Methyl Mercaptan

# 2.1.1 General/Industrial Hygiene

Methyl mercaptan [CAS # 74-93-1; methanethiol] is used as a gas odorant, an intermediate in the production of pesticides, jet fuels, and plastics, in the synthesis

of methionine, and as a catalyst. It is a flammable (flash point of 0°F), slightly water-soluble gas, with a disagreeable odor described as rotten cabbage (1). It has a boiling point of 5.96°C, a vapor pressure of 1520 mm Hg (26.1°C), and a vapor density of 1.66, relative to air. Methyl mercaptan occurs naturally in a wide variety of vegetables such as garlic and onion, in "sour" gas in West Texas oil fields, and in coal tar and petroleum distillates. It is a major contributor to normal human mouth odor (2). Methyl mercaptan can be prepared from sodium methyl sulfate and potassium hydrosulfide, catalytically from methanol and hydrogen sulfide, and from methyl chloride and sodium hydrosulfide (3-5). The human odor threshold is 2 ppb, and the level immediately dangerous to life or health (IDLH) is 400 ppm. The Occupational Safety and Health Administration (OSHA) permissible exposure level is a ceiling limit of 10 ppm/15 min and the American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value is 0.5 ppm. Sampling for personal or area air monitoring can be accomplished with glass fiber filters impregnated with mercuric acetate, with quantification by gas chromatography and flame photometric detection (6).

# 2.1.2 Toxicology

Methyl mercaptan is a central nervous system (CNS) depressant and acts like hydrogen sulfide on the respiratory center producing death by respiratory paralysis. Lower concentrations produce pulmonary edema (1.2). Chief signs and symptoms are eye and mucous membrane irritation, headache, dizziness, staggering gait, nausea, and vomiting (7), and more or less pronounced paralysis of the locomotor muscles and respiration (8). Human fatalities attributed to exposure to methyl mercaptan have been described: in one, a laborer handling tanks containing methyl mercaptan was hospitalized in a coma, with acute hemolytic anemia and methemoglobinemia. This man was later found to have a deficiency of glucose-6phosphate dehydrogenase (9). A second case involved a 24-year-old man working alone in a chemical factory that produced sodium methyl sulfhydrate. This man was found dead, and an autopsy revealed a large quantity of methyl mercaptan in his liver, kidneys, lungs, blood, and urine, and in the washout solution of his trachea (10). A third case involved a 19-year-old man overcome by a high concentration (probably in excess of 10,000 ppm) for only a few minutes. Death, attributed to respiratory arrest and heart failure, occurred within 45 min. The concentration of methyl mercaptan in this man's blood was measured at 2.5 nmol/cm3 of blood, but may have been higher because of inadvertent mishandling of the blood sample before analysis (11). Even though methyl mercaptan has an extremely unpleasant odor, at high concentrations, olfactory desensitization or fatigue occurs. Therefore, odor and symptoms of irritation may not adequately provide warning of high concentrations of methyl mercaptan.

An oral LD<sub>50</sub> in mice of 60.67 mg/kg has been reported (12). The acute 4-hr inhalation LC<sub>50</sub> value in mice is 1664 ppm (13). In rats the inhalation LC<sub>50</sub> values of 675 and 1680 have been reported for 4-hr and 1-hr exposure periods, respectively (14, 15). Clinical signs following acute exposure included initial hyperactivity, tachy-